

Charge Transport and Mass Transfer Processes

in Thin Films of Redox Polymers based on

Ruthenium and Osmium Poly(pyridyl) complexes.

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Declaration

I hereby declare that the contents of this thesis, except where otherwise stated, are based entirely on my own work

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Abstract

Charge Transport and Mass Transfer Processes in Thin Films of Redox Polymers based on Ruthenium and Osmium Poly(pyridyl) Complexes

Chapter 1 of this thesis provides a brief introduction to the electrochemical techniques used in the study of electrode modifying materials. A review of the synthesis, characterisation and application of redox polymers based on ruthenium and osmium poly(pyridyl) complexes is presented.

Chapter 2 describes the synthesis, characterisation and charge transport properties of $[M(N)_6]^{2+/3+}$ moleties coordinatively attached to a poly(4-vinyl pyridine) backbone (where M is Ru or Os and N is pyridine). The effect of electrolyte type and concentration on charge transport and heterogeneous electron transfer is studied using cyclic voltammetry, chronoamperometry and sampled current voltammetry. For M=Ru, the effect of redox site loading is also investigated. Activation parameters are used to aid the diagnosis of rate determining steps.

In Chapters 3 to 6 the Electrochemical Quartz Crystal Microbalance (EQCM) is used to probe mass transfer within modifying polymer layers. An introduction to the theory and application of the EQCM is first presented. This is followed in Chapters 3 and 4 by a study of the effect of electrolyte type and concentration on the polymer morphology and resident layer mass of $[Os(bipy)_2(PVP)_{10}Cl]$ + films. Impedance analysis of the quartz crystal \polymer film \electrolyte composite resonator is used to confirm the rigidity of the polymer layers and also to provide an insight into electrolyte-dependent morphology changes. The importance of the electrolyte / polymer interaction and the subsequent polymer solvation is stressed. A membrane model describing the osmotic transfer of solvent is considered.

In Chapter 5, the kinetic aspects of redox-induced mass transfer through $[Os(bipy)_2(PVP)_{10}Cl]^+$ are studied using cyclic voltammetry (under semi-infinite diffusion conditions) and potential step techniques A correlation between the rate of charge transport and the facility for solvent transfer is established. The origins of the previously reported dependency of charge transport rates on experimental time scale for $[Os(bipy)_2(PVP)_{10}Cl]^+$ is also explored.

In Chapter 6, the pH dependency of mass transfer for redox processes in films of $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ is used to evaluate the mechanisms for coupled proton and electron transfer Charge transport through this polymer is also considered

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This thesis is dedicated to my parents

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CHAPTER 1

Introduction, Theory and Review of

Polymer Modified Electrodes

based on

Ruthenium and Osmium Poly(Pyridyl) Complexes

1.1. INTRODUCTION

Modified electrodes differ from conventional electrodes in that a thin film of material is coated onto the electrode surface. In doing so, greater control of the electrode characteristics and surface reactivity can be achieved, thus enabling either the selective reaction of a particular analyte, or the mediation of redox reactions which are slow or not possible at a bare, unmodified electrode

The range of modifying species is vast, encompassing metal deposits and metal oxide layers, as well as organic compounds, enzymes and polymers [1-6]

The earliest method of attachment of the modifying layer to the electrode substrate involved the adsorption of unsaturated monomers [7] Subsequent methods were developed for direct covalent attachment and although multilayer coverages have been attempted in this way [8], monolayers are generally only achieved

Multilayers offer many advantages over monolayer coverage since the surface coverage can be greatly increased and a high concentration of electroactive centres can be attained [1] In addition, multilayers combine the advantages of monolayer derivatised electrodes with those of homogeneous catalytic systems. Like monolayers, multilayers offer a high localised concentration of catalytic sites with an easy separation of reaction products from the catalyst. However, because redox catalysis has been found to occur due to physical as well as chemical reasons [9], and may be unable to occur at the 2dimensional monolayer derivatised electrode [10,11], a 3-dimensional dispersion of catalytic centres may be advantageous [12]

Multilayer coverages are often achieved by modification of the electrode with a polymeric layer. For this reason polymer modified electrodes have received considerable attention [1-6]. Polymer materials offer synthetic flexibility and inherent stability as well as ease of application to electrode substrates. Methods that achieve this include electrochemical polymerisation of the monomer [13], gas phase polymerisation of the

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monomer onto the electrode surface [1,3], electrochemical precipitation of the preformed polymer [14], but most commonly, drop, dip or spin-coating of a solution of the polymer [1,3]

In addition to their use in electrocatalysis, polymer modified electrodes have also been developed in such diverse areas as photoelectrochemistry [15-18], macromolecular electronics [19,20], corrosion protection [21], electrochromics [22-24], energy storage [25], and solar energy conversion [26-28]

Electrochemical communication between the underlying electrode material and the electrolyte solution is generally achieved through the presence of an electroactive group within the layer, as in the case of electrostatically incorporated or coordinatively attached transition metal complexes [1-6] These are termed redox polymers. Alternatively, electronically conducting polymers, notably polypyrrole, polyaniline and polybithiophene, can be used

It is clear that for the successful application of polymer modified electrodes, and for the optimisation of their design and performance, the rate and mechanism of the charge transport process should be evaluated by a systematic investigation into the factors affecting it. This thesis is concerned with such a study for redox polymers based on ruthenium^{II} and osmium^{II} poly(pyridyl) complexes covalently attached to a preformed poly(4-vinylpyridine) polymer backbone. The effect of polymer morphology and its physicochemical characteristics is considered as a function of electrolyte type and concentration, redox site loading and the coordination sphere of ¹the covalently attached redox centre. The importance of the microenvironment of the redox centre, specifically its solvation and the extent of electrostatic interaction between counter-ions, redox sites and the polymer itself, is also addressed. The study involves the evaluation of charge transport and activation parameters for electron transfer using electrochemical techniques, while the Electrochemical Quartz Crystal Microbalance (EQCM) [29-31], is used to probe interfacial mass transfer during redox processes under a number of different kinetic

3

regimes, as well as to evaluate the resident layer mass

Much attention has been paid to polymer modified electrodes containing covalently attached poly(pyridyl) complexes of Ru¹¹ and Os¹¹ There is a well developed background of synthetic chemistry for these metal complexes. They have been found to exhibit high chemical stability in a series of oxidation states and have shown themselves to be useful in fundamental studies of ground- and excited-state electron transfer processes. The chemical diversity, the photochemical behaviour and reactions at the coordinated ligands of the complexes result in them exhibiting some useful catalytic properties. In this introduction a review of the synthetic procedures, characterisation, electrochemical properties and applications of redox polymers base on osmium and ruthenium poly(pyridyl) complexes will be given. Firstly, however, a brief description of charge transport within modifying layers, and the techniques utilised in the evaluation of charge transport rates, is presented. Particular emphasis will be placed on previous studies of the redox polymers which are the subject of this thesis, however reference to other modifying materials will be made. A description of the EQCM and its application to the study of electroactive polymer layers will be presented. In Chapter 3

1.2. MODIFIED ELECTRODE PROCESSES.

The accepted mechanism for charge propagation through redox polymer films is electron-hopping between neighbouring oxidised / reduced sites [32-36] This process can be frequently described by Fickian diffusion-based models [37-39] Allowance for pin-holes [40,41], structure within the film [42,43] and non-uniform film thickness [44] can also be made The role of migration has also received considerable attention [45-50] However, as will be discussed here and in later chapters, for redox polymers based on osmium and ruthenium poly(pyridyl) complexes, the application of a diffusion model to describe the charge transport process is appropriate

1.2.1. Evaluation of Charge Transport Rates.

<u>1211</u> Theory and use of Cyclic Voltammetry

Cyclic voltammetry has found routine application for the elucidation of electrochemical reaction mechanisms and the evaluation of diffusion coefficients for solution species. In the area of modified electrodes, however, its use was originally restricted to the evaluation of surface coverages and the provision of qualitative data regarding peak position, shape etc [51,52]

More recently, cyclic voltammetry has been used for the quantitative evaluation of charge transport parameters for modified electrodes [53-61] This requires the study of the current response of the electroactive film obtained at high sweep rates. Under these conditions the depletion layer of the redox conversion does not extend to the film / electrolyte interface and solution (i e semi-infinite diffusion) conditions prevail

For a modified electrode undergoing a reversible electrode reaction under a semiinfinite diffusion regime, the peak current is defined by the Randles-Sevcik equation [62],

$$u_{\rm p} = 0.4463 \,({\rm nF})^{3/2} \,{\rm A} \,{\rm D}_{\rm ct}^{1/2} \,{\rm C} \,{\rm v}^{1/2} \,({\rm RT})^{-1/2}$$
(1.2.1)

where 1_p is the peak current, n is the number of electrons transferred, F is the Faraday constant, A is the geometric electrode area, D_{ct} is the apparent charge transport diffusion coefficient, C is the concentration of redox sites within the film, V is the scan rate, R is the gas constant and T is the absolute temperature. Other features of the cyclic voltammogram are described by the equations,

$$E_p = E_{pa} - E_{pc} = 0.0592 / n V \text{ at } 25 \text{ °C}$$
 (1.2.2)

$$1_{pa} / 1_{pc} = 1$$
 (1.2.3)

where E_{pa} and E_{pc} , I_{pa} and I_{pc} are the anodic and cathodic peak potentials and current, respectively

The Randles-Sevcik equation has been successfully applied to the evaluation of charge transport rates in the osmium and ruthenium redox polymers under consideration here [56-61], as well as for other electrode-modifying materials [53-55] The apparent diffusion coefficient for the Os^{II} and Ru^{II} poly(pyridyl) polymers, termed D_{ct}(CV), is typically 10-11 to 10-10 cm²s-1, depending on the electrolyte type and concentration. In general, D_{ct}(CV) increases with increasing electrolyte concentration [57-61]. This is taken as qualitative proof of the absence of a significant migrational contribution to the charge transport process since migration is expected to result in a maximum value of D_{ct} at lower electrolyte concentrations [63]. In addition, migration is anticipated to yield a cubic dependency of D_{ct} on redox site loading when the mobility of counter-ions is much lower than the mobility of electrons [47]. In all studies of redox loading in these systems, where D_{ct}(CV) is found to increase with redox site concentration, it has never been observed to exceed a proportional relationship [58,60,61].

For surface-immobilised redox centres under certain circumstances the experimental

conditions may be such that all electroactive centres undergo redox transformation on the time scale considered. This may occur for slow cyclic voltammetric scan rates or for films exhibiting fast electron-transfer kinetics. The redox composition of the layer is thus in thermodynamic equilibrium with the electrode potential (the Nernst condition) and surface, or thin layer behaviour is observed. This is described by the equations [64],

$$u_{\rm p} = n^2 F^2 A \Gamma_{\rm T} v / (4RT)$$
(124)

$$E_{pa} = E_{pc} \tag{125}$$

$$FWHM = 906 / n mV at 25 \circ C$$
 (126)

where FWHM denotes full peak width at half height and Γ_T is the total surface coverage of redox centres Γ_T can be estimated from the integration of the anodic or the cathodic branch of a cyclic voltammogram exhibiting thin layer behaviour, using the relationship,

$$\Gamma_{\rm T} = Q / nFA \tag{127}$$

.

where Q is the background-corrected charge passed. The features of surface waves are typically observed for the ruthenium and osmium metallopolymers at scan rates less than 5 mVs^{-1} [56,57,59,65]

Because in modified electrodes the cyclic voltammogram may not exhibit pure diffusional or true surface wave characteristics, the diffusion equations within a finite diffusion space have been considered [66,67] The theory has been developed for modifying layers exhibiting Nernstian equilibrium processes [66] and for layers where kinetic limitations exist [67] The approach is beyond the scope of this thesis but has been observed to yield the same quantitative evaluation of $D_{cl}(CV)$ for these redox polymers as those obtained using Randles-Sevcik analysis [57]

<u>1212</u> Theory and use of Potential Step Techniques

The evaluation of charge transport processes is most commonly performed using potential step techniques (chronoamperometry and chronocoulometry)

Fig 1 2 1 illustrates the concentration profile of an electroactive species within a polymer film at various times, t, after application of a potential step. For the evaluation of charge transport rates the time scale of the experiment is generally chosen so that the depletion layer does not extend to the film / electrolyte interface. This ensures semi-infinite diffusion conditions and enables the application of the Cottrell equation to describe the current decay [62],

$$u(t) = nFAD_{ct}^{1/2} C(\pi t)^{-1/2}$$
(128)

where the symbols have their usual meaning

For polymers based on osmium and ruthenium poly(pyridyl) complexes, linear Cottrell plots with zero intercepts are obtained for times up to 20 ms [83-88] This, in conjunction with the absence of a peak in the it^{1/2} vs t^{1/2} plot [56,61], indicates the lack of a migrational contribution to the observed response [47,68-70] The apparent diffusion coefficient thus measured, designated $D_{ct}(PS)$, is the same (within experimental error) for anodic and cathodic processes [61] In addition, $D_{ct}(PS)$ has the same dependency on electrolyte concentration and redox site loading as those observed for $D_{ct}(CV)$ [58,60,61] These features are consistent with a current response which is primarily diffusional in character

The evaluation of D_{ct} through these redox polymers is often dependent on the experimental time scale of the electrochemical measurement, with $D_{ct}(PS)$ greater than $D_{ct}(CV)$ [56-61] It has been proposed that this is due to $D_{ct}(PS)$ reflecting different equilibria processes than those observed on longer time scales [61] The difference between $D_{ct}(PS)$ and $D_{ct}(CV)$ is determined by the redox site loading, the nature and

Fig 1 2 1Concentration profiles for electroactive species within a polymer filmafter application of an oxidising potential step



concentration of the electrolyte and the nature of the polymer backbone This suggests that it is the physico-chemical properties of the polymer layer which influences the mobility and availability of mobile species and, consequently, the equilibria established at different time scales

<u>1213.</u> Theory and use of Sampled Current Voltammetry

 $D_{ct}(CV)$ and $D_{ct}(PS)$ values are indicative of homogeneous charge transport For the evaluation of kinetic parameters associated with heterogeneous electron tranfer within modifying layers, Sampled Current Voltammetry (SCV) is used [58-60,71-82] This involves the application of a potential step waveform of increasing amplitude, covering a potential window where initially no redox reaction occurs, to one where the current response is diffusion controlled. The current decay is sampled at different times, τ , and for the limiting current a plot of η_{lim} vs τ -1/2 obeys the Cottrell equation (1.2.8). The current-potential relationship for the SCV of modified electrodes is found to exhibit typical Butler-Volmer kinetics and for oxidation processes is given by [83],

$$E = E^* + \frac{RT}{\alpha_+ nF} \ln \left\{ X \left[\frac{1.75 + X^2 [1 + \exp(-\xi)]^2}{1 - X [1 + \exp(-\xi)]} \right]^{1/2} \right\}$$
(1.2.9)

with

$$E^* = E^\circ - \frac{RT}{\alpha_+ nF} \ln \left\{ \frac{4}{\sqrt{3}} \frac{k^\circ \sqrt{\tau}}{\sqrt{D_{\text{CT}}} (\text{PS})} \right\}$$
(1 2 10)

where E is the electrode potential, E^o the reversible half wave potential, α is the anodic transfer coefficient, k^o is the standard rate constant for heterogeneous electron transfer, ξ a dimensionless parameter expressed as {(nF/RT)(E-E^o)}, τ the sampling time and x is the ratio of the current at potential E to the anodic limiting diffusion controlled current The other symbols have their usual meaning

A plot of the right hand side of Eqn 1 2 9 vs E is linear with a slope of $(\alpha nF/RT)$ and intercept E* Assuming $D_{ct}(PS)$ is the same for anodic and cathodic processes, and using the value of the formal potential obtained from CV, ko and α can be evaluated

Due to the non-conducting nature of the polymer backbone, initial charge injection can only take place at the immobilised metal centres [84,85] The rate of heterogeneous electron transfer, therefore, is generally found to be considerably less for metallopolymers than for solution phase species [58-60,76,82]

<u>1214</u> Evaluation of Activation Parameters

For a more definitive evaluation of the processes involved in charge transport, activation parameters are calculated [56-61,65,73,81,86-92]

Activation parameters for the homogeneous charge transport process can be determined from the temperature dependence of $D_{ct}(CV)$ and $D_{ct}(PS)$ The mechanisms involved in charge transport (i e electron hopping, polymer chain and counter-ion motion) are activated processes and can be described by an Arrhenius-type relationship [93],

$$D_{ct} = D_{ct} \circ \exp(-E_a / RT)$$
 (1 2 11)

where E_a is the activation energy (Jmol⁻¹), and D_{ct}^o is a pre-exponential factor for physical diffusion. The reaction enthalpy, $\Delta H^{\#}$, is given by,

$$\Delta H^{\#} = E_a - RT \tag{12.12}$$

The entropy of activation, $\Delta S^{\#}$ (Jmol⁻¹K⁻¹), can be estimated via the Eyring equation [94],

$$D_{ct^0} = e \,\delta^2 \,(k_b T/h) \exp(\Delta S^\# / R)$$
 (1 2 13)

where e is the base of the natural log, δ is intersite separation between redox centres, k_b is the Boltzmann constant and h is Planck's constant

Because the intersite separation can only be approximated, the absolute values of the activation parameters are of limited accuracy Despite this, the rate limiting cases of iondiffusion and polymer chain motion can be distinguished [56-61,95] The change in intersite distance expected due to polymer swelling at higher temperatures does not change the sign of the entropy term, and positive entropies can be assigned to disordering polymer chain motion [88] Negative entropies are associated with either electron self-exchange, or counter-ion motion rate determining steps [83-88,113]

1.3. REVIEW OF POLYMERS BASED ON Os^{II} AND Ru^{II} POLY(PYRIDYL) COMPLEXES

1.3.1. Synthetic Considerations.

For the successful application of Ru^{II} and Os^{II} poly(pyridyl) complexes the immobilization in a matrix has long been recognised as necessary [96] Metallopolymeric materials offer a convenient way of creating an interface by physical adsorption onto electrodes or onto particles in solution [1-6] The extension of homogeneous solution chemistry to polymeric materials also provides a facility for the incorporation of both catalytic and chromophoric sites, as well as the presence of multiple chromophoric sites, in a fixed chemical matrix [17] In the case of solar energy conversion, immobilisation may inhibit non-productive back reactions and thus promote more efficient energy capture [97,98]

Attachment of these complexes to preformed polymer backbones can be achieved through the electrostatic incorporation of the charged complexes into cationic / anionic polymer films [33,81,99-105], or through the covalent attachment of the metal centre to any polymer containing a pendant coordinating group [17,56,65,96,106-116] Alternatively, the reductive polymerisation of vinyl-containing metal complex monomers can lead to the formation of films of varying thickness [117-127], although extensive cross-linking is a feature of materials formed in this way. An important feature of these methods is that they enable the redox and excited state behaviour of the monomeric analogues to be carried over to the polymeric materials [107]. Preparation through covalent attachment, however, offers many advantages. These include a higher level of definition from characterisation as well as greater synthetic control and reproducibility.

The synthesis of metallopolymers containing poly(pyridyl) Ru and / or Os compounds by covalent attachment of the metal complex to a polymer backbone is based on the labile chloride ions in the complex cis-M(bipy)₂Cl₂, where M is either Ru or Os [128,129] The removal of the first chloride occurs readily by refluxing in methanol or ethanol, while removal of the second chloride requires aqueous-solvent mixtures [56,65,114,115] Consequently, for the synthesis of the mono-substituted metallopolymers (i e $[M(bipy)_2(Pol)Cl]^+$), refluxing in ethanol is sufficient, whereas for the bis-substituted materials (i e $[M(bipy)_2(Pol)_2]^{2+}$), water is added to the reaction mixture Because of the larger ligand-field splitting in osmium complexes they are much less reactive than their ruthenium analogues, and longer reaction times are therefore generally required [65] The coordination sphere for the bis- and mono-substituted polymers, based on poly(4-vinyl pyridine), (PVP), is shown in Fig 1 3 1

For the synthesis of the bis-substituted materials, the isolated bis-aquo complex cis- $[M(b_1py)_2(H_2O)_2]^{2+}$ [113,114,130] or $[M(b_1py)_2CO_3]$ [131,132] (which is converted to the bis-aquo complex in solution) may be used as starting materials [108,115,116] This is generally found to reduce reflux times. It has also been found that for the ruthenium metallopolymers a high concentration of polymer in the reaction mixture (*ca* 1 0 M) and / or a high polymer to metal ratio, yields the bis material [96,133]

These synthetic procedures offer considerable flexibility, with materials of different metal loadings being prepared simply by varying the relative molar amounts of the reactants [65,96,114,115] Loadings are expressed as the ratio, n, of the number of units in the polymer backbone to the number of metal centres. Thus, in the material [Ru(bipy)₂(PVP)₅Cl]Cl, n is 5, with one redox centre coordinatively attached to one out of every 5 monomer units. For the bis-substituted materials, two monomer units are coordinated per redox site, and n-2 will be free (see Fig 1 3 1). Routinely, metal loadings ranging from 1 5 (materials of the highest metal content) to 1 25 are only considered [58,60,61,71]. Although more dilute loadings have been synthesised [113,115], the presence of both bis- and mono-substituted centres prevents a precise evaluation of the metallopolymer composition. This, coupled to the necessarily smaller electrochemical

Fig 1 3 1 Coordination sphere of the metal centre for (a) mono- and (b) bissubstituted PVP-based redox polymers X varies from 5 to 25

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response of these materials, makes them unsuitable for detailed investigations

The polymer backbone can be changed, provided it has a pendant coordinating group, thus enabling materials of differing physico-chemical characteristics to be prepared Polymers that have been considered to date include include PVP [12,24,57-61,71,96,106-114], poly(N-vinylimidazole) (PVI) [65,115,116] and a series of 4-vinylpyridine / styrene copolymers (PVP / PS) [56] By reacting the metal complexes with preformed polymer, cross-linking during synthesis is avoided and soluble polymers are obtained The materials can therefore be characterised both in solution and as thin films on electrode surfaces

While the ligands in the metal complexes used as starting materials are almost exclusively bipy, the use of 2,2',2"- terpyridine (trpy), has also been investigated in the ruthenium polymer $[Ru(trpy)(bipy)(PVP)_n]^2+ [107]$ However, because of the unfavorable bite angle of the trpy ligand [134], the photolability of these complexes is greater and ligand loss is facilitated Indeed, Os^{II} trpy complexes are known to be photolabile [135] For this reason bis-bipyridyl complexes are preferred

The non-pyridyl ligand in the mono-substituted materials is usually chloride Other ligands can be introduced by the thermal substitution of the aquo group in the ruthenium polymer $[Ru(bipy)_2(PVP)(H_2O)]^{2+}$ [108] In this way the corresponding polymers $[Ru(bipy)_2(PVP)_nL]^{x+}$ have been prepared with L = N₃-, NO₂-, OH-, CN- (x=1), L = CH₃CN (x=2) and L = NO+ (x=3)

1.3.2. Characterisation.

The preformed polymer backbone can be characterised by conventional methods, such as spectroscopy and elemental analysis, while its molecular weight and glass transition temperature can also be determined. Although there is no evidence that the molecular weight has a strong influence on the electrochemical properties of the electroactive coatings, it has been found that high molecular weight materials adhere much better to the electrode substrate and so enhance the lifetime of the electrode. Thermal analysis of osmium and ruthenium polymers based on PVP has shown that the glass transition temperature of the metallopolymers is well above 100 °C [56,65]. This suggests that glass transitions do not have to be taken into account when analysing the electrochemical behaviour of these coatings. Analysis of thin layers of the metallopolymers can be carried out using normal surface analysis techniques. Both scanning tunnelling spectroscopy (STM) [136], and ESCA [107] have been used to investigate the surface structure. STM analysis has shown that the surface of the coatings does change considerably after electrochemical processes, most likely as a result of swelling of the metallopolymer film in the electrolyte used (H₂SO₄)

In these modifying materials the nature of the coordination around the central metal atom is of prime importance. For both ruthenium and osmium polymers the coordination sphere will greatly affect the redox potential of the metallopolymer obtained. During the synthesis of the materials, therefore, the reaction is continuously monitored. This is most conveniently done using electronic spectroscopy.

Both emission and absorption spectroscopy have proven useful in the characterisation of these metallopolymers [56,65,106-108,114-116,133] For the ruthenium materials especially, the visible absorption spectrum is characteristic of a particular ruthenium moiety Ruthenium compounds exhibit two bands in the visible region of the spectrum. These have been assigned to metal-to-ligand charge transfer

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(MLCT) transitions from Ru($d\pi$) to bipy(π^*) orbitals [137,138] The positions of the absorption maxima are governed by the σ -donor and π -acceptor properties of the ligands, and through comparison of the spectrum with those of monomeric model compounds, the coordination sphere of the ruthenium centre in the polymeric materials can be verified [17,56,65,96,107,108,114-116,133]

The absorption spectra of the osmium metallopolymers, while comparable to the monomeric models [65], are typically more complicated than those of the analogous ruthenium compounds. This is a consequence of the mixing of singlet and triplet excited states in Os¹¹ complexes which enable formally forbidden transitions, which are not seen for ruthenium complexes, to be observed for osmium [135]. Because of the complicated nature of the uv-vis absorption spectrum, definitive assignments to the coordination sphere of the osmium centre are rarely made by this technique alone [65].

In general, the ratio of metal centres to repeating units of the polymer backbone is based on the ratio of the starting materials, assuming complete reaction. However, approximate extinction coefficients, based on the mononuclear compounds, have been evaluated [17,65,107,133] and are useful in verifying the metal loading. Due to complications from the different levels of hydration in the homopolymer and the subsequent metallated polymer, this can only give an indication of the loading. In addition, subtle differences in the π -acceptor and σ -donor characteristics of the monomeric and polymeric ligands will affect the extinction coefficient [139]. Other considerations include steric effects in the polymer matrix [140], as well as changes in the microenvironment of the complex when confined to the polymer backbone [17]

The main features of the photophysical processes in poly(pyridyl) ruthenium¹¹ complexes are illustrated in Fig 1 3 2. The absorption, as already mentioned, is due to a ¹MLCT transition [137,138]. Due to the mixing of singlet and triplet spin states [138], fast intersystem crossing (ISC) occurs to a ³MLCT state with an efficiency of *ca* 1 [141]. Emission from this triplet state to the ground state (k_r) or, alternatively, radiationless

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Fig 1 3 2 Photophysical processes in ruthenium poly(pyridyl) complexes



deactivation (k_{nr}) can occur [137] Because of the strong similarities in the electronic spectra of the metallopolymers with those of the monomeric analogues, emission in the metallopolymers is also thought to originate from bipy-based ³MLCT states In general, for osmium complexes the ³MLCT state is lower in energy [135] and, consequently, no emission is observed for some osmium metallopolymers [65]

An alternative deactivation pathway from the ³MLCT state is the population of the ³MC state [142,143] In this state the electron occupies an antibonding, metal-based orbital resulting in distortion of the metal-ligand axes as well as the weakening of the Ru-N bonds Radiationless deactivation from this state may occur or, in some cases, photo-decomposition of the complex [142,143] In the case of unidentate ligands this results in ligand loss followed by coordination of a substitute ligand, often solvent [17] For the mono-substituted ruthenium polymers, with varying polymer backbones, the non-chromophoric, unidentate ligand is lost in aqueous acids and H₂O is coordinated [112,115,116] This can be observed for thin films of the metallopolymer by the change in the oxidation potential of the Ru^{II/III} couple due to the photochemically induced change in the coordination sphere

The ligand-exchange reactions for ruthenium redox polymers provide a useful pathway to polymeric materials which are difficult to synthesise by normal means [112] Upon photolysis of this polymer in acetonitrile based electrolytes CH₃CN is the substituting ligand, although in the presence of the perchlorate anion ClO₄- also becomes coordinated under certain conditions [110] For the analogous PVI polymer similar reactions are observed, although in H₂SO₄ electrolyte an equilibrium is established between the aquo and sulphate complex [115]

For the bis-substituted materials the only unidentate ligands present are the pyridine moleties of the polymer backbone Because of their close proximity they are readily available for coordination again and the facility of ligand recapture exists [17] However, as with mono-substituted materials, solvent molecules become coordinated [109,112]

Because the ³MC state for osmium is *ca* 30% higher in energy than in ruthenium [135], and the ³MLCT state lower, the energy gap for population of the ³MC is much greater Osmium complexes are thus rarely seen to undergo photosubstitution reactions This is graphically illustrated in Fig 1 3 3 which shows the photolysis of the mixed-metal polymer, $[Os(bipy)_2(PVP)_{10}Cl]$ +/ Ru(bipy)_2(PVP)_{10}Cl]+ The generation of the Ru aquo complex results in a shift in the formal potential of the Ru^{II/III} couple from *ca* 0 750 V to *ca* 0 90 V (vs SCE), while the Os^{II/III} redox couple is unaffected

The most important characteristic for these redox polymers is their electrochemical behaviour. The metallopolymers possess a metal based M^{II/III} oxidation. The first reduction of the M^{II} metallopolymers is thought to be bipy-based [128,137,138]. The potentials of these reductions can be empirically related to the potential of the M^{II/III} oxidation in that, the easier the metal oxidation is, the more difficult the reduction of the ligand becomes [135]. Because of the bonding interaction between the ligand π^* orbitals and the overlapping d π orbitals of the metal, the greater the electron density at the metal the more difficult it is to put an extra electron onto the ligand. This reduction occurs at quite negative potentials and has not been investigated in any great detail

As observed for the electronic spectroscopy of these materials, the formal potential of the Mu/III oxidation, coated as thin films on electrode surfaces, is sensitive to the nature of the metal coordination sphere [17,56-61,65,106-116] The nature of the moiety can be identified by comparison of the redox potential with those of analogous polymeric and monomeric compounds Typically, the oxidation for Os^{II/III} is easier, by 0 3 V to 0 5 V, compared to the analogous Ru^{II/III} oxidation [129,135] The Os^{III/IV} oxidation is also at a much lower potential and may be seen [65] For ruthenium complexes, however, the separation in potential of the Ru^{III/III} and Ru^{III/IV} couples is greater, and the Ru^{III/IV} oxidation is rarely observed [144]

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Fig 1 3 3 Photochemically-induced ligand exchange reactions within a polymer film of [Os(bipy)₂(PVP)₁₀Cl]+/Ru(bipy)₂(PVP)₁₀Cl]+ Electrolyte is 1 0 M HClO₄, scan rate is 100 mVs⁻¹ The interval between scans is 30 s [taken from Ref 65]



1.3.3. Applications.

The ultimate goal of polymer modified electrodes is their use in practical applications The rapid charge transfer rates, the chemical and physical robustness, and the synthetic flexibility of the metallopolymers under review here, make them ideally suited for such purposes

The excited-state electron transfer reactions of the Ru polymer $[Ru(bipy)_2(PVP)_2]^{2+}$, and the potential application of this material as a photosensitiser, has been investigated [17,18] In solution, both oxidative and reductive quenching of the metallopolymeric excited states is observed. However, in the polymer both the quenching process (which converts the excited-state energy to stored redox energy) and the back electron transfer recombination event, are slower than for the $[Ru(bipy)_3]^{2+}$ complex. This is attributed to the relatively more inaccessible redox sites in the polymeric material [17]. When coated as a thin film, using n-TiO₂ as the semiconductor electrode substrate, films of this ruthenium metallopolymer were found to yield sensitised anodic photocurrents [17]. With time a build up of Ru^{III} centres occured which reduced the photocurrent By the addition of hydroquinone (an electron donor) to the contacting electrolyte, these Ru^{III} sites were rereduced resulting in more prolonged and greater photocurrents. Similarly, using Pt as the electrode substrate and $[Co(C_2O_4)_3]^{3-}$ as the sacrificial oxidative quencher, large cathodic photocurrents are observed with this polymer [18]

Mediated electrodeposition of metal particles onto films has been demonstrated for both osmium and ruthenium metallopolymers [145,146] For $[Ru(bipy)_2(PVP)_nCl]$ + films on n-MoSe₂ and n-WSe₂ electrodes, the mediation of the charge transfer of a hole from the crystal valence band of the semi-conductor substrate to certain ions in solution has been shown [111]

However, it is the use and development of these metallopolymers as electroanalytical sensors that has received the greatest attention [116,147-158] As mentioned previously,

the use of surface modification can reduce, and even eliminate, the overpotential of a kinetically slow redox reaction at a bare electrode. In addition, modifying materials can increase the rate of the reaction. For redox polymer modifying materials, this is achieved by mediation of the analyte redox reaction by the self-exchange reaction of the redox centres of the modifying layer. For the mediating process involving the oxidation of the surface bound species RED, the reaction is,

RED _____
$$OX + e^-$$
 (1.3.1)

 $OX + Y \longrightarrow RED + Z$ (132)

where RED and OX are the reduced and oxidised forms of the redox polymer, and Y and Z are the reduced and oxidised forms of the analyte

The characterisation of such mediation reactions has been carried out for both osmium- [153] and ruthenium- [12] containing polymers Both the approach of Albery *et al* [159] and Saveant *et al* [12] allow for the diagnosis of the mediation kinetics in terms of the relative rates of electron transfer, substrate diffusion and the rate of the catalytic reaction itself

The mediated oxidation of the $Fe^{II/III}$ couple by $[Ru(bipy)_2(PVP)_nCI]^+$ in HCl electrolyte was found to be controlled, in thick coatings, by substrate diffusion from the bulk electrolyte to the polymer layer [12] As the layer thickness is reduced, kinetic limitations within the layer occur and the catalytic reaction becomes the rate determining step

For the mediated reduction of $Fe^{III/II}$ at $[Os(bipy)_2(PVP)_nCl]^+$ modified electrodes in sulphuric acid, for thinner layers the mediated reaction again occurs throughout the layer and is controlled by the layer thickness. With increasing coverages, total catalysis for the Fe^{III} reduction is observed, i.e. the diffusion of the substrate from solution is rate determining. In contrast to this, in perchloric acid electrolyte, where compaction of the
osmium polymer is expected, the mediated reduction of Fe^{III} is at the film / electrolyte interface for all surface coverages. This indicates little substrate permeation into the layer in this electrolyte. The mediation kinetics are therefore seen to be controlled, not only by electrode potential and film thickness, but also by the morphological changes imposed on the polymer structure by the contacting electrolyte and its subsequent effect on charge transport processes and substrate diffusion [153]. Similar electrolyte effects have been observed for the mediated oxidation of Fe^{III} by [Ru(bipy)₂(PVI)₅Cl]+ polymer films [116,148]

Because of the relative positions of formal potentials, Fe^{II} can only be oxidised at $[Ru(bipy)_2(PVP)_nCl]^+$ modified electrodes [12], while the Fe^{III} reduction can only proceed at $[Os(bipy)_2(PVP)_nCl]^+$ modified surfaces [153] This allows for the use of these materials for the simultaneous, and highly selective, speciation of Fe^{III} and Fe^{II} This has been achieved using a flow injection procedure, by the construction of a two-electrode sensor, one modified with the osmium polymer, the other with the ruthenium polymer [156]

 $[Ru(bipy)_2(PVP)_5Cl]^+$ has also been used in the determination of nitrite and a number of dithiocarbamate metal complexes in flow systems and an increase in sensitivity compared to the bare electrode is observed [150] Nitrite determination using the osmium polymer $[Os(bipy)_2(PVP)_{10}Cl]Cl$ has also been studied [155]

The diffusion of substrates within polymer films has been evaluated using doublecoated materials [12,160] With an underlying layer of polymeric 1-hydroxyphenazine, which can reduce Fe^{II/III}, the decrease in the limiting current observed at this layer, due to the presence of an overlying [Ru(bipy)₂(PVP)_nCl]+ layer, is indicative of the substrate diffusion through the ruthenium polymer For Fe^{III} ions, high diffusion rates were observed within the ruthenium polymer matrix. This was considered to be a result of the swelling of the polymer in acidic media due to the electrostatic repulsion of the protonated pyridine units of the polymer backbone The use of these metallopolymers in flowing systems can be restricted due to instability of the polymer layer and its gradual loss from the electrode surface A number of stabilisation procedures have been investigated [151,157] Crosslinking of the polymer using uv light, and the formation of bilayers using either a conducting or non-conducting polymer layer over the ruthenium polymer, have been attempted [151] Although these procedures reduce sensitivity, the lifetime in flowing solutions is very much enhanced An alternative approach to the stabilisation of the ruthenium polymer layers is the incorporation of hydrophobic styrene moleties into the PVP backbone [56,157] For the mediated oxidation of nitrite, it was found that a considerable improvement in stability is seen in the styrene-containing copolymers, compared to the PVP materials [157] Stability may also be enhanced by use of modified carbon paste electrodes [152]

Recently, the use of redox hydrogels has been reported [161-163] In the osmium polymer, $[Os(bipy)_2(PVP)_nCl]^+$, the PVP backbone has been quaternised, and both hydrophilic groups and groups capable of amide bond formation incorporated [161,162] In the presence of glucose oxidase and a polyamine cross-linking agent, robust, cross-linked, electroactive films are obtained. The polymer gel is stable on the electrode surface, and gives a highly active and selective response for the oxidation of glucose. The enzyme, however, is sensitive to oxidation by O₂ [161]. In an extension of this work, a similar hydrogel was formed using the osmium polymer and was immobilised on a microelectrode [162]. Compared to macroelectrodes based on the same redox epoxy hydrogel, the microelectrode yields a ten-fold increase in the current density, an improved signal-to-noise ratio, lower limits of detection, reduced sensitivity to oxygen and a more rapid response time to changes in glucose concentration. This is attributed to greater efficiency in the electrical communication, via the osmium centres, between the active enzyme and the electrode surface.

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1.4. CONCLUSIONS.

The above discussion clearly illustrates the many attractive features of metallopolymers based on ruthenium and osmium poly(pyridyl) complexes The ease of synthesis and the wide range of redox potentials that can be obtained make these polymers ideal materials for the modification of electrode surfaces Their use as electroanalytical sensors has been demonstrated and current investigations are concerned with stabilisation procedures to enable the development of a physically robust, practical sensor

This thesis, however, is concerned solely with a detailed investigation of the affects of polymer morphology on charge transport and mass transfer mechanisms within these electrode modifying materials. To date, from the results of electrochemical measurements, it has been shown that the charge transport rate is very much dependent on the physico-chemical properties of the film, as dictated by the metal loading, electrolyte type and concentration and the nature of the polymer backbone. In this study a more direct insight into polymer structure is sought through a combination of existing electrochemical data and EQCM analysis.

1.5. REFERENCES

- 1 A R Hillman, Electrochemical Science and Technology of Polymers, R G Linford (Ed), Elsevier, Amsterdam (1987), Chs 5 & 6
- 2 W J Albery and A R Hillman, R.S.C. Annual Report, (1981), 78, 377
- 3 R W Murray, Electroanalytical Chemistry, A J Bard (Ed), M Dekker, New York, (1984), 13, 191
- 4 H D Abruna, Coord Chem Rev., (1988), 86, 135
- 5 K D Snell and A G Keenan, Chem Soc Rev, (1979), 8, 259
- P N Bartlett, Busensors, Fundamentals and Applications, A P F Turner,
 G S Wilson and I Karube (Eds), Oxford University Press, New York (1987),
 Ch 13
- 7 R F Lane and A T Hubbard, J Phys Chem, (1973), 77, 1401, 1411
- 8 J M Bolts and M S Wrighton, J Am Chem Soc, (1979), 101, 6179
- 9 C P Andrieux, J M Dumas-Bouchiat and J M Saveant, J Electroanal Chem, (1978), 87, 39
- 10 C P Andrieux and J M Saveant, J Electroanal Chem, (1978), 93, 163
- 11 C P Andrieux, J M Dumas-Bouchiat and J M Saveant, J Electroanal Chem, (1981), 123, 171
- 12 C P Andrieux, O Haas and J M Saveant, J Am Chem Soc, (1986), 108, 8175
- 13 A Bettelheim, B A White, S A Raybuck and R W Murray, *Inorg Chem*, (1987), 26, 1009
- 14 A Merz and A J Bard, J Am Chem Soc, (1978), 100, 3222
- 15 D A Buttry and F C Anson, J Am Chem Soc, (1982), 104, 4824
- 16 I Rubenstein and A J Bard, J Am Chem Soc, (1981), 103, 5007

- 17 J M Calvert, J V Caspar, R A Binstead, T D Westmoreland and T J Meyer, J Am. Chem Soc, (1982), 104, 6620
- 18 T D Westmoreland, J M Calvert, R W Murray and T J Meyer, J Chem Soc Chem Commun, (1983), 65
- 19 C E D Chidsey and R W Murray, Science, (1986), 231, 25
- 20 R W Murray, A G Ewing and R A Durst, Anal Chem., (1987), 59, 379A
- 21 T Ohsaka, K Kanako and K Yoshino, Jap J Appl Phys, (1984), 23, L663
- 22 K Itaya, H Akahoshi and S Toshima, J Electrochem Soc , (1982), 129, 762
- 23 G F Kirkbright, R Narayanaswamy and N A Welti, Analyst, (1984), 109, 15
- 24 Z Zhujun and W R Seitz, Anal Chim Acta, (1984), 160, 47
- T Ohsaka, K Naoi, S Ogano and S Nakamura, J Electrochem Soc, (1987), 134,
 2096
- 26 N Oyama, S Yamaguchi, N Kaneko and A Yamada, J Electroanal Chem, (1982), 139, 215
- 27 D C Bookbinder and M S Wrighton, J Am. Chem Soc, (1980), 102, 5123
- 28 H D Abruna and A J Bard, J Am Chem Soc, (1981), 103, 6898
- 29 C Lu and A W Czanderna (Eds) Applications of Piezoelectric Crystal Microbalances, Vol 7, Elsevier, New York, (1984)
- 30 M R Deakin and D A Buttry, Anal Chem., (1989), 61, 1147A
- D A Buttry, Applications of the Quartz Crystal Microbalance to Electrochemistry,
 in A J Bard (Ed) Electroanalytical Chemistry, Marcel Dekker, New York, (1991),
 Vol 17, p 1-85
- 32 A Shroeder, F B Kaufman, V Patel and E M Engler, J Electroanal Chem., (1980), 113, 193
- 33 H S White, J Leddy and A J Bard, J Am Chem Soc, (1982), 104, 4811
- 34 T P Henning, H S White and A J Bard, J Am Chem Soc, (1981), 103, 3937

- N A Surridge, J C Jernigan, E F Dalton, R P Buck, M Watanabe, H Zhang,
 M Pinkerton, T T Wooster, M L Longmire, J S Facci and R W Murray, *Faraday* Discuss Chem Soc , (1989), 88, 1
- 36 I Fritsch-Faules and R W Murray, J Electroanal Chem, (1989), 263, 237
- 37 C P Andrieux and J M Saveant, J Electroanal Chem., (1980), 111, 377
- 38 E Laviron, J Electroanal Chem, (1980), 112, 1
- 39 K Shigehara, N Oyama and F C Anson, J Am. Chem. Soc, (1981), 103, 2552
- 40 J Leddy and A J Bard, J Electroanal Chem., (1983), 153, 223
- 41 J M Saveant, J Electroanal Chem, (1991), 302, 91
- 42 F C Anson, J M Saveant and K Shigehara, J Am Chem. Soc , (1983), 105, 1096
- 43 P He and X Chen, J Electroanal Chem, (1988), 256, 353
- K Aoki, K Tokuda, H Matsuda and N Oyama, J Electroanal Chem., (1984), 176,
 139
- 45 R P Buck, J Electroanal Chem, (1987), 219, 23
- 46 R P Buck, J Electroanal Chem., (1988), 258, 1
- 47 C P Andrieux and J M Saveant, J Phys Chem, (1988), 92, 6761
- 48 J M Saveant, J Electroanal Chem, (1988), 238, 1
- 49 J M Saveant, J Electroanal Chem, (1988), 242, 1
- 50 J M Saveant, J Phys Chem, (1988), 92, 4526
- 51 G Inzelt, J Backsai, J Q Chambers and R W Day, J Electroanal Chem, (1987), 201, 301
- 52 G Inzelt, L Szabo, J Q Chambers and R W Day, J Electroanal Chem, (1988), 242, 265
- 53 S B Khoo, J K Foley and S Pons, J Electroanal Chem, (1986), 215, 273
- 54 K M O'Connell, E Waldner, L Roullier and E Laviron, J Electroanal Chem., (1984), 162, 77
- 55 PK Ghosh and A J Bard, J Electroanal Chem., (1984) 169, 113

56 D Leech, R J Forster, M R Smyth and J G Vos, J Mater Chem, (1991), 1, 629

r

- 57 R J Forster, A J Kelly, J G Vos and M E G Lyons, J Electroanal Chem, (1989), 270, 365
- 58 R J Forster and J G Vos, J Electroanal Chem., (1991), 314, 135
- R J Forster and J G Vos, J Inorganic and Organometallic Polymers, (1991), 1,
 67
- 60 R J Forster and J G Vos, Electrochum Acta, (1992), 37, 159
- 61 R J Forster, J G Vos and M E G Lyons, J Chem. Soc Faraday Trans, (1991), 87, 3761
- 62 A J Bard and L R Faulkner, Electrochemical Methods, Fundamentals and Applications, Wiley, New York, (1980)
- 63 K Doblhofer, H Braun and R Lange, J Electroanal Chem, (1986), 206, 93
- 64 D Mohilner, J Electroanal Chem, (1966), 1, 241
- 65 R J Forster and J G Vos, Macromolecules, (1990), 23, 4372
- 66 K Aoki, K Tokuda and H Matsuda, J Electroanal Chem, (1983), 146, 417
- 67 K Aoki, K Tokuda and H Matsuda, J Electroanal Chem, (1984), 160, 33
- 68 P Daum and R W Murray, J Phys Chem, (1981), 85, 389
- 69 WTYap and RA Durst, J Electroanal Chem, (1987), 216, 11
- 70 W T Yap, R A Durst, E A Blubaugh and D D Blubaugh, J Electroanal Chem, (1983), 144, 69
- 71 R J Forster, J G Vos and M E G Lyons, J Chem Soc Faraday Trans, (1991), 87, 3769
- N Oyama, T Ohsaka, M Kaneko, K Sato and H Matsuda, J Am Chem Soc,
 (1983), 105, 6003
- N Oyama, T Ohsaka and T Ushirogouchi, J Phys Chem, (1984), 88, 5274
- T Ohsaka, N Oyama, K Sato and H Matsuda, J Electrochem Soc, (1985), 132,
 1871

- 75 N Oyama, T Ohsaka and T Shimidzu, Anal Chem., (1985), 57, 1526
- 76 T Ohsaka, T Okajima and N Oyama, J Electroanal Chem., (1986), 215, 191

7

- N Oyama, T Ohsaka, H Yamamoto and M Kaneko, J Phys Chem., (1986), 90,
 3850
- 78 T Ohsaka, H Yamamoto and N Oyama, J Phys Chem., (1987), 91, 3775
- 79 K Chiba, T Ohsaka and N Oyama, J Electroanal Chem., (1987), 217, 239
- 80 T Ohsaka, S Kunimara and N Oyama, Electrochum. Acta, (1988), 33, 639
- 81 N Oyama, T Ohsaka, T Ushirogouchi, S Sanpei and S Nakamura, Bull Chem Soc Jpn, (1988), 61, 3103
- T Ohsaka, M Nakanishi, O Hatozaki and N Oyama, Electrochim. Acta, (1990), 35,
 63
- 83 H Matsuda, Bull Chem Soc Jpn , (1980) , 53, 3439
- 84 C Amatore, J M Saveant and D Tessier, J Electroanal Chem, (1983), 146, 37
- 85 C Amatore, J M Saveant and D Tessier, J Electroanal Chem, (1983), 147, 39
- 86 M E G Lyons, H G Fay, J G Vos and A J Kelly, J Electroanal Chem, (1988), 250, 207
- 87 C P Andrieux, *Electrochemistry, Sensors and Analysis*, M R Smyth and J G Vos
 (Eds), Analytical Symposia Series, (1986), 25, 235
- 88 P Daum, J R Lenhard, D R Rolison and R W Murray, J Am Chem. Soc , (1980) , 102, 4649
- 89 J Q Chambers and G Inzelt, Anal Chem, (1985), 57, 1117
- 90 S M Oh and L R Faulkner, J Electroanal Chem, (1989), 269, 77
- 91 S M Oh and L R Faulkner, J Am Chem Soc , (1989), 111, 5613
- 92 N Oyama and F C Anson, J Electrochem Soc, (1980), 127, 640
- 93 A H Schroeder and F B Kaufman, J Electroanal Chem, (1980), 113, 209
- 94 R C Bowers and R W Murray, Anal Chem, (1966), 38, 461
- 95 R Lange and K Doblhofer, J Electroanal Chem., (1987), 237, 13

- 96 J M Clear, J M Kelly, D C Pepper and J G Vos, Inorg Chun Acta, (1979), 33, L139
- 97 T Nagamura, K Takuna, Y Tsutsui and T Matsuo, Chem. Lett , (1980), 503
- 98 D Meisel, M S Matheson and J Rabini, J Am. Chem. Soc, (1978), 100, 117
- 99 Y M Tsou and F C Anson, J Electrochem. Soc , (1984), 131, 595
- 100 ETT Jones and LR Faulkner, J Electroanal Chem., (1987), 222, 201
- 101 M Majda and L R Faulkner, J Electroanal Chem., (1984), 169, 77
- 102 X Chen, P He and L R Faulkner, J Electroanal Chem., (1987), 222, 223
- 103 M Sharp, B Lindholm and E L Lind, J Electroanal Chem, (1989), 274, 35
- 104 FC Anson, YM Tsou and JM Saveant, J Electroanal Chem, (1984), 178, 113
- 105 J Leddy and A J Bard, J Electroanal Chem, (1985), 189, 203
- 106 G J Samuels and T J Meyer, J Am Chem Soc, (1981), 103, 307
- 107 J M Calvert and T J Meyer, Inorg Chem, (1981), 20, 27
- 108 J M Calvert and T J Meyer, Inorg Chem, (1982), 21, 3978
- 109 O Haas and J G Vos, J Electroanal Chem, (1980), 113, 139
- 110 O Haas, M Kriens and J G Vos, J Am Chem Soc, (1981), 103, 1313
- 111 O Haas, N Muller and H Gerischer, Electrochim Acta, (1982), 27, 991
- 112 O Haas, H R Zumbrunnen and J G Vos, Electrochum Acta, (1985), 30, 1551
- 113 J M Clear, J M Kelly and J G Vos, Makromol Chem , (1983) , 184, 613
- J M Clear, J M Kelly, C M O'Connell and J G Vos, J Chem Res ,(M), (1981),
 3039
- 115 S M Geraty and J G Vos, J Chem Soc Dalton Trans, (1987), 3073
- 116 S M Geraty and J G Vos, J Electroanal Chem., (1984), 176, 389
- 117 H D Abruna, P Denisevich, M Umana, T J Meyer and R W Murray, J Am Chem Soc, (1981), 103, 1
- 118 T Ikeda, C R Leidner and R W Murray, J Am Chem Soc, (1981), 103, 7422

- 119 T Ikeda, R H Schmehl, P Denisevich, K W Willman and R W Murray, J Am Chem. Soc, (1982), 104, 2683
- 120 J S Facci, R H Schmehl and R W Murray, J Am. Chem Soc , (1982), 104, 4959
- 121 P Denisevich, H D Abruna, C R Leidner, T J Meyer and R W Murray, Inorg Chem., (1982), 21, 2153
- 122 J M Calvert, R H Schmehl, B P Sullivan, J S Facci, T J Meyer and R W Murray, Inorg Chem, (1983), 22, 2151
- 123 P G Pickup, W Kutner, C R Leidner and R W Murray, J Am. Chem. Soc, (1984), 106, 1991
- 124 C R Leidner and R W Murray, J Am Chem Soc, (1984), 106, 1606
- 125 J M Calvert, D L Peebles and R J Nowak, Inorg Chem, (1985), 24, 3111
- J C Jernigan, C E D Chidsey and R W Murray, J Am Chem. Soc, (1985), 107,
 2824
- 127 J Leddy, A J Bard, J T Maloy and J M Saveant, J Electroanal Chem, (1985), 187, 205
- 128 B P Sullivan, D J Salmon and T J Meyer, Inorg Chem, (1978), 17, 3334
- E M Kober, J V Casper, R S Lumpkin and T J Meyer, J Phys Chem, (1986), 90,
 3722
- B Durham, S R Wilson D J Hodgson and T J Meyer, J Am Chem Soc, (1980),
 102, 600
- 131 J M Calvert, R H Schmehl, B P Sullivan, J S Facci, T J Meyer and R W Murray, Inorg Chem, (1982), 21, 2153
- 132 E C Johnson, B P Sullivan, D J Salmon, S A Adeyemi and T J Meyer, Inorg Chem, (1978), 17, 2211
- 133 T Shimidzu, K Izaki, Y Akai and T Iyoda, Polym. J., (1981), 13, 889
- G Allen, B P Sullivan and T J Meyer, J Chem Soc, Chem. Commun, (1981),
 793

- E M Kober, J V Caspar, B P Sullivan and T J Meyer, Inorg Chem, (1988), 27,
 4587
- 136 N M D Brown, H X You, R J Forster and J G Vos, J Mater Chem., (1990), 1,
 517
- 137 (a) E M Kober and T J Meyer, *Inorg Chem*, (1982), 21, 3967
 (b) E M Kober and T J Meyer, *Inorg Chem*, (1983), 22, 1614
 (c) E M Kober and T J Meyer, *Inorg Chem*, (1984), 23, 3877
- 138 A Juris, V Balzani, F Barigelletti, S Campagna, P Belser and A von Zelewsky, Coord Chem Rev., (1988), 84, 85
- 139 T Shimidzu, H Chiba, K Yamazaki and T Minato, Macromolecules, (1976), 9, 641
- 140 E Tsuchida and K Honda, Polym J, (1975), 7, 498
- 141 J N Demas and D G Taylor, Inorg Chem, (1979), 18, 3177
- 142 J vanHouten and R J Watts, Inorg Chem, (1978), 17, 3381
- B Durham, J V Casper, J K Nagle and T J Meyer, J Am. Chem Soc , (1982) , 104,
 4803
- 144 B P Sullivan, D J Salmon, T J Meyer and J Peedin, Inorg Chem, (1979), 18, 369
- 145 PG Pickup, KN Kuo and RW Murray, J Electrochem Soc, (1983), 130, 2205
- 146 R Wang, R J Forster, A P Clarke and J G Vos, Electrochim Acta, (1990), 35, 1
- JF Cassidy, A G Ross and J G Vos, Electrochemistry, Sensors and Analysis,
 MR Smyth and J G Vos (Eds), Analytical Symposia Series, (1986), 25, 269
- S M Geraty, D W M Arrigan and J G Vos, *Electrochemistry, Sensors and Analysis*,
 M R Smyth and J G Vos (Eds.), Analytical Symposia Series, (1986), 25, 303
- 149 JF Cassidy and JG Vos, J Electrochem. Soc, (1988), 135, 863
- 150 J N Barisci, G G Wallace, E A Wilke, M Meaney, M R Smyth and J G Vos, Electroanalysis, (1989), 1, 245

- 151 G G Wallace, M Meaney, M R Smyth and J G Vos, *Electroanalysis*, (1989), 1, 357
- 152 T J O'Shea, M R Smyth and J G Vos, Talanta, accepted for publication
- 153 R J Forster and J G Vos, J Chem Soc Faraday Trans , (1991) , 87, 1863
- A P Doherty, R J Forster, M R Smyth and J G Vos, Anal Chim Acta, (1991), 55,
 45
- 156 A P Doherty, R J Forster, M R Smyth and J G Vos, Anal Chem., (1992), 64, 572
- 157 D Leech, Ph D Thesis, Dublin City University, (1992)
- 158 A P Doherty, Ph D Thesis, Dublin City University, (1992)
- 159 W J Albery, M G Boutelle, P J Colby and A R Hillman, J Electroanal Chem, (1982), 133, 135
- 160 O Haas and B Sandmeier, J Phys Chem, (1987), 91, 5072
- 161 B A Gregg and A Heller, Anal Chem, (1990), 62, 258
- 162 M V Pishko, A C Michael and A Heller, Anal Chem, (1991), 63, 2268
- 163 B A Gregg and A Heller, J Phys Chem , (1991) , 95, 5970, 5976

CHAPTER 2

Synthesis, Characterisation and

Charge Transport Properties of

Poly(4-vinylpyridine) Polymers Containing

 $[M(N)_6]^{2+/3+}$ Moieties

2.1. INTRODUCTION.

Charge transport within polymer modified electrodes based on the covalent attachment of Os and Ru poly (pyridyl) complexes has been extensively studied (see Section 1 2 1) However, it is the mono-substituted materials, $[M(N)_5Cl]^{+/2+}$, that have received most attention. In a study of the bis-substituted polymer $[Ru(bipy)_2(PVP)_n]^{2+}$, consideration of the X-ray crystal structures of the complex, $[Ru(bipy)_3]^{2+}$, and the PVP backbone, led to the conclusion that intra-chain coordination of each bis(bipyridyl) ruthenium centre to adjacent pyridine units was most likely, with the tertiary structure involving a helical arrangement of redox centres around the PVP polymer strand [1] The formation of soluble polymers containing bis-substituted complexes also provides evidence for this model of intra-chain coordination [1-6] The effect of the biscoordination of the metal complex to the polymer backbone thus results in a significant change in polymer structure. The +2 charge on each redox centre (compared to the +1 charge of the mono-substituted sites) is also expected to have an affect on polymer morphology due to the increase in electrostatic repulsion between adjacent fixed sites

It is the purpose of this chapter to investigate the effect of these structural changes on the charge transport within the bis-coordinated material $[Ru(bipy)_2(PVP)_n]^{2+}$ This metallopolymer has been shown to exhibit similar photochemical and photophysical properties to $[Ru(bipy)_3]^{2+}$ [7,8], with particular interest in its potential application to the photodissociation of water by visible light. The work presented here involves a systemmatic study of the effect of redox site loading, electrolyte type and electrolyte concentration on the homogeneous and heterogeneous electron transport through thin films of this polymer. Two experimental time scales are considered for homogeneous charge transport, cyclic voltammetry, which involves extensive redox switching throughout the bulk of the polymer layer, and short time scale chronoamperometry, which probes charge transport within a localised region at the electrode substrate / polymer film interface Activation paramaters are also calculated to enable the evaluation of the rate determining step in the charge transport process Comparison with previous studies of related Ru and Os polymers is made, and a preliminary study of the osmium analogue, $[Os(bipy)_2(PVP)_{10}]^{2+}$, is also presented

The electrochemical techniques used for the evaluation of heterogeneous kinetics and the apparent diffusion coefficient for homogeneous transport, D_{ct} , are as outlined in Section 1.2 The general features of charge transport within redox polymers based on poly(pyridyl) complexes of osmium and ruthenium have also been briefly introduced in Chapter 1 These will be addressed in greater detail in the course of the discussion of the work undertaken here A general discussion of some of the observed effects of redox site loading on D_{ct} and activation parameters is first presented

Where electron self-exchange makes a significant contribution to the observed charge transport rate, an increase in the rate of charge transport with an increase in redox site loading is anticipated (i e Dahms-Ruff theory) [9,10] This has been found for a number of modifying materials [11-18] However, because electron transfer within modifying layers reflects the availability and mobility of ions and solvent, as well as the facility for the electron self-exchange reaction itself. Dahms-Ruff behaviour is not always observed While electron transfer is favoured by a reduction in intersite separation, ultimately a trade off exists and ion motion limitations within the matrix may become significant [16-18] For some electroactive polymers, D_{c1} remains insensitive to changes in redox site loading [11,19,20] Of particular relevance to the present study, is the invariance of D_{c1} to changes in the concentration of [Ru(bipy)₃]^{2+/3+} electrostatically confined within poly(styrene sulphonate) [20], and [Ru(bipy)₂Cl]^{2+/3+} in quaternised PVP (Q-PVP) [19] For transition metal complexes electrostatically incorporated into polycationic films, D_{c1} is commonly found to decrease with increasing metal content [21-31] This reflects the

increased crosslinking of the polymer films by the metal redox centres as the loading increases

The activation energy for the charge transport process, E_a , has also been found to be affected by the redox site loading [14-19,32] The results of such work are often couched in terms of the polymer morphology changes associated with changing metal content However, for an electropolymerised osmium-containing polymer, bis(bipy) bis(N-4pyridyl cinnamamide)osmium^{II} hexafluorophosphate, the variation in E_a and D_{ct} with changing intersite separation was evaluated with the polymer phase metal content remaining constant through the use of ruthenium diluant sites [15] As the osmium intersite separation was decreased, a transition in the rate limiting process from polymer motion (low D_{ct}), to electron hopping (high D_{ct}), was found

For $[Ru(bipy)_2(PVP)_nCl]^{+/2+}$, E_a was observed to decrease with increasing redox site loading [14], while for $[Ru(bipy)_2Cl]^{2+/3+}$ in Q-PVP, E_a was found to be independent of the metal loading [19] However, increased crosslinking of the Q-PVP matrix, using α, α' -dibromo-m-xylene, resulted in an increase in the activation energy for charge transport [19] Similarly, the increased crosslinking due to increased metal loading of $[Fe(CN)_6]^{3-/4-}$ in Q-PVP, was also found to increase E_a [32]

The relationship between the physico-chemical characteristics of the polymer phase, as determined by the polymer backbone, and the activation energy for charge transport processes has been clearly demonstrated for the redox centre $[Ru(b_1py)_2(Pol)_nCl]^{+/2+}$, where Pol is a PVP based co-polymer [14,19,20,33,34] In a series of polymers of increasing polystyrene content, E_a was found to decrease in perchlorate based electrolyte The perchlorate anion has been observed to crosslink these polymers through the pyridine moleties of the polymer backbone [17,35] The decrease in E_a observed was attributed to the more facile ion permeation within the less crosslinked polymer structure of higher styrene content [33] The introduction of methyl methacrylate into the PVP backbone has been found to result in a change in behaviour in certain electrolytes [34] At low

temperatures counter-ion motion limitations exist, while at temperatures greater than 285 K, a shift to polymer chain motion limitations is found

The importance of the contacting electrolyte type and concentration in determining the effects of redox site loading on D_{ct} and activation parameters has been extensively studied for the osmium containing polymers [6,16-18,35] These will be discussed in terms of the results obtained in this chapter

The role of electrolyte in determining charge transport processes is also significant, and has been studied for many modifying materials, including poly(vinyl ferrocene) (PVF) [36], tetracyanoquinodimethane (TCNQ) [37], tetracyanoethylene (TCNE) [37], tetrathiafulvalene (TTF) [38] and poly(methylviologen) [39] For both [Ru(bipy)₃]^{2+/3+} confined within poly(styrenesulphonate) [20] and thionine [40], a decrease in D_{ct} with counter-anion size was considered to represent anion transport limitations for the charge transort process Despite early appreciation of the predominant role of polymer morphology in determining the mobility of ions within polymer layers [41], it is only relatively recently that explicit reference to the dependency of polymer structure on the contacting electrolyte has been made [19,32] This will be discussed in greater detail in Chapters 3 and 4

2.2. EXPERIMENTAL.

2.2.1. Apparatus.

Uv-visible spectra were recorded using a Hewlett-Packard 342A diode array spectrophotometer Emission spectra were recorded on a Perkin-Elmer LS-5 luminescence spectrometer, equipped with a red-sensitive Hamamatsu R928 detector Spectra were recorded with an emission slit width of 10 nm at room temperature and are uncorrected for photomultiplier response

Photochemical experiments were performed using a 300 W projector lamp as a light source Electrochemical measurements were performed using an EG&G 273 PAR potentiostat / galvanostat Data capture and interrogation for chronoamperometry was achieved using a Philips 311 digital oscilloscope interfaced to a BBC microcomputer

2.2.2. Materials.

Poly (4-vinylpyridine)

4-vinyl pyridine was distilled at 45 °C under reduced pressure Poly(4-vinylpyridine) was prepared by bulk polymerisation using 2,2'-azobisisobutyronitrile (500 1 w/w) as initiator The reaction was carried out at 80 °C under an N₂ atmosphere The polymer was purified by repeated precipitation in diethyl ether from methanol, and was dried at 60 °C *in vacuo* overnight The molecular weight was estimated by viscometry in absolute ethanol, utilising the Mark-Houwink equation, $[\eta] = 2.5 \times 10^{-4} M_V^{0.68}$ [42], and was found to be *ca* 250,000 gmol⁻¹

$c_{1s}-[M(b_{1}py)_{2}Cl_{2}]$

cis-[Ru(bipy)₂Cl₂] $2H_2O$ and cis-[Os(bipy)₂Cl₂] were prepared as described in the literature [43,44] The purity of the complexes was confirmed by high performance liquid chromatography on a cation exchange resin, with uv-visible detection using a photodiode array detector

Typical yield of cis-[Ru(bipy)₂Cl₂] 2H₂O from 3 9 g RuCl₃ 3H₂O, 70% Typical yield of cis-[Os(bipy)₂Cl₂] from 1 1 g K₂OsCl₆, 85%

$c_{1s}=[Ru(b_1py)_2(H_2O)_2](ClO_4)_2$

cis-[Ru(bipy)₂(H₂O)₂](ClO₄)₂ was prepared by heating cis-[Ru(bipy)₂Cl₂] 2H₂O in a minimum volume of H₂O for 15 minutes The diaquo complex formed was precipitated by addition of a 5-fold molar excess of LiClO₄, also dissolved in a minimum volume of H₂O The solution was allowed to stand for one hour, under refridgeration cis-[Ru(bipy)₂(H₂O)₂](ClO₄)₂ was isolated and dried by suction Its identity was confirmed using uv-visible spectrophotometry

Typical yield from 100 mg cis-[Ru(bipy)₂Cl₂] 2H₂O, 70-75%

$[\underline{Ru}(\underline{b1}py)_2(\underline{PVP})_n](\underline{ClO4})_2$

The metallopolymers were prepared by refluxing cis-[Ru(bipy)₂(H₂O)₂](ClO₄)₂ with an n-fold excess of PVP, where n = 5, 10, 15, 20 and 25 The reflux was performed in the dark in 80 20 ethanol H₂O, for up to 72 hours The reaction was continuously monitored using uv-visible spectrophotometry and cyclic voltammetry The product was solvent stripped into pure ethanol and used without purification Cyclic voltammetry confirmed the presence of a single redox centre, while molar extinction coefficient data confirmed the redox site loading

$[O_{s}(b_{1}py)_{2}(PVP)_{10}]Cl_{2}$

cis- $[Os(bipy)_2Cl_2]$ was dissolved in ethanol H₂O was added and the solution was boiled for *ca* 1 hour A ten fold excess of PVP, dissolved in a minimum volume of ethanol, was added The final solvent composition was *ca* 80 20 H₂O ethanol The solution was allowed to reflux for at least 10 days and was continuously monitored using cyclic voltammetry

2.2.3. Procedures.

Glassy carbon electrodes of 3 or 7 mm diameter, mounted in Teflon shrouds, were used throughout The electrode surface was prepared by mechanical polishing to a mirror finish using a 0.5 μ m alumina slurry on a felt bed, followed by thorough washing with Milli-Q H₂O and methanol The electrodes were modified by applying a few microlitres of a 0.2% (w/w) ethanolic solution of the metallopolymer and allowed to dry in a solvent saturated chamber This ensured the formation of homogeneous films The electrodes were then left to dry in air. For the ruthenium polymers the modification procedure was carried out in the dark

A conventional three-electrode electrochemical cell was used, thermostatted to \pm 1°C and blacked-out throughout the course of all experimental measurements Potentials are quoted versus a saturated calomel electrode (SCE), without correction for liquid junction potentials

For the ruthenium polymers a detailed study of charge transport processes was performed with the 1 5 and 1 10 loadings The total quantity of ruthenium centres immobilised on the electrode was maintained constant for both loadings This required layers of differing thickness Surface coverages were estimated by graphical integration of the background corrected slow sweep rate cyclic voltammogram (1 to 2 mVs⁻¹), and were typically 1 to 5 x 10⁻⁸ molcm ² Within these limits, the surface coverage was found

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to have no significant effect on the evaluation of charge transport parameters

The concentration of redox centres within the polymer films was evaluated from the individual densities of the dry metallopolymers measured by flotation in non-swelling solvents, tetrachloromethane and n-hexane. The concentrations determined for the ruthenium metallopolymers were, for n=5, 1 06 M and for n=10, 0 80 M For $[Os(bipy)_2(PVP)_{10}]Cl_2$ the concentration of centres was 0 70 M. These values were used for the calculation of D_{ct} from experimentally determined D_{ct}^{1/2}C

For the study of the affect of electrolyte type and concentration on charge transport parameters, a fresh polymer coating was used in each new electrolyte, thus avoiding the problem of memory-effects Prior to the evaluation of charge transport parameters, the polymer layers were continuously scanned for 15 min using cyclic voltammetry, followed by a determination of surface coverage at a scan rate of 1 or 2 mVs⁻¹ Diffusion coefficients for the M^{11/111} oxidation were obtained using linear sweep cyclic voltammetry at scan rates of 100 to 500 mVs⁻¹

Chronoamperometry, with signal averaging, was used to evaluate the charge transport process over the time scale of 0 to 20 ms. This was performed by applying a potential step from 0.0 V to *ca* 0.3 - 0.40 V positive of the formal potential of the redox couple Potential steps for background correction were made between 0.0 and 0.20 V, where no redox processes occur, and were linearly extrapolated IR compensation using positive feedback circuitry was employed, with 80-90% of cell resistance compensated for

Sampled current voltammetry was performed in an isothermal cell using the EG&G Model 273 potentiostat / galvanostat interfaced to a BBC microcomputer A pulse width of 200 ms and an interval of 20 s between successive pulses was employed The current was sampled at 1, 2, 4 and 10 ms after application of the potential step

2.3. RESULTS AND DISCUSSION.

2.3.1. Characterisation of Polymers.

<u>2311</u> [<u>Ru(bipy)2(PVP)n</u>]²⁺

As discussed in Section 1 3, the synthesis of redox polymers based on ruthenium poly(pyridyl) complexes is based on the lability of the chloride ligand in Ru(bipy)₂Cl₂ The reaction can be summarised by,

$$Ru(bipy)_{2}Cl_{2} + H_{2}O \longrightarrow [Ru(bipy)_{2}(H_{2}O)Cl]^{+} + Cl^{-} (2 \ 3 \ 1)$$

$$[Ru(bipy)_{2}(H_{2}O)Cl]^{+} + H_{2}O \longrightarrow [Ru(bipy)_{2}(H_{2}O)_{2}]^{2+} + Cl^{-} (2 \ 3 \ 2)$$

$$[Ru(bipy)_{2}(H_{2}O)_{2}]^{2+} + PVP \longrightarrow [Ru(bipy)_{2}(H_{2}O)(PVP)]^{2+} + H_{2}O (2 \ 3 \ 3)$$

$$[Ru(bipy)_{2}(H_{2}O)(PVP)]^{2+} + PVP \longrightarrow [Ru(bipy)_{2}(PVP)_{n}]^{2+} + H_{2}O (2 \ 3 \ 4)$$

The identity of the metallopolymer was confirmed from the electronic spectra of an ethanol solution of the product Room temperature emission at 610 ± 5 nm, and characteristic ¹MLCT absorption maxima in the uv-visible region at 345 ± 5 nm and 460 ± 5 nm are indicative of the [Ru(N)₆]²⁺ molety [1,7]

When applied as a coating on glassy carbon electrodes, the metallopolymers exhibit single-electron redox behaviour for the Ru^{11/111} oxidation in all electrolytes examined (see Fig 2 3 1) The formal potential for the redox couple, E^o, determined from slow sweep rate cyclic voltammetry, is around 1 0 V vs SCE (depending on electrolyte type and concentration) and is characteristic of $[Ru(bipy)_2(PVP)_n]^{2+}[1]$

The origins of the spectroscopic and electrochemical behaviour of this, and other Ru^{II} poly(pyridyl) compounds, have been discussed previously in Section 1.3

Fig 2 3 1 Cyclic voltammogram for an electrode modified with [Ru(bipy)₂(PVP)₅]²⁺ at a scan rate of (a) 5 mVs⁻¹ and (b) 100 mVs⁻¹ Surface coverage is 1 1 x 10⁻⁸ molcm⁻² Supporting electrolyte is 1 0 M HClO₄

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The metal loading, n, was based on the relative quantities of starting material and assumed complete reaction. This was confirmed through monitoring the reaction using spectroscopic and electrochemical techniques. For the highest loading synthesised (n=5), a redox centre must be coordinatively attached to 40% of all available pyridine moieties of the polymer backbone. This constitutes a very high metal content for coordinative attachment and a quantitative verification of the loading was required. This was achieved by the evaluation of the molar extinction coefficient of the ¹MLCT absorption of the [Ru(N)₆]²⁺ moiety at 460 nm. A typical determination is illustrated in Fig 2.3.2, where the absorption of 0.25 mgcm⁻³ solutions of [Ru(bipy)₂(PVP)_n]²⁺ is ploted versus the concentration of redox centres for n=10, 15, 20 and 25

The slope of the plot in Fig 2 3 2 yields a molar extinction coefficient of 7200 ± 200 M⁻¹cm⁻¹, which is in agreement with that quoted by Krause (7900 M⁻¹cm⁻¹) for the monomeric analogue [Ru(bipy)₂(py)₂]²⁺, where py is pyridine [45] The absorption for the highest loading, Abs₄₆₀ = 1 593, represents a chromophore concentration of 2 21 x 10-4 M For a 0 25 mgcm⁻³ solution, this yields a molecular weight for the metallopolymer unit of 1132 gmol⁻¹ This is indicative of [Ru(bipy)₂(PVP)₅](ClO₄)₂ predicted from reaction ratios

For reactions in which higher loadings were attempted (n=2 5), Abs₄₆₀ of the metallopolymer solution was also representative of $[Ru(bipy)_2(PVP)_5]^{2+}$, while the cyclic voltammogram demonstrated the presence of both bis- and mono-substituted redox centres. This has been observed previously for the synthesis of this metallopolymer [1] and it is considered that for bis-substituted materials of this type, n=5 represents the saturation loading.

Stable polymer layers coated as thin films on electrode surfaces could not be obtained for metallopolymers with metal loadings more dilute than n=10 This restricted an investigation of charge transport processes to films of higher metal content only Assuming a rigid rod structure for the PVP backbone, in which adjacent pyridine groups

Fig 2 3 2 Absorbance at 460 nm versus redox site concentration for ethanolic solutions of $[Ru(bipy)_2(PVP)_n]^{2+}$ The n = 10 to 25 loadings were used as standards (solid line) Concentration of all polymeric solutions was 0 25 mgcm⁻³



are 2 5 Å apart [1,46], the inter-site separation for the 1 10 loading is estimated to be 25 Å, for the 1 5 loading, 12 5 Å These estimates will be used below in the evaluation of activation parameters

<u>2312</u> [Os(bipy)₂(PVP)₁₀]²⁺

The synthesis of $[Os(bipy)_2(PVP)_{10}]^{2+}$ can be described in the same way as the ruthenium analogue (Eqn 2 3 1 to 2 3 4) The identity of the metallopolymer was confirmed from uv-visible spectrophotometry (¹MLCT transitions at 445 ± 5 nm and 615 ± 5 nm) and from room temperature emission (at 765 ± 5 nm) The polymer, when cast as a thin film on electrode surfaces, exhibits single-electron redox behaviour for the Os^{11/11} couple at around 0 60 V in aqueous acid electrolyte (depending on type and concentration) This is illustrated in Fig 2 3 3 The spectroscopic and electrochemical behaviour is consistent with the $[Os(N)_6]^{2+}$ molety [5,6,47] The redox site loading was based on reaction ratios and assumed complete reaction





i.

2.3.2. Effect of Photosubstitution reactions on Charge Transport [Ru(bipy)₂(PVP)_n]²⁺.

Charge transport and activation parameters for ruthenium-based redox polymers have been found to be subject to greater error than their osmium counter-parts [33] While structural inhomogeneity may result in irreproducible results for the evalution of charge transport parameters within modifying layers, it is considered that the most probable cause of experimental variation for ruthenium polymers is the photochemically-induced ligand-exchange reactions at the ruthenium redox centres (see Section 1 3 2)

[1,3,5,33,48,49]

The importance of the photosubstitution reaction lies in the dependency of the formal potential of the Ru^{II/III} couple on the coordination sphere Fig 2 3 4 and Fig 2 3 5 illustrate the change in voltammetric response observed during photolysis of a $[Ru(bipy)_2(PVP)_{10}]^{2+}$ modified electrode in 1 0 M HClO₄ and 0 1 M H₂SO₄, respectively For both figures the polymer surface coverage is 2 x 10⁻⁸ molcm⁻² and the scan rate is 100 mVs⁻¹ The Ru^{II/III} redox couple of the bis-substituted metallopolymer as cast (at *ca* 1000 mV) is seen to decrease with increasing photolysis time. This is accompanied by the emergence of the redox couple of the photoproduct at less positive potentials (*ca* 750 mV). In these aqueous acid electrolytes the ligand-exchange reaction at the Ru centre is [48,49],

$$[Ru(bipy)_2(PVP)_n]^{2+} + H_2O \longrightarrow [Ru(bipy)_2(PVP)_n(H_2O)]^{2+}$$
 (2.3.5)

The electrochemical behaviour of the photoproduct, the Ru-aquo metallopolymer, is the subject of Chapter 6 and is not considered further here

Compared to H₂SO₄ and pTSA electrolyte, in HClO₄, irradiation of the electrode for a longer period is required for a stable cyclic voltammetric response for the





Fig 2 3 4

Photochemically induced ligand exchange reaction in 1 0 M HClO₄ for an electrode modified with $[Ru(bipy)_2(PVP)_{10}]^{2+}$ Surface coverage is 2 x 10 8 molcm 2 scan rate is 100 mVs 1

Fig 2 3 5

Photochemically induced ligand exchange reaction in 0.1 M H₂SO₄ for an electrode modified with $[Ru(bipy)_2(PVP)_{10}]^{2+}$ Surface coverage is 2 x 10.8 molcm ² scan rate is 100 mVs ¹ photoproduct to be obtained In conjunction with Fig 2 3 4 and Fig 2 3 5, this clearly demonstrates that the ligand-exchange process is electrolyte dependent

In HClO₄, the emergence of the Ru^{II/III} redox couple of the aquo species does not occur until the bis-coordinated Ru^{II/III} couple has almost completely disappeared (Fig 2 3 4) In this electrolyte, the polymer layer is more compact and dehydrated [6,17,33,35] and the Ru-aquo centres initially generated are expected to be confined to the polymer / electrolyte interfacial region. Under semi-infinite diffusion conditions for voltammetric measurements charge transfer between widely separated Ru-aquo sites can not occur and they will remain kinetically isolated until photosubstitution has proceeded to a considerable extent throughout the layer

In H₂SO₄ (and pTSA), the collapse of the bis-coordinated Ru^{II/III} couple is more rapid (see Fig 2 3 5) and is closely paralleled to the immergence of redox couples for both the aquo species (at *ca* 850 mV) and a Ru-sulphato complex (at *ca* 700 mV) [3,49] In these electrolytes a more swollen polymer structure exists [3,6,16,17,35], which will facilitate the photosubstitution reaction throughout the entire layer. This results in reduced electrochemical isolation of the photoproduct(s) and the ability to detect the ligandexchange process more readily

The ligand-exchange reactions for $[Ru(bipy)_2(PVP)_n]^{2+}$ depicted in Fig 2 3 4 and Fig 2 3 5 differ from those observed for the mono-substituted analogue, $[Ru(bipy)_2(PVP)_nCl]+[5,48,49]$ Because of the relative positions of the formal potentials of the chloride and aquo complexes, the $[Ru - H_2O]^{2+/3+}$ couple can be mediated by the $[Ru - Cl]^{2+/3+}$ oxidation As a result, the electrochemical response of the aquo complex increases at the same rate at which the response of the chloride complex decreases, and an isosbestic point is obtained (see Fig 1 3 3, Chapter 1)

While all electrochemical measurements for the evaluation of charge transport through $[Ru(bipy)_2(PVP)_n]^{2+}$ were made in the dark, the generation of the Ru-aquo

complex, even in small quantities, is anticipated to affect the accuracy of the results [33] This will be of particular significance in HClO₄ electrolyte, where the presence of small quantities of the Ru-aquo complex will not be detected electrochemically Although in pTSA and H₂SO₄ the ligand-exchange is easily detected, because the Ru-aquo complex is generated more rapidly the error introduced to charge transport parameters is found to be of similar magnitude to that in HClO₄

Despite this, the errors in the charge transport and activation parameters calculated for $[Ru(bipy)_2(PVP)_n]^{2+}$ are considerably less than those found for the mono-substituted ruthenium polymer $[Ru(bipy)_2(Pol)_{10}Cl]^+$, where Pol is a PVP-PS copolymer of variable composition [33] In a study of the photophysical properties of the bis-coordinated polymer, $[Ru(bipy)_2(PVP)_{20}]^{2+}$, following solution phase photolysis in CH₃CN the facility for recapture of the lost ligand was found to exist due to the high concentration of pyridine moleties in the immediate vicinity of the metal centre [7] It is considered that while recapture of the Cl ligand of the mono-substituted polymers is unlikely, for the bissubstituted Ru polymers studied here, the photosubstitution reaction may be retarded by recapture of the PVP ligand

The error in the charge transport parameters quoted below are estimated as follows For D_{ct} measured using linear sweep voltammetry, designated D_{ct}(CV), the error is \pm 15% between films and \pm 5% for repeat determinations on a single film. For charge transport rates determined using chronoamperometry, denoted D_{ct}(PS), the error is \pm 20% between films and \pm 5% on a given film. For heterogeneous electron transfer, the error in the standard rate constant, k⁰, is \pm 20% while the error in the anodic transfer coefficient, α , is \pm 0.05. All values are measured over repeat determinations on at least 4 separate polymer coatings

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2.3.3. The effect of electrolyte and redox site concentration on Charge Transport through [Ru(bipy)₂(PVP)_n]²⁺.

2331. General Layer behaviour

At slow cyclic voltammetric scan rates (1 to 10 mVs⁻¹) the metallopolymer layers exhibit thin layer behaviour, while at scan rates greater than 50 mVs⁻¹ semi-infinite diffusion behaviour is observed (Fig 2 3 1) The plot of i_{pa} vs $v^{1/2}$ is linear for scan rates 100 to 500 mVs⁻¹, permitting the evaluation of the apparent diffusion coefficient, D_{ct}(CV), using the Randles-Sevcik equation (Eqn 1 2 1) The calculation of D_{ct}(CV) using the Aoki analysis for a finite diffusion space [50] yields the same result, within experimental error

For potential step experiments, the plot of 1(t) vs t^{-1/2} is linear over the timescale 0 to 20 ms and has a zero intercept. This enables the evaluation of $D_{ct}(PS)$ using the Cottrell equation (Eqn 1 2 8). Typical Cottrell plots for the n=5 and n=10 loadings in 0 1 M HClO₄ are shown in Fig 2 3 6.

The heterogeneous kinetics of electron transfer at the glassy carbon / modifying layer interface were examined using sampled current voltammetry Fig 2 3 7 illustrates a typical sampled current voltammogram for an electrode modified with $[Ru(bipy)_2(PVP)_{10}]^{2+}$, obtained in 1 0 M HClO₄ With decreasing sampling time, the diffusion-limited current for the Ru^{11/111} oxidation increases, while the half wave potentials for the voltammograms shift to more positive potentials. These sigmoid-shaped waves are similar to those observed for solution phase reactants at an unmodified electrode and are indicative of Butler-Volmer kinetics [51]. This allows for the conventional analysis of SCV, described in Section 1 2 1 3. For the limiting anodic currents in Fig 2 3 7, the value of D_{c1}(PS) calculated using the Cottrell equation is found to be similar to that obtained from chronoamperometry.

Fig 2 3 6 Typical chronoamperometric response for[Ru(bipy)₂(PVP)_n]²⁺ films presented as Cottrell plots (n=5, 10) Supporting electrolyte is 0 1 M HClO₄, surface coverage 1 8 x 10⁻⁸ molcm⁻²



Fig 2 3 7 Typical sampled current voltammogram for the Ru^{II/III} couple within $[Ru(bipy)_2(PVP)_n]^{2+}$ films (here n = 10) Supporting electrolyte is 1 0 M HClO₄, surface coverage 1 5 x 10⁻⁸ molcm⁻² Sampling times are, from top to bottom, 1, 2, 4 and 10 ms



2332 HClO4 electrolyte

Table 2 3 1 summarises the homogeneous and heterogeneous charge transport parameters obtained for films of $[Ru(bipy)_2(PVP)_n]^{2+}$ in HClO4 electrolyte These charge transport rates in HClO4 are found to be the highest of all electrolytes studied

With an increase in redox site loading, $D_{ct}(PS)$ and $D_{ct}(CV)$ increase by a factor of approximately 2 At low electrolyte concentrations this increase with loading becomes more significant. For the saturation loading of n=5, the rate of charge transport remains insensitive to electrolyte concentration, with $D_{ct}(PS)$ having a value of 6.7 ± 0.5 x 10⁻¹⁰ cm²s⁻¹ and $D_{ct}(CV)$ a value of 4.9 ± 0.5 x 10⁻¹⁰ cm²s⁻¹. For the 1 in 10 loading, $D_{ct}(CV)$ and $D_{ct}(PS)$ increase almost linearly with increasing HClO₄ concentration

The standard rate constant for heterogeneous electron transfer, k⁰, exhibits the same trends with redox site loading and electrolyte concentration as D_{ct} For the n=5 loading, k⁰ is independent of electrolyte concentration and has a value of 2 4 ± 0 1 x 10⁻⁴ cms⁻¹ For the 1 in 10 loading, k⁰ increases with HClO₄ concentration from 0 64 to 1 4 x 10⁻⁴ cms⁻¹ The anodic transfer coefficient, α , is insensitive to redox site loading and electrolyte concentration and has a value of 0 36 ± 0 02

[HClO4] (M)	D _{ct} (PS) (x 10 ¹¹ cm ² s ¹)	ko (x 104 cms ¹)	α	D _{ct} (CV) (x 10 ¹¹ cm ² s ¹)	E0 V vs SCE
01	68 8	24	0 34	40 6	1 045
02	66 3	24	0 36	51 8	1 070
04	717	26	0 32	54 9	1 060
06	73 8	23	0 33	52 4	1 040
08	63 4	23	0 34	50 1	1 035
10	60 6	23	0 36	44 2	1 010
n=10			١		
01	27 0	06	0 36	11 4	1 060
02	32 0	07	0 36	14 0	1 040
04	29 8	08	0 35	16 1	1 025
06	39 3	13	0 38	23 6	1 020
08	46 4	14	0 39	22 0	1 025
10	55 5	13	0 37	24 9	0 990

Table 2 3 1Charge transport parameters for [Ru(bipy)2(PVP)n]2+modified electrodes in HClO4 electrolyte
2333 H₂SO₄ electrolyte

The charge transport parameters obtained in H₂SO₄ electrolyte are summarised in Table 2.3.2 For the 1 in 5 loading, $D_{ct}(PS)$ and $D_{ct}(CV)$ are insensitive to H₂SO₄ concentration For the n=10 loading, while $D_{ct}(PS)$ is also independent of electrolyte concentration, $D_{ct}(CV)$ is observed to increase in the concentration range 0.1 to 0.6 M H₂SO₄, but decreases at higher concentrations

An increase in metal loading increases $D_{ct}(PS)$ by a factor of 3, from a value of *ca* 4 9 x 10⁻¹¹ cm²s⁻¹ (n=10) to 14 1 x 10⁻¹¹ cm²s⁻¹ (n=5) However, the evaluation of $D_{ct}(CV)$ is independent of redox site loading, with a value of *ca* 4 x 10⁻¹¹ cm²s⁻¹

For heterogeneous kinetics in H₂SO₄, k^o exhibits the same variation with electrolyte concentration and redox site loading as $D_{ct}(PS)$ and has a similar value to that found in HClO₄ electrolyte. The evaluation of α is also similar to that obtained in HClO₄ (0 34 ± 0 02), and remains constant for both loadings and all H₂SO₄ concentrations

2334 pTSA electrolyte

The charge transport behaviour in pTSA electrolyte is presented in Table 2.3.3 $D_{ct}(CV)$ is insensitive to redox site loading and electrolyte concentration and has a value of $3.5 \pm 0.3 \times 10^{-11} \text{ cm}^2\text{s}^{-1}$ $D_{ct}(PS)$ is of similar magnitude and is also insensitive to pTSA concentration. However, with an increase in redox site loading, $D_{ct}(PS)$ approximately doubles to a value of $7.6 \pm 0.4 \times 10^{-11} \text{ cm}^2\text{s}^{-1}$

k° exhibits the same trends with loading and electrolyte concentration as $D_{ct}(PS)$ and is similar to the values obtained in H₂SO₄ α is smaller than that observed in both HClO₄ and H₂SO₄ electrolytes (0 22 ± 0 02 versus 0 36) and is independent of redox site loading and pTSA concentration

[H ₂ SO ₄]	D _{ct} (PS)	ko	α	D _{ct} (CV)	Eo
(M)	(x 10 ¹¹ cm ² s ¹)	(x 10 ⁴ cms ¹)		(x 10 ¹¹ cm ² s ¹)	V vs SCE
n=5					
01	13 4	15	0 32	23	1 110
02	13 7	15	0 37	36	1 080
04	14 1	17	0 33	29	1 070
06	13 5	16	0 32	31	1 065
08	15 4	1 7	0 31	23	1 055
10	14 6	18	0 30	27	1 050
n=10					
01	43	07	0 36	47	1 070
02	4 5	07	0 37	48	1 060
04	4 5	06	0 36	74	1 050
06	49	07	0 32	95	1 050
08	56	06	0 34	32	1 035
10	54	06	0 32	39	1 040

Table 2 3.2Charge transport parameters for $[Ru(bipy)_2(PVP)_n]^2 +$ modified electrodes in H2SO4 electrolyte

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[pTSA]	D _{ct} (PS)	ko	α	D _{ct} (CV)	Eo	
(M)	(x 10 ¹¹ cm ² s ¹)	(x 10 ⁴ cms ¹)		(x 10 ¹¹ cm ² s ¹)	V vs SCE	
		·····				
n=5						
01	78	16	0 24	38	1 175	
0 2	8 0	17	0 23	4 1	1 165	
04	77	15	0 26	32	1 150	
06	70	15	0 25	37	1 065	
08	76	16	0 22	33	1 155	
10	73	15	0 21	30	1 155	
n=10						
01	4 5	05	0 22	3 5	1 165	
02	38	06	0 20	3 5	1 155	
04	26	06	0 21	34	1 145	
06	29	0 5	0 20	34	1 145	
08	27	05	0 18	34	1 140	
10	31	06	0 18	3 5	1 145	

Table 2 3 3 Charge transport parameters for [Ru(bipy)₂(PVP)_n]²⁺

modified electrodes in pTSA electrolyte

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2.3.4. Activation parameters for [Ru(bipy)₂(PVP)_n]²⁺.

The activation parameters for homogeneous charge transport were evaluated in 0 1 M and 1 0 M electrolyte in accordance with the methods described in Section 1 2 1 4 In H₂SO₄, the gradual loss of the polymer film in 1 0 M electrolyte prevented an accurate calculation of activation energies An intermediary concentration of 0 4 M H₂SO₄ was therefore used The temperature dependence of $D_{ct}(PS)$ and $D_{ct}(CV)$ was measured by varying the temperature of the contacting electrolyte over the range 273 - 308 K A typical Arrhenius plot, obtained for $D_{ct}(PS)$ in 0 4 M H₂SO₄ is shown in Fig 2 3 8 The activation parameters obtained using cyclic voltammetry and potential step methods are summarised in Table 2 3 4 and Table 2 3 5, respectively, and have an estimated error of \pm 5% on a given polymer coating and \pm 20% for analysis on different films

For all electrolytes and loadings, the activation energies, $E_a(CV)$ and $E_a(PS)$, are coupled to a negative entropy term, with the free energy, $\Delta G^{\#}$, remaining constant at 54 ± 4 kJmol-1 In HClO₄, $E_a(CV)$ and $E_a(PS)$ are independent of redox site loading and electrolyte concentration and have a common value of 23 ± 3 kJmol-1 In H₂SO₄ electrolyte, a decrease in $E_a(CV)$ and $E_a(PS)$ with increasing electrolyte concentration is generally observed $E_a(CV)$ and $E_a(PS)$ are once again similar, with a value of 36 ± 2 kJmol-1 in 0 1 M electrolyte and 25 ± 2 kJmol-1 in 0 4 M H₂SO₄ For the 1 in 5 loading however, $E_a(PS)$ decreases, particularly in 0 4 M H₂SO₄

In pTSA, $E_a(CV)$ is independent of electrolyte concentration and redox site loading and has the highest values obtained (*ca* 48 ± 5 kJmol⁻¹), although still coupled to negative entropy For the n=10 loading, $E_a(PS)$ is similar to $E_a(CV)$ However, as found for the n=5 loading in H₂SO₄, $E_a(PS)$ in pTSA also becomes significantly less than $E_a(CV)$, particularly at high electrolyte concentrations

Fig 2 3 8 Temperature dependence of D_{ct}, measured by chronoamperometry, for [Ru(bipy)₂(PVP)₁₀]²⁺ Supporting electrolyte is 0 4 M H₂SO₄, surface coverage is 1 x 10-8 molcm-2



Electrolyte Conc (M)	2/	E _a (CV) kJmol-1	ΔH(CV)# kJmol ⁻¹	ΔS(CV)# Jmol-1K-1	∆G(CV)# kJmol-1
n=5					
HClO4	01	23 0	20 5	- 890	47 1
	10	20 9	184	- 996	48 1
H ₂ SO ₄	01	- 34 1	31 7	- 797	55 4
	04	26 1	23 6	- 93 5	51 5
pTSA	01	5 5 1	52 6	- 168	57 6
	10	47 3	44 8	[*] - 37 7	56 1
n=10					
HClO ₄	01	20 1	17 6	-128 4	55 9
	10	23 3	20 8	-113 0	54 5
H ₂ SO ₄	01	38 2	35 7	- 612	54 0
	04	25 6	23 1	-115 6	57 5
pTSA	01	47 2	44 7	- 397	5 6 5
-	10	41 3	38 9	- 554	55 4

Table 2 3 4Activation parameters for charge transport through $[Ru(bipy)_2(PVP)_n]^{2+}$ films , obtained using cyclic voltammetry

Electrolyte Conc (M)	:/	E _a (PS) kJmol ⁻¹	ΔH(PS)# kJmol-1	ΔS(PS)# Jmol-1K-1	∆G(PS)# kJmol-1
n=5					
HClO ₄	01	29 3	26 8	- 657	46 4
	10	24 2	21 7	- 83 5	46 6
H ₂ SO ₄	01	24 2	21 8	-105 6	53 3
	04	12 1	97	-128 9	48 1
pTSA	01	23 4	20 9	-111 9	54 3
	10	15 4	13 0	-138 2	54 2
n=10					
HClO4	01	22 1	197	-121 1	55 7
	10	21 9	19 4	-109 8	52 1
H ₂ SO ₄	01	34 2	31 7	- 804	55 7
	04	21 9	19 4	-130 9	58 4
-770 4	0.1	42.5	41.0	5 4 0	ca 2
pisa	10	43 5 34 0	41 0 31 5	- 54 8 - 80 3	573 554

Table 2 3 5Activation parameters for charge transport through $[Ru(bipy)_2(PVP)_n]^{2+}$ films, obtained using chronoamperometry

2.3.5. Charge Transport and Activation parameters for [Os(bipy)₂(PVP)₁₀]²⁺

The general layer behaviour of $[Os(bipy)_2(PVP)_{10}]^{2+}$ modified electrodes is as described for $[Ru(bipy)_2(PVP)_n]^{2+}$ in Section 2 3 3 1 A preliminary study of homogeneous charge transport parameters in 0 1 M and 1 0 M HClO₄, H₂SO₄, and pTSA electrolyte is summarised in Table 2 3 6 These data are averaged over repeat determinations on two different polymer films and have an estimated error of $\pm 15\%$ A cyclic voltammogram under semi-infinite diffusion conditions and a typical Cottrell plot are illustrated in Fig 2 3 3 and Fig 2 3 9, respectively

Electroly	rte /	D _{ct} (PS)	D _{ct} (CV)	Eo	
Conc (M)	x10 ⁹ cm ² s 1	x10 ¹⁰ cm ² s ⁻¹	V vs SCE	
HClO ₄	01	8 5	0 5	0 555	
	10	88	04	0 520	
H ₂ SO ₄	01	12	30	0 585	
	10	22	24	0 580	
pTSA	01	33	12	0 635	
	10	3 5	16	0 630	

Table 2 3 6 Charge Transport parameters for [$[Os(b1py)_2(PVP)_{10}]^{2+}$ films
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Fig 2 3 9 Typical chronoamperometric response for[Os(bipy)₂(PVP)₁₀]²⁺ films presented as Cottrell plots Electrolyte is 1 0 M HClO₄, surface coverage 2 2 x 10⁻⁸ molcm⁻²



As found for the bis-coordinated ruthenium analogue, the rate of charge transport through $[Os(bipy)_2(PVP)_{10}]^{2+}$ films is insensitive to the electrolyte concentration However, unlike the ruthenium polymer, the data presented in Table 2 3 6 for $[Os(bipy)_2(PVP)_{10}]^{2+}$ demonstrate that D_{ct} is very much dependent on the experimental time scale In H₂SO₄ and pTSA electrolyte, $D_{ct}(PS)$ is at least an order of magnitude greater than $D_{ct}(CV)$, while in HClO₄, $D_{ct}(PS)$ exceeds $D_{ct}(CV)$ by a factor of over 200

The activation parameters for charge transport through $[Os(bipy)_2(PVP)_{10}]^{2+}$ are summarised in Table 2 3 7 and 2 3 8 for cyclic voltammetric and potential step measurements, respectively These were calculated as described for the ruthenium polymers in Section 2 3 4

In HClO₄ electrolyte $E_a(CV)$ is large (>100 kJmol⁻¹) and is coupled to positive entropy However, for potential step measurements, $E_a(PS)$ in 1 0 M HClO₄ is reduced to only 18 6 kJmol⁻¹ and has a negative entropy term In 0 1 M HClO₄ two regions of behaviour exist, as seen in the Arrhenius plot in Fig 2 3 10 At temperatures less than 298 K, $E_a(PS)$ is similar to that in 1 0 M electrolyte (i e 13 8 kJmol⁻¹) and has negative entropy, while at temperatures greater than 298 K, $E_a(PS)$ increases to 57 kJmol⁻¹ and the entropy term becomes positive

In H₂SO₄ electrolyte $E_a(CV)$ and $E_a(PS)$ are similar and are coupled to negative entropy This reflects the reduced difference in $D_{ct}(CV)$ and $D_{ct}(PS)$ in this electrolyte The activation energies are independent of H₂SO₄ concentration and have a value of 27 ± 2 kJmol⁻¹

In pTSA, significant differences in $E_a(CV)$ and $E_a(PS)$ exist $E_a(CV)$ is independent of pTSA concentration (54 ± 1 kJmol⁻¹) and has associated entropy approaching zero Jmol⁻¹K⁻¹ However, on the time scale of potential step measurements, $E_a(PS)$, although again insensitive to pTSA concentration, is reduced to a value of 11 ± 2 kJmol⁻¹, and has negative entropy of -123 ± 3 Jmol⁻¹K⁻¹

Electroly Conc (N	rte/ 1)	E _a (CV) kJmol ⁻¹	ΔH(CV)# kJmol ⁻¹	ΔS(CV)# Jmol-1K-1	∆G(CV)# kJmol ⁻¹
HClO ₄	01	115 1	112 7	187 4	56 8
	10	136 7	134 2	259 5	56 9
H₂SO₄	01	26 7	24 3	- 906	51 3
	10	24 4	22 0	-102 9	52 6
pTSA	01	52 3	49 9	- 14 3	54 1
•	10	54 9	52 4	- 74	547

Table 2 3 7Activation parameters for charge transport through $[Os(bipy)_2(PVP)_{10}]^{2+}$ films, obtained using cyclic voltammetry

 Table 2 3 8
 Activation parameters for charge transport through

[Os(bipy)₂(PVP)₁₀]²⁺ films, obtained using potential step methods

Electroly Conc (M	rte/ 1)		Ea(P S) kJmol ⁻¹	ΔH(PS)# kJmol ⁻¹	ΔS(PS)# Jmol ⁻¹ K ⁻¹	∆G(PS)# kJmol-1
HClO ₄	01 T	T>298	57 0	54 6	34 6	44 3
		T<298	138	11 3	-108 0	43 6
	10		18 6	16 1	- 91 8	43 5
H ₂ SO ₄	01		27 6	25 1	- 807	49 2
	10		29 5	27 1	- 65 4	46 6
pTSA	01		95	71	-125 6	44 5
-	10		12 9	10 5	-120 1	46 3

Fig 2 3 10 Temperature dependence of D_{ct}, measured by chronoamperometry, for [Os(bipy)₂(PVP)₁₀]²⁺ Supporting electrolyte is 0 1 M HClO₄, surface coverage is 1 9 x 10-8 molcm-2



Compared with the ruthenium analogue, $D_{ct}(PS)$ for $[Os(bipy)_2(PVP)_{10}]^{2+}$ is 50 to 100 times greater (*ca* 10⁻⁹ cm²s⁻¹ versus 10⁻¹¹ cm²s⁻¹) The electrolyte dependence of $D_{c1}(CV)$ for $[Os(bipy)_2(PVP)_{10}]^{2+}$ shows significant differences to that found for electrodes modified with $[Ru(bipy)_2(PVP)_{10}]^{2+}$, with increased charge transport rates in the swelling electrolytes and impeded charge transport in perchlorate In H₂SO₄ and pTSA electrolyte, $D_{ct}(CV)$ is greater for the osmium polymer, by a factor of approximately 5 In HClO₄, however, $D_{ct}(CV)$ for $[Os(bipy)_2(PVP)_{10}]^{2+}$ is approximately 5 times less than that seen for $[Ru(bipy)_2(PVP)_{10}]^{2+}$

2.3.6. General Discussion.

The accepted mechanism for homogeneous charge transfer through metallopolymer films is electron-hopping between neighbouring reduced / oxidised redox centres [52-54] The rate-determining step for charge percolation can be (i) the barrier to the electron selfexchange reaction, (ii) counter-ion motion into or out of the film required for the maintenance of electroneutrality, or (iii) segmental polymer chain motion required to juxtapose the redox centres [55]

In order to evaluate the apparent diffusion coefficient for charge transport using the Randles-Sevcik and Cottrell equations, the current response must be diffusional in character, with migrational effects absent. The cyclic voltammograms for the Ru^{11/111} and the Os^{11/111} couples under semi-infinite diffusion conditions, shown in Fig 2.3.1 and Fig 2.3.3, respectively, have an anodic to cathodic peak current ratio of unity. The plot of 1_{pa} vs $v^{1/2}$ is linear for scan rates 100 to 500 mVs-1, as predicted for a diffusion-controlled electrode process by the Randles-Sevcik equation

For potential step experiments, the Cottrell plots for the Ru^{II/III} and Os^{II/III} couples are linear over the 0 - 20 ms time scale and have zero intercepts (see Fig 2 3 6 and 2 3 9) A departure of the current decay from purely diffusional character may be evidenced by a non-zero intercept in the Cottrell plot [56] or by a peak in the $it^{1/2}$ vs $t^{1/2}$ plot [57] Neither are observed in this study

When electron mobility is greater than that of counter-ions and migration makes a significant contribution to the current response of a modifying layer, it has been shown that D_{ct} may take on a cubic dependence on redox site loading [58] In the study of $[Ru(bipy)_2(PVP)_n]^{2+}$ presented in this chapter, although only a limited range of loadings are considered, the effect of doubling the metal content is typically to increase D_{ct} by a factor of no more than 2 to 3, while for some electrolytes the predicted increase in D_{ct} with increasing metal content is not observed. This is in agreement with a previous study of loading for the polymer $[Os(bipy)_2(PVP)_nCl]^+$, where n was varied between 5 and 25 [16,17]. For this osmium polymer it was demonstrated that when D_{ct} increases with increased loading the increase never exceeds a proportional relationship, and, indeed, for the highest loadings considered, D_{ct} was found to decrease

The features of the current response for redox processes within $[M(bipy)_2(PVP)_n]^{2+}$ (where M is either Os or Ru), coupled to the loading effects discussed above, indicate that a diffusion model may be applied to charge transport through these metallopolymers The use of the Randles-Sevcik and Cottrell equations to calculate diffusion coefficients, therefore, is appropriate

The following discussion is primarily concerned with $[Ru(bipy)_2(PVP)_n]^2+$ The results are then compared with charge transport through $[Os(bipy)_2(PVP)_{10}]^2+$

The data presented in Table 2 3 1 to Table 2 3 3 demonstrate that although the rate of homogeneous charge transport through $[Ru(bipy)_2(PVP)_n]^{2+1}$ is dependent on the nature of the charge-compensating counter-anion, D_{ct} remains insensitive to the electrolyte concentration. In addition, both $D_{ct}(CV)$ and $D_{ct}(PS)$ are found to be of similar magnitude. This suggests that the rate limiting step in the charge transport process is unchanged over the concentration range studied and is the same on both experimental

time scales The thermodynamic data presented in Table 2 3 4 and Table 2 3 5 supports this interpretation, with the activation energies $E_a(CV)$ and $E_a(PS)$ both coupled to negative entropy terms for all electrolyte concentrations and loadings The free energy change during charge transport, $\Delta G^{\#}$, is the same for both cyclic voltammetry and potential step measurements and is observed to remain constant for all electrolyte / loading combinations These data indicate that the fundamental nature of the electron transfer process does not change, and that a common rate limiting process exists for all loadings, all electrolytes, all concentrations and all experimental time scales

Activation parameters have been used previously for diagnosing the rate determining processes for charge transport through modifying materials [6,14-20,32-35,55] Negative entropy reflects an ordering of the microstructure in the vicinity of each metal centre during redox switching and is associated with counter-ion motion or electron-hopping rate limiting steps [55] Positive entropy is indicative of disordering within the polymer layer and reflects the disruption of the layer structure caused by polymer chain movement [55]

The absolute values of entropy calculated in Table 2 3 4 and Table 2 3 5 are acknowledged to be of limited accuracy since the intersite separation of the redox centres (δ in Eqn 1 2 13) is only approximated using a rigid rod model of the polymer structure [46] However, even allowing for a large variation in polymer swelling, a significant departure from the assumed values of δ does not change the sign of the entropy terms calculated and the observed trends should remain valid [59] The negative entropy terms associated with homogeneous charge transport through [Ru(bipy)₂(PVP)_n]²⁺ can therefore be related to ion motion or electron-hopping limitations Using steady-state methods, the rate of electron self-exchange, D_E, for related osmium [60] and ruthenium [61] polymers is found to be 10-6 to 10-8 cm²s⁻¹ This is at least 3 orders of magnitude greater than the D_{c1} values measured in this work. It is therefore considered that the negative entropies associated with charge transport represent ion motion limitations The dependency of D_{ct} on counter-anion type supports this interpretation

A common observation for osmium and ruthenium metallopolymers of the type considered here, is the difference in the rate of charge transport measured on the different experimental time scales of chronoamperometry and cyclic voltammetry [6, 16-18,33,35] In previous studies, $D_{ct}(PS)$ has been routinely observed to be greater than D_{ct}(CV), often by 2 orders of magnitude This has been attributed to possible changes in the nature of the equilibrium established within the layer on different time scales, an interpretation that is supported by observed differences in activation parameters [6,16,17,35] It has also been proposed that the evaluation of D_{ct} reflects the region of the polymer layer through which charge transport is measured [16,17] Using potential step methods over a 20 ms timescale, for a typical film of surface coverage 10-8 molcm-2 and a $D_{ct}(PS)$ value of 10-10 cm²s⁻¹, the depletion layer is *ca* 10% of the total layer thickness [62] Hence, D_{ct}(PS) reflects charge transport processes within a thin region of the film at the electrode / polymer film interface, where localised movement of ions resident within the layer may be sufficient to satisfy electroneutrality on short time scales [16,17] In contrast to this, cyclic voltammetry involves redox switching throughout the bulk of the polymer layer, requiring more extensive interfacial movement of solvent and ions across the film These considerations have been evidenced in previous studies by the observation that when the Cottrell equation is valid for a depletion layer constituting the bulk of film thickness, the difference in $D_{ct}(CV)$ and $D_{ct}(PS)$ is significantly reduced [16]

However, for the $[Ru(bipy)_2(PVP)_n]^{2+}$ modified electrodes which are the subject of this study, the difference between $D_{ct}(PS)$ and $D_{ct}(CV)$ is negligible, typically a factor of less than two and never more than a factor of 5 As discussed above, this is borne out in the thermodynamic data which indicates that the rate determining step in the charge transport process remains unchanged on both experimental time scales

The results for $[Ru(b_{1}py)_2(PVP)_n]^{2+}$ indicate that an open polymer structure must

exist This is in agreement with the considerations by Meyer *et al* of the changes in polymer morphology caused by the bis-coordination of the metal centre to the polymer backbone [1] The intra-chain coordination of the bis-substituted ruthenium centres imposes a structural rigidity upon the polymer matrix, resulting in a lack of redox centre flexibility Adjacent redox sites must therefore maintain their fixed relative positions, leading to a more open layer structure. In the acid electrolytes considered here, protonation of the uncoordinated pyridine moleties of the polymer backbone (pKa 3 3) [63] is expected to swell the layer further. In such a film, the partition of all mobile species across the polymer / electrolyte interface should be unimpeded. This is seen in the invariance of D_{c1} and activation parameters to changes in electrolyte concentration and the general insensitivity of the formal potential of the Ru^{II/III} couple to changing anion activity in the bathing electrolyte solution. The consequence of this is not only the invariance of D_{c1} with changing electrolyte concentration, but, in increasing ion availability, the open structure will also suppress the contribution of migration to the current response

The nature of the electrolyte / polymer interaction has been found to be of importance in determining charge transport rates [6,16-19,32-41] The ClO₄- anion interacts strongly with polyelectrolytes [64], resulting in compact, highly crosslinked, dehydrated layers [19,32,65] This is thought to impede the extensive interfacial movement of counter-ions required during redox processes on the cyclic voltammetric time scale [17,35] Indeed, $D_{ct}(CV)$ has often been found to <u>decrease</u> as the HClO₄ electrolyte concentration <u>increases</u> [17,33,35] In contrast, in pTSA and H₂SO₄ electrolytes, the rate of charge transport is generally found to increase due to the more facile ion motion within the swollen polymer layers that exist in these electrolytes [6,35] The origins of these electrolyte effects on polymer morphology will be considered in greater detail in Chapters 3 and 4

For $[Ru(bipy)_2(PVP)_n]^{2+}$ polymer layers, the electrolyte dependent effects on charge transport rates are profoundly different to those seen previously in related polymers For $[Ru(bipy)_2(PVP)_n]^{2+}$, the highest values of $D_{ct}(CV)$ are observed in HClO₄, and for the 1 in 10 loading, $D_{ct}(CV)$ increases with increasing HClO₄ electrolyte concentration. In H₂SO₄ and pTSA, $D_{ct}(CV)$ is reduced in magnitude, particularly in pTSA. It is clear that the change in polymer structure due to the bis-coordination of redox centres affects the entire physico-chemical characteristics of the polymer layer

The extended configuration imposed by the bis-coordination results in a porous polymerc matrix Because this imparts an enhanced facility for ion partition and movement within the layer, in HClO₄ electrolyte the crosslinking which occurs merely results in a less open structure, with reduced inter-site separation. In addition, the strong interaction between the bis-coordinated Ru^{II} complex and the two ClO₄- counter-ions will decrease the electrostatic repulsion of the 2+ redox centres and will increase the configurational entropy of the polymer segments [66]. These structural changes in HClO₄ account for the higher rates of charge transport which are observed.

In pTSA and H₂SO₄, the electrolyte interaction with $[Ru(bipy)_2(PVP)_n]^{2+}$ exacerbates the porous structure of the film H₂SO₄ electrolyte solubilises redox polymers of this type [3,67], while in pTSA, from steric considerations alone, the incorporation of two pTS⁻ counter-anions per Ru^{II} redox centre will cause an increased strain on the polymer network More significantly, due to the longer distance of closest approach [68] between the bulky pTS⁻ anions and the fixed redox sites, there will be more complete solvation of polymer phase ions, greater polymer swelling and more widely separated redox centres

These swelling effects result in an increase in inter-site separation and, consequently, a decrease in charge transport rates. However, the activation parameters indicate that this swelling does not occur to an extent where segmental polymer chain motion becomes rate limiting.

The results in Tables 2.3.1 to Table 2.3.3 indicate that the nature of the polymer / electrolyte interaction also determines the way in which an increase in redox site loading influences charge transport rates. For the more swollen layers in pTSA and H₂SO₄, an increase in loading increases $D_{ct}(PS)$ yet has little affect on $D_{ct}(CV)$. In contrast, for HClO₄ electrolyte both $D_{ct}(CV)$ and $D_{ct}(PS)$ are affected in a similar way by a change in redox site loading. These data can be reconciled in terms of the polymer layer structure and the differing regions of the film through which $D_{ct}(CV)$ and $D_{ct}(PS)$ describe charge transport.

For metallopolymers of reduced loading, in pTSA and H₂SO₄ electrolyte the lower levels of metallation will result in a more swollen layer with a homogeneous structure across the entire layer thickness. Consequently, no difference between $D_{ct}(CV)$ and $D_{ct}(PS)$ is expected. This is indeed observed for the 1 in 10 loading of $[Ru(bipy)_2(PVP)_n]^{2+}$ in both pTSA and H₂SO₄ and is supported by the thermodynamic data, where $E_a(CV)$ and $E_a(PS)$ are identical, within experimental error

For the n=5 loading in H₂SO₄ and pTSA, the decreased solubility of the polymer matrix due to the saturation of metal centres may result in a more compact base layer morphology Because ion partition and diffusion within the polymer has been shown to be unimpeded, the charge transport rate in this base layer, as measured by $D_{ct}(PS)$, can increase with increasing redox site concentration and decreasing inter-site separation [8,9,17] However, because the polymer / electrolyte interfacial region of the layer in H₂SO₄ and pTSA is anticipated to remain swollen, an increase in redox site loading will not have as profound an effect on inter-site separation and $D_{ct}(CV)$ is observed to remain insensitive to the increase in metal loading

For the relatively more compact structures which exist in perchlorate electrolyte, differential swelling of the layer is expected to become less significant. Consequently, in HClO₄ both $D_{cl}(CV)$ and $D_{cl}(PS)$ increase with an increase in redox site loading

While the evaluation of D_{ct} is generally insensitive to electrolyte concentration for

 $[Ru(bipy)_2(PVP)_n]^{2+}$, in HClO4 for the 1 in 10 loading, both $D_{ct}(CV)$ and $D_{ct}(PS)$ increase as the electrolyte concentration increases. For $D_{ct}(PS)$ this increase with concentration results in a D_{ct} value in 1 0 M electrolyte similar to that found for the saturation loading. This strongly suggests that in the most compact state of $[Ru(bipy)_2(PVP)_n]^{2+}$, and with ion availability remaining facile, D_{ct} does not increase with a reduction in inter-site separation. This indicates that electron-hopping is not the rate determining step for charge transport within this modifying material

The standard rate constant for heterogeneous electron transfer into $[Ru(bipy)_2(PVP)_n]^{2+}$ layers is typically 10-4 to 10-5 cms-1. This is considerably greater than the values of D_{ct} obtained for homogeneous charge transport and confirms the view that charge injection into modifying layers is unlikely to be the rate limiting step in the charge transport process

This value of k⁰, however, is at least an order of magnitude less than that commonly obtained for electroactive species in solution [69] This has been observed previously for modified electrodes [6,16,18,27,70-72] and can be attributed to the partial blocking of the electrode surface by the modifying layer [73] The polymer backbone in $[Ru(bipy)_2(PVP)_n]^{2+}$ is non-conducting, hence interfacial electron transfer can only occur at the ruthenium redox centres. An increase in k⁰ with increasing redox site loading is therefore to be expected, and is observed for all electrolytes

For $[Ru(bipy)_2(PVP)_n]^{2+}$ polymer layers, k^o is affected by electrolyte type and concentration in a similar way to $D_{ct}(PS)$ The largest values of k^o are observed in HClO₄ electrolyte, with slightly reduced values in pTSA and H₂SO₄ Thus, the electrolyte dependent factors discussed for homogeneous charge transport also determine the rate of heterogeneous electron transfer This correlation between $D_{ct}(PS)$ and k^o has been noted previously for related osmium polymers [6,16,18,70] It is thought that because electron transfer is most likely to occur at the outer Helmholtz plane, the position of which is determined by ion availability within the layer, those factors which influence homogeneous charge transfer will also determine k^o [70] The insensitivity of k^o to changes in electrolyte concentration, therefore reflects the observation that in $[Ru(bipy)_2(PVP)_n]^{2+}$ an open, porous structure exists with a similar polymer phase ion population at all concentrations studied

The anodic transfer coefficient also remains insensitive to electrolyte concentration, and is found to be unaffected by redox site loading In HClO₄ and H₂SO₄, α is 0 33 ± 0 05, a value approaching the theoretical one of 0 50 Because the transfer coefficient also reflects the position of the reaction site at which electron transfer takes place, the invariance in α with electrolyte concentration is in agreement with the considerations of ion availability discussed previously for D_{ct} and k⁰

In pTSA, α is 0.20 ± 0.05, a value indicative of an asymmetric barrier to electron exchange. This is likely to be indicative of the bulky nature of the pTS- counter-ion and the increased difficulty for the redox sites to adopt the correct orientation required for the heterogeneous electron transfer process

The charge transport through $[Os(bipy)_2(PVP)_{10}]^{2+}$ is now considered This polymer provides a useful comparison with the ruthenium polymer discussed above Because osmium complexes to not undergo the photosubstitution reactions discussed in Section 2 3 2 [5,47], this source of error is illiminated. In addition, the extensive body of electrochemical data ammassed for related osmium polymers [5,6,16-18,70] enables a more direct assessment of the effect of the bis-coordination on charge transport to be made

The physico-chemical properties of the $[Os(bipy)_2(PVP)_{10}]^{2+}$ layers are dramatically different to those of $[Ru(bipy)_2(PVP)_{10}]^{2+}$ For the osmium polymer, the 1 in 10 loading represents the maximum loading that could be synthesised Reaction times for the metallopolymer were at least 10 days, while for ruthenium, the reaction is complete

within 24 hours and for lower loadings have even been observed to go to completion with 2 5 hours [1] The stability of the polymers, cast as films and immersed in aqueous acid electrolytes, is also different. The ruthenium polymer is swollen in high H₂SO₄ and low pTSA electrolytes and is gradually removed from the electrode surface. The osmium analogue is more stable, with the layer remaining unchanged over several hours. It is thus clear that the change in the central metal atom of the immobilised redox site results in profound differences in the properties of the metallopolymer layer.

These differences are manifested in the fundamentally different nature of charge transport through $[Os(bipy)_2(PVP)_{10}]^{2+}$ compared to that observed for $[Ru(bipy)_2(PVP)_{10}]^{2+}$ However, the charge transport data presented for $[Os(bipy)_2(PVP)_{10}]^{2+}$ in Table 2 3 6 demonstrate that D_{c1} remains insensitive to electrolyte concentration. This is supported by the thermodynamic data in Table 2 3 7 and Table 2 3 8 and is in contrast with the behaviour of the mono-substituted equivalent, $[Os(bipy)_2(PVP)_{10}Ci]^+$, where charge transport and activation parameters are influenced strongly by changing electrolyte concentration. The effect of the bis-coordination of the osmium redox centres on the overall polymer structure is therefore in agreement with the observations made above for $[Ru(bipy)_2(PVP)_n]^{2+}$

However, for $[Os(bipy)_2(PVP)_{10}]^{2+}$ the difference in the evaluation of D_{ct} on the two experimental time scales is large. It is possible that due to differential swelling across the film thickness the greater concentration of redox centres in the relatively more compact base layer results in an enhanced evaluation of $D_{ct}(PS)$. In H₂SO₄ and pTSA the difference in redox site concentration needed to equate $D_{ct}(CV)$ with $D_{ct}(PS)$ necessitates differential swelling of *ca* 300%. For these electrolytes it is possible that the outer regions of the polymer may be sufficiently swollen to account for this change in redox site concentration, with the equilibrium established on both time scales remaining unchanged This interpretation is supported by the activation parameters in H₂SO₄ and

pTSA, with $E_a(CV)$ and $E_a(PS)$ both representing ion motion limitations in high and low electrolyte concentration

In HClO₄ electrolyte, however, for the observed difference between $D_{ct}(PS)$ and $D_{ct}(CV)$ of two orders of magnitude, differential swelling of over 1500% is required For the values of $D_{ct}(PS)$ evaluated in $[Os(bipy)_2(PVP)_{10}]^{2+}$, for a film of surface coverage 2 x 10⁻⁸ molcm⁻², the depletion layer will extend to 30 to 40% of the layer thickness [62] This confirms that it is unlikely that changes in layer structure can adequately explain the differences in $D_{ct}(PS)$ and $D_{ct}(CV)$

It is therefore considered that the equilibrium established during charge transport on the potential step time scale in $[Os(bipy)_2(PVP)_{10}]^{2+}$ is different to that established during cyclic voltammetry. On longer time scales all mobile species, ions, electrons, polymer chains and solvent, can attain equilibrium positions For potential step methods it is possible that within the dehydrated, compact layer which exists in perchlorate, only redox equilibrium can be established for counter-ions and electrons. This is evidenced in the activation parameters in Table 2.3.7 and Table 2.3.8 In HClO₄, $E_a(CV)$ is large and is coupled to positive entropy, indicating that polymer chain motion is the rate limiting step This is thought to represent the crosslinking of the polymer network by the perchlorate anion and the subsequent requirement for extensive polymer motion to enable counter-anion diffusion However, for shorter time scales, the activation parameters represent a change in the rate limiting step to one of counter-ion diffusion An unusual dual slope behaviour is observed for D_{cl}(PS) in 0.1 M HClO₄ (see Fig 2.3.10) This has been observed previously for related metallopolymers in perchlorate media [34,35], and suggests that at temperatures below 298 K ion motion limits charge transport, while at higher temperatures polymer chain motion once again becomes the rate determining step

It is seen that substitution of ruthenium with osmium in $[M(bipy)_2(PVP)_{10}]^{2+}$ imparts a significant increase in layer stability. While the interaction of the contacting electrolyte with the metallopolymer structure is the same for both metal centres, the subsequent effect on charge transport rates are utterly different

For the osmium polymer, the perchlorate interaction impedes ion diffusion and $D_{cl}(CV)$ is reduced. For the ruthenium polymer, the crosslinking of the layer gives it an enhanced structural integrity, and charge transport rates are very much increased. In contrast, for pTSA and H₂SO₄ the swelling of the layer facilitates $D_{cl}(CV)$ for the osmium material, but merely exacerbates the open layer structure for $[Ru(bipy)_2(PVP)_n]^{2+}$ causing reduced $D_{cl}(CV)$

2.4. CONCLUSIONS.

The rate of charge transport is determined by the morphology of the polymer layer This, in turn, is dependent upon the coordination sphere of the immobilised redox centre and the specific interactions between the polymer and the contacting electrolyte. It has been demonstrated that the identity of the metal atom of the redox centre is also of fundamental importance in determining the overall physico-chemical properties of the layer

The bis-coordination imposes a structural rigidity upon the polymer segments, resulting in an open, porous structure. This results in D_{ct} values which are insensitive to changes in electrolyte concentration. In the case of the ruthenium polymer, the porous structure extends throughout the layer, resulting in the establishment of a common equilibrium during charge transport on all experimental time scales. For the osmium metallopolymer, however, this is not seen and $D_{ct}(PS)$ is greater than $D_{ct}(CV)$, possibly reflecting differential swelling in H_2SO_4 and pTSA, and the establishment of only electronic equilibrium on faster time scales in HClO₄.

For $[Ru(bipy)_2(PVP)_n]^{2+}$ (where n = 5 or 10), the rate limiting step in the charge transport process is the same in high and low electrolyte concentrations and is independent of redox site loading and electrolyte type. The activation parameters, the low rates of homogeneous charge transport and the sensitivity of D_{ct} to counter-anion type suggests that counter-ion motion is the rate limiting step. Because the increase in D_{ct} with increased redox site loading is small, it is thought that electron self exchange can not be rate limiting in this system.

For $[Ru(bipy)_2(PVP)_n]^{2+}$ the observation that k^o exhibits a similar trend with electrolyte and loading as $D_{cl}(PS)$ indicates that heterogeneous electron transfer and homogeneous charge transport are affected by ion availability and diffusion in the same way

2.5. **REFERENCES.**

- 1 J M Calvert and T J Meyer, Inorg Chem, (1982), 21,3978
- 2 J M Calvert and T J Meyer, Inorg Chem, (1981), 20, 27
- 3 S M Geraty and J G Vos, J Chem. Soc, Dalton Trans, (1987), 3073
- 4 J M Clear, J M Kelly, D C Pepper and J G Vos, Inorg Chum. Acta, (1979), 33, L139
- 5 R J Forster and J G Vos, Macromolecules, (1990), 23, 4372
- 6 R J Forster and J G Vos, J Inorganic and Organometallic Polymers, (1991), 1, 67
- J M Calvert, J V Caspar, R A Binstead, T D Westmoreland and T J Meyer, J Am Chem Soc, (1982), 104, 6620
- 8 T D Westmoreland, J M Calvert, R W Murray and T J Meyer, J Chem. Soc, Chem. Commun, (1983), 65
- 9 H Dahms, J Phys Chem, (1968), 72, 362
- 10 I Ruff, Electrochim Acta, (1970), 15, 1059
- A R Guadalupe, D A Usifei, K T Potts, H C Hurrell, A E Mogstad and
 H D Abruna, J Am Chem Soc, (1988), 110, 3462
- N Oyama, T Ohsaka, H Yamamoto and M Kaneko, J Phys Chem, (1986), 90,
 3850
- 13 T Ohsaka, H Yamamoto and N Oyama, J Phys Chem, (1986), 91, 3775
- 14 C P Andrieux in, *Electrochemistry, Sensors and Analysis*, Analytical Symposia Series, Elsevier, Amsterdam, (1986), Vol 25, 235
- 15 J S Facci, R H Schmehl and R W Murray, J Am Chem. Soc , (1982), 104, 4959
- 16 R J Forster and J G Vos, J Electroanal Chem, (1991), 314, 135

- 17 R J Forster, J G Vos and M E G Lyons, J Chem. Soc Faraday Trans, (1991), 87, 3761
- 18 R J Forster and J G Vos, Electrochim Acta, (1992), 37,159
- 19 S M Oh and L R Faulkner, J Am Chem. Soc , (1989), 111, 5613
- 20, M Majda and L R Faulkner, J Electroanal Chem, (1984), 169, 77
- N Oyama, S Yamaguchi, Y Nishiki, K Tokuda, H Matsuda and F C Anson,
 J Electroanal Chem, (1982), 139, 371
- 22 K Shigehara, N Oyama and F C Anson, Inorg Chem., (1981), 20, 518
- 23 H R Zumbrunnen and F C Anson, J Electroanal Chem, (1983), 152, 111
- 24 N Oyama and F C Anson, Anal Chem, (1980), 52, 1192
- 25 N Oyama, J Shimomura, K Shigehara and F C Anson, J Electroanal Chem, (1980), 112, 271
- 26 N Oyama, T Ohsaka and T Ushirogouchi, J Phys Chem, (1984), 88, 5274
- 27 T Ohsaka, T Okajima and N Oyama, J Electroanal Chem, (1986), 215, 191
- 28 N Oyama, T Ohsaka, M Kaneko, K Sato and H Matsuda, J Am Chem Soc, (1983), 105, 6003
- 29 C R Martin, I Rubenstein and A J Bard, J Am Chem. Soc, (1982), 104, 4817
- 30 N Oyama, T Ohsaka, T Ushirogouchi, S Sanpei and S Nakamura, Bull Chem Soc Jpn, (1988), 61, 3103
- 31 N Oyama, T Ohsaka and M Nakanishi, J Macromol Sci , (1987), A24, 375
- 32 S M Oh and L R Faulkner, J Electroanal Chem, (1989), 269, 77
- D Leech, R J Forster, M R Smyth and J G Vos, J Mater Chem, (1991), 1,
 629
- 34 M E G Lyons, H G Fay, J G Vos and A J Kelly, J Electroanal Chem, (1988), 250, 207
- 35 R J Forster, A J Kelly, J G Vos and M E G Lyons, J Electroanal Chem., (1989), 270, 365

- 36 G Inzelt and L Szabo, Electrochim Acta, (1986), 31, 1381
- 37 S B Khoo, J K Foley and S Pons, J Electroanal Chem., (1986), 215, 273
- 38 F B Kaufman, A H Schroeder, E M Engler, S R Kramer and J Q Chambers, J Am Chem. Soc, (1980), 10, 483
- 39 T Ohsaka, N Oyama, K Sato and H Matsuda, J Electrochem. Soc, (1985), 132, 1871
- 40 W J Albery, M G Boutelle, P J Colby and A R Hillman, J Electroanal Chem., (1982), 133, 135
- 41 A H Schroeder and F B Kaufman, J Electroanal Chem., (1980), 113, 209
- 42 J B Berkowitz, M Yamin and R M Fouss, J Polym Sci , (1958), 28, 69
- 43 B P Sullivan, D J Salmon and T J Meyer, Inorg Chem, (1978), 17, 3334
- 44 D A Buckingham, F P Dwyer, H A Goodwin and A M Sargeson, *Aust J Chem*, (1964), 17, 325
- 45 R A Krause, Inorg Chim Acta, (1977), 22, 209
- 46 D Ghesquiere, B Ban and C Chachaty, Macromolecules, (1977), 10,743
- 47 E M Kober, J V Caspar, B P Sullivan and T J Meyer, Inorg Chem, (1988), 27,
 4587
- 48 O Haas, M Kriens and J G Vos, J Am Chem Soc, (1981), 103, 1318
- 49 O Haas, H Zumbrunnen and J G Vos, Electrochim Acta, (1985), 30, 1551
- 50 K Aoki, K Tokuda and H Matsuda, J Electroanal Chem, (1983), 146, 417
- 51 K J Vetter, Electrochemical Kinetics, Academic Press, New York, (1987)
- 52 H S White, J Leddy and A J Bard, J Am. Chem Soc, (1982), 104, 4811
- 53 A Schroeder, F B Kaufman, V Patel and E M Engler, J Electroanal Chem, (1980), 113, 193
- 54 T P Henning, H White and A J Bard, J Am Chem Soc, (1981), 103, 3937
- 55 P Daum, J R Lenhard, D R Rolison and R W Murray, J Am Chem Soc, (1980), 102, 4649

- 56 WT Yap and R A Durst, J Electroanal Chem., (1987), 216, 11
- 57 W T Yap, R A Durst, E A Blubaugh and D D Blubaugh, J Electroanal Chem, (1983), 144, 69
- 58 C P Andrieux and J M Saveant, J Phys Chem., (1988), 92, 6761
- 59 R Lange and K Doblhofer, J Electroanal Chem., (1987), 237, 13
- 60 J C Jernigan and R W Murray, J Am. Chem. Soc, (1987), 109, 1738
- 61 M E G Lyons, H G Fay, T McCabe, J Corish, J G Vos and A J Kelly J Chem. Soc Faraday Trans, (1990), 86, 2905
- 62 A J Bard and L R Faulkner, Electrochemical Methods, Fundamentals and Applications, Wiley, New York, (1980)
- 63 P Ferruti and R Barbucci, Adv Polymer Sci , (1984), 58, 55
- 64 A Eisenberg, Macromolecules, (1970), 3, 147
- 65 E F Bowden, M F Dautartas and J F Evans, J Electroanal Chem, (1987), 219,91
- 66 S B Tuwiner, Diffusion and Membrane Technology, Chapman and Hall, New York, (1962)
- 67 G J Samuels and T J Meyer, J Am Chem Soc, (1981), 103, 307
- 68 T R E Kressman and J A Kitchener, J Chem Soc , (1949) , 1190, 1201, 1208
- 69 S Yamaguchi, H Matsuda, T Ohsaka and N Oyama, Bull Chem. Soc Jpn, (1983), 56, 2952
- 70 R J Forster, J G Vos and M E G Lyons, *J Chem Soc Faraday Trans*, (1991), 87, 3769
- 71 T Ohsaka, S Kunimara and N Oyama, Electrochim Acta, (1988), 33, 639
- T Ohsaka, M Nakanishi, O Hatozaki and N Oyama, Electrochim Acta, (1990), 35, 63
- C Amatore, J M Saveant and D Tessier, J Electroanal Chem, (1983), 146,
 37

CHAPTER 3

The effect of HClO₄ Electrolyte Concentration and Redox Site Oxidation State on the Resident Layer Mass of Thin Films of [Os(bipy)₂(PVP)₁₀Cl]+

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3.1. INTRODUCTION.

When a pressure is applied to the surface of some crystals a potential difference is generated across them. Conversely, the application of a potential across the crystal produces a corresponding deformation. First discovered in quartz in 1880 by Jacques and Pierre Curie, this phenomenon is termed the piezoelectric effect and is found to occur in crystals which do not have a centre of inversion in the ionic crystalline solid [1]

When an oscillating potential is applied, the crystal vibrates at the frequency of the exciting voltage This is the crystal resonator A typical crystal, with attached electrodes is shown in Fig 3 1 1. The amplitude of the mechanical vibration reaches a maximum when the frequency of the driving voltage is close to one of the mechanical resonances of the crystal. The crystal resonator can be made to oscillate at one of the crystal's resonant frequencies by incorporating the crystal unit into a circuit with suitable gain and feedback. This is the crystal oscillator circuit [1]. The mode of vibration of the crystal is dependent on many factors, but primarily on the crystallographic cut angle, the electrode configuration of the crystal resonator, the supporting structures and the oscillator circuitry employed [1].



Fig 3 1 1 Laboratory monitor quartz crystal

For a mechanical vibrational system, a change in the resonant frequency is often observed when material is added or removed from the vibrating body. In 1952, Sauerbrey demonstrated that the shift in the resonant frequency of an oscillating quartz crystal could be used to accurately determine the mass of rigidly attached material [2]. Since then, the Quartz Crystal Microbalance (QCM) has found routine use as a gas phase and vacuum technique [1]. However, in these early applications, the deleterious effects of liquid films on the QCM performance were noted and it was thought that the viscous dampening of the crystal oscillation would not only cause large frequency shifts, but also result in instability and cessation of oscillation [3]. It has only been in the last decade that it has been demonstrated that the QCM can be made oscillate in the liquid phase [4-7], monitoring not only changes in the mass attached to the electrode [8-10], but also changes in bulk solution properties such as viscosity [4,7,11-13].

In 1985, Bruckenstein and Shay demonstrated the use of one of the electrodes of the quartz crystal as the working electrode in a three-electrode electrochemical cell [14] The Electrochemical Quartz Crystal Microbalance, (EQCM), has since found considerable application for the *in situ* electrogravimetric investigation of electrode processes [8-10]

Previous studies of the polymer $[Os(bipy)_2(PVP)_{10}Cl]^+$ have indicated that the rate of charge transport is strongly influenced by electrolyte type and concentration [15-19], while the EQCM has shown considerable differences in the levels of solvent transferred during redox switching in different near-neutral pH electrolytes [20,21] These effects have been attributed to changes in polymer morphology

It is the purpose of this, and following chapters, to investigate the redox-induced mass changes within $[Os(bipy)_2(PVP)_{10}Cl]$ + films in electrolytes where significant differences in polymer morphology are anticipated. The electrolytes chosen are HClO₄, where dehydrated, compact layers exist [15], and para-toluene sulphonic acid, where the more facile movement of mobile species has been observed [15]. The study will first consider

the effect of electrolyte concentration on the resident layer mass and polymer morphology, and will attempt to relate these data with redox processes

As viscoelastic dampening of the quartz crystal oscillation prevents the accurate evaluation of mass from frequency data [21-24], in order to quantitatively assess the mass changes occuring within the polymer the rigidity of the layers must be first established This is achieved through the measurement of the crystal impedance [21-24] - i e the admittance (or conductance) response at a range of frequencies around the crystal resonance A decrease in admittance and a broadening of the resonance (as characterised by the peak width at half height), is a qualitative reflection of a decrease in the rigidity of the film, which may be equated with morphology changes occuring within the polymer

In this chapter, the equilibrium (or "thermodynamic") mass changes within films of $[Os(bipy)_2(PVP)_{10}Cl]^+$, as a function of HClO₄ electrolyte concentration and polymer redox state, are considered The theoretical background to the QCM will be presented first, and a brief review of its applications in electrochemistry will then be given

3.2. THEORETICAL BACKGROUND TO THE EQCM.

3.2.1. Piezoelectric Quartz Crystals.

 α -Quartz is the most commonly used piezoelectric material in routine applications [1]. The quartz crystal has a number of fundamental modes of resonance, overtones of each fundamental, as well as coupled resonances. However, the thickness-shear mode is the most sensitive to attached mass. This mode is illustrated in Fig.3.2.1. In order to suppress unwanted modes of crystal oscillation the quartz crystal slab must be cut (from a single crystal) at a precise crystallographic angle. The thickness-shear mode for α -quartz is observed in the "AT" and "BT" cuts. The cut used for the EQCM is the AT, and is illustrated in Fig.3.2.2. The cut angle also determines the temperature stability of the oscillation resonant frequency and the response of the crystal to surface stress [1]. The resonant frequency of the AT cut, which has an angle of 35 o 15', is insensitive to temperature variations around room temperature, as shown in Fig.3.2.3. This is obviously a desirable property.



Fig.3.2.1. Thickness-shear mode for quartz crystal oscillation.





AT-cut quartz crystal



Fig 3 2 3 Temperature-dependence of oscillation resonant frequency for quartz crystals of various cut angles

3.2.2. The Mass-Frequency Relationship.

The resonant frequency of the α -quartz crystal is such that a standing wave is set up within the crystal Thus for a crystal of thickness t (cm), with a fundamental frequency f_0 (Hz),

$$f_0 = V_q / 2t$$
 (3 2 1)

where V_q (cmHz) is the acoustic wave velocity within the quartz The thickness of the crystal slab may be defined by,

$$t = M_q / A \rho_q \tag{322}$$

where ρ_q (gcm⁻³) is the density of the quartz and M_q (g) is the mass of the quartz in the piezoelectrically active region between the two electrodes of area A (cm²) Combining Eqn 3 2 1 and 3 2 2,

$$f_0 = V_q A \rho_q / 2M_q$$
 (3 2 3)

Defining the areal mass of quartz by $m = M_q / A$,

$$f_0 = V_q \rho_q / 2m$$
 (3.2.4)

This equation clearly illustrates that the frequency of oscillation of a blank quartz crystal is dependent only the mass of the quartz between the two electrodes and that for a uniform crystal thickness only the areal mass is relevant

The addition of a uniform, rigid film, of areal mass Δm , to the one of the electrodes of the crystal will result in a decrease in the resonant frequency (Δf) Assuming that the attached mass can be treated as an equivalent mass change of the quartz itself,
$$f_0 + \Delta f = V_q \rho_q / 2(m + \Delta m)$$
 (3.2.5)

Eqn 3 2 5 can be rewritten as,

$$\Delta f = -\{ 2 f_0^2 / \rho_q V_q \} \{ \Delta m (1 + \Delta m/m) \}$$
(326)

When the change in areal mass, Δm (gcm⁻²), is considerably less than m, and substituting in for the constants $\rho_q=2.65$ gcm⁻³ and $V_q=3.34 \times 10^5$ cmHz [14], the change in frequency of an oscillating crystal, Δf (Hz), on addition of a small mass is given,

$$\Delta f = -2.26 \times 10^{6} f_{0}^{2} \Delta m \qquad (3.2.7)$$

This is the Sauerbrey equation [2], which was first formulated to describe vacuum metal deposition

3.2.3. Crystal Oscillation Immersed in Liquid.

When an oscillating crystal is immersed in liquid an oscillating boundary layer is set up due to the viscous coupling of the liquid medium. It has been shown that the change in frequency of the crystal, Δf , can be expressed as,

$$\Delta f = f_0^{3/2} \left(\eta_L \rho_L / \pi \rho_q \mu_q \right)^{1/2}$$
(328)

where η_L is the liquid viscosity, ρ_L is the liquid density and μ_q is the shear modulus of quartz. For thin rigid films attached to the immersed side of the crystal, the overall frequency change is simply the sum of of the frequency changes due to the attached film (Eqn 3 2 7) and the liquid (Eqn 3 2 8)

A more rigorous derivation of the mass-frequency relationship and the effect of liquid on the crystal oscillation can be obtained in Reference 1, and References 10 to 12

3.2.4. Secondary effects in mass-frequency relationship.

The frequency of the crystal oscillation is determined by the density, elastic stiffness and dimensions of the quartz [1]. All these quantities are affected by the existence of mechanical stress within the quartz resonator due to the attached electrodes and structural mounts, and more significantly, by stresses arising from films deposited on the electrode surface and from the liquid load of the contacting liquid phase [25].

The QCM has a radial mass-sensitivity function [26-28]. In air, the radial sensitivity has been calculated from the local damage produced in thin films by ion-beam sputtering [27], while in the liquid phase the sensitivity of the QCM has been investigated by the comparison of homogeneous silver deposition over the entire electrode with localised deposition in well-defined areas [28]. An investigation was also performed in the liquid phase by provoking frequency changes by placing a tungsten wire probe in contact with the quartz crystal [29,30].

In both liquid and air, for a crystal heavily stressed on one side it has been shown that the differential radial sensitivity of the crystal changes. Despite this, the integrated mass sensitivity of the crystal is found to remain constant [27,28]. This emphasises the importance of the need for homogenous, uniform attachment of mass over the entire electrode surface for the accurate application of Eqn.3.2.7. The centre of the crystal becomes more sensitive to changes in the attached mass, while the crystal edges, which are constrained in their movement, become less sensitive to mass [27]. This reflects the observation that maximum deformation of the crystal under stress occurs in the centre and that the resonant frequency is linearly related to the elastic energy stored within the crystal [25].

Because of the reduced mass sensitivity at the crystal edges, the mechanical dampening of the oscillation due to the electrical contacts to the quartz, becomes less significant. Similarly, electric field fringing effects [14] become inconsequential.

However, the fact that the radial mass sensitivity is stress-dependent results in quartz resonators of smaller active areas exhibiting smaller average sensitivity across the whole electrode [28]

The response of the crystal to surface stress depends on the crystallographic cut The AT-cut responds in an almost-equal but opposite way to BT-cut crystals [1,26] This property is utilised in the Double Resonator Technique, where both AT and BT cut crystals are used simultaneously [1] This enables the subtraction of the contribution from stress effects to the frequency changes measured

The height of the column of solution over the crystal has only a small effect on the frequency of oscillation [14] Of more importance is the change in the viscosity of the solution with increasing distance from the crystal surface [14,25] In deriving Eqn 3 2 8 the bulk viscosity of the liquid phase is used Any change in the viscosity of the solution within the boundary layer (which is *ca* 300 nm thick [31]), will be erroneously attributed to mass changes These changes cannot be accurately accounted for and may become significant in the diffuse double layer that exists at the coated-electrode / electrolyte interface

Of even greater significance is the roughness of the electrode in the presence of a viscous medium [10,32-34] The entrainment of the liquid within crevices on the electrode surface will contribute to the coupled viscous load. The effect has been studied for the changes in the roughness of gold, silver and copper electrodes following oxidation / reduction cycles in various aqueous electrolytes [32,33]. More recently a thorough investigation of the electrode microstructure was performed in conjunction with impedance analysis [34]. This enabled "rigidly" attached solvent in the channels of the roughnese to be distinguished from the viscously coupled solvent within the boundary layer.

In order to distinguish more clearly between mass changes occuring at the electrode surface and changes in the resonant frequency due to the contacting liquid, equivalent

electric circuits for the QCM have been considered [35-38] These circuits are based on the coupling of the mechanical displacement and electric potential within the piezoelectric quartz which results in mechanical interactions with the contacting liquid The QCM electrical characteristics are measured by an impedance analyzer at frequencies near resonance and have been sufficiently well defined in terms of equivalent circuit parameters to allow differentiation between mass and liquid loading. The models also enable other mechanical effects, such as viscosity, elasticity, density, dielectric constant, specific conductivity etc , to be evaluated in terms of their effect on the electrical characteristics of the QCM. These developments are beyond the scope of this thesis and the reader is referred to References 34 to 38.

3.2.5. Framework for the Interpretation of EQCM data.

The use of the QCM with one of the electrodes as the working electrode of an electrochemical cell enables the frequency changes due to an electrochemically driven process to be monitored [14] This is particularly useful for the evaluation of the interfacial movement of mobile species during charge transport processes within thin films of electroactive materials coated onto the crystal electrode surface [8-10] The EQCM cannot differentiate between the interfacial movement of charged and neutral species. However, for a known electrochemical reaction, the simultaneous capture of charge data will define the extent of the reaction and will provide information on the electroneutrality requirements for the movement of mobile ions. Thus, the combination of charge and mass transfer data may yield additional insight into the redox processes occuring within the polymer layer.

Interpretation of EQCM data requires the mass and charge relationship to be defined [31,39-41] The approach adopted in this work is that proposed by Hillman *et al* [31,39,40], and will be briefly outlined

The net total mass change per unit area of the electrode, occuring at the polymer / electrolyte interface is given by,

$$\Delta M = \Sigma m_{\rm m} \Delta \Gamma_{\rm m} \tag{329}$$

where $\Delta\Gamma_m$ is the change in the molar population of species m within the polymer film, and m_m is the molar mass. The change in mass of the polymer film is due to two components, the movement of ionic species and the movement of net neutrals. Therefore,

$$\Delta M = \Sigma m_1 \Delta \Gamma_1 + \Sigma m_n \Delta \Gamma_n \qquad (3 \ 2 \ 10)$$

where the subscripts 1 and n denote ionic and neutral species, respectively The total mass change 1s calculated from frequency measurements using the Sauerbrey equation The net charge passed at the polymer / electrode interface 1s,

$$Q = \int dt = -\Sigma z_1 F \Delta \Gamma_1 \qquad (3 2 11)$$

where z_1F is the charge carried per mole of the ionic species 1. In this analysis the charge is defined as positive for film oxidation. Combining Eqn 3 2 10 and 3 2 11, the total mass change per mole of redox sites can be obtained

$$\Delta MF / Q = \{ \Sigma m_n \Delta \Gamma_n + \Sigma m_1 \Delta \Gamma_1 \} / \{ \Sigma z_1 \Delta \Gamma_1 \}$$
(3 2 12)

This describes the net mass change per mole of redox sites converted and has units of gmol-1 For a film in a quasi-equilibrium state, Eqn 3 2 12 is referred to in future discussions as the normalised mass change

In order to evaluate the contribution of a particular ion j, to the observed mass change, an expression Φ_j is used This is a linear combination of the mass change

observed and the mass change that is associated with the movement of the ion j if it alone maintains electroneutrality for the charge passed Φ_j is therefore the weighted difference of the mass and charge responses, in units of gcm⁻², and is defined by,

$$\Phi_{\mathbf{j}} = \Delta \mathbf{M} + \mathbf{Q} \left(\mathbf{m}_{\mathbf{j}} / \mathbf{z}_{\mathbf{j}} \mathbf{F} \right) = \Sigma \mathbf{m}_{\mathbf{n}} \Delta \Gamma_{\mathbf{n}} + \Sigma \left(\mathbf{m}_{\mathbf{i}} - \mathbf{m}_{\mathbf{j}} \mathbf{z}_{\mathbf{i}} / \mathbf{z}_{\mathbf{j}} \right) \Delta \Gamma_{\mathbf{i}}$$
(3 2 13)

 Φ_j represents the additional mass transfer (either positive or negative), of all mobile species to that anticipated for the motion of the chosen ion j

For an evaluation of instantaneous mass fluxes, the differential forms of Eqn 3 2 10 to 3 2 13 can be used. The charge density is replaced by the current density, i, the areal mass becomes the rate of areal mass change (ΔM , gcm⁻²s⁻¹) and Φ_J becomes Φ_J (the mass flux of all species except the chosen ion j). These time-dependent parameters are useful for investigating mass changes under more dynamic experimental conditions and, for accurate comparisons, require normalisation to the time scale of the experiment

3.2.6. Review of EQCM applications.

The under-potential deposition (UPD) of metal films has been monitored *in situ* using the EQCM [42-46] In acid electrolytes the UPD of lead onto gold electrodes was found to proceed with an electrosorption valency of 2+ [43,44], as evidenced by the combination of mass and charge data For the UPD of lead on silver electrodes, in hydroxide [45] or borate buffer [46] solutions, the formation of Pb^{II} / anionic ligand complexes was found to result in significantly different mechanisms which could be clearly seen microgravimetrically at the EQCM

The deposition and dissolution of thin films has also been studied [47-53] The electrodeposition of silver onto gold, which proceeds with a current efficiency of unity, has been used for the calibration of the mass-sensitivity of the EQCM [14] For the corrosion [47] and electroless deposition [48,49] of copper onto gold electrodes, the EQCM has provided an insight into the submonolayer surface reactions that occur The copper phase formation and dissolution have also been investigated using combined ac-impedance and ac-quartz electrogravimetry [50] Corrosion kinetics have been investigated with the combined use of QCM and XPS techniques [51] The anodic dissolution of nickel [52] and nickel-phosphorous [53] films have been monitored using the EQCM and have been both shown to exist in two distinct phases

Metal oxide layers have also received considerable attention [32,33,54-60] Bruckenstein and Shay have demonstrated the formation of a monolayer of adsorbed oxygen at a gold electrode [55] Oxide layers on titanium [56] and aluminium [57] have also been investigated, as has the electrocatalysis of oxygen-transfer reactions at pure and bismuth doped beta-lead dioxide film electrodes [58] The intercalation of lithium into V_6O_{13} electrodes was investigated [59] and yielded mass changes at high lithium concentrations which reflected the formation of a second phase and / or morphology changes at the electrode surface The importance of electrode morphology changes has also been evident during oxidation / reduction cycles of metal electrodes in aqueous electrolytes [32-34] For copper electrodes in acid electrolytes no mass changes occur during electrochemical cycling [60] However, in neutral and alkaline electrolytes mass changes in excess of those required for oxygen incorporation into the copper electrode surface were observed [33] In conjunction with SEM, the EQCM data were found to reflect an increase in the electrode roughness and the entrainment of solution within the electrode crevices More pronounced roughening of the electrode was found to occur with silver electrodes [33,34], while for gold electrodes a relatively smaller change in electrode structure was observed [32]

The EQCM has provided insight into a similar phenomenon during the absorption of hydrogen (or deuterium) into palladium electrodes during electrolysis [61-63] The large frequency shifts observed were attributed to stresses within the palladium due to H_2 (D₂) adsorption / desorption and absorption processes

The EQCM has been used to study the adsorption of halides [64] as well as the adsorption of metal ions from buffered solutions [65] The preparation of Langmuir-Blodgett films [66-68], and the electrochemically mediated adsorption of redox surfactants [69], have also been monitored The use of adsorbed proteins and immunoglobulin G on the QCM have been used for gravimetric immunosensing devices [70-72], while the selective adsorption of odorous substances at lipid multibilayers has also been investigated [73] The use of the EQCM for recording adsorption isotherms has also been explored [74,75]

The EQCM has been used to monitor mass changes occuring within electroactive polymer layers As shown by a number of authors [21-24,76-79], the attachment of nonmetallic films to the EQCM electrode surface may present problems due to the viscoelastic rather than rigid character of the films However, considering a theoretical treatment of viscoelastic layers on an oscillator, it has been demonstrated that provided

the layer thickness is much smaller compared to the thickness of the quartz slab, viscoelastic films may be treated as rigid [54,80] This has been verified for Langmuir-Blodgett multilayers [66], Prussian Blue and its analogues [82;83], partially dinitrited poly(styrene) [24], the electropolymerised conducting polymers polyaniline [22], polypyrrole [81] and polybithiophene [23], and for the redox polymer $[Os(bipy)_2(PVP)_{10}Cl]+ [21]$ However, depending on the contacting electrolyte-polymer interaction and the subsequent level of polymer swelling, non-rigid behaviour may become significant and the mass-frequency relationship invalidated [21,24,78,79]

The EQCM has been used to study the deposition of inorganic polymer films. The deposition of Prussian Blue [82], the deposition / dissolution of electrochromic films of diheptylviologen bromide [41] and the electrocrystallisation of charge transfer salts [84,85] have been studied. Ion and solvent transport within Prussian Blue [82] and its nickel analogue [83] during electrochemical processes have been investigated, with solvent movement unambiguously quantified by isotopic substitution of H₂O with D₂O [83]. The selective intercalation of Na⁺ into Prussian Blue films, compared to Li⁺, was also determined using the EQCM [86].

The use of the EQCM in monitoring the electropolymerisation and deposition, of conducting polymers has been explored Ion and solvent movement during subsequent electrochemical processes within the formed polymers has also been investigated

Polyaniline films have been prepared both at the bare electrode [22,87,88] and within precast Nafion films [89] Simultaneous EQCM and ellipsometric measurements enabled differences in nucleation and growth of galvanostatically and potentiostatically electropolymerised films to be elucidated [87] Mass changes accompanying oxidation / reduction cycles in polyaniline have also been investigated [22] Anion insertion, with very little solvent movement, was observed during oxidation At more acidic pH proton expulsion mechanisms during oxidation were also in evidence, thus indicating the partial protonation of the amine groups of the polymer [22]

The electrosynthesis of polypyrrole has also been studied [81,90-95]. The simultaneous measurement of mass and charge enabled the efficiency of the polymerisation / deposition process to be determined as a function of film thickness and deposition rate [81,90]. Film formation, which was electrolyte dependent, was found to be affected by oligomer solubility and exhibited second order reaction kinetics with respect to monomer concentration [81,90]. The importance of the counter-anion size in polypyrrole has been investigated [92-95]. During electrochemical processes, for polypyrrole films grown with small anions, electroneutrality is maintained by anion insertion / expulsion [92,93]. However, for polymer films formed with large or polymeric anions, as in the case of polypyrrole / poly(styrene sulphonate) composites [95], electroneutrality is maintained by cation motion [92,93,95]. Other conducting polymers studied using the EQCM include poly(3-methylthiophene) [96], the self-doped polymer poly [3,6-(carbaz-9-yl propane sulphonate] [97] and polybithiophene [31,40,98-101]. In the latter, the kinetics of the doping / undoping process has been studied in great detail, with the movement of solvent (CH₃CN) and electrolyte salt in opposite directions being the rate limiting processes [31,40]. This involved the formalism outlined in Section 3.2.5.

A number of redox polymers have been investigated using the EQCM. Poly(vinyl ferrocene), (PVF), has received considerable attention [31,39,77-79,100-107]. Changes in the ion and solvent population within films of PVF during redox processes have been studied by a number of authors [31,39,78,80,100-104], while the ion-exchange of ferri (ferro) cyanide [106] and open circuit bimolecular reactions [107] in PVF have also been studied. From electrochemical data, Hillman *et al.* [102] and Inzelt [78] have demonstrated the permselectivity of PVF films in perchlorate electrolyte. The mass data accompanying redox processes, obtained at slow cyclic voltammetric scan rates, indicated that the mass transfer was due to the interfacial movement of a single perchlorate counter-anion and 4 - 5 solvent molecules [78,100,102]. In an earlier investigation [79] considerably less solvent movement with the perchlorate anion was observed. Co-ion

participation in PVF redox processes in perchlorate was not in evidence, as demonstrated by the invariance of the mass change with increasing cation molecular weight [102]. At higher concentrations, permselectivity fails and transfer of salt occurs during redox switching [31,39,102].

The importance of counter-anion type in PVF has been addressed [78,80,102]. An almost linear relationship between the observed mass change and anion molecular weight has been observed [102], with slight deviations attributed to variations in polymer structure affecting solvent movement. However, in a more recent study [78], more pronounced changes in PVF morphology with changes in counter-anion type have been observed. This has been graphically illustrated by the behaviour of PVF in PF₆- and Cl-electrolytes [79]. In PF₆- electrolyte no solvent movement was observed, while in Cl-electrolyte extensive delamination of the polymer from the electrode during oxidation occured due to the increased solvation of the polymer layer.

Similar counter-anion effects have been observed in the redox polymer, $[Os(bipy)_2(PVP)_{10}Cl]+ [20,21]$. In perchlorate no solvent transfer occurs, with the polymer layers behaving permselectively [21]. In para-toluene sulphonate, NO₃-, SO₄²⁻ and Cl- electrolytes, significant solvent transfer was observed. This was related to the increased solvent content of the polymer layers in the initial state when converted to these salt forms [22]. The large movement of solvent in pTS- electrolytes was confirmed from isotopic substitution of H₂O with D₂O [21].

The importance of polymer swelling and solvation has been clearly demonstrated in the "break-in" effects observed in many electroactive polymer systems. "Break-in" in PVF [78,105], tetracyanoquinodimethane (TCNQ) [108,109], nitrated polystyrene [24], poly(3-alkylthiophene) [110] and polyaniline [111] have been observed. Polymer swelling during the electrochemical deposition of PVF in CH₂Cl₂ has also been investigated [77]. For PVF transferred to aqueous electrolytes, where rigid layers exist [77], the solvation of the polymer in the reduced and oxidised layer has also been studied by the combined use of EQCM and ellipsometric measurements [100] A polymer layer comprising 55% polymer, 45% solution was found, with the polymer becoming more inhomogeneous and diffuse in the outer regions during oxidation of the layer. In nitrated polystyrene films increased solvation of the polymer with increasing redox cycling, as indicated by a decrease in the frequency of the working electrode, was observed [29]. This quickly lead to the loss of rigid layer behaviour

The effect of electrolyte concentration [78,108,109] and temperature [109] on polymer swelling has also been studied at the EQCM In TCNQ films cation motion maintains electroneutrality within the polymer during redox cycling and the mass changes observed were found to be dominated by the concomitant movement of water of hydration [108,109] At high electrolyte concentrations, where there is reduced levels of hydration, the mass changes observed decreased The kinetic limitations observed in the redox behaviour of TCNQ at high electrolyte concentrations were explained in terms of the decreased solvent activity and the compaction and restricted segmental polymer motion within the polymer layer [108] In variable temperature experiments, facilitated mass and charge transfer at higher temperatures was explained in terms of the increased swelling of the polymer layer [109] At intermediary electrolyte concentrations (ca 2 5 M LiCl), the increased swelling resulted in a loss of polymer rigidity At higher concentrations, however, layer compaction prevented swelling even at elevated temperatures In contrast to this was the behaviour of [Os(bipy)2(PVP)10Cl]+ films in high NapTS electrolyte concentrations [22] Here, the broadening of the conductance spectrum and the cessation of crystal oscillation in the active mode was interpreted in terms of excessive polymer swelling

The resident ion and solvent population within the polymer layer has been found to be of great importance in determining the mass changes observed at the EQCM [112] For the thermodynamic mass changes in polythionine films, the mass change observed were rationalised in terms of an ion-aggregation model in which ions resident within the

polymer layer provided a source of counter-anion [112] The transfer of large quantities of solvent in response to activity gradients was also evoked [112] This model was an extension of the approach outlined by Bruckenstein and Hillman, which describes the general features of mass and charge transfer processes [113]

The kinetics of mobile species transfer has been addressed for nitrated polystyrene [24], and has been systematically studied for PVF [31,39,103,104] and polythionine [103,104,114] In PVF, under potential step conditions, counter-ion motion maintains electroneutrality at short time scales [31,39] At low electrolyte concentrations solvent movement was found to be slower than ion motion. At fast cyclic voltammetric scan rates [103,104] this delineation of solvent transfer was termed "kinetic permselectivity", in which the mass change observed, due to the experimental time scale considered, was that of counter-anion only At high electrolyte concentrations salt transfer also occurs, but at a slightly faster rate than solvent movement [31,39] The kinetics of mass transfer has also been studied for polythionine. In this system at low pHs, three protons and one counteranion are transferred per redox site conversion [114], with solvent movement proceeding in the opposite direction in response to activity gradients. Here, the initial movement of two protons proceeds quickly, followed by the slower movement of the coupled proton / counter-anion and solvent [114] The conclusion in this system, and in others [24,103], is that transient non-equilibrium states are utilised to maintain electroneutrality under more dynamic conditions and that this may be achieved independently of the thermodynamic requirements of the charge transport process itself

3.3. EXPERIMENTAL.

3.3.1. Materials

 $[Os(bipy)_2Cl_2]$ was prepared as described by Buckingham *et al* [115] Its purity was verified using reverse phase chromatography, with a mobile phase of 80 20 acetonitrile H₂O (8% LiClO₄), with photo diode array detection in the uv-visible

Poly(4-vinylpyridine) was prepared as described previously (Section 2 2 2)

 $[Os(bipy)_2(PVP)_{10}Cl]Cl$ was prepared by refluxing a tenfold excess of PVP with $[Os(bipy)_2Cl_2]$ in ethanol for up to 36 hours. The reaction was monitored by uv-visible spectroscopy (using a Hewlett-Packard 342A diode array) and cyclic voltammetry (using an EG&G PAR 273 potentiostat / galvanostat). Although no photochemical reactions were observed, the reactions were routinely carried out in the dark. The metallopolymer was isolated by precipitation into diethyl ether and purified by repeated precipitation (x 3) in diethyl ether from methanol. The polymer was recovered by precipitation into diethyl ether and vacuum dried. The metal loading of the polymer was confirmed using molar extinction coefficient data for the ¹MLCT transition of the uv-visible spectrum at 350 nm

Electrolyte solutions were prepared using H₂O (purified using a Millipore Milli-Q water purification system)

3.3.2. Quartz Crystals and electrode preparation.

The quartz crystals employed were 10 MHz AT-cut laboratory monitor crystals (International Crystal Manufacturing Company Inc, Oklahoma City, USA) The crystals were supplied as standard and were either polished or finished with a 5 µm abrasive The crystals had a 90 nm thick layer of gold sputter coated onto each side, as shown in

Fig 3 1 1 One of the gold contacts to the quartz crystal served as the working electrode in a standard three electrode cell

The working electrode was coated with a visibly smooth, uniform layer of $[Os(bipy)_2(PVP)_{10}Cl]Cl$ by drop evaporation from an ethanol solution of the polymer The metallopolymer films were air dried for at least 24 hours The resonant frequency of the crystal oscillation was checked before and after the electrode coating procedure This enabled a gravimetric evaluation of the dry mass of the polymer

The polymer-coated crystals were fixed to the base of the electrochemical cell using non-corrosive silicone rubber sealant (RTV1000 Dow Corning), and allowed to cure for several hours The resonant frequency of the mounted crystal was also measured and compared with the dry mass evaluation of the unmounted coated crystal This was to ensure that the presence of sealant in close proximity to the circular mass-sensitive region of the electrode did not have a significant effect on the crystal oscillation [14] The geometric area of the exposed portion of the coated electrode was *ca* 0 23 to 0 24 cm² All current and charge data were thus normalised by the individually measured polymer-coated electrode areas

The active piezoelectric area of the electrodes was 0 21 cm², with a calibrated masssensitivity of 0 232 Hzcm²ng⁻¹ [14,116]

3.3.3. Instrumentation.

The oscillator circuit used for the measurement of the frequency difference between the reference crystal and the working crystal was, with minor modification, that outlined by Bruckenstein and Shay [14]

An Oxford Electrodes potentiostat was used for experiments carried out in potentiostatic mode All potentials were measured with respect to an aqueous potassium saturated calomel electrode (SCE), which was separated from the electrochemical cell by a Luggin capillary The counter electrode was a platinum mesh which was flamed and washed before use

The electrochemical cell, the oscillator circuitry and its power supply were enclosed in a faraday cage earthed to the potentiostat All measurements were made at ambient temperature ($20 \pm 2 \text{ oC}$) Although the electrochemical cell was not thermostatted, constant temperature could be assumed on the time scale of each experiment Temperature effects, which may alter electrolyte viscosity and influence frequency measurements [31], were therefore considered negligible

Frequency difference measurements were obtained using a Hewlett Packard 5334B frequency counter, which was accurate to ± 0.1 Hz in 10 MHz. For the mass changes associated with the redox switching of the polymer films, the frequency difference, the potential, current and charge were recorded on Bryans 6000 series xy-recorders or via a Keithley Data Acquisition System 570 interfaced to an IBM ATX computer. For recording on xy-recorders, the frequency was read as a voltage output from a frequency-voltage converter (with time constant of *ca* 5 ms). The computer-acquired data was stored in a compact binary file and was converted into an ASCII file suitable for importing into a Lotus 1-2-3 worksheet for analysis. All interfacing and computer programmes were written by M. J. Swann and D. C. Loveday of Bristol University

The rigidity of the polymer layers was evaluated as a function of electrolyte concentration and redox state from the shape of the admittance resonance of the polymercoated crystal Admittance analysis was performed in collaboration with Dr A Glidle

The frequency response of the crystal as a passive element was determined on a Hewlett-Packard 8753A network analyzer used in reflectance mode [23] The QCM was connected to the network analyser via a 50 Ω coaxial cable and a transmission / reflectance test unit (HP85044A) Scans were made over a 16 kHz bandwidth, with the computer software centred on the peak admittance maximum The sweep time was 400

ms, with a sweep repetition rate of 29 s Measurements were made at 801 points centred about the fundamental resonant frequency of the coated crystal giving a frequency resolution of 20 Hz

3.3.4. Procedures.

The equilibrium solvent and ion populations within the polymer layer, at open circuit, were measured as a function of electrolyte concentration (sic pH) The polymer films were first exposed to H_2O and the pH was adjusted by the dropwise addition of HClO₄ For all measurements the solution height above the electrode surface was maintained constant Equilibration times of up to 1 5 hours were required for a stable frequency reading to be obtained at each pH. The experiment was performed under a number of different experimental conditions. These will be discussed in greater detail in the relevant sections (Section 3 4 3 1 and 3 4 3 2).

The mass changes occuring during redox switching were determined over a concentration range of 10-4 M to 4 0 M HClO₄ Memory effects were minimised by continuously scanning over the Os^{II/III} redox couple for *ca* 30 minutes at 50 mVs⁻¹ and then several times at 1 mVs⁻¹ at each new electrolyte concentration. The electrole was then removed, rinsed with Milli-Q water, replaced in a fresh aliquot of the electrolyte and continuously scanned for a further 10 minutes at 50 mVs⁻¹ and once at 1 mVs⁻¹. The electrolytes were de-oxygenated with solvent-saturated argon prior to analysis. During data acquisition the Ar stream was directed over the electrolyte solution to ensure quiescent conditions. The normalised mass changes associated with redox conversion of the film were found to be independent of the order of the electrolyte concentrations to which the polymer layer had been previously exposed.

3.4. RESULTS AND DISCUSSION.

3.4.1. Surface coverage evaluation.

<u>3411</u> Dry mass

Table 3 4 1 Column A, summarises the gravimetric evaluation of surface coverage for a number of polymer coatings These were obtained from the shift in the resonant frequency of the working crystal on applying a polymer film

In these calculations the mass of the polymer unit, $[Os(bipy)_2(PVP)_{10}Cl]Cl$, is taken as 1741 gmol⁻¹ This includes a contribution from the water content of the polymer in the dry state, which contains two molecules of H₂O per osmium moiety and one molecule of H₂O for every two uncoordinated pyridine units of the PVP backbone

<u>3412</u> Electrochemical evaluation

Table 3 4 1, Column B, includes the electrochemical evaluation of surface coverage using slow scan cyclic voltammetry at 1 to 5 mVs⁻¹ in 0 1 M HClO₄ This is found to be*ca* 5 times smaller than the gravimetric evaluation Fig 3 4 1 shows a typical cyclic voltammogram (and mass potential plot) for a $[Os(bipy)_2(PVP)_{10}Cl]$ + film obtained at 5 mVs⁻¹ in 0 1 M HClO₄ The cyclic voltammogram does not represent true surface behaviour and an accurate evaluation of surface coverage cannot be obtained from the integrated charge of the cyclic voltammogram (see Section 1 2 1 1) For complete oxidation of the polymer layer in HClO₄ electrolytes, controlled potential coulometry must be used, with charge accumulation for up to 30 minutes [117] Although not performed with the experiments here, the increase in surface coverage evaluated in this way was confirmed later for a number of polymer films and was such to account for the discrepancy observed in Table 3 4 1

Table 3 4 1 Evaluation of [Os(bipy)2(PVP)10Cl]Cl surface coverage and

	Surface Coverage (molcm ⁻² x 10 ⁸)			Solvent Imbibition (c) (molcm ⁻² x 10 ⁸)	Solvent Content (d) (mol pol equiv -1)	
A 	Gravimetric (a)	B	Coulometric (b)			
	1 48		0 28	60 6	41	
	1 96		0 36	74 2	38	
	2 00		0 42	101 0	51	
	2 04		0 41	95 1	47	

layer solvent sorption on immersion in H₂O

- a) Calculated from shift in resonant frequency following coating procedure
- b) Calculated from background-corrected integrated anodic branch of cyclic voltammogram at 1 to 5 mVs⁻¹ in 0 1 M HClO₄
- c) Calculated from shift in resonant frequency on immersion of coated electrode in H₂O (corrected for solution viscosity)
- d) Calculated using gravimetric evaluation of surface coverage

Fig 3 4 1 Cyclic voltammetric and mass-potential response for a crystal modified with [Os(bipy)₂(PVP)₁₀Cl]⁺ Scan rate is 5 mVs⁻¹, supporting electrolyte is 0 1 M HClO₄, the coulometric surface coverage is 1 x 10⁻⁸ molcm⁻²



3.4.2. Solvent Imbibition on exposure of Layer to H₂O.

The coated electrodes were immersed in de-oxygenated Milli-Q H₂O and the frequency difference noted The increase in mass of the polymer layer, summarised in Table 3 4 1, represents the imbibition of 44 ± 5 molecules of H₂O per [Os(bipy)₂(PVP)₁₀Cl]Cl unit This is calculated on the basis of the gravimetric evaluation of the polymer surface coverage and represents 40 to 50% (w/w) of the polymer layer

In this calculation the liquid modulation layer is corrected for by subtracting the known mass change observed at a bare gold electrode in contact with H₂O. Due to the increase in the surface roughness at the polymer / solution interface, the entrainment of solvent within the polymer boundary layer is expected to be greater than at the bare gold electrode [32-34]. The correction for the coupled mass at the coated electrode, therefore, may be incomplete and the amount of solvent actually resident within the polymer layer is possibly less than that calculated in Table 3.4.1. The value of 44 ± 5 molecules of H₂O per polymer unit can be viewed as an upper limit of solvent imbibition by the polymer layer

As will be discussed in greater detail in Chapter 4, the swelling of the polymer on exposure to H₂O can be viewed as the tendency for the polymer segments and contacting solvent to inter-diffuse. Swelling is favoured by the electrostatic repulsion of the fixedcharge sites of the polymer backbone and by the tendency for the high ionic content of the internal pore liquid to be diluted [118,119]. The concentration of fixed-charge sites in the 1 10 loading of this osmium redox polymer, from flotation measurements in nonswelling solvents, is $ca \ 0.7 \ M \ [15,16]$, which is low in terms of ion-exchange resins, and the inter-site separation, assuming a rod-like structure for the PVP backbone, is 25 Å [120]. These features indicate that extensive swelling will not occur

The upper limit of 44 molecules of H_2O per polymer unit, although suggesting the need for substantial polymer expansion, is not, in fact, significant in terms of solvent

uptake by 10n-exchange resins, especially when one considers that the 44 molecules of solvent are distributed over 9 pyridine moleties and one osmium redox centre Ionexchange resins containing up to 50% (w/w) solvent are known to remain hard and brittle [121] Ellipsometric studies of PVF [100] and polythionine [112] films have shown them to contain up to 50% solution, while the osmium polymer itself has been found to contain 27% solvent in the chloride salt form when stored at 97% relative humidity [21] Appreciable swelling to form polymer gels, therefore, requires a considerably higher solvent content

Fig 3 4 2 illustrates the admittance-frequency response of a coated crystal and a bare crystal in contact with H_2O As discussed in the Section 3 1, the broadening of the crystal resonance represents an increase in viscoelasticity [21-24] In Fig 3 4 2 the presence of a polymer film results in only a slight broadening of the crystal resonance, indicating the absence of a significant departure from rigidity. The polymer coating is thus seen to remain rigid when exposed to H_2O



Fig 3 4 2Admittance spectra for (a) uncoated and (b) coated crystal immersedin H2OGravimetric polymer surface coverage is 2 x 10⁻⁸ molcm⁻²

3.4.3. HClO₄ concentration effects on layer mass and rigidity.

For this osmium redox polymer, activation parameters and the rate of charge transport have been found to be strongly influenced by the concentration of HClO4 electrolyte [15], and have been discussed in terms of changing polymer structure. The resident layer mass and structure are thus considered here for a range of HClO4 concentrations. As mass changes occuring within the polymer can only be quantitatively evaluated when layer rigidity has been established, the change in polymer morphology with changing electrolyte concentration is considered first, using impedance analysis [23]. This is followed by a more quantitative interpretation of the mass changes which occur within the polymer layer. Finally, the mass data are used in calculating the apparent pK_a of the pyridine moleties of the PVP backbone.

<u>3431</u> HClO₄ concentration effects on Polymer rigidity

Fig 3 4 3 illustrates the change in the admittance-frequency response for a polymercoated crystal, at open circuit, as the contacting solution concentration is increased from pure solvent to 1 0 M HClO₄ The polymer surface coverage was 2 x 10⁻⁸ molcm⁻², as determined by gravimetry No voltammetry of the redox polymer was performed in the course of acquiring this data Table 3 4 2 (Column A) summarises the admittance maximum, the peak width at half maximum and the shift in the resonant frequency at each electrolyte concentration

Fig 3 4 4 illustrates the corresponding series of admittance measurements for the same electrode, as the electrolyte concentration is decreased. At each concentration the polymer layer has been repeatedly scanned voltammetrically over the Os^{II/III} couple prior to obtaining the open circuit spectrum. The characteristic features of the resonance shape for these spectra are summarised in Column B of Table 3 4 2

Fig 3 4 3 Admittance spectra for an [Os(bipy)₂(PVP)₁₀Cl]⁺ film on exposure to increasing HClO₄ concentration (in the absence of any voltammetry)



Gravimetric surface coverage 2 x 10⁻⁸ molcm⁻²





(Ω-1 A	x 10 ²)	(kF		$\Delta f(a,c)$	
А		(kHz)		(Hz)	
	B	Α	B	A	В
0 478	0 402	6 096	7 681	0	- 518
0 468	0 402	6 096	7 681	- 52	- 518
0 456	0 406	6 304	7 681	- 104	-1036
0 460	0 412	6 304	7 526	- 466	-1192
0 460	0 420	6 304	7 3 7 2	- 933	-1554
0 464	0 414	6 356	7 681	-2435	-3057
0 444	0 412	6 825	7 836	-4249	-4404
0 468	0 470	6 304	6 444	-4508	-4663
0 448	0 442	6 721	6 908	-4663	-45 60
) 478) 468) 456) 460) 460) 464) 468) 448	0 478 0 402 0 468 0 402 0 456 0 406 0 456 0 406 0 460 0 412 0 460 0 420 0 464 0 414 0 468 0 470 0 468 0 442	0.478 0.402 6.096 0.468 0.402 6.096 0.456 0.406 6.304 0.456 0.406 6.304 0.460 0.412 6.304 0.460 0.420 6.304 0.464 0.414 6.356 0.444 0.412 6.825 0.468 0.470 6.304 0.448 0.442 6.721	0.478 0.402 6.096 7.681 0.468 0.402 6.096 7.681 0.456 0.406 6.304 7.681 0.460 0.412 6.304 7.526 0.460 0.420 6.304 7.372 0.460 0.412 6.356 7.681 0.464 0.414 6.356 7.681 0.464 0.412 6.825 7.836 0.468 0.470 6.304 6.444 0.448 0.442 6.721 6.908	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Table 3 4 2Admittance spectra at open circuit for an [Os(bipy)2(PVP)10Cl]+ coatedcrystal in HClO4Gravimetric surface coverage is 2 0 x 10-8 molcm-2

Uncoated electrode (air) 10 011088 MHz Coated electrode (air) 10 003180 MHz Coated electrode (H₂O) 9 999150 MHz (zero value, Column A)

- a) Data interpolated from points of 20 Hz resolution
- b) Admittance maximum (at resonant frequency)
- c) Δf is the shift in centre frequency with respect to value on initial exposure to H₂O (Corrected for viscous load of electrolyte)
- d) Column A is data for first exposure to electrolyte without electrochemical cycling
 Column B is open circuit data after electrochemical cycling at each concentration

Fig 3 4 3 and Table 3 4 2 show that as the concentration of HClO₄ is increased, there is a large decrease in the resonant frequency of the coated crystal, indicating an increase in the mass of the polymer layer. All frequency data are corrected for solvent viscosity changes and the decrease in frequency is considered to represent the protonation of the pyridine moleties of the polymer backbone [122] and the influx of perchlorate counteranions required to maintain electroneutrality. The mass increase occurs at open circuit, thus illustrating that protonation is associated solely with the physico-chemical properties of the metallopolymer and, as such, is a feature of all PVP-based redox polymers of this type

In Fig 3 4 3, with the exception of 0 01 M HClO₄, the crystal resonance shape becomes slightly sharper as the electrolyte concentration is increased from 10-4 M to 0 1 M HClO₄ The sharpening of the crystal resonance shape for the polymer-coated crystal suggests that, despite the increased viscous load of the contacting electrolyte, and despite the increase in the number of fixed-charge sites of the polymer backbone and the insertion of ClO₄- counter-anions, the polymer layer becomes more rigid. The broadening of the admittance spectrum in 1 0 M HClO₄ (Fig 3 4 3 - I) is not thought to represent polymer expansion, but can be attributed to the large increase in the electrolyte viscosity at this concentration. The effect of increasing HClO₄ electrolyte concentration on the resonance shape of an <u>uncoated</u> crystal is illustrated in Fig 3 4 5 for HClO₄ concentrations ranging from 10^{-5} M to 4 0 M

The increase in polymer rigidity represents the compaction of the film due to the crosslinking of polymer segments by the perchlorate anion [123-129] In addition, the disruption of hydrogen bonding between water molecules by ClO₄- [130] can result in dehydrated and deswollen polymer structures, as observed previously for quaternised PVP [124,125] Deswelling of the polymer phase at high electrolyte concentrations, due to the decreased activity of the solvent in the external solution [108,109,119] is also to be expected

In 0 01 M HClO₄, however, a broadening of the coated crystal resonance is observed (Fig 3 4 3 - G) This cannot be attributed to the viscous liquid load of the electrolyte and must represent the expansion of the polymer layer. As will be discussed below and in Section 3 4 3 2, at this electrolyte concentration there is incomplete protonation of the polymer backbone. The ionic content of the polymer film increases without the extensive inter-chain crosslinking which occurs at higher HClO₄ concentrations, resulting in an increased tendency for the polymer matrix to swell

The admittance spectra obtained with decreasing electrolyte concentration (Fig 3 4 4) do not retrace those obtained on initial exposure (Fig 3 4 3) This is clearly illustrated in Fig 3 4 6, where the resonant frequency is plotted against the electrolyte pH Graph A represents the frequency change as the electrolyte is initially increased, while Graph B corresponds to the frequency changes as the electrolyte concentration is decreased. The frequency data have been converted to mass, and normalised to the dry mass estimation of the polymer surface coverage. These mass changes per polymer equivalent are also illustrated in the ordinate in Fig 3 4 6, and represent the change in the ion and solvent content of the polymer phase relative to the initial level of imbibed solvent.

The change in resonant frequency at concentrations more dilute than 0 01M HClO₄, coupled with the broadening of the resonance shape, indicates that the polymer layer has expanded and that a structural change (i e a "break-in" effect) has occured These data are considered to reflect the difficulty in attaining equilibrium levels of solvation of the inner polymer layer [119] which is only facilitated by the extensive interfacial counter-anion and solvent transfer that occurs during electrochemical cycling "Break-in" effects have been observed for many electroactive polymers, where the initial low polymer phase solvent and / or electrolyte content results in an electrochemical response for the first redox cycles which differ from those subsequently seen [78,105,108-111, 130]



The effect of HClO₄ concentration on the uncoated crystal resonance Fig 3 4 5



Fig 3 4 6 The shift in resonant frequency for $[Os(bipy)_2(PVP)_{10}Cl]^+$ coated crystal on (a) initial exposure to increasing HClO₄ concentration (without voltammetry) and (b) exposure to decreasing $HClO_4$ concentration (with voltammetry) Data taken from Table 3 4 2



At concentrations greater than 0 01 M HClO₄, the increase in rigidity afforded by the crosslinking of the pyridine units of the fully protonated backbone by ClO₄-, results in no change in the polymer structure or layer mass before or after the break-in (see Fig 3 4 6) However, on re-exposure to lower HClO₄ concentrations, the increased level of polymer solvation established by electrochemical cycling, results in an increase in layer mass. In addition, the reduced crosslinking due to the lower ClO₄- content, coupled to the increased swelling pressures which exist in dilute electrolyte concentrations [119], results in further polymer solvation and expansion.

Although there are changes in the morphology of this metallopolymer with changes in HClO4 concentration, these changes are small and are insignificant in comparison with the swelling of this polymer in contact with pTSA electrolyte (see Chapter 4) The maintenance of rigid structures for polymer films which are only partially protonated, suggests that crosslinking occurs at all concentrations and indicates that perchlorate must exist in clusters within the polymer matrix when present in small quantities This is in agreement with the observed behaviour of perchlorate in quaternary ammonium anion exchangers [131] Having demonstrated the rigidity of this polymer at all HClO4 electrolyte concentrations it is now possible to give a quantitative assessment of mass changes occuring within the layer

<u>3432</u> <u>HClO4 concentration effects on polymer layer mass</u>

For a quantitative evaluation of the layer mass dependency on HClO₄ electrolyte concentration, the experiment was performed with the working crystal in the active mode The "titration" was performed as before. However, in order to ensure the expulsion of chloride from the polymer layer and the conversion of the polymer to the perchlorate salt form, the film was scanned voltammetrically for several hours at 1 mVs⁻¹ at pH 3 50. The electrode was then rinsed a number of times, stored in Milli-Q water and the experiment continued at this pH. The increase in mass associated with the counter-anion exchange of the polymer salt was corrected for in all subsequent mass calculations. Although the hydration numbers of the two anions differ [132], no change in the solvent content of the film due to these differences was corrected for. This is due to the lack of detailed knowledge of the level of solvation of anions in polymeric membranes.

At each pH below pH 3 50 the mass of the electrode was measured at open circuit before and after continuous voltammetric scanning of the Os^{11/111} couple The mass evaluated did not change significantly, indicating that the "break-in" effect was absent This was attributed to the establishment of equilibrium levels of solvation within the polymer layer by electrochemical cycling at each preceding HClO₄ concentration

The effect of the changing viscous load of the electrolyte was corrected for by subtraction of the frequency shift observed at each pH at an uncoated gold electrode This correction assumes polymer layer rigidity, which has been established in Section 3 4 3 1, and will be addressed further in Section 3 4 4 2a

Fig 3 4 7 (Graph A) and Table 3 4 3 summarise the mass data obtained at open circuit as the electrolyte concentration is increased from pure solvent to ca 4 0 M HClO₄ All masses quoted are in addition to the initially imbibed solvent estimated in Section 3 4 2 and thus represent the further incorporation of ions and solvent within the polymer layer The mass changes per polymer equivalent, based on the gravimetric estimate of surface

Fig 3 4 7 The change in resident layer mass of a [Os(bipy)₂(PVP)₁₀Cl]⁺ coated crystal as a function of HClO₄ electrolyte concentration (sic pH), for (A) Os^{II} and (B) Os^{III} oxidation states Gravimetric surface coverage is 8 7 x 10⁻⁸ molcm⁻²



HClO ₄ pH	∆f (a) (kHz)	ΔM (b) (ugcm ⁻²)	Mass per pol unit (c) (g pol equiv -1)	ClO ₄ - content (d) (mol pol equiv -1)	
				A	В
6 00	0	0	0	0	0
5 15	- 0 429	1 849	21	0 2	01
4 00	- 2 326	10 028	116	10	07
3 50	- 3749	16 161	184	16	11
3 00	- 6303	27 169	314	27	19
2 50	- 8759	37 756	436	37	26
2 00	-14 393	62 040	716	61	43
1 50	-16 234	69 975	808	68	49
1 00	-17 323	74 669	862	73	52
0 50	-17 411	75 048	867	74	53
0 00	-18 133	78 161	903	76	55

Table 3 4 3 Change in resident layer mass with increasing HClO4

concentration for data illustrated in Fig 3 4 7 (A)

a) Decrease in resonant frequency, corrected for changing electrolyte viscosity

- b) Calculated from calibrated mass sensitivity of 0 232 Hzcm²ng⁻¹
- c) Calculated from gravimetric surface coverage (8 7 x 10-8 molcm-2)
- d) Column A assuming insertion of dehydrated ClO₄- and H₃O+ per uncoordinated pyridine moiety

Column B assuming insertion of hydrated ClO₄- (hydration number 2 6)

and H_3O^+ per uncoordinated pyridine moiety

coverage, are in excellent agreement with those obtained in Fig 3 4 6 Fig 3 4 7 (Graph B) represents the mass of the fully oxidised layer and will be discussed later in Section 3 4 4

Table 3 4 3 summarises the estimated number of perchlorate anions per $[Os(bipy)_2(PVP)_{10}Cl](ClO_4)$ unit at increasingly acidic pH Assuming the insertion of H₃O+ with solvated perchlorate, using the solution hydration number of 2 6 [132], an upper limit of *ca* 6 anions per polymer unit is obtained. This suggests incomplete protonation of the polymer backbone, which is considered unlikely at pH much more acidic than the pK_a of the PVP homopolymer (pK_a 3 30) [122]. For the incorporation of H₃O+ with an unsolvated anion, an upper limit of *ca* 8 perchlorate anions per polymer unit is obtained. This almost corresponds to the electroneutrality requirement for the 9 protonated, uncoordinated pyridine moieties of each polymer unit

Since the EQCM can only detect the <u>net</u> interfacial mass transfer, the discussion thus far has assumed that the initial solvent imbibition of *ca* 44 molecules of H₂O per polymer unit remains constant. This may not be so. The disruption of the H₂O structure by ClO₄may result in a reduction of the polymer phase solvent content [123,124]. This may be evidenced by the layer compaction and increased polymer rigidity with increasing levels of protonation, as observed in Fig 3 4 3 and Fig 3 4 4. It is also possible that, while the overall level of polymer phase solvent content remains constant, the sorption of solvated ClO₄- and H₃O+ may occur at the expense of the forced expulsion of the initially imbibed free solvent [126-128]. The increased electrostriction of the same quantity of interstitial solvent is also anticipated to result in deswelling of the polymer layer.

However, there is no evidence for the transfer of solvent either into or out of the polymer layer, if occuring at all Furthermore, it is clear that while some solvation of perchlorate ions is expected within the polymer, solution values for anion hydration are inappropriate Regardless of the level of protonation, it is seen that for a polymer exhibiting a 6 to 10 fold increase in ionic content, the extent of solvent movement is

considerably less than would be expected

In Fig 3 4 7 (Graph A), at pH less than 0 5 the resident mass within the polymer layer begins to increase further. This is attributed to a breakdown of permselectivity and the influx of co- and counter- ions into the polymer layer. The lowering of solvent activity at increased concentrations, coupled with the increase in the perchlorate content within the layer, is expected to result in a more compact, dehydrated polymer structure

<u>3433.</u> The evaluation of the pKa^{app} of PVP.

The plot of the change in polymer layer mass with increasing HClO₄ concentration in Fig 3 4 7 (Graph A) can be viewed as the gravimetric titration of the free pyridine groups of the PVP backbone of the polymer Assuming that the pH of the resin phase in the equilibrated polymer layers is the same as that of the contacting electrolyte, the apparent pK_a of the protonated pyridine groups, pK_a^{aPP} , may be calculated using the Henderson-Hasselbach equation [119,133],

$$pH = pK_a^{app} + \log \{\alpha / (1 - \alpha)\}$$
(3.4.1)

where the pK_a^{app} is defined by,

$$pK_{a}app = -\log_{10} \{ [PVP][H+] / [PVP H+] \}$$
(3 4 2)

 α is the degree of dissociation of the protonated polymer backbone and is determined by,

$$\alpha = (\Delta M_{\text{total}} - \Delta M) / \Delta M_{\text{total}}$$
(3 4 3)

where ΔM_{total} is the total mass change observed on increasing the pH from *ca* 6 00 to pH 0 5, and ΔM is the mass change at a given pH Substituting into Eqn 3 4 1,

$$pH = pK_a^{app} + \log_{10} \{ (\Delta M_{total} / \Delta M) - 1 \}$$
(344)

Fig 3 4 8 shows the plot of $\log_{10} \{ (\Delta M_{total} / \Delta M) - 1 \}$ vs pH for the rising portion of the layer mass-pH profile Two areas of differing behaviour exist, with a transition occuring at pH 2 54 (± 0 10) At this pH log₁₀ { ($\Delta M_{total} / \Delta M$) - 1 } is zero and, according to Eqn 3 4 4, defines the pK_a^{app} of the PVP backbone Significantly, as discussed in Section 3 4 3 1, it is at electrolyte concentrations corresponding to this pH (*ca* 0 01 M HClO₄) that morphology changes within this polymer are also found to occur

At pH above pH 2 50, the slope of the plot in Fig 3 4 8 is 0.60 ± 0.10 Eqn 3 4 4 predicts a slope of unity, thus the calculated slope indicates that there is a lesser dependence of polymer protonation on the solution pH than expected In this region the concentration of the contacting electrolyte is 10^{-5} M to 10^{-3} M, while the concentration of the osmium fixed sites is *ca* 0.7 M [15,16] Consequently, there will be a significant Donnan potential at the membrane / solution interface which will exclude electrolyte and prevent protonation of the polymer backbone

At pH more acidic than pH 2 50, the slope of the plot is $1\ 20\pm0\ 07$ This is in nearagreement with the predicted protonation-pH behaviour in Eqn 3 4 4 and suggests that electrolyte partition into the polymer layer is not retarded by membrane potentials. In this lower pH range there will be less efficient electrolyte exclusion and the increased ion association within the layer, as manifested by the increased polymer rigidity in Section 3 4 3 1, will serve to reduce the Donnan potential further [119] Protonation can thus proceed as dictated by the pH of the external solution and the pK_aapp of PVP

While the development of membrane potentials and polymer morphology changes undermine the assumptions for the application of the Henderson-Hasselbach equation, it is clear that the pK_a^{app} for the PVP backbone of the metallopolymer is more acidic than the pK_a of the homopolymer in solution (2.54 versus 3.30 [122]) This reflects the exclusion of electrolyte from the polymer layer. Of greater significance, however, is the increased difficulty in the protonation of the PVP due to the electroneutrality requirement for counter-anion insertion within the finite void volume of the compact and rigid polymer films



Fig 3 4 8 Graph of $\log_{10} \{ (\Delta M_{total} / \Delta M) - 1 \}$ vs HClO₄ electrolyte pH for rising portion of resident layer mass data in Fig 3 4 7 (A)

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3.4.4. Mass changes accompanying Os^{II/III} couple.

<u>3441</u> General description of the redox process

In Section 3 4 3 the affect of the electrolyte concentration in determining the anion, co-ion and solvent population within the polymer layer in the reduced Os^{II} state was examined. The changes in layer mass due to the one-electron oxidation of Os^{II} to Os^{III} in a 1 1 acid electrolyte (H₃O+)(ClO₄-), is now considered. The description of redox switching in polymer films outlined here is one which requires the polymer phase and solution phase species to be distinguished. In this regard the EQCM is particularly suited to an investigation of redox-induced transfer of mobile species.

The reduced state of the polymer contains a counter-anion, A-, and an undetermined amount of electrolyte, b, for each (Os^{11}) + centre The total polymer population of anion is thus (1+b) A_p-, and that of the hydronium ion, (b) H₃O_p+, where the subscript p denotes the polymer phase Due to the protonation of the polymer backbone, up to *ca* 8 counteranions may be required within the polymer film Hence, values for b at different electrolyte pHs can be assumed to be those given in Table 3 4 3 The Os¹¹ state of the polymer also contains a quantity of solvent, (w) H₂O_p, which may be assumed to be the initially imbibed solvent, as discussed in Section 3 4 2

On oxidation of the osmium centres electroneutrality is maintained by the influx of counter-anion from the bathing solution,

$$\{ (O_{S^{II}})^+ (A^-) \}_p + A_{S^-}$$
 $(O_{S^{III}})^{2+} (A^-)_2 \}_p + e^-$ (3 4 5)

The bathing solution is denoted by the subscript s The polymer phase population of A- therefore increases to (2+b) A_p -, and that of the solution phase decreases by 1

An alternative mechanism for maintaining electroneutrality within the layer is the expulsion of hydronium ions,

(y) { (Os^{II})+PVP H₃O+ (A-)₂ }
$$_{p}$$
 + (y) H₂O_s (3 4 6)
(y) { (Os^{III})²+PVP (A-)₂ + H₂O } $_{p}$ + (y) H₃O_s+ + e-

In this way the hydromum ion population within the film is decreased to (b-y) H_3O_p +, while that of the solution phase is increased by y. For every osmium centre oxidation electroneutralised in this way, the requirement for anion ingress during oxidation is negated. Hence, the polymer phase population of anion on oxidation is correspondingly reduced to (2+b-y) A_p - The overall solution phase condition for the anion after oxidation is therefore (y-1) A_s -

1

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The change in the ionic concentration of the internal polymer pore liquid during redox processes is expected to result in a change in the activity of the interstitial solvent [113] Solvent movement into or out of the layer, defined by the coefficient x, is therefore expected As can be seen from Eqn 3 4 6, cation loss during oxidation can result in the generation of a solvent molecule within the film. The polymer phase condition for solvent on oxidation can be summarised by $(w+x+y) H_2O_p$, with the solution phase necessarily changing by $(-x-y) H_2O_s$

Combining Eqn 3 4 5 and 3 4 6, the half reaction for Os¹¹ oxidation can be described by,

{
$$(O_{S^{11}})^+ + (1+b) A^- + (b) H_3O^+ + (w) H_2O$$
 } p (3 4 7)

{
$$(O_{SIII})^{2+} + (2+b-y) A^{-} + (b-y) H_{3}O^{+} + (w+x+y) H_{2}O$$
 } p + e-

There is no requirement for integral relationships between the number of electrons transferred and any of the neutral mobile species entering or leaving the film [113] However, because an integer number of electrons are transferred for each redox centre, integer relationships will exist between the stoichiometric coefficients for the charged species [40] Thus, in Eqn 3 4 7, (b-y) will equal 1

It can be seen that movement of solvent on redox switching is expected The transport of other net neutrals, such as ion pairs and undissociated molecules, is also possible and can be included in the overall equation. All these mass transfer processes are driven by their associated electrochemical potentials. For charged species the electrochemical potential contains both an activity gradient and a potential gradient term. Solvent molecules and net neutrals are only transferred in response to activity considerations [31,39,104]

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<u>3442</u>, Effect of HClO₄ concentration on Redox-induced mass changes

Table 3 4 4 summarises the normalised mass changes associated with redox switching in a series of HClO₄ electrolytes at cyclic voltammetric time scales of 1 and 5 mVs⁻¹ These data are averaged over analysis of at least two different polymer coatings and the results obtained repeatedly on a given film

It is considered that the trends in the normalised mass change observed during redox processes at different electrolyte concentrations reflect the changing composition of the polymer layer and are not due to differences in the ionic strength of the contacting electrolyte This is seen in Fig 3 4 7, which illustrates the layer mass as a function of osmium redox state and electrolyte concentration

Fig 3 4 1 shows a typical cyclic voltammetric response for the Os^{II/III} couple at 5 mVs⁻¹ in 0 1 M HClO₄ (see Section 3 4 1 2) This figure also includes the mass change within the polymer layer associated with the maintenance of electroneutrality during the charge transport process While true surface behaviour is not observed in HClO₄ electrolytes at these cyclc voltammetric time scales, Fig 3 4 1 shows that the mass change within the polymer has attained a steady state value. The results in Table 3 4 4 indicate that for most electrolyte concentrations there is little difference in the normalised mass changes obtained at 1 and 5 mVs⁻¹. These time scales are thus sufficiently long for all mobile species to attain their quasi-equilibrium state, as dictated by the extent of oxidation of the polymer layer.

Table 3 4 5 summarises the potential for the half-total-mass-change, $E_{1/2}(m)$, and the half-total-charge-change, $E_{1/2}(q)$ [20,103] for the oxidation and reduction of the polymer at 1 mVs⁻¹ at each electrolyte concentration. At all but the lowest and highest concentrations, $E_{1/2}(m)$ and $E_{1/2}(q)$ coincide for both anodic and cathodic processes, indicating concomitant mass and charge transfer [20,103]

HClO ₄ Conc	Normalised Mass Change (gmol-1)				
(Molar)	A 1 mVs-1 (a)		B 5 mVs-1 (a)		
0 001	91	(20)	60	(12)	
0 01	186	(5)	-		
0 03	-		155	(2)	
0 10	143	(1)	142	(3)	
0 30	147	(1)	143	(1)	
0 70	146	(1)	145	(1)	
1 00	142	(1)	142	(2)	
2 00	186	(3)*	183	(3)*	
3 00	-		479	(5)*	
4 00	-304	(10)*	-221	(40)	

Table 3 4.4.Normalised mass for redox switching in $[Os(bipy)_2(PVP)_{10}Cl]^+$ modified crystals at 1 & 5 mVs-1 in a series of HClO4 electrolytes

a) Normalised mass averaged on at least three repeat determinations of each polymer film and on at least two different polymer coatings (standard deviation from the mean value is quoted in brackets)

,

* denotes three repeat determinations on a single film only

HClO ₄ Conc	E'app (a,b)	Oxidation (b)		Reduction (b)	
(Molar)	(mV vs SCE)	E _{1/2} (m)	E _{1/2} (q)	E _{1/2} (m)	E _{1/2} (q)
0 001	337	408	389	318	297
0 01	282	292	292	278	278
0 03	248	268	269	223	223
0 10	212	216	220	208	210
0 30	190	188	191	180	180
0 70	170	178	182	155	157
1 00	165	16 6	179	145	149
2 00	130	127	132	131	130
3 00	90	98	104	93	99
4 00	80	128	98	116	65

Table 3 4 5The formal potential of the Os^{II/III} couple and the half-mass and
half-charge potentials for oxidative and reductive processes

- a) Taken as the average of the anodic and cathodic peak potentials
- b) All potentials (mV vs SCE) measured at 1 mVs⁻¹ at ambient temperature ($20 \pm 2 \text{ oC}$)

The change in the formal potential of the Os^{11/11} couple, E'_{app}, with electrolyte concentration is also shown in Table 3.4.5 E'_{app} is taken as the average of the anodic and cathodic peak potentials of the cyclic voltammogram at 1 mVs⁻¹ Fig 3.4.9 shows a plot of E'_{app} versus the logarithm of the bathing solution ClO₄- activity, spanning 3 decades of HClO₄ electrolyte concentration. Activities at concentrations less than 0.03 M were calculated using the Debye-Huckel equation [136], while at higher HClO₄ concentrations activities were obtained from Reference 118

The variation in E'_{app} with electrolyte ionic strength is due to the change in free energy associated with the transfer of the anion from the bathing solution to the polymer phase [134,135], and is given by the Nernstian expression [134],

$$E'_{app} = E^{o} - (RT/nF) \ln \{ (a_{A-s}) / (a_{A-p}) \}$$
(348)

where E^o is the formal potential of the redox couple and a_{A-s} and a_{A-p} are the activities of the counter-anion in the external solution and the polymer phase, respectively Provided that a_{A-p} remains essentially constant as the electrolyte concentration is varied, and that there is no significant change in polymer swelling, Eqn 3 4 8 has a predicted slope of -59 mV decade-1 of anion activity. The slope of the plot in Fig 3 4 9 for the concentration range 0 001 M to 1 0 M HClO4, is -61 ± 3 mV decade-1, and has an intercept at unit activity of 153 ± 5 mV vs SCE. The near-Nernstian slope is indicative of permselective behaviour for the osmium metallopolymer in this concentration range, with httle co-ion participation in the charge transport process. Similar behavior has been observed in near-neutral pH perchlorate electrolyte for this polymer [21] and for PVF [78,102]

Fig 3 4 9 Nernst plot for [Os(bipy)₂(PVP)₁₀Cl]+ polymer films in HClO₄ electrolyte (i e E'_{app} versus solution ClO₄⁻ anion activity)



<u>3442a</u> Concentration range 01 M to 10 M HClO4

In the concentration range 0 1 M to 1 0 M HClO₄, the layer mass in the reduced Os^{II} state is essentially constant, and has been found to represent the complete protonation of the uncoordinated pyridine moleties of the PVP backbone. The incorporation of ClO₄- in the fully protonated polymer has been shown to cause an increase in rigidity and, consequently, a lowering of the free volume of the polymer matrix. Both the mechanical forces involved in anion insertion [126-128] and the movement of solvent in response to activity gradients [113], indicate that significant changes in layer morphology may occur during redox processes in this polymer. Indeed, morphology changes have been observed previously for this polymer in a highly swelling electrolyte, H₂SO₄ using STM [137].

In order to determine whether significant polymer layer morphology changes occur during redox processes, the admittance-frequency response of the crystal was measured during redox switching. The shape of the crystal resonance for the polymer layer in the fully reduced and fully oxidised states, for a series of HClO₄ electrolytes, is summarised in Table 3 4 6 Fig 3 4 10 and Fig 3 4 11 show the change in the admittance spectrum during polymer oxidation in 0 1 M and 1 0 M HClO₄, respectively. The monotonic decrease / increase in the resonant frequency as redox switching occurs is indicative of the anion and solvent insertion / expulsion, while the constant resonance shape (see Table 3 4 6) indicates that there is little change in the viscoelasticity of the polymer layer and that no significant redox-induced mrphology changes occur. Therefore, in the concentration range 0 1 M to 1 0 M HClO₄, the rigidity of the polymer layer is maintained during redox switching and the frequency-mass relationship of Section 3 2 2 is not compromised

Fig 3 4 12 shows the variation of mass change with surface coverage of oxidised centres (i e anodic charge), obtained in 0 1 M HClO4 at 5 mVs⁻¹ for films of varying thickness This plot is linear, with a zero intercept The result in 1 0 M HClO4 is similar

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Table 3 4 6The change in admittance spectrum during redox switching for a $[Os(bipy)_2(PVP)_{10}Cl]$ + coated crystal in a series of HClO4 electrolytesScan rate 5 mVs-1, gravimetric surface coverage is 2 8 x 10-8 molcm-2

HClO4 Conc (Molar)	∆f (a,b) (Hz)	Admittan (Ω-1	ce Maxımum x 10 ²)	PWHM (a) (kHz)	
		OsII	OsIII	OsII	OsIII
0 001	- 254	0 444	0 444	6 669	6 669
0 004	- 351	0 420	0 414	7 086	7 346
0 01	- 897	0 424	0 406	7 138	7 763
0 10	- 780	0 462	0 456	6 252	6 356
1 00	- 741	0 450	0 450	6 460	6 460

(a) Data interpolated from points of 20 Hz resolution

(b) Δf is the shift in centre frequency during oxidation Negative values imply mass gain during polymer oxidation

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Fig 3 4 10 Admittance spectra for an [Os(bipy)₂(PVP)₁₀Cl]+ coated crystal during redox switching in 0 1 M HClO₄ at 5 mVs⁻¹ Coulometric surface coverage 2 x 10⁻⁸ molcm⁻²



Fig 3 4 11 Admittance spectra for the same [Os(bipy)₂(PVP)₁₀Cl]+ coated crystal in Fig 3 4 10, but for redox switching in 1 0 M HClO₄ at 5 mVs⁻¹



Fig 3 4 12 The end-to-end mass change accompanying polymer oxidation at 5 mVs⁻¹ in 0 1 M HClO₄ versus the surface coverage of oxidised centres (i e the charge passed)



A significant change in polymer structure in different oxidation states would result in a change in the coupled viscious liquid load [32-34] and a non-zero intercept in Fig 3 4 12 would result Fig 3 4 12 and the data presented in Table 3 4 6 indicate that, in this concentration range of HClO₄, minimal structural changes occur

For non-rigid polymer layers, viscoelasticity becomes more pronounced as the surface coverage is increased [23] The evaluation of mass from the dampened oscillation, although not strictly related to the frequency changes measured due to the violation of the Sauerbrey equation, is less than the true mass change occuring [23] The linear relationship between the mass and charge data in Fig 3 4 12 confirms that the polymer behaves as a rigid, thin layer for the range of film thickness employed in this study and that mass changes are accurately evaluated from frequency measurements

Table 3 4 4 shows that in the concentration range 0 1 M to 1 0 M HClO₄ there is little variation in the mass change associated with the oxidation of each osmium redox centre The potentiometric data in Fig 3 4 9 indicate the existence of a permselective film. This reflects the layer properties in the Os^{II} state. The Os^{II} layer mass in this concentration range also remains invariant (see Fig 3 4 7), with no change in polymer structure occuring (Section 3 4 3 1). In addition, the layer mass is only sufficient to account for the perchlorate required for electroneutrality within the protonated polymer (see Section 3 4 3 2), and no free electrolyte resides within the polymer at concentrations less than 1 0 M HClO₄.

Because of this permselectivity of the layer, the normalised mass change of *ca* 144 gmol⁻¹ can be equated to the movement of a single perchlorate counter-anion and 2 -3 solvent molecules per osmium centre oxidation. This level of solvent transfer is close to the hydration number of ClO₄- of 2 6 [132]. However, it has been shown that solution values for anion hydration are not applicable to the ion within polymer films. Indeed, for mass transfer within this polymer in NaClO₄, no solvent transfer with the counter-anion was observed [20,21]. As will be discussed in Chapter 5, under more dynamic

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experimental conditions solvent movement and perchlorate anion movement are resolved, indicating that the solvent is not specifically associated with the anion. The solvent transfer can thus be viewed as being in response to the activity gradient established by the decrease in the interstitial solvent activity during oxidation of the polymer layer [113]

The mechanism of co-ion expulsion, from either interstitual co-ion in the pore liquid or from deprotonation of the polymer backbone, can be further discounted on inspection of the Φ_{CIO4} - and mass-charge plots shown in Fig 3 4 13 and Fig 3 4 14 for 0 1 M and 1 0 M HClO4, respectively These were obtained at a 1 mVs⁻¹ scan rate The slight assymmetry in the charge in Fig 3 4 14, and the subsequent non-closure of the Φ plot is a feature of the behaviour of this metallopolymer in HClO4 (*vide infra*), and has been observed previously in a study of polybithiophene [40] Non-closure of the plot may arise from trace oxygen in solution, or instrumental drift in the integrator offset, which can become significant during the slow scan rates used here. However, it is thought that the drift in charge is most probably due to incomplete charge recovery from the compact polymer structures which exist in HClO4 electrolyte

The Φ_{ClO4} - plot, as defined in Section 3.2.5, is indicative of the movement of all mobile species, except the chosen ion (in this case, the counter-anion) In Fig 3.4.13 and Fig 3.4.14, the monotonic change in Φ_{ClO4} - represents the concomitant movement of all mobile species with the anion. This, as well as the $E_{1/2}(m)$ and $E_{1/2}(q)$ data in Table 3.4.5, indicates that the mass changes are due to a single mass transfer mechanism and are not the net result of several different processes

Fig 3 4 13 Φ_{ClO4}- and mass-charge plot for [Os(bipy)₂(PVP)₁₀Cl]+ in 0 1 M HClO₄ at a scan rate of 1 mVs ¹ The coulometric surface coverage is 2 x 10⁻⁸ molcm⁻²



Fig 3 4 14 Φ_{ClO4} - and mass-charge plot for $[Os(bipy)_2(PVP)_{10}Cl]$ + in 1 0 M HClO4 at a scan rate of 1 mVs-1 Polymer film as in Fig 3 4 13



The stoichiometric coefficients for the Os^{II} oxidation, described in Section 3 4 4 1, for the HClO₄ concentration range 0 1 M to 1 0 M, are thus determined from the charge and mass changes, and the half reaction given by,

{ (Os^{II})+A⁻}
$$_{p}$$
 + A_s⁻ + 2 6 H₂O_s $=$ { (Os^{III})²⁺(A⁻)₂ + 2 6 H₂O } $_{p}$ + e⁻ (3 4 9)

Because co-ion expulsion is not observed (i e y=0) the polymer ion content due to PVP protonation (i e b=8) is not included in the above equation

<u>3 3 4 2b</u> Concentration range 0 1 M to 0 001 M HClO4

From Section 3 4 3, it was seen that in the concentration range 0 001 M to 0 1 M HClO4 there is considerable variation in the levels of protonation of the polymer backbone. It is clear from Table 3 4 4 that the subsequent effect on film structure has a profound influence on the normalised mass changes occuring during redox processes

The inter-relationship between polymer morphology and the extent of solvent transfer is evident in Fig 3 4 15, which shows the change in the admittance-frequency response of the coated crystal during redox switching in 0 01 M HClO₄ at 5 mVs⁻¹ Table 3 4 6 shows that of all concentrations studied, it is only in 0 01 M HClO₄ that a significant broadening of the crystal resonance occurs on polymer oxidation. It has been found in Section 3 4 3 1 that the decreased levels of protonation within the polymer matrix, coupled with the increased swelling pressures which exist in more dilute electrolytes, ultimately results in conditions which favour swelling at *ca* 0 01 M HClO₄ Fig 3 4 15 clearly illustrates how this change in morphology is exacerbated during oxidation of the polymer layer, where the increase in the ionic content of the layer increases the tendency to swell further. The normalised mass change of 186 gmol⁻¹ thus represents the increased level of solvent

Fig 3 4 15 Admittance spectra for an [Os(bipy)₂(PVP)₁₀Cl]+ coated crystal during redox switching in 0 01 M HClO₄ at 5 mVs⁻¹ Coulometric surface coverage 2 x 10⁻⁸ molem⁻²



movement facilitated by the change in polymer structure and is, in turn the cause of further swelling

The morphology change in 0 01 M HClO₄ affects the evaluation of normalised mass For thick layers, with surface coverage greater than 1 x 10⁻⁸ molcm⁻², the value of 186 gmol⁻¹ is obtained For thin polymer films (less than 10⁻⁸ molcm⁻²), a mass change of only 126 gmol⁻¹ is observed These observations are at variance with what is expected for films which exhibit significant viscoelasticity, where an increase in film thickness would result in a reduction in the mass change observed [23]

Fig 3 4 16 (a) illustrates the Φ_{CIO4} - and mass-charge plot obtained in 0 01 M HCIO4 at 1 mVs⁻¹ for a thin film, with surface coverage 5 x 10⁻⁹ molcm⁻² The Φ_{CIO4} - plot clearly shows that for the first 20% of redox conversion there is no net movement of solvent across the polymer / electrolyte interface. The corresponding plot for a thicker film (with surface coverage 2 x 10⁻⁸ molcm⁻²), is shown in Fig 3 4 16 (b), where Φ_{CIO4} is indicative of the concomitant movement of solvent and anion throughout all stages of oxidation. It is thought that the morphology changes occuring during redox processes at this HCIO4 concentration may result in an under-evaluation of mass changes occuring initially. These effects will be more pronounced for thinner films and the apparent normalised mass change subsequently reduced.

Fig 3 4 16. Φ_{ClO4}- and mass-charge plot for [Os(bipy)₂(PVP)₁₀Cl]+ in 0 01 M HClO₄ at a scan rate of 1 mVs⁻¹ The coulometric surface coverages are (A) 5 x 10⁻⁹ molcm⁻² and (B) 2 x 10⁻⁸ molcm⁻²



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At electrolyte concentrations below 0 01 M HClO₄ the normalised mass change decreases Fig 3 4 17 shows the mass-potential plot and the cyclic voltammogram at a scan rate of 5 mVs⁻¹, for a polymer of surface coverage 2 x 10⁻⁸ molcm⁻² in 0 001 M HClO₄ The cyclic voltammogram exhibits slow kinetics, with large peak-to-peak separation and broad, poorly defined waves This figure also shows that during both oxidation and re-reduction of the polymer layer the net interfacial mass transfer lags behind the passage of charge This is also seen in Table 3 4 5, where $E_{1/2}(m)$ and $E_{1/2}(q)$ do not coincide

The kinetic limitations evident in the cyclic voltammogram of Fig 3 4 17 indicate that charge transport within the polymer is slow. In Section 3 4 3 3 it was seen that Donnan exclusion of electrolyte operates at concentrations less than *ca* 0 01 M HClO₄. While this has significant implications for electrolyte sorption, which requires co-ion transfer, it is not anticipated to result in the kinetic limitations for anion transfer during redox switching which are indicated from the cyclic voltammogram in Fig 3 4 17.

Fig 3 4 18 illustrates the corresponding Φ_{ClO4} - and mass-charge plots for the data in Fig 3 4 17 The continued decrease in Φ_{ClO4} - with the passage of anodic charge indicates that the mass gain observed at the electrode is insufficient to account for the interfacial movement of a counter-anion per redox site conversion

If anion insertion does maintain electroneutrality, the Φ_{CIO4} - plot represents the net movement of large quantities of solvent from the layer. This cannot be in response to activity gradients. The activity of solvent in the bathing electrolyte, which also defines the activity of the solvent within the polymer layer at equilibrium, is not expected to change significantly at concentrations less than 0.1 M HClO₄ and the activity gradient established by polymer oxidation should be similar [112,113]

In Table 3 4 6 there is no change in the admittance spectrum of the coated crystal during redox switching in 0 001 M HClO₄ at 5 mVs⁻¹ The constant shape of the crystal resonance indicates that there is no contribution from changes in viscoelastic

Fig 3 4 17 Cyclic voltammogram and mass-potential plot for [Os(bipy)₂(PVP)₁₀Cl]+ coated electrode in 0 001 M HClO₄ Scan rate is 5 mVs⁻¹, coulometric polymer surface coverage is 2 x 10⁻⁸ molcm⁻²



Fig 3 4 18 Φ_{ClO4} - and mass-charge plot for $[Os(bipy)_2(PVP)_{10}Cl]$ + in 0 001 M HClO4 at a scan rate of 5 mVs⁻¹, for data in Fig 3 4 17



characteristics to the change in mass occuring during redox switching Changes in the flux of solvent induced by redox-dependent structural changes, as observed for 0 01 M electrolyte, therefore do not occur here

The end-to-end mass change of ca 90 gmol⁻¹ in 0 001 M electrolyte at 1 mV⁻¹ (Table 3 3 4), is approximately the mass change observed at 0 01 M HClO₄ minus the molar mass of the perchlorate anion (i e 186 - 99 5 gmol⁻¹) The mass change in 0 001 M electrolyte may therefore represent the transfer of solvent due to the activity gradient established on film oxidation, with the slow continued rise in mass after completion of the oxidation of osmium centres in Fig 3 4 17 corresponding to the slow, continued influx of solvent This is in agreement with the theoretical considerations of Bruckenstein *et al* [112], which predict that at infinite dilution the redox factors governing ion transfer vanish, and a mass change due only to solvent transfer will be seen

However, this suggests that electroneutrality may be maintained by rapid interfacial proton exchange, while the slow rate of charge transport in 0 001 M HClO₄ (see Chapter 5), and the potentiometric data in Fig 3 4 9, indicate that it is anion activity which determines the redox behaviour of the Os^{II/III} couple

In order to evaluate whether co-ion expulsion is likely to be responsible for the maintenance of electroneutrality in dilute electrolytes, it is necessary to consider the time required for the diffusion of a counter anion from the bulk electrolyte to the polymer layer. This is given by [139],

$$t = L^2 / (D_s \pi)$$
 (349)

where t is the time required for diffusion (s), D_s is the diffusion coefficient for solution species (typically 5 x 10⁻⁶ cm²s⁻¹ [139]) and L is the diffusion layer thickness L is estimated in terms of the volume of solution needed to contain the number of counteranions required for electroneutrality within a polymer layer with a surface coverage of *ca* 10-8 molcm-2 For 0 001 M solutions L is *ca* 10-2 cm, yielding a time required for diffusion of 6 s Thus, on the experimental time scale (corresponding to voltammetric scan rates of 1 to 5 mVs⁻¹), there will be sufficient anion available from solution to satisfy electroneutrality within the film Alternative, faster mechanisms for satisfying electroneutrality may operate but are not necessary

However, it is clear from the cyclic voltammogram obtained at 5 mVs⁻¹ in 0 001 M electrolyte, that kinetic limitations do exist and that co-ion participation may be utilised In dilute HClO₄ electrolytes the level of protonation of the polymer decreases, so a_{ClO4} p (Eqn 3 4 8), can no longer be assumed to be much greater than the concentration of osmium centres and may change significantly in the course of redox switching [133] Thus, although the polymer film remains permselective, the potentiometric data are not unambiguous proof of anion activity control It is thought, therefore, that the redox-induced mass transfer behaviour in 0 001 M HClO₄ reflects both counter-anion insertion and co-ion expulsion mechanisms

Irrespective of the contribution to the maintenance of electroneutrality from each ion, severe limitations on the interfacial movement of ions exist in 0 001 M HClO₄. This is surprising considering the relatively more expanded polymer structure which exists at HClO₄ concentrations below 0 01 M (see Section 3 4 3).

<u>3442c</u> Concentration range 10 M to 40 M HClO4

As the electrolyte concentration is increased from 1 0M to 3 0 M HClO₄ the normalised mass changes become greater (see Table 3 4 4) This is attributed to the failure of permselectivity and the ingress of $(H_3O^+)(ClO_4^-)$ into the polymer layer during redox switching [31,39,102]

The loss of permselectivity at high concentrations is evidenced by the increase in layer mass data (Section 3 4 3), and by the breakdown of the Nernstian relationship between ClO₄- activity and E'_{app} (Fig 3 4 9) As has been observed throughout for the redox-induced mass changes in HClO₄, and will be seen in Chapter 4 for the behaviour of this metallopolymer in para-toluene sulphonic acid, any change in the properties of the polymer in the reduced state are highlighted during redox switching

Assuming that the solvent transfer due to activity considerations is the same as for lower concentrations (*ca* 2 - 3 solvent molecules per redox site conversion), the increase in the normalised mass observed in Table 3 3 4 at higher concentrations is due to neutral perchloric acid transfer Thus, at 3 0 M HClO₄, the transfer of acid is (479 - 99 5 - 45) gmol⁻¹, which is equivalent to 2 8 moles of (H₃O+)(ClO₄-) per mole of osmium sites The reaction for osmium oxidation, considering only the net changes of the species within the polymer layer, is therefore now described by,

{ (Os^{II})+ A- } $_{p}$ + (1+b)_s A- + (b)_s H₃O+ + 2 6 H₂O_s (3 4 10)

$$\{(O_{SIII})^{2+}(A^{2-}) + 2 6 H_2O + b (H_3O^+A^-)\}_p + e^{-1}$$

where the value of b is 28

In 4 0 M HClO₄ the mass transport process changes, and a large net mass loss is observed for the overall oxidation, Fig 3 4 19 shows the cyclic voltammogram and the mass-potential plot at 5 mVs⁻¹ in 4 0 M HClO₄ Fig 3 4 20 illustrates the corresponding Φ_{ClO4} - and mass-charge plots For the first 30 - 40% of redox conversion there is a mass influx into the polymer layer, equivalent to *ca*. 594 gmol⁻¹, yielding a value of 3 8 for the stoichiometric coefficient b in Eqn 3 4 10 This large value of (H₃O+) (ClO₄-) transfer into the film reflects the breakdown of permselectivity, as observed in both 2 0 M and 3 0 M electrolyte concentrations However, during continued oxidation there is a mass exodus from the polymer layer

The fixed site concentration of osmium centres is *ca* 0 7 M On complete protonation of the PVP backbone the fixed site concentration will increase tenfold to *ca* 7 0 M Film compaction in HClO4 will increase this concentration further [131] Thus, at 4 0 M HClO4 the concentration of bathing electrolyte is a significant fraction of the polymer phase fixed-site concentration. In a model developed for ion-exchange membranes by Gregor [138], the partial exclusion of free electrolyte from the membrane, in contact with bathing solution concentrations approaching the fixed site concentration, results in the movement of solvent from the low free electrolyte concentration within the membrane to the high concentration in the contacting solution. This "counter-Donnan" osmotic flux not only results in deswelling, but also serves to exclude electrolyte further and thus cause further flux of material from the layer [138]

The initial mass increase in 4 0 M HClO₄ reflects the threshold level of charge density within the polymer film that can be tolerated before the osmotic flux of solvent becomes thermodynamically favoured. The establishment of this flux not only reduces the polymer phase solvent content but may also include the movement of free electrolyte from the polymer layer and the partial re-attainment of permselectivity

Fig 3 4 19 Cyclic voltammogram and mass-potential plot for [Os(bipy)₂(PVP)₁₀Cl]+ coated electrode in 4 0 M HClO₄ Scan rate is 5 mVs⁻¹, coulometric polymer surface coverage is 1 5 x 10⁻⁸ molcm⁻²



Fig 3 4 20 Φ_{CIO4} - and mass-charge plot for $[Os(bipy)_2(PVP)_{10}Cl]$ + in 4 0 M HClO4 at a scan rate of 5 mVs⁻¹, for data in Fig 3 4 19



3.5. CONCLUSIONS.

Exposure of $[Os(bipy)_2(PVP)_{10}Cl]$ + films to increasing HClO4 concentration, results in protonation of the PVP polymer backbone. The change in polymer phase mass reflects the electroneutrality requirement for counter-anion insertion, while the the change in layer structure is indicative of the increased rigidity of the layer due to the crosslinking of the polymer matrix by ClO4-. The strong interaction of the counter-anion with the polymer results in reduced levels of polymer solvation and rigid polymer structures at all electrolyte concentrations

The more acidic value for the pK_a^{app} of the uncoordinated pyridine groups of the metallopolymer compared to that of the homopolymer, reflects the reduction in volume within the polymer layer and the difficulty for counter-anion insertion. A change in morphology of the layer with changing electrolyte concentration is manifested in two distinct regions of differing behaviour which exist during the protonation process, and indicates the exclusion of HClO₄ from the layer at low electrolyte concentrations

A break-in of the polymer is in operation in which an equilibrium level of solvation of the underlying base layer is only facilitated by the extensive interfacial movement of counter-anion and solvent during redox processes

Equilibrium mass changes during polymer oxidation show that ion and solvent transfer are greatly influenced by the contacting electrolyte concentration and, consequently, by the polymer layer morphology The movement of solvent is determined by two finely balanced opposing forces, the tendency for increased polymer solvation due to the increase in ionic content during film oxidation, and the tendency for solvent exclusion due to the increased polymer phase perchlorate content. At HClO4 electrolyte concentrations below 0.1 M the reduced levels of polymer protonation allow solvation requirements to dominate, while at higher concentrations it is the restraints imposed on the polymer network by the crosslinking ClO4- anion that dictate the reduced solvent

movement

The combination of potentiometric and EQCM data show that electroneutrality is maintained by counter-anion motion in the concentration range 0 01 M to 1 0 M HClO₄ Solvent transfer, in response to the decrease in activity of the interstitial solvent in the oxidised layer, also occurs At very low HClO₄ concentrations kinetic limitations exist for interfacial mass transfer and normalised mass changes are indicative of mixed transport of co- and counter-ion during redox switching

At electrolyte concentrations greater than 1 0 M HClO₄, permselectivity fails At the highest electrolyte concentration investigated, the mass loss during exhaustive oxidation reflects a maximum level of charge density within the polymer layer that can be tolerated, and the partial re-establishment of permselectivity

The ClO₄--polymer interaction is strong. This reduces the number of free ions within the polymer layer and the requirement for solvation, i.e. the osmotic activity of ions in the interstitial pore liquid is low. In Chapter 4, however, the behaviour of $[Os(bipy)_2(PVP)_{10}Cl]$ + in para-toluene sulphonic acid is studied. The counter-anion polymer interaction is anticipated to be quite different, and it will be seen how the development of osmotic pressure gradients across the polymer / electrolyte interface will strongly affect solvent transfer and polymer structure

3.6. REFERENCES.

- 1 C Lu and A W Czanderna (Eds), Applications of Piezoelectric Crystal Microbalances, Vol 7, Elsevier, New York, (1984)
- 2 G Sauerbrey, Z Phys , (1959) , 155 , 206
- 3 J Hlavay and G G Guilbault, Anal Chem., (1977), 49, 1890
- 4 T Nomura and M Okuhara, Anal Chim Acta, (1982), 142, 281
- 5 T Nomura and M Maruyama, Anal Chim. Acta, (1983), 147, 365
- 6 T Nomura and T Nagmune, Anal Chim Acta, (1983), 155, 231
- 7 PL Konash and GJ Bastiaans, Anal Chem, (1980), 52, 1929
- 8 M R Deakin and D A Buttry, Anal Chem, (1989), 61, 1147A
- D A Buttry, Applications of the Quartz Crystal Microbalance to Electrochemistry,
 in A J Bard (Ed) Electroanalytical Chemistry, Marcel Dekker, New York, (1991),
 Vol 17, p 1-85
- 10 R Schumacher, Angew Chem (Int Ed Engl), (1990), 29, 329
- 11 K K Kanazawa and J G Gordon, Anal Chem, (1985), 57, 1770
- 12 K K Kanazawa and J G Gordon, Anal Chim Acta, (1985), 175, 99
- 13 R Beck, U Pittermann and K G Weil, Ber Bunsenges Phys Chem, (1988), 92, 1363
- 14 S Bruckenstein and M Shay, Electrochum Acta, (1985), 30, 1295
- 15 R J Forster, A J Kelly, J G Vos and M E G Lyons, J Electroanal Chem, (1989), 270, 365
- 16 R J Forster and J G Vos, J Electroanal Chem, (1991), 314, 135
- 17 R J Forster and J G Vos, Electrochim Acta, (1992), 37, 159
- 18 R J Forster, J G Vos and M E G Lyons, J Chem Soc Faraday Trans, (1991), 87,
 3761

- 19 R J Forster, J G Vos and M E G Lyons, *J Chem. Soc Faraday Trans*, (1991), 87, 3769
- 20 A J Kelly, T Ohsaka, N Oyama, R J Forster and J G Vos, *J Electroanal Chem*, (1990), 287, 185
- 21 A J Kelly and N Oyama, J Phys Chem, (1991), 95, 9579
- 22 D Orata and D A Buttry, J Am Chem. Soc , (1987), 109, 3574
- A Glidle, A R Hillman and S Bruckenstein, J Electroanal Chem., (1991), 318,
 411
- 24 R Borjas and D A Buttry, J Electroanal Chem., (1990), 280, 73
- 25 K E Heusler, A Grzegorzewski, L Jackel and J Pietrucha, Ber Bunsenges Phys Chem., (1988), 92, 1218
- 26 D M Ullevig and J F Evans, Anal Chem, (1980), 52, 1467
- 27 D M Ullevig, J F Evans and M G Albrecht, Anal Chem, (1982), 54, 2341
- 28 C Gabrielli, M Keddam and R Torresi, J Electrochem. Soc , (1991), 138, 2657
- 29 B A Martin and H E Hager, J Appl Phys, (1989), 65, 2627
- 30 B A Martin and H E Hager, J Appl Phys, (1989), 65, 2630
- 31 A R Hillman, D C Loveday, M J Swann, S Bruckenstein and C P Wilde, J Chem Soc Faraday Trans, (1991), 87, 2047
- 32 R Schumacher, G Borges and K K Kanazawa, Surf Sci , (1985), 163, L621
- R Schumacher, J G Gordon and O Melroy, J Electroanal Chem, (1987), 216,
 127
- 34 R Beck, U Pittermann and K G Weil, J Electrochem Soc, (1992), 139, 453
- 35 R Beck, U Pittermann and K G Weil, Ber Bunsenges Phys Chem., (1988), 92, 1363
- 36 H Muramatsu, E Tamiya and I Karube, Anal Chem, (1988), 60, 2142
- 37 Z Tiean, N Liehua and Y Shouzhuo, J Electroanal Chem, (1990), 293, 1
- 38 S J Martin, V Edwards Granstaff and G C Frye, Anal Chem., (1991), 63, 2272

- 39 A R Hillman, D C Loveday and S Bruckenstein, J Electroanal Chem, (1991), 300, 67
- 40 A R Hillman, M J Swann and S Bruckenstein, J Phys Chem., (1991), 95, 3271
- 41 G S Ostrom and D A Buttry, J Electroanal Chem., (1988), 256, 411
- 42 M Shay and S Bruckenstein, Langmuir, (1989), 5, 280
- O R Melroy, K K Kanazawa, J G Gordon and D A Buttry, *Langmusr*, (1986),
 2, 697
- 44 M Deakin and O Melroy, J Electroanal Chem., (1988), 239, 321
- 45 M Hepel, K Kanige and S Bruckenstein, J Electroanal Chem, (1989), 266, 409
- 46 M Hepel, K Kanige and S Bruckenstein, Langmuir, (1990), 6, 1063
- 47 R Schumacher, A Muller and W Stockel, J Electroanal Chem., (1987), 219, 311
- 48 R Schumacher, J Pesek and O Melroy, J Phys Chem, (1985), 89, 4338
- 49 B J Feldman and O R Melroy, J Electrochem Soc, (1989), 136, 640
- 50 S Bourkane, C Gabrielli and M Keddam, Electrochum Acta, (1989), 34, 1081
- 51 S Zakipouly, C Leygraf and G Portnoff, J Electrochem. Soc, (1986), 133, 873
- 52 M Benje, M Eiermann, U Pittermann and K G Weil, Ber Bunsenges Phys Chem, (1986), 90, 435
- 53 M Benje, U Hofmann, U Pittermann and K G Weil, Ber Bunsenges Phys Chem, (1988), 92, 1257
- 54 W D Hinsberg, C G Wilson and K K Kanazawa, J Electrochem Soc, (1986), 133, 1448
- 55 S Bruckenstein and M Shay, J Electroanal Chem, (1985), 188, 131
- 56 A Muller, M Wicker, R Schumacher and R N Schindler, Ber Bunsenges Phys Chem, (1988), 92, 1395
- 57 M R Deakin and O Melroy, J Electrochem Soc, (1989), 136, 349

- 58 L A Larew, J S Gordon, Y -L Hsiao, D C Johnson and D A Buttry, J Electrochem Soc, (1990), 137, 3071
- 59 H-K Park, K Podolske, Z Munshi, W H Smyrl and B B Owens, J Electrochem Soc, (1991), 138, 627
- 60 W Stockel and R Schumacher, Ber Bunsenges Phys Chem., (1987), 91, 345
- 61 L Grasjo and M Seo, J Electroanal Chem., (1990), 296, 233
- 62 N Yamamoto, T Ohsaka, T Terashima and N Oyama, J Electroanal Chem., (1990), 296, 463
- 63 GT Cheek and WE O'Grady, J Electroanal Chem, (1990), 277, 341
- 64 M R Deakin, T T Li and O R Melroy, J Electroanal Chem, (1988), 243, 343
- 65 T Nomura and T Kanazawa, Anal Chim Acta, (1991), 245, 71
- 66 R R McCaffrey, S Bruckenstein and P N Prasad, Langmuir, (1986), 2, 228
- N Oyama, K Mishima, S Ikeda, O Hatozaki, M Shimomuro and K Kasuga,
 J Electrochem. Soc , accepted for publication
- 68 V V Erokhim, R L Kayushina, Y Lvov and L A Feigin, Il Nuovo Cimento, (1990), 12, 1253
- 69 JJ Donohue and DA Buttry, Langmuir, (1989), 5, 671
- 70 E S Grabbe, R P Buck and O R Melroy, J Electroanal Chem., (1987), 223, 67
- 71 R C Ebersole and M D Ward, J Am Chem Soc, (1988), 110, 8623
- 72 J Ngeh-Ngwainbi, A A Suleiman and G G Guilbault, Biosensors and Bioelectronics, (1990), 5, 13
- 73 Y Okahata, H Ebato and X He, J Chem. Soc, Chem. Commun, (1988), 1037
- 74 M Laatikainen and M Lindstrom, J Coll Int Sci , (1988), 125, 610
- 75 A W Czanderna and T M Thomas, J Vac Sci Technol, (1987), 5, 2412
- 76 Y Okahata and H Ebato, Anal Chem, (1989), 61, 2185

Ĩ

77 A R Hillman, D.C Loveday and S Bruckenstein Langmuir, (1991), 7, 191

- 78 G Inzelt and J Bacskai, Electrochim Acta, (1992), 37, 647
- 79 PT Varineau and DA Buttry, J Phys Chem., (1987), 91, 1292
- 80 W D Hinsberg and K K Kanazawa, Rev Sci Instrum., (1989), 60, 489
- 81 C K Baker and J R Reynolds, J Electroanal Chem., (1988), 251, 307
- 82 B J Feldman and O R Melroy, J Electroanal Chem., (1987), 234, 213
- 83 S J Lasky and D A Buttry, J Am. Chem Soc, (1988), 110, 6258
- 84 M D Ward, Synth Met , (1988), 27, B211

í

- 85 M D Ward, J Electrochem. Soc , accepted for publication
- 86 K Aoki, T Miyamoto and Y Ohsawa, Bull Chem. Soc Jpn , (1989), 62, 1658
- 87 J Rishpon, A Redondo, C Derouin and S Gottesfeld, J Electroanal Chem, (1990), 294, 73
- 88 H Daifuku, T Kawagoe, N Yamamoto, T Ohsaka and N Oyama, J Electroanal Chem, (1989), 274, 313
- 89 D Orata and D A Buttry, J Electroanal Chem, (1988), 257, 71
- 90 C K Baker and J R Reynolds, Synth Met, (1989), 28, C21
- J H Kaufman, K K Kanazawa and G B Street, Phys Rev Lett, (1984), 53,
 2461
- 92 K Naoi, M M Lien and W H Smyrl, J Electroanal Chem., (1989), 272, 273
- 93 K Naoi, M Lien and W H Smyrl, J Electrochem Soc, (1991), 138, 440
- J R Reynolds, N S Sundaresan, M Pomerantz, S Busak and C K Baker,
 J Electroanal Chem, (1988), 250, 355
- 95 C K Baker, Y -J Qiu and J R Reynolds, J Phys Chem, (1991), 95, 4446
- 96 S Sarvagent and E Vieil, J Electroanal Chem, (1990), 280, 227
- 97 Y-J Qiu and J R Reynolds, J Electrochem Soc, (1990), 137, 900
- 98 A R Hillman, M J Swann and S Bruckenstein, J Electroanal Chem, in press
- 99 A R Hillman and M J Swann, Electrochim Acta, (1988), 33, 1303

- 100 A R Hillman, R M Eales, D C Loveday, M J Swann, A Hamnet, S J Higgins, S Bruckenstein and C P Wilde, *Faraday Discuss*, Chem. Soc, (1989), 88,151
- 101 A R Hillman, D C Loveday, M J Swann and S Bruckenstein, J Chem. Soc, Faraday Trans, (1990), 86, 233
- 102 A R Hillman, D C Loveday and S Bruckenstein, J Electroanal Chem., (1989), 274, 157
- S Bruckenstein, C P Wilde, M Shay, A R Hillman and D C Loveday,
 J Electroanal Chem., (1989), 258, 457
- 104 A R Hillman, D C Loveday, S Bruckenstein and C P Wilde, J Chem. Soc Faraday Trans, (1990), 86, 437
- 105 A R Hillman, N A Hughes and S Bruckenstein, J Electrochem. Soc, (1992), 139, 74
- 106 M D Ward, J Electrochem Soc , (1988) , 135 , 2747
- 107 M D Ward, J Phys Chem, (1988), 92, 2049
- 108 G Inzelt, J Electroanal Chem, (1990), 287, 171
- 109 G Inzelt and J Bacskai, J Electroanal Chem, (1991), 308, 255
- 110 T Kawai, T Kuwabara, S Wang and K Yoshino, J Electrochem Soc, (1990), 137, 3793
- 111 S Gottesfeld, A Redondo, I Rubinstein and S W Feldberg, *J Electroanal Chem*, (1989), 265, 15
- S Bruckenstein, C P Wilde, M Shay and A R Hillman, J Phys Chem, (1990),
 94, 787
- 113 S Bruckenstein and A R Hillman, J Phys Chem., (1988), 92, 4837
- 114 S Bruckenstein, A R Hillman and M J Swann, J Electrochem. Soc , (1990), 137, 1323
- D A Buckingham, F P Dwyer, H A Goodwin, A M Sargeson, *Aust J Chem*,
 (1964) 17, 325

- 116 M J Swann, Ph D Thesis, University of Bristol, (1991)
- 117 R J Forster, Ph D Thesis, Dublin City University, (1990)
- 118 S B Tuwiner, Diffusion and Membrane Technology, Chapman and Hall, New York, (1962)
- 119 F Heltferich, Ion Exchange, McGraw-Hill, New York, (1962)
- 120 D Ghesquiere, B Ban and C Chachaty, Macromolecules, (1977), 10, 743
- 121 J A Kitchener in Ion exchange, J A Marinsky Ed, Marcel Dekker, New York, (1969), 1, Chp 2
- 122 P Ferruti and R Barbucci, Adv Polym Sci , (1984), 58, 55
- 123 S M Oh and L R Faulkner, J Electroanal Chem, (1989), 269, 77
- 124 S M Oh and L R Faulkner, J Am Chem Soc, (1989), 111, 5613
- 125 A Eisenberg, Macromolecules, (1970), 3, 147
- 126 E F Bowden, M F Dautartas and J F Evans, J Electroanal Chem, (1987), 219, 49
- 127 M F Dautartas, E F Bowden and J F Evans, *J Electroanal Chem*, (1987), 219, 71
- 128 E F Bowden, M F Dautartas and J F Evans, J Electroanal Chem, (1987), 219,91
- 129 G E Walrafen, J Chem Phys , (1970), 52, 4176
- 130 A H Schroeder, F B Kaufman, V Patel and E M Engler, J Electroanal Chem, (1980), 113, 193
- 131 H P Gregor, J Belle and R A Marcus, J Am Chem Soc, (1954), 76, 1984
- 132 Y Marcus, Ion Solvation, Wiley-Interscience, New York, (1985)
- 133 JA Marinsky, J Phys Chem, (1985), 89, 5294
- 134 R Naegli, J Redepenning and F C Anson, J Phys Chem, (1986), 90, 6227
- 135 J Redepenning and F C Anson, J Phys Chem, (1987), 91, 4549
- 136 J Koryta and J Dvorak, Principles of Electrochemistry, Wiley, New York, (1987)

- 137 N M D Brown, H X You, R J Forster and J G Vos, J Mater, Chem, (1991), 1,517
- 138 H P Gregor, J Am. Chem. Soc , (1951), 73, 642
- 139 A J Bard and L R Faulkner, Electrochemical Methods, Fundamentals and Applications, Wiley, New York, (1980), Ch 4, p 128
CHAPTER 4

The effect of pTSA Electrolyte Concentration and Redox Site Oxidation State on the Resident Layer Mass of Thin Films of [Os(bipy)2(PVP)10Cl]+

4.1. INTRODUCTION.

With the development of synthetic organic ion-exchange resins, in which crosslinking, capacity etc can be controlled, a systemmatic investigation into the effects of membrane structure on ion-exchange equilibria has been undertaken [1-4]. The results from this work have demonstrated the importance of the counter-ion interaction with the fixed-charge sites of the polymer backbone and its consequent effects on the selectivity exhibited by the exchange sites and the level of solvent-swelling of the membrane [4].

From the earliest days of polymer modified electrodes, solvent transfer accompanying counter-ion motion during charge transport processes has been known to occur [5] The membrane properties of the polymer modifying layer have been recognised [6], and the counter-ion dependency of polymer structure [7,8], and the effect of swelling [9] investigated. However, despite this, early thermodynamic models describing the electrochemical processes failed to consider the solvent population within the polymer layer [10-12]. It has been through the increased use of the EQCM in probing mass changes accompanying redox switching that the role of solvent has become increasingly evident (see Section 3.2.6). Recent thermodynamic models [13,14] for equilibrium solvent and ion-aggregate populations within electroactive polymers have been developed and have utilised earlier models for ion-exchange membranes [10] and polyelectrolyte systems [15].

Previous electrochemical studies of the redox polymer $[Os(bipy)_2(PVP)_{10}Cl]$ + have indicated that the rate of charge transport is strongly influenced by the nature of the contacting electrolyte [16-20] An EQCM study has shown considerable differences in the levels of solvent involved in the mass transfer during redox switching in different near-neutral pH electrolytes [21,22] These effects have been attributed to changes in polymer morphology as dictated by the metallopolymer-electrolyte interaction, and a correlation between the polymer phase solvent content and the rate of charge transport has been proposed [22]

In Chapter 3, the equilibrium mass changes within the osmium metallopolymer in HClO₄ were investigated as a function of redox state and electrolyte concentration. The role of solvent was observed to be minimal, due to the dehydrating nature of the counteranion. In this chapter a similar study is performed in a more swelling electrolyte, paratoluene sulphonic acid (pTSA). It is the purpose of this work to investigate the origin of morphology changes within this metallopolymer as a function of electrolyte type and concentration. The approach adopted views the metallopolymer as an anion-exchange membrane with the protonated pyridine moieties of the polymer backbone, as well as the osmium redox centres themselves, being the fixed cationic sites. The model considers those factors which will affect the internal osmotic pressure within an ion-exchange structure and thus influence the level of swelling and solvent transfer

This approach is used primarily to explain electrolyte dependent changes in polymer morphology in the absence of redox processes. However, the general features of the treatment provide a basis for the understanding of the mass changes which occur during charge transport through membranes. In this regard, the behaviour of an ion-exchange membrane in an electric field will be considered

To understand the origin of osmotic pressure within membranes it is useful to first consider the nature of osmosis The importance of osmosis in ion-exchange membranes will be emphasised and a brief review of the early literature concerning membrane swelling and ion-association effects will be given

4.1.1. Osmotic Transport of Solvent.

The osmotic transport of solvent is demonstrated by the classical experiment in which two solutions of differing solute concentration are separated by a semi-permeable membrane through which the solute cannot pass Solvent flows from the more dilute solution (c_1) to the more concentrated (c_2) In an open system, the pressure gradient generated by the solute concentration gradient is eventually counter-balanced by the increase in hydrostatic pressure on the more concentrated solution side of the membrane, and solvent flow ceases

From a thermodynamic point of view, osmotic flow proceeds from high solvent activity, in the dilute solution, to lower activity in the more concentrated solution. This is stated in the Van't Hoff equation [1], which for dilute solutions is given by,

$$P_2 - P_1 = RT(c_2 - c_1) \tag{411}$$

R is the gas constant and T is the temperature P_1 and P_2 are the pressures at equilibrium associated with solutions of concentration c_1 and c_2 , respectively [1]

A molecular theory describing the osmotic flux has been proposed which considers the intermolecular forces between solute and solvent molecules [23] A net force per unit area acts upon the membrane pore liquid only when a solute molecule resides at the pore mouth. The osmotic flux of solvent is thus viewed as spurts of solvent lasting the length of time that a solute molecule resides, on average, at the pore. The time-averaged force per unit area is found to be given by the conventional osmotic pressure of the solution (Eqn 4 1 1)

4.1.2. Osmotic Transport in Ion-exchange Membranes.

The osmotic movement of solvent as outlined in Section 4.1.1 pertains to membranes which are non-ionic or which are completely impermeable to solute. The osmotic transport of solvent in such systems is termed "normal" osmosis [2]

For ion-exchange membranes, the pressure gradient established, when in contact with electrolyte solutions, is derived from the swelling pressure within the membrane Because of the high ionic concentration within ion-exchange membranes there is a strong tendency for the internal ionic populations to become diluted, i e a high internal osmotic pressure exists. When in contact with dilute electrolyte solutions or pure solvent, the matrix expands as the polymer segments and solution inter-diffuse. The swelling, as defined by the osmotic pressure (which may be of the order of 1000 atm.), is opposed by the swelling tension imposed on the polymer segments by the overall polymer structural framework [1,2].

For the situation in Section 4.1.1 the swelling pressure is greater for the membrane face in contact with the more dilute electrolyte. A purely pressure gradient across the membrane, therefore, always results in osmotic solvent transfer from low to high electrolyte solutions, i.e. positive osmosis

The interstitial pore liquid of ion-exchange membranes contains mobile counter-ions and relatively few mobile co-ions. The pore liquid thus carries a net electric charge. The osmotic movement of solvent in this case is not only in response to pressure gradients across the membrane but is also profoundly affected by the presence of electric fields. Where this occurs the transfer of solvent is invariably against its chemical potential gradient and the solvent flux is termed "anomalous" osmosis [1,2]

Due to differences in the mobilities of the counter- and co-ions, strong diffusion potentials may arise in the contacting solution. These increase with increasingly dilute solutions. If the counter-ion diffuses faster, the space charge developed at the solution / membrane interface results in an electric field which drives the pore liquid to the more concentrated solution. The greatly enhanced osmotic flux which results is termed "anomalous positive osmosis". Conversely, if the co-ion diffuses faster, the electric field established causes the pore liquid to be pulled back towards the more dilute solution, giving rise to "negative anomolous osmosis".

The application of a potential field across an ion-exchange membrane will similarly result in solvent movement, with a net solvent flux in the direction in which the counterions within the membrane are transferred. In such circumstances, the solvent transfer is termed "electro-osmosis" [24]

The extent of both anomalous and electro-osmosis is determined by the flow resistance of the ion-exchange material, the fixed-site concentration, the extent of co-ion exclusion from the membrane pores, the ionic mobilities of the mobile ions and the extent of specific interactions between the counter-ions within the membrane and the fixed membrane sites and / or the polymer backbone [2]

4.1.3. Counter-ion effects in Ion-exchange Membranes.

Much of the literature concerning the structure of ion-exchange resins has been motivated by the need to determine those factors which govern selectivity coefficients for the exchanging ions [2,4,25-27] The results obtained, however, have yielded significant insight into the effect of the counter-ion fixed site interaction on the resin structure [26,27]

The interaction between counter-ions and the fixed sites of the polymer matrix has been visualised by Manning in an "ion-condensation" model for polyelectrolytes [28] This model sees the counter-ions condensed in a thin layer about the fixed sites of the polymer backbone. The mobile counter- ions are territorially bound within this layer as long as the mean separation of fixed sites does not exceed a critical value. For water at 25 °C the critical charge spacing along the polymer is z_1 (7 135 Å), where z_1 is the valence of the counter-ion The nature of the two-phase properties of polyelectrolyte-salt mixtures has also been investigated by Marinsky [15]

In a mechanical model for ion-exchange membranes proposed by Gregor *et al* [29-31], the membrane is viewed as a network of elastic springs, against which the interstitial pore liquid exerts a force due to its osmotic pressure. These mechanical models have shown the relationship between the activity of the mobile counter-ions within the ionexchange resin and the pressure-volume free energy changes involved in the swelling process [30]. The swollen resin volume is related to the solvent activity within the membrane and is thus dependent on the size of the unhydrated counter-ion, ion-solvent interactions and ion-pair formation [32].

The size of the counter-ion is of obvious importance. The mechanical model of ionexchange resins anticipates that an increase in the molar volume of the counter-ion will increase the volume of the resin phase slightly. However, because there is a decrease in the membrane interstitial volume which can be occupied by solvent, a sharp increase in the osmotic pressure of the resin phase occurs [30]. These pressure-volume considerations are found to be most important in cation-exchange resins [33], and for a 10% crosslinked poly(styrenesulphonatre) cation-exchanger the level of swelling was found to increase with increasing size of the hydrated cation [33].

Specific ion interactions and the formation of ion-pairs results in reduced electrostriction of solvent and decreases the osmotic activity of the internal pore liquid A reduction in swelling is thus predicted as ion association proceeds [32,33] Van der Waals forces may increase with increasing counter-ion size, and for a series of quaternary ammonium cations, the level of swelling of 10% crosslinked poly (styrenesulphonate) resin was observed to decrease for the larger counter-ions due to the increased counterion fixed site interaction [33] In anion-exchange resins, ion-pair formation and anionspecific interactions have been found to be the dominant factor in determining the level

of swelling of the resin [26,32] In a quaternary-ammonium anion-exchanger a decrease in the resin volume was observed with increasing unhydrated halide ionic size Similarly, for a series of substituted acetate counter-ions a decrease in resin volume with increasing anion size was seen [32]

The valency of the counter-10n has been found to be of importance in determining structure in polyelectrolytes and 10n-exchange membranes. Counter-10ns of high valency are generally observed to produce low levels of swelling due to their increased association with the fixed sites [2,4]. For highly cross-linked gels of poly(methacrylic acid), multivalent salts were found to result in marked deswelling, compared with the H+ form of the gel [34]. This was attributed to the contraction of the polymer chains due to cross-linking of the polymer carboxyl groups by the polyvalent counter-10ns

The importance of these interactions on ion transport has been addressed in a series of contributions from Boyd and Soldano [35-38], concerning the self-diffusion of counterions in cation and anion exchange resins. Multivalent cations in sulphonated polystyrene cation-exchangers were found to have negative entropies for their self-diffusion. This was rationalised in terms of these cations having to first dissociate from the resin in order to form the activated complex of the molecular diffusion process [35]. Such a dissociation resulted in electrostriction of solvent molecules and a subsequent decrease in entropy. Univalent counter-ions, however, were not considered to be associated and the entropy of self-diffusion was positive, merely reflecting the disturbance in the micro-environment of the diffusing ion [35]. Significantly, for similar experiments in various quaternary ammonium type exchangers, neither the rate of self-diffusion nor the entropy of activation for self diffusion of anions was found to be affected by valency [36]. In all cases, only the disordering of the anion environment was observed. This was reconciled in terms of the weak hydration of anions in comparison to cations.

Increasing the concentration of the electrolyte in contact with the ionic polymer may result in a number of effects. In general, however, as the electrolyte concentration increases the reduction in the osmotic pressure gradient across the polymer / electrolyte interface will reduce the driving force for solvent uptake and deswelling will result [2,4]. Alternatively, the breakdown in permselectivity of the membrane at high electrolyte concentrations will result in penetration of the electrolyte into the resin phase. This may serve to increase the osmotic effect of the resin and cause further swelling [2]. In yet another possibility, the partial exclusion of the electrolyte from the resin phase will result in a concentration gradient for electrolyte across the membrane interface. A counter-Donnan osmotic pressure is established which results in the transfer of solvent out of the resin [30]. This solvent flux further increases the exclusion of electrolyte from the membrane, as well as causing deswelling.

4.2. EXPERIMENTAL.

 $[Os(bipy)_2(PVP)_{10}Cl]Cl$ was synthesised as described previously in Chapter 3 Electrode preparation and the experimental procedures for frequency measurement, impedance analysis and voltammetry were also as described in Chapter 3

4.3. RESULTS AND DISCUSSION.

4.3.1. pTSA concentration effects on the resident layer mass.

Before the pTSA concentration effects on the layer mass and layer rigidity were studied, the metallopolymer was first converted to the para-toluene sulphonate salt form This was achieved by repeated voltammetric cycling of the $Os^{11/11}$ couple in 0 1 M pTSA The polymer films were then stored in Milli-Q H₂O for several days prior to further analysis

The change in the resonant frequency of the polymer-coated working crystal in the active mode, at open circuit, with increasing pTSA electrolyte concentration is shown in Fig 4 3 1 (Graph A) The polymer surface coverage, by gravimetry, was 2 9 x 10⁻⁸ molcm⁻² The mass change per polymer equivalent, assuming the frequency-mass relationship (Eqn 3 1 7), is also presented on the ordinate of Fig 4 3 1, where the zero value represents the pTS- salt form of the polymer plus initially imbibed water The contribution of changing electrolyte viscosity was corrected for at each pH by subtraction of the frequency shift observed at an uncoated crystal

Although no voltammetry was performed in the course of this experiment, Fig 4 3 1 also includes the frequency change observed during the oxidation of the polymer layer (Graph B) This will be discussed later in Section 4 3 2

Graph A in Fig 4 3 1 is retraced when increasing or decreasing the electrolyte pH, thus indicating that no irreversible changes in layer structure occur. However, in order to evaluate any change in polymer structure with changing electrolyte concentration, impedance measurements were made. These were obtained using a different polymer film, with surface coverage 5 x 10-9 molcm⁻², and are illustrated in Fig 4 3 2 to Fig 4 3 4 Table 4 3 1 summarises the crystal resonance shape and position.

Fig 4 3 1 The effect of pTSA electrolyte concentration and osmium oxidation state on the layer mass of a [Os(bipy)₂(PVP)₁₀Cl]+ polymer film The surface coverage is 2 9 x 10-8 molcm-2



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Fig 4 3 2 to 4 3 4

The admittance spectra at open circuit for a polymer-coated crystal (surface coverage 5×10^{9} molcm⁻²) in a series of pTSA electrolytes Fig 4 3 2 H₂O to 10 ³ M pTSA, Fig 4 3 3 10 ³ M to 0 1 M pTSA and Fig 4 3 4 0 1 to 1 0 M pTSA Data are summarised in Table 4 3 1



Table 4 3 1The effect of pTSA electrolyte concentration on the admittance
spectrum for [Os(bipy)2(PVP)10Cl](pTS) coated crystals at open
circuit Gravimetric surface coverage 5 x 10-9 molcm-2

lectrolyte conc	Admittance Maximum	PWHM (a)	Δf (a,b)
(Molar)	(Ω-1 x 10 ²)	(kHz)	(Hz)
H ₂ O	0 374	8 958	0 0
1 x 10-5	0 342	10 781	- 416
1 x 10-4	0 336	10 833	- 521
4 x 10-4	0 324	11 615	- 755
1 x 10-3	0 332	10 573	+ 313
4 x 10-3	0 290	14 375	- 573
1 x 10-2	0 294	13 750	- 833
4 x 10-2	0 338	10 625	- 938
01	0 392	8 281	-2135
04	0 378	8 906	-2292
10	0 336	10 469	-3229

- (a) Interpolated from data points at 20 Hz resolution
- (b) Shift in resonant frequency with respect to value of [Os(bipy)₂(PVP)₁₀Cl](pTS) polymer-coated crystal in H₂O Negative values imply layer becomes heavier

The shift in the crystal resonance centre frequency with changing pTSA concentration in Table 4.3.1 exhibits the same qualitative trends as the data depicted in Fig 4.3.1 (Graph A) While layers of differing thickness may show a slight variation in the exact electrolyte pH at which there is a dramatic change in resonant frequency, the same layer mass-pTSA pH profile is observed for all polymer films studied. The following discussion, therefore, is general

<u>4 3.1.1.</u> pH range 4 00 to 2 75

The decrease in the resonant frequency of the coated crystal in the pH range 4 00 to 2 75 (Fig 4 3 1), is indicative of a large increase in mass of the polymer phase Fig 4 3 2 and Table 4 3 1 illustrate the change in the crystal resonance as the contacting liquid is changed from pure H₂O to 4 x 10⁻⁴ M pTSA. The broadening of the resonance with increasing pTSA concentration represents an increase in polymer film viscosity. There is no contribution to this broadening from the changing viscous liquid load of the contacting electrolyte, as evidenced by the invariance of the admittance-frequency response of an uncoated crystal in contact with pTSA electrolytes in this pH range.

While the increased viscoelasticity of the polymer layer may contribute to the observed decrease in the resonant frequency of the working crystal starting at pH 4 00, the changes in polymer morphology alone are suggestive of polymer swelling. The decrease in resonant frequency, therefore, must reflect an increase in the ionic content of the polymer phase and the subsequent increase in the level of solvation. This is considered to be due to the protonation of the pyridine moleties of the PVP backbone and the influx of pTS- counter-anions required for electroneutrality.

The decrease in the resonant frequency attains a near plateau level in this narrow pH range Assuming that the fractional change in the resonant frequency can be related to the level of protonation, the pK_a^{app} of PVP can be evaluated, as described previously in

Section 3 4 3 3 The graph of log { $(\Delta f_{total} / \Delta f) - 1$ } vs pTSA electrolyte pH is shown in Fig 4 3 5 Here, Δf_{total} is taken to be the frequency change at pH 0 5, while Δf is the frequency change at a given pH

The plot in Fig 4 3 5 exhibits two distinct regions As with HClO₄, this is thought to indicate a change in polymer morphology as the protonation of the polymer proceeds beyond a certain point However, in pTSA the transition occurs with less extensive protonation. This is in agreement with the immediate swelling of the polymer on exposure to pTSA, evidenced by the broadening of the admittance spectra in Fig 4 3 2.

In the pH range 5 60 to 3 35 the slope of Fig 4 3 5 is 1 70 \pm 0 04 and yields a pK_aapp of 2 84 \pm 0 15 At more acidic pH (pH range 3 35 to 2 75) the slope is 2 81 \pm 0 07, giving a value of pK_aapp of 3 02 \pm 0 02 The evaluation of pK_aapp in pTSA is more basic than those obtained in HClO₄ In addition, the slopes greater than unity indicate a much stronger dependence of polymer protonation on electrolyte pH than that predicted by Eqn 3 4 4 Both these features reflect the facile movement of counter-anions into the polymer structure that exists in pTSA electrolyte

<u>4312</u> pH range 275 to 175

On increasing the concentration of the pTSA electrolyte to pH below pH 2 75, the resonant frequency of the coated crystal in Fig 4 3 1 shifts to a higher frequency, indicating the loss of material from the electrode surface (see also the entry for 0 001 M pTSA in Table 4 3 1) This cannot be due to the dissolution of the polymer layer, since the mass of the electrode, once returned to pure solvent, retains its original value. In addition, the electrochemical evaluation of the polymer surface coverage remains constant at all pHs (*vide infra*)

Table 4 3 1 and Fig 4 3 2 show that there is a sharpening of the crystal resonance at 0 001 M pTSA This suggests that there is a decrease in the viscoelasticity of the medium

Fig 4 3 5 Plot of log { $(\Delta f_{total}/\Delta f) - 1$ } vs pTSA electrolyte pH for the rising layer mass in the pH range 6 0 to 2 75 in Fig 4 3 1 (A)



in the immediate vicinity of the working crystal. The observed frequency increase, therefore, must represent a dramatic swelling of the polymer layer and its delamination from the electrode surface. A similar QCM response has been observed during phase transitions within lipid multibilayers [40], for the electrochemical cycling of PVF in chloride electrolytes [41], as well as for the break-in of nitrated polystyrene films [42]

The polymer swelling can be explained in terms of the swelling of ion-exchange resins. In accordance with the ion-condensation effect for polyelectrolytes [28], the concentration of counter-ions within the protonated polymer phase will proceed regardless of the ionic strength of the contacting electrolyte. At pH 3 00, the concentration of pTS- within a fully protonated polymer layer is 4 - 7 M, depending on the level of swelling, while that of the contacting electrolyte is only *ca* 0 001 M. A large osmotic pressure gradient is thus established and the movement of solvent into the polymer phase is expected.

From steric considerations alone, the large molar volume of the pTS- anion (*ca* 120 cm³mol⁻¹ [43]) will result in a greater "distance of closest approach" [44] to the fixed protonated pyridine sites Consequently, a lower level of ion-pair formation is expected Incomplete shielding of the fixed-charge sites will also result, leading to electrostatic repulsion and further stretching of the polymer segments [1,2] Specific interactions between the aromatic anion and the hydrocarbon matrix of the PVP backbone, which can become significant [32], are considered to be of minor importance, since each polymer unit bears a fixed-charge site. The absence of ion aggregates within the polymer layer will lead to a greater osmotic activity, more complete solvation of all ions, and increased swelling. An increase in the swelling pressure of the interstitial pore liquid is also anticipated due to the pressure-volume effect of the bulky pTS- counter-anion [30]. It is clear, therefore, that extensive polymer swelling is expected in low pTSA electrolyte concentrations.

<u>4313</u> pH range 1 75 to 1 00

As the concentration of pTSA in the external solution is increased further, the resonant frequency of the polymer coated crystal decreases sharply (Fig 4 3 1), representing an increase in the polymer layer mass. The admittance spectra in this pH range are illustrated in Fig 4 3 3 and summarised in Table 4 3 1. Despite the increased viscosity of the more concentrated electrolyte solutions the resonance of the coated crystal becomes sharper, clearly indicating that the polymer layer in this pH range becomes more rigid.

The compaction of the polymer layer may be a consequence of the decreased activity of solvent in the bathing solution and the subsequent lowering of the osmotic pressure difference between the interstitial pore liquid and the contacting pTSA electrolyte However, the solvent activity is not expected to change that significantly in this range of electrolyte concentration. The abrupt nature of the layer compaction in Fig 4.3.1 suggests that other deswelling mechanisms must be in operation.

Due to the mobility of the co-ion (H₃O+) compared to the larger counter-ion (pTS-), the development of a positive space charge at the electrolyte / polymer interface is likely While the polymer phase is unlikely to be permselective when so extensively swollen, the pore liquid will bear a net negative charge due to the greater number of mobile anions The positive space charge will thus drive the pore liquid as a whole out of the polymer phase This is negative anomolous osmosis (Section 4 1)

The extensive involvement of solvent in this metallopolymer in para-toluene sulphonate based electrolytes [21,22] suggests that there is facile movement of solution species and minimal flow resistance, while the presence of a protonated pyridine moiety every 2 5 Å (assuming a rigid rod structure [45]) results in an ionic polymer film of high capacity This, in addition to the high swelling pressures within the polymer due to the influx of large quantities of pTS⁻ counter-anion, and the absence of strong ion-pairing interactions, results in a situation where negative anomolous osmosis is strongly favoured [2]

Deswelling, due to the establishment of a counter-Donnan osmotic flux [30], as discussed in Section 4.1.2, may also be in evidence here. Because the concentration of free electrolyte within the pore liquid is less than that in the external solution, the osmotic movement of solvent from the layer, to the region of higher electrolyte concentration in the external solution, may occur. This will augment the deswelling process and, in turn, will increase the exclusion of electrolyte from the polymer phase. The process is selfperpetuating, since this further electrolyte exclusion serves to exacerbate the counter-Donnan osmotic solvent movement from the polymer. In this way, it can be seen how such a rapid deswelling process can occur and how permselective films may be reestablished

<u>4314</u> pH less than pH 1 00

The change in the admittance spectrum for the coated crystal in this concentration range is shown in Fig 4 3 4. The broadening of the spectra is considered to represent the increased viscous load of the electrolyte. In Fig 4 3 1 the resonant frequency (corrected for changing liquid load), remains essentially constant, and represents the plateau value being approached at higher pH (Section 4 3 1 1). This suggests that despite the increased viscous liquid load at higher electrolyte concentrations, the same decrease is observed in the crystal resonant frequency for an attached layer mass which is thought to represent a fully protonated polymer film. Because of this, it is thought that frequency measurements may be related quantitatively to mass changes occuring within the layer.

At pH less than 0 00 the frequency of the working crystal increases abruptly and indicates a mass loss from the electrode It is unlikely that polymer swelling is responsible for this, as suggested in a previous study in NapTS [22] However, while mechanisms for swelling or deswelling may be invoked to account for this apparent mass change, it is more likely that the combination of a highly viscous electrolyte solution and the polymer film results in such a broadened crystal resonance that the crystal oscillator circuit cannot accurately follow the centre resonant frequency

The swelling of the osmium polymer and the protonation of PVP in pTSA electrolyte is in sharp contrast with that observed for HClO₄ The anion-dependency of structure, as observed previously for quaternised PVP [7,8], can be attributed to the differing interaction of these anions with the polymer backbone. The changes in structure in pTSA indicate that when swollen, the layer morphology becomes more strongly dependent on electrolyte concentration. This has also been noted for PVF films [46]

4.3.2. Mass changes accompanying Os^{II/III} couple in pTSA.

The effect of the changing layer structure on mass transfer during redox processes is now considered. The mass changes accompanying redox processes for the osmium polymer were investigated at cyclic voltammetric scan rates of 1 and 5 mVs⁻¹. The requirements for solvent transfer and the maintenance of electroneutrality are as described previously in Section 3.4.4.1. Additional considerations for solvent transfer in ion-exchange membranes are as discussed in Section 4.1.

Fig 4 3 6 shows a typical cyclic voltammogram of the Os^{11/11} couple in 0 1 M pTSA at 1 mVs⁻¹ The anodic and cathodic peak potentials converge, and the peak current ratio is one The plot of peak current versus sweep rate is linear, up to sweep rates of *ca* 20 mVs⁻¹, and has a normalised slope of unity These features are indicative of a surface wave [47], with all redox sites being oxidised on the experimental time scale. This is evidenced by the close agreement of the gravimetric and electrochemical evaluations of surface coverage.

Fig 4 3 6 also includes the change in frequency, Δf , during redox processes. The attainment of a steady-state resonant frequency during oxidation, representing a mass gain, and the re-establishment of the baseline value following re-reduction, indicate that a pseudo-equilibrium state for all mobile species is attained. The frequency change is thus representative of the thermodynamic mass transfer associated with the oxidation / reduction of the layer [48]

Table 4 3 2 summarises the frequency change and the charge passed at 1 and 5 mVs⁻¹ for a range of pTSA electrolytes Table 4 3 2 also includes the evaluation of the normalised mass, assuming the validity of the Sauerbrey equation

Table 4 3 3 summarises the potentials for the half-total-mass-change, $E_{1/2}(m)$, and the half-total-charge-change, $E_{1/2}(q)$, for the oxidation and reduction of the polymer at

Fig 4 3 6 Cyclic voltammogram and frequency-potential plot in 0 1 M pTSA for [Os(bipy)₂(PVP)₁₀Cl]+ Scan rate is 1 mVs⁻¹, polymer surface coverage is 2 x 10⁻⁸ molcm⁻² The data are presented to reflect the direction of mass transfer, and not the shift in resonant frequency (i e a decrease in frequency is shown as positive)



Meq (c) pTSA Conc (Molar) Charge (a) ∆f (b) / Scan Rate (µC) (gmol-1)(Hz)0 01 399 1 mVs⁺ 1727 - 414 391 1880 - 460 5 mVs⁺ 0 02 3049 400 - 729 1 mVs ' 0 05 1 mVs1 408 -1007 236 402 - 962 229 5 mVs+ 0 10 365 476 1 mVs⁺ -1816 5 mVs⁺ 368 -1777 462 0 20 1 mVs¹ 408 -2030 476 5 mVs+ 402 -1988 473 0 40 1 mVs¹ 385 -1948 484 5 mVs^{\perp} 382 -1845 462 0 60 1 mVs^{\perp} 375 -1975 504 5 mVs⁺ 380 -1955 492 0.80 350 1 mVs+ 1376 - 376 5 mVs⁺ 364 1001 - 263 1 00 1 mVs¹ 358 2044 - 546 5 mVs1 391 1799 - 440

Table 4 3 2Frequency shifts accompanying redox switching at 1 and 5 mVs⁻¹for a series of pTSA electrolytesGravimetric surface coverage2 x 10⁻⁸ molcm⁻²

(a) From the anodic branch of the cyclic voltammogram

(b) The end-to-end frequency shift accompanying oxidation

(c) Normalised mass calculated assuming the validity of the Sauerbrey equation

pTSA Conc	E'app (a,b)	Oxidation (b)		Reduction (b)	
(Molar)	(mV vs SCE)	E _{1/2} (m)	E _{1/2} (q)	E _{1/2} (m)	E _{1/2} (q)
0 01	335	332	343	322	318
0 02	320	300	330	305	310
0 05	305	271	303	267	286
0 10	275	268	277	264	267
0 20	260	260	264	255	250
0 40	233	229	236	220	223
0 60	223	221	225	217	220
0 80	220	239	220	224	213
1 00	215	224	218	205	199

Table 4.3 3The formal potential of the Os^{11/111} couple and the half-mass and
half-charge potentials for oxidative and reductive processes

- (a) Taken as the average of the anodic and cathodic peak potentials
- (b) All potentials (mV vs SCE) measured at 1 mVs⁻¹ at ambient temperature $(20 \pm 2 \text{ oC})$

1 mVs⁻¹ The formal potential of the Os^{11/111} redox couple, E'_{app} , is also included in Table 4 3 3 E'_{app} is taken as the average of the anodic and cathodic peak potential of the cyclic voltammogram at 1 mVs⁻¹

Table 4 3 4 summarises the change in the admittance spectra due to redox switching, obtained using a different polymer film. It is evident from these data that there is a broadening of the crystal resonance on oxidation of the polymer at all electrolyte concentrations. While the correct evaluation of mass from frequency measurements in Table 4 3 2 is subject to this increased polymer viscoelasticity, it remains clear that interfacial mass transfer is very much influenced by the pTSA electrolyte concentration. The data in Table 4 3 2 were generated with the film used for the determination of the open circuit layer mass-pH profile in Section 4 3 1. Graph B in Fig 4 3 1 illustrates the layer mass-pH profile for the fully oxidised polymer layer. This figure demonstrates that the redox-induced mass transfer processes are directly related to the morphology of the polymer layer, with mass loss occuring during oxidation in swollen polymer structures and mass gain processes being observed in more compact layers.

Although for polymer layers of differing thickness there is variation in the exact pTSA concentrations at which there is a transition from a mass gain process during oxidation to one of mass loss, the trend in mass transfer as a function of polymer morphology in the reduced state is observed for all polymer films. The following discussion, therefore, although based on the data in Table 4.3.2, applies to the general behaviour of this osmium redox polymer in pTSA. For quantitative analysis of the normalised mass change the estimated error is $\pm 2\%$ for repeat analysis on a given film and, for films of similar surface coverage (i.e. $\pm 1 \times 10^{-8}$ molcm⁻²) the between film variation is $\pm 15\%$

Table 4 3 4The change in admittance spectrum during redox switching for a
[Os(bipy)2(PVP)10Cl]+ coated crystal in a series of pTSA
electrolytes Scan rate 5 mVs-1, surface coverage 5 x 10-9 molcm-2

pTSA Conc (Molar)	∆f (a,b) (Hz)	$\Delta f(a,b)$ Admittance Maximum(Hz)(Ω-1 x 102)		PWHM (a) (kHz)	
		OsII	OsIII	OsII	OsIII
H ₂ O	-	0 370	-	8 808	-
4 x 10-4	- 100	0 358	0 350	9 534	9 847
1 x 10-3	60	0 318	0 300	11 931	13 859
4 x 10-3	0	0 284	0 270	15 005	16 672
0 01	254	0 316	0 294	12 608	14 431
0 04	- 98	0 402	0 400	8 128	8 128
0 10	- 273	0 382	0 376	8 701	8 909
0 40	- 273	0 376	0 372	9 118	9 170
1 00	- 273	0 336	0 332	10 993	11 410

- (a) Data interpolated from points of 20 Hz resolution
- (b) Δf is the shift in centre frequency during oxidation Negative values imply mass gain during polymer oxidation

4321 pTSA concentrations less than 01 M

Fig 4 3 7 shows the cyclic voltammogram for the Os^{11/111} couple in 0 01 M pTSA at 5 mVs⁻¹ and also includes the frequency change observed during redox switching The change in the admittance-frequency response, for a different film, at 5 mVs⁻¹, is illustrated in Fig 4 3 8 The frequency shift during oxidation in these figures represents a mass loss from the polymer layer

As discussed in Section 4.3.1, at concentrations below 0.1 M pTSA the polymer is swollen. On oxidation of the osmium redox centres the ion population of the polymer phase is increased. In addition to ion solvation, the osmotic effect, discussed in Sections 4.1, will result in an increase in the solvent content within the polymer phase during oxidation, and swelling of the polymer layer is anticipated. This is evidenced by the broadening of the crystal resonance in Fig 4.3.8

However, the mass loss cannot be attributed to the swelling of the polymer Where delamination of the polymer from the electrode surface has been observed during redox processes, the frequency decreases again during the reverse scan with a diffusion-like (i e $t^{1/2}$) dependency, indicative of the diffusion-controlled redeposition of the material [41,42] It is clear from the frequency (sic mass)-potential plot of Fig 4 3 7 that this is not the case for the osmium redox polymer Despite the viscoelasticity of the swollen polymer layer, the increase in frequency during oxidation is considered to be representative of a redox-induced mass loss from the layer and not due to layer morphology changes

As discussed in Chapter 3, the supply of counter-anions from the bulk solution is not anticipated to be rate-limiting on the experimental time scale under investigation here. In addition, in 0 01 M pTSA the polymer layer is swollen and is not expected to provide any barriers to interfacial mass transport. The mass loss, therefore, is not considered to represent co-ion expulsion during polymer oxidation. It is clear that the existence of

Fig.4.3.7. Cyclic voltammogram and frequency-potential plot in 0.01 M pTSA for [Os(bipy)₂(PVP)₁₀Cl]+. Scan rate is 5 mVs⁻¹ and the polymer surface coverage is 2 x 10⁻⁸ molcm⁻².







"pools" of electrolyte within the swollen polymer layer may provide a source of counteranion which will not contribute to the observed mass change [42] However, this can not account for the net transfer of mobile species from the layer which is observed

In order to determine the identity of the mobile species involved, the experiment was repeated, using the same polymer film, with D₂O as the solvent. Table 4.3.5 summarises the electrochemical and frequency data obtained in H₂O and D₂O at 5 mVs⁻¹, while Fig 4.3.9 (a) and Fig 4.3.9 (b) illustrate the Φ_{pTS} - versus potential plot for H₂O and D₂O, respectively This Φ plot, as defined in Section 3.2.5, represents the flux of all mobile species except pTS-, assuming that counter-anion motion is responsible for the maintenance of electroneutrality [49,50] The cyclic voltammograms are also included in these figures. For presentation purposes, the mass loss flux during oxidation is superimposed on the anodic branch of the cyclic voltammogram

During oxidation with H₂O as solvent, the difference in $E_{1/2}(m)$ and $E_{1/2}(q)$ (Table 4.3.3 and 4.3.5) indicates that mass and charge transfer are delineated [21,51]. During rereduction, $E_{1/2}(m)$ and $E_{1/2}(q)$ coincide, indicating concomitant charge and mass transfer. This is graphically illustrated in the Φ_{pTS} - plot in Fig 4.3.9 (a) and can be attributed to the observation that for electroactive polymer films solvent egress from the layer is more rapid than solvent entry [52].

Following isotopic substitution of hydrogen with deuterium, a greater mass loss is observed during oxidation. However, the Φ_{pTS} - plot in Fig 4 3 9 (b) indicates that the mass flux coincides more with the passage of current. This is also seen from the half-potential data for D₂O in Table 4 3 5 and is due to the slower rate of transport for the higher molecular weight solvent species [53]

Assuming the mass-frequency relationship, the increase in the normalised mass loss on isotopic substitution is ca 17% (see Table 4 3 5), compared to the predicted increase of 11% if the mass change was due to solvent only However, if counter-anion motion into the layer is to be considered, with the normalised mass loss reflecting the net

	0.01 M pTSA		0.5 N	1 pTSA	A
	H ₂ O	D20	H ₂ O	D ₂ O	
			<u> </u>	- <u> </u>	
$E_{1/2}$ (m) _{OX} .(a)	341	381	242	263	
$E_{1/2}(q) = O(x) O(x)$	363	386	260	271	
$E_{1/2}$ (m) _{RED.} (a)	298	303	227	224	
$E_{1/2}$ (q) _{RED.} (a)	294	297	225	216	
$\Delta Q \ (\mu C) \ (b)$	375	371	350	352	
Δf (Hz) (c)	1842	2146	- 929	- 980	
Meq (gmol-1) (d)	- 470	- 553	254	266	
Δf (solvent) (e)	2512	2809	- 303	- 351	
MOLES SOLVENT (f)	- 35.6	-36.2	4.6	4.8	
Φ_{pTS} (max) (g)	-380	-480	75	80	

Table 4.3.5.Electrochemical and frequency data for isotopic substitutionof H2O with D2O in 0.01 M and 0.5 M pTSA at 5 mVs⁻¹.

- a) Potentials measured at $20 \pm 2 \text{ °C}$, (mV vs SCE).
- b) From anodic branch of cyclic voltammogram.
- c) Frequency shift accompanying polymer oxidation.
- d) Normalised mass change, assuming validity of Sauerbrey equation.
- e) Frequency shift due to solvent, assuming counter-ion motion IN during oxidation
- f) Solvent transfer per redox site conversion, assuming counter-ion motion in.
- g) Flux of solvent in ngcm-2s-1, assuming counter-ion motion in.

Fig 4 3 9 Φ_{pTS}- vs potential plot and cyclic voltammogram in 0 01 M pTSA for [Os(bipy)₂(PVP)₁₀Cl]+ with (a) H₂O and (b) D₂O as solvent Surface coverage 2 x 10-8 molcm⁻², scan rate is 5 mVs⁻¹



movement of solvent out, the mass loss in H₂O represents the movement from the layer of *ca* 35 moles per redox site conversion, while in D₂O the mass loss represents *ca* 36 moles of D₂O per redox site conversion. The close agreement of these figures not only suggests that it is solvent movement that is responsible for the frequency change, but that despite the viscoelasticity of the polymer layer, mass changes may be evaluated from frequency measurements

The domination of swelling effects during redox switching has been observed to result in a delay in the observed mass transfer [46,42] However, in Fig 4 3 9, the flux of both H_2O and D_2O from the layer commences as soon as redox processes begin. This suggests that the polymer swelling during oxidation does not adversely affect the frequency response, and provides further evidence that frequency changes occur primarily in response to mass transfer processes

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Thermodynamic requirements for equilibrium levels of solvent cannot be predicted *a* prion [13] It is possible that under the conditions prevailing in 0 01 M pTSA, oxidation of the layer results in changes in solvent activity coefficients which require the loss of solvent from the polymer film. However, this is considered to be unlikely, and the solvent loss in this instance is thought to have kinetic rather than thermodynamic origins. This is evidenced by the difference in the position of the flux maxima (in relation to the passage of current) in H₂O and D₂O, and the observation that once the flux has been established, it is rapid and ceases before complete oxidation of the polymer occurs. This is manifested in the difference in $E_{1/2}(m)$ and $E_{1/2}(q)$ for the oxidation and reduction of the layer in 0.01 M pTSA in Table 4.3.3 and indicates delineation of mass and charge transfer.

The swollen polymer layer are not expected to be permselective and will contain free electrolyte In the presence of an electric field the electro-osmotic flux of solvent in the direction of movement of the more mobile hydronium ions will be expected (see Section 4.1) Because electro-osmosis is more pronounced in swollen membranes at low electrolyte concentrations [1,2], it is considered to be a possible explanation for the rapid flux of solvent from the polymer layer once anodic processes have begun

While it has been demonstrated that morphology changes during redox-switching in 0 01 M pTSA do not adversely affect frequency measurements, the admittance spectra in Fig 4 3 10, obtained in 0 001 M pTSA at a scan rate of 5 mVs-1, using a different polymer film, illustrate that subtle variations in polymer structure can occur in swollen films during redox processes. The mass loss, indicated by the shift of the resonant frequency to higher values, has been discussed above. However, the "saddle" effect for the admittance peak maxima is indicative of changes in structure at different stages of polymer oxidation. These changes are dependent solely on the extent of redox conversion, as they are retraced during re-reduction.



Fig 4 3 10 Admittance spectra for [Os(bipy)₂(PVP)₁₀Cl]+ during redox switching in 0 001 M pTSA, polymer surface coverage is 5 x 10⁻⁹ molcm⁻²

Fig 4 3 1 illustrates how the mass changes during redox-switching are influenced by the resident layer mass and polymer morphology Although not performed on the same polymer film, it is seen in Table 4 3 4 that in 0 0004 M pTSA a mass gain accompanying polymer oxidation is observed. This electrolyte concentration falls into the pH range where the initial increase in layer mass due to polymer backbone protonation occurs (see Fig 4 3 1 Graph A). As has been discussed in Section 4 3 1 1, in this pH range extensive polymer swelling has not yet occured. The mass gain on oxidation in 0 0004 M pTSA thus confirms the general observation for this polymer in pTSA electrolyte that within swollen structures, mass loss processes dominate while in more compact layers a mass gain during oxidation is observed.

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The transition from a mass loss process during oxidation to one of mass gain is not a sharp one, and the actual electrolyte concentration may vary for polymer layers of differing thickness. In all cases, however, the transition occurs when the layer becomes deswollen (Section 4 3 1 2)

Fig 4 3 11 (a) illustrates the cyclic voltammogram and the frequency (sic mass)potential trace obtained at 5 mVs⁻¹ in 0 05 M pTSA, for a polymer layer of surface coverage 2 9 x 10⁻⁸ molcm⁻² This figure is typical for all films at which the change over in mass transfer behaviour occurs At the pH corresponding to 0 05 M pTSA, the polymer layer is deswollen (see Fig 4 3 1) and the mobile co-ion population within the polymer is thus substantially reduced Electro-osmotic flux of solvent from the layer is consequently expected to be less, while the reduced levels of interstitial pore electrolyte will result in the requirement for interfacial counter-anion motion for electroneutrality which will be detected by the EQCM This results in the mass increase in Fig 4 3 11 (a) as oxidation proceeds

Fig 4 3 11 (b) illustrates the corresponding plot of Φ_{pTS} - versus potential The initial value of zero for Φ_{pTS} - indicates that there is no net movement of solvent into or out of

Fig 4 3 11 (a) Frequency vs potential plot and cyclic voltammogram in 0 05 M pTSA for an [Os(bipy)₂(PVP)₁₀Cl]+ film of surface coverage 2 x 10-8 molcm⁻², scan rate is 5 mVs⁻¹





the layer in the early stages of oxidation While this may represent polymer swelling effects [42,46], it may also be indicative of the counter-balancing of the lower level of electro-osmotic flux and the concomitant solvent movement with the counter-anion into the layer

On more exhaustive oxidation, a frequency change, indicating a mass loss, is observed and the attainment of a new plateau, "steady-state" layer mass in the Os^{III} state is established (see Fig 4 3 11 a). It is considered that this shift in frequency represents a morphology change within the layer

In Fig 4 3 11 (b), during the initial stages of polymer re-reduction, Φ_{pTS} - increases, indicating that the mass change observed is insufficient to account for the movement of anion from the polymer layer. This may represent layer viscoelasticity, which results in an underestimation of the mass change from frequency measurements [54]. Alternatively, the positive value for Φ_{pTS} - may reflect the increased levels of electro-osmotic movement of solvent into the layer in the more swollen structure existing in the Os^{III} state. In either case, a more swollen (sic solvated) polymer layer in the Os^{III} state is responsible.

On complete re-reduction of the layer in Fig 4 3 11 (a), a new, lighter baseline in the Os^{11} state is established. After allowing the polymer layer sufficient time to equilibrate, there is a return to the original layer mass. This indicates that the swelling of the polymer in the oxidised form is reversed on conversion to the reduced state on a time scale much longer than that of the 5 mVs⁻¹ scan rate

While no direct evidence for the substantial swelling of the polymer layer during oxidation was obtained for the polymer film depicted in Fig 4 3 11, it has been observed for other polymer layers that the change in the polymer structure in the concentration range 0 01 M to 0 1 M pTSA may result in dramatic changes in layer morphology during redox switching This is seen in Fig 4 3 12, which shows the change in the admittance spectra during redox processes for the sequence of electrolytes 0 04 M, 0 07 M and
0 05 M pTSA In 0 04 M pTSA (Fig 4 3 12a), oxidation results in only minimal changes in rigidity, while in 0 07 M (Fig 4 3 12b), significant swelling is observed. However, for this polymer film transferred to 0 05 M pTSA (Fig 4 3 12c), oxidation results in such extensive swelling that delamination from the electrode surface occurs. This is seen in the flattening of the crystal resonance followed by a shift in resonant frequency to such higher frequencies (due to loss of material) that the subsequent admittance spectra are off-scale.

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That this dramatic change can occur in such a narrow pTSA concentration range is evidence of how important the electrolyte concentration is in determining the layer properties of $[Os(bipy)_2(PVP)_{10}Cl]^+$, and how redox switching may result in the combining of factors where swelling is greatly favoured

Fig 4 3 12 Admittance spectra accompanying redox switching at 5 mVs ¹ in (a) 0 04 M pTSA, (b) 0 07 M pTSA and (c) 0 05 M pTSA Polymer surface coverage is 2 5 x 10⁻⁸ molcm ²



4322 pTSA concentration range 01 M to 1.0 M.

Table 4 3 2 shows that the mass transfer accompanying redox switching in the concentration range 0 1 M to 0 6 M remains constant There is little variation in the normalised mass change evaluated at both 1 and 5 mVs-1, indicating that kinetic effects are absent The $E_{1/2}(m)$ and $E_{1/2}(q)$ values in Table 4 3 3 are in close agreement for both the oxidation and reduction processes, suggesting that there is concomitant mass and charge transfer with only a single mass transfer process in operation. This is illustrated in Fig 4 3 13 where the cyclic voltammogram and the $\hat{\Phi}_{pTS}$ - potential plot in 0 2 M pTSA at 5 mVs-1 are shown. It is of note that the flux of solvent under these conditions is *ca* 300 ngcm-2s-1, while the electro-osmotic flux of solvent from the layer at low electrolyte concentrations is *ca* 400 ngcm-2s-1 (Fig 4 3 9a). This clearly illustrates the additional driving force established for the latter solvent transport process.

Table 4 3 4 shows that there is a broadening of the crystal resonance during oxidation of the polymer, indicative of swelling, in this concentration range This is shown in Fig 4 3 14 for a film of surface coverage 1×10^{-8} molcm⁻² in 0 1 M pTSA

This swelling, in conjunction with the large frequency (sic mass) changes, suggests that there is a large movement of mobile species with the counter-anion. To investigate this, isotopic substitution of H₂O with D₂O was performed in 0.5 M pTSA. Table 4.3.5 summarises the features of the mass change in D₂O and H₂O, obtained at cyclic voltammetric scan rates of 5 mVs⁻¹.

Assuming that electroneutrality is maintained by counter-anion insertion, the normalised mass change in H₂O represents the concomitant movement of 4 8 moles of H₂O per counter-anion, while for D₂O, a value of 4 6 moles is obtained. It should be noted that this solvent transfer is almost five times less than that evaluated by Oyama *et al* for this polymer in NapTS electrolytes [21]. The mass changes evaluated here were obtained using a polymer film of lower surface coverage than that used in Ref 21. As will

Fig 4 3 13 \$\vec{\Phi}_{pTS}\$- vs potential plot and cyclic voltammogram in 0 2 M pTSA for an [Os(bipy)₂(PVP)₁₀Cl]+ film of surface coverage 2 x 10 ⁸ molem ², scan rate is 5 mVs 1



Fig 4 3 14 The change in the admittance spectrum for [Os(bipy)₂(PVP)₁₀Cl]+ during redox switching at 5 mVs ¹ in 0 1 M pTSA. The polymer surface coverage is 1 x 10 ⁸ molem ²



be discussed below, for thinner polymer films in pTSA a lower normalised mass change is obtained For polymer films of comparable thickness to those used in Ref 21, the solvent transfer is of similar magnitude (see Table 4 3 6)

The result from the isotopic substitution experiment in 0.5 M pTSA is considered to provide unambiguous proof of the role of solvent transfer during redox processes for all polymer layers in the concentration range 0.1 M to 0.6 M pTSA. The close quantitative agreement also indicates that while the polymer layers are viscoelastic, the approximation to rigidity may be valid [55] and that the evaluation of mass is an accurate reflection of interfacial mass transfer processes. Irrespective of the morphology changes during redox, the conclusion that a large influx of solvent occurs during oxidation remains valid

At pTSA concentrations greater than 0 6 M there is a gradual transition to mass loss processes predominating during redox switching Fig 4 3 15 (a) shows the mass-potential plot and cyclic voltammogram in 0 8 M pTSA at 5 mVs⁻¹ for a polymer of surface coverage 2 x 10⁻⁸ molcm⁻² The normalised mass change evaluated for the oxidation is lower due to the reduced level of mass transfer in the latter stages of oxidation (see Table 4 3 2) This is illustrated in the corresponding $\hat{\Phi}_{pTS}$ - plot in Fig 4 3 15 (b), where, after *ca* 50% oxidation, the mass change is insufficient to account for the insertion of the pTScounter-anion and the frequency measurements suggest a net movement of solvent from the polymer layer

Fig 4 3 16 (a) illustrates the mass-potential and cyclic voltammogram for the same film, obtained in 1 0 M pTSA at 5 mVs⁻¹ A mass loss is observed throughout film oxidation However, at these high pTSA electrolyte concentrations there is a strong viscoeleastic contribution to frequency measurements. This is seen in Fig 4 3 16 (b), which shows the admittance spectra obtained during redox switching at 5 mVs⁻¹ in 1 0 M pTSA for a different film but of similar surface coverage (*ca* 2 x 10⁻⁸ molcm⁻²). The spectra are so broadened that the centre resonant frequency is not expected to be

- Fig 4 3 15 (a) Frequency vs potential plot and cyclic voltammogram in 0 8 M pTSA for an [Os(bipy)₂(PVP)₁₀Cl]+ film of surface coverage 2 x 10-8 molcm⁻², scan rate is 5 mVs⁻¹
 - (b) The corresponding $\dot{\Phi}_{pTS}$ vs potential plot



- Fig 4 3 16 (a) Cyclic voltammogram and frequency-potential plot in 1 0 M pTSA for [Os(bipy)₂(PVP)₁₀Cl]+ Scan rate is 5 mVs⁻¹ and the polymer surface coverage is 2 x 10⁻⁸ molcm⁻²
 - (b) Admittance spectra during redox switching at 5 mVs⁻¹ in 1 0 M pTSA for polymer of similar surface coverage



accurately followed by the oscillator circuitry At this concentration a reduction in the resident layer mass is also observed (see Fig 4 3 1) and it is considered that the combination of highly viscous electrolyte and heavy polymer loading results in frequency changes which can not be accurately related to mass changes occuring within the layer

For thinner polymer layers a mass gain during oxidation is observed in 0.8 M and 1.0 M pTSA (see entry for film of surface coverage 5×10^{-9} molcm⁻² in Table 4.3.4 and data for film of surface coverage 1.1 x 10⁻⁸ molcm⁻² in Chapter 5, Table 5.3.4) For these films the resident layer mass retains a value representative of a fully protonated, solvated film. It is only at concentrations as high as 2.0 M pTSA that the transition to a mass loss is observed. This suggests that a maximum crystal loading can be tolerated, beyond which interpretation of frequency data cannot be made

4323 Surface coverage effects

Table 4 3 6 summarises the frequency shift during redox switching in 0 1 M pTSA at 5 mVs⁻¹ for polymer layers of differing thickness. The evaluation of the normalised mass is also included Below *ca* 2 x 10⁻⁸ molcm⁻² (i e 450 μ C), the normalised mass increases with increasing polymer layer surface coverages. This is contrary to the expectation in viscoelastic polymer layers, where increased film thickness is anticipated to exacerbate the underevaluation of mass from frequency measurements [54]

The solvent interaction with the osmium metallopolymer is strong in pTSA electrolyte. It is likely that the outer regions of the films at the polymer / electrolyte interface have attained an equilibrium level of solvation, which, for thinner polymer layers, will constitute a greater proportion of the total layer. Because concomitant mass and charge transfer is observed for all polymer surface coverages, an increasing viscoelastic contribution to frequency measurements for thinner layers is not thought to be responsible for the decrease in the normalised mass calculated. Instead, the more

Table 4 3 6The effect of [Os(bipy)2(PVP)10Cl]+ surface coverage on the end-to-
end frequency changes accompanying redox switching at 5 mVs-1 in
0 1 M pTSA

Charge (a) (µC)	∆f (Hz)	M _{eq} (b) (gmol ⁻¹)	Moles H ₂ O (c) (per redox site)
795	6990		56 1
625	3511	- 537	-39 4
555	1168	- 201	-20 6
460	-3610	751	32 2
390	-2392	587	23 1
338	-1725	488	17 6
255	-1157	434	14 6
154	- 510	317	8 1
60	- 146	232	34

- a) From the anodic branch of the cyclic voltammogram at 5 mVs⁻¹
- b) Normalised mass for Osil/ill couple assuming the Sauerbrey equation
- c) Solvent transfer for Os^{11/111} couple assuming counter-anion motion IN for electroneutrality

complete solvation of thinner films reduces the requirement for solvent transfer accompanying anion motion This dependency of interfacial solvent transfer on morphology has also been seen in the surface coverage effects for this polymer in 0 01 M HClO₄ (Section 3 4 4 2b)

For polymer films with surface coverages greater than $2 \ge 10^{-8}$ molcm⁻², a mass loss occurs during oxidation in 0.1 M pTSA. A typical cyclic voltammogram and frequency-potential plot at 5mVs⁻¹ for such a film (surface coverage $3.2 \ge 10^{-8}$ molcm⁻²) is shown in Fig 4.3.17

Since the layer mass in 0 1M pTSA is representative of a more compact structure (see plateau region in the pH range 1 00 to 0 00 in Fig 4 3 1) the polymer is not anticipated to contain large quantities of electrolye. The mass loss therefore cannot represent the electro-osmotic flux of solvent and electroneutrality is maintained by interfacial counteranion motion.

In a series of papers by Evans *et al* [55], dealing with the electro-mechanical considerations for counter-ion insertion during redox processes in PVF, it was observed that the shear forces due to internal stress are expected to increase with film thickness [55] Internal pressures during redox processes as great as *ca* 3000 atm may be exerted It is possible that up to surface coverages of 2×10^{-8} molcm⁻², the osmium metallopolymer matrix can tolerate the increases in swelling pressure and maintain the same level of initial solvent sorption. For thicker films, with more compact underlayers, the mechanical strains may become too great and redox switching can only occur by the ejection of large quantities of solvent from the polymer layer. Unlike plasma polymerised PVF, where thick films may be observed to burst [55], no such effect is in evidence here, as seen in the by the minimal hysteresis in the mass-potential plot in Fig 4 3 17

This interpretation is evidenced by the mass transfer behaviour of all polymer layers, irrespective of thickness, when transferred from perchlorate to pTSA electrolyte

Fig 4 3 17 Cyclic voltammogram and frequency-potential plot in 0 1 M pTSA for an [Os(bipy)₂(PVP)₁₀Cl]+ film with surface coverage is 3 2 x 10-8 molcm⁻² The scan rate is 5 mVs⁻¹



Fig 4 3 18 illustrates the mass-potential traces for a film of surface coverage 2 x 10^{-8} molcm⁻² in 0 1 M pTSA, having previously been exposed to 1 0 M HClO₄ electrolyte (and subsequently stored in H₂O for several days) The scan rate is 50 mVs⁻¹, with continuous scanning over 4 hours

In this figure, it is seen that the initial mass transfer accompanying oxidation (Scan A) represents a mass loss During repeated cycling, mass gain processes gradually begin to predominate, until eventually a mass gain process during oxidation is observed (Scan B) Throughout these repeated scans no change in the voltammetry of the Os^{II/III} couple is seen (Fig 4 3 18 inset) It is of note that the mass baseline in the Os^{II} state becomes gradually lighter in the course of the electrochemical cycling, although for presentation purposes this has been ommitted in Fig 4 3 18

Having been exposed to HClO₄ electrolyte, the polymer layer will be extensively crosslinked (see Section 3 4 3 1) This imposes a rigid structure on the polymeric matrix which will result in a finite void volume. The insertion of the bulky pTS- anion on exposure to, and initial redox cycling in pTSA can thus only proceed at the expense of the existing interstitial solvent. However, on equilibration of the layer in pTSA, all ClO₄⁻ ion-pairs from the layer are removed, volume limitations within the layer no longer exist, and pTS- anion and solvent transfer can proceed unimpeded by steric constraints. This transition in mass transfer behaviour is directly analagous to the surface coverage effects discussed above

Fig 4 3 18 Frequency-potential plot at 50 mVs⁻¹ for a [Os(bipy)₂(PVP)₁₀Cl]+ film in 0 1 M pTSA, having previously exposed to HClO₄ The surface coverage is 2 x 10⁻⁸ molcm⁻² Inset is the corresponding voltammetric response



4.4. CONCLUSIONS.

It has been shown for the redox polymer, [Os(bipy)₂(PVP)₁₀Cl]+ that the layer morphology, when swollen, becomes more sensitive to electrolyte concentration. These structural changes have been verified using admittance analysis and EQCM data, and have been explained in terms of solvent transfer and swelling mechanisms developed for ion-exchange membranes. It has been demonstrated that the counter-anion molar volume is of only secondary importance in determining the level of swelling. It is the osmotic activity of the anion, as determined by specific ionic interactions which is of primary importance. The increased swelling of the osmium metallopolymer in pTSA results in easier protonation of the polymer backbone due to the ease with which counter-anions can enter the more open polymer matrix.

The flux of solvent into or out of the polymer during oxidation reflects the layer morphology However, in all cases, increased polymer expansion accompanies oxidation due to the increased osmotic effect of the Os^{III} centres. While the existence of solvated polymer layers undermines the validity of the Sauerbrey equation in certain circumstances, the results of the isotopic substitution experiments confirm the predominance of solvent transport during redox switching. When swollen at dilute concentrations, electro-osmotic flux of solvent is observed. As the pTSA concentration is increased, compact layers are re-established, and solvent flux concomitant with counteranion motion occurs. At the highest electrolyte concentrations studied the combined viscosity of the electrolyte and the polymer layer prevents an accurate assessment of interfacial transport from being made

Because of the differences in the polymer structure that exists in pTSA and HClO₄, these electrolytes provide a useful comparison in studying the effect of polymer morphology on redox and mass transfer processes. These will now be considered in the context of charge transport rates within this metallopolymer

4.5 **REFERENCES.**

- 1 S B Tuwiner, Diffusion and Membrane Technology, Chapman and Hall, New York, (1962)
- 2 F Helfferich, Ion Exchange, McGraw-Hill, New York, (1962)
- 3 J Koryta, Ions, Electrodes and Membranes, Wiley-Interscience, New York, (1982)
- 4 JA Kitchener in, Ion exchange, JA Marinsky Ed, Marcel Dekker, New York, (1969), 1, Chp 2
- 5 R W Murray, Electroanalytical Chemistry, A J Bard (Ed), Marcel Dekker, New York, (1984), 13, p302
- 6 K Doblhofer and R D Armstrong, Electrochim Acta, (1988), 33, 4534
- 7 S M Oh and L R Faulkner, J Electroanal Chem, (1989), 269, 77
- 8 S M Oh and L R Faulkner, J Am Chem Soc, (1989), 111, 5613
- 9 JF Parcher, CJ Barbour and R W Murray, Anal Chem., (1989), 61, 584
- 10 R P Buck, J Electroanal Chem, (1987), 219, 213
- 11 R P Buck and P Vanysek, J Electroanal Chem, (1990), 292, 73
- 12 P Vanysek and R P Buck, J Electroanal Chem, (1991), 297, 19
- 13 S Bruckenstein and A R Hillman, J Phys Chem, (1988), 92, 4837
- S Bruckenstein, C P Wilde, M Shay and A R Hillman, J Phys Chem, (1990), 94,
 787
- 15 J A Marinsky, J Phys Chem , (1985) , 89, 5294
- 16 R J Forster, A J Kelly, J G Vos and M E G Lyons, *J Electroanal Chem*, (1989), 270, 365
- 17 R J Forster and J G Vos, J Electroanal Chem, (1991), 314, 135
- 18 R J Forster and J G Vos, Electrochim Acta, (1992), 37, 159
- R J Forster, J G Vos and M E G Lyons, J Chem Soc Faraday Trans, (1991), 87,
 3761

- 20 R J Forster, J G Vos and M E G Lyons, *J Chem Soc Faraday Trans*, (1991), 87, 3769
- 21 A J Kelly, T Ohsaka, N Oyama, R J Forster and J G Vos, J Electroanal Chem, (1990), 287, 185
- 22 A J Kelly and N Oyama, J Phys Chem, (1991), 95, 9579
- 23 J Dainty and J Ferrier, Studia Biophysica, (1989), 133, 133
- 24 R J Hunter, Zeta Potential in Colloid Science Principles and Application, Academic Press, London, (1981)
- 25 H P Gregor, J Am Chem Soc , (1951), 73, 3537
- 26 H P Gregor, J Belle and R A Marcus, J Am Chem Soc, (1955), 77, 2713
- 27 D Reichenberg, K W Pepper and D J McCauley, J Chem Soc, (1951), 493
- 28 G S Manning, J Chem Phys , (1969) , 51 , 924, 934
- 29 H P Gregor, J Am Chem. Soc , (1948), 70, 1293
- 30 H P Gregor, J Am Chem Soc , (1951), 73, 642
- 31 L Lazare, B R Sundheim and H P Gregor, J Phys Chem., (1956), 60, 641
- 32 H P Gregor, J Belle and R A Marcus, J Am Chem Soc, (1954), 76, 1984
- H P Gregor, B R Sundheim, K M Held and M H Waxman, J Colloid Sci , (1952) ,
 7, 511
- 34 PG Howe and JA Kitchener, J Chem Soc , (1955), 2143
- 35 G E Boyd and B A Soldano, J Am Chem Soc, (1954), 75, 6091
- 36 B A Soldano and G E Boyd, J Am. Chem. Soc , (1954), 75, 6099
- 37 G E Boyd and B A Soldano, J Am Chem Soc, (1954), 75, 6105
- 38 B A Soldano and G E Boyd, J Am Chem Soc, (1954), 75, 6107
- 39 P Ferruti and R Barbucci, Adv Polym Sci , (1984), 58, 55
- 40 Y Okahata and H Ebato, Anal Chem, (1989), 61, 2185
- 41 PT Varineau and DA Buttry, J Phys Chem, (1987), 91, 1292
- 42 R Borjas and D A Buttry, J Electroanal Chem, (1990), 280, 73

- 43 Y Marcus, Ion Solvation, Wiley-Interscience, New York, (1985)
- 44 T R E Kressman and J A Kitchener, J Chem Soc , (1949), 1190, 1201, 1208
- 45 D Ghesquiere, B Ban and C Chachaty, Macromolecules, (1977), 10, 743
- 46 G Inzelt and J Bacskai, Electrochum. Acta, (1992), 37, 647
- 47 A R Hillman, Electrochemical Science and Technology of Polymers, Ed R Linford, Elsevier Applied Science Publishers, London, (1987), Vol 1, Ch 5 & 6
- 48 A R Hillman, D C Loveday and S Bruckenstein, J Electroanal Chem., (1989), 274, 157
- 49 A R Hillman, D C Loveday, M J Swann, S Bruckenstein and C P Wilde, J Chem Soc Faraday Trans, (1991), 87, 2047
- 50 A R Hillman, M J Swann and S Bruckenstein, J Phys Chem., (1991), 95, 3271
- 51 S Bruckenstein, C P Wilde, M Shay, A R Hillman and D C Loveday, J Electroanal Chem., (1989), 258, 457
- 52 A R Hillman, D C Loveday, S Bruckenstein and C P Wilde, J Chem. Soc, Faraday Trans, (1990), 86, 437
- 53 S Bruckenstein, A R Hillman and M J Swann, J Electrochem. Soc, (1990), 137, 1323
- A Glidle, A R Hillman and S Bruckenstein, J Electroanal Chem, (1991), 318,
 411
- 55 S J Lasky and D A Buttry, J Am Chem Soc, (1988), 110, 6258
- a) E F Bowden, M F Dautartas and J F Evans, J Electroanal Chem, (1987),
 219, 49
 - b) M F Dautartas, E F Bowden and J F Evans, J Electroanal Chem, (1987), 219, 71
 - c) E F Bowden, M F Dautartas and J F Evans, J Electroanal Chem, (1987), 219, 91

CHAPTER 5

The Effect of Electrolyte and Experimental Time Scale on Mass Transfer and Charge Transport through Thin Films of [Os(bipy)2(PVP)10Cl]+

5.1. INTRODUCTION.

The rate of charge transport through electrode modifying materials is of fundamental importance to their successful application. As discussed in previous chapters, for redox polymers containing osmium bis(bipyridyl) complexes, an extensive study of the electron transfer process has been undertaken. What has emerged has been the primary importance of the physico-chemical properties of the polymer film in determining electron transfer rates, with layer structure influenced by the contacting electrolyte type and concentration, polymer backbone and redox site loading [1-3]

In Chapters 3 and 4, the effect of the contacting electrolyte on the structure of $[Os(bipy)_2(PVP)_{10}Cl]$ + has been demonstrated through the combined use of the EQCM and impedance analysis In both HClO₄ and pTSA, application of the Sauerbrey equation was found to be permissable

It is the purpose of this chapter to investigate the effect of these structural changes on interfacial mass transfer under more dynamic conditions and to relate this to previously determined diffusion coefficients and activation parameters for the charge transport process. The dynamic aspects of mass transfer in HClO4 and pTSA is first considered using cyclic voltammetry under semi-infinite diffusion conditions. Transient mass transfer in response to a potential step is then investigated on the 100 ms to 10 s time scale for both oxidation and reduction of the polymer film. For $[Os(bipy)_2(PVP)_{10}Cl]^+$ the apparent charge transport diffusion coefficient measured from potential step techniques, $D_{ct}(PS)$, has been observed to be significantly different from those obtained using cyclic voltammetry, $D_{ct}(CV)$ [1-3]. This has been discussed previously in Chapter 2. It is hoped that the study of mass transfer on these differing time scales will enable the origin of the time scale dependence of D_{ct} to be better understood

5.2. EXPERIMENTAL.

 $[Os(bipy)_2(PVP)_{10}Cl]Cl$ was synthesised as described in Chapter 3 The electrode preparation for the EQCM and the experimental procedures for mass measurement are also as described in Chapter 3 For potential step techniques, the potential was controlled via an IBM ATX computer The frequency was input as a voltage via a F/V converter, which had a time constant of 5 ms

Apparent charge transport diffusion coefficients were evaluated as described in Chapter 2

5.3. **RESULTS AND DISCUSSION.**

5.3.1. Cyclic Voltammetry- General Layer behaviour.

In Chapters 3 and 4, the thermodynamic mass transfer during redox processes in HClO₄ and pTSA was considered for slow cyclic voltammetric scan rates. Under more dynamic conditions kinetic limitations for the interfacial transfer of one or more mobile species may become evident. A simple qualitative method for illustrating this is the scan rate dependence of the potentials of half-mass-change, $E_{1/2}(m)$, and half-charge-change, $E_{1/2}(q)$ [4-7]. This is shown in Fig 5.3.1 and Fig 5.3.2 for oxidation and reduction of $[Os(bipy)_2(PVP)_{10}Cl]$ + in 0.1 M HClO₄ and 0.2 M pTSA, respectively. The scan rate was varied from 1 to 500 mVs⁻¹ (log scan rate is used for presentation purposes). The polymer surface coverage for both sets of data is 2 x 10-8 molcm-2. 0.2 M pTSA is chosen for comparison as it has been demonstrated in Chapter 4 that mass transfer during redox switching at this electrolyte concentration represents a simple counter-ion and solvent transfer into / out of the layer during polymer oxidation / reduction, with no complications to frequency measurements from polymer swelling effects, electro-osmosis or redox-dependent morpholgy changes.



Fig 5 3.1 Scan rate dependency of (\Box) $E_{1/2}(m)$ and (+) $E_{1/2}(q)$ in 0.1 M HClO₄

Fig 5 3 2 Scan rate dependency of ([]) $E_{1/2}(m)$ and (+) $E_{1/2}(q)$ in 0 2 M pTSA



The scan rate dependence of mass and charge transfer in Fig 5 3 1 and Fig 5 3 2 exhibits the same trends in both electrolytes. At slow scan rates, $E_{1/2}(m)$ and $E_{1/2}(q)$ tend to the same limiting value and, as discussed in previous chapters, represents the attainment of global equilibrium of all mobile species (i e electrons, ions and solvent). In HClO₄, at a scan rate of 1 mVs⁻¹, $E_{1/2}(m)$ and $E_{1/2}(q)$ for polymer oxidation converge at 221 mV, while for reduction the common value is 193 mV. In pTSA electrolyte, the halfpotentials for both the anodic and cathodic branches of the cyclic voltammogram at 1 mVs⁻¹ converge to the same value of 259 ± 4 mV. This reflects the true surface wave behaviour of [Os(bipy)₂(PVP)₁₀Cl]+ in pTSA electrolyte, which is not observed in HClO₄

The "equilibrium" redox potentials are clearly dependent on electrolyte type The less positive potential for redox processes in HClO₄ may be attributed to the ion-association between the perchlorate counter-ion and the fixed charge sites of the polymer layer [8,9] In a recent study, it has been proposed that the more positive redox potential of $[Os(bipy)_2(PVP)_{10}Cl]$ + in pTSA electrolyte reflects the increased requirement for organisation of solvent during redox conversion [10]

For both electrolytes, at faster cyclic voltammetric scan rates, $E_{1/2}(m)$ and $E_{1/2}(q)$ deviate from these "equilibrium" potentials, with $E_{1/2}(m)$ deviating more strongly This illustrates the introduction of kinetic limitations to mass and charge transfer, particularly interfacial mass transfer [5,6] For the films depicted in Fig 5 3 1 and Fig 5 3 2, kinetic limitations are evidenced at scan rates faster than 5 mVs⁻¹ in 0 1 M HClO₄ and 50 mVs⁻¹ in 0 2 M pTSA. This departure from equilibrium is therefore electrolyte dependent and, although qualitatively similar for all films, is also found to be dependent on polymer surface coverage

5.3.2. Scan Rate dependency of Mass transfer.

5321 HClO4 electrolyte

The half-potential data in Fig 5 3 1 demonstrate that global equilibrium is only attained during redox processes at slow cyclic voltammetric scan rates. The identity of the slowest of the mobile species is now addressed.

Fig 5 3 3 illustrates the current-potential, mass-potential and charge-potential plots for the initial and repeat cyclic voltammetric scans at 200 mVs⁻¹ in 0 1 M HClO₄ The coulometric polymer surface coverage is 2 x 10⁻⁸ molcm⁻² The corresponding Φ_{ClO4^-} and mass-charge plots for the first and second cycles are illustrated in Fig 5 3 4

During the first redox cycle, as soon as polymer oxidation commences there is a mass ingress. This is seen in the mass-charge plot in Fig 5.3.4 and is observed for redox switching at all HClO₄ concentrations (*vide infra*). Because counter-ions within the layer are anticipated to take temporal precedence over solution phase sources [7], this immediate interfacial mass transfer illustrates that no polymer phase counter-anion source is readily available. For concentrations less than 1.0 M HClO₄, this is in agreement with the permiselectivity of the layer in the Os^{II} state discussed in Chapter 3. For concentrations greater than 1.0 M, where permiselectivity fails, it suggests that counter-anion is not supplied from the dissociation of the polymer phase ion-pair, $(H_3O)+(ClO_4)$ -[11]

The passage of anodic charge is almost complete during the forward scan of the cyclic voltammogam (Point A, Fig 5 3 3c) However, the mass continues to increase until the onset of re-reduction of the Os¹¹¹ centres during the reverse sweep (Point B, Fig 5 3 3b) This is clearly seen in the mass-charge plot in Fig 5 3 4, but is particularly evident in the corresponding Φ_{ClO4} - plot As discussed previously, Φ_{J} represents the movement of all mobile species except the ion j, assuming ion j is responsible for the

Fig 5 3 3 (1) Cyclic voltammogram, (11) mass-potential and (111) charge potential plots at a scan rate of 200 mVs⁻¹ in 0 1 M HClO₄ The polymer surface coverage is 2 x 10⁻⁸ molcm⁻²







maintenance of electroneutrality [12-14] In Chapter 3, it was shown, that for $[Os(bipy)_2(PVP)_{10}Cl]$ + in 0 1 M HClO₄, Φ_{ClO4} -represents solvent movement

Due to the requirement for electroneutrality within the layer, an electrochemical potential gradient for counter-ion motion is established during redox processes [12] Consequently, ion motion is anticipated to be coupled to the passage of charge with solvent transfer occuring more slowly [12-15] The continued mass increase in Fig 5 3 3 and Fig 5 3 4, therefore, represents the slower transfer of solvent into the layer under the activity gradient established by the Os^{11/11} oxidation [16]

This interpretation is confirmed from the features of the mass and charge transfer data in Fig 5 3 3 and Fig 5 3 4 Neither the mass-potential nor charge-potential plots track (i e a given potential does not uniquely define a value for layer mass or charge) Similarly, the mass-charge plot does not track, indicating that the transfer of mobile species is not in equilibrium with the instantaneous oxidation state of the layer. Using a diagnostic scheme proposed by Hillman *et al* [12-14] for the interpretation of EQCM data, these features of mass and charge transfer in HClO₄ indicate that it is activity control by net neutrals which is the rate determining step. It can therefore be concluded that it is retarded solvent movement which causes the greater divergence of $E_{1/2}(m)$ with increasing scan rate in Fig 5 3 1

In Fig 5 3 3, during the reverse scan neither mass nor charge re-attain their initial zero values (Points C) This is attributed to the kinetic isolation of Os^{III} centres on the time scale of the 200 mVs⁻¹ scan rate and the subsequent requirement for counter-anion and solvent to be retained within the polymer. For the redox sites that remain in the Os^{III} oxidation state at Point C, the retained mass corresponds to a single ClO₄- anion plus 2 7 moles of H₂O per osmium centre. This is the thermodynamic solvent requirement for polymer oxidation discussed in Chapter 3

In Fig 5 3 3, following repeated cyclic voltammetric scanning, a "steady-state" value

for mass and charge transfer is eventually reached on approximately the third or fourth repeat scan. While all other features of the data depicted in Fig 5 3 3 and Fig 5 3 4 are found for all HClO₄ electrolytes, the attainment of this "steady-state" is very much dependent on electrolyte concentration. This will be discussed later in Section 5 3 3 in relation to the observed dependency of $D_{cl}(CV)$ on HClO₄ concentration.

The normalised <u>end-to-end</u> mass for the forward scan (corresponding to points A in Fig 5 3 3) is summarised in Table 5 3 1 for different scan rates in a range of HClO₄ electrolytes This mass change occurs between the "<u>end-to-end</u>" potentials of the applied potential ramp (i e the linear sweep), and is designated M_{eq}(ETE) The normalised mass for the <u>total</u> mass change accompanying the <u>total</u> anodic charge passed (corresponding to points B in Fig 5 3 3), is designated M_{eq}(TOT), and is also included in Table 5 3 1 These data have been averaged over repeat analysis on a single coating and, with the exception of 0 001 M and 4 0 M, for analysis on at least two different polymer films The values of M_{eq}(TOT) are independent of surface coverage for the range studied (0 5 to 5 x 10-8 molcm⁻²) and have an estimated error of ± 5% M_{eq}(ETE) values are quoted for polymer films of coulometric surface coverage greater than 1 x 10-8 molcm⁻² and also have an estimated error of ± 5%

For films of gravimetric surface coverage less than 1 x 10⁻⁸ molcm⁻², $M_{eq}(TOT)$ and $M_{eq}(ETE)$ are quantitatively similar and yield the value of $M_{eq}(TOT)$ quoted in Table 5 3 1. This indicates that the interfacial transfer of solvent occurs more readily within thinner films and can accompany counter-anion motion throughout. As discussed in Chapter 3, the polymer in perchlorate media is extensively cross-linked and dehydrated and it has been considered that it is only through extensive polymer chain motion that counter-ion can enter the film [1,2]. Because the relaxation rates for diffusional processes and polymer morphology changes are expected to be dependent on film thickness.

HClO ₄ Conc	D _{ct} (CV) (a)	ν	M _{eq} (ETE) (b,d)	M _{eq} (TOT) (c,d)	
(Molar)	(x 10 ¹¹ cm ² s ¹)	(mVs ¹)	(gmol ¹)	(gmol ¹)	
0 001	0 47	5	42	60	
		50	42	46	
		200	39	46	
0 01	1 25	1	185	*	
• • •		50	143	176	
		200	99	150	
0 03	4 76	5	155	*	
		50	156	164	
		200	140	165	
01	3 88	5	142	*	
		50	136	148	
		200	113	136	
03	2 67	5	143	*	
		50	135	143	
		200	121	140	
10	1 32	5	142	*	
		50	127	141	
		200	112	139	
30	6 75	5	479	*	
		50	481	*	
		200	479	*	
40	11 30	5	-221	*	
· •		50	-522	*	
		200	-516	*	

Table 5 3 1Scan rate dependency of normalised mass in HClO4 electrolyteThe variation in $D_{ct}(CV)$ with HClO4 concentration is also included

a) Evaluated from anodic peak current of cyclic voltammogram using the Randles-Sevcik equation

b) Evaluated from data obtained on completion of linear sweep of the cyclic voltammogram

- c) Evaluated from the maximum value of mass and charge attained before onset of re-reduction of Os^{III} to Os^{III} * denotes the same evaluation as obtained for $M_{eq}(ETE)$
- d) Averaged for two different polymer coatings Error is $\pm 2\%$ for a given film, $\pm 10\%$ between films

[6,17,18], it is thought that for thinner films such processes will be less impeded and the transfer of all mobile species correspondingly facilitated

The data in Table 5.3.1 indicate that $M_{eq}(ETE)$ is significantly reduced at faster scan rates, reflecting the reduced solvent transfer discussed above. In the range 0.01 to 1.0 M HClO₄, with the exception of 0.03 M HClO₄, $M_{eq}(ETE)$ has a value approaching that of the perchlorate anion and a single solvent molecule. However, even on time scales corresponding to 200 mVs⁻¹, solvent transfer occurs before onset of re-reduction of the layer, to yield $M_{eq}(TOT)$ values which are similar to the "thermodynamic" mass changes obtained on the longer time scales of 5 mVs⁻¹ scan rates. The thermodynamic data have been discussed previously in Chapter 3 and are also included in Table 5.3.1 for comparison

For electrolyte concentrations greater than 1 0 M HClO₄, $M_{eq}(ETE)$ and $M_{eq}(TOT)$ values are similar, with all mass and charge transfer occuring during the end-to-end anodic sweep As discussed in Chapter 3, at these electrolyte concentrations permselectivity of the layer fails and transfer of the neutral acid, (H₃O)+(ClO₄)-, occurs The transfer of perchlorate salt has been observed to be faster than solvent transfer in PVF [13,14] Similarly, neutral acid transfer is expected to be faster than that of solvent and for [Os(bipy)₂(PVP)₁₀Cl]+ films appears to occur concomitantly with the counter-anion

For 4 0 M HClO₄, the development of the counter-Donnan osmotic flux [19], discussed in Section 3 4 4 2c, results in a <u>net</u> mass loss which is almost independent of scan rate Consequently, because of the kinetic limitations for the passage of charge at faster scan rates, the evaluation of the normalised mass is observed to increase with increasing scan rate

5322 pTSA electrolyte

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Fig 5 3 5 illustrates the cyclic voltammogram, mass-potential and charge-potential plots obtained in 0 2 M pTSA for the first and subsequent scans at 200 mVs-1 The corresponding Φ_{pTS} - and mass-charge plots are illustrated in Fig 5 3 6 The coulometric polymer surface coverage is 2 x 10-8 molcm⁻²

Mass and charge transfer in all pTSA concentrations exhibit the same general features as those in Fig 5 3 5 and Fig 5 3 6 On the time scale of the forward scan complete transfer of solvent occurs as dictated by the extent of polymer oxidation. The evaluation of $M_{eq}(ETE)$ is therefore found to be equal to that of $M_{eq}(TOT)$ (calculated from Points A and B in Fig 5 3 5, respectively)

The immediate mass increase with the passage of charge in Fig 5 3 6, demonstrates that an anion source does not exist within the polymer film. This suggests that despite being more swollen, the polymer layers in pTSA may remain permselective in the concentration range 0 1 M to 1 0 M. If this is so, then it is only the levels of solvation dictated by the electrolyte / polymer interaction and the pTS- counter-anion requirement for the protonated polymer backbone that contribute to the resident layer mass in the pTSA concentration range corresponding to pH 0 0 to 1 0 (see Section 4 3 1 4 and Fig 4 3 7).

The minimal hysteresis in both the Φ_{pTS} - and mass-charge plots in Fig 5.3.6, confirms that all mobile species are transferred at a similar rate. The facile mass transfer in pTSA electrolyte and the concomitant transfer of large quantities of solvent with the counter-anion may be attributed to the polymer morphology which results from the pTSA / polymer interaction discussed in Chapter 4. Using the diagnostic scheme for the analysis of EQCM data, the mass and charge transfer in Fig 5.3.5 and Fig 5.3.6 indicate that the charge transport process is under electroneutrality control [12-14]. For a nonpermselective film this would represent electron self exchange as the rate limiting step

Fig 5 3 5 (1) Cyclic voltammogram, (11) mass-potential and (111) charge potential plots at a scan rate of 200 mVs⁻¹ in 0 2 M pTSA The polymer surface coverage is 2 x 10⁻⁸ molcm⁻²



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Fig 5 3 6 Φ_{pTS} - and mass-charge plot for data presented in Fig 5 3 5

Due to the loading effects that have been found for $[Os(bipy)_2(PVP)_nCl]^+$, where n was varied from 5 to 25 [2,3], this is considered unlikely. For a permselective polymer film, however, electroneutrality control represents counter-anion motion as the rate limiting step. This interpretation is evidenced by the absence of a counter-anion source within $[Os(bipy)_2(PVP)_{10}Cl]^+$ films and is in agreement with activation parameters for $D_{ct}(CV)$ previously reported for this polymer in pTSA electrolyte [1]

Table 5 3 2 summarises the <u>end-to-end</u> frequency shift, anodic charge and the normalised mass for scan rates ranging from 1 to 500 mVs⁻¹ in a series of pTSA electrolyte concentrations. The data presented are for a film of coulometric surface coverage 2 x 10⁻⁸ molcm⁻² and are averaged for repeat analysis on that film (error \pm 2%) For films of similar surface coverage, the between film variation is \pm 10%

5322a pTSA concentrations less than 01 M

As discussed in Section 4.3.2.1, the swelling of the layer at pTSA concentrations below 0.1 M results in different mass transfer behaviour. At the transition concentration of 0.05 M pTSA, redox-induced morphology changes on more exhaustive oxidation of the polymer were found to result in such polymer swelling that an apparent mass loss is observed (Fig 4.3.14, Chapter 4). From Table 5.3.2 it can be seen that at faster scan rates this morphology change is "frozen out" of the observed mass change, and consequently, $M_{eq}(ETE)$ increases with increasing scan rate up to a scan rate of 200 mVs⁻¹. This may be attributed to the reduced levels of polymer oxidation under semi-infinite diffusion conditions effecting reduced polymer swelling. It also represents the liklihood that polymer swelling processes are slower than the time scale of the electrochemical transformation of the layer. This was evidenced in Chapter 4 by the slow re-establishment of the baseline layer mass following the complete redox-switching cycle (see Fig 4.3.11

		•		4QUA	
(Molar)	$(x \ 10^{11} \ cm^2 s^1)$	(mVs ¹)	(Hz)	(μC)	(gmol 1)
0.01	3.80 (1.0)	1	1727	300	_414
001	360 (10)	50	1800	330	-414
		200	1360	220	-505
		500	1041	170	-586
0.05	5 70 (0 7)	1	-1007	408	236
	- (,	50	-1068	365	280
		200	-1214	285	407
		500	- 758	193	377
0.10	12 90 (0 6)	1	-2391	390	587
	· · /	50	-2300	375	586
		200	-1552	285	521
		500	- 913	200	437
0 20	12 60 (0 9)	1	-2030	408	476
		50	-2027	405	479
		200	-1515	315	460
		500	-1004	235	409
0 40 12	12 50 (0 8)	1	-1926	340	541
		50	-1862	368	484
		200	-1515	328	442
		500	-1041	252	395
0 60	12 30 (0 7)	1	-1975	375	504
		50	-1990	370	514
		200	-1625	330	505
		500	-1095	255	438
0 80	13 90 (0 9)	1	1376	350	-376
		50	1634	393	-398
		200	1424	340	-401
		500	849	210	-387
1 00	14 10 (0 9)	1	2044	358	-546
		50	1826	375	-466
		200	1387	340	-390
		500	895	260	-329

Table 5 3 2	Scan rate dependency of frequency shift, charge and normalised mass in pTSA electrolyte
	D _{ct} (CV) evaluation at each concentration is also included

a) Calculated from anodic peak current of cyclic voltammogram using Randles-Sevcik equation

b) Change in resonant frequency on completion of linear sweep for oxidation

c) Calculated assuming the validity of the Sauerbrey equation

and related text)

In 0 01 M pTSA the mass loss occuring throughout polymer oxidation was shown to be due to the electro-osmotic flux of solvent from the extensively swollen polymer film (see Section 4 3 2 1) In Table 5 3 2, while the <u>absolute mass</u> (sic frequency) change is smaller at faster scan rates, the normalised mass becomes greater This reflects the kinetic aspects of the electro-osmotic flux and its dependence on current density rather than the total charge passed [20] Although this solvent flux has been demonstrated to be real, using solvent isotopic substitution, its quantification is recognised to be subject to the viscoelasticity of the swollen polymer layer in dilute pTSA electrolyte

<u>5322b</u> pTSA concentration range 0.1 M to 1.0 M

In the concentration range 0 1 M to 0 6 M pTSA, the mass change is due to counteranion motion and solvent transfer (Section 4 3 2 2) The normalised mass in Table 5 3 2 is constant for scan rates ranging from 1 to 200 mVs⁻¹, decreasing only slightly at a scan rate of 500 mVs⁻¹ For polymer films exhibiting viscoeleastic behaviour, the evaluation of normalised mass is expected to be greater at faster scan rates, with viscoelastic dampening of frequency measurements more severe on longer time scales The observation that $M_{eq}(ETE)$ is quantitatively similar at scan rates of 1 to 200 mVs⁻¹ suggests that the frequency shifts associated with complete polymer oxidation in Chapter 4 are not subject to a significant viscoelastic contribution and accurately represent the mass changes associated with the attainment of global equilibrium

At the fastest scan rate of 500 mVs⁻¹, the slight decrease in normalised mass indicates that it is only under these dynamic conditions that the thermodynamic solvent requirement for solvent transfer cannot occur However, in the concentration range 0 1 M to 0 6 M, the M_{eq}(ETE) value at 500 mVs⁻¹ is 420 ± 18 gmol⁻¹ This represents the concomitant transfer of *ca* 14 solvent molecules per redox site conversion, while in HClO₄ electrolyte, the value of $M_{eq}(ETE)$ at 200 mVs⁻¹ typically represents the transfer of only 1 solvent molecule, rising to a maximum value of 2 3 in 0 03M HClO₄ This clearly illustrates the anion dependency of polymer structure and the subsequent differences in the facility for the movement of solvent This will be illustrated more clearly in Section 5 3 3

For the data presented in Table 5 3 2, at electrolyte concentrations greater than 0 6 M pTSA, mass loss processes appear to be in operation. However, as discussed in Chapter 4, this mass loss is not considered to be real and no change in mass transfer mechanisms actually exist. It is thought that for all $[Os(bipy)_2(PVP)_{10}Cl]^+$ films, irrespective of thickness, a concentration of pTSA is ultimately reached where the coupled viscous load of polymer film and viscous electrolyte results in unpredictable crystal oscillations which cannot be reliably related to mass changes. Obviously, this will occur in more concentrated pTSA electrolytes for thinner films. This is confirmed for a film of lower surface coverage (1 1 x 10-8 molcm-2), where the <u>apparent</u> mass loss processes only become evident at concentrations greater than 1 0 M pTSA. These data will be presented later in Tables 5 3 4 and Table 5 3 5

The EQCM data presented thus far have demonstrated the effect of electrolyte type and concentration on the mechanisms and nature of mass transfer in pTSA and HClO₄ A more detailed evaluation of the effect of mass transfer on charge transport rates under potential sweep and potential step conditions is now undertaken

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5.3.3. Cyclic voltammetry - Mass transfer and D_{ct}(CV).

5331, HClO₄ electrolyte

The change in the apparent diffusion coefficient, $D_{ct}(CV)$, with changing HClO₄ concentration is summarised in Table 5 3 1 $D_{ct}^{1/2}C(CV)$ was calculated from the slope of the Randles-Sevcik plot for scan rates 100 to 500 mVs⁻¹, as described in Section 1 2 1 $D_{c1}(CV)$ was estimated using a concentration of redox sites of 0 7 M. This concentration was determined from the dry density of the polymer, measured by flotation in non-swelling solvents [1-3]. The error in $D_{c1}(CV)$ is $\pm 2\%$ on a given film and $\pm 10\%$ between films. With the exception of 1 0 M HClO₄, the values for $D_{ct}(CV)$ are in agreement to within $\pm 20\%$ with previously reported values [1]. The effect of changing perchlorate concentration on $D_{c1}(CV)$ is illustrated in Fig 5 3 7, with log electrolyte concentration used for presentation purposes.

In Chapter 3 it was found that, as the electrolyte concentration is increased, the polymer phase mass increases due to protonation of the polymer backbone and the insertion of perchlorate counter-ion Despite this, impedance measurements indicated that no significant polymer morphology changes occur Consequently, no change in redox site concentration is expected and the trends evident in $D_{ct}(CV)$ in Fig 5 3 7 are considered to be real

The decrease in $D_{ct}(CV)$ over the concentration range 0 03 M to 1 0 M HClO₄ has been observed previously for $[Os(bipy)_2(PVP)_{10}Cl]+[1,2]$ From the characteristics of the current response for potential sweep and potential step techniques, as well as the effect of redox site loading on D_{ct} [2,3], it has been demonstrated that the decrease in $D_{ct}(CV)$ cannot be attributed to a migrational enhancement of the current at lower concentrations (see Section 1 2 1 and Section 2 3 6) The reduced $D_{ct}(CV)$ in 0 01 M and 0 001 M HClO₄ support this view

Fig 5 3 7 The effect of HClO₄ electrolyte concentration on $D_{ct}(CV)$



The temperature-dependence of $D_{ct}(CV)$ within $[Os(bipy)_2(PVP)_{10}Cl]$ + has been used to aid the diagnosis of the rate determining step in the charge transport process [1-3] The large activation energies and positive entropy in the concentration range 0 01 M to 2 0 M HClO₄ are indicative of segmental polymer chain motion limiting charge percolation rates. The decrease in $D_{cl}(CV)$ has therefore been thought to represent the increased crosslinking and dehydration of the polymer matrix by the increasing concentration of perchlorate [1]. In Chapter 3 it was shown that the polymer phase perchlorate content does not change in this concentration range. Similarly, the activity of solvent will not be significantly different in 0 03 and 1 0 M electrolyte [11] and the levels of polymer solvation are expected to remain constant. An alternative explanation for the decrease in $D_{ct}(CV)$ is therefore required

Fig 5 3 8 illustrates the cyclic voltammogram, the mass-potential and the chargepotential plots obtained at 200 mVs⁻¹ for a polymer of coulometric surface coverage 2 x 10^{-8} molcm⁻² in 0 01 M HClO₄ Fig 5 3 9 shows the corresponding plots for the same film when transferred and equilibrated in 0 03 M HClO₄, while Fig 5 3 10 illustrates the behaviour in 1 0 M electrolyte The data in 0 1 M HClO₄ has been shown previously in Fig 5 3 3 and Fig 5 3 4

Fig 5 3 8 illustrates that in 0 01 M HClO₄ mass and charge transfer are very much impeded, particularly mass. It is only after 7 cycles that a "steady-state" mass response is attained. In contrast, in 0 03 M HClO₄ (Fig 5 3 9) both mass and charge transfer is relatively more facile, with the steady-state accomplished after the first scan. The behaviour in 0 1 M electrolyte (Fig 5 3 3) is similar. However, in 1 0 M HClO₄ there appears to be a return to impeded mass transport (Fig 5 3 10).

The data are more clearly represented by the corresponding Φ_{ClO4} - and mass-charge plots These are illustrated in Fig 5 3 11 (a) to Fig 5 3 11 (c) for 0 01 M, 0 03 M and 1 0 M HClO4, respectively In 0 01 M electrolyte, during the forward anodic scan no transfer

Fig 5 3 8 (1) Cyclic voltammogram, (11) mass-potential and (111) charge potential plots at a scan rate of 200 mVs⁻¹ in 0 01 M HClO₄ The polymer surface coverage is 2 x 10⁻⁸ molcm⁻²



Fig 5 3 9 (1) Cyclic voltammogram, (11) mass-potential and (111) charge potential plots at a scan rate of 200 mVs⁻¹ in 0 03 M HClO₄

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Fig 5.3 10 (1) Cyclic voltammogram, (11) mass-potential and (111) charge potential plots at a scan rate of 200 mVs⁻¹ in 1 0 M HClO₄



Fig 5 3 11 Φ_{ClO4} - and mass-charge plot for data presented in Fig 5 3 8 to 5 3 10 (a) 0 01 M, (b) 0 03 M and (c) 1 0 M HClO₄



of solvent occurs, with Φ_{ClO4} - remaining near-zero throughout. It is only on cessation of the passage of anodic charge that solvent ingress is observed. Similarly, in 1.0 M HClO4 (Fig 5.3.11 c) there appears to be retarded solvent transfer, with Φ_{ClO4} - only becoming positive after *ca* 60 µC (i e. 25% of the total redox conversion). In contrast, in 0.1 M and 0.03 M HClO4, (Fig 5.3.4 and 5.3.11 b, respectively), Φ_{ClO4} - becomes positive almost immediately with the passage of anodic charge, indicating that interfacial solvent transfer occurs throughout the redox conversion

While the origins of this change in the facility for solvent transfer remain unclear, it is considered that they must also be responsible for the decrease in $D_{ct}(CV)$ with increasing HClO₄ concentration in the range 0.03 M to 1.0 M

At concentrations greater than 1 0 M HClO₄, $D_{ct}(CV)$ increases sharply (Fig 5 3 7) The current response for the polymer films under semi-infinite diffusion conditions exhibits a migrational enhancement of the anodic branch. The measurement of charge transport diffusion coefficients from Randles-Sevcik plots is therefore inappropriate While the contribution from migration to the current decay of electroactive films following a potential step has been addressed [21-23], little has been proposed for the current response for cyclic voltammetry. No attempt to extract charge transport diffusion rates at these concentrations was therefore attempted

Migration is normally found to become more significant at low supporting electrolyte concentrations [24] That it is encountered at high concentrations of perchlorate is thought to reflect the increased crosslinking and compaction of the layer due to the presence of free electrolyte. It is proposed that charge transfer becomes so impeded that a potential gradient is established across the film, changing the nature of counter-ion motion from a predominantly diffusional one to one with migrational character

5332 pTSA electrolyte

The effect of pTSA electrolyte concentration on $D_{ct}(CV)$ is shown in Table 5.3.2 For concentrations greater than 0.1 M pTSA, $D_{ct}(CV)$ has a value of $13 \pm 1 \ge 10^{-11} \text{ cm}^2\text{s}^{-1}$ At concentrations less than 0.1 M pTSA, $D_{ct}(CV)$ decreases to $5 \pm 1 \ge 10^{-11} \text{ cm}^2\text{s}^{-1}$ This reduction in the apparent charge transport diffusion coefficient may reflect the excessive swelling of the layer in low pTSA concentrations and the subsequent reduction in redox site concentration

For concentrations greater than 0 6 M pTSA, $D_{ct}(CV)$ is independent of both film thickness and whether a mass "loss" or gain is observed to accompany polymer oxidation This supports the contention that the mass loss indicated from frequency measurements is an artefact of the excessive viscous load of thicker films at high pTSA electrolyte concentrations

The invariance of $D_{ct}(CV)$ to pTSA concentrations greater than 0.1 M is not in agreement with previously reported data, where a monotonic increase with concentration was found [1] However, at all electrolyte concentrations, $D_{ct}(CV)$ in pTSA is greater than that observed in HClO₄ by a factor of *ca* 5 Because the more solvated polymer layer in pTSA is expected to result in a lower redox site concentration, this increase in $D_{ct}(CV)$ represents the lower limit for the enhanced charge transport rates in pTSA

Despite the considerable variation in the levels and mechanisms for solvent transfer within $[Os(bipy)_2(PVP)_{10}Cl]^+$ when exposed to pTSA, it is clear that the movement of solvent is more facile than in perchlorate electrolyte. The inter-relationship between polymer structure, solvent transfer and the rate of charge transport is graphically illustrated in Fig 5 3 12. In part (a) of this figure a typical voltammetric response in pTSA and HClO₄ electrolyte at 50 mVs⁻¹ is shown. The concentrations are 0.2 M pTSA and 0.1 M HClO₄ and the polymer surface coverage is 2 x 10⁻⁸ molcm⁻². In Fig 5 3 12 (b) Fig 5 3 12 (a) Cyclic voltammogram obtained for an [Os(bipy)₂(PVP)₁₀Cl]+ film of surface coverage 2 0 x 10-8 molcm-2 in 0 2 M pTSA and 0 1 M HClO₄ Scan rate is 50 mVs-1

(b) The corresponding $\dot{\Phi}_j$ vs potential plots, representing the concomitant solvent flux



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the corresponding $\dot{\Phi}_{j}$ plots are presented As it has been demonstrated the counter-anion j is responsible for the maintenance of electroneutrality, $\dot{\Phi}_{j}$ represents the flux of solvent occuring during redox switching

In perchlorate electrolyte charge transport kinetics are clearly slower than those in pTSA The cyclic voltamogram has broader, more ill-defined waves, with reduced peak current and wider peak-to-peak separation [25] This more impeded charge transport in perchlorate media, is mirrored in the minimal levels of solvent flux accompanying redox-switching The electrolyte-dependence of polymer morphology and the subsequent facility for solvent transfer, discussed in previous chapters, is therefore seen to determine the relative charge transport rates This inter-relationship between solvent movement and charge transport has also been demonstrated for this polymer by Oyama *et al* [10]

5.3.4. Potential Step - Mass transfer and D_{ct}(PS).

As discussed in Chapter 2, a common observation for $[Os(bipy)_2(PVP)_nCl]^+$ and related polymers is the dependence of D_{ct} on the experimental time scale $D_{ct}(CV)$ is frequently 2 orders of magnitude less than the value of $D_{ct}(PS)$ evaluated within 20 ms of pulse application. In this study, the resolution of data points was only 5 ms, thus precluding an accurate assessment of interfacial mass transfer on the sub-20 ms time scale. The EQCM study was limited to 100 ms, a time scale over which chronocoulometry was found to yield a value for D_{ct} similar to that obtained using cyclic voltammetry. Normally for $[Os(bipy)_2(PVP)_{10}Cl]^+$ in HClO4 $D_{ct}(PS)$ is greater than $D_{ct}(CV)$ by a factor of over 100, while in pTSA the difference is a factor of *ca*. 10 [1] However, despite the inability to reproduce previously reported $D_{ct}(PS)$ values for $[Os(bipy)_2(PVP)_{10}Cl]^+$, a number of observations regarding mass transfer in response to a potential step can be made

5341 HClO4 electrolyte

The normalised mass for both oxidation and reduction of $[Os(bipy)_2(PVP)_{10}Cl]^+$ on the 100 ms and 10 s time scales following pulse application is summarised for a range of HClO4 electrolyte concentrations in Table 5 3 3 The data were collected for two different polymer films and have an error of $\pm 20\%$ Repeat determinations on a given film have an error of $\pm 2\%$ For HClO4, the features of mass transfer accompanying polymer oxidation are similar (but opposite) to those for polymer reduction The mass transfer accompanying oxidation is therefore only considered in the following discussion

Over the 100 ms time scale the normalised mass in the concentration range 0 03 M to 1 0 M HClO₄ is approximately that of the ClO₄- anion Over 10 s, $M_{eq}(OX)$ increases to a value approaching that of $M_{eq}(ETE)$ quoted in Table 5 3 1 for the 200 mVs⁻¹ scan rate

HClO4 Conc (Molar)	M _{eq} (OXIDATION) (a)		M _{eq} (REDUCTION) (b)	
	100 ms	10 s	100 ms	10 s
0 001	- 25	27	13	- 20
0 01	0	78	66	- 90
0 03	76	162	- 124	- 166
0 10	76	123	- 65	- 120
0 30	117	123	- 110	- 118
0 70	102	119	- 112	- 114
1 00	112	114	- 111	- 120
2 00	162	142	- 138	- 161
3 00	597	425	- 651	- 529
4 00 (c)	- 1940	- 892	1361	1358

Table 5 3 3Normalised mass for the Osit/III couple on application of a
potential step in HClO4 electrolyte

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- a) Potential pulse from -0 25 to 0 8 V vs SCE
- b) Potential pulse from 0 8 to -0 25 V vs SCE
- c) Mass influx for first 20 ms ca 350 gmol-1

The exception, as before, is in 0 03 M HClO₄, where, even on the 10 s time scale, global equilibrium appears to be established and the "thermodynamic" mass change occurs This is in agreement with the relatively more facile solvent transfer in $[Os(bipy)_2(PVP)_{10}Cl]$ + films in 0 03 M HClO₄ observed using cyclic voltammetry in Section 5 3 3 1

The features of solvent and $(H_3O)+(ClO_4-)$ transfer in $[Os(bipy)_2(PVP)_{10}Cl]+$ films discussed in previous sections, also pertain to mass transfer on the potential step time scales considered here However, a number of important features exist at low HClO₄ electrolyte concentrations

Fig 5 3 13 illustrates a typical mass and charge response (vs time) for a 10 s oxidation pulse from -0 25 V to 0 8 V in 0 1 M HClO4 The Φ_{ClO4} - and mass-charge plots are depicted in Fig 5 3 14, where the value of Φ_{ClO4} - is negative for the first 30% of polymer oxidation This indicates that during the initial stages of polymer oxidation insufficient interfacial mass transfer occurs to account for the transfer of one perchlorate anion per Os^{II/III} conversion The corresponding $\dot{\Phi}_{ClO4}$ - and $\dot{\Phi}_{H^+}$ vs time plots are shown in Fig 5 3 15 (a) and 5 3 15 (b), respectively As outlined previously, $\dot{\Phi}_{ClO4}$ - represents the flux of all mobile species except that of ClO4⁻, assuming that ClO4⁻ is responsible for the maintenance of electroneutrality within the layer $\dot{\Phi}_{H^+}$ is the corresponding plot assuming proton movement is the charge compensating ion In Fig 5 3 15 (a), the initial mass flux for the $\dot{\Phi}_{ClO4}$ - plot is negative, while for the $\dot{\Phi}_{H^+}$ plot in Fig 5 3 15 (b), a net mass influx is seen. It is through the minimisation of Φ that the identification of the main charge carrier during redox switching of electroactive films may be established [12-14] However, as can be seen in Fig 5 3 15, both $\dot{\Phi}_{ClO4}$ - and $\dot{\Phi}_{H^+}$ are of similar magnitude (although opposite in sign)

While the contribution from double layer charging prevents accurate quantitation [14], it appears that in HClO₄ electrolyte partial co-ion expulsion must exist as a mechanism for the maintenance of electroneutrality within $[Os(bipy)_2(PVP)_{10}Cl]$ + on short time scales



Fig 5 3 13 (a) Mass and (b) charge transients for [Os(bipy)₂(PVP)₁₀Cl]+ in 0 1M HClO₄, following a 10 s oxidising pulse



Fig 5 3 15 (a) $\dot{\Phi}_{ClO4}$ - vs time plot for data presented in Fig 5 3 13 (b) $\dot{\Phi}_{H}$ + vs time plot for data presented in Fig 5 3 13



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In more dilute electrolytes, the reduced availability of counter-anion results in the coion expulsion mechanism taking temporal precedence. This is illustrated in Fig 5.3.16 which shows a typical mass-time transient obtained in 0.01 M HClO4 on the 100 ms time scale. While no <u>net</u> mass change is observed overall (see Table 5.3.3) this figure shows that there is a mass <u>loss</u> during the first 50 ms of oxidation, presumably due to the domination of H+ expulsion, with mass ingress due to anion insertion only occuring in the latter stages of the pulse

For $[Os(bipy)_2(PVP)_{10}Cl]$ + in 0 1 M to 1 0M HClO₄ electrolyte, the activation parameters for charge transport on the time scale of potential step techniques have been proposed to represent the localised movement of counter-ion which is available within the layer [1-3] The fact that interfacial mass transfer is observed on all time scales studied and that the polymer layers are permselective, makes this interpretation unlikely

At all HClO₄ electrolyte concentrations below 1 0 M, the interfacial mass transfer in the 20 ms following pulse application is insufficient to account for counter-ion motion. While quantitative arguements cannot be made due to the difficulty in extracting the contribution from double layer charging and the limited resolution for data capture, *it is* considered that co-ion expulsion mechanisms are utilised. Where counter-anion supply from the bulk electrolyte is slower (see Section 3 4 4 2b) co-ion expulsion occurs to a greater extent. Thus, it is probable that different equilibria processes do exist for $[Os(bipy)_2(PVP)_{10}Cl]$ + in HClO₄ on different experimental time scales, and the enhanced $D_{cl}(PS)$ values that have been reported may reflect the unique nature of proton exchange mechanisms

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Fig 5 3 16 Mass transient in response to a 100 ms oxidising potential step for a [Os(bipy)₂(PVP)₁₀Cl]+ film of surface coverage 2 x 10⁻⁸ molcm⁻² The electrolyte is 0 01 M HClO₄



<u>5342</u> p<u>TSA electrolyte</u>

Fig 5 3 17 illustrates the mass and charge (vs time) response in 0 2 M pTSA for a 10 s oxidation pulse from -0 25 V to 0 8 V The coulometric polymer surface coverage is 2 x 10^{-8} molcm⁻² The corresponding Φ_{pTS} - and mass-charge plots are shown in Fig 5 3 18 Both the mass and Φ_{pTS} - remain positive throughout redox conversion, indicating that in pTSA electrolyte co-ion expulsion mechanisms are not utilised, even on potential step time scales

The $\dot{\Phi}_{pTS}$ - and $\dot{\Phi}_{H}$ + vs time plots for these data are illustrated in Fig 5 3 19 Both $\dot{\Phi}_{j}$ plots demonstrate an immediate influx of material during polymer oxidation following application of the potential pulse However, the value of $\dot{\Phi}_{j}$ is significantly reduced for j = pTS-, confirming that in pTSA electrolyte the counter-anion is the major charge compensating ion

The data presented in Fig 5 3 17 to 5 3 19 show that there is immediate interfacial mass transfer following pulse application. This indicates that an anion source does not exist within the polymer layer and provides evidence that the enhanced values of D_{ct} , which have been observed previously fo $[Os(bipy)_2(PVP)_{10}Cl]$ + in pTSA on potential step time scales [1], is unlikely to be due to localised counter-anion motion resident within the polymer layer

The Φ_{pTS} - and mass-charge plots in Fig 5 3 18 exhibit no hysteresis This demonstrates clearly the concomitant influx of solvent and anion on all time scales in pTSA and is in sharp contrast to the behaviour of this polymer in HClO4 electrolyte (see Fig 5 3 13 and 5 3 14) For the potential step time scales considered here, the charge transport process through [Os(bipy)₂(PVP)₁₀Cl]+ in pTSA is under electroneutrality control and, as discussed for the cyclic voltammetric data in Section 5 3 2 2, it is considered that the rate limiting process remains counter-anion motion



Fig 5 3 17 (a) Mass and (b) charge transients for [Os(bipy)₂(PVP)₁₀Cl]+ in 0 2 M pTSA following a 10 s oxidising pulse



Fig 5 3 19 (a) $\dot{\Phi}_{pTS}$ - vs time plot for data presented in Fig 5 3 17 (b) $\dot{\Phi}_{H}$ + vs time plot for data presented in Fig 5 3 17



Table 5 3 4 summarises the frequency shift, charge and normalised mass for polymer oxidation on the 100 ms, 1 s and 10 s time scale in a series of pTSA electrolytes for a $[Os(bipy)_2(PVP)_{10}Cl]$ + film of coulometric surface coverage 1 1 x 10-8 molcm-2 The data are averaged for 3 repeat determinations at each time scale, with an error in the normalised mass of ± 5% The corresponding data for reduction of the polymer layer are given in Table 5 3 5, and have similar error The thermodynamic mass change accompanying polymer oxidation for this film, obtained using cyclic voltammetry at 2 mVs-1, is also included in Table 5 3 4 in order to aid comparison with the transient mass data These thermodynamic data are in excellent agreement with those presented for a thicker film in Chapter 4, Table 4 3 2

The data for polymer oxidation and reduction in pTSA are qualitatively similar However, in the concentration range 0 1 to 1 0M pTSA, on the 100 ms time scale the normalised mass for polymer oxidation is greater than that for reduction by *ca* 25%, on the 1 s time scale this difference is narrowed to only *ca* 10%, while on the 10 s time scale the normalised mass changes are identical, within experimental error As discussed in Chapter 4, for all $[Os(bipy)_2(PVP)_{10}Cl]^+$ polymer films in pTSA, the layer is more swollen in the fully oxidised state. The increase in polymer viscoelasticity will therefore result in a greater under-evaluation of mass from frequency measurements during reduction of the Os¹¹¹ centres, particularly on shorter time scales. On more exhaustive redox switching of the polymer the viscoelastic contribution to mass measurement is expected to become similar for both oxidation and reduction of the layer, as observed for a 10 s potential step

In the following discussion reference to polymer oxidation is only made However, the general features for mass and charge transfer outlined are equally applicable to polymer reduction

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pTSA Conc (Molar)	Time Scale	Δf	ΔQox	Mea(OX)
		(Hz)	(µC)	(gmol-1)
0 05	a) 100 ms	+1060	84	-1204
	b) 1 s	+1228	148	- 792
	c) 10 s	+1214	225	- 514
	d) 2 mVs-1	+1103	170	- 620
0 10	a) 100 ms	- 551	108	+ 489
	b) 1 s	- 1133	189	+ 574
	c) 10 s	- 1169	230	+ 486
	d) 2 mVs-1	- 1157	235	+ 471
0 20	a) 100 ms	- 401	98	+ 393
	b) 1 s	- 854	178	+ 459
	c) 10 s	- 951	208	+ 437
	d) 2 mVs-1	- 953	200	+ 456
0 40	a) 100 ms	- 357	96	+ 357
	b) 1 s	- 782	175	+ 428
	c) 10 s	- 891	210	+ 406
	d) 2 mVs-1	- 891	189	+ 452
0 80	a) 100 ms	- 399	100	+ 382
	b) 1 s	- 858	183	+ 433
	c) 10 s	- 948	225	+ 403
	d) 2 mVs-1	- 905	184	+ 471
1 00	a) 100 ms	- 345	96	+ 343
	b) 1 s	- 696	1 77 '	+ 375
	c) 10 s	- 716	215	+ 319
	d) 2 mVs ⁻¹	- 694	180	+ 369
1 50	a) 100 ms	- 108	97	+ 108
	b) 1 s	+ 359	176	- 194
	c) 10 s	+ 632	206	- 293
	d) 2 mVs-1	+2045	180	- 328

Table 5 3 4Frequency, anodic charge and normalised mass for potential step from-0 25 to 0 8 V vs SCE in pTSASurface coverage 1 1 x 10-8 molcm-2

pTSA Conc (Molar)	Time Scale	Δf (Hz)	ΔQ _{RED} (μC)	M _{eq} (RED) (gmol ⁻¹)
0 05	a) 100 ms	- 671	- 98	+ 544
	b) 1 s	- 1290	- 141	+ 877
	c) 10 s	- 1232	- 213	+ 533
0 10	a) 100 ms	+ 451	- 124	- 349
	b) 1 s	+1067	- 197	- 522
	c) 10 s	+1165	- 235	- 475
0 20	a) 100 ms	+ 380	- 119	- 305
	b) 1 s	+ 849	- 193	- 423
	c) 10 s	+ 951	- 218	- 418
0 40	a) 100 ms	+ 342	- 119	- 275
	b) 1 s	+ 784	- 194	- 388
	c) 10 s	+ 893	- 220	- 388
0 80	a) 100 ms	+ 341	- 126	- 260
	b) 1 s	+ 835	- 209	- 384
	c) 10 s	+ 945	- 225	- 401
1 00	a) 100 ms	+ 268	- 121	- 212
	b) 1 s	+ 644	- 213	- 290
	c) 10 s	+ 674	- 220	- 293
1 50	a) 100 ms	+ 15	- 121	- 13
	b) 1 s	- 435	- 202	+ 206
	c) 10 s	- 683	- 210	+ 311

Table 5 3 5Frequency, cathodic charge and normalised mass for potential stepfrom 0 8 to -0 25 V vs SCE in pTSA for the film shown in Table 5 3 4

5342a pTSA concentrations less than 01 M

As discussed previously, at low pTSA concentrations, [Os(bipy)₂(PVP)₁₀Cl]+ polymer films are extensively swollen and mass transfer during polymer oxidation represents the electro-osmotic flux of solvent from the layer. This is anticipated to be greatest for high current densities [20] and, consequently, the largest mass losses are observed on the shortest experimental time scales following potential step application However, due to the swollen nature of the films at pTSA concentrations below 0.1 M, the viscoelastic contribution to frequency measurements will be significant, and quantitative judgements regarding mass changes cannot be accurately made

The effect of layer thickness on polymer swelling at these low concentrations is also illustrated by the data in Table 5 3 4 For this thinner film of surface coverage 1 1 x 10⁻⁸ molcm⁻², the swelling of the layer occurs at 0 05 M pTSA For thicker $[Os(bipy)_2(PVP)_{10}Cl]$ + polymer films discussed previously (Table 5 3 2 and Table 4 3 2) mass loss occurs only at 0 01 M pTSA. This confirms the surface coverage effects discussed in Section 4 3 2 3, where it was considered that swelling of the layer occurs more readily in thinner films

53.42b pTSA concentration range 01 M to 10 M

As discussed in Chapter 4, for pTSA concentrations at and above *ca* 0 1 M, mass transfer reflects counter-anion motion and the concomitant movement of large quantities of solvent Because of the rapid interfacial mass transfer in pTSA, it has been shown how, on cyclic voltammetric time scales, global equilibrium can be established quickly

In the concentration range 0 1 M to 1 0 M pTSA, in Table 5 3 4 the normalised mass on the 100 ms time scale is 388 ± 50 gmol⁻¹ This indicates that even on this time scale, the interfacial transfer of up to 12 moles of solvent per redox site conversion can take place On the 1 s time scale, the normalised mass increases to a value which is identical, within experimental error, to the thermodynamic data obtained at a cyclic voltammetric scan rate of 2 mVs⁻¹ That global equilibrium can be established on an experimental time scale of 1 s for $[Os(bipy)_2(PVP)_{10}Cl]$ + in pTSA electrolyte demonstrates the polymer morphology that exists in this electrolyte and the enhanced facility for mass transfer More importantly, however, the same evaluation of normalised mass on the 1 s time scale and that corresponding to 1 to 5 mVs⁻¹ scan rates, confirms the thermodynamic data presented in Chapter 4 and demonstrates that the viscoelastic contribution to frequency measurements does not prevent an accurate evaluation of redox-induced interfacial mass changes

In Table 5 3 4, there is a reduction in the normalised mass evaluated for the 10 s pulse For an $[Os(bipy)_2(PVP)_{10}Cl]$ + film of surface coverage 1 1 x 10⁻⁸ molcm⁻², with a redox site concentration of 0 7 M, the layer thickness is *ca* 1 6 x 10⁻⁵ cm With a diffusion coefficient for charge transport of *ca* 2 x 10⁻¹⁰ cm²s⁻¹, the time required for the depletion layer to extend to the electrolyte / film interface is *ca* 0 4 s (Eqn 3 4 9) [24]

The Φ_{pTS} - and mass-charge plots for a 1 s and 10 s pulse in 0 2 M pTSA are shown in Fig 5 3 20 On the 1 s time scale (Plot A), the data is as described for the thicker film depicted in Fig 5 3 18 However, for a 10 s pulse (Plot B), mass transfer is complete with the passage of *ca* 170 µC and remains constant thereafter. The Φ_{pTS} - plot decreases after 170 µC, representing the lower mass change per redox site conversion. While a viscoelastic contribution to mass measurement from the increased polymer swelling in the Os^{III} may be responsible for this, it is noted that the coulometric surface coverage (from slow scan cyclic voltammetry) is only approximately 180 µC. The reduced M_{eq} for the 10 s pulse, therefore, is thought to reflect a drift in charge after complete polymer

Fig 5 3 20 Φ_{pTS} - and mass-charge plots obtained for a layer of surface coverage 1 1 x 10-8 molcm-2 in 0 2 M pTSA for a 1 s oxidation pulse (Plot A) and a 10 s oxidation pulse (Plot B)



oxidation This is considered likely for a gold electrode potentiostatted at 0 8 V in high concentration acid electrolyte [26] It is of note that this drift in charge introduces significant hysteresis into Fig 5 3 20 Plot B, and thus results in a mis-interpretation of mass transfer data This illustrates how it is the measurement of charge, not mass, which limits the accuracy of the quantitative analysis of EQCM data

A number of important differences exist in the data presented in Table 5 3 4, compared with data presented in pTSA in Table 5 3 2 and Table 4 3 2 A mass gain accompanying polymer oxidation is in evidence up to pTSA concentrations of 1 0 M. In addition, in 1 5 M pTSA, although the thermodynamic mass change at 2 mVs⁻¹ is a mass loss for polymer oxidation, on the 100 ms time scale a mass ingress is observed. These features of mass transfer for the thinner polymer coating confirm that no change in mass transfer processes occur at higher pTSA electrolyte concentrations and, as discussed previously, the lower viscous load of the thinner film merely allows for the crystal oscillation to be related to mass in more viscous electrolytes.

5.4. CONCLUSIONS.

The differences in the extent and facility of solvent transfer in different electrolytes is directly related to charge transport rates. This is determined by the nature of the electrolyte / polymer interaction, which, in turn, determines the nature of the rate determining step in the charge transport process.

In HClO₄ the difficulty in solvent transfer results in the slow attainment of a steadystate mass and charge response during repeat scanning. There is evidence for 0.01 M and 1.0 M HClO₄ that this impeded solvent transfer reduces $D_{ct}(CV)$. In the intervening electrolyte concentrations solvent transfer is marginally easier, resulting in an increase in the charge transport diffusion coefficient. This contrasts with the transfer of solvent in pTSA, where concomitant movement with the counter-anion occurs on all time scales and at all concentrations

The difference in $D_{ct}(CV)$ and $D_{ct}(PS)$ cannot be attributed to a difference in the sources / sinks of charge compensating counter-anion, as no free electrolyte exists within the polymer layer at concentrations less than 1 0 M However, in HClO₄, co-ion expulsion is utilised as a mechanism for the maintenance of electroneutrality on short time scales In pTSA the same equilibria appear to be established on all time scales

The EQCM has been demonstrated to provide a useful insight into the origins of electrolyte-dependent differences in electrochemical behaviour. The results presented here have shown how the evaluation of charge transport and mass transfer processes can only be understood by a systematic investigation of the effects of electrolyte type, concentration and experimental time scale

5.4. REFERENCES.

- 1 R J Forster, A J Kelly, J G Vos and M E G Lyons, J Electroanal Chem., (1989), 270, 365
- 2 R J Forster, J G Vos and M E G Lyons, *J Chem. Soc Faraday Trans*, (1991), 87, 3761
- 3 R J Forster and J G Vos, J Electroanal Chem, (1991), 314, 135
- 4 A J Kelly, T Ohsaka, N Oyama, R J Forster and J G Vos, J Electroanal Chem., (1990), 287, 185
- 5 A R Hillman, D C Loveday, S Bruckenstein and C P Wilde, J Chem Soc Faraday Trans, (1990), 86, 437
- 6 S Bruckenstein, C P Wilde, M Shay, A R Hillman and D C Loveday, J Electroanal Chem., (1989), 258, 457
- A R Hillman, D C Loveday, M J Swann, R M Eales, A Hamnett, S J Higgins,
 S Bruckenstein and C P Wilde, *Faraday Discuss*, Chem Soc, (1989), 88, 151
- 8 G Inzelt and L Szabo, Electrochim Acta, (1986), 31, 1381
- 9 G Inzelt and J Bacskai, Electrochim Acta, (1992), 37, 647
- 10 A J Kelly and N Oyama, J Phys Chem, (1991), 95, 9579
- S Bruckenstein, C P Wilde, M Shay and A R Hillman, J Phys Chem, (1990), 94,
 787
- 12 A R Hillman, M J Swann and S Bruckenstein, J Phys Chem, (1991), 95, 3271
- 13 A R Hillman, D C Loveday, M J Swann, S Bruckenstein and C P Wilde, J Chem Soc Faraday Trans, (1991), 87, 2047
- 14 A R Hillman, D C Loveday and S Bruckenstein, J Electroanal Chem, (1991), 300, 67
- 15 R Borjas and D A Buttry, J Electroanal Chem, (1990), 280, 73
- 16 S Bruckenstein and A R Hillman, J Phys Chem, (1988), 92, 4837

- 17 A R Hillman, D C Loveday and S Bruckenstein, J Electroanal Chem., (1989), 274, 157
- 18 S Bruckenstein and A R Hillman, Faraday Trans, submitted
- 19 H P Gregor, J Am. Chem. Soc , (1951), 73, 642
- 20 M W Verbrugge and R F Hill, J Electrochem Soc , (1990) , 137, 1131
- 21 J M Saveant, J Electroanal Chem, (1988), 238, 1
- 22 C P Andrieux and J M Saveant, J Phys Chem, (1988), 92, 6761
- 23 R P Buck, J Electroanal Chem., (1988), 258, 1
- 24 A J Bard and L R Faulkner, Electrochemical Methods, Fundamentals and Applications, Wiley, New York, (1980), Ch 4, p 128
- A R Hillman, Electrochemical Science and Technology of Polymers,
 R G Linford (Ed), Elsevier, Amsterdam (1987), Chs 5 & 6
- 26 D T Sawyer and J L Roberts in Experimental Electrochemistry for Chemists, Wiley, New York, (1974)

CHAPTER 6

Redox and Mass Transfer Processes

through Thin Films of

 $[Ru(b_1py)_2(PVP)_{10}(H_2O)]^{2+}$

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6.1. INTRODUCTION.

As outlined in Chapter 1, the photophysical processes in poly(pyridyl) ruthenium¹¹ complexes may lead to the photo-decomposition of the complex by a ligand substitution process. The extension of such photo-induced ligand-exchange reactions to ruthenium-based metallopolymers has long been recognised [1-5] and has been found to provide a useful route to ruthenium polymers which may be otherwise difficult to synthesise [2,3,5]. As discussed in Chapter 2, this photo-sensitivity has important consequences for the accurate evaluation of charge transport mechanisms within ruthenium polymer-modified electrodes [6].

For polymers based on bis(bipyridyl) ruthenium complexes, in aqueous acid electrolyte the main photo-substitution product is the aquo complex [1-5], $[Ru(bipy)_2(Pol)_n(H_2O)]^{2+}$, where Pol is the polymer backbone and n is the redox site loading (see Section 2 3 2) Both the polymeric and monomeric [7-10] aquo complex have received considerable attention. This derives from the reversible, net two electron oxidation to form a ruthenium-oxo complex at easily accessible potentials. The stabilisation of the 4+ ruthenium centre is attributed to the proton loss from the aquo ligand to form the ruthenyl complex [7,8], which for the polymer-bound species, has the formula, $[Ru^{IV}=O(bipy)_2(Pol)_n]^{2+}$

The importance of transition metal oxo complexes is seen in their use as strong oxidising agents Ruthenium-oxo complexes have been shown to be active catalysts for the oxidation of organic [11-14] and inorganic [14-19] substrates, as well as for H₂O splitting [20-22] As discussed in Chapter 1, the immobilisation of such catalytic sites within a polymeric matrix may provide many advantages [12]

It is the purpose of this chapter to investigate the mechanism for redox processes within polymer films of $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ coated on electrode surfaces The coupled proton and electron transfer of the $Ru^{11/111}$ and $Ru^{111/11}$ couples is investigated in

acid electrolytes over the pH range 0 0 to 2 0 An EQCM study of the redox behaviour of $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ is first presented The kinetic aspects of polymer oxidation will then be addressed Through the combination of EQCM data and charge transport and activation parameters, the rate determining step for charge transport through $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ under semi-infinite diffusion conditions is discussed

6.2. EXPERIMENTAL.

1

 $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ was prepared *in situ* by the photolysis of electrodes modified with either $[Ru(bipy)_2(PVP)_{10}]^{2+}$ or $[Ru(bipy)_2(PVP)_{10}Cl]^{+}$ The Ru-aquo polymer was also synthesised from the diaquo monomer, $[Ru(bipy)_2(H_2O)_2]^{2+}$, as described in the literature [12] In all cases, the electrochemical behaviour of the resulting $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ metallopolymer was identical

For the evaluation of mass transfer accompanying redox switching, the electrode preparation, mass measurement and data capture were as described in Chapter 3 Charge transport and activation parameters for the Ru^{II/III} couple were determined using cyclic voltammetry and chronoamperometry, as described in Chapter 2 $D_{ct}(CV)$ was evaluated using scan rates of 100 to 500 mVs⁻¹ and $D_{ct}(PS)$ was determined over the 20 ms time scale following pulse application D_{ct} values were estimated from experimentally determined $D_{ct}^{1/2}C$ using a redox site concentration of 0.8 M, (the concentration of sites determined for the mono-substituted material [Ru(bipy)₂(PVP)₁₀Cl]+ [6])

Because of the difficulty in resolving the electrochemical response of the Ru^{11/111} and Ru^{111/12} couples (*vide infra*), polymer surface coverages were determined from graphical integration of the slow scan cyclic voltammogram obtained for the polymer layers before photolysis In the study of mass transfer, in order to facilitate the resolution of the Ru^{11/111} and Ru^{111/12} couples, polymer surface coverages were kept at *ca* 1 0 x 10⁻⁸ molcm⁻² For [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ polymer layers thicker than this, the oxidation to higher

ruthenium oxidation states was not clearly seen

While the oxidation of $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ by O₂ is thermodynamically favourable, in an early study of the monomeric material $[Ru(bipy)_2(py)(H_2O)]^{2+}$ no evidence for air oxidation was found [7] Similarly, in this study of the polymeric analogue no precautions for the exclusion of air from the electrochemical cell were required However, for the EQCM study the electrolytes were routinely purged with Ar and a steady stream of Ar directed over the electrolyte throughout the course of electrochemical and mass measurements

6.3. RESULTS AND DISCUSSION.

6.3.1. Redox and Mass Transfer Processes within Modifying layers of [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺.

6311 General layer behaviour

The Ru^{1v}=O species is a strong catalytic agent for oxidation [11-22] and in electrolytes of high acid concentration it is possible that H₂O may be oxidised to O₂ [7] However, in this and earlier studies [7], no evidence for the oxidation of water has been found In more recent work on Ru-oxo compounds it has been established that it is the oxo-bridged dimeric species, Ru-O-Ru, which is required for the active catalysis of water [20-22] While the formation of μ -oxo species has been found to occur for the monomeric analogue, [Ru(bipy)₂(py)(H₂O)]²⁺, if left standing for several days or if heated [7], because the oxo-bridge formation is thermodynamically unfavourable [7], it is not considered to be of any significance for the freshly generated metallopolymer films used in this study

However, in this work, the oxidising properties of the Ru^{IV}=O group were observed in pTSA electrolyte, where a catalytic current for the oxidation of the toluene sulphonate anion was seen at [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ modified electrodes at slow cyclic voltammetric scan rates This, coupled to the photochemical generation of a sulphatocomplex in sulphate-based electrolytes [3,4,23], results in further complication of the redox behaviour of [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ in pTSA Furthermore, because of the expected increase in viscoelasticity of polymer films of this type in pTSA electrolyte (see Chapter 4), an EQCM study of mass transfer was restricted to perchlorate-based electrolytes only
For these reasons, in the following discussion of the redox behaviour of $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$, specific reference is made only to HClO₄. However, it should be noted that the cyclic voltammetric response for the electrochemical processes within $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ was found to be qualitatively similar in all acid electrolytes studied (i e pTSA, HClO₄ and H₂SO₄) and the following discussion of redox processes should be generally applicable

6312. General features of mass transfer

It is the purpose of this section to illustrate the mass transfer found in differing ClO₄electrolytes and to explain it in terms of the pH dependency of the coupled proton and electron transfer in $[Ru(bipy)_2(PVP)_{10}(H_2O)]^2+[5,7,8,12]$ A more quantitative discussion of mass changes is considered in Section 6.3.3

Fig 6 3 1 (a) illustrates a typical mass-potential and cyclic voltammogram obtained for a $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ polymer film at a scan rate of 5 mVs⁻¹ in 1 0 M HClO₄ The polymer layer was prepared *in situ* by photolysis and has a surface coverage of 1 13 x 10⁻⁸ molcm⁻² Fig 6 3 1 (b) shows the mass-potential and cyclic voltammogram obtained at 5 mVs⁻¹ for the same film when transferred to 0 1 M HClO₄

The cyclic voltammogram in both HClO₄ electrolytes exhibits a voltammetric wave at *ca* 800 mV for the Ru^{II/III} couple The formal potential of this couple shows a slight dependency on the contacting electrolyte concentration (or more correctly, the electrolyte pH), shifting to less positive potentials at lower HClO₄ concentrations For [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ polymer films, a further oxidation to form the ruthenyl complex, Ru^{IV}=O, occurs [7] This <u>net</u> oxidation of Ru^{III} to Ru^{IV}=O is clearly observed in 1 0 M HClO₄, and is centred at *ca* 940 mV in Fig 6 3 1 (a) The formal potential of the Ru^{III/IV} couple exhibits a more marked dependency on pH than the Ru^{III/III} couple and in 0 1 M HClO₄, it is not resolved However, the existence of the Ru^{III/IV} couple in 0 1 M Fig 6 3 1 Cyclic voltammogram and mass-potential plot for an electrode modified with [Ru(bipy)2(PVP)10(H2O)]²⁺ in (a) 1 0 M HClO₄ and (b) 0 1 M HClO₄ Polymer layer prepared *in situ* in 1 0 M HClO₄ from photolysis of [Ru(bipy)2(PVP)10Cl]⁺ Polymer surface coverage is 1 13 x 10 8 molcm⁻², scan rate is 5 mVs⁻¹



HClO₄ is evidenced by the enhanced cathodic branch of the voltammetric wave in Fig 6 3 1 (b)

From the data presented in Fig 6 3 1, it is seen that not only is the resolution of the Ru^{II/III} and Ru^{III/IV} couples influenced by the contacting electrolyte pH, but the accompanying redox-induced mass transfer is profoundly different in 1 0 M and 0 1 M HCiO₄ electrolyte For 1 0 M HCiO₄ in Fig 6 3 1 (a), a mass gain is seen for the Ru^{III/III} oxidation at 810 mV, but on commencement of the Ru^{III/IV} couple at *ca* 890 mV a mass loss occurs In contrast, for 0 1 M HCiO₄ in Fig 6 3 1 (b), a mass loss accompanies all anodic processes

The transition in mass transfer behaviour over the concentration range 0.1 M to 1.0 M HClO4 is not a sharp one. This is shown in Fig 6.3.2 which illustrates the mass-charge plots for the data presented in Fig 6.3.1, and also that for the film when transferred to 0.3 M HClO4. At this intermediary concentration of 0.3 M (Fig 6.3.2 (b)), there is no net interfacial mass transfer throughout the entire Ru^{II/III} couple and it is only during the <u>net</u> oxidation of Ru^{III} to Ru^{IV} that a mass loss is observed.

The transition in the mass transfer behaviour with changing HClO₄ electrolyte concentration is further illustrated in Fig 6 3 3, where the normalised mass for both the Ru^{11/11} and Ru^{111/1V} couples, obtained at 1 mVs⁻¹, is plotted against minus log HClO₄ concentration These data are typical for all [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ films studied and were obtained for a film of surface coverage 1 13 x 10⁻⁸ molcm⁻² The data are taken from Table 6 3 1 which is presented in Section 6 3 3, below

In Fig 6 3 3, the normalised mass for $Ru^{II/III}$ couple <u>decreases</u> almost linearly with <u>increasing HClO4</u> concentration, from a mass gain of *ca* 167 gmol⁻¹ in 1 0 M HClO4 to a mass loss of -55 gmol⁻¹ in 0 1 M HClO4 For the $Ru^{III/IV}$ couple, a mass loss accompanies oxidation at all concentrations, but the magnitude of this mass loss decreases from -136 gmol⁻¹ in 1 0 M electrolyte to -55 gmol⁻¹ in 0 1 M HClO4

Fig 6 3 2 Mass-charge plots for the data presented in Fig 6 3 1 and also that obtained when the [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ film was transferred to 0 3 M HClO₄ The plots are, from top to bottom, (a) 1 0 M, (b) 0 3 M and (c) 0 1 M HClO₄



Fig 6 3 3 The effect of HClO₄ concentration on the normalised mass for the Ru^{11/11} and Ru^{111/1V} couples for [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ The data are presented for polymer oxidation and are taken from Table 6 3 1 (Section 6 3 3) for a scan rate of 1 mVs⁻¹



The differing redox behaviour and the change in interfacial mass transfer over this electrolyte concentration range derives from the coupled proton and electron transfer for the Ru^{II/III} and Ru^{III/IV} redox couples Each ruthenium couple will now be considered separately

6313 The RuII/III Couple

The redox chemistry of the monomeric anologue, $[Ru(bipy)_2(py)(H_2O)]^{2+}$, has been extensively studied [7-10] The Ru^{II}-H₂O monomeric complex is a weak base (pK_a 10 2), while Ru^{III}-H₂O is a strong acid (pK_a 0 85) [7] The protonation of the aquo ligand of the Ru^{III} molety will therefore be strongly influenced by the contacting acid electrolyte concentration

6313a pH below the pK_a of RuIII-H₂O

At pH below the pK_a of Ru^{III}-H₂O, the aquo ligand is protonated in both redox states and the Ru^{II/III} couple may be described by,

$$[Ru^{II}(bipy)_2(PVP)_{10}(H_2O)]^{2+} \xrightarrow{-e} [Ru^{III}(bipy)_2(PVP)_{10}(H_2O)]^{3+}$$
(6 3 1)

Therefore, in 1 0 M HClO₄ (measured pH 0) the initial mass gain in Fig 6 3 1 (a) represents counter-anion motion required for the maintenance of electroneutrality within the layer. The normalised mass for this mass gain is 167 gmol⁻¹, representing the concomitant transfer of *ca* 68 gmol⁻¹ of net neutrals. Because there is an increase in charge of the Ru complex from $[Ru^{II}]^{2+}$ to $[Ru^{III}]^{3+}$, this additional transfer of net neutrals most probably represents the transfer of solvent in response to the activity gradient established during polymer oxidation [24]

6312b pH above the pK_a of RuIII-H₂O

For the Ru^{II/III} couple at pH above the pK_a of Ru^{III}-H₂O, the aquo ligand will not be protonated in the Ru^{III} state, and the Ru^{II/III} couple becomes,

$$[Ru^{II}(b_{1}py)_{2}(PVP)_{10}(H_{2}O)]^{2+} = e [Ru^{III}(b_{1}py)_{2}(PVP)_{10}(OH)]^{2+} + H^{+} (6 3 2)$$

This equation predicts the expulsion of a proton per redox site conversion For 0.1 M HClO₄ (measured pH 1.05), the mass-charge plot in Fig 6.3.2 (c) shows that a mass loss occurs on the immediate passage of anodic charge This suggests that Eqn 6.3.2 describes the Ru^{11/111} couple for [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ in 0.1 M HClO₄ The mass loss, corresponding to -55 g electron equiv -1, therefore represents the expulsion of a proton and *ca* three solvent molecules per redox site conversion from [Ru¹¹-H₂O]²⁺ to [Ru¹¹¹ OH]²⁺

The decrease in the normalised mass for the Ru^{II/III} couple with decreasing electrolyte HClO₄ concentration in Fig 6 3 3, therefore represents the change in the mass transfer mechanisms required for the maintenance of electroneutrality within the layer In 0 5 M HClO₄ the normalised mass gain accompanying Ru^{II/III} oxidation is significantly reduced, reflecting the existence of the Ru^{III} redox centres as both [Ru^{III}-H₂O]³⁺ and [Ru^{III}-OH]²⁺ and the partial utilisation of proton expulsion mechanisms during redox conversion. The behaviour in 0 3 M electrolyte represents the balancing of proton expulsion mechanisms and counter-anion insertion during the oxidation of [Ru^{III}-H₂O]²⁺ to [Ru^{III}-OH]²⁺ and [Ru^{III}-H₂O]³⁺, respectively. This figure clearly illustrates that for the Ru^{III} oxidation mass transfer mechanisms are dependent upon the pK_a of Ru^{III}-H₂O

That this gradual shift in the mechanism dominating mass transfer occurs in the concentration range 1.0 M to 0.1 M HClO₄ is surprising. With a pK_a for the Ru^{III}-H₂O

complex of 0 85, in 0 1 M HClO₄ (measured pH 1 05), the ratio of Ru^{III}-H₂O to Ru^{III}-OH will be *ca* 2 3 (using the Henderson-Hasselbach equation [25]) Consequently, in 0 1 M HClO₄, for the oxidation of Ru^{II} H₂O, both anion insertion (Eqn 6 3 1) and proton expulsion mechanisms (Eqn 6 3 2) should be in operation, with anion insertion dominating to yield an observed <u>net</u> mass ingress. Indeed, for a pK_a of 0 85, for proton expulsion mechanisms to dominate the observed net mass transfer, the ratio of Ru^{III}-H₂O to Ru^{III}-OH required will be at least 1 99 (assuming only ion movement). This will occur at a predicted pH of 2 85

That proton loss is observed at a pH of 1 05 demonstrates that the solution phase value for the pK_a of Ru^{111} -H₂O is inappropriate for the polymeric analogue and that the actual pK_a value within the polymer film is likely to be more acidic. This is in agreement with the protonation behaviour of the PVP backbone of $[Os(bipy)_2(PVP)_{10}Cl]^+$, discussed in Chapter 3, where it was found that the pK_a of the uncoordinated pyridine moleties within the metallopolymer was significantly more acidic than that observed for the homopolymer in solution

To gain a more unambiguous insight into the mass transfer associated solely with proton expulsion, redox-induced mass transfer in $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ was investigated in 1 0 M NaClO₄ electrolyte with pH adjusted to pH 1 and 2 Analysis at higher pH was not performed due to the deterioration in the cyclic voltammetric response

The data at pH 1 and 2 were obtained for the same film as that used in Fig 6 3 1 and are summarised for scan rates ranging from 1 to 100 mVs⁻¹ in Table 6 3 1 (see Section 6 3 3) The cyclic voltammograms and mass-potential plots at pH 1 and 2 at 5 mVs⁻¹ are illustrated in Fig 6 3 4 (a) and Fig 6 3 4 (b), respectively As seen for 0 1 M HClO₄ above, in pH 1 and 2 electrolyte a mass loss is observed throughout the anodic scan However, the magnitude of the mass loss increases at higher pH

The value of the normalised mass loss in 1 0 M NaClO₄ (pH 1) electrolyte is less than that obtained in 0 1 M HClO₄ (i e -21 g electron equiv -1 vs -55 g electron equiv -1) This is not surprising considering the dehydrating effect of perchlorate on redox polymer films of this type Indeed, for the polymer $[Os(bipy)_2(PVP)_{10}Cl]^+$ in NaClO₄, it has been found that there is no concomitant solvent transfer during redox switching [26,27] Thus the reduced value of -21 g electron equiv -1 for $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ in 1 0 M NaClO₄ (pH 1) most probably reflects a reduction in solvent transfer to *ca* a single H₂O molecule expelled per redox site conversion

Significantly, the mass loss in 1 0 M NaClO₄ (pH 2) increases to -58 g electron equiv ⁻¹ This suggests that at this higher pH the proton expulsion mechanism is utilised to a greater extent. However, even at pH 2, with a pK_a of 0 85 the ratio of Ru^{III}-H₂O to Ru^{III}-OH will be *ca* 1 14 and there should be sufficient Ru^{III}-H₂O centres (requiring anion inserion) to overshadow the proton expulsion required for Ru^{III}-OH centres Therefore, despite the greater mass loss at higher pH, all data confirm that the pK_a of Ru^{III}-H₂O must be far removed from pH 1 and significantly more acidic than that of the monomeric analogue Fig 6 3 4 Cyclic voltammogram and mass-potential plot for an electrode modified with [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ in 1 0 M NaClO₄ with pH adjusted to (a) pH 1 and (b) pH 2 The scan rate is 5 mVs⁻¹ The polymer layer is that used in Fig 6 3 1 (surface coverage 1 13 x 10 8 molcm⁻²)



6313 The Rull/IV Couple.

As mentioned previously, for $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ the stabilisation of the 4+ oxidation state of ruthenium through proton loss from the aquo ligand results in the generation of the ruthenyl complex, $[Ru^{IV}=O(bipy)_2(PVP)_{10}]^{2+}$ [7,8]

Due to the distribution of protons in the products, it is thermodynamically unfavourable for the Ru^{III}-H₂O / Ru^{IV}=O oxidation to proceed *via* a simple electron transfer [9] For the polymer-bound complex, the peak height of the anodic branch of the Ru^{III/IV} couple is significantly reduced in comparison to that of the Ru^{II/III} couple (see Fig 6 3 1 (a)) and is only clearly seen at slow scan rates (< 20 mVs⁻¹) These features have been observed previously [2-5,12] and are indicative of slow kinetics typical of an "EC" electrochemical process It has been proposed that Ru^{IV}=O is generated *via* the disproportionation of Ru^{III} centres into Ru^{II} and Ru^{IV}, with the observed electrochemical response due to the diffusion controlled oxidation of the Ru^{III} centres at the electrode [7,9]

At pH below the pK_a of Ru^{III} -H₂O, the disproportionation reaction is given by,

$$2 [Ru^{III}(b_{1}py)_{2}(PVP)_{10}(H_{2}O)]^{3+}$$
(6 3 3)

 $[Ru^{II}(b_{1}p_{2})_{10}(PVP)_{10}(H_{2}O)]^{2+} + [Ru^{IV}=O(b_{1}p_{2})_{2}(PVP)_{10}]^{2+} + 2H^{+}$

with the electrochemical response due to the oxidation of the $Ru^{II}-H_2O$ to $Ru^{III}-H_2O$ as described by Eqn 6.3.1

For the maintenance of electroneutrality during the initial disproportionation reaction (Eqn 6 3 3), the expulsion of two counter-anions and two protons for each Ru^{IV} redox centre generated is required. The diffusion controlled oxidation of the resulting Ru^{II} centre necessitates the retention of one of these counter-anions. Thus, considering only electroneutrality, for the net oxidation of Ru^{III}-H₂O to Ru^{IV}=O, a net mass egress of a

single counter-anion and two protons per redox site conversion is required Assuming the Grotthus-type transfer of protons [28], the net mass loss predicted for the Ru^{III/IV} couple is -101 gmol⁻¹

In Fig 6 3 1 (a), the normalised mass loss for the Ru^{III/IV} couple in 1 0 M HClO₄ is -136 gmol⁻¹ This reflects the predicted mass loss in Eqn 6 3 3 plus the additional transfer of *ca* 2 solvent molecules For the Ru^{III/IV} oxidation the overall charge of the polymer phase decreases from a film containing two [Ru^{III}]³⁺ redox centres to a film containing a [Ru^{III}]³⁺ and a [Ru^{IV}=O]²⁺ centre It is therefore expected that the activity gradient established for the transfer of net neutrals will be in the opposite direction to that established during the initial Ru^{II/III} oxidation and the transfer of solvent from the layer will occur [24]

Significantly, the mass-charge plot in 1 0 M HClO₄ in Fig 6 3 2 (a) shows that, for the Ru^{III/IV} couple, the mass loss is almost uniquely defined by the instantaneous oxidation state, (i e the mass-charge plot almost tracks) This provides evidence that, despite the differing shapes of the anodic and cathodic branches of the cyclic voltammogram in Fig 6 3 1 (a), Eqn 6 3 3 is reversible, with the net re-reduction of Ru^{IV}=O to Ru^{III}-H₂O following the comproportionation pathway

At pH above the pK_a of Ru^{III}-H₂O, disproportionation is similar to that in Eqn 6 3 3, but will have differing proton requirements due to the existence of Ru^{III} as Ru^{III}-OH,

$$2 [Ru^{II}(b_{1}py)_{2}(PVP)_{10}(OH)]^{2+}$$

$$[Ru^{II}(b_{1}py)_{2}(PVP)_{10}(H_{2}O)]^{2+} + [Ru^{IV}=O(b_{1}py)_{2}(PVP)_{10}]^{2+}$$
(6 3 4)

Again, the observed electrode reaction is the oxidation of the Ru^{II}-H₂O centres which are formed during the disproportionation step. The subsequent oxidation to Ru^{III}-OH is as described by Eqn 6.3.2 For the disproportionation reaction in Eqn 6.3.4, there is no net change in the mass requirements within the layer However, for the oxidation of the Ru^{II}-H₂O centres generated, further proton loss is expected Consequently, the interfacial mass transfer characteristics seen for the net oxidation of $[Ru^{III}-OH]^{2+}$ to $[Ru^{IV}=O]^{2+}$ are identical to those for the Ru^{II/III} couple

Fig 6 3 2 (c) shows the mass-charge plot obtained in 0 1 M HClO₄ The linear relationship between mass and charge throughout all redox processes provides evidence for the existence of a single mass transfer mechanism throughout redox conversion and confirms the mechanisms for redox switching outlined in Eqn 6 3 4 In addition, the tracking of the mass-charge plot indicates that Eqn 6 3 4 is reversible and that the comproportionation pathway is utilised during polymer reduction

That Eqn 6.3.4 adequately describes the mass transfer behaviour for the Ru^{III/IV} couple in an electrolyte with pH so close to the pK_a of the Ru^{III}-H₂O complex is once again a surprising result. However, the mass transfer behaviour for the Ru^{III/IV} couple is in agreement with the observations concerning the pK_a of the polymer-bound Ru^{III}-H₂O complex, discussed above

In Fig 6 3 3, the normalised mass for the RuIII/IV oxidation is plotted as a function of minus log HClO₄ concentration. The observed decrease in the extent of mass loss with decreasing HClO₄ concentration reflects the transition in the disproportionation reaction from one requiring both counter-anion and proton expulsion at high HClO₄ concentrations (Eqn 6 3 3), to one which requires only proton expulsion at lower HClO₄ concentrations (Eqn 6 3 4)

6.3.2. On the Wave Shape of the Ru^{III/IV} Couple.

In Fig 6 3 1, the Ru^{11/111} couple exhibits the predicted surface behaviour for a reversible one-electron redox process [29] However, the Ru^{111/1V} couple clearly does not While the anodic and cathodic charge passed for the Ru^{111/1V} couple is identical, within experimental error, the cathodic wave, corresponding to the the reverse of Eqn 6 3 3 and 6 3 4 (the comproportionation reaction between Ru¹¹ and Ru^{1V}), is sharp and has a pwhm significantly less than that expected for a surface-immobilised reversible one-electron process [29]

For the coupled proton and electron transfer required for the interconversion between higher oxidation states of ruthenium, the nature and pretreatment of the electrode has been found to be significant [13,23] For $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ polymer films, glassy carbon has been found to be a better electrode substrate for the resolution of the $Ru^{11/111}$ and $Ru^{111/112}$ couples

Fig 6 3 5 (a) illustrates a typical cyclic voltammogram for a glassy carbon electrode modified with $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ The film was prepared *in situ* in 1 0 M HClO4 and the scan rate is 5 mVs⁻¹ Fig 6 3 5 (b) shows a cyclic voltammogram under the same conditions for a $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ polymer layer prepared *in situ* in 0 1 M HClO4 While the redox behaviour in Fig 6 3 5 is qualitatively similar to that observed in Fig 6 3 1 on gold electrodes, the Ru^{III/IV} couple is clearly better defined

The origins of the dissymmetry of the anodic and cathodic peak shapes of the Ru^{III/IV} couple remain unclear Interaction models have been used to describe the narrowing and broadening of the wave shape of immobilised electroactive materials [30-33], particularly the reversible one-electron redox process in PVF [33] However, for $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$, where the redox site separation is *ca* 25 Å (assuming a rigid rod structure) [34], no significant interaction is expected This is supported by the absence of such interactions in all metallopolymers of this type, even in materials of

Fig 6 3 5 Cyclic voltammogram for a [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ modified glassy carbon electrode in (a) 1 0 M HClO₄ and (b) 0 1 M HClO₄
The polymer layers were prepared *in situ* in each electrolyte from photolysis of a [Ru(bipy)₂(PVP)₁₀Cl]⁺ film The polymer surface coverages are both *ca* 2 0 x 10⁻⁸ molcm⁻², the scan rate is 5 mVs ¹



higher metal loading [35]

A possible explanation for the observed cathodic wave shape lies in the need for both $Ru^{IV}=O$ and $Ru^{II}-H_2O$ centres for the comproportionation reaction. True surface wave behaviour for the $Ru^{II/III}$ couple ensures complete oxidation to Ru^{III} . Consequently, the <u>net</u> re-reduction of $Ru^{IV}=O$ to $Ru^{III}H_2O$ (or $Ru^{III}-OH$) cannot occur until a source of $Ru^{II}-H_2O$ exists within the layer

Because the disproportionation reaction during polymer oxidation is slow, even during cyclic voltammetric scan rates of 1 to 5 mVs⁻¹ complete oxidation of the layer to Ru^{IV}=O is unlikely. Some ruthenium centres are therefore expected to exist in the Ru^{III} oxidation state throughout. During the reverse sweep, it is only when these centres are rereduced that a source of Ru^{II} H₂O will exist within the layer. The Ru^{IV}=O centres are forced to exist at potentials less positive than the formal potential of the Ru^{III/IV} couple and once the comproportionation can proceed it will do so rapidly. In many respects, the reduction of Ru^{IV}=O is "mediated" by the Ru^{III/II} couple

6.3.3. Mass Transfer accompanying Redox processes.

6331 General Layer behaviour

Table 6.3.1 summarises a set of data for the normalised mass for the Ru^{II/III} and Ru^{III/IV} couples in a series of HClO₄ electrolytes for a [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ film of surface coverage 1.13 x 10-8 molcm⁻². The <u>net</u> mass change for the combined redox processes (i.e. the "end-to-end" mass change), is also included and is calculated as the mass per electron equivalent. The data is presented for cyclic voltammetric scan rates ranging from 1 to 200 mVs⁻¹.

The data for $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ in Table 6.3.1 is qualitatively identical for all films studied. The mass changes observed are independent of the electrolyte concentration in which the photolysis was performed (either 0.1 M or 1.0 M HClO4). The normalised mass is independent of the sequence of previous exposure to different electrolytes and is reproducible for a given film to within \pm 5%. On changing the electrolyte, redox and mass transfer mechanisms immediately revert to those predicted from the electrolyte pH, with no "break-in" required. This rapid transfer of electrolyte properties to the layer has been observed previously for $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ at pH below the pK_a of PVP [12].

The evaluation of mass from frequency measurements assumes the Sauerbrey equation For $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ polymer films the rigidity of the layer was not unambiguously established using impedance analysis However, as seen in Chapter 3, in perchlorate media, metallopolymers of this type are dehydrated, compact structures, in which the approximation to rigidity can be made Furthermore, in Table 6 3 1 the normalised mass is similar at all scan rates. It is generally considered that for non-rigid layers the normalised mass will increase for measurements made on shorter time scales.

HClO ₄	Scan Rate	Meq Ru11/111	Meq RuIII/IV	End-To-End (a)
(Molar)	(mVs-1)	(g mol-1)	(g mol-1)	(g electron equiv ⁻¹)
10	1	167	-136	20
	5	162	-122	32
	50	160	-	108
	200	176	-	133
0 5	1	91	- 86	19
	5	86	- 64	37
	50	61	- 13	39
	200	45	-	45
03	1	8	- 71	- 32
	5	13	- 60	- 25
	50	0	- 30	- 8
	200	0	-	0
01	1	*	*	- 55
	5	*	*	- 44
	50	*	*	- 40
	200	*	*	- 36
pH 1	1	*	*	- 21
	5	*	*	- 26
	50	*	*	- 12
	100	*	*	- 0
pH 2	1	*	*	- 58
	5	*	*	- 39
	50	*	*	- 18
	100	*	*	- 0

Table 6 3 1.Normalised mass data for $[Ru(bipy)_2(H_2O)(PVP)_{10}]^{2+}$ in a series of
HClO4 electrolytes for a film of surface coverage 1 13 x 10-8 molcm-2

a) Normalised mass for <u>net</u> mass change on completion of all anodic processes

* Denotes common mass transfer for both couples

This suggests that the data presented in Table 6 3 1 is an accurate evaluation of interfacial mass transfer during redox switching

However, the normalised mass for $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ is subject to greater between film variation than that observed for $[Os(bipy)_2(PVP)_{10}Cl]^+$ in Chapter 3 For the Ru^{II/III} couple in 0 3 M and 0 1 M HClO₄ the between film variation at slow scan rates is $\pm 20\%$ In 1 0 M and 0 5 M HClO₄ the normalised mass increases with increasing surface coverage (0 8 to 2 x 10⁻⁸ molcm⁻²), to give a between film variation at slow scan rates of $\pm 30\%$ This is contrary to what would be expected for a viscoelastic film, where for thicker layers the under-evaluation of mass due to excessive dampening of crystal oscillations will increase [36] Instead, the between film variation in 0 5 M and 1 0 M HClO₄ reflects the fact that for thicker films of $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ only the Ru^{II/III} couple is in evidence. As a result, the mass loss associated with the Ru^{III/IV} couple does not occur to the same extent as in thinner layers and only the mass gain accompanying the Ru^{II/III} couple is measured

Considering the complicated redox and mass transfer processes within $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$, the dependence of the resolution of the two redox couples on film thickness, as well as the possibility of between film variation due to incomplete photolysis, the errors here are considered to be acceptable

6332 Kinetic aspects of interfacial mass transfer

The disproportionation reaction is slow and it is generally found that at increasing cyclic voltammetric scan rates the net oxidation of Ru^{III} to Ru^{IV}=O does not occur [1-5] Fig 6 3 6 (a) and Fig 6 3 6 (b) illustrate the cyclic voltammogram and the mass-potential plot obtained at 200 mVs⁻¹ in 1 0 M and 0 1 M HClO₄, respectively The slow scan rate data for this polymer film are depicted in Fig 6 3 1 The absence of a voltammetric response for the Ru^{III/IV} couple in Fig 6 3 6 demonstrates the kinetic limitations of the

bimolecular oxidation pathway The mass-potential plot in 1 0 M HClO₄ confirms this, with no mass loss occuring during the anodic sweep

For the data in 0 1 M HClO₄, mass transfer for the Ru^{II/III} and Ru^{III/IV} couples is identical (see Section 6 3 13), and it is not possible to monitor the isolation of the Ru^{III/IV} couple using the EQCM However, considering the isolation of the disproportionation reaction in 1 0 M HClO₄ at 200 mVs⁻¹, it is thought that the behaviour in 0 1 M HClO₄ will be similar

Significantly, mass transfer through $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ shows no kinetic limitations This is seen in Table 6.3.1, where the normalised mass at 200 mVs⁻¹ represents the "thermodynamic" mass transfer requirement. The absence of kinetic limitations is also shown in Fig 6.3.7, which illustrates the corresponding mass-charge plots for the 200 mVs⁻¹ data shown in Fig 6.3.6. In 0.1 M HClO4, even at 200 mVs⁻¹, the mass-charge plot exhibits no hysteresis. This may reflect the quicker rates of transport for protons. For 1.0 M HClO4, apart from the introduction of hysteresis during the latter stages of oxidation, due possibly to partial Ru^{111/11} redox switching, the mass-charge plot for the Ru^{11/111} couple also tracks

This facile mass transfer behaviour is in sharp contrast to that found in Chapter 5 for $[Os(bipy)_2(PVP)_{10}Cl]$ + in HClO₄ electrolyte, where the transfer of net neutrals (specifically solvent) was found to become increasingly difficult under more dynamic regimes That the transfer of all mobile species through $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+1}$ is facile at all scan rates studied suggests that a more open polymer structure exists

In Chapter 2 it was established that the physico-chemical characteristics of the metallopolymer layers are profoudly different for ruthenium and osmium metal complexes. The differing facility for solvent transfer in HClO₄ electrolyte for $[Ru(bipy)_2(PVP)_{10}(H_2O)]^2$ + and $[Os(bipy)_2(PVP)_{10}Cl]$ + demonstrates this

Fig 6 3 6 Cyclic voltammogram and mass-potential plot at a scan rate of 200 mVs ¹ for a [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ modified electrode in (a) 1 0 M HClO₄ and (b) 0 1 M HClO₄ The polymer surface coverage is 1 13 x 10 ⁸ molcm⁻² and is that used for the slow scan rate data in Fig 6 3 1 and Fig 6 3 4



Fig 6 3 7 Mass-charge plots for the data presented at a 200 mVs-1 scan rate in Fig 6 3 6 for a [Ru(bipy)2(PVP)10(H2O)]²⁺ film The plots are
(a) 1 0 M HClO₄ and (b) 0 1 M HClO₄



The data presented in Table 6 3 1 clearly illustrate that in 1 0 M HClO₄ the contribution of the mass loss associated with the Ru^{III/IV} couple decreases at faster scan rates Fig 6 3 8 plots the normalised end-to-end mass and the normalised mass for the Ru^{II/III} oxidation versus log scan rate. At faster scan rates the end-to-end normalised mass approaches the mass transfer requirements of the Ru^{II/III} couple only. Therefore, under semi-infinite diffusion conditions (i.e. at scan rates greater than 100 mVs⁻¹), it may be assumed that the voltammetric response is due only to the Ru^{II/III} couple



Fig 6 3 8 The effect of the cyclic voltammetric scan rate on the normalised mass for the Ru^{II/III} couple and the net end-to-end mass change in 1 0 M HClO₄ The data are taken from Table 6 3 1

6.3.4. Charge Transport and Activation Parameters for the $Ru^{II/III}$ couple (oxidation).

63.41. General Layer Behaviour

The EQCM study of redox-induced mass transfer in [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ polymer films demonstrates that under semi-infinite diffusion conditions the voltammetric response in HClO₄ represents the reversible one-electron Ru^{it/III} couple The evaluation of the apparent charge transport diffusion coefficient and activation parameters for this oxidation, using chronoamperometry and cyclic voltammetry, as described in Chapter 2, is therefore appropriate

In this work, the charge transport parameters for $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ films under semi-infinite diffusion conditions is only considered for polymer oxidation. The effect of experimental time scale and electrolyte type is addressed and a comparison with other ruthenium metallopolymers is made. Preliminary work has shown that activation and charge transport parameters for polymer reduction are similar to those presented below for oxidation. This is surprising, considering the requirement of Ru^{II} centres for the comproportionation reaction in Eqn 6.3.3 and the absence of such Ru^{II} centres in a fully oxidised polymer film. Cathodic processes within $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ films therefore require further investigation.

Table 6 3 2 summarises $D_{c1}(CV)$ and $D_{c1}(PS)$ for the Ru^{II/III} oxidation obtained on glassy carbon electrodes at 25 °C in 0 1 M and 1 0 M concentrations of pTSA and HClO₄ electrolyte The [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ films were freshly prepared *in situ* in each electrolyte The error in D_{c1} values is \pm 20% and is independent of polymer surface coverage in the range 0 5 to 5 x 10⁻⁸ molcm⁻² However, to ensure the kinetic isolation of the Ru^{III/IV} couple, surface coverages were routinely kept greater than 2 x 10⁻⁸ molcm⁻² Although the redox behaviour in pTSA is complicated by the presence of small quantities of the toluene sulphonato-complex, the charge transport data for the $Ru^{11/11}$ - H_2O centres are of similar reproducibility to those in HClO₄ electrolyte

Table 6 3 3 summarises the activation parameters for the Ru^{II/III} couple in 0 1 M and 1 0 M concentrations of pTSA and HClO₄ The error in the activation energy, calculated over the temperature range 278 to 313 K, is \pm 5% for a given film and \pm 20% between films While the Ru^{III/IV} couple is isolated at 25 °C, at higher temperatures the disproportionation reaction becomes increasingly evident, irrespective of film thickness This is illustrated in Fig 6 3 9 (a) which shows the temperature dependence of the cyclic voltammetric response at 100 mVs⁻¹ for the Ru-aquo polymer in 1 0 M HClO₄ The polymer surface coverage is *ca* 2 0 x 10⁻⁸ molcm⁻² Fig 6 3 9 (b) illustrates the data for a different film prepared in 0 1 M HClO₄, under the same experimental conditions

The slope of the Arrhenius plot for the temperature-dependence of $D_{ct}(CV)$ and $D_{ct}(PS)$ is linear across the entire temperature range, i.e. the activation parameters calculated at lower temperatures, where the disproportionation reaction is kinetically isolated, are identical to those evaluated at higher temperature, where the disproportionation reaction is seen to occur. The activation parameters quoted in Table 6.3.3 are therefore considered to be representative of the Ru^{II/III} couple

Because the EQCM study of redox-induced interfacial mass transfer was restricted to HClO₄ electrolyte, the following discussion of charge transport through $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ deals primarily with HClO₄ The effect of electrolyte type on D_{ct} and activation parameters will then be addressed

Table 6 3 2Charge Transport parameters for [Ru(bipy)2(PVP)10(H2O)]2+

Electrolyte/		D _{ct} (PS)	D _{ct} (CV)	Eº
Conc (M)		(x 10 ¹⁰ cm ² s ⁻¹)	(x 10 ¹⁰ cm ² s ⁻¹)	V vs SCE
HClO4	01	13 1	0 4	0 800
	10	14 2	0 6	0 780
pTSA	01	4 8	15	0 880
	10	4 5	14	0 835

films for a series of electrolytes

Table 6 3 3Activation parameters for charge transport through
[Ru(bipy)2(PVP)10(H2O)]2+

Electrolyte/ Conc (M)		Ea	ΔH#	ΔS#	∆G#				
		kJmol-1	kJmol-1	Jmol-1K-1	kJmol-1				
A Cyclic Voltammetry									
HClO4	01	208	206	484	62				
	10	172	170	382	56				
pTSA	01	244	242	630	54				
	10	48	45	- 35	56				
B Chro	noamperc	ometry							
HClO ₄	01	20	18	- 106	49				
	10	55	52	14	48				
pTSA	01	43	41	- 35	51				
	10	57	55	13	51				

Fig.6.3.9. Temperature dependence of the cyclic voltammetric response (at a scan rate of 100 mVs⁻¹) for [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ modified glassy carbon electrodes in (a) 1.0 M HClO₄ and (b) 0.1 M HClO₄. Each polymer layer was prepared *in situ* and has a surface coverage of *ca*. 2 x 10⁻⁸ molcm⁻².



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6342 General Discussion of Charge Transport.

The charge transport for the Ru^{11/11} couple on the cyclic voltammetric time scale is first considered $D_{cl}(CV)$ is found to be relatively insensitive to HClO₄ electrolyte concentration, increasing slightly from 4 0 to 6 0 x 10⁻¹¹ cm²s⁻¹ over the concentration range 0 1 to 1 0 M HClO₄ (Table 6 3 2) This is surprising since in Sections 6 3 1 it was found that the mechanisms for the maintenance of electroneutrality following polymer oxidation are strongly dependent on the contacting electrolyte pH, changing from proton expulsion in 0 1 M HClO₄ to anion insertion in 1 0 M HClO₄ However, the insensitivity of D_{ct}(CV) to electrolyte concentration indicates that the rate determining step in the charge transport remains invariant. This is further evidenced by the activation parameters in Table 6 3 3, where for both 0 1 M and 1 0 M HClO₄ $\Delta G^{\#}$ (CV) has a constant value of 59 ± 3 kJmol⁻¹ and E_a(CV) and $\Delta S^{\#}$ (CV) are of similar magnitude

In Section 6 3 3, the mass data indicated the concomitant movement of all mobile species, irrespective of the mechanism required for the maintenance of electroneutrality The minimal hysteresis in the mass-charge plot under semi-infinite diffusion conditions (Fig 6 3 8) suggests that it is electroneutrality control which is the rate limiting process [37-39] According to the diagnostic scheme for the interpretation of EQCM data, for non-permiselective films the tracking of the mass-charge plot represents that electron-hopping is the rate-limiting step, while for permiselective films it is counter-ion motion [37-39]

The magnitude of $D_{c1}(CV)$ in Table 6.3.2 is considerably less than the rate of electron self-exchange, D_E , evaluated for related metallopolymers using steady state methods (typically 10-6 to 10-8 cm²s⁻¹) [40,41] It is thus unlikely that electron-hopping between adjacent redox centres is the rate limiting step for charge percolation through [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ The limiting of charge transport by counter-ion motion also seems to be an inappropriate interpretation, since the counter-ion requirements have been shown to be different for the Ruil/III couple in 0 1 M and 1 0 M HClO4

The activation energies obtained for the cyclic voltammetric response in HClO₄ electrolyte are very large (greater than 150 kJmol⁻¹), and are coupled to strongly positive entropy terms (in excess of 350 Jmol⁻¹K⁻¹). It is therefore considered that the common rate limiting step in 0.1 M and 1.0 M HClO₄ is the segmental polymer chain motion required to juxtapose adjacent redox centres [42]. This identification of the rate limiting step is supported by the facile transfer of all mobile species indicated from mass measurements. Such an observation reflects an open polymer structure in which ion motion limitations should not exist. The high activation energy may also explain why the disproportionation reaction at high temperatures does not adversely affect the evaluation of D_{c1}(CV). The bimolecular reaction between Ru¹¹¹ centres is also anticipated to have a high activation energy associated with the requirement to juxtapose adjacent sites.

Significantly, unlike the Ru^{II/III} couple for the bis-coordinated polymer, $[Ru(bipy)_2(PVP)_{10}]^{2+}$ in Chapter 2, where ion motion remains rate limiting despite the extended configuration imposed by the bis-coordination, for the mono-substituted Ruaquo polymer ion motion limitations are apparently lifted. The significance of the change in coordination sphere on charge transport is further illustrated by the emergence of a time scale dependence on the evaluation of D_{ct} in the mono-substituted $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ polymer (see Table 6.3.2)

In HClO₄, $D_{ct}(PS)$ for the Ru^{II/III}-H₂O couple is *ca* 13 5 ± 0 5 x 10⁻¹⁰ cm²s⁻¹ and is greater than $D_{ct}(CV)$ by a factor of approximately 30 For the bis-substituted material in Chapter 2, the difference in $D_{ct}(PS)$ and $D_{ct}(CV)$ is a factor of only 2

As discussed in previous chapters, the difference in the evaluation of D_{ct} on differing time scales may reflect the establishment of different equilibria [43,44] It is only over the longer time scales of cyclic voltammetry that polymer chains can attain their equilibrium positions On the time scale of potential step measurements only redox equilibrium may be established [45] For [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ films in HClO₄, this is evidenced by the activation parameters in Table 6.3.3 On the time scale of chronoamperometry, $E_a(PS)$ is significantly reduced in magnitude and $\Delta S^{\#}(PS)$ becomes negative in 0.1 M HClO₄ and approaches zero in 1.0 M HClO₄, indicating a shift in the rate limiting step to one of ion motion

In Table 6.3.2 it is seen that for $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$, $D_{ct}(CV)$ increases in pTSA by a factor of *ca* 4 compared to the value in HClO₄ As discussed in Chapter 5, the increased solvation of the polymer layer in pTSA electrolyte is anticipated to result in the more facile movement of all mobile species. The increase in $D_{ct}(CV)$ reflects this

The more solvated polymer layer in pTSA electrolyte is further evidenced by the absence of a time scale dependence for the evaluation of D_{ct} For the Ru^{II/III} couple, $D_{ct}(PS)$ is greater than $D_{ct}(CV)$ by a factor of only *ca* 3 It is likely that this is due to differential swelling resulting in a higher concentration of redox centres in a more compact base layer morphology. Consequently, in pTSA the equilibrium process established on the differing time scales remains the same and D_{ct} is independent of the experimental time scale. This interpretation is supported by the activation parameters in Table 6.3.3, where, with the exception of cyclic voltammertric measurements in 0.1 M pTSA, $E_a(CV)$ and $E_a(PS)$ are similar with a value of *ca* 49 ± 6 kJmol-1. The entropy term is approximately zero, tending towards a negative value. These data represent a cross-over between counter-ion and polymer chain motion limitations. Irrespective of what exactly the rate limiting step is, it is clear that the change in polymer solvation in pTSA electrolyte results in different charge transport behaviour.

The importance of differential swelling as a consideration for the time scale dependence of D_{c1} and activation parameters is further demonstrated by the data for pTSA in Table 6.3.2 and 6.3.3 In 1.0 M pTSA, although still solvated, the layers are anticipated to become more compact due to the polyelectrolyte effect (see Section 4.3.1.4). The more homogeneous film throughout the entire thickness is evidenced by the

similarity in $E_a(CV)$ and $E_a(PS)$ However, in 0 1 M pTSA, where the polymer layers may become extensively swollen (see Section 4 3 1 3), $E_a(CV)$ becomes large (244 kJmol⁻¹) and is coupled to a very positive entropy term (630 Jmol⁻¹K⁻¹). This most probably represents the dramatic swelling of the exterior of the layer and the subsequent shift in the rate limiting process to one of segmental polymer chain motion required in the juxtapositioning of adjacent redox sites. For the base layer, however, the swelling is less extensive, and no significant change in activation parameters for potential step measurements is found.

The data obtained in HClO₄ electrolyte in Table 6 3 2 and Table 6 3 3 for $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ are in near-quantitative agreement with that obtained for the mono-substituted ruthenium metallopolymer, $[Ru(bipy)_2(PVP)_{10}Cl]^+$ [6] A comparison of these data with those presented in Chapter 2 for the analogous bis-substituted ruthenium polymer, $[Ru(bipy)_2(PVP)_{10}]^{2+}$, clearly demonstrates the profound effect that a change in the coordination sphere of the ruthenium moiety has on charge transport and activation parameters In HClO₄ electrolyte, for the mono-substituted materials there is evidence that a different equilbrium is established on differing experimental time scales For the bis-substituted $[Ru(bipy)_2(PVP)_{10}]^{2+}$ polymer films, this is not found

6.4. CONCLUSIONS.

The coupling of proton and electron transfer for redox processes within [Ru(bipy)₂(PVP)₁₀(H₂O)]²⁺ polymer modified electrodes has been demonstrated by the pH dependency of the voltammetric response and interfacial mass transfer

The EQCM has provided unambiguous evidence of the disproportionation pathway for the net oxidation of Ru^{III} to Ru^{IV}=O. The EQCM has also demonstrated the importance of the pK_a of Ru^{III} -H₂O in determining the mechanism for the maintenance of electroneutrality within the polymer films during Ru^{II/III} redox switching. Below the pK_a of Ru^{III} -H₂O counter-anion insertion is required, above the pK_a proton expulsion mechanisms are utilised

The slow kinetics associated with the "EC" mechanism of the Ru^{III/IV} couple has been shown by its kinetic isolation under semi-infinite diffusion conditions. This allows for a study of the oxidation for the Ru^{II/III} couple using a diffusion model for a one-electron reversible process

The concomitant transfer of all mobile species under dynamic conditions (either into or out of the layer), coupled to the insensitivity of activation parameters and D_{ct} to HClO₄ electrolyte concentration, indicates that an open polymer structure exists For cyclic voltammetric measurements it is the segmental polymer chain motion required to juxtapose redox sites which limits the charge percolation rate In HClO₄, on short time scales a different equilibrium is established, with a subsequent increase in the charge transport rate

In pTSA electrolyte the more solvated polymer layer results in an increase in $D_{ct}(CV)$ and enables a common equilibrium to be established on all experimental time scales As a result, the difference between $D_{cl}(CV)$ and $D_{ct}(PS)$ is negligible in this electrolyte

The similarity in charge transport behaviour for the mono-substituted polymers $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ and $[Ru(bipy)_2(PVP)_{10}Cl]^+$ indicates that the overall charge

of the ruthenium complex is of minimal significance in determining charge transport rates and activation parameters. Of primary importance is the coordination sphere and the subsequent effects on polymer structure. This is evidenced by the fundamental differences exhibited in the behaviour of $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ and the bissubstituted polymer in Chapter 2

Although this work has provided further insight into the redox processes within $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$ polymer modified electrodes, a more rigorous study of cathodic processes is required While the Ru-aquo polymer does not undergo further photolysis reactions, it is considered that the inherently more stable and reproducible behaviour of osmium complexes may provide a route to a more detailed understanding of the redox chemistry of the aquo ligand This is currently under investigation

6.5. REFERENCES.

- 1 O Haas and J G Vos, J Electroanal Chem., (1980), 113, 139
- 2 O Haas, M Kriens and J G Vos, J Am Chem. Soc, (1981), 103, 1318
- 3 O Haas, H R Zumbrunnen and J G Vos, Electrochum. Acta, (1985), 30, 1551
- 4 S M Geraty and J G Vos, J Chem. Soc Dalton Trans, (1987), 3073
- 5 J M Calvert and T J Meyer, Inorg Chem., (1982), 21, 3978
- 6 D Leech, R J Forster, M R Smyth and J G Vos, J Mater Chem., (1991), 1, 629
- 7 B A Moyer and T J Meyer, Inorg Chem, (1981), 20, 436
- 8 B A Moyer and T J Meyer, J Am Chem Soc, (1978), 100, 3601
- 9 R A Binstead, B A Moyer, G J Samuels and T J Meyer, J Am. Chem Soc, (1981), 103, 2897
- 10 K J Takeuchi, G J Samuels, S W Gersten, J A Gilbert and T J Meyer, *Inorg* Chem, (1983), 22, 1407
- B A Moyer, M S Thompson and T J Meyer, J Am. Chem. Soc , (1980) , 102,
 2310
- 12 G J Samuels and T J Meyer, J Am Chem Soc, (1981), 103, 307
- 13 C M Che, K Y Wong, W O Lee and F C Anson, J Electroanal Chem., (1991), 309, 303
- 14 C M Che and W H Leung, J Chem Soc, Chem Commun, (1987), 1376
- 15 B A Moyer and T J Meyer, J Am Chem. Soc, (1979), 101, 1326
- 16 B Durham, S R Wilson, D J Hodgson and T J Meyer, J Am Chem. Soc, (1980), 102, 600
- 17 B A Moyer, B K Sipe and T J Meyer, Inorg Chem, (1981), 20, 1475
- 18 C D Ellis, J A Gilbert, W R Murphy and T J Meyer, J Am Chem Soc, (1983), 105, 4842
- 19 W J Vining and T J Meyer, Inorg. Chem., (1986), 25, 2023

- J A Gilbert, D S Eggleston, W R Murphy, D A Geselowitz, S W Gersten,
 D J Hodgson and T J Meyer, J Am Chem Soc, (1985), 107, 3855
- 21 F P Rotzinger, S Munavalli, P Comte, J K Hurst, M Gratzel, F J Pern and A J Frank, J Am. Chem. Soc, (1987), 109, 6619
- 22 M K Nazeeruddin, F P Rotzinger, P Comte, and M Gratzel, J Chem. Soc, Chem. Commun, (1988), 872
- 23 R C McHatton and F C Anson, Inorg Chem., (1984), 23, 3935
- 24 S Bruckenstein and A R Hillman, J Phys Chem., (1988), 92, 4837
- 25 F Hellferich, Ion Exchange, McGraw-Hill, New York, (1962)
- 26 A J Kelly, T Ohsaka, N Oyama, R J Forster and J G Vos, J Electroanal Chem, (1990), 287, 185
- 27 A J Kelly and N Oyama, J Phys Chem, (1991), 95, 9579
- 28 S Bruckenstein, A R Hillman and M J Swann, J Electrochem. Soc , (1990), 137, 1323
- A R Hillman, Electrochemical Science and Technology of Polymers, R G Linford
 (Ed), Elsevier, Amsterdam (1987), Chs 5 & 6
- 30 A P Brown and F C Anson, Anal Chem, (1977), 49, 1589
- 31 H Gerischer and D A Scherson, J Electroanal Chem., (1985), 188, 33
- 32 H Daifuku, K Aoki, K Tokuda and H Matsuda, J Electroanal Chem., (1985), 183, 1
- 33 E Laviron and L Roullier, J Electroanal Chem., (1980), 115, 65
- 34 D Ghesquiere, B Ban and C Chachaty, Macromolecules, (1977), 10, 743
- 35 R J Forster, Ph D Thesis, Dublin City University, (1990)
- A Glidle, A R Hillman and S Bruckenstein, J Electroanal Chem, (1991), 318,
 411

- 37 A R Hillman, M J Swann and S Bruckenstein, J Phys Chem., (1991), 95, 3271
- 38 A R Hillman, D C Loveday, M J Swann, S Bruckenstein and C P Wilde, J Chem Soc, Faraday Trans, (1991), 87, 2047
- 39 A R Hillman, D C Loveday and S Bruckenstein, J Electroanal Chem, (1991), 300, 67
- 40 J C Jernigan and R W Murray, J Am Chem Soc, (1987), 109, 1738
- 41 M E G Lyons, H G Fay, T McCabe, J Corish, J G Vos and A J Kelly J Chem. Soc Faraday Trans, (1990), 86, 2905
- 42 P Daum, J R Lenhard, D R Rolison and R W Murray, J Am Chem Soc, (1980), 102, 4649
- 43 R J Forster, J G Vos and M E G Lyons, *J Chem. Soc Faraday Trans*, (1991), 87, 3761
- 44 R J Forster and J G Vos, J Electroanal Chem, (1991), 314, 135
- 45 S Bruckenstein, C P Wilde, M Shay, A R Hillman and D C Loveday, J Electroanal Chem, (1989), 258, 457
CHAPTER 7

Concluding Remarks

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7.1. CONCLUDING REMARKS.

Redox polymers based on ruthenium and osmium poly(pyridyl) complexes have many desirable properties which make them ideally suited for fundamental studies of charge transport mechanisms within electrode-modifying layers. In all cases (with the exception of the ruthenium aquo complex in Chapter 6), the metallopolymers exhibit a reversible, single electron redox reaction, indicative of a surface-bound species. The polymer layers are stable for long periods in high concentrations of acid electrolyte, enabling small variations in experimentally determined parameters to be reproducibly observed. The redox polymers are easily prepared with a high degree of synthetic control and can be rigorously characterised to a high level of definition through comparison with the well documented chemistry of monomeric analogues. Many structural parameters for the polymers can be systemmatically and accurately varied, yielding materials of differing redox site loading, coordination sphere, metal centre, etc

In this work, particular emphasis is placed on the importance of the polymer layer morphology in determining charge transport rates. Surprisingly, the identity of the central metal atom is of fundamental importance in determining the physico-chemical characteristics of the entire layer. This is seen in the quite differing charge transport behaviour for the bis-substituted osmium polymer, $[Os(bipy)_2(PVP)_{10}]^{2+}$, and the analogous ruthenium material in Chapter 2. However, of greater importance, is the coordination sphere of the metal centre. For both osmium and ruthenium bis-substituted polymers, the rate of charge transport is insensitive to the electrolyte concentration. This is derived from the more open polymer structure due to the rigidity imposed on the polymer segments by this coordination.

For all redox polymers of this type, the dependence of the rate of charge transport on the nature of the contacting electrolyte is profound. The origins of this lie in the nature of

the polymer / electrolyte interaction Through the measurement of the resident layer mass using the EQCM, and the evaluation of film rigidity using impedance analysis, electrolyte dependent morphology changes have been studied for [Os(bipy)₂(PVP)₁₀Cl]+ polymer films

The polymer layer can be considered an anion-exchange membrane For counteranions which interact strongly with the fixed charged sites, eg ClO₄⁻, there is a decrease in the "free-ion" population of the polymer phase and, consequently, a decrease in the requirement for polymer solvation On the otherhand, for electrolytes which do not form close ion-pairs with the fixed sites of the polymer, eg pTSA, the levels of polymer solvation increase The solvation of polymer layers is therefore determined by the activity gradient established by the relative ion populations across the polymer layer / electrolyte interface

When polymers are solvated in a particular electrolyte they become more sensitive to the electrolyte concentration For $[Os(bipy)_2(PVP)_{10}Cl]$ + polymer films in pTSA, this gives rise to dramatic morphology changes in response to relatively small changes in the pTSA concentration At concentrations greater than *ca* 0 1 M, the activity of solvent within the system is reduced and the polymer layers are relatively compact. However, at pTSA concentrations less than *ca* 0 1 M, the osmotic transfer of solvent into the layer occurs, resulting in such an increase in polymer swelling that there is delamination of the polymer film from the electrode surface. In contrast, in HClO4 electrolyte, where the role of solvent is minimised, there is only a small expansion of the polymer matrix at low HClO4 concentrations

The evaluation of the resident layer mass of $[Os(bipy)_2(PVP)_{10}Cl]$ + polymer films as a function of electrolyte concentration enables the protonation of the uncoordinated pyridine moleties of the polymer backbone to be monitored. The mass increase accompanying protonation in both pTSA and HClO₄ accounts only for the counter-anion requirement for the maintenance of electroneutrality plus the demands for ion solvation

The existence of polymer phase pools of electrolyte is unlikely and the layers may be considered to be permselective However, at low pTSA concentrations, where extensive polymer swelling occurs this may not remain the case

One of the major factors in determining swelling of redox polymer films is the overall charge of the ionic membrane. This changes during redox switching, therefore changing the solvent requirement within the layer. In HClO4, the minimal role of solvent is reflected in the low solvent transfer accompanying the Os^{11/11} couple and the maintenance of a constant polymer morphology in both oxidation states. However, where a slightly expanded layer exists at low HClO4 concentrations (0 01 M to 0 1 M), the redox-induced solvent transfer increases. This represents the conflicting forces which determine the level of solvent transfer in HClO4. On the one hand there is the tendency for increased solvation of the oxidised layer. Opposing this is the tendency for the perchlorate anion to crosslink the polymer, thus restricting solvent movement and causing dehydration. It is only in the partially protonated layers at low HClO4 concentration, where the polymer phase perchlorate content is reduced, that the driving force for increased polymer solvation predominates. This occurs with dramatic results in 0.03 M HClO4, where solvent transfer is not only higher than in most other HClO4 electrolytes, but more significantly, it is much more facile.

In pTSA, the increased levels of polymer solvation in the reduced state are reflected in the increased solvent requirement accompanying polymer oxidation. However, because no restrictions on polymer expansion exist in this electrolyte, at all pTSA concentrations, the increased solvation of the layer in higher oxidation states results in further polymer swelling

One of the most important aspects of this work is the investigation of the dynamics of mass transfer on the time scales over which apparent charge transport diffusion coefficients are measured. In pTSA, using cyclic voltammetry, the greater solvation of

the layer facilitates the transfer of all mobile species, allowing for the concomitant transfer of the "thermodynamic" solvent requirement with the counter-anion However, in HClO₄, although the requirement for solvent transfer is significantly smaller, because of the more dehydrated polymer structure in this electrolyte, solvent is not transferred with the counter-anion and the rate of charge transport is reduced This is evidenced by the increased difficulty for solvent transfer and a corresponding decrease in $D_{ct}(CV)$ as the HClO₄ concentration increases from 0 03 M to 1 0 M

In previous studies of $[Os(bipy)_2(PVP)_{10}Cl]^+$, for potential step experiments, the apparent charge transport diffusion coefficient has been frequently observed to be greater than that obtained using cyclic voltammetry. The study of mass transfer accompanying redox switching provides a fresh insight into this observation. Using chronoamperometry, charge transport is measured in a region of the film close to the polymer layer / electrode interface. In this study, in both swelling and dehydrating electrolytes, a net transfer of mass occurs within 5 ms of pulse application. This demonstrates unequivocally that a source of counter-anion localised within the layer does not exist in significant quantities and that the high values of $D_{cl}(PS)$ which are observed, can not be attributed to such localised ion movement

Significantly, in more swelling electrolytes, the difference in $D_{ct}(CV)$ and $D_{ct}(PS)$ decreases In pTSA, the concomitant transfer of solvent with counter-anion occurs on all time scales In such circumstances, the equilibrium established for all mobile species is identical, and any difference between $D_{ct}(CV)$ and $D_{ct}(PS)$ may be attributed to differential polymer swelling, with a higher concentration of redox sites in the more compact base layer morphology

In HClO₄, however, the difference between $D_{ct}(PS)$ and $D_{ct}(CV)$ has been found to be much greater (in excess of two orders of magnitude) The mass transfer in HClO₄ on potential step time scales is insufficient to account for counter-anion motion, while at low HClO₄ concentrations, a net mass loss occurs This represents the utilisation of co-ion expulsion mechanisms in HClO₄ on short time scales Therefore, it is considered that when a significant difference in $D_{cl}(CV)$ and $D_{cl}(PS)$ exists, this reflects the establishment of different equilibria during redox switching on the differing time scales Such a scenario is only envisaged when there are restrictions to ion motion, such as those existing in materials of high redox site loading (as observed in previous studies), or those due to the compaction and crosslinking of the polymer layer by specific electrolyte interactions (as observed here in HClO₄)

This interpretation is confirmed for all redox polymers considered in this thesis For $[Ru(bipy)_2(PVP)_n]^{2+}$ no difference in $D_{ct}(PS)$ and $D_{ct}(CV)$ exists in any electrolyte, activation parameters are similar and the polymer structure is considered to be open, facilitating the transfer of all mobile species on all time scales. For both $[Os(bipy)_2(PVP)_{10}]^{2+}$ and $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$, the difference in $D_{ct}(PS)$ and $D_{ct}(CV)$ in swelling electrolytes is small (typically a factor of *ca* 5 to 10), activation parameters are similar on both time scales and the data indicate a common rate determining step. However, for these redox polymers in HClO4 electrolyte, the difference in $D_{ct}(PS)$ and $D_{ct}(CV)$ is a factor of *ca* 30 to 200 and activation parameters indicate a shift in the rate determining step from one of segmental polymer chain motion for cyclic voltammetric measurements, to one of counter-ion motion for chronoamperometry

In this thesis, the combined use of the EQCM, impedance analysis and conventional electrochemical measurements, results in a more complete picture of the many processes which may occur within electroactive polymer films. The powerful combination of simultaneous electrochemical and mass transfer measurements are most graphically illustrated in the evaluation of the proposed mechanism for the coupled proton and electron transfer within films of $[Ru(bipy)_2(PVP)_{10}(H_2O)]^{2+}$

In conclusion, the use of purely electrochemical quantities, D_{ct} , α and k^{0} , in conjunction with activation parameters, goes some way in elucidating the underlying

factors which affect charge transport in these systems Indeed, such electrochemical measurements may be considered a way for studying polymer structure through the use of "redox probes" However, techniques which directly probe the physical structure of the modifying layers are clearly advantageous. In this regard the EQCM has been shown to provide not only an evaluation of mass changes taking place, but, in conjunction with impedance analysis, also provides a means of obtaining a direct insight into the type of structure in which such mass changes would be expected to occur