Organic Phase Cyclopentadienylnickelthiolate Sensor System for Electrochemical Determination of Sulfur Dioxide

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Abstract
A series of cyclopentadienylnickelthiolate complexes, $[Ni(PBu_3)(\eta^5\text{-}C_5H_5)(SC_6H_4X\text{-}4)]$ (X = F, Cl, Br, NH_2), were shown to express stable reversible electrochemical properties even after formation of SO_2 adducts in organic phase consisting of argon purged CH_2Cl_2/0.1 M $[n\text{-}Bu_4N][BF_4]$. The formal potentials ($E^{\circ\prime}$) values of the compounds ranged from 265 to 431 mV/Ag-AgCl depending on the para substituent of the benzene thiolate ligand. Electrochemical, UV-vis and ^{1}H NMR spectroscopic analyses show that the formation of SO_2 adducts causes the perturbation of the electronic density of the nickel metal center, indicated by shifts in the $E^{\circ\prime}$ values of the $Ni^{II/III}$ redox couple that is dependent on SO_2 concentration. The detection limits of the resulting organic phase electrochemical gas sensor system was as low as 0.56 ppm SO_2 for the fluoro complex, while the linear range was as high as 700–2000 ppm SO_2 for the amino complex.

Keywords: Sulfur dioxide determination, Electrochemical sulfur dioxide sensor, Organic phase sulfur dioxide sensor, Cyclopentadienylnickelthiolate complex, Potentiometric SO_2 sensor

1. Introduction

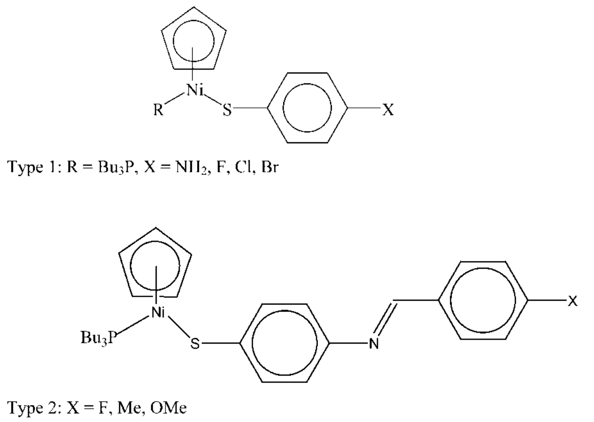
Environmental and health hazards associated with sulfur dioxide pollution mandate stringent monitoring of atmospheric sulfur dioxide in many countries [1]. A number of instrumental methods are available to monitor SO_2 levels in the environment. These include ultraviolet fluorescence [2], flame photometry [3] and ion chromatography [4,5]. These instrumental techniques require sample treatment steps that provide additional scope for error. Conductometric gas sensors have also been used for SO_2 detection [5–7]. However, most conductometric gas sensors rely on alterations (or modulation) in the electronic conductivity of the sensing layer, or change in the ionic conductivity of the electrolyte by interaction with the analyte.

Another SO_2 detection method that has been reported [8] is the use of electrochemical (or amperometric) gas sensor, which measures the current associated with electro-oxidation/reduction of the gas. In aqueous media, the oxidation of SO_2 at modified electrode results in the formation of sulfate ions through sulfite and bisulfite intermediates. This reaction is sluggish and requires high overpotential [9, 10]. In non-aqueous media, SO_2 is reduced to dithionate through a free-radical (SO_2^-) intermediate [11].

In this study we present an electrochemical method for the determination of SO_2 that does not involve SO_3^{2-}, HSO_3^{2-}, and SO_2^- intermediates. This method involves the complexation of SO_2 with electroactive metal thiolates, such as cyclopentadienylnickel thiolates, followed by the determination of the change in formal potential associated with the binding of SO_2. Complex formation between metal thiolates and SO_2 is very well documented [12–17]. The SO_2 adducts of the metal thiolate complex contain a generally weak sulfur–sulfur bond between the thiolate and SO_2 sulfur atoms which ensures reversible absorption of SO_2. One question that is yet to be answered is whether the SO_2 adducts are electroactive and stable enough for SO_2 determination. This paper contains preliminary studies of some cyclopentadienylnickelthiolates screened for application as organic phase electrochemical sensors for SO_2 that answers the above question. In order to assess the ability of cyclopentadienylnickelthiolates as electrochemical sensor systems for sulfur dioxide, two types of thiolato complexes (Scheme 1) were investigated. Cyclic and square wave voltammetry experiments were performed with each type of the nickel thiolate complexes before and after reaction with sulfur dioxide.

2. Experimental

All preparations were carried out in reagent grade solvents. Dichloromethane used for electrochemical experiments was refluxed twice over P_2O_5 for 24 h, distilled under nitrogen and stored over activated molecular sieves. Complexes $[Ni(PBu_3)(\eta^5\text{-}C_5H_5)(SC_6H_4X\text{-}4)]$ (X = F, Cl, Br, NH_2) [16, 18] and $[Ni(PBu_3)(\eta^5\text{-}C_5H_5)(SC_6H_4NC(H)C_6H_4X\text{-}4)]$ (X = F, Me, OMe) [19–22], were prepared as previously reported. All reactions were performed under a nitrogen atmosphere, but the air and moisture stable complexes that were formed were worked-up in air.


Type 1: R = Bu$_3$P, X = NH$_2$, F, Cl, Br

Type 2: X = F, Me, OMe

Scheme 1. Structures of complexes screened as SO_2 sensors materials.

^{1}H NMR spectra were run on a Varian Gemini 2000 spectrometer at 200 MHz and referenced internally to residual $CDCl_3$ at 7.26 ppm. Elemental analyses were carried out with a CARLO EBER CHN analyzer. The electrochemical measurements were performed with a BAS 50 W potentiostat. A conventional three-electrode cell system which was used consisted of a glassy carbon working electrode (1 mm diameter), Ag/AgCl reference electrode and a platinum wire auxiliary electrode. Prior to use, the glassy carbon electrodes were cleaned by successive polishing on aqueous slurries of 1 μm, 0.3 μm and 0.05 μm alumina powder, followed by thorough rinsing with deionised water and acetone. The experiments were carried out at room temperature under an argon atmosphere in an organic phase consisting of degassed dichloromethane containing 0.1 M tetrabutylammonium tetrafluoroborate [n-Bu_4N][BF_4] as supporting electrolyte. A 2 mM solution of cyclopentadienylnickelthiolate complex was used in all electrochemical determinations. Cyclic voltammetry experiments were carried out at a scan rate of 50 mV s^{-1}, under diffusion-limiting conditions. After performing the initial run under argon the working electrode was removed and polished, prior to the bubbling of SO_2 through the solution for 2 minutes. The voltammetry experiment was immediately repeated on the SO_2 saturated solution under the same conditions.

3. Results and Discussion

3.1. Type 1 Electrochemical SO_2 Sensors: [Ni(PBu_3)(η^5-C_5H_5)(SC_6H_4X-4)]

The formation of SO_2 adduct of the Type 1 complexes, [Ni(PBu_3)(η^5-C_5H_5)(SC_6H_4X-4)] (X = F, Cl, Br, NH_2), in the organic phase reaction medium was confirmed by ^{1}H NMR and UV-vis spectroscopy. All the Type 1 complexes formed stable SO_2 adducts in solution, initially observed by a distinct color change from a dark brown to a reddish color after bubbling excess SO_2 through the solutions. ^{1}H NMR spectrum showed that the cyclopentadienyl singlet attached to the Ni(II) center for PBu_3 ligand complexes, was observed at 5.15 ppm in the original spectrum, but shifted downfield to a value of 5.53 ppm, upon exposure to SO_2 . This was a deshielding effect as a result of a decrease in electron density around the nickel center.

Typical UV-vis spectra are shown in Figure 1 for [Ni(PBu$_3$)(η^5-C_5H_5)($SC_6H_4NH_2$-4)]. The UV-vis spectra show increases in absorption and shifts in absorption wavelength on the formation of SO_2 adduct of the complex. In the UV region (Fig. 1a), the absorption peaks of the complex at 260 and 320 nm were replaced by a large peak at 290 nm ($A_{(290\,nm)} \approx 2A_{(260\,nm)}$ and $4.5A_{(320\,nm)}$) after SO_2 adduct formation. These transitions in the UV region are ligand-based and indicate the attachment of SO_2 to a site on the ligand. In the visible region (Fig. 1b), the d – d transition of the Ni center in the complex occurs at about 400 nm. The wavelength of this transition shifts only slightly to about 390 nm ($A_{(390\,nm)} \approx 3A_{(400\,nm)}$) after adduct formation, indicating that it is most likely the SO_2 is not directly bonded to the metal and the electronic state of the metal is only affected secondarily.

Figure 2 shows typical voltammograms observed for Type 1 complexes in CH_2Cl_2 solvent medium containing 0.1 M [n-Bu_4N][BF_4] as electrolyte. Type 1 series of compounds exhibited quasi-reversible redox behavior before and after the formation of sulfur dioxide adducts. As shown in the data in Table 1, the ratio of the cyclic voltammetric anodic to cathodic peak currents ($I_{p,a}/I_{p,c}$) was approximately unity in both the thiolate complexes and their sulfur dioxide adducts. The peak separation ΔE_p ($\Delta E_p = E_{p,a} - E_{p,c}$) values ranged from 57 mV for [Ni(PBu_3)(η^5-C_5H_5)(SC_6H_4F-4)] to 119 mV for [Ni(PBu_3)(η^5-C_5H_5)(SC_6H_4Cl-4)], as would be expected for quasi-reversible diffusion controlled electrochemical processes. However, within limits of experimental error, the ΔE_p values for each compound remained essentially the same before and after SO_2 adduct formation. This shows that the Faradaic process being observed in both SO_2-free and SO_2-containing compound is the same, namely the diffusion-controlled $Ni^{II/III}$ electrochemistry of the [Ni(PBu$_3$)(η^5-C_5H_5)(SC_6H_4X-4)] (X = F, Cl, Br, NH_2). The standard rate constant (k°) value of a typical SO_2-adduct (X =

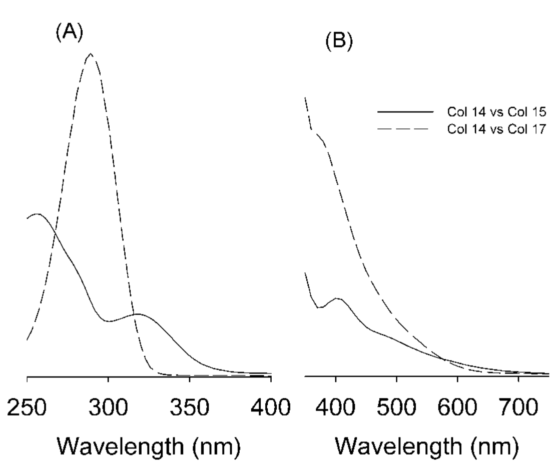


Fig. 1. UV-vis spectra for [Ni(PBu_3)(η^5-C_5H_5)($SC_6H_4NH_2$-4)]. A) UV region showing the ligand-based transitions. B) Visible region showing the metal-based transition.

NH$_2$) calculated by the analysis of the Tafel region of the cyclic voltammogram is 2.54×10^{-9} cm s^{-1}. This low k° value is in agreement with what has been reported for electron transfer reaction at the electrode that is coupled to other chemical and physical processes [23]. In the present study the reversible binding of SO$_2$ is coupled to [Ni(PBu$_3$)(η^5-C$_5$H$_5$)(SC$_6$H$_4$NH$_2$-4)] electrochemistry.

As shown in Table 1, the formal potentials of the SO$_2$ adducts were generally higher than for the thiolate complexes by up to 60 mV/Ag-AgCl for the case of [Ni(PBu$_3$)(η^5-C$_5$H$_5$)(SC$_6$H$_4$NH$_2$-4)], which is indicative of the perturbation of the redox properties of the thiolate complex by the binding of SO$_2$. The magnitude of formal potential shift ($E^{\circ\prime}_{\text{shift}}$) varied with the substituent on the thiolate ligand. The NH$_2$ ($E^{\circ\prime}_{\text{shift}} = 57$ mV) and F ($E^{\circ\prime}_{\text{shift}} = 60$ mV) substituents exhibited the largest shift in formal potential after SO$_2$ binding. The data suggests a relationship between the electron withdrawing ability of the substituent and the formal potential of the complex. This was verified by the analysis of the Hammett constants of the substituents. Figure 3 shows that the $E^{\circ\prime}$ value of the Type 1 compounds varied in accordance with the value of the Hammett constant (σ_p) of the substituent in the para-position of the thiolate ligand. The formal potentials of the SO$_2$ adduct increase in the order Br $\cong$ Cl $>$ F $>$ NH$_2$. It is important to emphasis that Br and Cl substituents which have the same σ_p value of 0.23, show remarkable similarity in their $E^{\circ\prime}$ values for the SO$_2$ adducts ($E^{\circ\prime}_{\text{Br}} = 413$ mV and $E^{\circ\prime}_{\text{Cl}} = 412$ mV) even though the formal potentials of their SO$_2$-free analogues differ by up to 47 mV. This behavior of Br- and Cl-substituted SO$_2$ adducts confirms the observed linear relationship between σ_p and $E^{\circ\prime}$ as shown in Figure 3. It has been proposed that SO$_2$ adducts of [Ni(PBu$_3$)(η^5-C$_5$H$_5$)(SC$_6$H$_4$X-4)] have the SO$_2$ bonded to the sulfur of the thiolate ligand [16]. Since the value of σ_p is a measure of the electron-withdrawing ability of the substituent in the para-position of the benzene ring to which the sulfur donor atom is attached [24], the increased formal potential of the SO$_2$ adducts confirms the behavior of SO$_2$ as a Lewis acid that binds to the thiolate sulfur by accepting electrons. This bonding mode in turn reduces electron density at the metal center, hence the increase in formal oxidation potentials of SO$_2$ adducts.

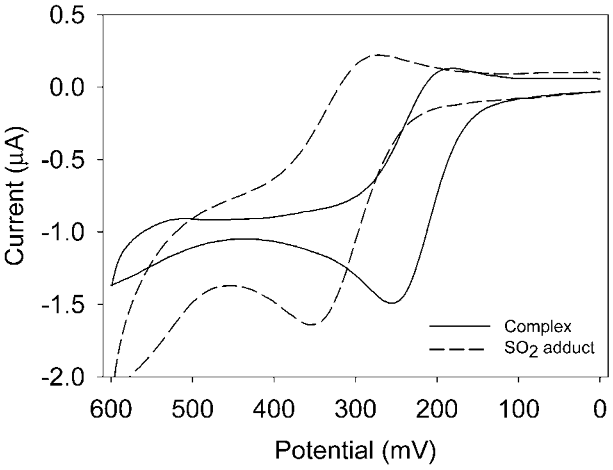


Fig. 2. Cyclic voltammograms for the complex [Ni(PBu$_3$)-(η^5-C$_5$H$_5$)(SC$_6$H$_4$NH$_2$-4)] and its SO$_2$ adduct.

3.2. Type 2 Electrochemical SO$_2$ Sensors: [Ni(PBu$_3$)(η^5-C$_5$H$_5$)(SC$_6$H$_4$NC(H)C$_6$H$_4$X-4)]

Type 2 complexes represent a modification of Type 1 compounds in which the substituent on the thiolate ligand has an imine functionality. Typical voltammograms of the Type 2 compounds are shown in Figure 4 for [Ni(PBu$_3$)-(η^5-C$_5$H$_5$)SC$_6$H$_4$NC(H)C$_6$H$_4$CH$_3$-4] and its SO$_2$ adduct. Electrochemical data for F, OCH$_3$ and CH$_3$ substituents of the SO$_2$-free complex are contained in Table 1. The compounds exhibit the quasi reversible electrochemistry ($I_{p,a}/I_{p,c}$ values are approximately unity and the ΔE_p values for X = F and OCH$_3$ are within 59 ± 6 mV) of a diffusion controlled system, as has been reported for related compounds [19]. The formal potential values of the complexes are 345, 345 and 351 mV/Ag-AgCl for the F, OCH$_3$ and CH$_3$ substituents, respectively. Unlike Type 1 compounds, the

Table 1. Electrochemical data for cyclopentadienylnickel thiolate complexes screened for SO$_2$ adduct formation.

Sensor material	$E_{p,a}$ (mV)	$E_{p,c}$ (mV)	ΔE_p (mV)	$E^{\circ\prime}$ (mV)	$I_{p,a}/I_{p,c}$
Type 1 Complexes and SO$_2$ Adducts					
[Ni(PBu$_3$)(η^5-C$_5$H$_5$)(SC$_6$H$_4$NH$_2$-4)]	283	223	59	256	1.50
[Ni(PBu$_3$)(η^5-C$_5$H$_5$)(SC$_6$H$_4$NH$_2$-4)]SO$_2$	342	283	59	313	1.34
[Ni(PBu$_3$)(η^5-C$_5$H$_5$)(SC$_6$H$_4$F-4)]	359	302	57	331	1.07
[Ni(PBu$_3$)(η^5-C$_5$H$_5$)(SC$_6$H$_4$F-4)]SO$_2$	422	359	63	391	1.22
[Ni(PBu$_3$)(η^5-C$_5$H$_5$)(SC$_6$H$_4$Br-4)]	434	333	101	384	1.08
[Ni(PBu$_3$)(η^5-C$_5$H$_5$)(SC$_6$H$_4$Br-4)]SO$_2$	461	364	97	413	1.15
[Ni(PBu$_3$)(η^5-C$_5$H$_5$)(SC$_6$H$_4$Cl-4)]	488	374	114	431	0.91
[Ni(PBu$_3$)(η^5-C$_5$H$_5$)(SC$_6$H$_4$Cl-4)]SO$_2$	471	352	119	412	1.08
Type 2 Complexes					
[Ni(PBu$_3$)(η^5-C$_5$H$_5$)(SC$_6$H$_4$NC(H)C$_6$H$_4$F-4)]	376	313	64	345	1.10
[Ni(PBu$_3$)(η^5-C$_5$H$_5$)(SC$_6$H$_4$NC(H)C$_6$H$_4$OCH$_3$-4]	354	297	57	326	1.04
[Ni(PBu$_3$)(η^5-C$_5$H$_5$)(SC$_6$H$_4$NC(H)C$_6$H$_4$CH$_3$-4]	369	332	37	351	1.01

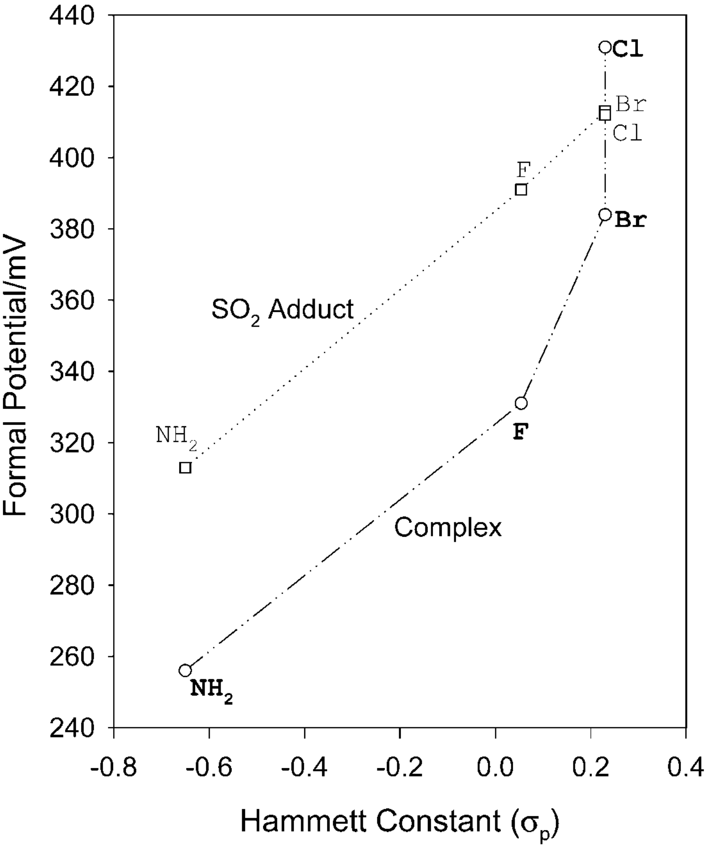


Fig. 3. The dependence of the formal potentials of $[Ni(PBu_3)(\eta^5\text{-}C_5H_5)(SC_6H_4X\text{-}4)]$ ($X = NH_2$, F, Cl, Br) complexes and SO_2 adducts on the Hammett constants of the para-substituents on the thiolate ligand.

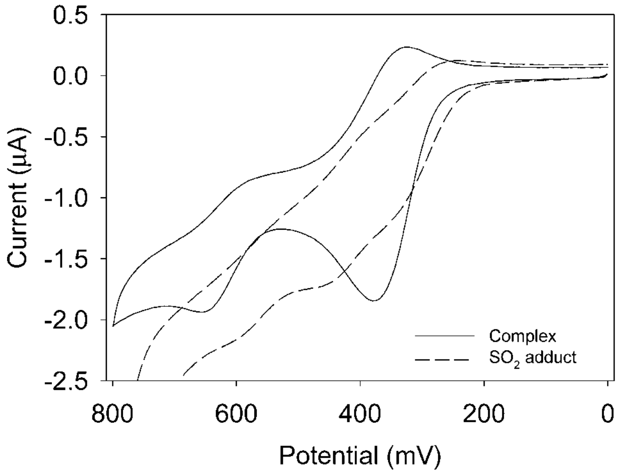


Fig. 4. Cyclic voltammograms for the complex $[Ni(PBu_3)(\eta^5\text{-}C_5H_5)(SC_6H_4NC(H)C_6H_4CH_3\text{-}4]$ before and after bubbling of SO_2.

electrochemistry of the SO_2 adducts depicts the coupling of a chemical reaction to electron transfer process. The CV's of $[Ni(PBu_3)(\eta^5\text{-}C_5H_5)(SC_6H_4NC(H)C_6H_4CH_3\text{-}4)]$ before and after addition of SO_2 confirmed that the SO_2 products do not form stable SO_2 adducts. Time dependent ^{1}H NMR experiments showed that the cyclopentadienyl singlet, originally at 5.27 ppm, shifted as expected to 5.53 ppm 20 min after bubbling SO_2. Subsequently, the peak at 5.53 ppm was replaced by a new aldehyde peak at 9.99 ppm indicative of the decomposition of the SO_2 adduct. Type 2 series of compounds were therefore found to be unsuitable as electrochemical (potentiometric) SO_2 sensor materials that would be based on well-defined electrochemistry of both the complexes and their SO_2 adducts. However, this class of compounds could still be useful as amperometric SO_2 sensor materials.

3.3. Quantifying SO_2 Uptake by Nickel Thiolate Complexes

Type 1 complexes were used in the quantitative determination of SO_2. Experiments were performed by reacting 2 mM cyclopentadienylnickelthiolate (in argon degassed CH_2Cl_2 solvent medium containing 0.1 M $[n\text{-}Bu_4N][BF_4]$) with varying amounts of gaseous SO_2, measured with a gas tight syringe. Concentration of SO_2 gas was calculated in parts per million (ppm) by assuming ideal gas conditions. The performance of the sensor system depended on the complex used. For example, the $[Ni(PBu_3)(\eta^5\text{-}C_5H_5)(SC_6H_4NH_2\_4]$ sensor system gave a linear relationship between electrochemical potential and the amount of SO_2 from 700 to 2000 ppm with r^2 value of 0.993. The sensitivity of the complex, calculated as the slope of linear calibration plot, was 0.02 mV ppm^{-1}. An SO_2 detection limit of 25 ppm was estimated for the nickel thiolate sensor system from the signal to noise ratio. On the other hand the $[Ni(PBu_3)(\eta^5\text{-}C_5H_5)(SC_6H_4F\text{-}4)]$ sensor system had a low saturation point resulting in a short linear range (0 – 20 ppm) with r^2 values of 0.989. The fluoro complex exhibited greater sensitivity than its amino analogue with a slope of 0.88 mV ppm^{-1}. A detection limit of 0.56 ppm was calculated for the $[Ni(PBu_3)(\eta^5\text{-}C_5H_5)(SC_6H_4F\text{-}4)]$ sensor system.

4. Conclusions

Both the SO_2-free and SO_2 adducts of the Type 1 series of cyclopentadienylnickel thiolate complexes, $[Ni(PBu_3)(\eta^5\text{-}C_5H_5)(SC_6H_4X\text{-}4)]$, exhibited stable reversible electrochemistry in CH_2CH_2 used as organic phase. However, a shift in formal potential upon the formation of SO_2 adduct showed that the compounds were suitable for application as organic phase potentiometric SO_2 sensor materials. The linear range for free SO_2 determination with the cyclopentadienylnickelthiolate sensor system in organic phase range from 0 – 20 ppm to 700 – 2000 ppm, for the flouro and amine derivatives, respectively. A linear range value of 2 – 75 ppm (free SO_2) been reported for spectrophotometric method in HCl solution [25]. What this means is that the cyclopentadienylnickelthiolate complexes can be tailored to exhibit high or low capacities for SO_2 depending on the nature of the para substituent of the thiolate benzene ring. Also the detection limits of the organic phase SO_2 sensor system can be as low as 0.56 ppm for the fluro or as high as 25 ppm for the amino substituents. The detection limit of the Type 1 fluoro substituted cyclopentadienylnickelthiolate complex compares favorably with the value of 1.0 ppm for free SO_2 determined spectrophotmetrically [25]. Within limits of experimental error, CO_2, N_2 and O_2 do not interfere with the detection of SO_2 with the sensor system. The effect of nitrogen oxides on the sensor was not covered in this study.

5. Acknowledgement

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6. References

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