PHYSICOCHEMICAL STUDIES OF CLAY-ORGANIC INTERACTIONS

by

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ABSTRACT

The acidity of Al-, Cr(III)- and Fe(III)-exchanged montmorillonite was characterised utilising the bases pyridine and n-butylamine which occupy three different sites in the interlamellar space:
(i) physisorbed base (ii) base bound to Lewis sites and (iii) protonated base. The Al- and Cr(III)-forms were found to be very temperature stable whereas the Fe(III)-form was not. Isothermal gravimetry in the temperature range 18 - 105 °C was used to measure the rate of sorption of three alcohols, methanol (MeOH), propan-2-ol (i-PrOH), and 2-methylpropan-2-ol (t-BuOH), and three cyclic ethers, 1,4-dioxan (DIOX), tetrahydropyran (THP) and tetrahydrofuran (THF), from the vapour phase, onto the three cation exchanged forms. The rate of alcohol uptake increased as t-BuOH $<$ i-PrOH $<$ MeOH with integral diffusion coefficients, $\bar{D}$, ranging from $3.0\text{-}16.0 \times 10^{-17}\ m^{2}s^{-1}$. The sorption rate for i-PrOH and t-BuOH following the sequence Fe(III) $<$ Cr(III) $<$ Al whereas the cyclic ethers follow the sequence Cr(III) $<$ Fe(III) $<$ Al. Activation energies for all the solvents lie between 2.0 kJ mol^{-1} and 13.0 kJ mol^{-1}. In the adsorption of cyclic ethers from binary liquid mixtures with methanol the isotherm type is dominated by the binary mixture whereas the amplitude, which follows the sequence DIOX $<$ THP $<$ THF is further influenced by the exchanged cation. Altering the level of hydration shifts the azeotropic point in favour of the cyclic ethers DIOX and THP, but only affected the amplitude of the THF/MeOH system.

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CHAPTER 1.

CLAY MINERALS: STRUCTURES AND PROPERTIES.

1.1 Introduction

Although the uses of clay minerals are numerous it has not been possible until recently to adequately analyse the nature of the fundamental structure of most clay materials. With the advent of a large number of instrumental techniques, such as infra-red spectroscopy, x-ray diffraction and modern methods of elemental analyses, for example atomic absorption spectroscopy, a clearer picture of the structure and properties of the different clay minerals has been produced.[1] With the growing amount of information concerning the clay minerals a greater understanding of the relationship between structure and properties may be established.[2] This leads to the conclusion that before any useful information, concerning the properties of any clay material, can be obtained a knowledge of the clay structure is imperative.

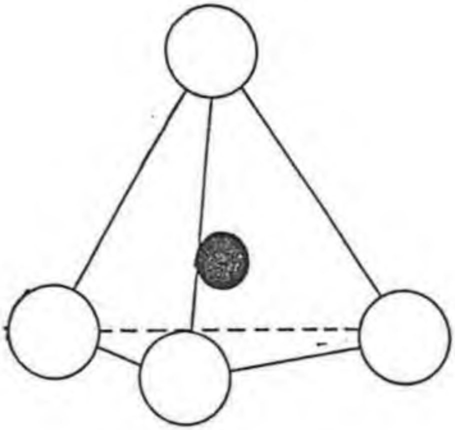
1.2 Basic Structure of Clay Minerals.

The basic structure of clay minerals consists of two major units. These are a two-dimensional array of $Si(O,OH)_4$ tetrahedra, and a two-dimensional array of either $M_2(OH)_6$ or $N_3(OH)_6$ where M is a trivalent cation and N is a divalent cation. These form layers or sheets and are superimposed, by condensation, in different ways to form the various clay mineral structures, hence their name 'layer silicates'.[1]

The tetrahedral layer consists of units which may be described, assuming no distortions, as follows: the tetrahedron is formed by four oxygen atoms or hydroxyl groups with a silcon atom at its centre (Fig.1a). These tetrahedral units form a hexagonal group by corner sharing of a basal oxygen. This may be repeated indefinitely to form one sheet. Thus this sheet is referred to as the 'tetrahedral layer' or 'silica layer'.[1]

The second unit, called the octahedral layer normally consists of a M (or N) cation, which is usually Mg or Al, directly co-ordinated to six oxygen atoms or hydroxyl groups which form an octahedron. The oxygen or hydroxyls form two planes, one above and one below the cation (Fig.1b). The symmetries of both the octahedral and tetrahedral layers allow the sharing of oxygen atoms between the sheets. The apical oxygen atom protruding from the tetrahedral sheet, pointing into the layer, is shared by the octahedral sheet. This may occur between one octahedral and one tetrahedral sheet as in the 1:1 layer minerals, for example kaolinite (Fig.1c), or may occur between one octahedral sheet and two tetrahedral sheets as in the 2:1 layer minerals, for example montmorillonite (Fig.1d). Ideally the layers are "continuous" in the a and b directions and are stacked on the top of one another in the c direction.[1]

Fig. 1a.



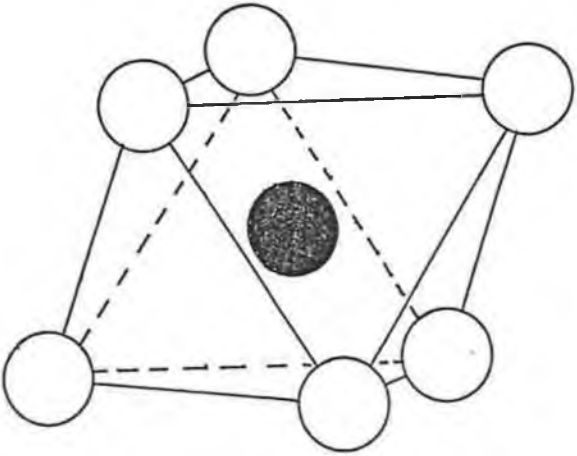
A single silica tetrahedron unit.

● SILICON

● ALUMINIUM

○ OXYGEN

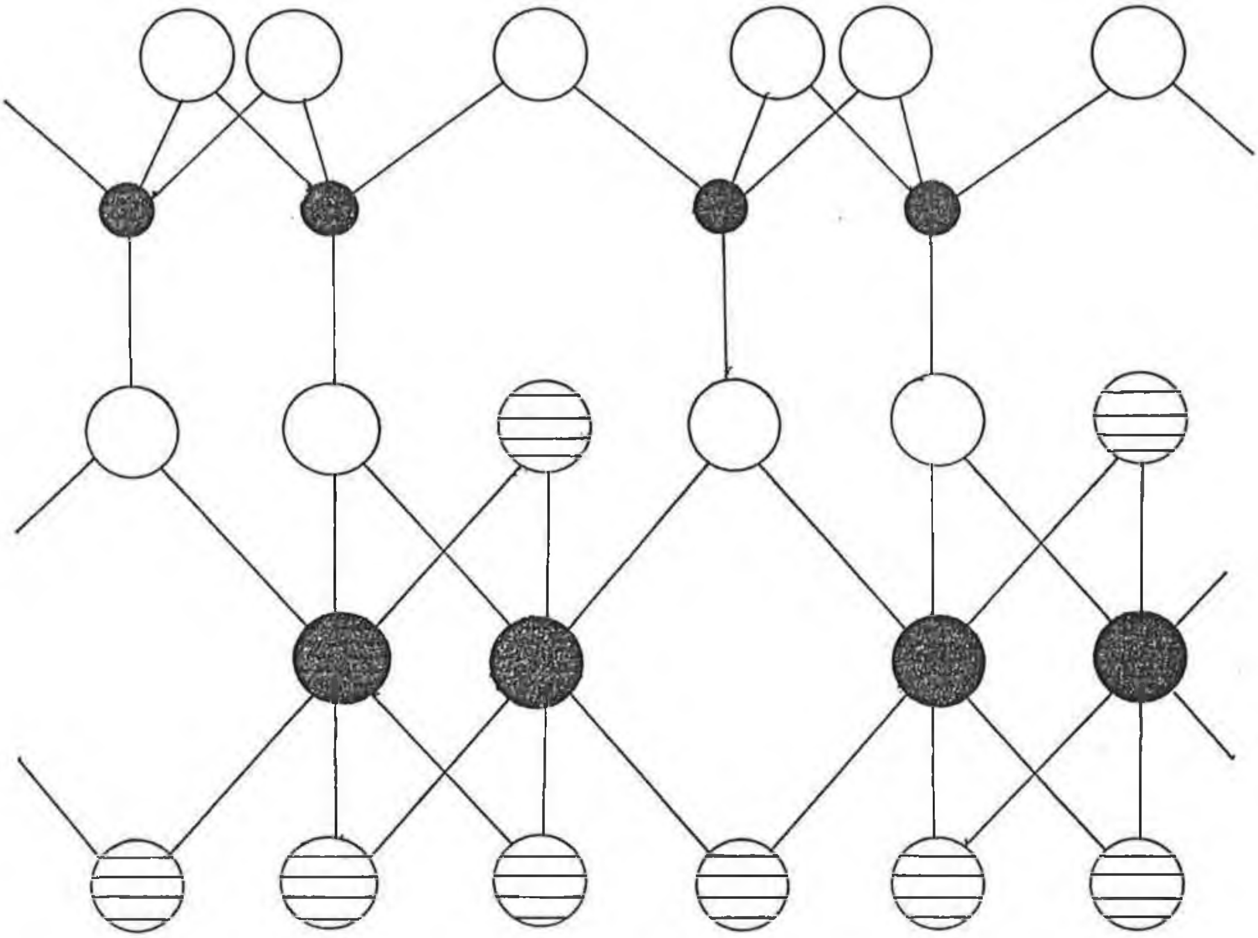
Fig. 1b.



A single alumina octhedron unit.

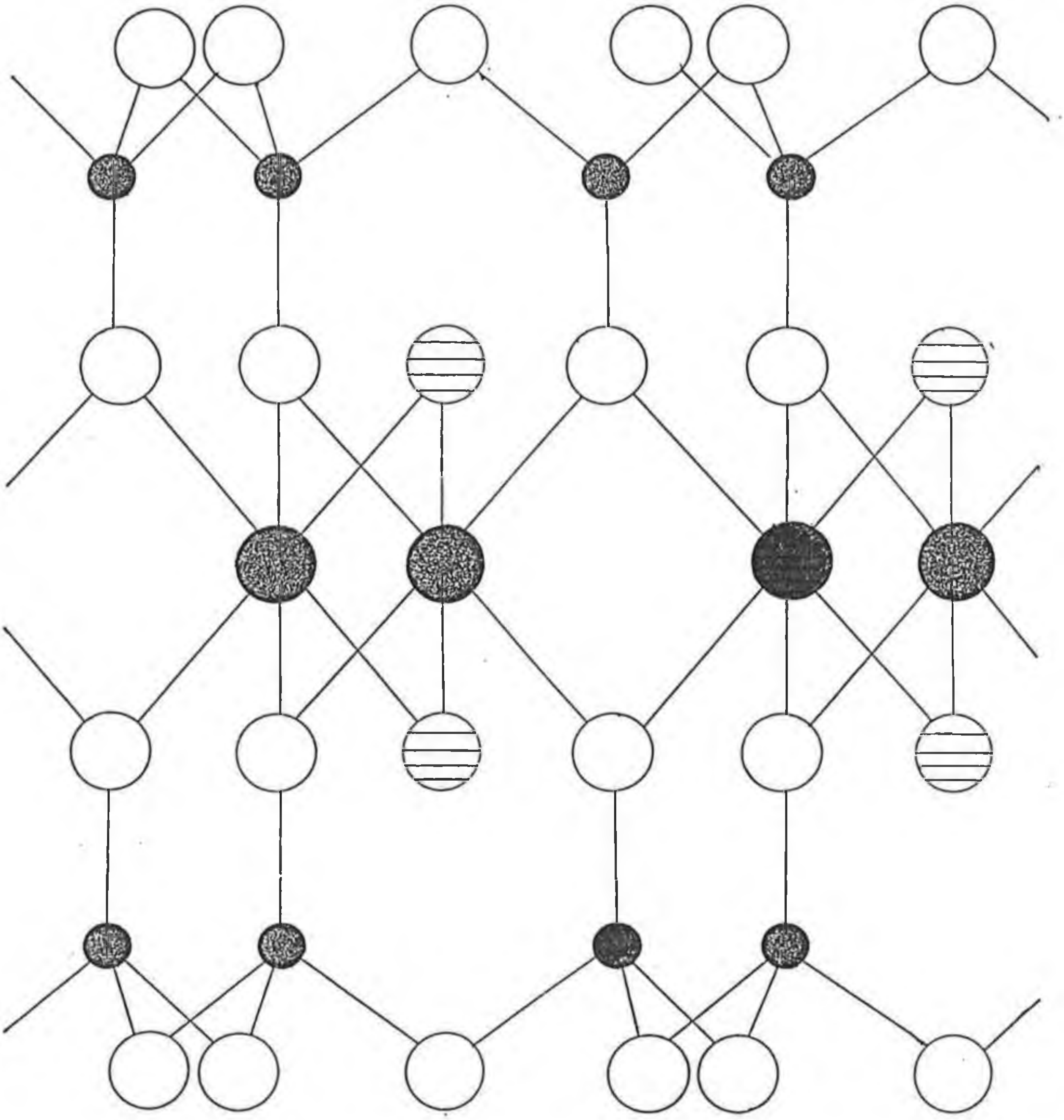
▤ HYDROXYL

Fig. 1c.



Diagrammatic sketch of the structure of a kaolinite layer projected onto the 'a' plane.

Fig. 1d.



Diagrammatic sketch of the structure of a montmorillonite layer projected onto the 'a' plane.

○ OXYGEN

● ALUMINIUM

▤ HYDROXYL

• SILICON

The layer silicates may also be subdivided into di- and tri-octahedral forms. In the ideal cases, the octahedral layers contain only Al or Mg cations. However, due to the valency of the Al cation, the layer only requires 2 out of 3 octahedral cation sites to be filled in a clay containing only Al cations. This is referred to as a di-octahedral mineral, (D). If, on the other hand, all the Al is replaced by Mg, all 3 octahedral cation sites need to be filled, thus a tri-octahedral (T) mineral is formed.[2] Therefore in the ideal cases all the charges are balanced and the minerals are electrically neutral. The formula units in these cases are, for the di-octahedral mineral, $Al_2\ Si_4\ O_{10}\ (OH)_2$, and for the tri-octahedral mineral, $Mg_3\ Si_4\ O_{10}\ (OH)_2$.

However, since the clay minerals occur in nature their formation is usually under non-ideal conditions. This leads to isomorphous substitution within the clay layer, that is the replacement of Si and/or octahedral cations by cations of similar size but different, usually lower, valency.[1] This substitution in turn leads to a net negative charge, or positive charge deficiency, on the clay layer. To counteract this charge imbalance the clay layers separate and sorption of exchangeable cations occurs within the space between the layers (for the discussion of cation exchange see section 1.4.2). The amount as well as the site of isomorphous replacement influences the surface properties, for example swelling in water, of the layer silicates since they determine the surface density of charge as well as the cation-silicate layer attraction. The charge per formula unit, x, is thus an important parameter which enters into the classification of the layer silicates.[1]

1.3 Classification of Layer Silicates.

The charge on the aluminosilicate layer is widely used as a means of classification within the main types of structures and these are presented here in order of increasing charge per formula unit, x.

1.3.1 The 1:1 Type Minerals.

Almost no substitution occurs in this group thus the layers are electrically neutral. The main difference between various species in this group is a different stacking geometry of the clay layers. The minerals in this group do not expand in water and the interactions between the different layers consist mainly of van der Waal's forces and a certain degree of hydrogen bonding. There is a small but determinable cation exchange capacity on these clay minerals which is attributed to the adsorption of cations on the external surfaces of the stacked layers because little expansion of the clay layers occurs in the c direction and only then in the presence of strongly polar solvents e.g. Hydrazine and NMF. Clay minerals of this type are kaolinite, $Al_2 Si_2 O_5 (OH)_4$,
which is a dioctahedral mineral and chrysotile,

$Mg_3\ Si_2\ O_5\ (OH)_4$, which is trioctahedral.

1.3.2 The 2:1 Type Minerals.

The next type of layer silicates are the 2:1 type minerals. There are numerous examples of this type of mineral and because of their varying properties they have received the most attention of any type of clay mineral.

In this main group there are a number of different sub-groups, each of which may be identified by the different layer charge.

Pyrophyllite-Talc group.

There is no layer charge in this sub-group since isomorphous substitution does not occur and therefore no charge balancing interlayer cation is required, the charge per formula unit, x, is 0. In the absence of cation adsorption the introduction of water or organic molecules between the layers is a difficult process. An example of a dioctahedral clay mineral in this sub-group is pyrophyllite, $Al_2\ Si_4\ O_{10}\ (OH)_2$, and that of a trioctahedral one in this sub-group is talc, $Mg_3\ Si_4\ O_{10}\ (OH)_2$.

Smectite group.

The structures of the layer silicates in this sub-group are similar to the pyrophyllite-talc sub-group except that isomorphous substitution occurs. The charge per formula unit, x, is between 0.25 - 0.6 and arises from both octahedral and tetrahedral substitution. The exchangeable cations sorbed at the interlamellar surface are readily replaced causing a separation of layers between which adsorption of polar liquid or vapour molecules may occur, the swelling of these minerals has been widely reported.[1,2] Examples of clay minerals in this sub-group are, in the dioctahedral case, montmorillonite, assuming Na is the exchangeable cation, $Na_{0.3}\ (Al_{1.7}\ Mg_{0.3})\ Si_4\ O_{10}\ (OH)_2$, and in the trioctahedral case saponite, with a formula of $Na_{0.3}\ Mg_3\ (Si_{3.8}\ Al_{0.3})\ O_{10}\ (OH)_2$.

Vermiculite group.

The structures of the clay minerals in this sub-group are similar to the smectite group. These clays have a higher charge per formula unit, x, of about 0.6 - 0.9 which arises solely from isomorphous replacement in the tetrahedral sheet i.e. replacement of Si by Al. Due to the greater charge deficiency compared to the smectites the separation of layers is more difficult in this sub-group but sorption does occur in the interlayer space.[1] Examples of clay minerals in this sub-group, with Mg in the exchange position, are dioctahedral vermiculite $Mg_{0.3}\ Al_2\ (Si_{3.4}\ Al_{0.6})\ O_{10}\ (OH)_2$ and trioctahedral vermiculite $Mg_{0.3}\ Mg_3\ (Si_{3.4}\ Al_{0.6})\ O_{10}\ (OH)_2$.

Illite group

With a charge per formula unit, x, of approximately 0.8 the illite sub-group have the next highest layer charge. With such a high charge on the layer the adsorbed cations are strongly bound to the basal surface therefore intercalation is extremely difficult.[1] Examples of clay minerals in this sub-group are, using K as the interlayer cation, dioctahedral illite $K_{0.8}\ Al_2\ (Si_{3.2}\ Al_{0.8})\ O_{10}\ (OH)_2$ and trioctahedral illite $K_{0.8}\ Mg_3\ (Si_{3.2}\ Al_{0.8})\ O_{10}\ (OH)_2$.

Mica group.

Once again this sub-group has a similar structure to the smectites but there is a greater amount of isomorphous replacement in the layers. With a charge per formula unit, x, of about 1.0 the adsorbed interlayer cations are held very strongly to the surface making substitution extremely difficult and intercalation seldom occurs. Again with K as the exchangeable cation examples of clays in this group are, muscovite, $K\ Al_2\ (Si_3\ Al)\ O_{10}\ (OH)_2$, which is a dioctahedral layer silicate and, phlogopite $K\ Mg_3\ (Si_3\ Al)\ O_{10}\ (OH)_2$, a trioctahedral layer silicate.

Brittle Mica group.

The layer silicates of this sub-group are similar to the micas in structure except that there is a higher level of isomorphous replacement leading to a higher charge per formula unit, x, which is about 2.0 . The charge deficiency lies mainly in the tetrahedral layer. Again the interlamellar cations are so strongly held that substitution does not occur and swelling is very rare. Some clay minerals of this type, with Ca in the exchange position, are margarite, $Ca\ Al_2\ (Si_2\ Al_2)\ O_{10}\ (OH)_2$, which is dioctahedral and xanthophyllite, $Ca\ Mg_3\ (Si_2\ Al_2)\ O_{10}\ (OH)_4$, which is trioctahedral.

1.3.3 The Modified 2:1 Type Minerals.

Chlorite group.

This sub-group is formed by layers of alternate mica-like and brucite-like sheets. The mica layer is usually unbalanced by substitution of Al for Si but this deficiency is counteracted by an excess charge in the brucite layer. Various members of this sub-group differ from each other in the type and amount of substitutions within the layers. The bonding is partly electrostatic because of substitutions within the lattice and partly due to hydrogen bonding between pairs of adjacent oxygen atoms in the mica layer and hydroxyl ions in the brucite layer. The charge per formula unit, x, is between 0.5 and 1.5, but the range may be wider depending on the modification of the layers. Some examples of this type of clay mineral are donbassite $Al_4\ Si_{2.5}\ O_{11}\ (H_2O)_{3.5}$, which is dioctahedral, and clinoclore, $Mg_6\ Si_4\ O_{10}\ (OH)_3$,which is trioctahedral.

1.4 Montmorillonite

It may be seen from the previous discussion that only certain types of clay minerals have the ability to swell and intercalate both water and organic molecules. As a potentially good clay catalyst the surface area available to the reactants must be at a maximum, therefore only certain clay minerals have received attention[3] in this area. Since the research work carried out here concentrated on a particular clay mineral, i.e. montmorillonite, this layer silicate will be discussed in further detail.

1.4.1 Structure.

Montmorillonite, a member of the smectite group is derived from the ideal pyrophyllite-talc structure by substitution of certain atoms within the clay layer. These are (i) the replacement of the Al by other cations (e.g. Mg, Fe(II) or Fe(III)) in the octahedral positions and (ii) less frequently of Si by Al in the tetrahedral positions.

The generally accepted structure of montmorillonite was first proposed by Hofmann, Endell and Wilm,[4] with modifications made by Maegdefrau and Hoffmann,[5] Hendricks[6] and Marshall[7] (Fig.1d). According to this structure montmorillonite is a 2:1 type clay mineral which has a positive charge deficiency due to the isomorphous substitution. To compensate for this isomorphous substitution cations are sorbed between the layers and consequently water or other polar solvents may enter between the unit layers causing the lattice to expand in the c direction.[1] The c direction in montmorillonite is not fixed but varies from about 9.6Å in the totally dehydrated form to complete separation in some cases.[1]

Charge imbalance in either basic units may be compensated for in part, but only in part, by substitution in the other basic units of the layer or by substitution of hydroxyl for oxygen. It is significant that the substitutions within the lattice always result in about the same net charge (about 0.33 - 0.45 per formula unit i.e. 0.6 - 0.9 per unit cell) on the lattice. The negative charge is then, as explained earlier, balanced by exchangeable cations being taken up between the unit layers and around the edges. The location of these intercalated cations can be assumed to be in close proximity to the negative charge although the actual position depends on the valency, size and level of hydration of the exchangeable cation, and also the level of substitution within the lattice. In the case of monovalent cations they would be associated with the hexagonal hole above or below the substitution site.[8] However, the di- and trivalent cations would approach the hexagonal hole nearest one negative charge, but unlike the monovalent cations, are readily hydrated in the presence of water thus leaving the hole.[9]

1.4.2 The Cation Exchange Capacity (C.E.C.).

Clay minerals have the ability to sorb certain cations and anions which may be replaced by other cations or anions by treatment with those ions in solution. Although this cation exchange phenomenon has been known for hundreds of years it is only recently that any systematic studies have been carried out.[10] Even so the quantity of information for cation exchange is much greater than for anion exchange and the present work concerns the former.

The exchangeable cations are held around the outside of the silica-alumina clay-mineral structural unit, and the exchange reaction generally does not affect the structure of the silica-alumina packet.[1] The cation exchange capacity of clays is measured in terms of milliequivalents per gram or more frequently per 100 grams of clay. The factors influencing the cation exchange capacity are discussed in the next section. However, a much wider discussion of cation exchange and its importance in numerous fields of study is given by Grim.[1]

1.4.3 Cation Exchange Sites.

The cation exchange capacity of a clay arises from the combination of three types of exchange site.

(a) Broken bonds.

Broken bonds around the edges of the silica-alumina sheets give rise to a charge deficiency resulting in the adsorption of cations. The number of broken bonds and hence the exchange capacity due to them would decrease as the particle size increases. In montmorillonites broken bonds are responsible for about 20% of the cation exchange capacity. In kaolinite minerals, on the other hand, broken bonds are probably the major cause of cation exchange capacity. The broken bonds tend to be on non-cleavage surfaces hence they are parallel to the c-axis of montmorillonites.

(b) Lattice Substitution.

Lattice substitution or isomorphous substitution of trivalent aluminium for tetravalent silicon in the tetrahedral sheet and of lower valency ions, particularly magnesium, for the trivalent aluminium in the octahedral sheet can be a major contributor. Sometimes such substitutions are balanced by other lattice changes for example a hydroxyl replacing an oxygen, but frequently they are balanced by adsorbed cations. Exchangeable cations resulting from lattice substitutions are usually to be found on the cleavage surfaces i.e. the basal surfaces. Substitution in the tetrahedral sheet is much closer to the exchangeable cation than substitution in the octahedral sheet, therefore it would be expected that the cations held because of the former substitutions would be bonded by a stronger force leading to these cations being harder to exchange. This type of substitution within the lattice accounts for about 80% of the total cation exchange capacity of expandable clays.

(c) The hydrogen of exposed hydroxyls.

The hydrogen of exposed hydroxyls may be replaced by a cation which may be exchangeable. However, this seems unlikely since these hydrogens would be tightly bonded and hence, in the main, not replaceable. This cause of cation exchange would be important for kaolinite type minerals because of the presence of the sheet of hydroxyls on one side of the clay layer, but is of little importance for montmorillonites.

1.4.4 Position of the Exchangeable Cation.

As previously mentioned the position of the cation depends on both the charge it is satisfying and on the valency of the cation. If the cation is held by a broken bond then it will be held on the edge of the clay sheet next to the negative charge, whereas if the cation is held by lattice substitution then the cation will be held next to the silica-alumina basal layer.

If a clay contains small amounts of water it is likely that the cations adsorbed at the edges will be held directly next to or very close to the broken bond. The cations adsorbed between the basal surfaces will be held in different positions depending on the nature of the cation and the water content of the clay.

In Na-montmorillonite with more than one layer of water adsorbed the cation will be separated from the clay layer by a water molecule, if less water is present then the cation will occupy the hexagonal hole on the surface of the clay layer. The positions of all exchangeable cations in such systems are not the same. Ca will occupy the hole if no water has been adsorbed but leaves this position immediately upon hydration of the clay.[1]

1.4.5 Rate of the Exchange Reaction.

The rate of the cation exchange reaction depends on the clay and on the nature and the concentration of the cations. In general, exchange of the edge-sited cation can take place quickly, as in kaolinite, but penetration between the sheets of montmorillonites takes longer.

Ion exchange is a diffusion controlled process and its rate depends on the mobility of the ions.[1] When accompanied by swelling an activation energy is needed and a hysteresis phenomenon may be observed. Ion exchange in clays may also be accompanied by a change in basal spacing,[11] that is an expansion in the c direction of the unit cell and this may also influence the rate of exchange. For example, in replacing magnesium ions by strontium ions in vermiculite an increase in d_{001} spacing from 14.4Å to 15Å occurs because of the larger size of the strontium ion.

The surface charge density on the clay also has an effect on the rate of exchange, as the charge increases the rate decreases.[12]

1.4.6 The Replaceability of Exchangeable Cations.

All cations do not have the same replaceability or replacing power. Although cation exchange has been widely studied [13,14] no simple replaceability series has been found. There are various factors which are believed to influence the cation replaceability, among these are:-

(a) Effect of concentration.[15]

That is the increased concentration of the replacing cation causes greater exchange by that cation.

(b) Nature of exchanging cation.[15]

All other things being equal the higher the valency of the incoming cation the greater its replacing power, and also the more difficult it is to be replaced. One exception is hydrogen as it behaves like a di- or trivalent cation. This is possibly due to the migration of the hydrogen into the clay layer and followed by the displacement of Al from the internal sheets of the clay. The smaller ions are held less tightly than the larger ions of the same valency. The only exception are those cations which fit in the hexagonal holes on the basal oxygen sheet of the clay layers.

There are numerous other factors which influence the replaceability of the exchanging cation such as

(c) Preheating of Clay.[1]

(d) Nature of the anion in the exchange[1] solution.

(e) Population of exchange sites.[1]

All these affect the position of each cation in any replaceability series but not in a uniform manner thus making the task of finding a replaceability series difficult.

1.5 Clay-Water Systems.[2]

Under normal conditions of temperature and humidity water is the most common polar solvent in the interlayer space of the clay minerals. The nature of this water is of great importance since it gives the clay many of its characteristics and hence leads to its use in numerous spheres. In montmorillonites the interlayer cation is considered to have a large effect on the uptake and retention of water.[16] The water adsorbed by montmorillonites may be classified into two categories:

(a) The water in pores, on the surface and around the edges of the discrete particles of the mineral.

(b) The interlayer water between the unit cell layers which causes swelling.

The former type of water requires little energy for its displacement, for example drying at temperatures just above room temperature is usually sufficient for its removal. The latter type, however, requires much greater energy for its displacement and if removal is complete, that is total dehydration of the clay layers, then rehydration is difficult if not impossible. If traces of interlayer water remain then rehydration is easily achieved.[2]

Although it is accepted that the interlayer water has a definite configuration no agreement has been reached on the precise nature of this configuration. Hendricks and Jefferson,[20] suggested that initially adsorbed water hydrated the alkali-earth metals, used in the study, with six water molecules. Further hydration led to hydrogen-bonded water on the surface of the clay layers. Barshad[21] went further to suggest that the water initially adsorbed on the clay layer, as distinct from that adsorbed at the interlayer cation, was arranged in a tetrahedral arrangement placed on the oxygens at the top layer of the silica sheet, upon further hydration the adsorbed water forms into a hexagonal sheet on the oxygens of the silica lattice. Using X-ray diffraction, Walker[12] demonstrated the presence of two distinct types of interlayer water in vermiculites. The first type, type I, being the hydration shell of the cation and the second type, type II, not directly co-ordinated to the cation thus having greater mobility and also being more labile than type I.

1.6 Dehydration and Rehydration of Clay minerals.

When hydrated layer silicates are heated to high temperatures a progressive contraction of the clay layers occur, that is a decrease in basal spacing. The mechanism involved in dehydration of vermiculite has been studied in some detail by Walker.[17] It was discovered that the space between the lattice contracted in a series of steps which are thought to correspond to the basal spacings of stable hydrates of the interlayer cation until eventually no interlayer water remains.

All natural montmorillonites dehydrate between 100 - 200°C giving the 9.6Å basal structure. The exact temperatures of dehydration, as in the vermiculite clay, depends on the exchangeable cation.[18]

The rehydration of the expanding layer silicates also depends on the nature of the interlayer cation. Few of the montmorillonite clays rehydrate when heated above 600°C. There are a number of exceptions such as Mg- and Li- clay which will not rehydrate when heated above 250°C, but this is probably due to cation migration into the clay layers where they neutralise the negative charge.[19]

Rehydration is impossible when a clay has been heated above its dehydroxylation temperature which for montmorillonites starts between 500° - 600°C. This is due to the collapse of the clay structure to facilitate the removal of the hydroxyl groups. The loss of this lattice water does not begin or end abruptly but is usually complete by 800°C. The dehydroxylation temperature is not dependent on the interlayer cation.[18]

As dehydration of a metal-cation exchanged montmorillonite proceeds there comes a stage when the remaining water molecules, which are in the primary hydration shell and which dissipate the polarising power of the cation, will become dissociated. The extent of dissociation depends on the cation involved. This property of montmorillonites give the clays an 'acidic' character which has been used in numerous organic reactions.[1,22]

1.7 Intercalation of Organic Species

The intercalation of organic species into clay minerals may be classified under two headings:

(a) Organic Cation Exchange.

When organic cations are adsorbed by raw clay they do so by cation exchange thus replacing the inorganic species in the interlamellar space. The most common molecules used, that can acquire a positive charge, contain nitrogen, for example ammonium salts or amines. Quantitive exchange of the interlayer cations by alkylammonium ions provides a useful method for the characterisation of smectites and determination of their layer charge density.[23] The distance between ammonium groups gives the surface charge density and the different types of structures can easily be distinguished by their basal spacings. The monolayer has a basal spacing of 13.6Å and the bilayer has a basal spacing of

17.7Å.

(b) Intercalation of organic molecules.

The organic molecule does not have to be ionic before adsorption into the inorganic cation exchanged clay layer may take place, in fact, a large number of organic molecules will be adsorbed, particularly if the molecule is polar.[22] It has been shown that polar organics, particularly short-chained compounds, interact with the exchangeable cations rather than with the silicate surface.[2] They are either bonded directly to the cation or linked to it by a bridging water molecule similar to the interactions in the clay-water system. Indeed the introduction of infra-red spectroscopy to clay studies has led to major advances in understanding and accurate interpretation of such clay/organic interactions.[24]

Numerous studies on the intercalation of polar organic molecules have been carried out. The adsorption of alcohols being the most widely studied in recent years.[22] With the recent increase in investigations of the catalysis of organic reactions by clays[1,25] a much larger of number organic molecules need to be investigated with regard to the clay/organic interactions.[2,24]

CHAPTER 2.

PHYSIOCHEMICAL STUDIES OF CLAY CATALYSIS.

2.1 Introduction

Clay minerals have been shown to act as efficient catalysts for a variety of organic reactions.[1] Thus suitably cation exchanged (Al, Cr(III), Fe(III)) montmorillonites have been successfully used as catalysts in ethylene hydration,[2] the esterification of organic acids by alkenes,[3] and the synthesis of methyltertiary butyl ether (MTBE) from isobutene and methanol.[4]

As the number and diversity of these catalysed reactions grows so does the realisation that little information is available concerning both the dynamic and steady state behaviour of these reaction systems. The lamellar nature of the sheet silicate structure suggests that the diffusion of reactants to and products away from reaction sites will play an important role[5] (see Section 2.2).

2.2 Organic Reactions Using Clay Catalysts.

Montmorillonite clays, or, more often, acid treated montmorillonites have been used as catalysts for numerous reactions over the last few decades, ranging from reactions on an industrial scale, for example the dimerization of unsaturated fatty acids to dicarboxylic acids,[6] and alkylation of phenols.[7] Others have been employed in laboratory synthesis for example the production of bis-secondary ethers such as di- 2,2/ hexyl ether using the corresponding alkene.[8] The efficiency and wide variety of such catalysts for organic reactions are discussed in greater detail by Thomas.[1] Acid treated montmorillonite results in the breakdown of the clay layer so in effect they are high surface area solids therefore they are not included in the subsequent discussion.

It has been shown in some cases of catalysis by ion-exchanged montmorillonites there is shape selectively[9,10] similar to that exhibited by zeolites.[11] This is due to spacial requirements for the bonding of reactive species around the interlayer cation. In most cases, however, the clay appears to act as a solid source of protons,[3,12] (see section 2.4). The yield of such organic reactions seem to depend on a variety of factors some of which will be studied in this work.

Since the protons responsible for the acid character of the cation-exchanged clays are produced by polarisation of the interlayer water (section 2.4) trivalent cations in the interlayers would be expected to be more active than divalent or monovalent exchanged montmorillonites. The cations chosen are therefore usually Al, Cr(III) and Fe(III).[2-5]

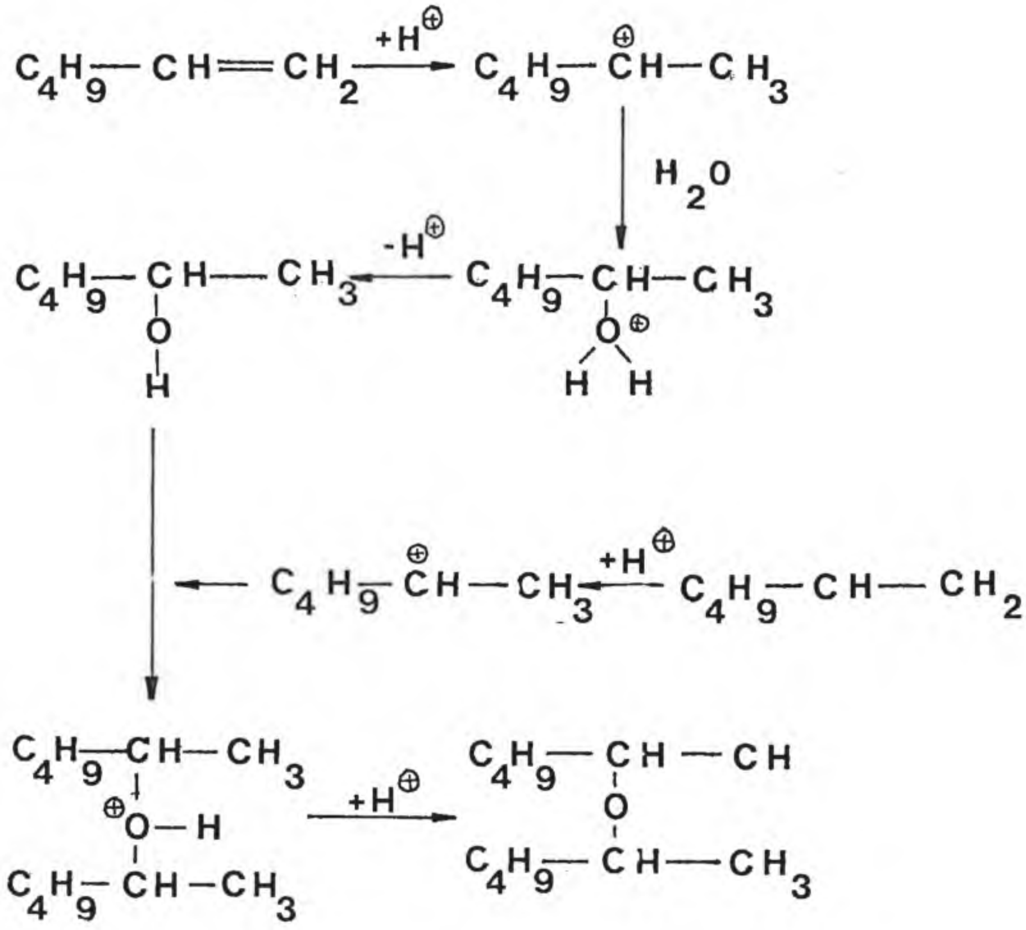
2.2.1 Restrictions on Possible Reactions.

Type of carbocation intermediate.

Certain reactions of alcohols with alkenes over cation-exchanged montmorillonites below 100 °C readily occur whereas others do not.[13] A study of the type of reactions that proceed leads to the conclusion that at these temperatures the only reactions that occur involve a tertiary carbocation being formed from the reactants directly on protonation[9] (Fig. 2a). Possibly one exception to this rule is in the addition of water to alk-1-enes to form di-2,2' alkyl ethers over cation-exchanged montmorillonites which seems to involve secondary carbocations but this reaction is not truly catalytic since the water is derived from the clay interlayer and cannot be replenished directly.[8]

At temperatures above 100 °C the products of reaction of alcohol and alkenes[13] shows evidence of involvement of primary or secondary carbocation intermediates in the reaction. These carbocations are derived directly from alkene protonation or by protonation of the alcohol followed by dehydration. Two possible causes of such reactivity have been proposed[3] (i) the interlayer environment is sufficiently acidic to protonate tertiary species but insufficient, below 100 °C to protonate either secondary or primary species or (ii) primary and secondary carbocations are formed along with the tertiary species but are too short lived to react.[5] It is known that processes involving primary and secondary carbocations require a high proton

Fig. 2a



Production of di-2,2'-hexyl ether from hexene.

concentration.[14] The first explanation seems, at temperatures below 100 °C, to be more reasonable.

2.2.2 Reaction Sites

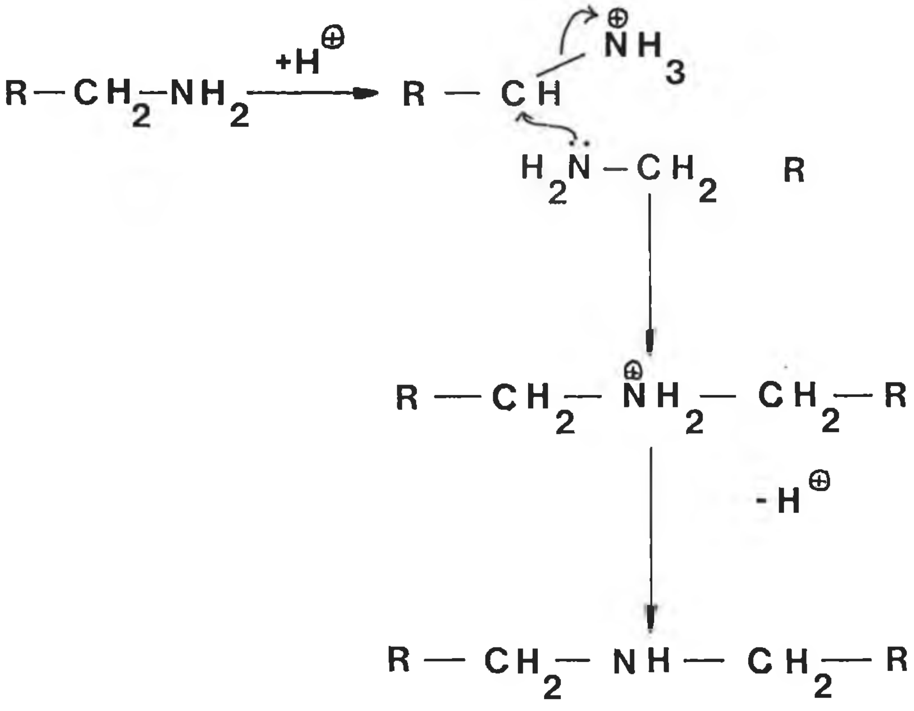
Although the protons necessary for acid-catalysis are produced in the clay interlayer region, reaction need not, in principle, occur there. In the interlayer region the protonation of an organic molecule, R, can be described as

$$M(OH_2)_n^{m+} + R \rightleftharpoons [M(OH_2)_{n-1}\ OH\ ]^{(m-1)+} + RH^+$$

where M^{m+} is an interlayer cation, the relative probability of such a reaction occuring depends on the number of water and organic molecules present in the interlayer space and also upon the basicity of the organic species relative to water. The situation becomes more complicated when more than one organic reagent is present. One example of these proton mediated reactions is the intermolecular elimination of ammonia from intercalated primary amines[15] as described in Fig. 2b. The primary amine freely enters the interlamellar region of the clay species which contains, in this case, cations such as Al, Cr(III) or Cu(II). The amine is protonated and combines with a second unprotonated amine molecule which reacts by nucleophilic displacement of ammonia to form the protonated secondary amine. Such a reaction scheme is unknown in solution where all the amino groups would normally be protonated and spati-ally separated by solvent.

A second type of reaction site is described by

Fig. 2b



Intermolecular elimination of ammonia from intercalated primary amines.

Adams et al.,[16] using the reaction of 2 methylpent-1-ene with butan-1-ol at 95 °C and 150 °C over Al-montmorillonite. They found that at 95 °C the clay gave t-ether and t-alcohol products formed from the reaction of the tertiary carbocation (from the alkene) with alcohol or water. At 150° C products included: ethers, C_{10}- alkenes formed by attack of n-$C_4H_9^+$ ions on the alkene and di-(but-1-yl)ether formed by dehydration of the butanol and dimers of the alkene. These results suggest that after the production of carbocations by protonation of the alkene reactions can take place at two different sites. The first, as described earlier is in the interlamellar region where reaction may occur between the carbocations formed and the alkenes and second being a surface site where the carbocation can react with oxygenated (polar) species such as alcohols and water but not with unsaturated hydrocarbons.

2.2.3 Solvent Effects

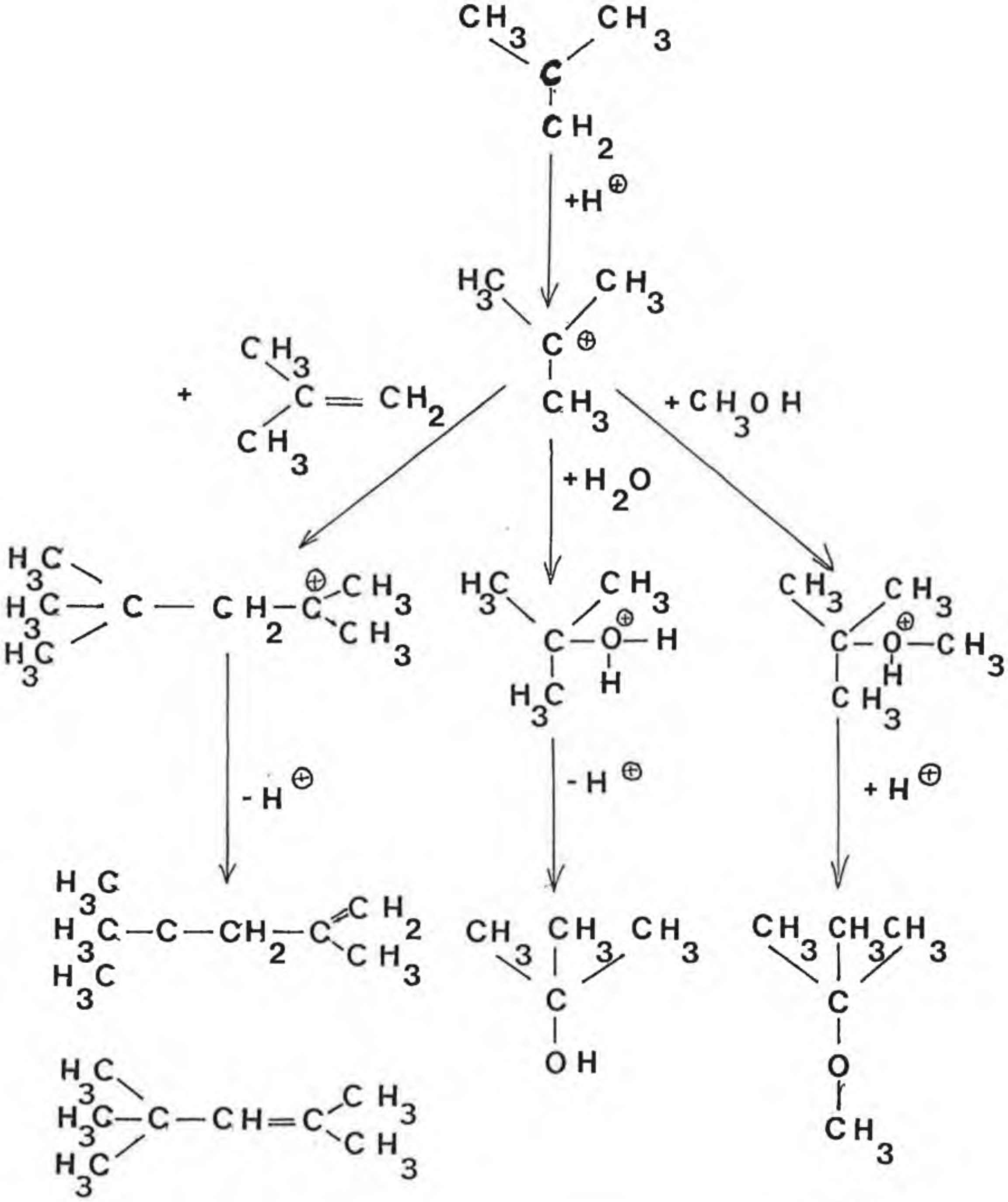
Saturated hydrocarbon solvents have been used in liquid phase cation exchanged clay reactions to avoid the possibility of co-ordination of the solvents to the interlayer cations.[4,12] Methyl t-butyl ether (MTBE) is an effective additive to petrol for improving the antiknock and antismog properties. It is usually synthesised from isobutene and methanol using a suitable acid catalyst such as sulphuric acid, ion-exchanged resins or doped molybdic acids.[13] It has been shown that a montmorillonite can be an effective catalyst for the process provided that ions such as Al, Fe(III) and Cu(II) have been exchanged into the interlamellar space of the clay.[4,5] However, it has been observed that the production of methyl-t-butyl ether (MTBE) from methanol and isobutene (as shown in Fig. 2c) is greatly influenced by the choice of solvent and the use of cyclic ether-type solvents, such as 1,4-dioxan, resulted in comparable yields of MTBE at temperatures ~30 °C lower than when hydrocarbon solvents were used.As mentioned earlier, (section 2.2.3), this lowering of the reaction temperatures has the effect of reducing the production of dimers. One explanation for the differences in yield of MTBE using different solvents is the degree of miscibility of all the products and reactants with the solvent to either increase or decrease the yield. Although the displacement of some interlayer water by the solvent may additionally affect the interlayer acidity. Table 2.1 shows that there are also some specific cation-solvent pairing effects observed by Adams et al.[5] which are not readily explained by the above comments.

Solvent effects complicate as indicated by Adams et. al.[13] the low temperature reaction of alcohols to form t-butyl ethers using clay catalysts. The reaction may be described

$$\text{ROH} + \text{t-BuOH} \xrightarrow{60\text{-}90\ ^\circ\text{C}} \text{RO(t-Bu)}$$

where R = methyl, propyl, i-propyl but not t-butyl. This reaction reaches equilibrium quickly and was found to depend on which alcohol was used in conjunction with

Fig. 2c



t-butanol
9.5%

MTBE
61%

Production of MTBE.

the t-butanol. The equilibrium was such as to give yields in the order methanol > propanol > i-propanol (>>t-butanol). This seems to suggest some correlation between the rate of reaction with the rate of diffusion of these molecules or inversely with the steric hindrance which would occur during the reaction step when the alcohol attacks the carbocation.

The final yields of the various products of these cation-exchanged montmorillonite catalysed reactions depend upon the reactivity of the various reactants and the distribution of reactants and products between the clay and the surrounding medium. The representation of the various equilibria in the clay/external system is quite complex and is further complicated when the various equilibria between the liquid medium surrounding the clay and the vapour phase existing above the clay/liquid mixture is taken into account. Quantitative information about these equilibria are not available so much work needs to be done before the network of interconnecting equilibria is traceable. The following sections discuss some of the factors considered to influence these equilibria.

TABLE 2.1

THE SOLVENT AND CATION DEPENDENCE OF THE PERCENTAGE YIELD OF MTBE.[4]

CLAY	SOLVENT		
	1,4-Dioxan	THP	THF
Al-mont.	61	4	0
Cr(III)-mont.	63	42	28
Fe(III)-mont.	65	35	32

Experimental conditions used:
1g clay, 1cm^3 MeOH, 3 cm^3 solvent, 25 mmol isobutene.
60° C for 4 hours.

2.3 Sorption into Zeolites and Clay Minerals.

2.3.1 Equilibrium Sorption

Sorption, involving the removal of molecules from the liquid or gas phase by the attractive field of a solid surface may occur where such molecules are allowed to diffuse to the solid.[17] This may take the form of sorption at the surface (adsorption) or occlusion by the solid (absorption). It is usual to distinguish between physical sorption where the sorbate-sorbent interactions involve van der Waal's forces and chemisorption which involve chemical interactions and electron transfer.[17] This distinction is valuable in certain cases, but in numerous others the distinction is neither clear nor useful, for example the difference is necessarily defined for gases on metals but in the area of clays and zeolites no clear difference is observed. It is probably more important in clay and zeolite chemistry to differentiate between mobile and immobile sorption onto localised and non-localised sorption sites.

When adsorption takes place the molecules are restricted to two-dimensional motion. Gas adsorption processes are, therefore, accompanied by a decrease in entropy. Since adsorption also involves a decrease in free energy then from the thermodynamic relationship

$$\Delta G = \Delta H_{ads} - T\Delta S \qquad 2.3.1$$

it is evident that ΔH_{ads} must be negative, i.e. the adsorption of gases and vapours onto solids is always an exothermic process. The extent of gas adsorption (under equilibrum conditions) therefore increases with decreasing temperature.[17]

2.3.2 Adsorption onto Montmorillonite Clays.

Vapour phase adsorption.

Vapour phase adsorption onto the layer silicates in general and cation exchanged montmorillonite in particular has long been studied. Barrer[18,19] was among the first to perform major studies in this area. For example, Barrer and MacLeod[18] followed the adsorption of some polar and non-polar gases and vapours on a sodium-exchanged montmorillonite and showed that non-polar species are not intercalated but that the polar molecules may be. It was pointed out that the shape of the polar species may mitigate against adsorption between the clay layers. Early studies were confined to the naturally occurring cations within the clay layers, mainly sodium or calcium. Subsequently, however, other cations, both organic and inorganic, were examined. Barrer and Perry[19] showed that a great increase in effective area of the clay could be obtained by replacing the monovalent inorganic cations by larger organic cations for example $Me\ NH_3^+$, $Me_2NH_2^+$, Me_3NH^+ and Me_4N^+. It was also discovered that many non-polar molecules could be accommodated within the increased space between the layers.[20]

The surface areas of the various cation-exchanged montmorillonite may be determined by the adsorption of nitrogen into the interlamellar space under controlled conditions a technique used by many authors[21,22] in the elucidation of the cation-exchanged clay. Although this data is not completely necessary for all studies a knowledge of the effective area of a clay surface helps in determining for example the number of water molecules at the surface of the clay. One of the major drawbacks in this method is that it is only effective for a small size range of interlayer cations. These cations must cause large enough layer separations to allow nitrogen to reach the inner cavities but must not be large enough to block the interlamellar voids.[21]

In 1979, Annabi-Bergaya et al., reported several studies[23-25] regarding the desorption of alcohols by a series of charge-deficient calcium-montmorillonites using gravimetry and X.R.D.. They found that about half of the adsorbed alcohol molecules are occluded in micropores between the particles. They also suggested that the apparent molecular packing of the alcohol in the interlamellar space is related specifically to the nature of the exchange cation.

Another area of vapour phase adsorption to receive much attention in recent years has been the study of surface acidity. This area is discussed in greater detail in section 2.4.

2.3.3 Sorption Dynamics in Zeolites and Clay Minerals.

Since zeolites are rigid crystals with windows of peripheral oxygen atoms, access to and diffusion within the zeolites is controlled by these windows. In practice these openings usually consist of 8, 10 or 12 oxygen atoms and their arrangement depends on the zeolite. As it has been discovered by numerous authors[26-32] diffusion within zeolites is also influenced by several other factors including the geometry and dimensions of the channel network; the size, shape, concentration and location of the adsorbed cations within the lattice; the shape, size, polarity and flexibility of adsorbent molecules and the presence of preadsorbed 'impurity' molecules. In addition it has been shown that counter-diffusion of reactants and products out of zeolite catalysts may seriously affect the apparent activity and selectivity for a specific reaction because of intermolecular interaction between the counter-diffusing molecules.[31] As may be expected diffusion in layer silicates will be influenced to some extent by all of these factors. In contrast to zeolites the geometry and dimensions of the interlamellar network of clay minerals are not fixed but are governed by the size of the occluded molecules. This makes it extremely difficult to predict the diffusional characteristics, particularly in systems where counterdiffusion of molecules of dissimilar size is involved.[33]

Diffusion coefficients and activation energies for gases (or liquids) adsorbed on zeolite crystals have often been calculated from experimental transient uptake curves on the assumption that the system may be regarded as isothermal. Because of the heat of adsorption this approximation is only valid when the adsorption rate is slow compared with the rate of heat transfer.[34] There are two distinct effects, caused by the heat of adsorption, on the diffusivity of vapours into solid lattices. The initial increase in the rate of uptake is due to the temperature dependence of the diffusion coefficient while in the later phases of adsorption the sorption rate is decreased by the temperature dependence of the equilibrium position. The relative importance of the various possible thermal resistances indicate that the major thermal resistance is heat transfer from the external surfaces of the sample (which may be either a pellet or a loose aggregate of crystals).[34]

The application of pulsed field gradient n.m.r.[35] to the determination of intracrystalline self-diffusion coefficients in zeolites were initially thought to show large discrepancies between the values measured using this technique and the diffusivities derived from sorption rate data.[36] Since the n.m.r. technique measures the rate of intracrystalline migration of adsorbed molecules under equilibrium conditions[37] it is necessary to correct any values obtained using such a technique. Consequently, the dramatic differences noted may be eliminated by accounting for the external heat- and mass-transfer resistance of uptake curves and using uniform samples in both sets of experiments, since factors such as grain size[38] and/or crystal size[39] have also been found to play an important part in the diffusion of gases onto zeolites.[40a,b]

Zeolites, because of their structural order, have lent themselves to this kind of study and this is reflected in the number of publications concerning diffusion studies in zeolites. Clay minerals on the other hand, not having the almost rigid structure, tend to have been neglected. The areas of work reported have been mainly confined to the equilibrium studies of the selective sorption of specific absorbates from binary mixtures in the gas and vapour phase[41] and from solution.[40b,42]

In the area of clay catalysis however, the information derived from single sorbate/sorbent studies inadequately describes the complex systems involved. However, such studies of diffusion in clay intercalates containing mixtures of both reactants and products are important in the determination of reaction pathways, particularly in determining the possible rate limiting process. For this reason the techniques of neutron scattering and quasielastic neutron scattering have received attention in recent years.[33] These techniques have been utilized to investigate the diffusion characteristics of single species such as ammonia[43,44] and pyridine[45] in tantalum disulphide, and water in various cation exchanged phyllosilicates.[46,47] The use of Neutron Scattering techniques for the determination of diffusion co-efficients is greatly facilitated by the dissimilar incoherent scattering cross-sections for hydrogen and deuterium (79.7×10^{28} m^2 and 2.0×10^{28} m^2 respectively). This dissimilarity results in neutrons being extremely sensitive to hydrogen-containing species. Deuteration of hydrogen compounds markedly reduces the incoherent scattering enabling isotopic exchange to be followed by neutron diffraction under favourable conditions. In contract, incoherent quasielastic neutron scattering (QENS) utilizes the large incoherent cross-section of hydrogen atoms .

It has been reported[46-47] from QENS that the water diffusion process, in the one-, two- and three-layer hydrates of various cation-exchanged montmorillonite, is simultaneous rotation and translation characterised by translational diffusion co-efficients of $3 - 10 \times 10^{-10}$ m^2/sec, the magnitude being dependent on the water content of the clay. In a similar study utilising a Na-montmorillonite/pyridine/water system[48] the interlamellar water was found to have a translational diffusion coefficient of 6×10^{-11} m^2/sec which is considerably less than the 10^{-9} m^2/sec found for water in clays with 18Å basal spacings.[47] Obviously the immobile pyridine in the pyridine/water intercalate markedly affects the diffusion of the interlayer water. The Na-montmorillonite/pyridine/water system has been used as a model system for studying the factors which influence the diffusion of species into and out of the interlayer region of clays.[33,48] Using this model it has been suggested that at high water contents the rate of 'reaction' depends on progress of the reactants through the interparticulate water barrier whereas at lower water contents the diffusion of the bulky organic species through the lower spacing intercalate appears to be the slowest diffusion step.[48]

The open structure of an outgassed zeolite allows the rapid uptake of most organic molecules with diameters $\leq$ 8Å and the diffusion coefficients follow the trend alkanes $>$ alkenes $>$ polar compounds. The increased affinity of polar sorbates for the zeolite results in longer residence times at each site and therefore slower transport rates. Consequently the presence of preadsorbed 'impurity' molecules in zeolites can reduce diffusion coefficients by a factor of 10^3 to 10^4 by forming periodic barriers in the narrow channels of the zeolites.[40b] In clay catalysis, however, the presence of a small number of preadsorbed molecules is essential because the Bronsted acidity which gives rise to the catalytic activity (section 2.4) results from the polarisation of solvent water molecules by the interlayer cations. In contrast to the situation in zeolites, a small number of preadsorbed water molecules are likely to accelerate the initial rate of ingress of certain molecules by propping the layers apart.[48]

Liquid phase adsorption.

As in vapour phase adsorption the liquid phase adsorption properties of clays have been extensively studied in the past.[49] Major work has been carried out in this area by Dekany and his collaborators[50-52] who have dealt with the adsorption from benzene/alkane and benzene/alcohol binary liquid mixtures onto montmorillonites and kaolinites treated to varying extents with hexadecylpyridinium chloride. Using the Schay-Nagy system of classification,[53] they found that the surface excess isotherms for methanol from benzene, for example, was of type II although pretreatment with water + isopropanol was found to cause a shift to less alcohol uptake in the isotherm.[51] Traditionally, adsorption from binary solutions is determined as the difference between the adsorbate concentration in the solution before and after contacting with the solid adsorbent, for example cation-exchanged clays. The bulk composition may be measured by means of a differential liquid refactometer[51] or by gas chromatography.[54] The specific excess adsorption of the mixtures, n_i, is then calculated as:[53]

$$n_i = n_0 (X_{i,0} - X_i) = n_0 \triangle X_i$$

where n_0 is the total amount of the liquid mixture referred to unit mass of the adsorbent, $X_{i,0}$ is the mole fraction of the i^{th} component before adsorption, and X_i is the mole fraction in liquid mixture of the i^{th} component at equilibrium. It should also be noted that the dynamic technique of frontal analysis, utilising high performance liquid chromatorography, despite the finite mass transfer resistance and adsorption kinetics,[55] has also been used in this area. A comparative study of both a static and a dynamic technique for the system n-hexane/n-hexanol/silica gel showed agreement over the whole mole fraction range.[56]

The adsorption of vapours, gases and from liquid mixtures onto the cation exchanged clays has been found to be strongly influenced by the size, shape and valency of the interlayer cation, and by the presence of preadsorbed molecules such as water. Theng[30] suggested that the presence of water in the coordination positions causes adsorbate molecules to compete directly with these water molecules. In the case of liquid adsorption the type of the isotherm obtained seems to be influenced largely by the solvent system used although the amount adsorbed and the isotherm curve maximum and minimum are influenced by the exchangeable cation and the presence of preadsorbed molecules.[49-52]

With the present interest in cation exchanged montmorillonites as clay catalysts the role of the coordination shell water is considered to be vital to the clays activity as a solid source of protons.[1] The active sites derived in this manner are discussed in greater detail in the next section.

2.4 Acidity

Since most of the reactions performed over montmorillonite clays utilise the acid properties of the clay it is therefore necessary to include in any discussion of the factors influencing such reactions a description of the acidic properties of these catalysts. This involves determining the nature, strength and number of acid centres which exist on the solid acid.

2.4.1 Active Sites

Unlike most of the solid acid catalysts in use the cation-exchanged montmorillonite clays do not possess acid centres caused by defects or alterations to the lattice structure directly, the acid centres are considered to be caused by the polarisation of hydration shell water by the interlayer cations. Mortland et al.[57] found that the interlayer water is dissociated to a much greater extent than bulk water and Weiss[58] has shown that the hydrogen ion concentration in the interlayer regions of some cation (eg Ca^{2+},Mg^{2+}) exchanged clays may be as high as 10 mol dm^{-3}. The acidity of this water was also higher than was achieved for these ions in aqueous solutions.[59]

2.4.2 Acid Strength

The acid strength of a solid acid is described as 'the ability of the surface to convert an adsorbed neutral base into its conjugate acid'.[60] This process may occur via a proton transfer (Brønsted acidity) or an electron transfer (Lewis Acidity). Since the water of hydration dissociates in the interlayer of the clays it is considered that only Brønsted acidity occurs within these regions.

The following equilibrium describes the acid strength of hydrated ions:

$$[\,M\,(H_2O)_x]^{+n} + H_2O \rightleftharpoons [\,MOH(H_2O)_{x-1}\,]^{+n-1} + H_3O^+$$

Thus the production of protons from water molecules coordinated to the metal ion depends on the nature of the metal. The extent to which the O-H bond is weakened determines the extent to which the equilibrium is displaced to the right. This is a very simplified view of what happens in cation-exchanged montmorillonites and there are a number of other factors which have also been considered to affect the acidity of the clay mineral. For example the pk_b of the base used in the acidity determination has been found to influence the number of acid sites in any cation exchanged clay. Mortland[60] described, from the work of Russell,[59] Farmer and Mortland[61] and Mortland[62] how different yields were obtained over Mg^{2+}- montmorillonite, along with other cation exchanged forms, using bases of different values. Three bases were considered, ammonia, pKa = 4.74; pyridine, pKa = 8.85; urea, pKa = 13.82; the amounts of protonated species formed in the order ammonia (80meq/100gms clay) > pyridine (41meq/100gms clay) > urea (none formed). It was also noted that bases requiring low pH's to be protonated, for example acetamide, may be protonated by trivalent cation exchanged montmorillonites.

There are a wide variety of techniques used to determine the acid strength of solid acid catalysts. Probably the most widely used method was that of Hammett indicators[63] which despite their drawbacks are still frequently employed.[64-68] The acid strength being described by the Hammett acidity function[69]

$$H_o = pk_a + \text{Log}\,[B]/[BH^+]$$

where $[B]$ and $[BH^+]$ are the concentrations of the base and its conjugate acid respectively. The technique involves the addition of an indicator of known pk_a value and observing the colour change, if any occurs, until the pk_a of the solid acid is found to lie between two indicator values. Although several alterations to this technique have been developed it still is very difficult to perform accurately. Most of the other methods used in the determination of acid strength are also used in estimating the amount of acid and/or in the differentiation of the types of acid site.

2.4.3 Amount of Acid.

There are two major areas of study in obtaining the amount of acid in a solid acid catalyst. The first is exposure of the surface to a liquid and allowing equilibrium to be reached. The amine titration method is one such technique but this tends to lead to a titration of at least two or three days duration to ensure equilibrium has been reached after each addition.

Modifications to the techniques by using indicators and successive approximation [70] to the end point of the titrations speed up these techniques.

The acid amount may also be obtained by introducing a gas or vapour onto the surface. Numerous bases have been employed in such techniques including ammonia,[71] pyridine,[72,73] and n-butylamine.[74] Techniques using such basic vapours include i) reduced pressure gravimetry, which involves the introduction of excess base vapour over the solid, the system then being subjected to prolonged evacuation at reduced pressures until no further weight change of the sample is recorded.[75] ii) Thermal analysis has also been used in this area in recent years. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) being used to study zeolites[74,76] and clay minerals.[77] Together with an estimation of the acid amount, DTA and TGA may be used to calculate the acid strength of the solid acid.[75] These techniques involve the exposure of the solid sample to a base vapour followed by thermal treatment to determine both the amount of vapour adsorbed and the temperatures at which the physi- and chemisorbed species desorb, and iii) Gas chromatography (GC) has also been used under similar circumstances.[78,79]

Some of the major advantages of the vapour phase adsorption/desorption techniques are that the number of acid sites may be determined at the working temperature of the catalyst.

2.4.4 Types of Acid Sites.

The number of acid sites as well as their strength have been considered to be a summation of all acid sites on a solid acid. Distinction between the two types of sites, Brønsted acid and Lewis acid sites, also helps in determining reaction pathways over solid acid catalysts. Although a number of different techniques have been described in the literature[80-82] probably the most widely used technique is infra-red spectroscopy. The infra-red technique allows identification of the various bands associated with the two different types of sites and in this area both ammonia[83] and pyridine[84] have been used. In zeolites,[85] for example, pyridine gives rise to bands at $\sim 1545\text{cm}^{-1}$ and $\sim 1450\text{cm}^{-1}$ among others and these are assigned to Bronsted interactions and Lewis interactions, respectively. Other techniques exist for aiding the classification of acid sites such as spectroscopic studies of reaction intermediates and exchange reactions involving hydrogen.[86] These methods are by their nature specialised and are adapted to suit the individual catlayst under study.

2.5 Thermal Analyses.

Since the major technique used in this work was the method of thermogravimetry a brief discussion of its application is included here. Thermal methods of analysis are defined as techniques which measure the change of some property of a material as it is subjected to a defined temperature programme. Since their introduction, and with the increasing sensitivity of the instruments being used, a wide variety of areas have been investigated, such as chemical reactivity, thermal constants and structural changes.[87] Indeed thermogravimetry, along with differential thermal analysis, has been frequently used in the identification and characterisation of the clay minerals.[77,88]

2.5.1 Thermogravimetry (TG).

The thermal analyses technique of thermogravimetry is one in which the change in sample mass is recorded as a function of temperature. The resultant mass-change versus temperature curve, or thermogram, provides information about the thermal stability and composition of the initial sample, any intermediates formed and the composition of the residue. Except for mass-changes, much of the information obtained from the TG curves are empirical in nature in that transition temperatures are dependent on the parameters involved, though with the increased use of commercial instruments this problem has been improved.

In conventional thermogravimetry the mass of a sample, m, is continuously recorded as a function of temperature, T, or time, t, i.e.

$$m = f\ (T \text{ or } t)$$

Quantitative measurements can be obtained for mass-changes by determining distances between the points of interest on the curves' mass axis. A second method of displaying the data obtained is to record the derivative of the mass change, m, with respect to time, against temperature, T, or time, t, i.e.

$$\frac{dm}{dt} = f\ (T \text{ or } t)$$

This curve may be obtained by manual differentiation methods or by electronic differentiation of the TG curve. This technique is called derivative thermogravimetry (DTG). Although this technique contains no more information than thermogravimetry it is sometimes easier to interpret the derived thermograms.

As with any instrumental technique, the results derived from thermogravimetry are affected by a large number of factors. Such factors are usually grouped as instrumental or sample. Some, such as heating rate, furnace geometry and balance sensitivity are fixed for any given thermobalance, but others such as particle size, packing and solubility of evolved gases are difficult to repeat continuously. Although much work has been done on such factors[87] still no uniform standard sample is available for comparing one given apparatus with another.

2.5.2 Thermogravimetry in Clay Minerals Studies.

Since its development, thermogravimetry has been used as a tool in the identification and classification of the clay minerals.[88] While the TG curves alone do not usually provide sufficient information to identify a species with certainty, quite often the observation of characteristic thermal events will identify to which group a clay mineral belongs. With the increased interest in using clay minerals in general, and cation exchanged-montmorillonites in particular, in the area of heterogeneous catalysis, greater interest has been expressed in the use of such thermal methods to the investigations of both the solid acid surfaces[89] and the interactions of the various reactants with such surfaces.[90,91] In the area of solid acid surfaces the thermal technique of temperature programmed desorption has received much attention. By using thermogravimetry and/or derivative thermogravimetry it is possible to follow the loss in mass due to the linearly increasing temperature of the solid onto which a basic vapour has been previously adsorbed and protonated.[92] Such techniques may be used to aid in the description of the acid strength and amount since the increase in the temperature necessary to evolve a particular species from the surface indicates a higher energy of activation and hence a stronger bond between adsorbent and adsorbate.[88] Other techniques must be used in the identification of evolved gases since TG/DTG only record a change in mass of the sample.

With the large number of cations incorporated at the exchange sites of montmorillonite another application of TG, similar to that mentioned for the determination of surface acidity, has been used in the study of hydration state of the clay and cations. Studies have shown that the level of hydration of the cation exchanged clay depends on the cation present[93] and is directly related to the polarising power of that cation.[94]

Methods have also been developed, using TG, to study the kinetics of thermal decomposition reactions. Doyle[95] suggested that, for dynamic thermogravimetry, one mass-loss curve is equivalent to a large number of isothermal mass-loss curves. It should be noted however, that non-isothermal thermogravimetric data is only narrowly definitive in that the kinetic parameters are obtained using a particular set of experimental conditions. The advantages of determining kinetic parameters by these methods are that considerably fewer data are required; that the kinetics can be calculated over the entire temperature range and that only a single sample is required. One decided disadvantage as compared with isothermal methods is that the reaction mechanism cannot usually be determined, and hence, the meaning of the activation energy, order of reaction and frequency factor are uncertain. The use of such non-isothermal methods have therefore been questioned[96] and criticised.[97]

2.6 Infra-red Spectroscopy in Clay Mineral Studies.

Since its development, infra-red spectroscopy has been applied to a large number of areas with much success in aiding the identification and clarification of a wide variety of chemical species. It has found much use in organic chemistry as a fundamental tool and the general theory, experimental techniques and instrumentation used in examining the infra-red spectra have been widely studied. Until the development of infra-red spectroscopy, x-ray diffractometry[98] was used almost exclusively to study the structure of the interactions between the expanding layer silicates and organic compounds.[98] While this technique yielded much information regarding the arrangement of the organic species within the clay layer, its inability to reveal most of the changes occuring in the adsorbed species led to the wide application of infra-red spectroscopy to this area of clay-organic interactions.[30]

The principle behind the application of infra-red spectroscopy to the study of clay-organic systems is that the vibrational spectrum of the adsorbed species is directly comparable to that species in the "free" state, that is, when that species is in the solid, liquid or dissolved state. Therefore, any interactions with the clay surface could lead to changes in the position and/or the intensity of the bands in the spectrum. These observations assist in determining the mode of bonding of the adsorbed or intercalated organic molecules.

As indicated in Chapter 1 montmorillonite and vermiculite minerals readily form interlayer complexes with a wide variety of uncharged polar organic molecules and much work has been carried out involving montmorillonite-organic complexes. Infra-red spectroscopy has been therefore, in conjunction with x-ray diffraction, instrumental in clarifying many of the mechanisms underlying the formation of complexes between layer silicates and organic substances.[30]

The presence of interlayer water in montmorillonite has been extensively studied since not only is it the most common polar compound present in the interlayer spacing but also for its role in the use of such clays as acid catalysts.[1,31,42] The presence of the two types of water, discussed in Chapter 1, have been identified using this technique since the more labile water (type II) that is the outer shell about the cation, gives a spectrum similar to liquid water whereas the inner coordination shell water (type I), due to weak hydrogen bonding, yield a different spectrum.[99]

Since montmorillonite clay contains a number of hydroxyl groups within its structure assignment of the appropriate bands has not always been easy.[100] Difficulties are often encountered in assigning the origins of differences in spectra since even closely related clay minerals may differ in geometry and regularity of their structure. But generally the montmorillonite clays exhibit some distinguishing features. A large sharp peak at $\sim 3600\text{cm}^{-1}$ is assigned to the lattice hydroxyls. This peak is usually partly surpressed by the presence of the interlayer water which gives rise to a very broad peak ranging from 3500 - 2900cm^{-1}. This water also gives rise to a much smaller but sharper peak centred at $\sim 1640\text{cm}^{-1}$. Probably the most distinguishing feature of the layer silicates are the broad and very large series of overlapping peaks between $1150\text{-}960\text{cm}^{-1}$ arising from Si - O stretching vibrations.[101] Below 960cm^{-1} vibrations involving the hydroxyl groups and the octahedral cations give rise to a number of bands. For example a band at 850cm^{-1} is assigned to by a bending frequency of hydroxyl groups shared between Al- and Mg- in the layer.[101] Bands in this area are usually very close together and thus are often difficult to determine and assign due to overlapping.

The use of infra-red spectroscopy to identify and quantify the chemical interactions between layer silicates and organic solvents has rapidly increased the ability of the chemist to identify reaction pathways. Another major field of use has been in the determination of the clay acidity as mentioned earlier.[60]

CHAPTER 3

CHARACTERISATION OF A MONTMORILLONITE CLAY.

3.1 Introduction.

With the growth in applications of clay minerals, such as in clay catalysis[1] and ceramics, the characterisation of the clay minerals involved has become increasingly important. The elemental structure[2] as well as such properties as basal spacing,[3] cation exchange capacity,[1] exchangeable cation present in the interlayer[4] and layer charge distribution[5] all give the layer silicates their individual properties. These properties should, therefore, be determined so that any subsequent data concerning the clay minerals involved can be significantly compared.

There are a large number of techniques used to characterise the layer silicates and these may be divided into two major categories:

(i) Elemental analyses,[6] which involve the digestion of the clay mineral samples and yield the elemental composition of the clay.

(ii) Clay mineral properties, which involve the determination of the surface properties of clay minerals. Techniques such as X-ray diffraction (X.R.D.),[3] infra-red (I.R) spectroscopy[8] and particle size analysis[2] would be included in this category.

The work reported in this chapter uses a number of different techniques to characterise the montmorillonite clay used in these studies and will be discussed in the appropriate sections.

3.2 General Theory.

In the early years of clay mineral identification and characterisation "wet" chemical analysis was the major approach available to the clay chemist. Following the introduction of X-ray diffraction major advances were made in the classification of clay minerals.[9] As new techniques emerged, such as infra-red spectroscopy[8] and a variety of thermal methods,[10] they too were used for clay mineral characterisation.[7] Despite the availability of these other techniques X-ray diffraction is still a basic tool for studying clay minerals.[9]

3.2.1 X-ray Diffraction.[7]

X-rays are produced when fast moving electrons impinge on matter. The X-rays result from two general types of interaction of the electrons with the atoms of the target material. Firstly the displacement of an inner shell electron from the atom thereby ionising the atom. Following this an outer shell electron may fall into the vacant place with the resulting emission of X-ray radiation, which is characteristic of the target atom involved. Secondly the high speed electrons may be slowed simply in passing through the strong electric field near the nucleus of the atom. The decrease in energy, ΔE, of the electron appears as an X-ray photon of frequency, ν , and is given by Einsteins equation

$$\Delta E = h\nu$$

where h is Plancks constant. X-rays produced in this manner are independent of the atom involved and appear as a continuous band of radiation whose lower limit is a function of the maximum energy of the bombarding electrons.[7]

3.2.2 The Bragg Relationship.

Most metals emit a wide band of X-ray wavelengths but superimposed on this are two intense peaks at characteristic wavelengths. These are the K_α and K_β radiation, the wavelengths of which are related to the element (usually a metal) used. Monochromatic x-rays can be produced if a filter, usually another metal, is selected which transmits the K_α radiation and adsorbs the K_β radiation.

The atoms or ions in a crystal are arranged symmetrically and form planes or groups of planes between which there is a constant separation distance. The collimated beams of x-rays are focussed on the sample at an incident angle, θ. Constructive interference occurs when a set of crystal planes are in the correct orientation to satisfy the Bragg relationship

$$n\lambda = 2d \sin\theta.$$

where n = the order of diffraction

λ = the wavelength of radiation

d = basal spacing

θ = angle of diffraction.

This predicts that all planes in a crystal will diffract x-rays when inclined at certain angles to the incident beam and from a knowledge of the angle of diffraction, θ, and the wavelength of radiation, λ, the spacing between the planes, d, can be calculated.[7]

3.2.3 Thermogravimetry.[10]

The technique of thermogravimetric analysis (TGA) is based on recording the change in sample mass as the temperature is increased. There are three different modes (a) isothermal, in which the sample mass is recorded as a function of time at a constant temperature, (b) quasistatic, in which the sample is heated to constant mass at each of a series of increasing temperatures and (c) dynamic, in which the sample is heated in an environment where the temperature is changing in a predetermined manner, preferably at a linear rate. The resulting mass-change versus temperature curve is called a thermogram and provides information concerning the thermal stability and composition of the initial sample, and any intermediates formed and residues remaining following heating. Wendlandt[10] has given a detailed discussion of all aspects of thermal analysis.

3.3 Experimental.

3.3.1 Pretreatment of Clay.

All clays invariably contain impurities which must be removed before any worthwhile measurements can be made.[11] The most convenient way of removing these impurities is a method based on Stoke's law. This states that for particles of radius, a, falling with a terminal velocity, v, through a liquid medium of viscosity, η , the force on the particle, F, is given by

$$F = 6\pi a \eta v$$

The raw clay is stirred with water and left to stand for 24 hours , after which the top 10cm (which should contain particles of $< 2\,\mu m$)is siphoned off and mixed with a 0.3 M sodium chloride solution. After a suitable exchange period this clay is washed free of excess salt, centrifuged, air-dried and ground to a powder, then stored for further use. This clay will be referred to as 'base' clay. The various cation exchanged clays were produced by the addition of a quantity of 'base' clay to a 0.3 M chloride salt solution containing the appropriate cation. This suspension was then allowed to stand before washing with deionised water until free of excess salt. These clays are then air dried, ground and stored or alternatively made into X.R.D. slides or I.R. films by evaporating a clay suspension on a glass slide or polythene backing, respectively. The polythene backing is subsequently removed and the films stored.

3.3.2 Elemental Analysis.

Two techniques of elemental analysis were employed in these studies. The first method will only be described briefly since a more complete description of the procedure is given by Bennet and Reed.[6]

The main part of the analysis was carried out on a portion of 120 °C dried clay fused into sodium hydroxide. This melt was decomposed with boiling water and dissolved in hydrochloric acid. Following digestion, aliquots were taken to determine the different elements in the 'base' clay. Silica was determined gravimetrically by producing the yellow quinoline silicomolybdate which was precipitated out of solution, filtered and dried to constant weight. The amount of alumina present was determined by the formation of the aluminium oxinate complex following removal of iron from the solution, again the quantitation of alumina was performed gravimetrically. Ferric oxide was determined by the addition of 1,10-phenanthroline thus forming an iron (II): 1,10-phenanthroline complex which may be measured spectrophotometrically at a wavelength of 515 nm. The presence of calcium and magnesium was determined by titrating with EDTA using the appropriate indicators. Finally, the loss of ignition was determined by heating the sample to 1000 °C for 30 minutes.

The second method used was atomic absorption spectrophotometry. The instrument used was an Instrumentation Laboratory (I.L.) model 357 spectrophotometer with either an air/acetylene or nitrous oxide/acetylene burner head. The instrument used hollow cathode lamps which emit radiation at the resonance wavelength of the element under investigation. The details of the instrument and lamp conditions are given in the appropriate manual.[12]

Following digestion of the clay mineral sample,[6] as in the previous method, aliquots of the digestion solution were investigated using the appropriate operating conditions in the atomic absorption spectrophotometer. A standard curve was plotted, using a series of standard solutions and the concentration of the unknown sample determined by interpolation.

3.3.3 Structural Properties.

Cation Exchange Capacity.

The cation exchange capacity was measured as follows:

approximately 0.25 g of the powdered 'base' clay sample was shaken up at room temperature with 0.2 M calcium chloride solution and allowed to stand overnight. The sample was repeatedly washed and centrifuged until no Cl^- ions could be detected using $AgNO_3$. The clay was then dried at 120 °C overnight (16 hours) and allowed to cool in a desiccator before being ground. Approximately 50 mg of this clay was then weighed accurately and added to 10 cm^3 of 0.4 M potassium chloride solution. 5 cm^3 of the supernatant solution was removed and, following dilution, the amount of calcium present was determined by atomic absorption spectrophotometry.

The percentage exchange-site occupancy of the three trivalent cation exchanged clays was also determined. The method was similar to that above except that the clays were not washed free of excess salt, instead the trivalent metal was determined in the supernatant in the presence of the calcium ions. Since the pH of these exchange solutions was found to be 0.8, the method was repeated using a calcium exchange solution at pH 4 to determine the effect of pH on the determination of the cation exchange capacity. The pH has been found by Maes et al.,[13] to influence the cation exchange capacity.

3.3.4 Determination of Layer Charge.

Preparation of n-Alkylammonium Chlorides.[14]

Gaseous HCl was bubbled through a mixture of equal volumes of the appropriate n-alkylamine and 95% ethanol. The temperature of the mixture was kept below 65 °C. As the end point of the reaction was approached (that is $pH \sim 7$) the gas flow was stopped and the mixture placed in a rotary evaporator at 60 °C. The mixture was evaporated to almost complete dryness and then washed with cooled (< -20 °C) acetone. The resulting salt was dried at 60 °C overnight and stored until needed.

Intercalation and Preparation of Samples.

Known weights of the base clay were added to the appropriate n-alkylammonium chloride solutions and the suspensions shaken in a water bath at 60 °C for 24 hours. After this they were centrifuged and washed with ethanol (95%). The samples were resuspended in the appropriate alkylammonium salt solution and shaken for a further 24 hours centrifuged and washed at least six times with 95% ethanol until free of excess salt. After the final wash the clay suspension was smeared onto glass slides, allowed to dry and placed in a dessicator. The samples were dried under vacuum prior to X-ray analysis.

3.3.5 Determination of Layer Spacing .

X-ray slides, prepared as in section 3.3.1 (either in the air-dried or 120 °C dried form as appropriate) were exposed to the vapour of the required solvent for 16 hours prior to the X-ray diffraction studies. The diffraction traces were recorded at 2°(2θ) minute^{-1} between 2°(2θ) and 10°(2θ). The instrument used in all these studies was a Jeol model JDS 8X diffractometer using Ni filtered copper K_{α} radiation (λ = 1.5418 Å) at 40 kV and 20 mA.

3.3.6 Thermogravimetric Analysis.

The clays for thermogravimetric analysis were prepared as for the X-ray diffraction experiments except that the clay suspensions were not smeared onto glass slides. The clay samples were ground when air dried and stored. 8 - 10 mg of each air-dried cation exchanged clay was added to the sample pan and allowed to reach equilibrium in the N_2 gas flow. The furnace was raised and the temperature ramp initiated. As the temperature increased the sample weight loss was recorded as a function of temperature either directly or as the first derivative. A purge gas, N_2, was used to prevent any readsorption of the evolved vapours.

The instrument used in these studies was a Stanton Redcroft TG 750 thermobalance, a detailed description of which is given in Chapter 4. The conditions of a typical experiment were, purge gas, N_2; flowrate, 20 cm^3 $minute^{-1}$; chart speed, 20 cm $hour^{-1}$; heating rate, 20 °C $minute^{-1}$; sample holder, inconel. Each sample was run between room temperature (18 °C) and $\sim$800 °C which is known to be above the dehydroxylation temperature of this clay mineral.[15]

3.3.7 Particle Size Analysis.

Two methods of particle size analysis were employed for the different trivalent metal exchanged montmorillonites. The first method used a Cilas Granulator model 715 equipped with a 1.5 mV Helium/Neon laser operating at a wavelength of 632.8 nm. The clay sample (0.1 - 0.2 g) which had previously been ground to pass through a $<$45 µm sieve, was placed in the upper chamber in deionised water. After dispersion, in the built-in ultrasonic bath for 2 minutes, the clay suspension was measured optically for the particle size distribution and the range of sizes plotted out. The instrument was then washed free of clay suspension with deionised water prior to analysing the next sample. This method gives the particle size distribution of the different cation exchanged clays when they are in aqueous suspension.

The second particle size investigation utilised a scanning electron microscope, (S.E.M.) The samples, which had been passed through a 45 μm sieve, were deposited onto the holders by evaporation from an alcohol slurry, coated with gold and the micrograph recorded photographically. The instrument used was a Jeol JXA-50A electron probe microanalyser.

3.4 Results.

The results of elemental analyses reported in Table 3.1 are the mean values derived from three samples of the base, montmorillonite, clay. The computation of a molecular formula from these chemical analyses is explained in section 3.5.1. Table 3.2 gives the cation exchange capacities of the different cation exchanged montmorillonite which have been determined at two pH values using different exchange solutions indicating the amount of deviation found not only with varying pH but also when different exchangeable cations are present in the interlayer. The results of the layer charge distribution for the 'base' montmorillonite clay are given in Table 3.3 and plotted in Fig. 3a. The heterogeniety of the charge density of the clay mineral used in this study is shown by the presence of two peaks in the X.R.D. profiles for the n-alkylammonium chains of 9, 10 and 11 CH_2 units long, showing the co-existence of single and double layer spacings (see section 3.5.2). The basal spacings collected in Table 3.4 indicate the range of interlayer spacings that the several cation exchanged derivatives exhibit when the clays are exposed to a wide variety of solvents. The solvents chosen have all been used as solvents or reactants in clay catalysed organic reactions or as bases used in the studies of clay acidity. Table 3.4 records only the most stable of the intercalated forms but Lagaly[16] has shown that other spacings occur particularly for the amines using a variety of

TABLE 3.1.

ELEMENTAL ANALYSIS

Constituent oxide	Wet method wt. %*	Atomic absorption wt. %*
SiO_2	57.4	58.5
Al_2O_3	19.8	19.2
Fe_2O_3	1.8	1.6
MgO	3.1^x	6.5
CaO	2.8^x	0.0
Cr_2O_3	0.0	0.0
K_2O	N.D.	0.8
exchangeable cations	5.2	3.7
$- H_2O$	8.3	8.3

* - averaged over three clay samples. Analyses carried out on 120 °C dried, base clay cooled in air.

x - in the 'wet' method used these figures are related as they are determined as magnesia and lime.

N.D. - not determined

$-H_2O$ - weight lost from clay when heated to 1000 °C for 30 minutes.

TABLE 3.2

CATION EXCHANGE CAPACITIES (C.E.C.)
IN MILLIEQUIVALENTS
PER 100g OF CLAY (meq/100g CLAY).

Clay	Exchanging solution	pH of solution	C.E.C.
Na - mont	$CaCl_2$	N.D.	69.0
Fe(III)-mont	$CaCO_3$	0.8	90.0
Cr(III)-mont	$CaCO_3$	0.8	76.0
Al -mont	$CaCO_3$	0.8	69.0
Fe(III)-mont*	$CaCO_3$ + $Ca(OH)_2$	4.0	0.0
Cr(III)-mont*	$CaCO_3$ + $Ca(OH)_2$	4.0	69.0
Al - mont*	$CaCO_3$ + $Ca(OH)_2$	4.0	69.0

N.D. - not determined.

* - dried at 120 °C for 16 hours prior to C.E.C. determination.

TABLE 3.3

DETERMINATION OF LAYER CHARGE BY n-ALKYLAMMONIUM METHOD.

n-alkylammonium salt chain length	conc.* of exchange solution/M	basal spacing(s)Å
5	2.0	13.8
6	2.0	13.9
7	0.5	14.3
8	0.5	18.5
9	0.5	18.8, 14.5⁺
10	0.1	18.8, 14.5⁺
11	0.1	18.8, 14.9⁺
16	0.05	13.6
18	0.03	13.6

* - optimium concentrations used are those of Ruehlicke and Kohler.[14]

\+ - indicated by ■ in Fig. 3a.

Figure 3a. Transition from the monolayer to bilayer form in alklammonium exchanged montmorillonites as found by x-ray diffraction.

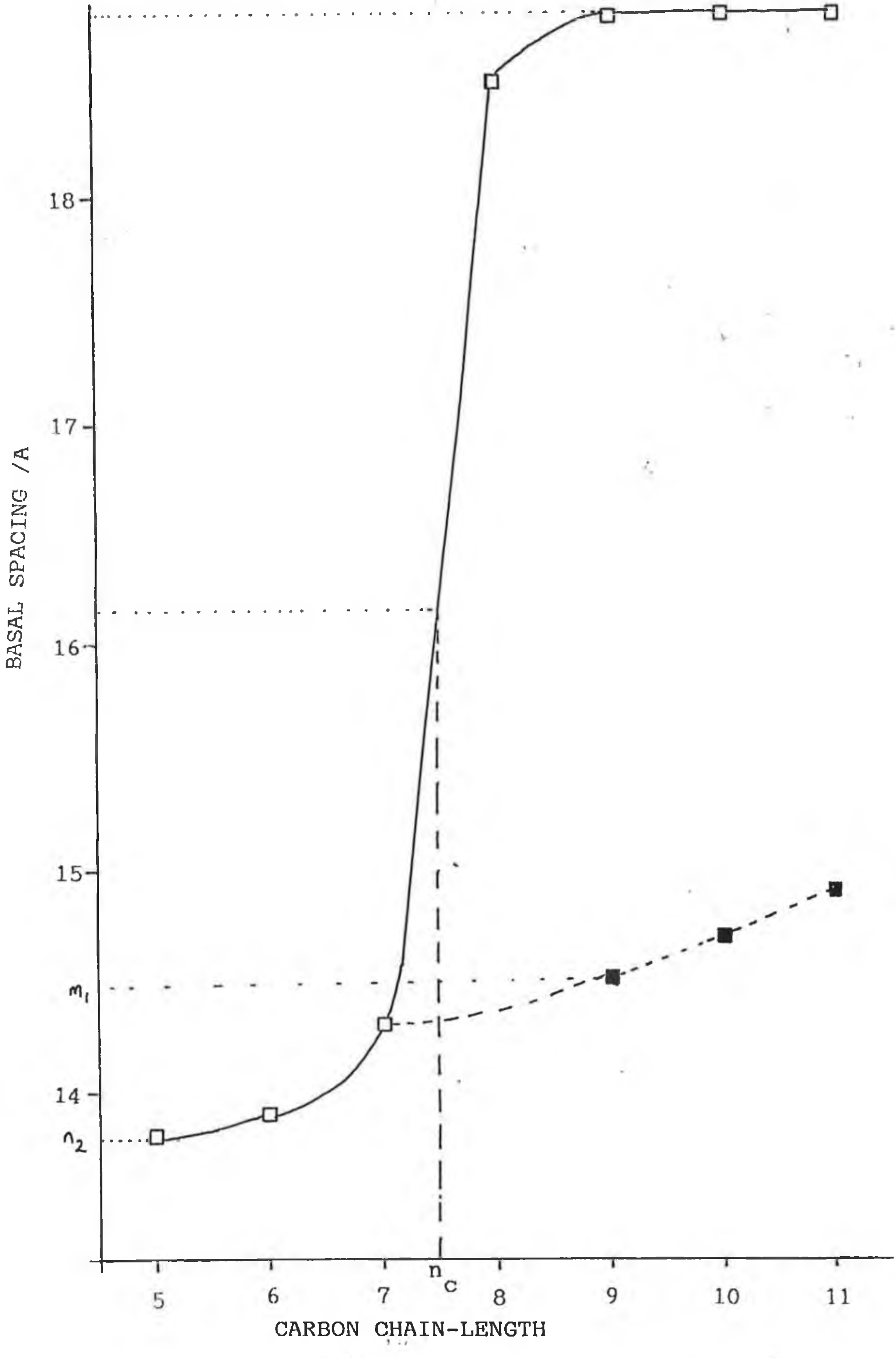


TABLE 3.4.

BASAL SPACINGS* FOR VARIOUS CATION EXCHANGED CLAYS HEATED TO 120 °C PRIOR TO EXPOSURE TO THE SOLVENTS LISTED.

Exchange cation solvents	Fe(III) - mont.	Cr(III) - mont.	Al-mont.
120°C dried	9.6	12.6	12.6
methanol	15.5	15.0	14.0
i-propanol	16.0	15.8	14.3
t-butanol	17.7	17.4	15.3
1,4 - dioxan	15.5	17.6	17.6
THP	15.5	15.0	15.0
THF	15.5	15.0	14.5
Pyridine	15.8^{x}	15.5	16.0
n-butylamine	14.5^{x}	16.1	15.0^{x}
ammonia	13.2	13.2	13.2

* - calculated from the d_{001} spacings and are given in Å.

x - only the most stable spacing is given although further discussion of other spacings is given in the text.

conditions of both temperature and amine partial pressure.

Table 3.5 contains the slopes of the thermogravimetric curves of some mono-, di- and trivalent cation exchanged forms calculated from the dehydration region (120 °C - 520 °C) of the clay. A plot of these slopes against the charge density on the surface is shown in Fig. 3b. It has been shown[1,9] that the amount of water present in the interlayer region has a profound effect on the properties of montmorillonite. It was necessary to dry all cation exchange forms to ensure uniform levels of hydration. Table 3.5 shows that the charge density on each surface after being air dried in excess of 1 week may be dependent on the interlayer cation.

Since many of the experiments carried out in this work involved preheating the different cation exchanged clay to 120 °C the results in Table 3.6 indicate the amount of water lost by 550 °C as a percentage of the original weight of clay sample used and the amount of water lost by 120 °C as a percentage of the total water lost by the clay.

The results of the particle size analysis of the aqueous clay solution are given in Table 3.7 and plotted in Fig. 3c. The results of the scanning electron microscope study showed that all the powdered clay samples studied exhibit similar grain size. However, since the particle size of the base clay was 1 - 2 μm and all the cation exchange forms were prepared

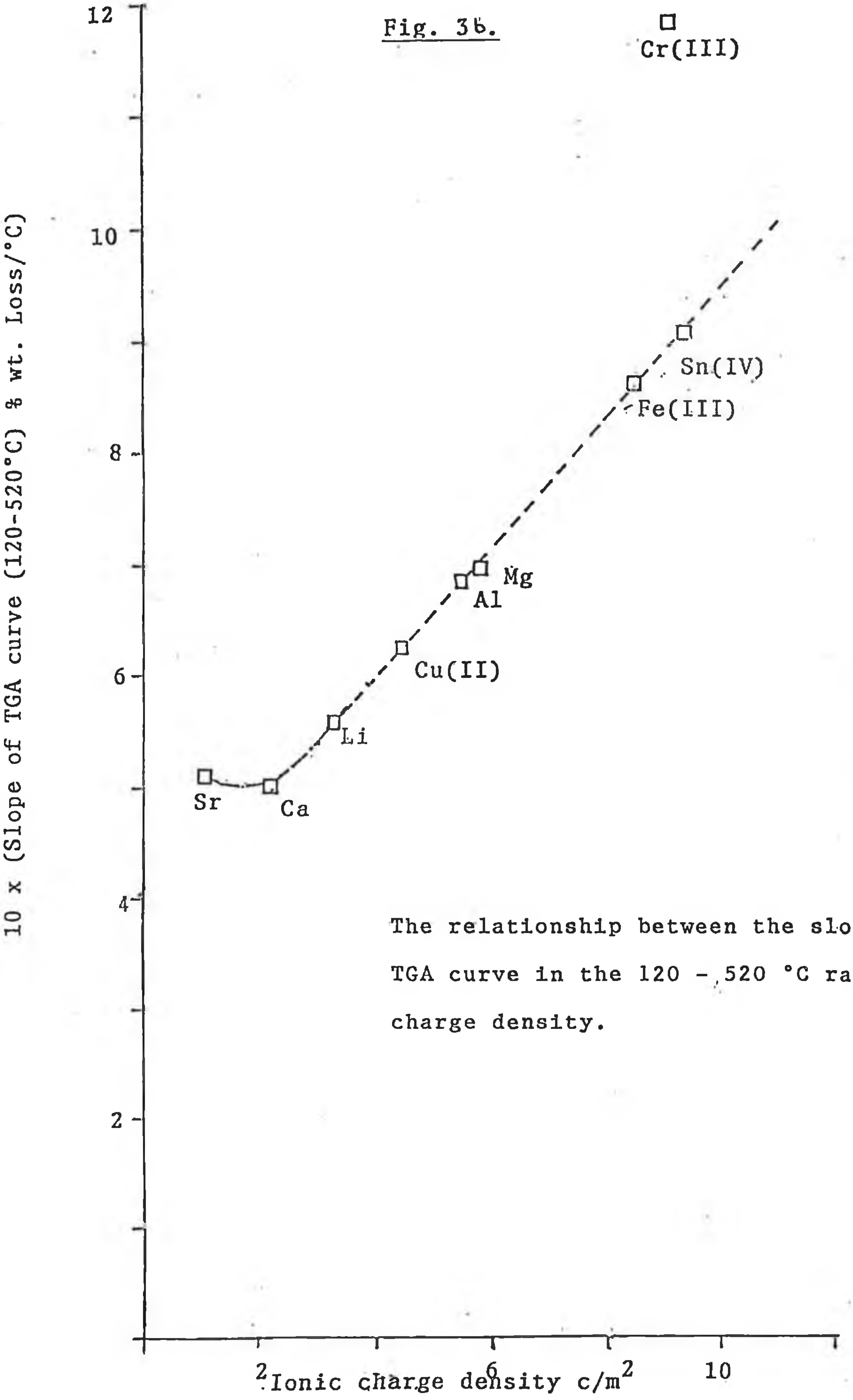


Fig. 3b.

The relationship between the slope of the TGA curve in the 120 - 520 °C range ionic charge density.

TABLE 3.5.

VALUES OF CHARGE DENSITY ON EACH CATION SURFACE AND THE CORRESPONDING SLOPE* OF THE T.G. CURVE.

Exchangeable cation	ionic radius	cationic$^{\Delta}$ surface area $(4\pi r^2)$/ $m^2 \times 10^{20}$	Charge density^{x} on cation surface	slope* of T.G. curve
Li	0.65	7.65	3.019	5.6
Mg	0.67	5.64	5.683	6.9
Ca	1.06	14.10	2.270	5.0
Sr	1.29	20.20	1.590	5.1
Cu(II)	0.76	7.26	4.417	6.25
Fe(III)	0.67	5.60	8.600	8.5
Cr(III)	0.65	5.30	9.070	11.8
Al	0.83	8.70	5.530	6.8
Sn(IV)	0.74	6.88	9.318	9.0

* - slopes calculated between 120°C and 520°C except where migration of the cation into the octahedral layer may occur for example Li-mont. in which case a range of 120 °C - 250 °C was used.

x - The charges were taken as 1.603, 3.206, 4.809 and 6.412×10^{-19} C for the mono-, di-, tri- and tetravalent cations respectively.

Δ - ref. 17.

TABLE 3.6.

PERCENTAGE HYDRATION OF THE VARIOUS CATION EXCHANGED MONTMORILLONITES.

Cation	percentage wt lost on heating*	percentage water lost by 120 °C[x]
Na	18.8	80
Sr	19.5	86
Ca	21.8	95
Fe(III)	18.8	76
Cr(III)	19.7	71
Al	16.8	66

* - Clays air-dried for 1 week then heated to 800 °C.

x - expressed as a percentage of total amount of water lost by heating to ~ 550 °C.

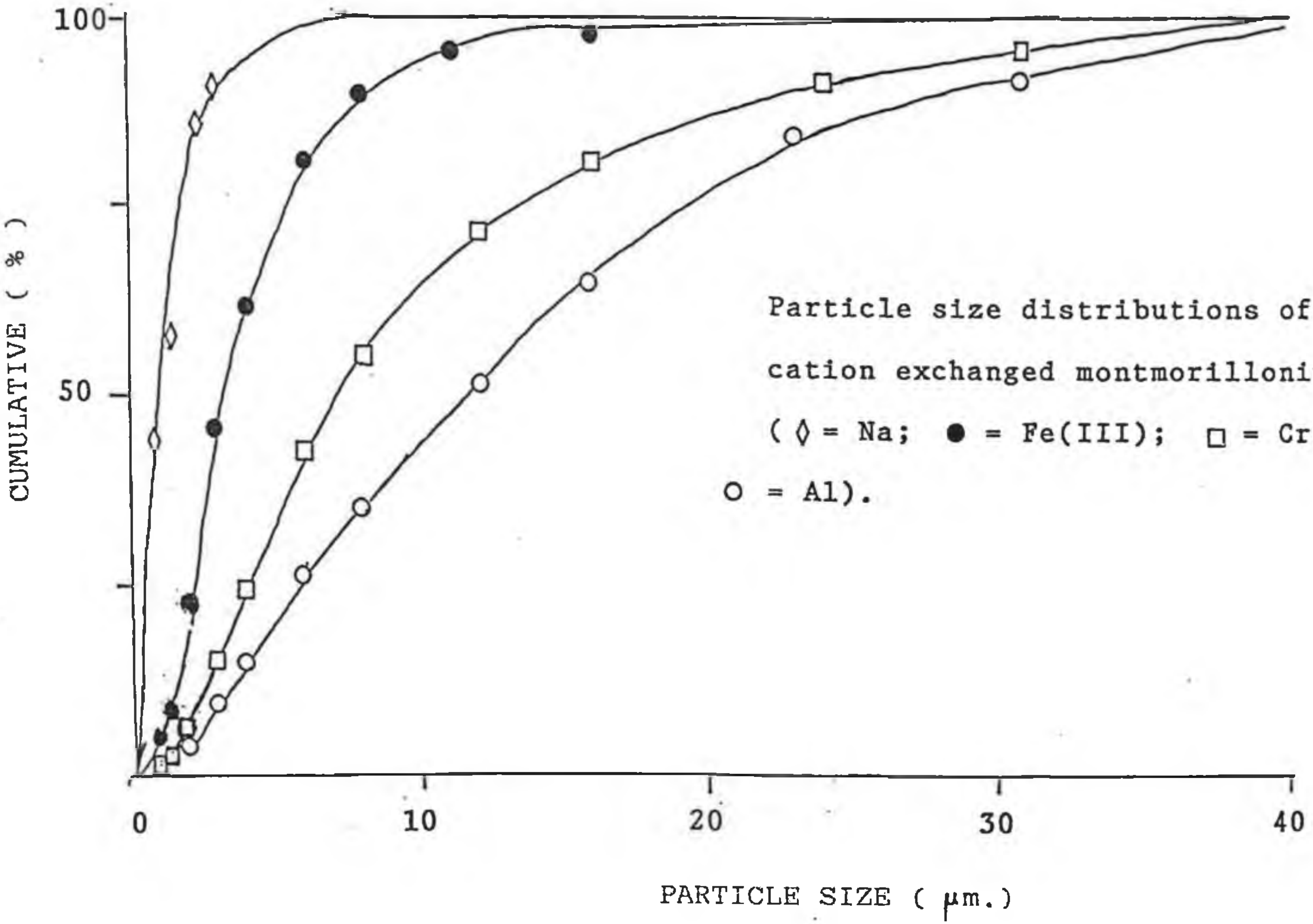
TABLE 3.7.

THE MEDIAN PARTICLE SIZE FOR THE DIFFERENT CATION EXCHANGED MONTMORILLONITES.

Cation	Median particle size*/ m in aqueous solution
Na	1.2
Sr	3.3
Fe(III)	2.0
Cr(III)	7.2
Al	11.7

* - median particle size at a cumulative volume of 50%.

Fig. 3C.



Particle size distributions of some cation exchanged montmorillonites. (◊ = Na; ● = Fe(III); □ = Cr(III); ○ = Al).

from this, then the particle size must be 1 - 2 μm and the granulometer results must reflect the aggregation or simultaneous passage of the individual particles.

3.5 Discussion.

3.5.1 Structural Formula and Cation Exchange Capacity.

The theoretical formula for the smectites, without considering lattice substitutions, is $Al_2Si_4O_{10}(OH)_2$ and the theoretical composition neglecting the interlayer material is SiO_4, 66.7 %; Al_2O_3, 28.3 %; H_2O, 5 %.[11] As explained in Chapter 1 smectites in general, and montmorillonite in particular, always differ from the above idealised formula because of substitution within the lattice. The general formula for montmorillonite is given by

$(Si_{4-y}\ Al_y)(Al_{a-y}\ Fe_b\ Mg_c\ Cr_d\ Mn_e\ Li_f)\ O_{10}(OH)_2\ -\ X_g$

where X are the exchangeable cations. If it is assumed that the consistuent oxides (Table 3.1) are the only ones present then a molecular formula for the montmorillonite clay used in this study may be determined using the following rationale. If it is assumed[11] that there are 20 oxygen atoms and 4 hydroxyl groups per unit cell, that is there are 10 oxygen atoms and 2 hydroxyl groups per formula unit, and all the silicon atoms are in the tetrahedral sheet, the remainder of sites being occupied by aluminium then the molecular formula derived from the results in column 2 of Table 3.1 is

$$(Si_{3.86}\ Al_{0.14})(Al_{1.35}\ Fe_{0.08}\ Mg_{0.6})\ O_{10}(OH)_2\ -\ K_{0.07}\ Na_{0.59}.$$

From the results in Table 3.2 the cation exchange capacity of this clay was 68 ± 2 (meq/100 g). This value was affected by both the cation present in the interlayer and the pH of the back exchange experiments. At a pH = 0.8, when the interlayer cation was (nominally) Fe(III) this figure rose to 90 ± 2 meq/100g clay and with Cr(III) present this figure was 76 ± 2 meq/100g clay. This is probably due to the partial dissolution of some hydroxy or oxyhydroxy species formed on the clay surface during the exchange process. In addition at low pH (0.8) the leaching of cations from within the clay lattice is also a possibility, although this is unlikely to be a cause for an increase in C.E.C. in the Cr(III)- form because no Cr(III) was found in the analysis of the clay (see Table 3.1). At a pH equal to 4.0 the exchange solution removes those Cr(III) cations which occupy the exchange sites but is not acidic enough to dissolve the hydroxy or oxyhydroxy species present. In the case of the Fe(III)- exchanged clay the formation of $Fe(OH)_3$ from the Fe(III) cations may occur therefore making it non-exchangeable.

However, the cation exchange capacity estimated in this fashion, only yields an average value computed over the entire clay surface and does not give any indication about the heterogeniety of that surface. This aspect will be considered in the next section.

3.5.2 Determination of Layer Charge Heterogeniety.

The surface charge density distribution in smectites is one of the most important parameters in understanding adsorption behaviour. It has been shown, by Maes et al.,[13] that in montmorillonite the exchange of simple inorganic ions is very much dependent upon charge density. One method for measuring the isomorphic layer charge is the quantitative exchange of the interlayer cations of smectites by alkylammonium ions. This approach also helps in the characterisation of montmorillonites.[16]

Alkylammonium ions in montmorillonite.

The results of the alkylammonium cation exchange experiments collected in Table 3.3 and illustrated in Fig. 3a show that the layer charge on the montmorillonite clay used in these studies is not very uniform. Ideally as the complexes are formed the alkylchains from opposing surfaces move over one another and interpenetrate so as to form a single layer of ions and thus form a discrete repeat distance with a unique d_{001} spacing of 13.6 Å. As the alkylchain length increases this interpenetration becomes more difficult until a chain length is reached at which a single layer of ions can no longer be accommodated on the clay surface thereby causing a second layer or a bi-layer complex to be formed, again with a discrete distance, resulting in a unique d_{001} spacing of 17.6 Å. This means that the monolayer (13.6 Å form) rearranges into the bilayer (17.6 Å form) if the area of the flat-lying alkylammonium ion becomes larger than the equivalent area. However the chains tend to interlock at some point short of this interpenetration. The opposing forces acting at the clay surfaces determine this 'stable' point for each complex of different alkylchain lengths.[18] In an alkylchain methylene groups occur at 2.52 Å intervals. There are, therefore, free energy maxima at similar intervals along the chain and it is believed that the chains tend to stick at these maxima when drying. The result is that each complex will interpenetrate to give d_{001} spacings which may be slightly higher than would be calculated for both the mono- and bilayers at 13.6 Å and 17.6 Å respectively. The broad diffraction peaks found in the diffraction profile indicate that interpenetration has taken place but in a random fashion.[18]

From the results collected in Table 3.3 and plotted in Fig. 3a, it can be seen that for alkylammonium ions with chain length of 5, 6 and 7 carbons a discrete monolayer spacing is observed and the slight deviation of the distances found is explained above. The d_{001} spacings for units of 8, 9, 10 and 11 carbons show a double or bi-layer spacing as was expected (represented by the open squares for the bi-layer and the closed squares for the mono-layer). From the transition point, n_c in Fig. 3a, the charge density of the surface of these clay particles was calculated to be 81 meq/100g clay. This figure is higher than the cation exchange capacity found by the other method used in this study. Assuming that the internal surface charge contributed approx 80% to the cation exchange capacity of the clay, this figure yields a C.E.C. for this clay in the region of 101 meq/100 g clay. But Table 3.3 and Fig. 3a also indicate the continued presence of a monolayer complex, m_1, the open squares, with a d_{001} spacing of 14.5 Å at chain lengths of 9, 10 and 11 carbons. Using the method employed by Lagaly[5] at the point n_2 this suggests the presence of clay particles with a low charge density distribution which in this case was found to be less than 31 meq/100 g clay and therefore, assuming this to be about 80 % of the total C.E.C., these clay layers have a total C.E.C. of ~37 meq/100 g clay. It is obvious that the C.E.C. of the montmorillonite clay used in this study is an average of these two extreme values.

In studying reduced charge montmorillonites (RCM's) Maes et al.,[13] suggested that no bilayer spacing was observed because when the larger chain compounds are taken up into the interlayer space they only displace the cations close to the edges leaving the inorganic cation at the interlayer surface. The alkylammonium ions with 16 and 18 carbon units seem to have been intercalated here in such a manner.

3.5.3 X-ray Diffraction Studies of Solvent Exposed Clay.

The results given in Table 3.4 indicate the large number of different basal spacings found when each of the trivalent cation-exchanged derivatives were exposed to the different solvents utilised in later sections of this work. As the clay samples were all dried at 120 °C and cooled in a desiccator prior to exposure to the solvent vapour the basal spacings for the three derivatives immediately after drying were obtained. It should be noted from Table 3.4 that the basal spacings for the three clay forms are not all identical. The spacing of 9.6Å for the Fe(III)- derivative suggested complete dehydration of the clay but as indicated in Chapter 1 if such an event occurred the rehydration would be very difficult if not impossible but this basal spacing would only represent an average value and there was probably some water remaining at the clay interface to facilitate adsorption of the various solvents.

The solvents used here were the solvents used in further studies contained in this thesis and represent three types of general solvents, (i) the alcohols, (ii) the cyclic ethers and (iii) bases, each of which vary in their orientation relative to the clay layer and interlayer cation present.

i) The Alcohols.

As it is known that alcohols compete directly with hydration shell water for ligand positions[1] the differing basal spacings are caused by numerous factors such as solvent orientation with respect to the interlayer cation, whether they are adsorbed in single or double layers etc. The actual basal spacing obtained for each clay is dependent on the solvent used.

Methanol, being both the smallest of the three and linear, causes the smallest change in the basal spacings for each cation exchange form and t-butanol being the most non-linear of the three causing the largest change in the basal spacing.

ii) The cylic ethers.

The next three solvents in Table 3.4 are cylic ethers. Here the Fe(III)- derivative seems to have been affected by removal of most of its hydration shell water and the three solvents all yield identical basal spacings of 15.5 Å. The other two exchange forms yield different spacings for each of the three solvents studied with the largest being due to 1,4-Dioxan.

iii) Bases.

The third group of solvents were found to have the most diverse range of basal spacings of any of the three solvent groups studied.

The Fe(III)- montmorillonite gives a number of different spacings for pyridine and n-butylamine suggesting a number of different orientations for these molecules within this exchange form. Upon subsequent exposure to air the Fe(III)-clay/base complex reverts to the more stable form with spacing of 15.8 Å and 16.0 Å for pyridine and n-butylamine, respectively. The instability of the higher spacing, 23.3 Å form with pyridine and its conversion to the 15.0 Å form in the Na^+- exchange form has been the subject of an extensive study by Breen et al.[20]

Similarly, the Cr(III) and Al forms exhibited a single spacing for both pyridine and n-butylamine following exposure to air. The ammonia intercalate of the M(III) exchange forms exhibited a single, uniform basal spacing which was so similar to that of a water clay that corroborative evidence through infra-red spectroscopy was necessary to confirm that adsorption of NH_3 onto the clay had occurred.[21]

3.5.4 Thermogravimetric Analysis of Clays.

Using thermogravimetric curves for various air-dried cation exchanged montmorillonites the number of major thermal events, as well as their length and steepness can be related to the number of water molecules liberated and the binding energy holding them to the interlayer cation or on the clay surface.[22] Other polar solvents, for example alcohols and cylic ethers have also been studied in this way, see Chapter 4.

These water molecules can be classified into three types: (i) The "free water" which is found in the case of pastes and gels and is easily removed at a temperature slightly above room temperature. This phase is required when cation exchange is performed. (ii) The "surface water" which is physically bound to the clay surface and requires slightly higher energy to be removed. (iii) The water molecules which are in the primary coordination sphere which are attracted to the positively charged cations and are electrostatically bound to them. These molecules require the highest energy to overcome these attractive forces.[22] It is generally accepted that these water molecules are the source of the clay's surface acidity[21,23] discussed in Chapter 4.

Below ~100 °C the curves were found to be almost identical to each other and have very steep slopes. In this temperature range both the free water and surface water would be expected to be desorbed and the presence of a large volume of these types of water is indicated by the size of the in the first peak derivative thermogravi-metric curves.

Each TG curve exhibits a different slope in the temperature region 120 °C to 520 °C which is considered to be the dehydration region of montmorillonite clays. The different slopes may be explained by the fact that the hydration shells of the various interlayer cations require different temperatures for their removal. Fig. 3b shows the relationship between the slopes and the charge density on the cation surface. There is only one point which deviates from the expected linear relationship. This may be explained either by the much longer residence time for water molecules around the Cr(III) cation,[24] thereby increasing the energy needed to displace any water from the primary coordination shell of this cation to a level above that expected from its charge density. Or, secondly, it could be due to the formation of hydroxy and oxyhydroxy Cr(III)-derivatives in the interlamellar region of the clay and the degradation of these species upon heating.

Fig. 3d

Derivative thermograms of air-dried trivalent cation-exchanged montmorillonites.

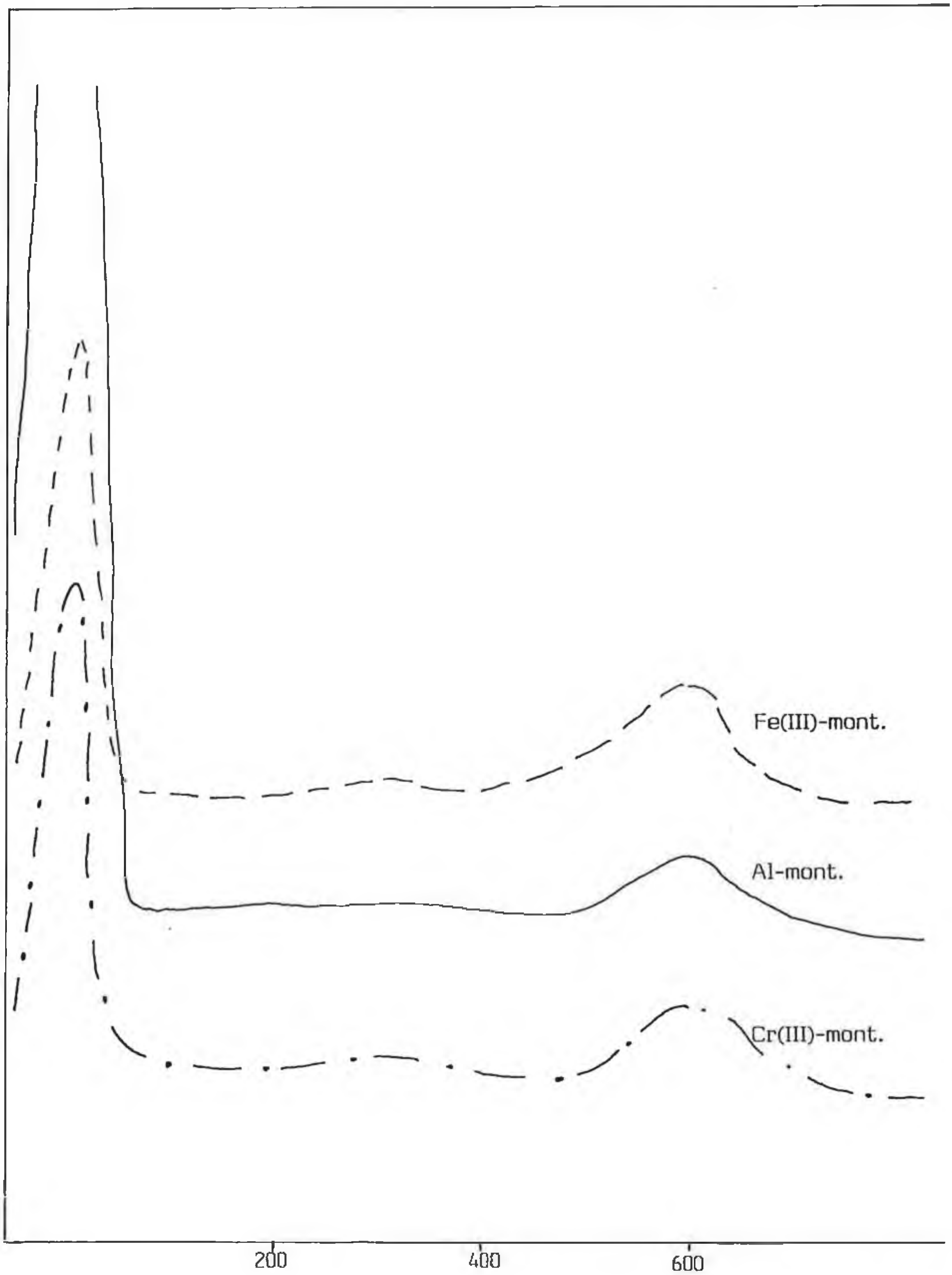
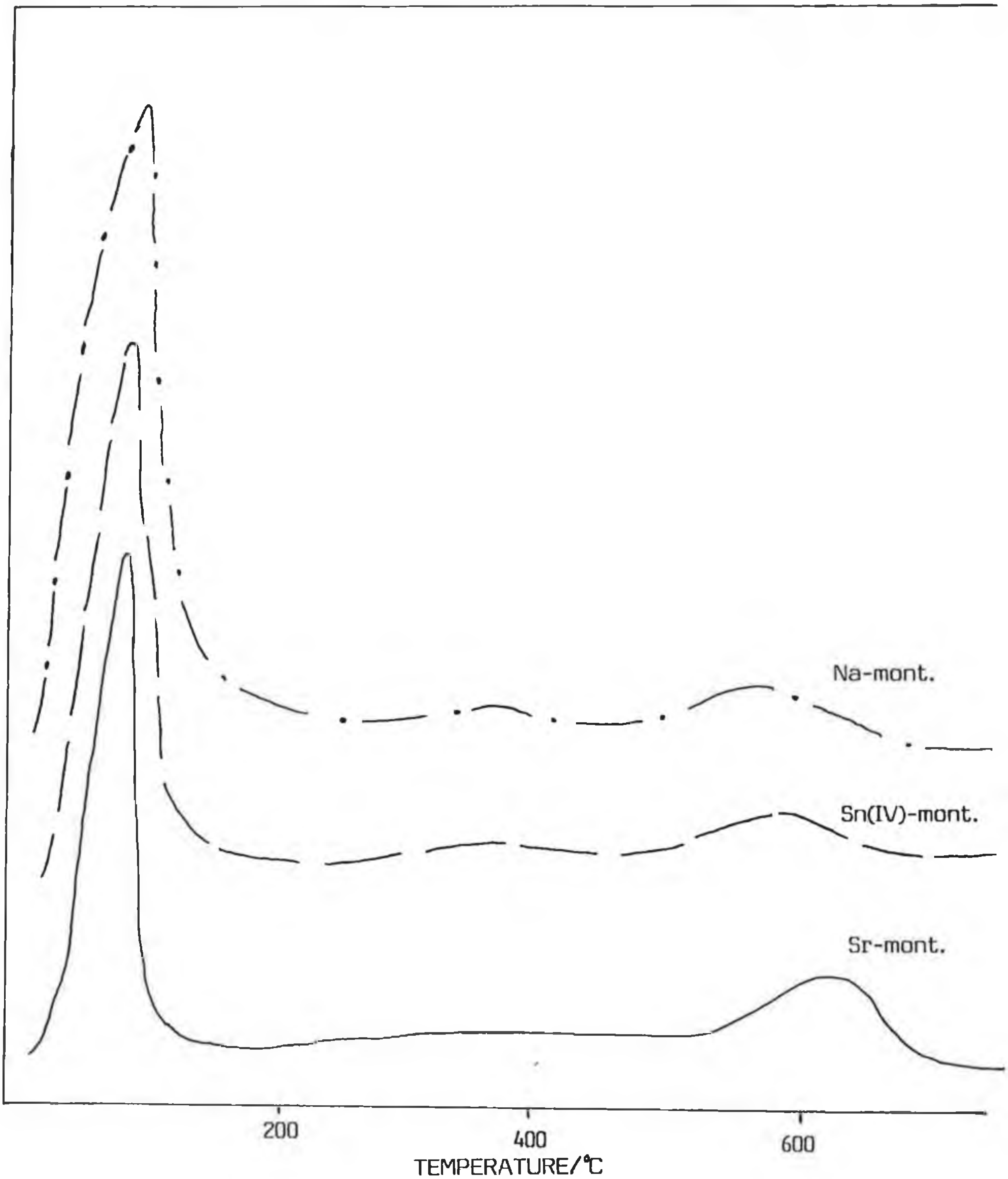


Fig. 3e.

Derivative thermograms of some cation-exchanged montmorillonites of varying valencies.



In the derivative thermograms collected in Figs. 3d and 3e the removal of the hydration shell water is not observed because there is no change in slope during the desorption process. This unchanging slope may be caused, in part by incomplete removal of the water molecules from the clay interlayer in the temperature range 20-250 °C, the presence of which has been confirmed by infra-red spectroscopy.[21] A water molecule which is tightly held may become trapped at the surfaces following collapse of the clay layers and therefore cannot be recovered rapidly by using high heating rates but are removed slowly and continuously from the narrow channels formed after collapse.

The dehydroxylation of all the various cation exchanged montmorillonites under investigation seems to occur in almost the same temperature range and the peaks in the derivative thermograms all have approximately the same shape and intensity. This is because the dehydroxylation of the clay mineral is directly related to the clay used and does not depend upon the exchangeable cation present in the interlayer. The dehydroxylation region was between 550 °C and 750 °C as expected.[3]

3.5.5 Thermal Pretreatment of Samples.

Many of the experiments carried out in this work involved predrying the different cation exchanged montmorillonites to 120 °C and consequently the amount of water removed by this treatment is of relevance.

The results in Table 3.6 fall into two categories; the trivalent cation exchanged clays and the mono- and divalent cation exchanged forms. The amount of water lost by the trivalent cation exchange derivatives by 120 °C is approximately 70 % of the total amount lost by 550 °C, which contrasts with the mono- and divalent exchanged forms which lose in excess of 80 %. It must, therefore, be assumed that a substantial proportion of the layers are collapsed in the mono- and divalent cation exchanged derivatives at this temperature. The effect is probably due to the smaller charge density on the cationic surface of the lower valency forms as opposed to the trivalent cation exchanged derivatives.

3.5.6 Particle Size Analysis.

i) Particles in aqueous suspension.

The results of the particle size analysis in aqueous suspension display a wide variety of particle sizes which was unexpected as all the clay derivatives were made from the one sample of base clay. The results given in Table 3.7 give the median particle size for five different cation exchanged forms and a plot of the particle size distribution is shown in Fig. 3c. Because of the variety of particle sizes it must be assumed that the introduction of the various cations into the interlayer and the subsequent generation of oxyhydroxides leads to greater edge to edge and edge to face interactions which may not be broken down by the reintroduction of water. The stability of these associations is demonstrated by the fact that even ultrasonic treatment failed to cause a complete dispersion of the clay.

ii) Particles in powder form.

The results of the scanning electron microscopy study showed that when the clays are in the powdered form they all seem to have about the same average grain size after passage through a <45 μm sieve.

3.6. Conclusions.

The montmorillonite clay used in these studies was found to differ from the ideal smectite structure with replacement of silicon by aluminium in the octahedral sheet and of aluminium by iron and magnesium in the tetrahedral sheets. It was found to have a structural formula of

$$(Si_{3.86}\ Al_{0.14})(Al_{1.35}\ Fe_{0.08}\ Mg_{0.6})\ O_{10}\ (OH)_2 - K_{0.07}\ Na_{0.59}$$

The replacable cations in the 'unrefined' form being potassium and sodium. The cation exchange capacity of 68± 2 meq/100 g clay was found to be an average value of the charge density on the clay layer with some layers having a cation exchange capacity as high as 101 meq/100 g clay whilst others were as low as 37 meq/100 g. The determination of this capacity was found to be pH dependent only when the clay contained certain exchangeable cations, such as Fe(III)- ions.

The structural properties of the clay mineral depend largely on the presence or absence of interlayer water as well as on the exchangeable cation. This water exists as three distinct species at the clay surface. The water in the coordination shell is directly related to the exchangeable cation and its removal is characteristic of the surface charge density of the cation.

The effect of different metal ions exchanged into the interlayer can be seen to be extensive. It not only varies the amount of hydration shell water present on a clay but also the adsorption of different solvents used in the following studies. The work reported in this Chapter therefore shows how important characterisation of the clay used in any study is before direct comparision of data can be made.

CHAPTER 4.

A STUDY OF THE ACIDITY OF SOME TRIVALENT CATION-EXCHANGED MONTMORILLONITE.

4.1 Introduction

Most, if not all, of the reactions catalysed by clay minerals use the 'acidic' nature of the clay mineral surface to carry out such reactions.[1-4] In fact, it is currently accepted that this 'surface acidity' is not on the clay surface itself but is caused by the dissociation of the hydration shell water polarised by the exchangeable metal cation. Many techniques have been used in the study of 'surface acidity' of acid catalysts in general and clay acidity in particular. These techniques range from infra-red spectroscopy, which detects, as suggested by Mortland et al.,[5] Russell,[6] and Mortland and Raman,[7] the production of a protonated ion in the interlayer space, to the adsorption of coloured compounds and the absorption intensity at the wavelengths characteristic of protonated species analysed by ultra-violet spectroscopy.[8]

A technique which has received wide attention in the study of catalytic activity in general and acidic activity in particular is temperature programmed desorption (TPD). This technique has been used to considerable advantage in the elucidation of the number and type of adsorption sites on a wide range of solid surfaces which exhibit catalytic properties.[9-11] Because of the required high sensitivity of the instruments adapted to this technique it has only become widely used in recent years. However as with most techniques, the TPD results should only be interpreted with the aid of corroborative evidence from one or more of the other techniques.

The acidity measurements carried out in this work were done using the temperature programmed desorption technique and infra-red spectroscopy. The purpose of the studies reported here was to determine the type and relative strength of acid sites on a number of trivalent cation-exchanged montmorillonites which have been used in a number of novel organic reactions.[2]

4.2 The Thermobalance.

The instrument used in this study was a Stanton-Redcroft TG750 thermobalance. It is a sensitive apparatus designed to give a direct plot of weight versus temperature for any sample in the temperature range ambient to 1000°C. The thermobalance may be used for isothermal studies (as in Chapter 5) or for controlled heating (or cooling) studies. A derivative thermogravimetric unit was used in conjunction with the thermobalance. This unit gives the rate of weight loss versus temperature curve which is referred to as the derivative thermogravimetric curve or DTG curve. Specifications of the thermobalance are given in Table 4.1.

TABLE 4.1.

SPECIFICATIONS OF THE STANTON-REDCROFT 750.

Temperature range:	Ambient to 1000°C
Heating rate:	1, 2, 3, 5, 10, 15, 20, 30, 50, 100 °C/min.
Programme modes:	Heat-hold; heat-off; cool-hold; cool-off; isothermal.
Sample size:	0.1mg - 100 mg.
Balance ranges:	Between 0-1mg f.s.d. and 0-250mg f.s.d.
Temperature measurement:	Pt V Pt 13% Rh platform thermocouple.
Atmosphere control:	Static air or gas flowing air or gas.

4.3 The Infra-red Spectrophotometer.

The instrument used in these studies was a Perkin-Elmer 983 Infra-red Spectrophotometer. It is a double beam, optical null precision instrument. Specifications of which are given in Table 4.2.

TABLE 4.2.

Principle:	Real-time, double-beam, ratio-recording with presample chopping.
Optics:	F4.2 monochromator with 4 gratings and 9 filters, purgeable.
Source:	Oppermans Source (self-igniting and self regulating).
Detector:	Coated caesium iodide lens thermocouple.
Abscissa range:	5000cm^{-1} to 180cm^{-1}.
Ordinate Accuracy:	Better than 0.1%T.
I_o flatness:	Better than ± 0.5%T
Abscissa repeatability:	0.005cm^{-1}.
Scan Time:	usually 8 mins.

4.4 Experimental

The clay samples were prepared as described in Chapter 3. Clay flakes for the infra-red studies were prepared by air-drying the different cation exchanged clay suspensions on sheets of plastic which were later removed. Before exposure to the bases the clays were either exposed to air or dried at 120°C for 16 hours, then exposed to the solvent vapours for a minimum of 16 hours. The clay samples were then transferred to the thermobalance as quickly as possible and the TPD spectra recorded.

Following exposure to these basic vapours a sample was transferred to the micro-balance and the DTG curve recorded using the following instrumental conditions: Heating rate, 20 °C min^{-1}; sample holder, inconel; N_2 purge gas dried by passage through 4Å molecular sieve and P_2O_5, flow-rate of N_2; $20cm^3min^{-1}$.

4.4.1 Temperature Programmed Desorption.

In this study the method of temperature programmed desorption used was that of derivative thermogravimetry (DTG). The present study involves the exposure of the trivalent cation exchanged montmorillonite samples to the vapour of bases of different pK_b values,[12] as given in Table 4.3.

TABLE 4.3.

Base	pK_b
t-butylamine	3.17
n-butylamine	3.23
Cyclohexylamine	3.34
Octylamine	3.35
n-decylamine	3.36
hexylamine	3.44
Benzylamine	4.67
Pyridine	8.79

4.4.2 Infra-red Spectroscopy.

Having obtained a clay film the infra-red spectra were recorded at room temperature, then after one hour at 50, 100, 150 and 200° C using an evacuable variable-temperature cell with a maximum operating temperature of 200° C. The variations in thickness of clay film were compensated for by using IR bands arising from the clay matrix itself as internal standards as suggested by Russell [6] and described by Mortland and Raman.[7] X-Ray diffraction profiles were recorded on a Jeol JDS 8X diffractometer using CuK_{α} radiation at 40mV and 20mA.

4.5 Results

The desorption thermograms and corresponding IR spectra which are individually and collectly discussed later, are collected in Fig. 4a - 4i. The most obvious feature of the TPD profiles is the excellent resolution between different thermal events. This indicates that the different adsorption sites have well characterised desorption energies which greatly facilitated the interpretation of the experimental data.

Table 4.4 collects together the basal spacings and their relative intensities (with the most intense peak in any profile being given a value of 10) of the various samples studied in this work. The sample numbers refer to the figures in which the TPD profiles are presented. It has been shown that in a Na^+-montmorillonite/pyridine:water system[13] four different intercalates exhibiting basal spacings of 29.3, 23.3, 19.4, and 14.8Å can be formed depending on the pyridine/water ratio. Under conditions utilised in this study, i.e. clay saturated with pyridine, the Na^+-montmorillonite contains 34% by weight of pyridine and exhibits a rational series of 001 reflections commensurate with a 23.3Å form. This high spacing intercalate converts to the 14.8Å form over a period of 2 - 3 hours.[14] In general the TPD profiles for pyridine and n-butylamine represent a weight loss in excess of 20% which in conjunction with the basal spacing data summarised in Table 4.4, confirm that the bases are intercalated and not just surface species.

TABLE 4.4.

SUMMARY OF BASAL SPACING DATA
OF SAMPLES DESCRIBED IN TEXT

Cation /Solvent	d-spacing /Å	Sample No.^{x}	Relative^y Intensities
Fe(III)/pyridine	23.0	4a.4	10
	19.2		5
	15.0		7
Al/pyridine	15.0	4a.2	10
Cr(III)/pyridine	15.0	4a.3	10
Fe(III)/ n-butylamine	21.0	4e.4	10
	13.0		9
Al/n-butylamine	21.0	4e.2	10
	13.0		4
Cr(III)/ n-butylamine	21.0	4e.3	10
	13.0		--

x = sample number is the same as the number of the figure in which the TPD profile is presented.

y = most intense peak given intensity equal to 10

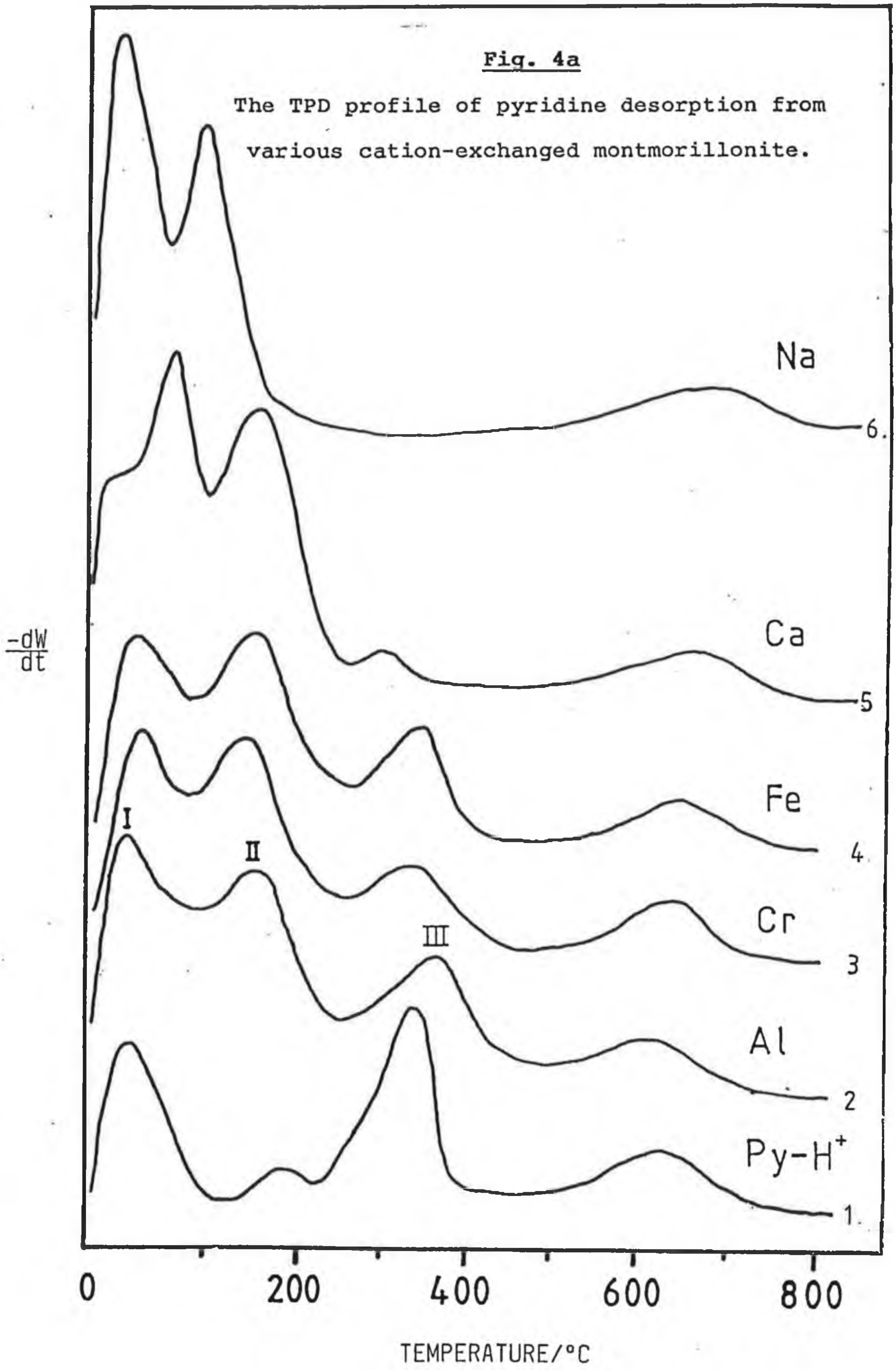
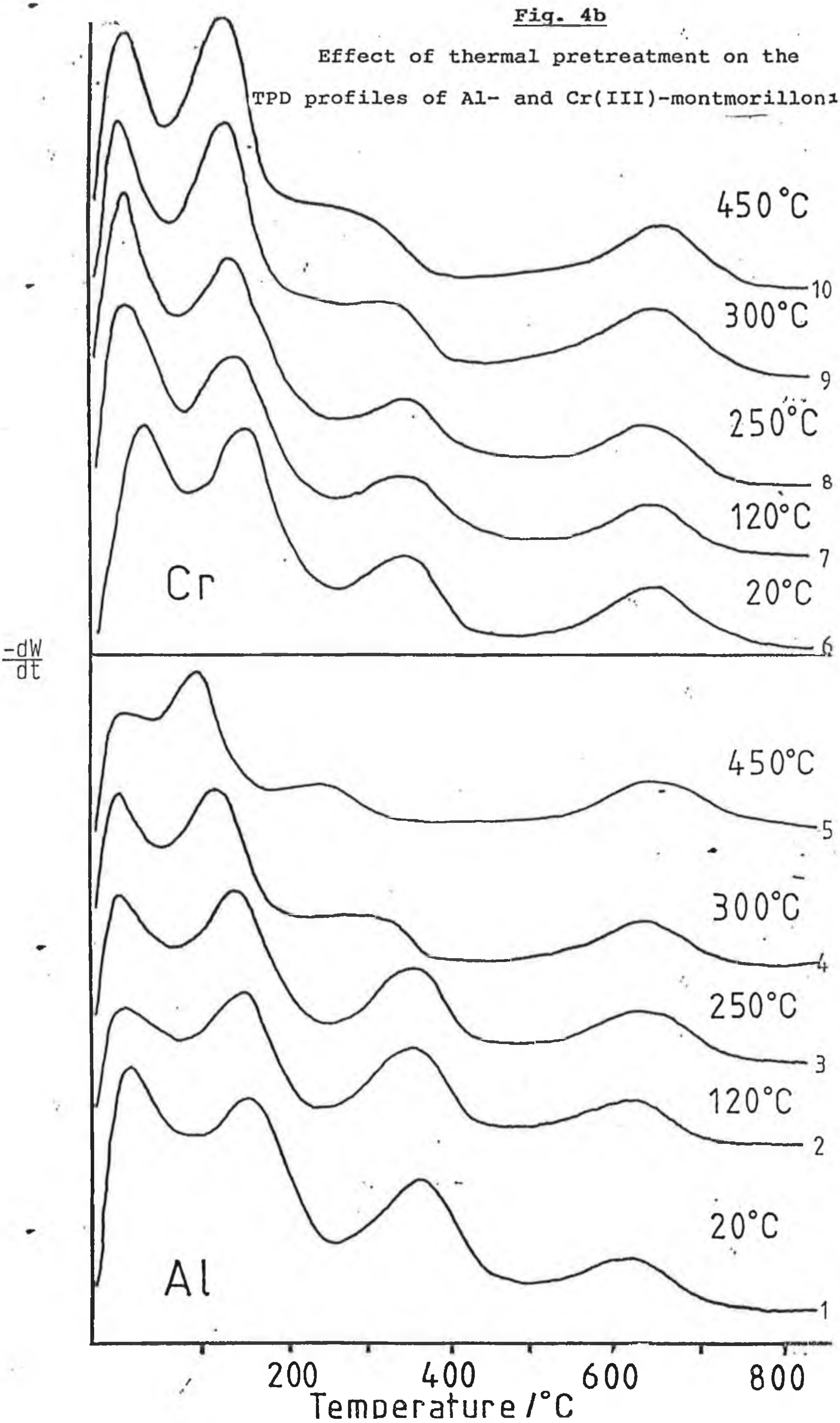


Fig. 4a

The TPD profile of pyridine desorption from various cation-exchanged montmorillonite.

Fig. 4b

Effect of thermal pretreatment on the TPD profiles of Al- and Cr(III)-montmorillonite



Before considering any specific results an overview should be taken to highlight some of the most obvious features from the many spectra obtained during the course of this work. Pyridine with a pk_b value of 8.79 was adsorbed onto the various cation-exchanged derivatives of the montmorillonite clays. The TPD spectrum of a pyridinium - exchanged montmorillonite (Fig. 4a.1) has four desorption peaks with maxima at 30, 190, 340 and 620° C. It is assumed that, the peaks at 30 and 620° C represent the loss of hydration water and lattice dehydroxylation respectively. The thermograms for the Al-, Cr(III)- and Fe(III)- montmorillonite (Fig. 4a.2 - 4a.4 respectively) are all very similar with three predehydroxylation peaks at 40, 150 and 340 °C, although the third peak for the Al- form occurs at 360 °C. Fig. 4a.5 and 4a.6 represent the desorption of pyridine from Ca- and Na- exchanged montmorillonite respectively. Only the peak at 150 °C in the Ca- form is common to the trivalent exchanged clays, although it does have a very weak peak centered at 300 °C

The types of adsorption sites in the Cr(III)- and Al- forms were found to be affected by the pretreatment temperature (Fig. 4b.4, 5, 9, 10) only if that temperature was above 300 °C. Pretreatment at this temperature shifts peaks II and III in both exchange forms to lower temperatures, the effect being more marked in the Al- form (Fig. 4b.4, 5). This lowering of peak temperatures continues up to pretreatment temperatures of 450 °C. The effect of thermal pretreatment on the Fe(III)- exchanged form is similar to the other two trivalent forms but it required much longer exposure times to reexpand, after heating to pretreatment temperatures even as low as 40° C. Several days were needed to re-establish peak III whereas peaks I and II quickly reappear.

The high pk_b of pyridine means that it should only react with strong sites. Therefore it was considered that other bases with lower pk_b should be used to study the interaction with weaker sites. The desorption spectra from an Al- exchanged montmorillonite of the other strong bases investigated, n-butylamine t-butylamine, cyclohexylamine and benzylamine, all with similar pk_b values, are shown in Fig. 4c.1-4c.5 respectively. These TPD profiles all exhibit three pre-dehydroxylation peaks and the peak position especially that of peak $III^{/}$ depended on the base used. Fig. 4d illustrates how the position and intensity of peak $III^{/}$ in the desorption profile varies when montmorillonite is exchanged with C_4 - C_{18} alkylammonium ions. This plot shows that C_4 - C_7 alkylammonium ions exhibit a desorption maximum at the same temperature and with similar intensities. This correlation did not hold for chain lengths in excess of seven carbon atoms.

Consequently Fig. 4c and 4d show that many bases exhibit desorption maxima indicative of a protonated species and would be useful in determining the protonating ability of the clay. However, it is

Fig. 4c

The desorption profile from Al-montmorillonite of some strong bases.

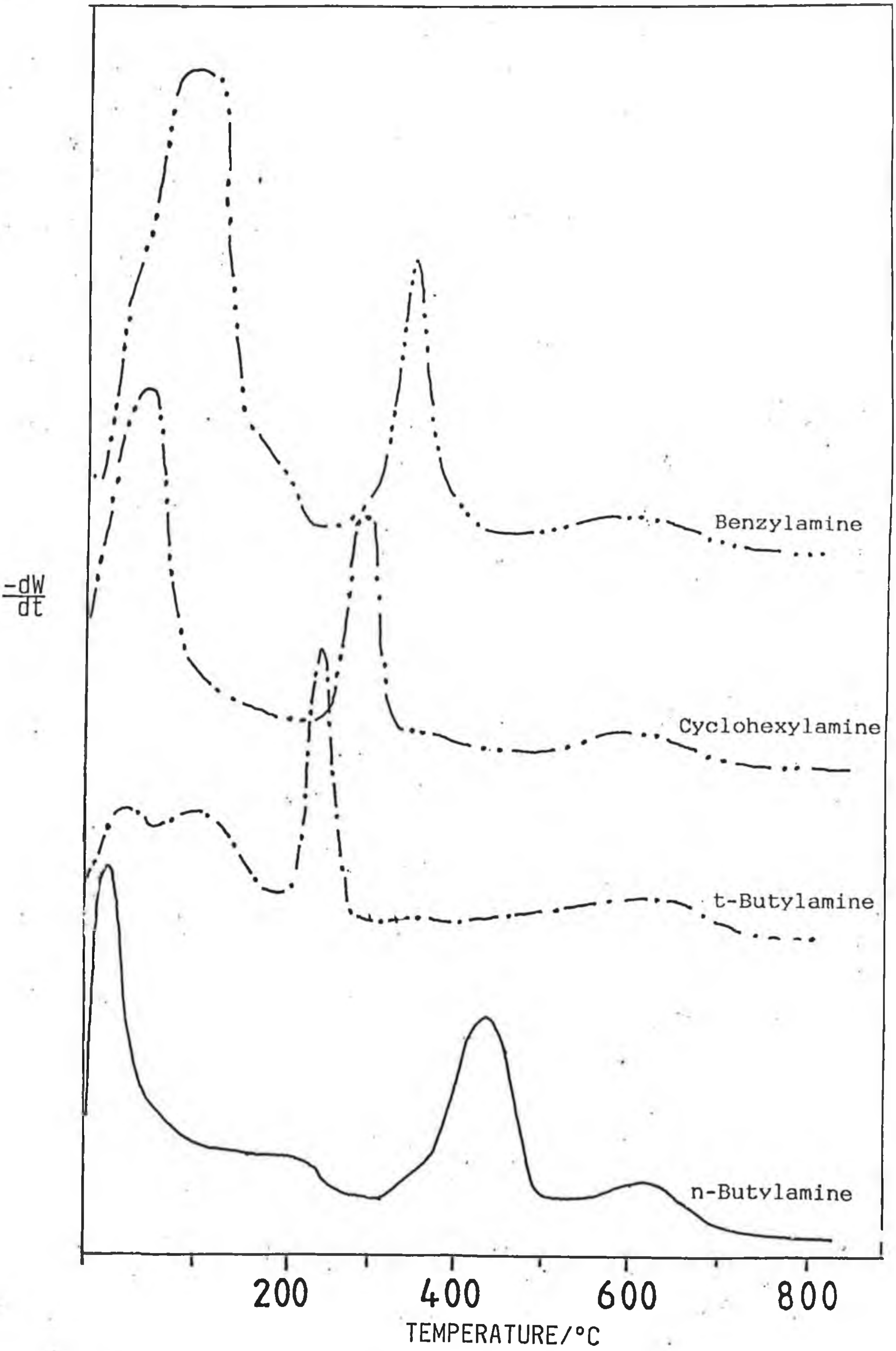
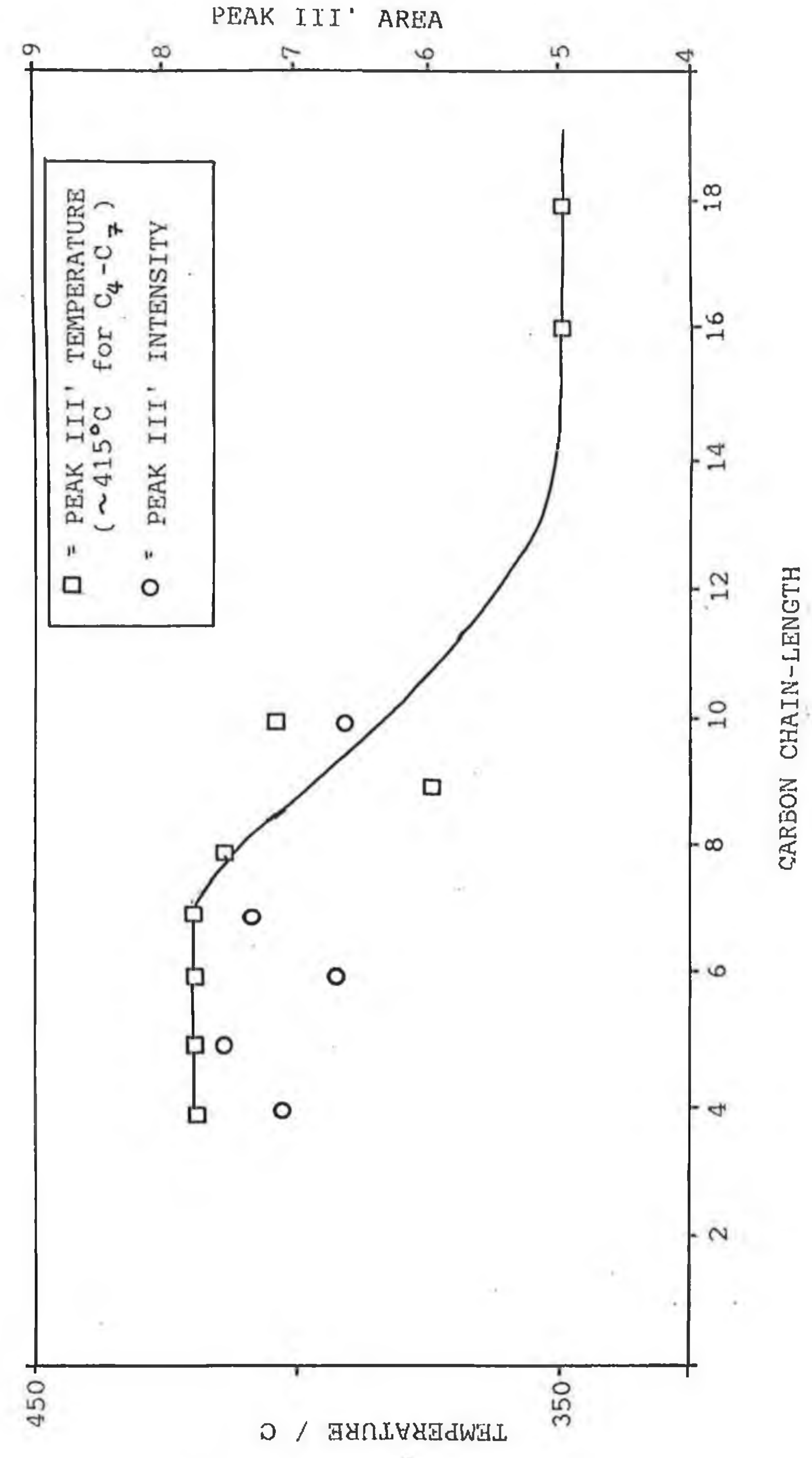


Fig. 4d

The variation in position and intensity of peak III/ in the TPD profile for C_4 - C_{18} Alkylammonium exchanged montmorillonite.



difficult to reconcile how the protonated form of bases which are stronger than pyridine (t-butylamine, cyclochexylamine and benzylamine) should desorb at lower temperatures. Therefore, n-butylamine was chosen because the protonated form desorbed at 50 °C above that of pyridine and because its small size should make more sites accessible due to reduced steric hindrance.

4.5.1 Desorption from Samples of Varying Grain Size.

Fig. 4e and 4f represent the thermal desorption profiles of pyridine and n-butylamine, respectively, from a room-temperature dried Al-montmorillonite of varying grain size. Fig. 4e shows that the pyridine desorption peaks become sharper with decreasing grain size but the temperature of the peak maxima are only slightly affected by grain size. However, Fig. 4e and 4f show that the dehydroxylation peak exhibits a marked shift to lower temperatures with decreasing grain size. The best resolution is obtained with grain sizes of $< 63\ \mu m$. The clay samples used in this study are known to be $< 45\ \mu m$.

4.5.2 n-Butylamine Desorption.

Fig. 4g collects together the desorption profiles of n-butylamine from the various cation-exchanged forms. The n-butylammonium exchanged montmorillonite (Fig. 4g.1) shows two desorption maxima, before the dehydroxylation peak, at 40° C and 410°C. The peak at 410 °C is very assymetric on the low temperature side. The Al-, Cr(III)-, Fe(III)- and Ca-

Fig. 4e.

The TPD profiles of pyridine from an air-dried Al-montmorillonite of varying grain size.

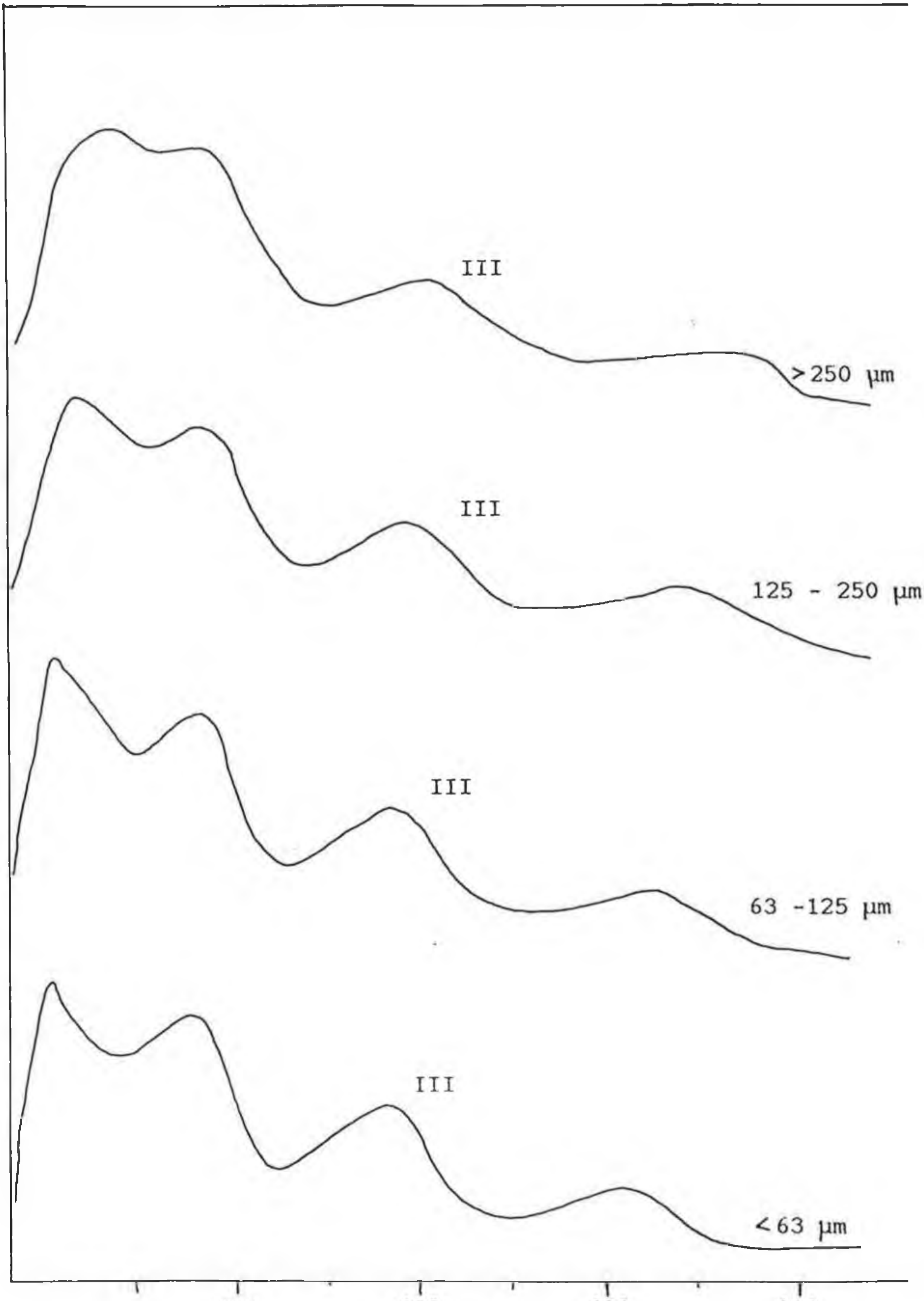


Fig. 4f.

The TPD profiles of n-butylamine from an air-dried Al-montmorillonite of varying grain size.

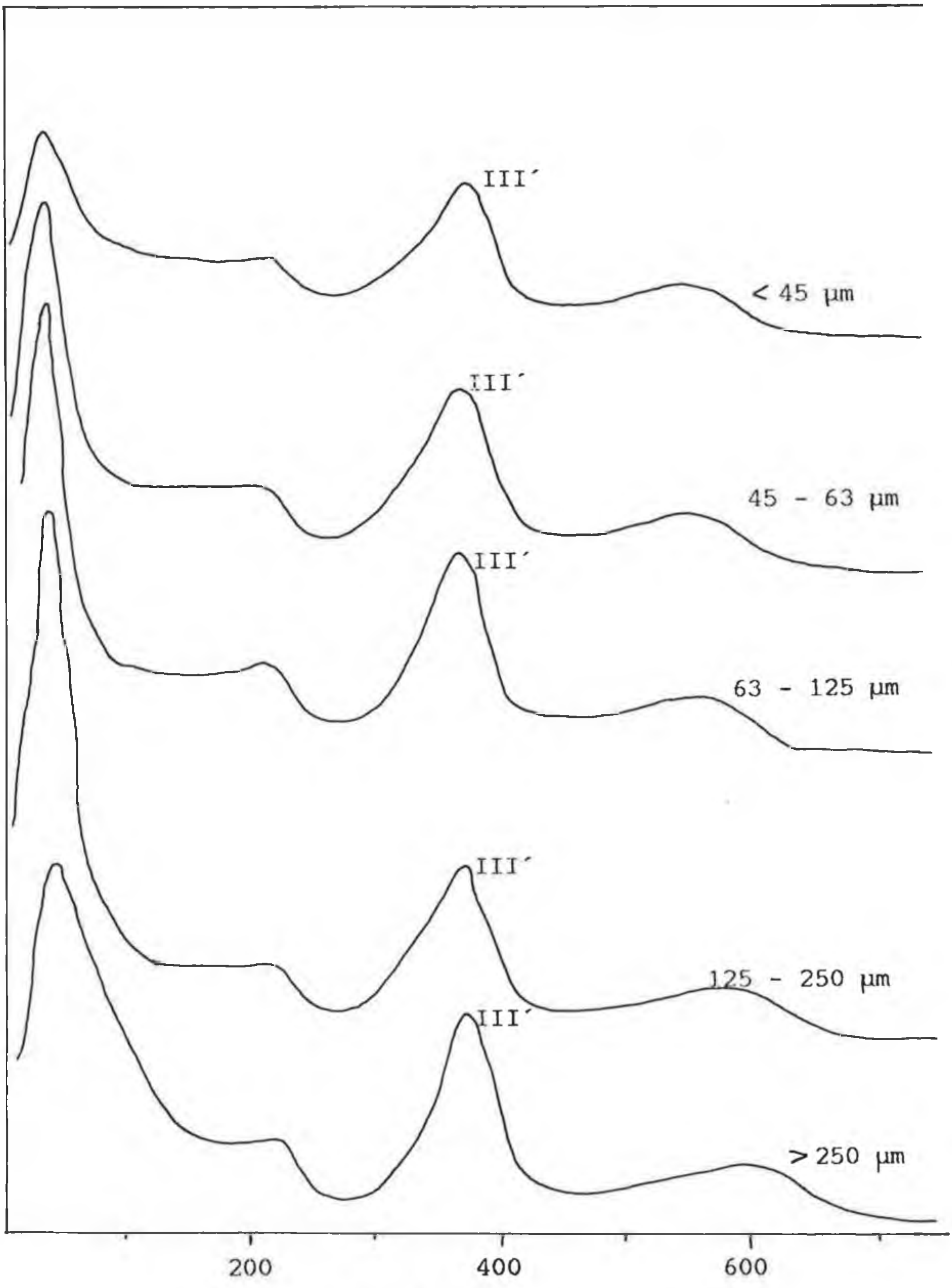


Fig. 4g

The TPD profiles of n-butylamine from the various cation-exchanged montmorillonite.

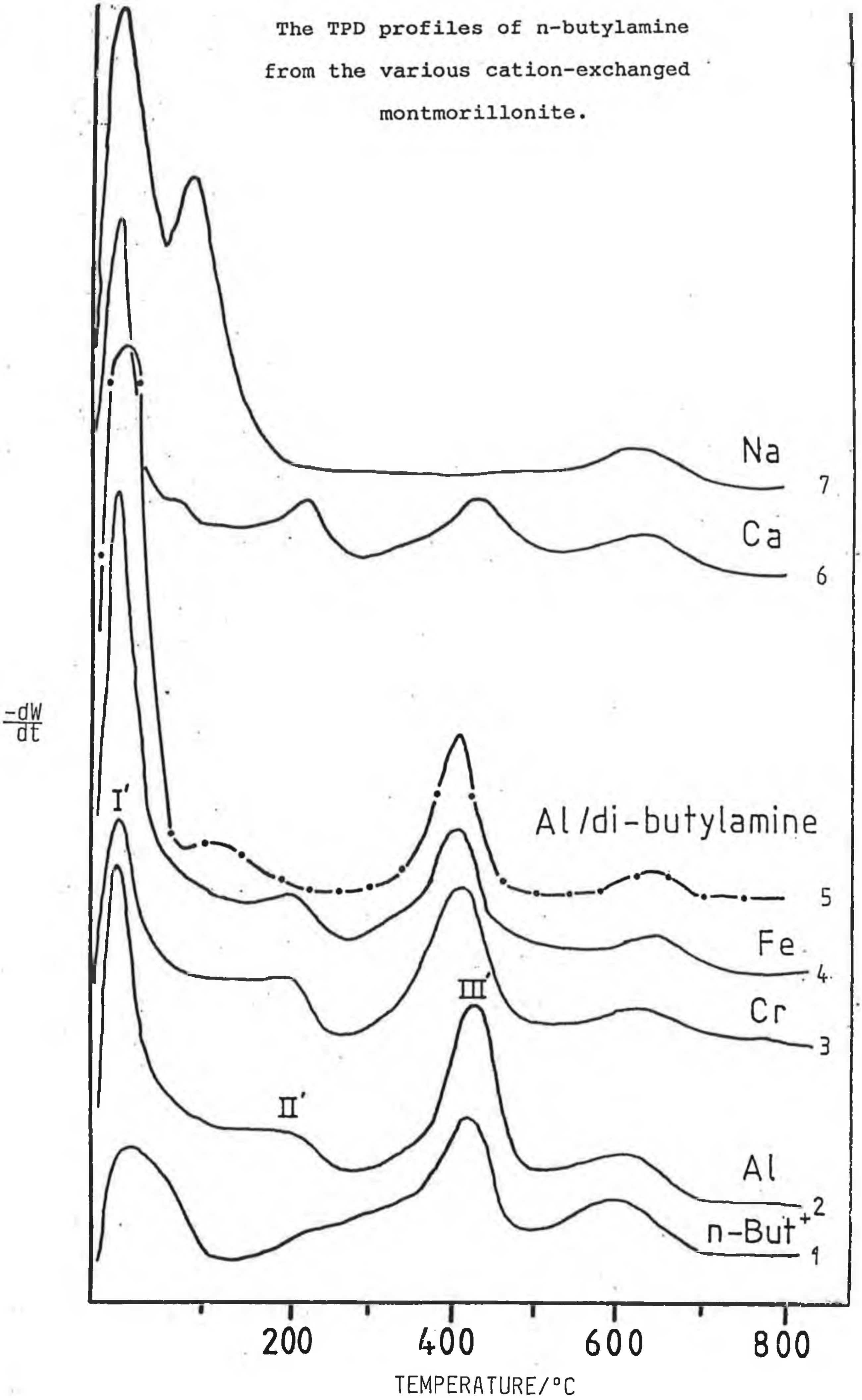
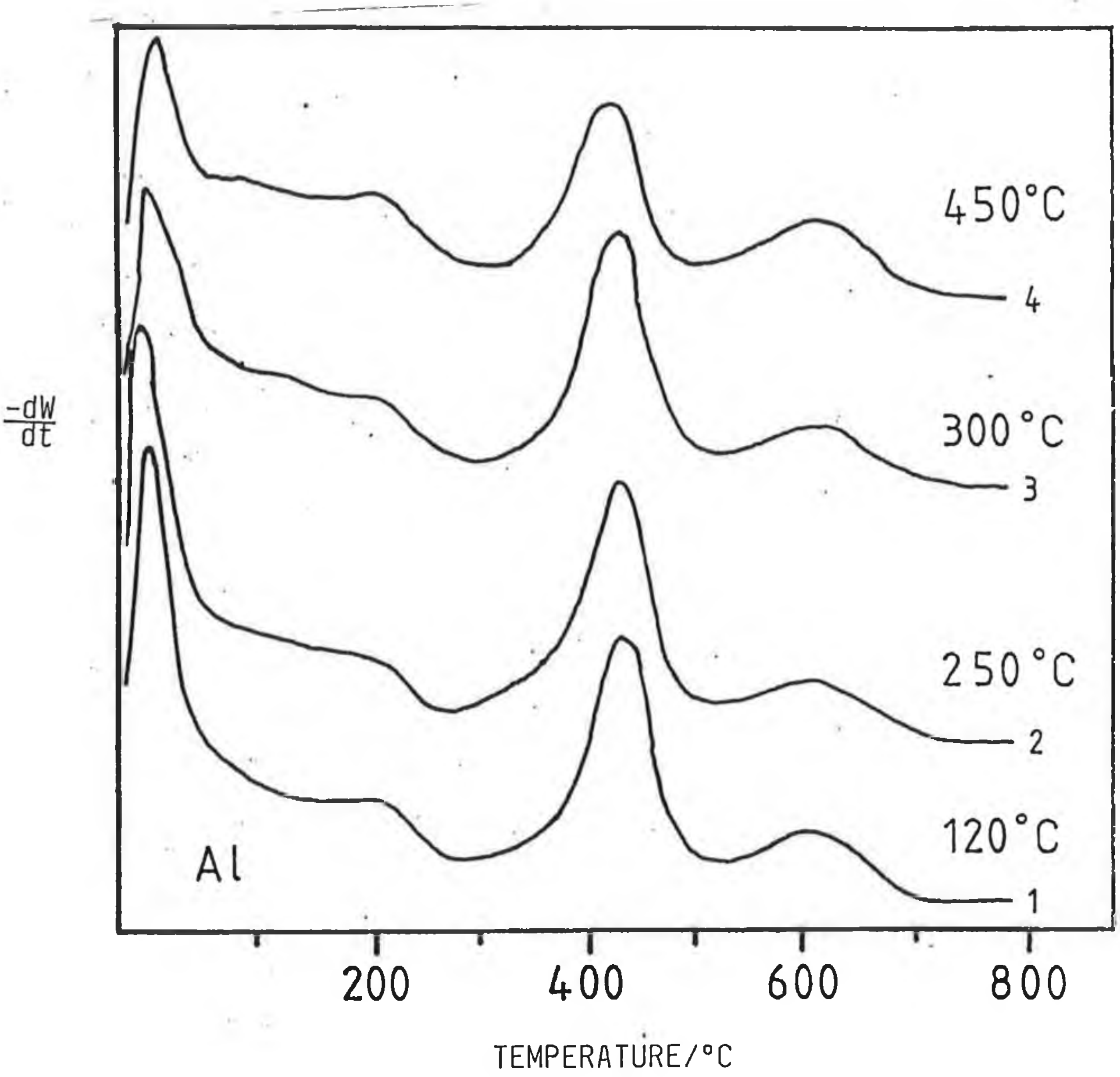


Fig. 4h

The effect of thermal pretreatment on the TPD profiles of n-butylamine from Al-montmorillonite..



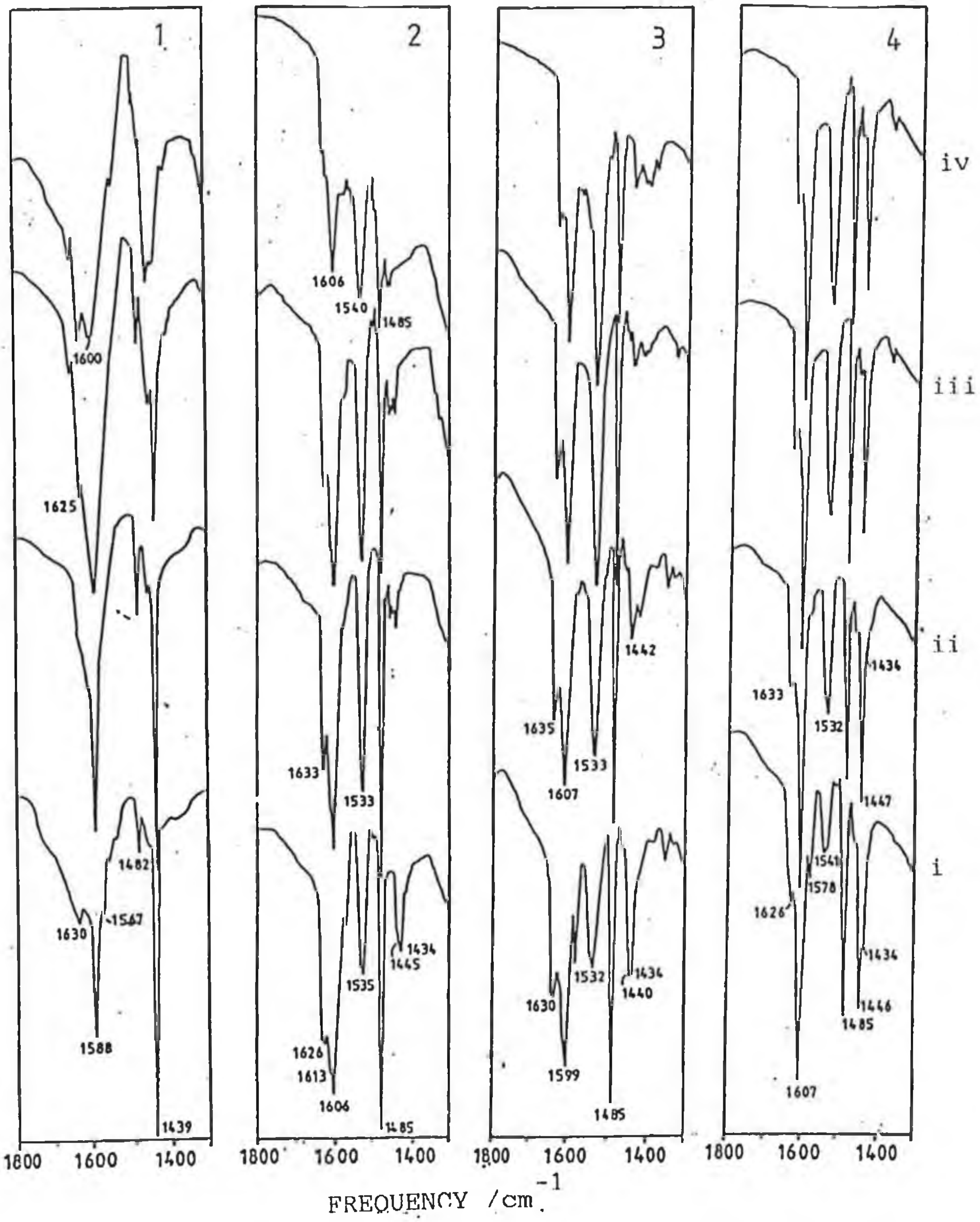
montmorillonite (Fig. 4g.2 - 5 respectively) all have three pre-dehydroxylation peaks at, or near 30,200 and 410 °C. Na- montmorillonite exhibits only two peaks at 30 and 90 °C. Thermal pretreatment at 450 °C does not seriously affect the number or position of the desorption peaks in the desorption profile of n-butylamine desorbed from Al- montmorillonite (Fig. 4h). The Cr(III)- and Fe(III)- forms behaved identically following thermal pretreatment at these temperatures.

4.5.4 Infra-red Studies.

The infra-red spectra of the air-dried Na-, Al-, Fe(III)- and Cr(III)- montmorillonite, following exposure to pyridine and subsequent evacuation at increasing temperatures are represented in Fig. 4i.1 - 4. Samples exhibit absorption bands when taken fresh from pyridine vapour, which using the assignments of Ward,[15] indicate the presence of physically adsorbed pyridine (1440 and 1487 cm^{-1}), hydrogen bonded pyridine (1590 and 752 cm^{-1}), Lewis bound pyridine (1445, 1485, 1578, 1590 and 1613 cm^{-1}) and the pyridinium cation (1485, 1540, 1606 and 1635 cm^{-1}). Subsequent to degassing at 50, 100, 150 and 200 °C it is apparent that (i) the Na- form (Fig. 4g.1) contains no Bronsted sites only coordinatly bound pyridine and that this is virtually removed by 200 °C, (ii) the Al- and Fe(III)- exchanged forms (Fig. 4i.2,3) contain predominantly Bronsted sites and that (iii) the Cr(III)- form (Fig. 4i.4) shows the presence of both Bronsted and

Fig. 41

The infra-red spectra of the air-dried Na-, Al-, Fe(III)- and Cr(III)-montmorillonite, following exposure to pyridine and subsequent evacuation at elevated temperatures.



i Evacuation at 50 °C.

ii Evacuation at 100 °C.

iii Evacuation at 150 °C.

iv Evacuation at 200 °C.

Lewis acid centres which are stable up to 200 °C. The presence of the Lewis centres being indicated by the persistence of the band at 1445 cm^{-1} which disappears in the Al- and Fe(III)- derivatives. The increase in the number of Bronsted acid sites as the degassing temperature is elevated is indicated by the development of the peak at 1540 cm^{-1}. This may be expected since the removal of surface water (and indeed interlayer water) makes for easier penetration of the bulkier pyridine molecules.

4.6 Discussion.

The adsorption of pyridine and its subsequent protonation to produce pyridinium ions by various acidic surfaces is a well documented process for the measurement of acidity.[15,16] This acidity is considered to be caused by the polarisation of hydration shell water by the interlayer cation. The equilibrium for the acid strength of hydrated ions is described by

$$[M\ (H_2O)_x]^{+n} + H_2O \rightleftharpoons [MOH\ (H_2O)_{x-1}]^{+n-1} + H_3O^+$$

The hydration state of the interlayer cation is of prime importance in the study of clay acidity. The dissociation constants, given in Table 4.6, should therefore indicate the acid strength of these cations:-

TABLE 4.6.

HYDROLYSIS DATA FOR SOME METAL IONS.[17]

Acid	Conjugate base	pKa (25°C)
$Fe(H_2O)_x{}^{3+}$	$FeOH(H_2O)_{x-1}{}^{2+}$	2.15
$Cr(H_2O)_x{}^{3+}$	$CrOH(H_2O)_{x-1}{}^{2+}$	3.9
$Al(H_2O)_x{}^{3+}$	$AlOH(H_2O)_{x-1}{}^{2+}$	5.02

This scheme gives a sequence of Fe(III) < Cr(III) < Al for the ions in aqueous solution but does not reflect the observed sequence of catalyst activity.

The low desorption temperature of peak I (40 °C) in the pyridine desorption profile (Fig. 4.b) and the fact that its intensity is reduced in a flow of dry nitrogen at room temperature indicates that it arises from physisorbed pyridine and water (which is not completely removed on degassing). The desorption maximum in the pyridine desorption thermograms at approximately 150 °C has the strongest intensity in the Ca- form, is roughly equal in the trivalent cation-exchanged forms and does not occur in the Na- or pyridinium forms. Moreover it is present in all the trivalent cation exchange forms irrespective of the pretreatment temperature. Furthermore it is not removed in a dry nitrogen gas flow (as peak I is) but is removed following exposure to atmospheric moisture. This evidence together with the almost complete removal of this Lewis band at 1445 cm^{-1} by 200 °C in the Al- and Fe(III)- exchanged forms implies that peak II represents pyridine coordinated to lewis sites.

The TPD profile of the pyridinium-exchanged form (Fig. 4.a1) together with the spectroscopic evidence presented in Fig. 4i show quite definitely that pyridinium ion is the predominant species in the Al- and Fe(III)- derivatives subsequent to heating at 200 °C. It is therefore assumed that the desorption maximum near 340 °C is due to the loss of the pyridinium ion. This desorption temperature agrees closely with the value of 360 °C found for the desorption of pyridine from Silica-alumina.[18] The presence of Lewis sites above 200 °C in the Cr(III)- form seems only to cause peaks II and III to be less well resolved than they are in the Al- and Fe(III)- forms.

The strong acid sites, as represented by the pyridine desorption peak near 340 °C, are quite stable to thermal pretreatment requiring temperatures > 300 °C to modify them. This temperature agrees well with the dehydration temperature of these cations. The heating of pillared clays to temperatures > 300 °C has been found to convert Bronsted acid sites to Lewis sites[19] and this seems to be the case here. The thermal pretreatment of the Cr(III)- and Al- forms at temperatures in excess of ~ 300 °C give rise to a broad peak centred at 300 °C (Fig. 4c.4, 5, 9 and 10) which are therefore considered to be caused by the desorption of pyridine from Lewis sites caused by the essentially complete dehydration of the interlamellar cation.

By analogy with the pyridine desorption profiles in Fig. 4c the TPD profiles of the other bases, (Fig.

4d) n-butylamine, t-butylamine and benzylamine can be attributed to physisorbed, Lewis and protonated base. The variation in intensity of peak II′, which is assigned to the Lewis acid sites, is probably due to steric hindrance in so far as the nitrogen in the bulky secondary and tertiary forms cannot approach the Lewis acid site closely. In the other thermogram the absence of peak II′, for the cyclohexylamine, seems to confirm the hindrance caused by the shape and size of the adsorbed molecules.

The high desorption temperatures of peaks II′ and III′ in Fig. 4g compared with the values for pyridine reflect the increased interaction between the strong base n-butylamine and the acid centres. The low intensity of peak II′ (Fig. 4f) may be due to the enhanced interaction with these Lewis sites shifting their desorption maxima to coincide with the desorption from Bronsted sites. It has been reported,[20] however, that 5% of n-butylamine is converted to di-n-butylamine upon heating at 215 °C for 14 hours over Al- montmorillonite in a sealed reaction vessel. The yield of dicyclohexylamine from cyclohexylamine over Al-, Cr(III)-, Ca and Na- exchanged bentonite is 91, 72, 35 and 22% respectively, indicating that all these exchange forms are capable of producing di-n-butylamine. It may be noted that Fig. 4g.5 representing the derivative thermogram of di-n-butylamine from Al-montmorillonite has an intense peak maximum coinciding with the peak assigned to protonated butylamine. Consequently, peak

$II^{/}$ may be weak because most of the n-butylamine has been converted to the dimer. Further evidence to support this interpretation is found in that rigorous thermal pretreatment (Fig. 4h), resulting in the dehydration of the interlayer cations, does not remove the peak tentatively assigned to the protonated amine, as was the case for pyridine desorption (Fig. 4b). However, it has recently been reported[21] that treating calcined pillared clays with strong bases such as ammonia can abstract protons which have migrated into the clay layer during the calcination process at 500 °C. It is, therefore, suggested that peak $III^{/}$ in the n-butylamine desorption spectra is mainly due to the protonated amine and partly as a result of the formation of the dimer.

4.7 Conclusions

The thermal desorption profile indicates the presence of both Lewis and Bronsted acids sites on the three trivalent cation exchanged derivatives studied. There appears to be little difference in the number of these sites, although the desorption temperature maximum of the protonated base from Al- montmorillonite does occur at a higher ($\sim$ 20 °C) temperature indicating stronger acidity. A wide variety of bases may be used and the desorption temperature of the protonated base depends on the base involved. Heating the trivalent cation-exchanged derivatives to $>$ 300°C causes the cation to dehydrate leading to the formation of Lewis acid sites following the destruction of the Bronsted acid sites. This dehydration, however, also results in the migration of protons into the clay layer and strong bases such as n-butylamine can abstract them but weaker bases such as pyridine cannot.

CHAPTER 5

VAPOUR PHASE DIFFUSION ONTO SOME TRIVALENT CATION EXCHANGED MONTMORILLONITES.

5.1 Introduction.

In the light of recent advances in the study of clays as catalysts and the interest shown by industry, it must be realised that directly measured sorption kinetics are of considerable technical importance because they determine rates of diffusion in practical applications. A number of techniques are already in use, for example, neutron scattering studies and field gradient methods in nuclear magnetic resonance, to determine the actual rates of diffusion of occluded species in a host structure.[1-3] However, these techniques do not determine the rates of diffusion under the reaction conditions of the catalyst.

The work described in this chapter involves the measurement of the direct rate of sorption and the calculated activation energies of a number of organic solvents (alcohols and cyclic ethers) in an attempt to determine the relative importance of the numerous factors, such as (i) the size, charge and concentration of the cations, (ii) the size, shape, polarity and flexibility of the diffusing molecule and (iii) the geometry and dimensions of the adsorbent network, all of which have been found to affect diffusion into zeolites.[4] The actual organic solvents were chosen because of their use in clay-catalysed organic reactions either as reactants (alcohols) or solvents (cyclic ethers) as described by Adams et al.,[5,6] see also section 2.2.

5.2 Diffusion and Diffusion Coefficients.

Diffusion was first described quantitatively by Fick[7] by using the analogous equations for heat conduction derived by Fourier.[8] Ficks hypothesis was that

$$J = -D \frac{\delta C}{\delta x} \qquad 5.2.1$$

where J is the rate of transfer per unit area of section

C is the concentration of the diffusing substance

x is the space co-ordinate measured normal to the section

D is the diffusion coefficient.

It follows directly from equation 5.2.1 that

$$\frac{\delta C}{\delta t} = \frac{\delta \left[D \frac{\delta C}{\delta x} \right]}{\delta x} \qquad 5.2.2$$

which is usually called Ficks's diffusion equation.

In order that use may be made of the above equations it is necessary to describe the section through which diffusion is measured or considered and this area has received much attention.[9,10]

5.2.1 Ficks diffusion equations.[13]

It is also important that the units of J, C and x are equally well defined. Frames of reference, definitions and units have all been discussed by

Crank,[11] Carmen and Stein[12] and Barrer.[13] If for example, we consider diffusion using cylindrical polar coordinates (r, θ, z) then equation 5.2.2 becomes

$$\frac{\delta C}{\delta t} = D\left[\frac{\delta C}{\delta r} + \frac{1}{r}\frac{\delta C}{\delta \theta} + \frac{\delta C}{\delta z}\right] \qquad 5.2.3$$

It is easier for the following discussion therefore to initially restrict ourselves to one-dimensional diffusion using equations 5.2.1 and 5.2.2. Solutions of these differential equations can be obtained by the separation of variables method or by making use of the Laplace Transformation method. The relevant solutions of the diffusion equation are outlined below.

5.2.2 Diffusion In a Plane Sheet.

Diffusion in a plane sheet represents one-dimensional diffusion in a medium bounded by two parallel planes e.g. planes at x = 0 and x = a. No transfer of diffusing substance occurs at the edge of the sheet. The surface concentration is constant with an initial distribution of some function of x, say f(x) and the diffusion coefficient is constant then the concentration satisfies the equation

$$\frac{\delta C}{\delta t} = \frac{\delta}{\delta x}\left[D\frac{\delta C}{\delta x}\right] \qquad 5.2.2$$

with boundary conditions:

$C_x = C_1, \quad x = 0, \quad t \geqslant 0$

$C_x = C_2, \quad x = a, \quad t \geqslant 0$

and an initial condition

$C_x = f(x), \; 0 < x < a, \; t = 0$

The solution in the form of a trignometrical series is

$$C_x = C_1+(C_2-C_1)\frac{x}{a} + \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{C_2\cos(n\pi)-C_1}{n}\sin\frac{n\pi x}{a}\exp\frac{-Dn^2\pi^2t}{a^2} + \frac{2}{a}\sum_{n=1}^{\infty}\sin(n\pi)\ldots\ldots\ldots\ldots\ldots\ldots \qquad 5.2.4$$

as may be seen from this example the mathematics of a solution are quite involved to perform.

One further set of conditions which is useful in the study of diffusion in a plane sheet has constant initial concentration, surface concentration of zero, between the planes at x = -a and x = +a, the diffusivity D again assumed to be independent of concentration; the relevant boundary condition are therefore

$C = 0 \quad x = -a \quad t \geqslant 0$

$C = 0 \quad x = +a \quad t \geqslant 0$

$C = C_o \quad -a < x < a \quad t = 0$

A much more useful solution for this problem can be obtained by expressing

$$M_t = \int_{-a}^{a} C_x \, dx \qquad 5.2.5$$

where M_t is the amount of diffusing substance present after time t and M_∞ is thereby defined as the amount of diffusing substance in the plane sheet; i.e.

$$M_\infty = C_{o\rightarrow 2a}$$

therefore

$$\frac{M_t}{M_\infty} = \sum_{n=1}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp\left[\frac{-D(2n+1)^2\pi^2t}{4a^2}\right] \qquad 5.2.6$$

and Mt/M_∞ may be obtained from adsorption data.

Diffusion into other regions leads to a wide variety of solutions depending on both the initial and boundary conditions and the diffusion equation used to describe such diffusion. Diffusion in a rectangular parallelpiped utilises the equation in the form

$$\frac{\delta c}{\delta t} = D\left[\frac{\delta c}{\delta x^2} + \frac{\delta c}{\delta y^2} + \frac{\delta c}{\delta z^2}\right] \qquad 5.2.7$$

Radial diffusion in a sphere may be described by the equation

$$\frac{\delta c}{\delta t} = D\left[\frac{\delta^2 c}{\delta r^2} + \frac{2}{r}\,\frac{\delta c}{\delta r}\right] \qquad 5.2.8$$

again assuming that the diffusion coefficient is independent of concentration.

In this work a model is presented for a gas diffusing isothermally at constant pressure into a cylindrical clay pellet through its curved lateral surface in the absence of chemical reactions. In order that the diffusion equation can be solved it is necessary to make a number of assumptions. These are that i) the initial concentration of the diffusant at the pellet surface is zero, ii) the cylinder is exposed to a uniform atmosphere of gas concentration and iii) the surface concentration approaches the ambient concentration in a exponential manner. As the clay platelet is used then it was also assumed that the flat circular surfaces of the cylinder are impermeable.

Using Cylindrical Polar coordinates (r, θ, z) let the concentration of the gas at time t at the point (r, θ, z) be represented by $C(r, \theta, z, t)$. If we suppose that the clay pellet occupies the fixed right-circular cylinder as defined by

$0 \leqslant r \leqslant a, \quad 0 \leqslant \theta \leqslant 2\pi, \quad -L \leqslant z \leqslant L$, the concentration then satisfies the Fickian diffusion equation (5.2.2) i.e.

$$\frac{\delta C}{\delta t} = D\left[\frac{\delta^2 C}{\delta r^2} + \frac{1}{r}\frac{\delta C}{\delta r} + \frac{1}{r^2}\frac{\delta^2 C}{\delta \theta^2} + \frac{\delta^2 C}{\delta z^2}\right] \qquad 5.2.9$$

From the previous assumptions:-

Initially at time, $t = 0$, the concentration satisfies

$$C\ (r,\ \theta,\ z,\ o) = 0 \qquad 5.2.10$$

on the flat impermeable circular surfaces

$$C\ (a,\ \theta,\ \pm L,\ t) = 0 \qquad 5.2.11$$

and the concentration on the lateral surfaces is given by

$$C\ (a,\ \theta,\ z,\ t) = C_{\infty}\ (1 - e^{-\beta t}) \qquad 5.2.12$$

$\beta > 0$ is expected to be large so that the concentration at the surface rapidly approaches C_{∞}.

The solution to equations 5.2.9 under the boundary conditions of equations 5.2.10 and 5.2.11 given that equation 5.2.11 holds for any concentration of gas, $C(a,\ \theta,\ z\ t,)$, has been described in detail by Crank.[11] It may be shown that

$$C(r, \theta, z, t) = C_{\infty}\left[1 - e^{-\beta t}\frac{J_0(rd)}{J_1(ad)}\right] \cdot \frac{-2\beta C_{\infty}}{a} \cdot \sum_{n=1}^{\infty} \frac{1}{{}_{n}(\beta - D\alpha_n^{2})} \cdot \frac{J_0(\alpha_n r)}{J_1(\alpha_n a)} \cdot e^{-\alpha_n^2 D t} \qquad 5.2.13$$

where $d = \sqrt{\beta/D}$ and α_n is the increasing sequence of positive roots to the equation

$$J_0(a\alpha) = 0$$

where J_0 and J_1 are the Bessel functions of the first kind, of order zero and one respectively. Obviously, β cannot assume the values $D\alpha_1^2$, $D\alpha_2^2$, ...

The mass of adsorbed gas on the clay surface at the time = t is given by

$$M_t = 2L\pi a^2 \int_{-L}^{L} \int_{0}^{2} \int_{0}^{a} C(r, \theta, z, t) r \, dr \, d\theta \, dz$$

given the equation 5.2.13 then it may be shown that

$$M_t = \left[1 - 2e^{-\beta t} \frac{j_1(ad)}{ad j_0(ad)}\right] - 4 \frac{\beta}{a} \sum_{n=1}^{\infty} \frac{L \bar{e}xp \alpha_n^2 Dt}{\alpha_n^2(\beta - D\alpha_n^2)} \qquad 5.2.14$$

where M_∞ ($= L\pi a^2 C_\infty$) is the mass of gas adsorbed when the system reaches equilibrium. Here again the values of β may not be $\alpha_1^2, \alpha_2^2, \alpha_3^2$......... The values of ΔE and of D may, therefore be obtained from kinetic adsorption data for M_t/M_∞, which were derived in this work using a gravimetric technique.

In order that numerical solutions may be obtained for equation 5.2.14 it is necessary to truncate the series thereby leading to inaccuracies particularly for small times. Since no data were included for M_t/M_∞ at such times the numerical truncated solutions were considered satisfactory, and although approximations for the small time data have been obtained[14] none have been included in the calculations here.

The integral diffusion coefficient, $\bar{D}$, represents only a mean value of the diffusion coefficient D(C) if it is found to vary with concentration and is described by the relationship

$$\overline{D} = \frac{1}{C_\infty}\int_0^{C_\infty} D(c)dc \qquad 5.2.15$$

The temperature dependence of the diffusion into porous crystals is usually represented by the Arrhenius equation

$$\overline{D} = \overline{D}_o \exp\left({}^{-\Delta E}/RT\right) \qquad 5.2.16$$

therefore values of the integral diffusion coefficients, $\overline{D}$, and the activation energies, ΔE, may be obtained.

5.3 Experimental.

The parent clay used was a Wyoming montmorillonite with the < 2 μm fraction collected by sedimentation. The cation-exchange procedure and elemental analyses have been described in Chapter 3.

The thermobalance used for the isothermal and dynamic thermogravimetric studies was a Stanton Redcroft TG 750 which is described in detail in Chapter 4 and only the pertinent experimental details are given here. The temperature of the furnace in the range 42 - 240°C was calibrated using the known melting points of materials listed in Table 5.1, which were recrystallised to the constant melting points shown. The flow rate of nitrogen gas, which was dried by passing through 4Å molecular sieve and P_2O_5, is calibrated by using an external bubble flow meter. The thermograms were obtained using a heating rate of 20°C min^{-1} and a flow rate of purge nitrogen gas of 20 cm^3 min^{-1}.

In the isothermal sorption kinetics studies the alcohol or cyclic ether vapour was introduced into the dry nitrogen gas stream by passing the nitrogen through a bubble chamber containing the organic solvent. This saturated gas stream was directed over the clay sample suspended in the furnace and then passed out of the system via the external bubble meter. Preliminary experiments indicated that increasing the nitrogen carrier gas flow rate above 100 cm^3 min^{-1} did not increase the rate of sorption of any of the solvents.

The following indicates the procedure of a typical run. A sample of clay (6 - 7mg) was placed in the sample pan and preheated to 120°C at 3°C min^{-1}, in a flow rate of nitrogen of 100 cm^3 min^{-1}. The temperature being maintained at 120°C for 15 mins or until no further weight change occurred. The sample was then allowed to cool to a known temperature (18, 43, 72 or 105°C) and the nitrogen gas diverted through the solvent then over the clay sample. This was taken as time zero for the mass uptake experiments. The reproducibility of the method is indicated in Fig. 5a and 5b.

Between runs (particularly when a change of solvent was necessary) the thermobalance was purged with dry nitrogen at a rate in excess of 150 cm^3 min^{-1} whilst heating the furnace at 250°C over a period of 30 minutes and then allowed to cool. After cooling the furnace, a clay sample was added to the sample pan and if no deviation from the baseline occurred within 10 minutes further purging was deemed unnecessary.

The solvents used in these studies were:- three alcohols, Methanol, MeOH; propan-2-ol, i-PrOH; and t-butanol, t-BuOH; and three cyclic ethers, 1,4-dioxan, DIOX; tetrahydrofuran, THF; and tetrahydropyran, THP.

TABLE 5.1

MATERIALS USED TO CALIBRATE FURNACE TEMPERATURE IN THE RANGE 40°C - 240°C

Material	Melting Range /°C
Diphenyltindichloride	42 - 44
2.2'-bipyridyl	70 - 73
Triphenyltinchloride	104 - 105
Triphenyltinhydroxide	119 - 121
4-aminobenzoic acid	187 - 189
3.5-dinitrobenzoic acid	205 - 207
dimethylglyoxime	237 - 241

Fig. 5a

Reproducibility of experimental method. The sorption of methanol on Fe(III)-montmorillonite at 72 °C.

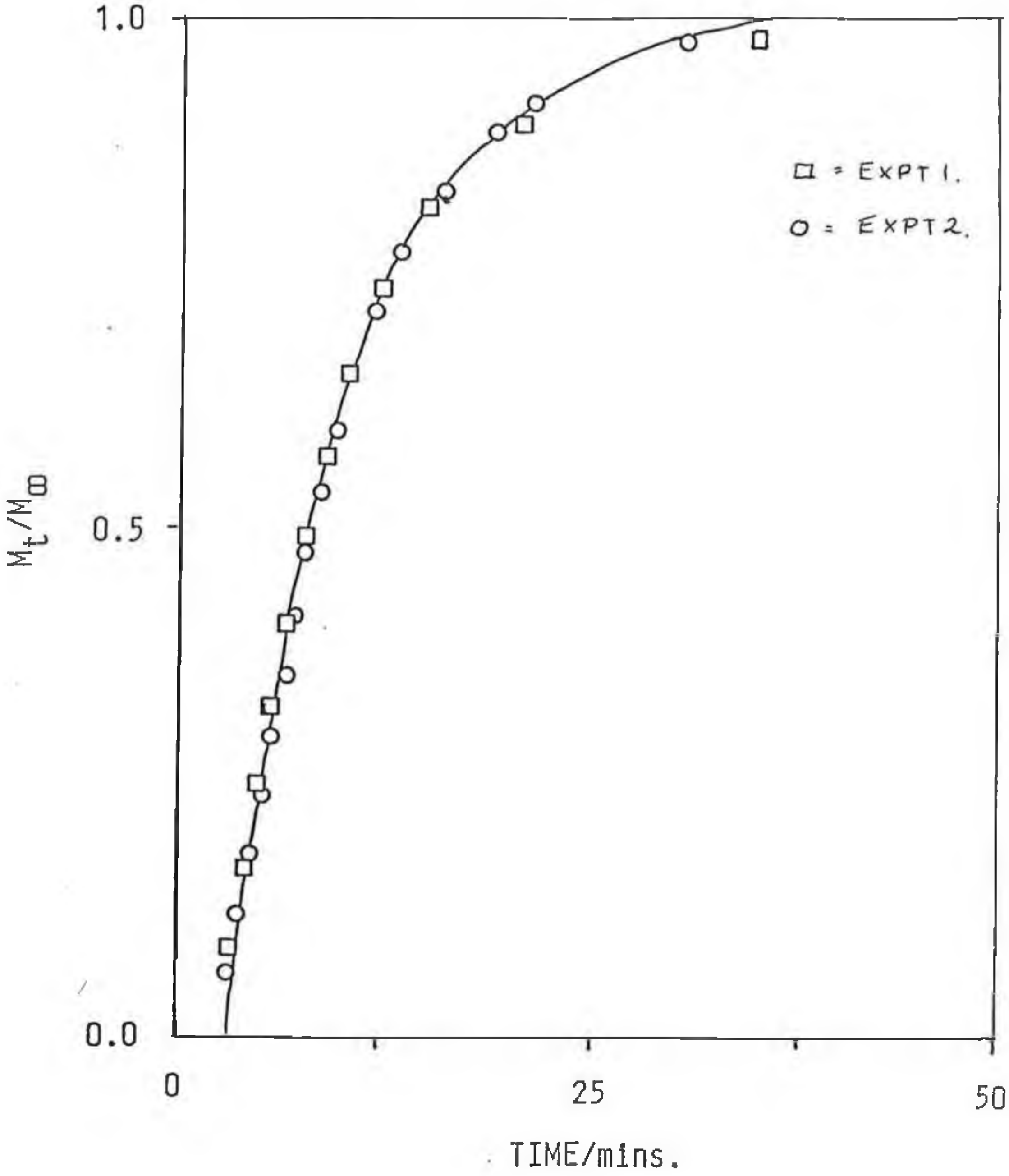
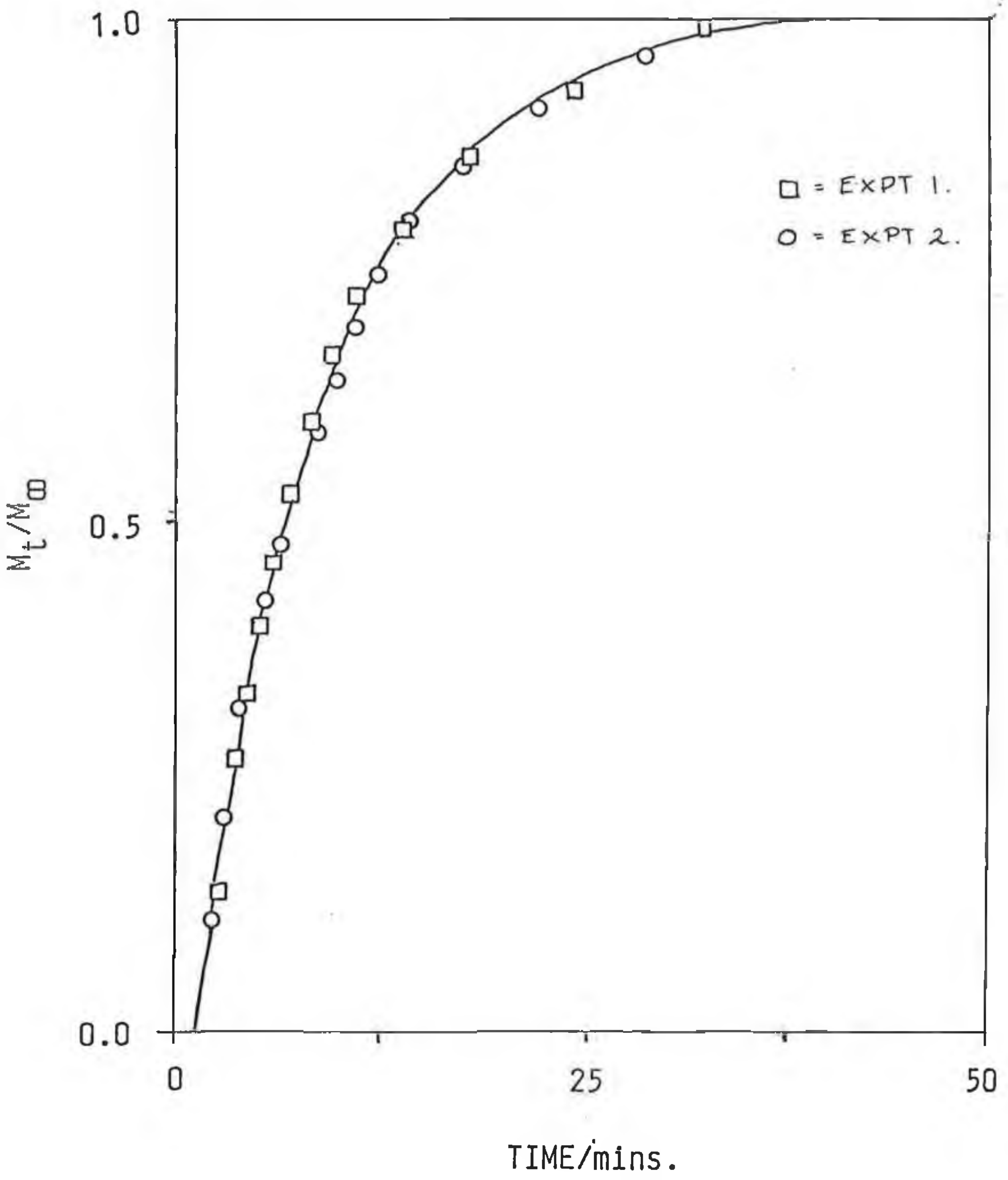


Fig. 5b

As in Fig. 5a except the methanol is adsorbed onto Cr(III)-montmorillonite at 42 °C.



5.4 Results

Sorption kinetic data are usually presented as plots of $(Q_t - Q_o)/(Q_\infty - Q_o)$ against time, t, where Q_t, Q_o and Q_∞ are the amounts of vapour sorbed at time, t, at the start of the experiment (t = 0) and at equilibrium ($t = \infty$), respectively. In the results presented here Q_o is invariably zero and since a gravimetric method has been employed the data are presented as plots of M_t/M_∞ versus time where M_t and M_∞ are the mass adsorbed at time t and at equilibrium.

Figures 5a and 5b indicate the excellent fit of the adsorption data to the 2-dimensional sorption equation 5.2.14. Fig. 5c represents the temperature dependence of the diffusion of propan-2-ol in Cr(III)-montmorillonites. Fig. 5d shows how the uptake of this alcohol was affected by the different exchange cations at 18°C. Fig. 5e shows the relative rates of sorption of the three alcohols on Cr(III)-montmorillonite at 18°C. Fig. 5f illustrates the temperature dependence of the diffusion of 1,4-dioxan in Fe(III)-montmorillonite and Fig. 5g represents how the uptake of this cyclic ether was affected by the presence of the various exchange cations.

The integral diffusion coefficients, $\bar{D}$, derived from the experimental data are collected in table 5.2 for the alcohols and table 5.3 for the cyclic ethers together with the values of the activation energy ΔE calculated from them. Table 5.2 indicated that in the temperature range studied the uptake of i-PrOH and t-

Fig. 5c

The uptake of i-PrOH on Cr(III)-montmorillonite derivative as a function of temperature. (□ = 18 °C; ○ = 42 °C; Δ = 105 °C). The 2-D diffusion model yields the lines.

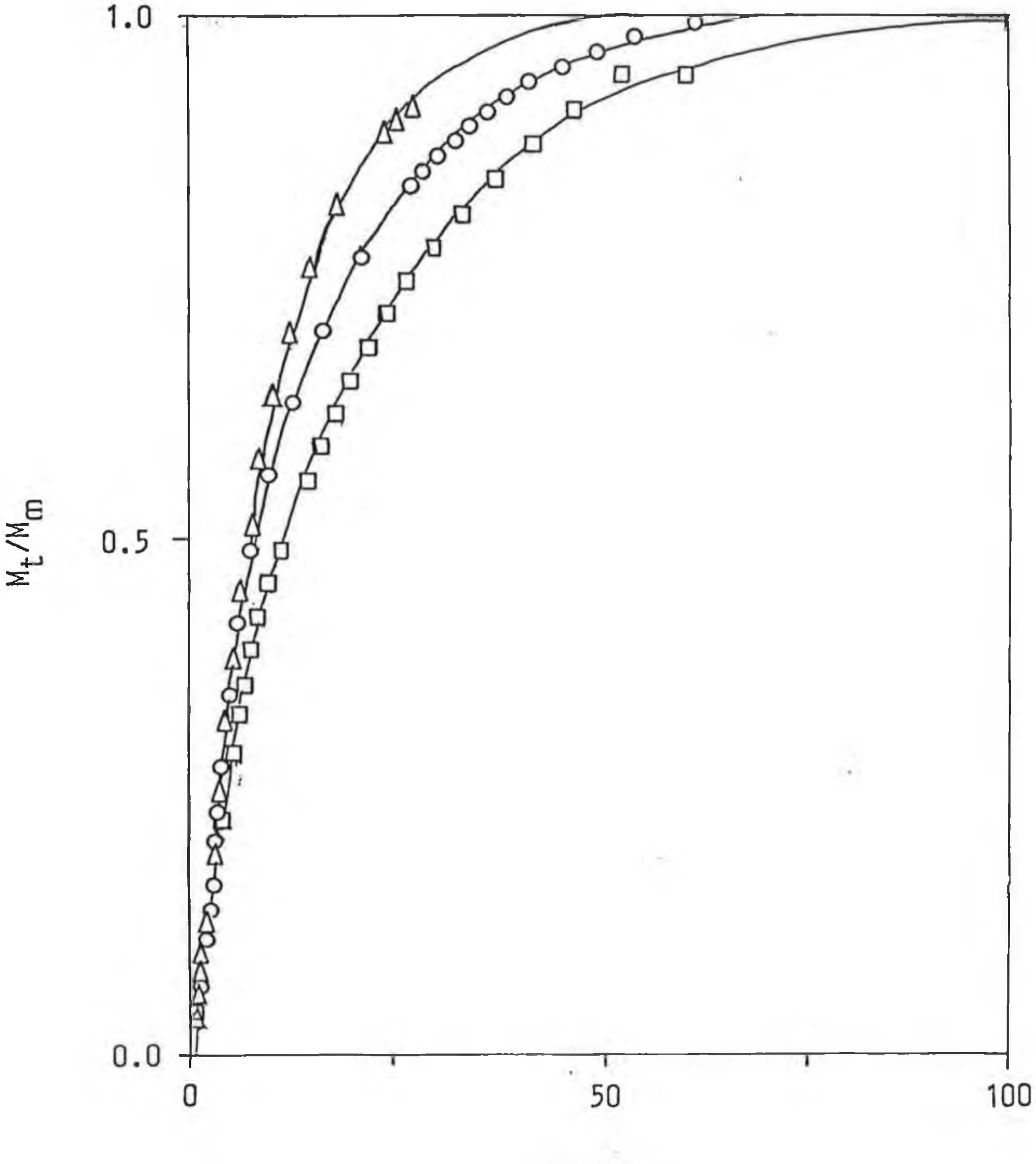


Fig. 5d

The uptake of i-PrOH on trivalent cation exchanged montmorillonite (△ = Fe(III); □ = Cr(III); ○ = Al) lines as in Fig. 5c.

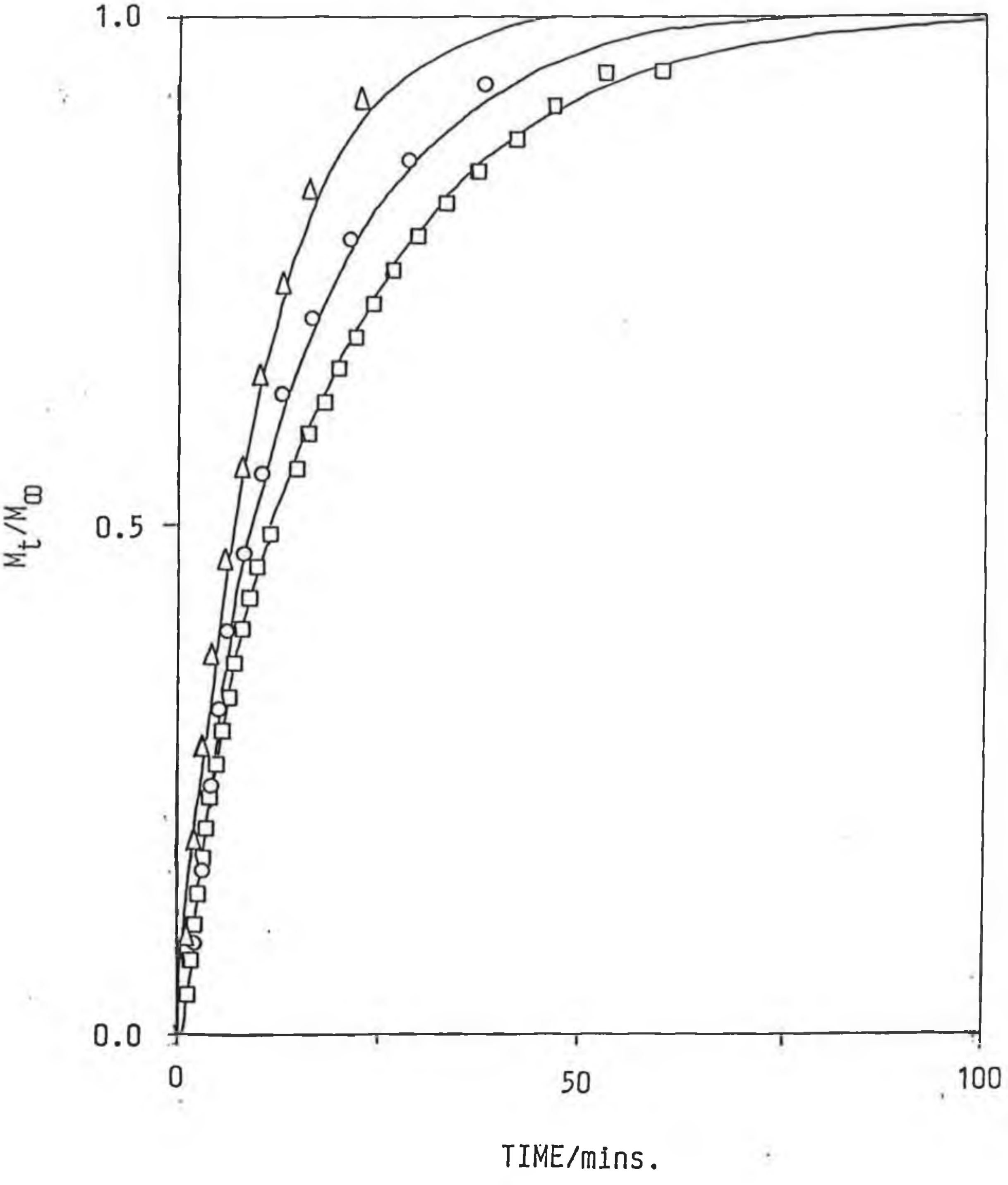


Fig. 5e

The uptake of the three alcohols on Cr(III)- form at 18 °C. (Δ = MeOH; □ = i-PrOH; ○ = t-BuOH). lines as in Fig. 5c.

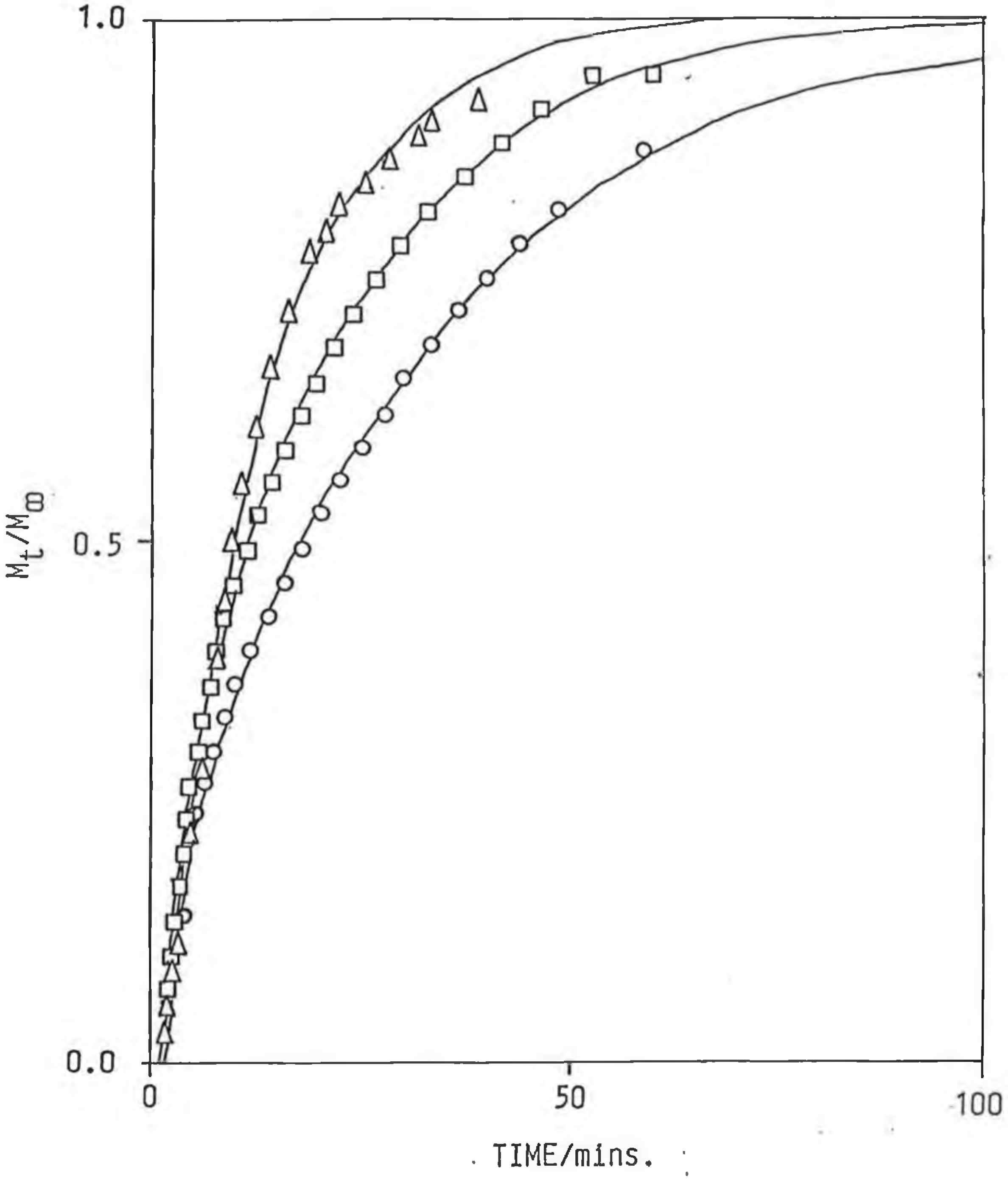


Fig. 5f

The uptake of 1,4-dioxan on Fe(III)- form as a function of temperature. (□ = 18 °C; ○ = 42 °C; Δ = 105 °C) lines as in Fig. 5c.

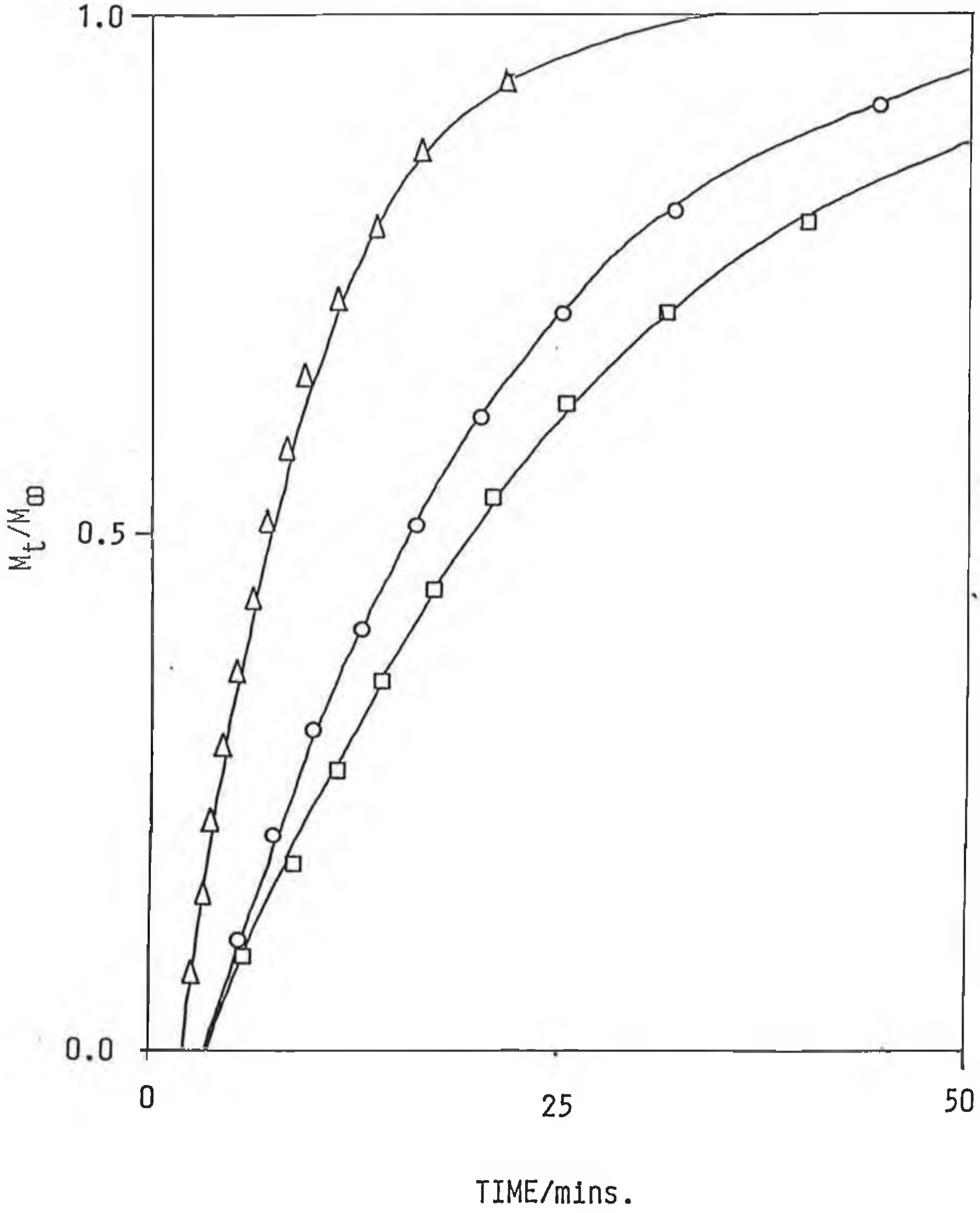


Fig. 5g

The uptake of 1,4-dioxan on trivalent cation exchanged montmorillonite (Δ = Fe(III); □ = Cr(III); ○ = Al) lines as in Fig. 5c.

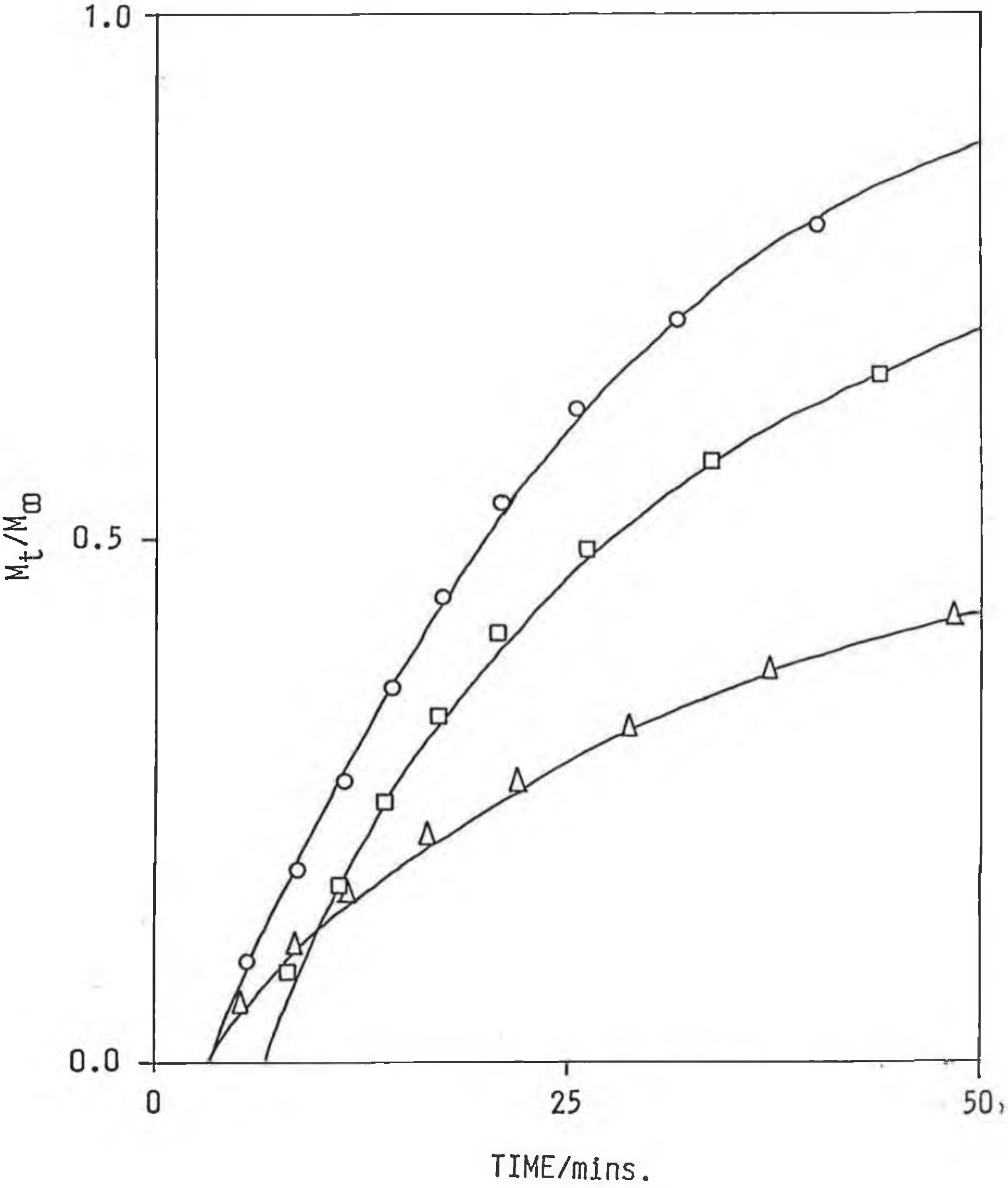


TABLE 5.2

DIFFUSION COEFFICIENTS, $\overline{D}$, AND ACTIVATION ENERGIES, ΔE, FOR ALCOHOLS IN TRIVALENT CATION-EXCHANGED MONTMORILLONITE .

Cation/Sorbate	T/°C	$\overline{D}$ $/10^{16}$ m^2s^{-1}	ΔE /kJ mol^{-1}.
	18	0.80	
Fe(III)/MeOH	72	1.16	4.0
	105	1.27	
	18	1.10	
Fe(III)/i-PrOH	43	1.27	4.0
	105	1.64	
	18	0.55	
Fe(III)/t-BuOH	43	0.67	6.0
	72	0.79	
	18	0.79	
Cr(III)/MeOH	43	0.97	7.0
	105	1.58	

TABLE 5.2 PART II

Cation/Sorbate	T/°C	$\bar{D}$ $/10^{16}$ m^2s^{-1}	ΔE /kJ mol^{-1}.
Cr(III)/i-PrOH	18	0.58	7.0
	43	0.73	
	105	1.22	
Cr(III)/t-BuOH	18	0.30	11.0
	72	0.55	
	105	0.85	
Al/MeOH	18	1.09	3.0
	43	1.22	
	72	1.34	
Al/i-PrOH	18	0.61	3.5
	72	0.73	
	105	0.85	
Al/t-BuOH	18	0.55	4.0
	72	0.67	
	105	0.79	

TABLE 5.3

DIFFUSION COEFFICIENTS, $\bar{D}$, AND ACTIVATION ENERGIES, ΔE, FOR CYCLIC ETHERS IN TRIVALENT CATION-EXCHANGED MONTMORILLONITE.

Cation/sorbate	T/°C	$\bar{D}$ /10^{16} m^2 s^{-1}	ΔE /kJ mol^{-1}
Fe(III)/THF	18	1.03	2.0
	43	1.06	
	105	1.10	
Fe(III)/THP	43	0.91	3.0
	72	0.97	
	105	1.03	
Fe(III)/DIOX	18	0.43	13.0
	43	0.67	
	105	1.22	
Cr(III)/THF	18	0.36	11.0
	43	0.55	
	72	0.79	
	105	1.03	

TABLE 5.3 PART II

Cation/sorbate	T/°C	$\bar{D}$ /10^{16} m^2 s^{-1}	ΔE /kJ mol^{-1}
	18	0.30	
Cr(III)/THP	43	0.43	9.0
	72	0.55	
	18	0.07	
Cr(III)/DIOX	43	0.13	13.0
	105	0.24	
	18	0.67	
Al/THF	43	0.73	3.0
	105	0.85	
	18	0.52	
Al/THP	72	0.67	3.0
	105	0.73	
	18	0.21	
Al/DIOX	43	0.24	13.0
	72	0.55	

BuOH by the M^{3+}-exchanged clays increased as Cr(III) < Al < Fe(III) whereas for MeOH the sequence was Fe(III) < Cr(III) < Al and for a given cation the rate of sorption increases as t-BuOH < i-PrOH < MeOH. In addition the activation energies, represented by Fig. 5h and 5i in the $M^{3\pm}$ exchanged derivatives increased as Al < Fe(III) < Cr(III). With regard to the cyclic ethers the observed sequence of the diffusion coefficients, collected in table 5.3, increase as Cr(III) < Al < Fe(III). Fig. 5j and 5k represent the observed rate of sorption of the cyclic ethers in the temperature range studied. For all cationic forms the sorption rate increased as DIOX < THP ≤ THF, except at 105 °C when the sequence for the Cr(III)- and the Al- exchange forms was THP ≤ THF < DIOX. The activation energies (Fig. 5k) show that the Cr(III)-montmorillonite presented the greatest potential barrier to the sorption of THF and THP but that DIOX has the highest activation energy and that it has the same value for all the exchange forms.

Fig. 5h

Arrhenius plots for the uptake of MeOH (———), i-PrOH (—·—), t-BuOH (- - - -), onto Δ = Fe(III) and O =Al. lines as in Fig. 5c.

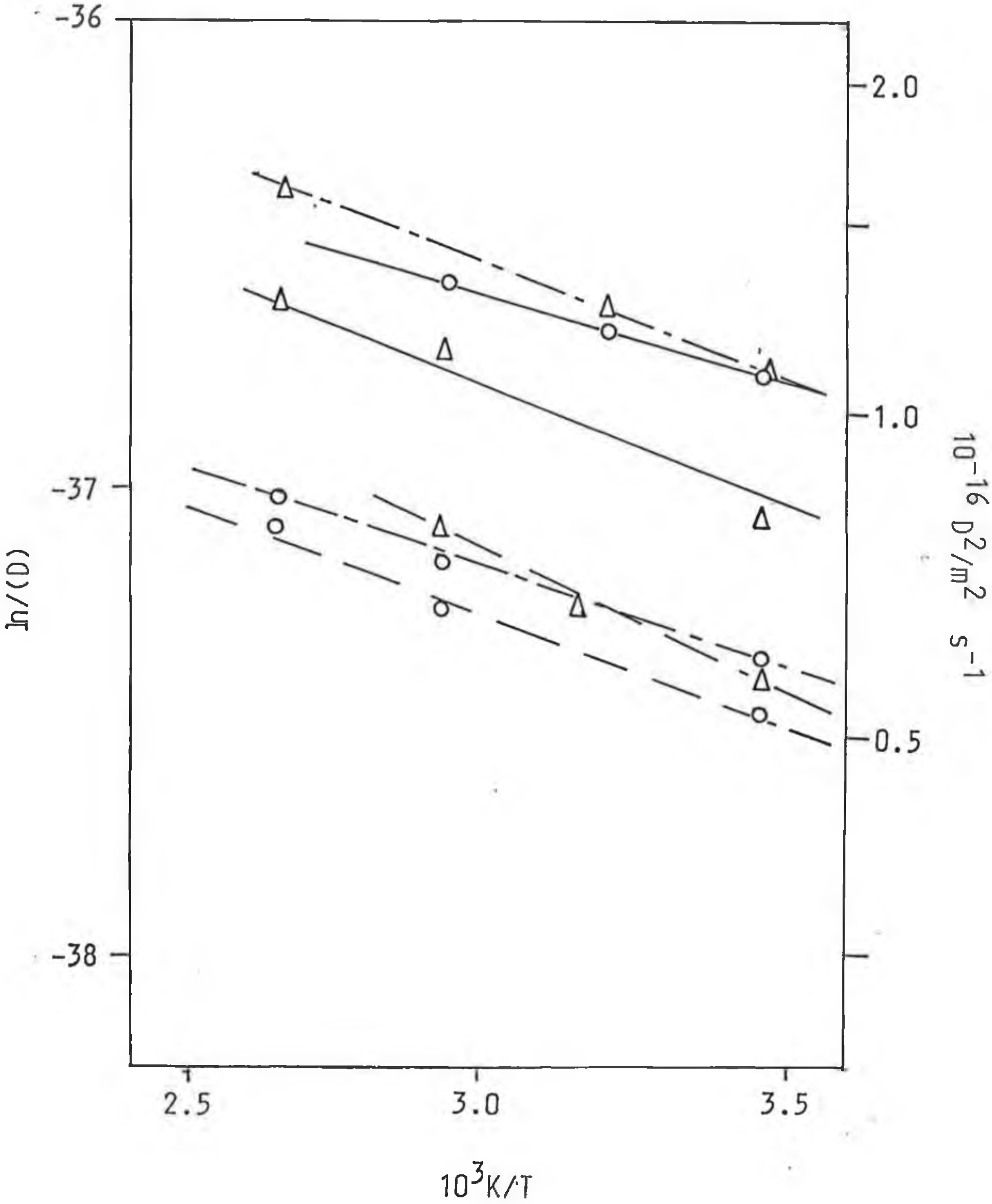


Fig. 5i

Arrhenius plots as in Fig. 5h onto Cr(III)-montmorillonite.

MeOH (——), i-PrOH (—·—), t-BuOH (- - -).

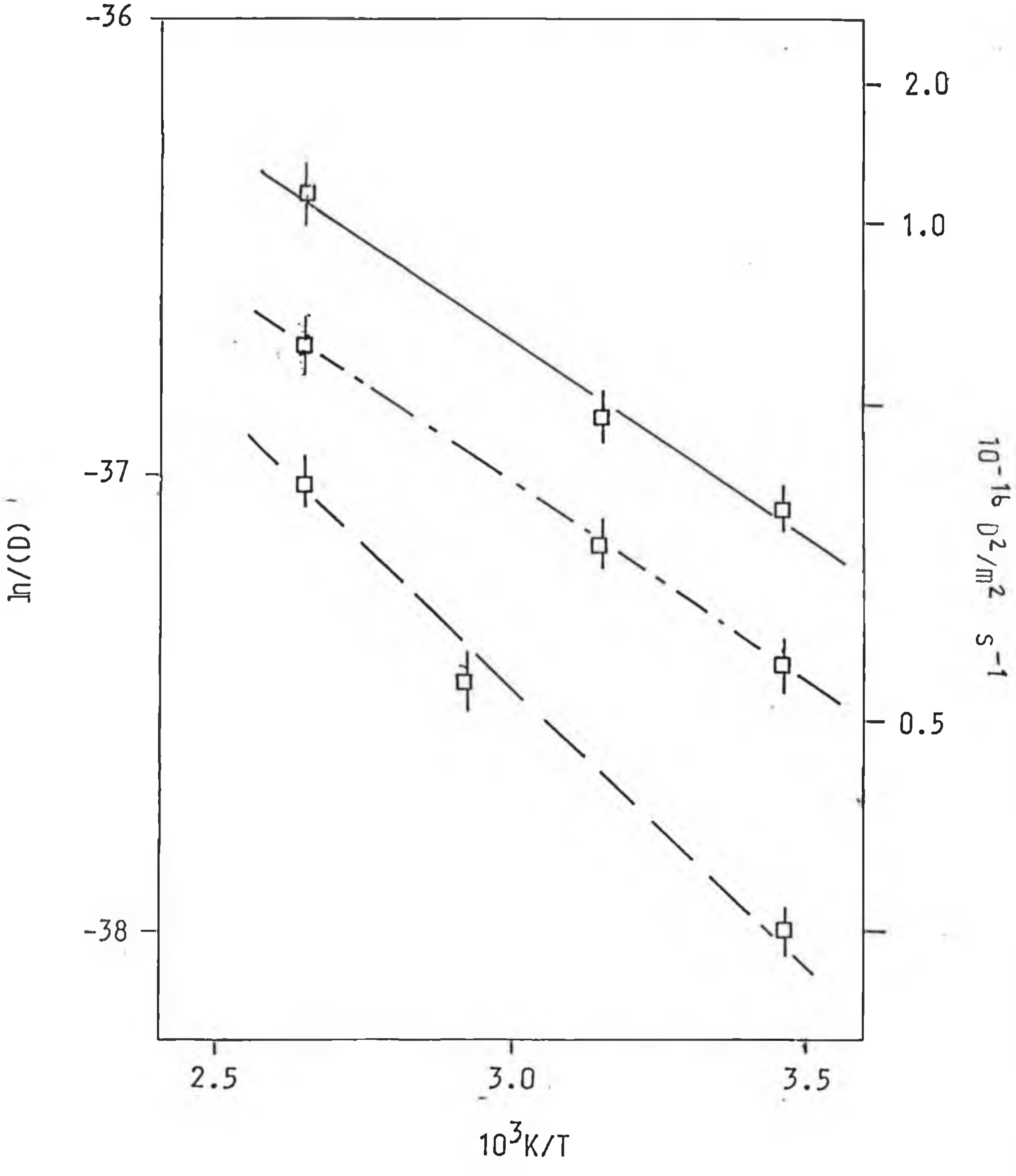


Fig. 5j

Arrhenius plots for the uptake of THF (———), THP (—·—) and DIOX (- - - -) on Δ = Fe(III), and □ = Al. lines as in Fig. 5c.

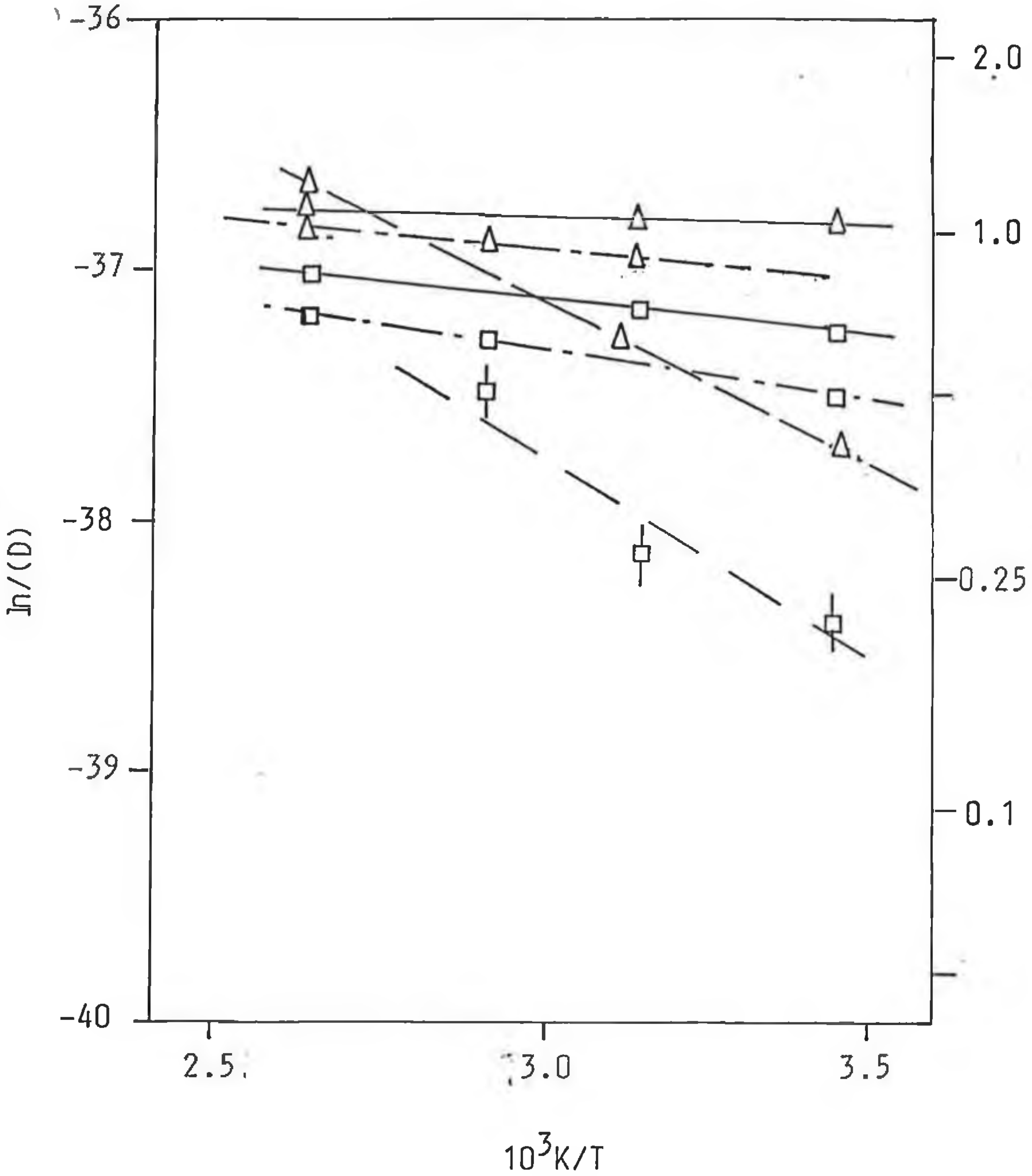
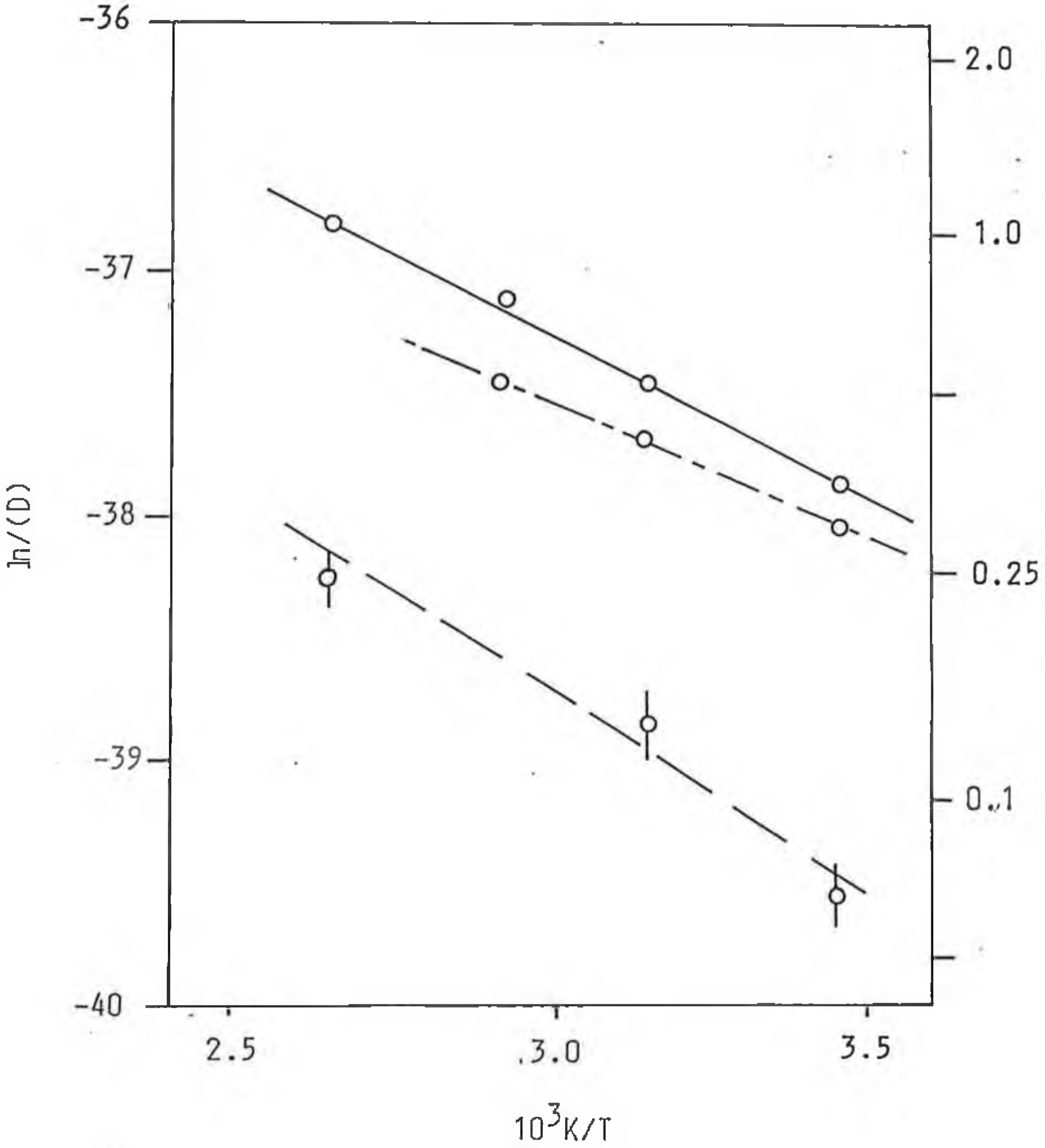


Fig. 5k

Arrhenius plots (cyclic ethers) onto Cr(III)-montmorillonites.

THF (——), THP (—·—), DIOX (- - -).



5.5 Discussion

Before interpretation of data could be attempted it was necessary to determine whether the adsorption process was one-dimensional (1-D) or two-dimensional (2-D). It has been suggested by Weiss[15] that if the particle size of the adsorbent was less than the cooperative elastic action length then the adsorption process was a 1-D process, as for example with urea and dimethylsulfoxide onto kaolin from aqueous solution. Whereas if the particle size exceeded this value then the process was 2-dimensional in nature. Attempts were made therefore to fit the rate of uptake of the three alcohols by the various cation-exchanged clays to both one- and two-dimensional solutions of the diffusion equation. Weiss[15] suggests that the strain produced in the lamellae in the vicinity of the kaolin sheets where adsorption takes place causes the adsorption to be one-dimensional. This strain inhibits the access of other molecules around the outside of the kaolin lamellae. In all the systems considered here, complete dehydration has not taken place (Section 3.4), therefore, the simultaneous adsorption at all points around the layers is facilitated by the water molecules acting as supports to keep the platelets apart thereby reducing the barrier presented by the cooperative elastic action length.

As discussed in a Chapter 4 the thermal pretreatment at 120 °C of the trivalent cation-exchanged forms does not totally dehydrate the clay. The remaining water molecules give the clay its Bronsted acidity and mimics the surface of the clays used in clay catalysis. It has been found (Chapter 3) that between 65 and 75 per cent of the water present in the air dried cation-exchange form is removed by this pretreatment and the presence of this water could affect the adsorption of solvent molecules by the various cation-exchanged forms. If however, the solvent molecules compete successfully for the coordination sites about the exchangeable cations then the removal of the water molecules must occur, and in this case, the mass uptake curve represents the difference between the mass of solvent taken up and the mass of water lost, i.e. ($M_{solvent} - M_{water}$). It is probable that a combination of these factors occur. Although to facilitate the initial discussion it was assumed that the trivalent exchanged clays behave identically with respect to the hydration shell water.

5.5.1 Adsorption of Alcohols.

The most obvious difference between the six solvents used in this work is the fact that three, MeOH, i-PrOH and t-BuOH, are alcohols whilst the remainder, DIOX, THP and THF are cyclic ethers. The mass uptake data are therefore discussed under these separate headings.

Diffusion Coefficients.

The trends obtained for the diffusion coefficients for the three alcohols in the various cation-exchanged montmorillonite provide considerable insight regarding the factors which influence diffusion in layered silicates. In contrast to the fixed size and shape of the channel network in the outgassed zeolites, the interlayer space of the clay minerals are not fixed but are governed by the size of the adsorbed molecules.[1] For a given cation it has been shown that the rate of alcohol sorption increases as t-BuOH $<$ i-PrOH $<$ MeOH. However, a disparity exists between the partial pressures of MeOH (100 mm Hg) and i-PrOH (40 mm Hg) and t-BuOH (40 mm Hg) consequently the rate of sorption of MeOH is therefore, not strictly comparable with the other two alcohols, although the size difference of MeOH compared to i-PrOH and t-BuOH should allow a higher rate of sorption for the smaller alcohol. Since the polarites of the three alcohols are almost identical the sequence for the rate of sorption must be due partly to the difference in molecular size.

Much work has been carried out in the area of diffusion of organic molecules into zeolites but none determining rate of diffusions of alcohols into zeolites. It is therefore not possible to compare the values obtained in these studies to diffusion rates into the zeolite network. However, it should be stated that diffusion coefficients of the order of those determined here (10^{-16} m^2 s^{-1}) generally indicate hindered diffusion such as that of n-butane in 4A zeolite at ~ 20 °C.[17] Using quasi-elastic neutron scattering studies, Tuck[18,19] states that the effective diffusion coefficient of water not bound to the exchangeable cation in calcium exchanged montmorillonite is ~ 1 - 4.5 x 10^{-10} m^2 s^{-1} and an activation energy of ~ 11 kJ mol^{-1}. In a mixed system, pyridine/water adsorbed by a sodium-montmorillonite as discussed by Adams et al.[20] utilising similar techniques to Tuck[18,19] the effective diffusion of water was found to be reduced by an order of magnitude. In comparable alcohol diffusion studies conducted by Adams and coworkers[21,22] it was found that the displacment of water molecules bound to the exchangeable sodium cation by CD_3OD, in the presence of a large excess of pyridine, a diffusion coefficient for the CD_3OD molecule of ~ 1 x 10^{-16} m^2 s^{-1} at 25 °C. This diffusion coefficient is similar to those found in this work at that temperature. It also suggests that the alcohol molecules may be competing successfully for the coordination sites of the exchangeable cation.

Activation Energies.

There are two main features concerning the activation energies for the alcohol adsorption collected in Table 5.3. It may be observed that they are cation dependent in the order Al $<$ Fe(III) $<$ Cr(III) and also their values are quite small ($\leq$ 11.0 kJ mol^{-1}) thus indicating that there is a low potential barrier to diffusion for these alcohols into these trivalent cation -exchanged clays. It may also be seen that even though the activation energies are quite low there is a distinct trend underlying the values in each of the cation-exchanged forms. MeOH and i-PrOH seem to meet with a potential barrier of equal proportions, whereas t-BuOH needs a slightly higher activation energy in each of the exchanged forms for diffusion to occur. This may be due to the alteration of the spatial arrangement of the groups in the t-BuOH compared to the i-PrOH, forming a bulky molecule which in turn requires the clay layer separation to be increased.

As mentioned earlier the cation dependence of the activation energies for the diffusion of alcohols increases as Al $<$ Fe(III) $<$ Cr(III). It has been stated that for the exchange of water molecules about the Cr(III) ion the relaxation times have a half life of approximately 4 days, and an activation energy in the order of 112 kJ mol^{-1}.[23] If it is considered, as suggested earlier, that some of the coordination shell water is replaced when the three alcohols are adsorbed by the clay, then the increase in activation energies for the Cr(III)-exchanged clay/alcohol systems is caused, if only in part, by the added potential barrier encountered by the alcohol molecule in attempting to remove such a firmly held water molecule form the ligand positions. For the Al ion the half life for the exchange of water from the coordination positions is 73 ms. No information is available for the Fe(III) ion, since these rates of interaction are influenced by the alterations in the d-electron energies as the coordination changes from the reactant to the transition species, and no information concerning this is available. Also there exists the possibility of other species being formed on exchange of the Fe(III) ions onto the cation sites. Utilising the Mossbauer effect Helsen and Goodman showed evidence that following the thermal treatment at 120 °C some oxy- or oxyhydroxy-species are formed at the clay surface.[24] These factors may influence the activation energies.

5.5.2 Adsorption of Cyclic Ethers

The adsorption of cyclic ethers by the trivalent cation-exchanged montmorillonite was investigated to give further information regarding the diffusion of organic molecules by this layered silicate. Adams and co-workers[6] have found that in their studies of the production of methyl-t-butyl ether (MTBE) from methanol and isobutene using trivalent cation-exchanged montmorillonites as catalysts that cyclic ethers, of the type studied here, give similar yields to hydrocarbon solvents but at lower temperatures from ~90 °C to ~60 °Cand that the yield of MTBE was dependent on the cyclic ether used.

Diffusion Coefficients.

From Table 5.3 it may be observed that for given cation the diffusion coefficient increases as DIOX $<$ THP $\leq$ THF. As with the alcohols studied, there is a large difference in the partial pressures of DIOX (30mm Hg), THP (110mm Hg) and THF (110mm Hg). The uptake of methanol was found to be faster than the other two alcohols which may be assumed to be partly caused by their size difference, however, the difference was not as great as was observed for DIOX, THP and THF (Fig. 51). Since the cyclic ethers are all of equal size, with no bulky groups attached it may be expected that they should interact with the exchangeable cations in a similar manner. Along with the difference in partial pressures which may account in part for the observed sequence it is also considered from experimental observation that the interactions of THP and THF with the exchangeable interlayer cations is much less than for the DIOX molecules. This greater interaction for the DIOX leads to greater residence times about the cations and consequently to slower diffusion rates.

The diffusion coefficients for each of the cyclic ethers into the individual cation-exchanged forms show influences similar to the alcohols but were found to increase as Cr(III) $<$ Al $<$ Fe(III). Here again the diffusion coefficients were of the order of 1×10^{-16} m^2 s^{-1}.

Activation Energies.

As was found for the alcohols the main features concerning the activation energies of the cyclic ethers, collected in Table 5.3, were that (i) the magnitude of the activation energies were quite small thereby indicating a low potential barrier to diffusion into the trivalent exchanged derivatives, and (ii) it may be seen that the activation energies for the cyclic ethers exhibit the same cation dependence as the alcohols as in Al $<$ Fe(III) $<$ Cr(III). Further investigation of the values given in Table 5.4 indicates that the activation energies for the Al- and Fe(III)- exchanged montmorillonite were almost identical within experimental error and were very low for THP and THF $\sim$ 2-3 kJ mol^{-1} . The relatively high rate of diffusion and low activation energies for THF and THP into these cation forms suggests little or no cation/solvent interaction. The decrease in diffusion rate and rise in activation energies for the THP and THF on the Cr(III)-montmorillonite indicate greater interaction occuring between the Cr(III)- forms and the cyclic ethers, THP and THF. The magnitude of the interactions between the DIOX molecules and the trivalent cation-exchanged montmorillonite may be deduced from the large increase in the activation energies for these solvent/cation systems as well as the decreased diffusion rates mentioned earlier.

A comparison of the diffusion rates of the cyclic ethers and alcohols onto Cr(III)- montmorillonite at 18 °C is shown in Fig. 51. This represents the trend found for all the trivalent cation-exchanged forms and decreases as MeOH > i-PrOH > t-BuOH ≥ THF ≥ THP >> DIOX. On consideration of the vapour pressures the solvent form two separate groups: MeOH > THF ≥ THP and i-PrOH > t-BuOH >> DIOX. Upon inspection it may seem easy to assume that the first group follows a sequence of molecular size and the second being due to the much greater DIOX/cation interaction but it is probable that a combination of these factors apply.

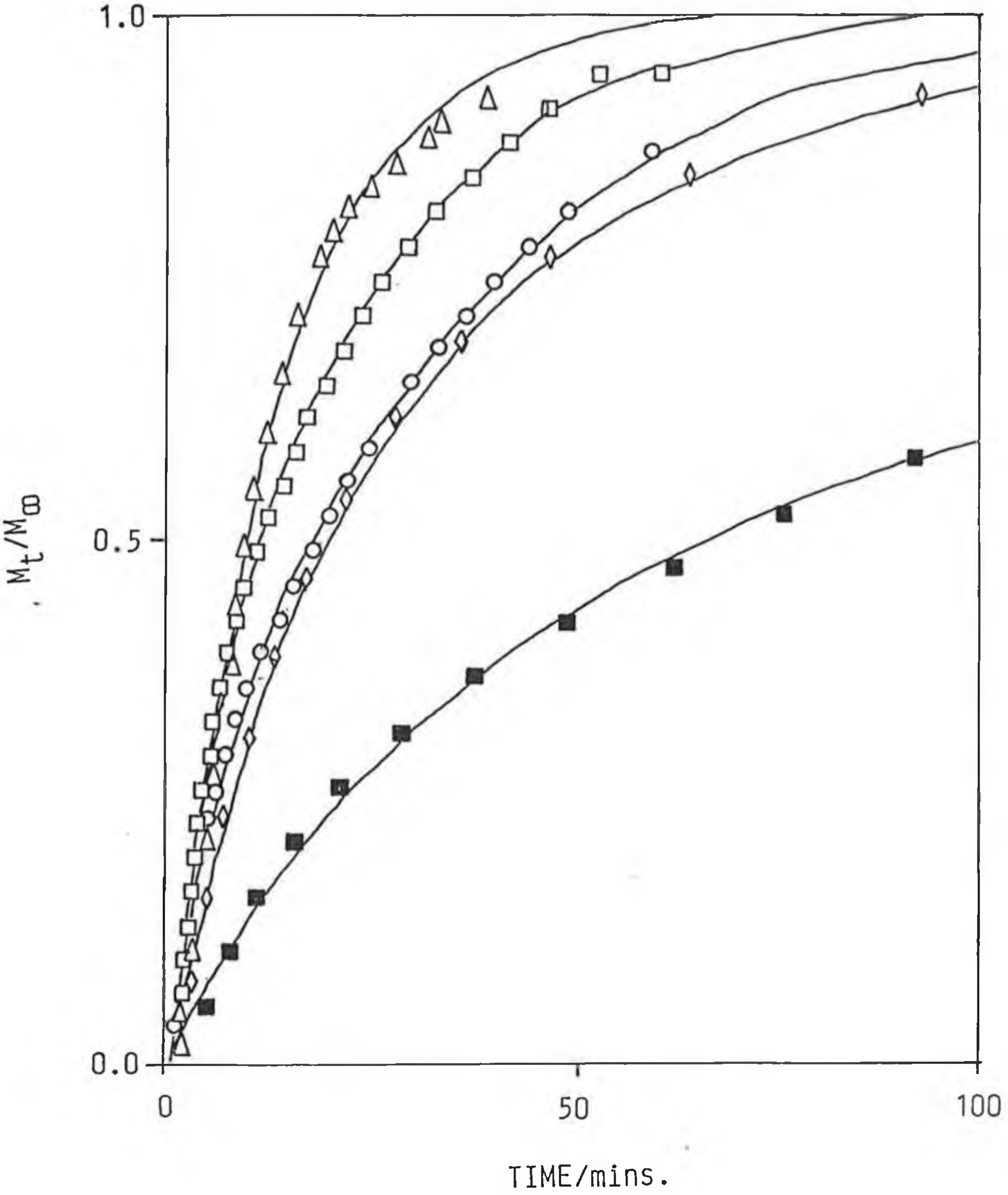
5.6 Conclusions.

The rate of uptake of the alcohols onto the three cation-exchanged forms of montmorillonite included in this work was characterised by a temperature dependent integral diffusion coefficient, $\overline{D}$, in the range 0.3 - 1.64 x 10^{-16} m^2 s^{-1} and required activation energies in the range 3 - 11 kJ mol^{-1}. The activation energies were found to be dependent on the exchange cation and increased as Fe(III) < Al < Cr(III), this was considered to be caused by the displacement of some water molecules from the coordination shell of the cation. The alcohol sorption increased as t-BuOH < i-PrOH ≤ MeOH and the activation energies for MeOH and i-PrOH for the three exchanged derivatives are similar whereas that for the t-BuOH is slightly higher in all cases, this was thought to be caused by the difference in both molecular size and shape of the three alcohols.

Since there is little difference in the molecular size and shape of the three cyclic ethers it

Fig. 51

Comparison of the sorption rates for alcohols and cyclic ethers on the Cr(III)-montmorillonite at 18 °C (Δ = MeOH; □ = i-PrOH; ○ = t-BuOH; ◊ = THF; ■ = DIOX). lines as in Fig. 5c.



was expected that the diffusion rates and activation energies would give similar results for each solvent. With rates of diffusion between the values 0.07 - 1.22 x 10^{-16} m^2 s^{-1} and activation energies between 3 - 13 kJ mol^{-1}, these ranges were found to be bigger than for the alcohols. The DIOX was shown to diffuse at a slower rate than both the THP and THF in all three cation-exchanged forms and with the same activation energy in each case. It was therefore suggested that there is enhanced DIOX/cation interaction which props the clay layers apart more efficiently, thereby leading to greater possibility of catalysis occuring when this solvent is used in conjunction with these trivalent exchanged clays.

It should be noted that the results obtained for the Fe(III)-montmorillonite should be considered carefully since the possibility of the presence of some oxyhydroxy species in the interlayer could lead to some misleading results as mentioned in Chapter 4.

CHAPTER 6

ADSORPTION FROM BINARY SOLUTION ONTO SOME TRIVALENT CATION EXCHANGED MONTMORILLONITE.

6.1 Introduction

Numerous investigations have been carried out concerning clay-organic interactions.[1] However most data collected to date have been on the quantitative aspects of adsorption of organic molecules from aqueous and non-aqueous solutions by alkali-metal and alkali-earth cation exchanged clays.[2,3] Moreover, little information is available regarding the dynamic and steady state behaviour of reactions catalysed by trivalent cation exchanged montmorillonites. As in any heterogeneous catalytic system the efficiency of the catalyst may not be governed by its own intrinsic activity but may be subject to other controlling factors such as distribution of reactants, solvent and products between the bulk phase and the adsorbed phase where reaction occurs. Although several novel organic syntheses occur in the interlayer space of some transition metal exchanged montmorillonites (for example the ready dimerisation of diphenylethylene,[4] elimination of ammonia from amines[5] and the conversion of 1-hexene to di-2-hexyl ether[6]) it was in the production of methyl tertiary butyl ether (MTBE)[7] that the yield of product was first reported to be altered by the particular type of solvent used. Using three cyclic ethers, namely 1,4-dioxan (DIOX), tetrahydropyran (THP) and tetrahydrofuran (THF) the percentage yield was found to be reduced from 65% over a Fe(III)- exchanged montmorillonite using DIOX as solvent to 0% over an Al-exchanged form using THF as solvent (see table 6.1). In the case of using DIOX as solvent then the order of percentage yield is Al < Cr(III) < Fe(III) although the actual percentages are very similar. Using THP or THF as solvents, however, yield sequences of Al < Fe(III)< Cr(III) and Al < Cr(III) < Fe(III) with the production of MTBE over Al-montmorillonite being much smaller than the percentage yield over the other two exchanged forms. Obviously these catalytic systems need to be characterised and the effect of equilibrium on the yield investigated.

Work reported in this chapter represents the adsorption, from binary liquid mixtures, of the alcohol, i.e. methanol, from the cyclic ethers DIOX, THP or THF onto an Al- or Cr(III)- exchanged montmorillonite in the presence or absence of a rehydrated clay surface. The results are reported in the form of composite isotherms the use of which, in this area, have been largely restricted to studies involving tetra-alkylammonium and hexadecylpyridinium exchanged clays as reviewed by Davis and Everett.[8]

TABLE 6.1

The solvent and cation dependence of the percentage yield of MTBE.

Clay	Solvent		
	1,4-Dioxan	THP	THF
Al-mont	61	4	0
Cr(III)-mont	63	42	28
Fe(III)-mont	65	35	32

Experimental conditions used:

1g clay, 1cm^3 MeOH, 3cm^3 solvent, 25 mmol isobutene.

60 °C for four hours.

After Adams, Clement & Graham.[7]

6.2 Theory

When a binary liquid mixture of solvents A and B, say, is shaken up with m grams of an adsorbent C, having an appreciable surface area, the concentration of solvent A remaining in solution usually diminishes by an amount ΔC_A, say, in consequence of the preferetial adsorption of the molecules of A on the surface of C. A plot of $\Delta C_A/m$ against the concentration of A remaining in solution is then the isotherm of apparent adsorption of A on C. The word apparent being used since the solvent B can also be adsorbed and the quantity ΔC_A which is measured represents the resultant of the differing extents of adsorption of A and B. It is more appropriate to express results of adsorption measurements in terms of mole fractions rather than concentrations. The isotherm of apparent adsorption - called the specific surface excess (composite) isotherm - of A is then the curve of Δx_A against x_A, where Δx_A is the change in mole fraction of component A in the mixture when adsorption occurs, and x_A is the mole fraction of A in the mixture which is in equilibrium with the solid C. An indication of the number of moles of each component adsorbed and the forces involved in adsorption can be obtained from such composite isotherms. Indeed the two individual isotherms may be calculated although a knowledge of the specific surface area or mono-layer capacity is required.

The number of moles of each component adsorbed is calculated as follows:-[9] Henceforth suffix 1 will refer to component A and suffix 2 to component B.

Let n_1^0 and n_2^0 be the number of moles of the two components A and B present originally, the total n^0 is therefore:-

$$n_1^0 + n_2^0 = n^0 \qquad 6.2.1$$

Let the mole fraction of each be x_1^0 and x_2^0 before and x_1 and x_2 after adsorption equilibrium has been achieved. Assuming a mass, m, of 1 gram, let the number of moles of each component adsorbed be n_1^s and n_2^s respectively.

Since the number of moles of each component adsorbed must equal the number originally present less the number remaining in solution we have

$$n_1^s = n_1^0 - n_1 \qquad 6.2.2$$

and

$$n_2^s = n_2^0 - n_2 \qquad 6.2.3$$

but since

$$n_2/n_1 = x_2/x_1 \qquad 6.2.4$$

then

$$n_2^s = n_2^0 - n_1 \frac{x_2}{x_1} \qquad 6.2.5$$

$$\Rightarrow \quad n_2^s x_1 = n_2^0 x_1 - n_1 x_2 \qquad 6.2.6$$

multiplying equation 6.2.2 by x_2 we get

$$n_1^s x_2 = n_1^0 x_2 - n_1 x_2 \qquad 6.2.7$$

subtracting equation 6.2.6 from 6.2.7 we obtain

$$n_1^s x_2 - n_2^s x_1 = n_1^0 x_2 - n_2^0 x_1 \qquad 6.2.8$$

but

$$x_1 + x_2 = 1 \quad \text{and} \quad n_2^0 = n^0 - n_1^0$$

then

$$n_1^s x_2 - n_2^0 x_1 = n_1^0 (1-x_1) - (n^0 - n_1^0) x_1 \qquad 6.2.9$$

$$
\begin{aligned}
n_1^s\, x_2 - n_2^s\, x_1 &= n_1^0 - n^0\, x_1 \\
&= n^0\, x_1^0 - n^0\, x_1 \\
&= n^0\, (x_1^0 - x_1)
\end{aligned}
$$

let $\Delta x_1 = x_1^0 - x_1$

then $n^0\, \Delta x_1 = n_1^s\, x_2 - n_2^s\, x_1$ 6.2.10

A plot therefore of $n^0 \Delta x_1$, where Δx_1 is the change in mole fraction occuring in the mixture and may be measured by experiment, against x_1 is the composite isotherm for component 1.

The adsorption excess isotherms calculated as above may be classified into basic types by the Schay-Nagy system of classification.[10]

Adsorption excess isotherms of type I, Fig. 6a, in the Schay-Nagy system arise where there is a notable difference in the adsorption energies of the two components. An example of such an isotherm is described by Dekany et al.[11] for the adsorption of benzene from benzene/n-heptane mixtures onto a sodium exchanged montmorillonite. Although it is indicated that the adsorption occurs on the external surface of the clay.

Composite isotherms of type II, Fig. 6b, in the Schay-Nagy system occur when one of the components is preferentially adsorbed on the surface similar to type I but the adsorption capacities are much higher than for values calculated for the type I isotherms. Dekany et al.[11] described the adsorption from some alcohol/Benzene mixtures onto Na-montmorillonite. It was found that the alcohol was not only adsorbed on the surface but

Fig. 6a

Shape of type I isotherm in the Schay-Nagy classification.

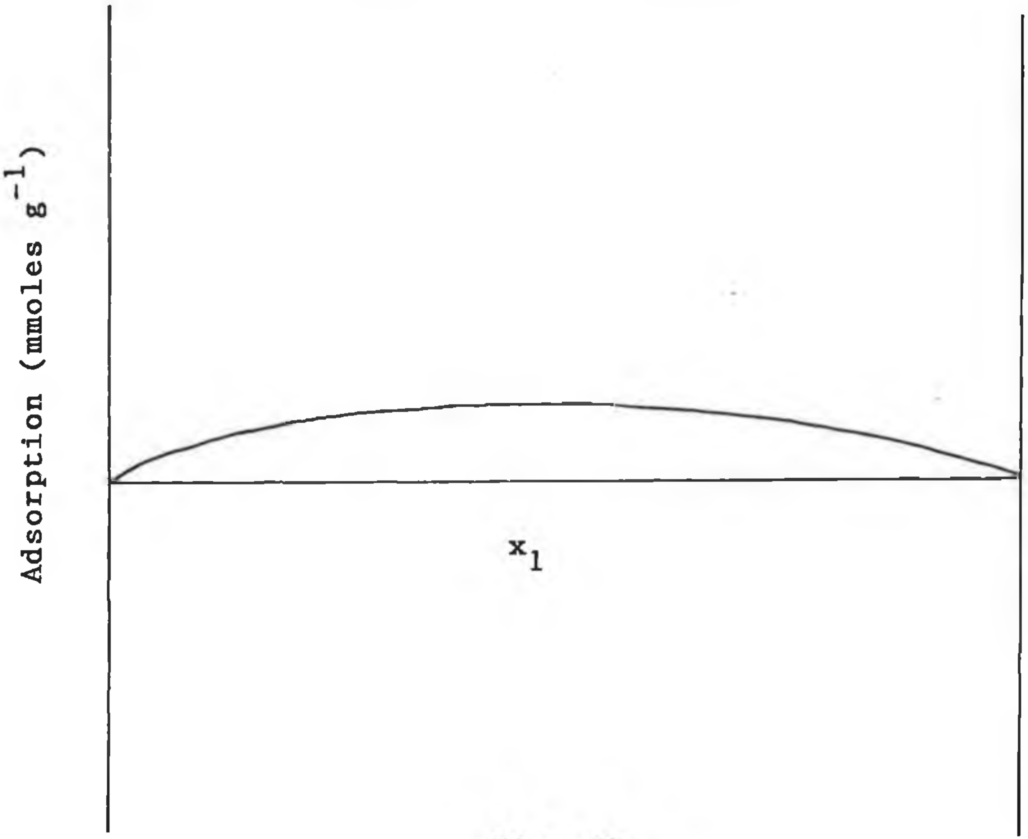
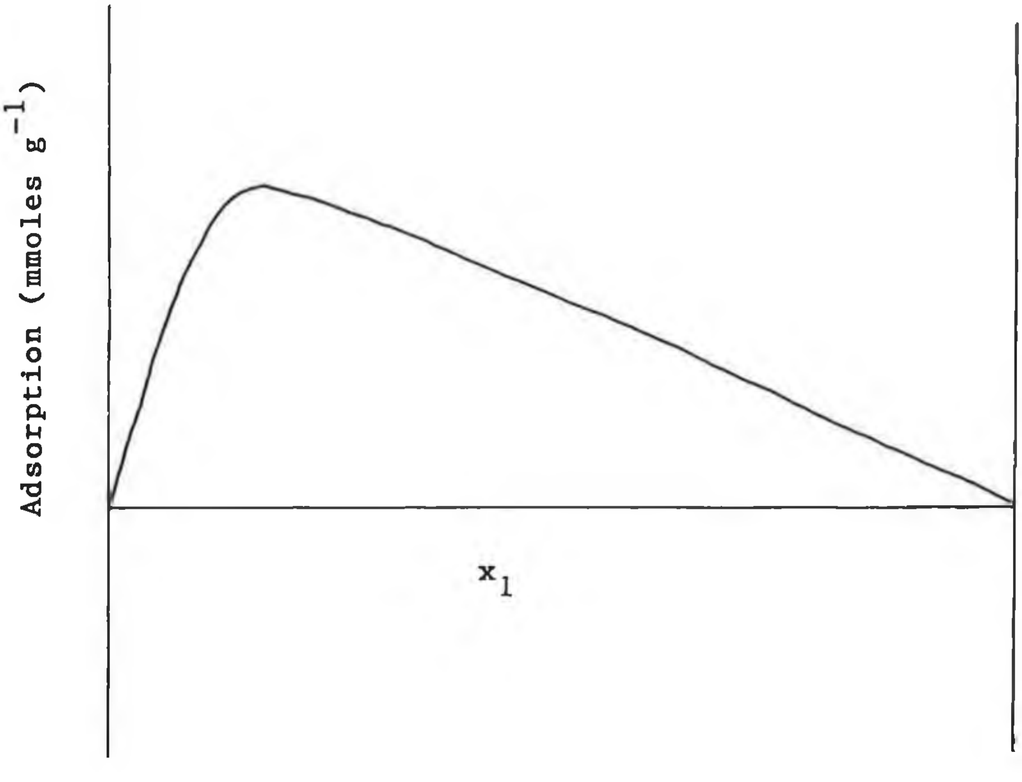


Fig. 6b

Shape of type II isotherm in the Schay-Nagy classification.



also penetrated the clay layers and was adsorbed onto the internal surfaces.

Adsorption excess isotherms of type III, Fig. 6c, occur when there is a small difference in the adsorption energies of the two components. Such an isotherm was found[12] for the adsorption of methanol/benzene mixtures on bentonite which had been previously extracted with a 50% mixture of water-i-propanol (although the isotherm is a transition between types III and IV). Here again the adsorption capacity is much greater than the benzene/n-heptane mixtures.[11] Because of the alcoholic extraction, the surface is alkylated, due to the chemisorption of the alcohol. Therefore, besides the alcohol, benzene is adsorbed on the alkylated surface.

As with isotherms of type III, the adsorption excess isotherms of type IV, Fig. 6d, arise when the two components have sorption energies and distribution coefficients of similar magnitudes.[17] An example of such an isotherm is observed with the adsorption from methanol/benzene onto charcoal.[13] The S-shape of the curve yields negative values on the right-hand side of the diagram, a negative value of methanol merely implies that the methanol is being adsorbed to a lesser extent than is benzene in that concentration range of the mixture.

Isotherms of type II, III and IV of the Schay - Nagy classification[10] have the common characteristic that a fairly long section of the isotherm is practic-

Fig. 6c

Shape of type III isotherms in the Schay-Nagy classification.

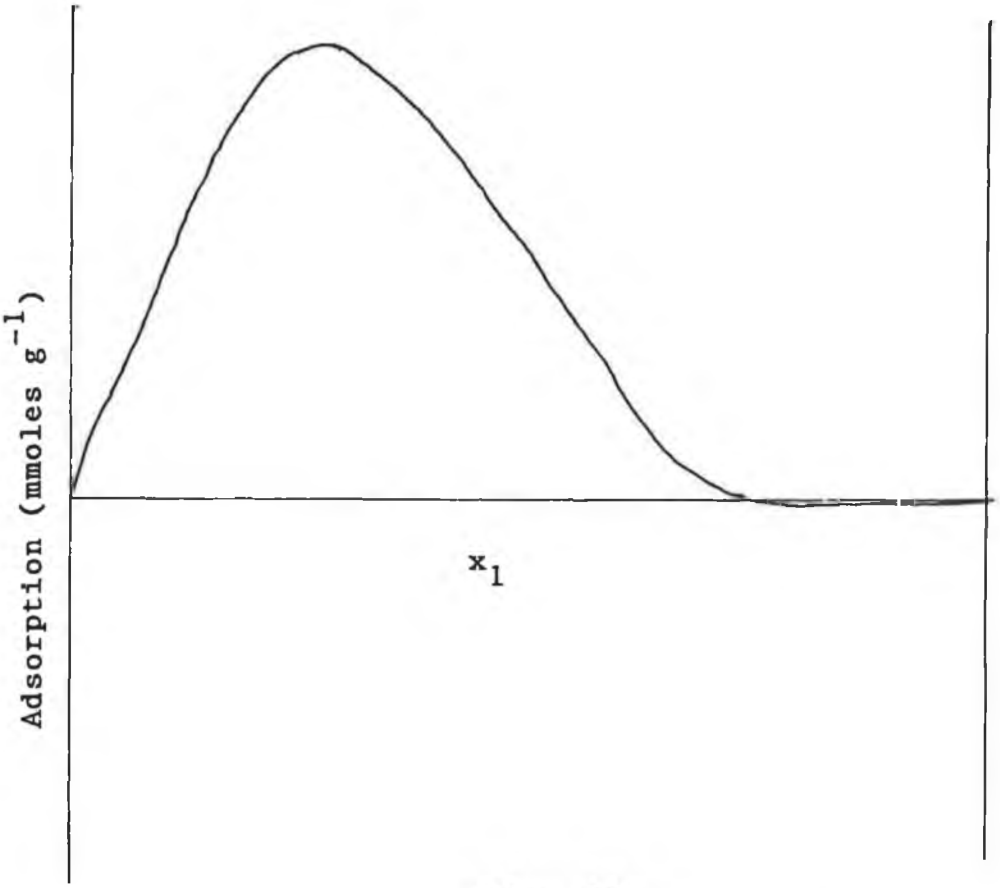
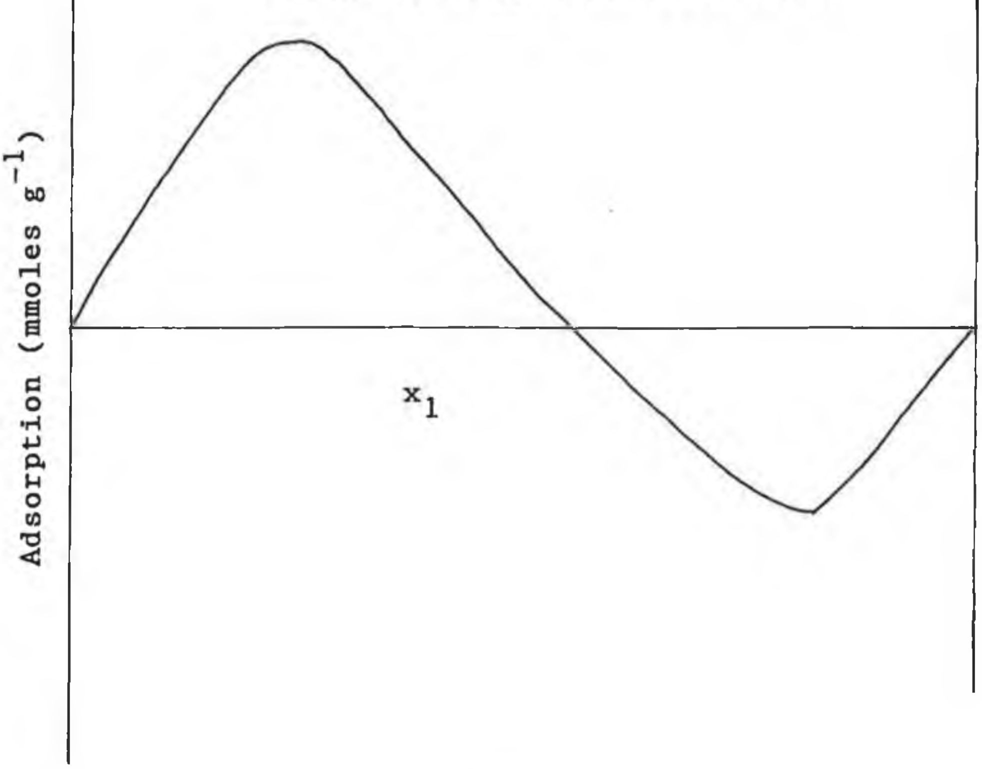


Fig. 6d

Shape of type IV isotherms in the Schay-Nagy classification.



ally linear. It has also been suggested that the adsorbed layer is of constant composition for this linear portion of the isotherm.[14] For the linear section we may write

$$n^o \Delta x_1 = a - b\, x_1 \qquad 6.2.11$$

therefore combining equations 10 and 11 gives

$$a - b\, x_1 = n_1^s - (n_1^s + n_2^s)\, x_1 \qquad 6.2.12$$

now, assuming that the intercepts of the linear parts are equal to the adsorption of the components at the points $x_1 = 0$ and $x_1 = 1$,[10] it may be written for the $x_1 = 0$ intercept

$$a = (n_1^s)_c \qquad 6.2.13$$

and for the $x_1 = 1$ intercept

$$a - b = -(n_2^s)_c \qquad 6.2.14$$

which define the adsorbed layer over the linear region. It should be noted that although the assumption of constant composition over the linear region is not the only explanation of this phenomenon[14] it was used to obtain the semiquantitative values for type III and IV isotherms collected in Table 6.2.

6.3 Experimental.

The trivalent cation exchanged montmorillonites used in these studies were prepared as described in Chapter 3. The clay samples used were either dried at 120 °C for 16 hours, cooled in a dessicator and immediately added to 10 cm^3 of the required binary mixture of known mole fraction or alternatively were dried at 120 °C cooled in a desiccator and equilibrated at 12% relative humidity (over saturated LiCl solution maintained at 20 °C) for a further 16 hours prior to immersion in the binary solution. Following the addition of the clay the centrifuge tubes were stoppered with rubber septa and shaken at 27 °C for 48 hours. After this equilibration period the liquid mixtures/clay suspension were centrifuged until a clear supernatant was obtained and a sample removed via syringe. The supernatant was analysed for both solute and solvent using a pye unicam G.C.D. gas chromato-graph with a one meter column packed with 10% SE 30 on chromosorb W (60-80 mesh). A calibration curve was set up by analysing for both the solute and solvent, using the same G.C. conditions, from liquid mixtures of known composition. Using the values obtained to find which of the liquids were taken up in excess and by how much.

As in previous studies in this work the technique of x-ray diffraction was used to examine the basal spacings of some representative samples of the clay/binary mixture systems. These samples were obtained by immersing glass-slide supported clay films (either dried at 120 °C or dried at 120 °C and equilibrated at 12% RH) into a mixture of 2 cm^3 of cyclic ether plus 1 cm^3 of methanol or into the pure cyclic ether or methanol. The instrument with which the diffraction traces were recorded was a Jeol JDS 8X diffractometer using copper K_{α} radiation at 40kV and 20mA.

6.4 Results

The specific surface excess adsorption isotherms for both the Al and Cr(III) exchanged clays are collected in Fig. 6e to 6j where the surface concentration of the cyclic ether (in mmoles g^{-1}) is plotted against its mole fraction in the supernatant liquid.

6.4.1 Samples Pretreated at 120 °C.

These samples can be identified by the open circles in Fig. 6e to 6j. A type I isotherm, in the Schay - Nagy classification,[10] was obtained for the adsorption of THF from MeOH on both the Al- and Cr(III)-derivatives as represented in Fig. 6g and 6j respectively. The curves have a very small amplitude with THF being preferentially adsorbed over the entire range. The adsorption of DIOX or THP from MeOH on 120°C dried Al-montmorillonite, as shown in Fig. 6e and 6f, describe type IV isotherm with the azeotropic point near a 1:1 mole ratio. Adsorption of DIOX from MeOH onto 120 °C dried Cr(III)-montmorillonite (Fig. 6h) also adopts a type IV isotherm but with lower amplitude. The adsorption of THP from MeOH on the Cr(III) form (Fig. 6i) yields a type III isotherm.

6.4.2 Samples Rehydrated at 12% RH.

The presence of the preadsorbed water, in excess of that present after the predrying of samples at 120 °C, was found to have a major effect on both the amount adsorbed and the azeotropic point, as represented by the

Fig. 6e

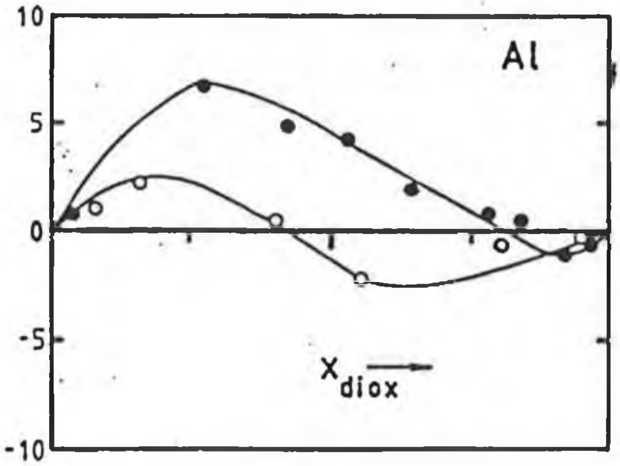


Fig. 6f

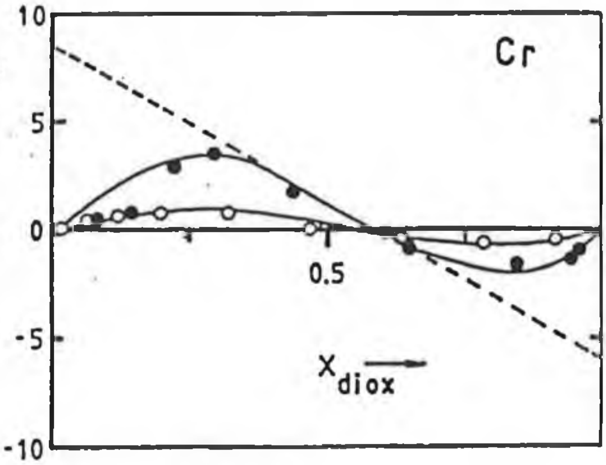


Fig. 6g

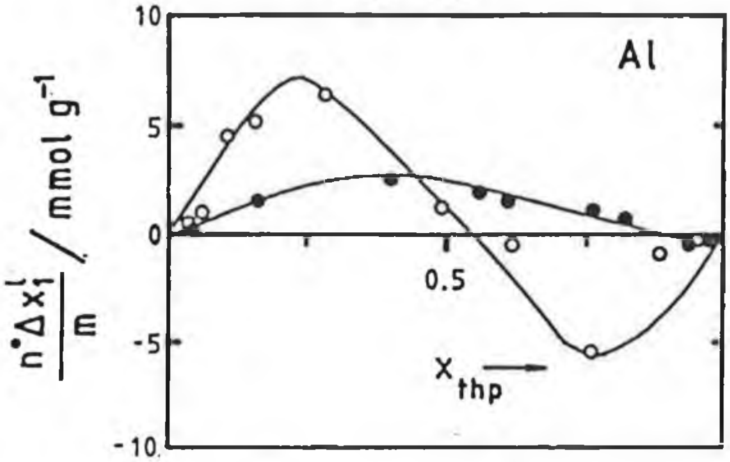


Fig. 6h

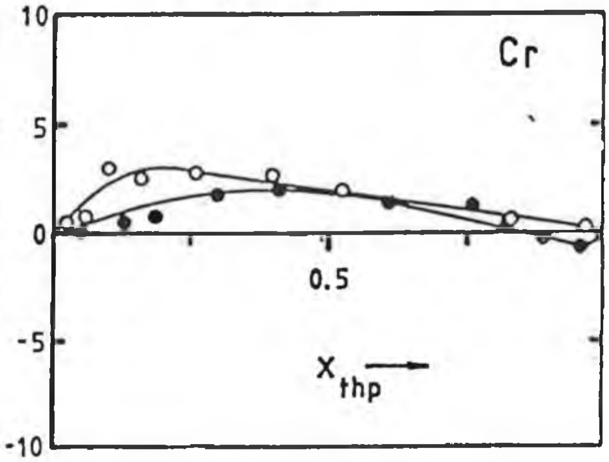


Fig. 6i

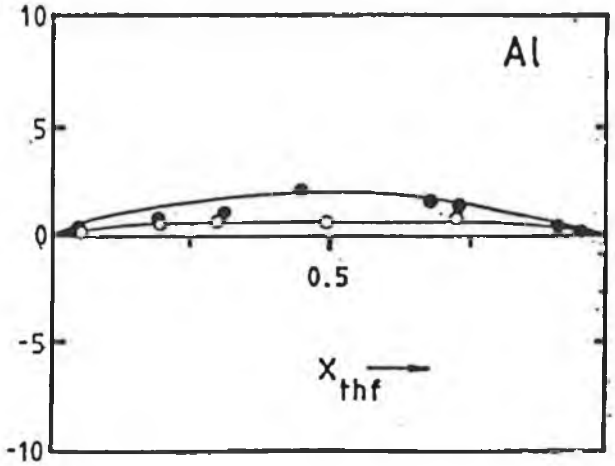


Fig. 6j

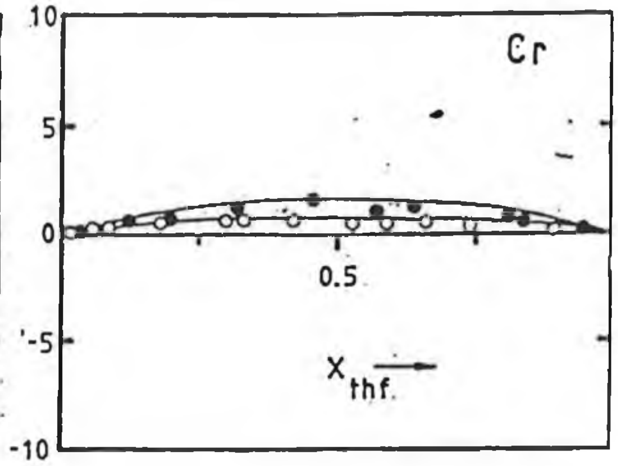


TABLE 6.2

THE AZEOTROPIC POINTS AND ADSORBED LAYER COMPOSITION FOR 1,4-DIOXAN (DIOX) AND TETRAHYDROPYRAN (THP) FROM METHANOL (MeOH).

Exchange Cation	Rehydrated at 12%RH	Solvent System	n_1^s /mmol g^{-1}	n_2^s /mmol g^{-1}	x_1^a
Al	NO	DIOX/ MeOH	7.5	10.5	0.43
Al	YES		11.8	3.0	0.81
Cr(III)	NO		1.8	1.6	0.52
Cr(III)	YES		8.5	5.5	0.58
Al	NO	THP/ MeOH	14.0	10.5	0.54
Al	YES		6.0	0.8	0.88
Cr(III)	NO		-	-	-
Cr(III)	YES		4.3	0.6	0.87

full circles in Fig. 6e to 6j, but was not found to alter the general classification of the isotherms. There is an increase in the amount of THF taken up from MeOH relative to the 120 °C dried samples for both the Al and Cr(III) forms (Fig. 6g and 6j respectively). The uptake of DIOX from MeOH also increased on both forms (Fig. 6e and 6h respectively) with the effect of the added water being much more obvious in the former case resulting in DIOX being preferred for $\sim$80% of the composition range. In the THP/MeOH mixtures the preadsorbed water was found to reduce the amount of THP preferentially adsorbed, although THP was found to be preferred for 90% of the composition range. This represents an increase of some 35% for the Al- form (Fig. 6f) but a decrease of 10% for the Cr(III) form (Fig. 6i). Moreover, the additional water leads to the adoption of a type IV isotherm for the Cr(III) form. No attempt was made to compensate for the inclusion of the enhanced water content or its possible expulsion into the supernatant mixture. It is also assumed that the depletion of the components in the mixture equals the amount adsorbed in the interlayer region since there is little possibility of direct determination of the amount associated with the external clay surfaces.

6.4.3 X-ray Diffration.

The x-ray diffraction results for the 120 °C and 12% rehydrated samples of Al- and Cr(III)- forms exposed to the various liquid mixtures and pure solvents are

TABLE 6.3

BASAL SPACINGS OF THE Al- AND Cr(III)- EXCHANGE FORMS IN PURE SOLVENTS AND BINARY MIXTURES.

Exchange Cation	X_{MeOH}	Cyclic Ether	d/Å Peak 1	d/Å Peak 2
Al^a	1.00	-	18.4	-
	0.00	DIOX	15.6	-
	0.00	THF	15.5	-
	0.45	DIOX	15.5	-
	0.45	THF	15.6	19.2
Cr^a	1.00	-	18.4	-
	0.00	DIOX	15.2	-
	0.00	THF	14.3	-
	0.45	DIOX	15.5	-
	0.45	THF	15.5	18.4
Al^b	0.45	DIOX	15.0	-
	0.45	THF	15.0	17.7
Cr^b	0.45	DIOX	15.2	-
	0.45	THF	15.0	16.8

a = dried at 120 °C

b = dried at 120 °C and rehydrated in 12% R.H.

gathered in Table 6.3. It can be seen from table 6.3 that the x-ray diffraction profiles of the DIOX/MeOH mixtures are all dominated by a DIOX intercalate. Although the d_{001} peaks were very broad and may indeed mask a weak interstratified complex. Only the THF/MeOH systems show any signs of interstratified complexes with 2 diffraction maxima indicative of THF (15.5Å) and MeOH (18.4Å) intercalates. The mole fraction used in all liquid mixtures was 0.45 of MeOH.

6.5 Discussion

Generally the isotherm type is greatly affected by the binary system involved whereas the amplitude, which follows the sequence DIOX $>$ THP $>$ THF, is not only influenced by the binary mixture but also by the exchangeable cation. An increase in the amount of preadsorbed water leads not only to a shift of the azeotropic point in favour of DIOX or THP but also to a change in amplitude. Similar effects have been described when increasing the number of layers of water on a rutile surface for the uptake of p-xylene from some binary mixtures with ethanol, dodecan-1-ol, octan-1-ol and n-heptane.[15,16]

The isotherms obtained for the binary mixture of THF and MeOH were found to be of type I in the Schay - Nagy classification for both the Al- and Cr(III)-exchanged montmorillonites, as shown in Fig. 6g and 6j. This type usually occur when there is a notable difference between the adsorption energies of the two components.[17] The adsorption energy of THF must therefore exceed that of MeOH in both the Al- and Cr(III)- forms. With the addition of water to the clay interlayer prior to exposure to the mixtures the uptake of THF is increased by 50% in both exchange forms. It should be noted however, that from the x-ray diffraction data in Table 6.2 the exclusive presence of MeOH in some interlayers has been shown. Thus suggesting that the adsorption of THF and MeOH may segregate into separate layers. These results emphasise that this type of investigation gives only the surface excess of one component and does not mean that this component is adsorbed to the exclusion of the other. A possible explanation for these results is that although THF and MeOH compete for the same sites it is energetically more favourable for adsorption to occur in layers consisting of one component of the binary mixture. This overall preference for THF over MeOH, although slight, may explain why a relatively poor yield of MTBE was obtained when THF is used as a solvent.

Type III and IV excess isotherms are obtained when the sorption energies and the distribution coefficients of the two components in the binary mixture are of similar magnitudes.[14] This suggests that DIOX, THP and MeOH have similar adsorption energies in both the Al- and Cr(III)- exchanged montmorillonites. DIOX was found to be adsorbed more than THP in both forms although the Al- form adsorbed more of both cyclic ethers than the Cr(III)- form. The preadsorbed water was found to have opposite effects on each exchanged form in that it increases the adsorption of DIOX and reduces that of THP.

Assuming that the condition of constant composition over the linear range holds then the molar ratio of DIOX:MeOH is 4:1 in the Al- form and 3:2 in the Cr(III)- form while that for THP:MeOH is 7.5:1 in the Al-form and 7:1 in the Cr(III)- form. These figures are all obtained for the rehydrated clays. The ratio for THF:MeOH may not be easily determined. Examination of the percentage yields of MTBE[7] quoted in the introduction leads to the conclusion that the yield decreases with increasing cyclic ether:MeOH ratio. Obviously there may be some variation of the extent of adsorption with temperature and pressure and these may affect the ratios obtained. Moreover, the presence of the other reactants, intermediates and products will have an influence on the system. It is therefore concluded that although an introduction has been made into the complex reaction systems many further studies need to be carried out before these reaction mechanisms can be understood.

CHAPTER 7

A SUMMARY.

SORPTION KINETICS AND SORPTION ISOTHERMS OF TRIVALENT CATION-EXCHANGED MONTMORILLONITES

The fact that di- and trivalent cation exchanged clays can be utilised as efficient catalysts in both the production of industrially significant chemicals[1,2,3] and novel one step syntheses[4,5] has been unequivocally demonstrated in recent years. However, the dynamic and steady state factors which affect the position and rate of attainment of equilibrium have received little attention by comparison.[6] The lamellar nature of the sheet silicate structure in which the hydrated cations (which constitute the active sites) are dispersed suggests that the diffusion of the requisite organic moieties to and product molecules away from the active centre will play an important, if not rate limiting, role.[7] In the light of the recent advances in the study of clays as catalysts and the interest shown by industry it must be realised that directly measured sorption kinetics are of considerable technical importance because they determine rates in practical applications. It is because of this scarcity of information regarding the factors influencing such properties as the acidity of the trivalent exchange forms and the diffusion of organic species in montmorillonites that has prompted this investigation.

The base clay used in these studies was a Wyoming montmorillonite with a layer formula, following sedimentation, of

$(Si_{3.86}Al_{0.14})(Al_{1.35}Fe_{0.08}Mg_{0.6})\ O_{10}\ (OH)_2\text{-}\ K_{0.07}Na_{0.59}$

The Bronsted acidity which gives rise to the catalytic activity of clays is derived from the polarisation of solvent water molecules by the small, highly charged interlayer cations. There is little difference in the number of acid sites on the three cation-exchanged forms studied here (Al-, Cr(III)- and Fe(III)-), although the thermal desorption studies show that the desorption temperature of the protonated base does occur at higher temperatures in the Al- montmorillonite than the other two forms thus indicating stronger acidity. Heating the trivalent cation exchanged forms to $>$ 300° C results in the dehydration of the cation and the formation of Lewis acid sites of a strength intermediate to those of the naturally occurring Lewis sites and the Bronsted sites destroyed by the high pretreatment temperatures. This dehydration however, also results in the migration of protons into the clay layer and strong bases such as n-butylamine can abstract these protons but weaker bases such as pyridine cannot.

The trends obtained for the diffusion coefficients for the three alcohols in the trivalent cation forms provide considerable insight regarding the factors which influence diffusion in layered silicates. For a given cation it is shown that the rate of alcohol sorption increases at t-BuOH $<$ i-PrOH $<$ MeOH and is characterised by temperature dependent integral diffusion coefficients, $\overline{D}$, in the range

$$0.3\text{-}1.64 \times 10^{-16}\ m^2\ s^{-1}.$$

Unfortunately, due to the dissimilarity in the partial pressures exerted by MeOH (100 mm Hg), i-PrOH (40 mm Hg) and t-BuOH (40 mm Hg) the rate of sorption of MeOH is not strictly comparable with that of the remaining two alcohols. However, since the polarities of the three alcohols are almost identical, the small size of MeOH molecule should allow more rapid ingress than that exhibited by t-BuOH and i-PrOH. Therefore, this sequence may, be partly attributed to the difference in molecular size. It is worth noting that diffusion coefficients of the order $10^{-16}\ m^2\ s^{-1}$ generally reflect quite hindered diffusion such as that of n-butane in 4Å zeolite at $\simeq$ 20° C.[8]

The values for the activation energies may be seen to be cation dependent and increase as Al $<$ Fe(III)$<$ Cr(III). The values of the activation energy are also very small ($\leq$ 11.0 $kJmol^{-1}$) indicating that the potential barrier to diffusion is quite low. MeOH and i-PrOH appear to meet a potential barrier of approximately equal magnitude but t-BuOH requires marginally more energy to initiate diffusion which is probably due to its bulky nature necessitating further separation of the clay lamellae. This observed dependence of the activation energy on the exchange cation may result from the displacement of some water molecules from the primary hydration sphere of the cation by the incoming organic molecules.

The retention of a certain amount of water by the trivalent-cation exchanged clays may affect the observed rate of alcohol uptake in both a positive and a negative manner. Firstly, if all the remaining water is contained within the cations co-ordination sphere then those hydrated ions will act as props making the internal surfaces of the clay more readily available to the incoming alcohol. Secondly, if the alcohol competes successfully with water for sites in the primary co-ordination sphere of the cation and the displaced water is expelled into the vapour phase. It is possible that some combination of these effects occur.

It has been observed in the production of methyltertiarybutylether (MTBE), from methanol and isobutene using trivalent cation-exchanged montmorillonites as catalysts[1,7], that cyclic ether type solvents give comparable yields of MTBE at temperatures ~30 °C lower than when hydrocarbon solvents are used. More specifically it was found that the yield of MTBE depends on the actual cyclic ether used as solvent.[1] The efficiency of the catalytic process is optimised when 1,4-dioxan (DIOX) is used as a solvent, although the Cr(III)- and Fe(III)- exchange forms give respectable yields with tetrahydrfuran (THF) and tetrhydropyran (THP). It was suggested that DIOX was the best solvent because all the reactants and products were completely miscible in it thus facilitating the rapid distribution of all the participating moieties between the clay interlayer and the external medium thus preventing phase transfer becoming a rate controlling step. If, however, a Langmuir-Hinshelwood or Rideal-type mechanism is assumed then the diffusion of molecules to and from the catalytic site must be considered as possible rate controlling steps as well as the reaction at that site. Consequently the study of the sorption dynamics of the three cyclic ethers THF, THP and DIOX is pertinent for several reasons. The molecules are of approximately the same size with no bulky substituents and should interact with the exchange cations in a similar manner. Secondly, since they play no obvious role in the catalytic mechanism, their purpose could be envisaged as propping the layers apart thereby presenting the participating molecules with a uniform channel network.

For a given cation the rate of cyclic ether diffusion follows the general trend THF $\gg$ THP > DIOX. This observed sequence may well reflect the greater partial pressures of THF and THP (100 mm Hg) compared to that of DIOX (40 mm Hg). A similar disparity exists in the partial pressures for the alcohols but the difference in diffusion is not as marked as that between THF and THP on the one hand and DIOX on the other. A more realistic explanation is therefore, that THF and THP experience a weaker interaction with the cation than DIOX enjoys. The diffusion coefficients of the individual cyclic ethers in the various cation-exchanged forms exhibit the same dependence as that observed for the alcohols and increases as Cr(III) $<$ Al $<$ Fe(III) characterised by integral diffusion coefficients, $\bar{D}$, between 0.07 - 1.22 x 10^{-16} m^2 s^{-1}. The activation energies for cyclic ether diffusion also mimic those of the alcohols as in Al $<$ Fe(III) $<$ Cr(III) with values between 2 - 13 kJ mol^{-1}. It should be noted that the activation energies for both the Al- and Fe(III)- montmorillonite are identical and are almost negligible for THF and THP (2-3 kJ mol^{-1}). This comparatively fast sorption rate and low activation energy for THF and THP indicate negligible cation/solvent interaction. The slower diffusion rates and higher activation energies for the Cr(III)- form suggests that there is an increased, but nevertheless weak, interaction between Cr(III) and the cyclic ethers THF and THP.

In the optimisation of the MTBE yield when DIOX is used as solvent it may well be attributed to the greater interaction energy the DIOX enjoys with the respective cations making it more effective as a prop than THF and THP which may be readily displaced due to their weak cation/solvent interaction.

The rates of uptake on all the cation exchange forms gives a sequence of MeOH $>$ i-PrOH $>$ t-BuOH $\geqslant$ THF $\geqslant$ THP $>>$ DIOX. Grouping these solvents by comparable vapour pressures yields the two following trends: MeOH $>$ THF $\geqslant$ THP and i-PrOH $>$ t-BuOH $>>$ DIOX. It is possible that the former sequence is attributable to molecular size and the latter to the residence time of the DIOX molecule at the cationic site, however, it must be realised that a combination of these factors may apply.

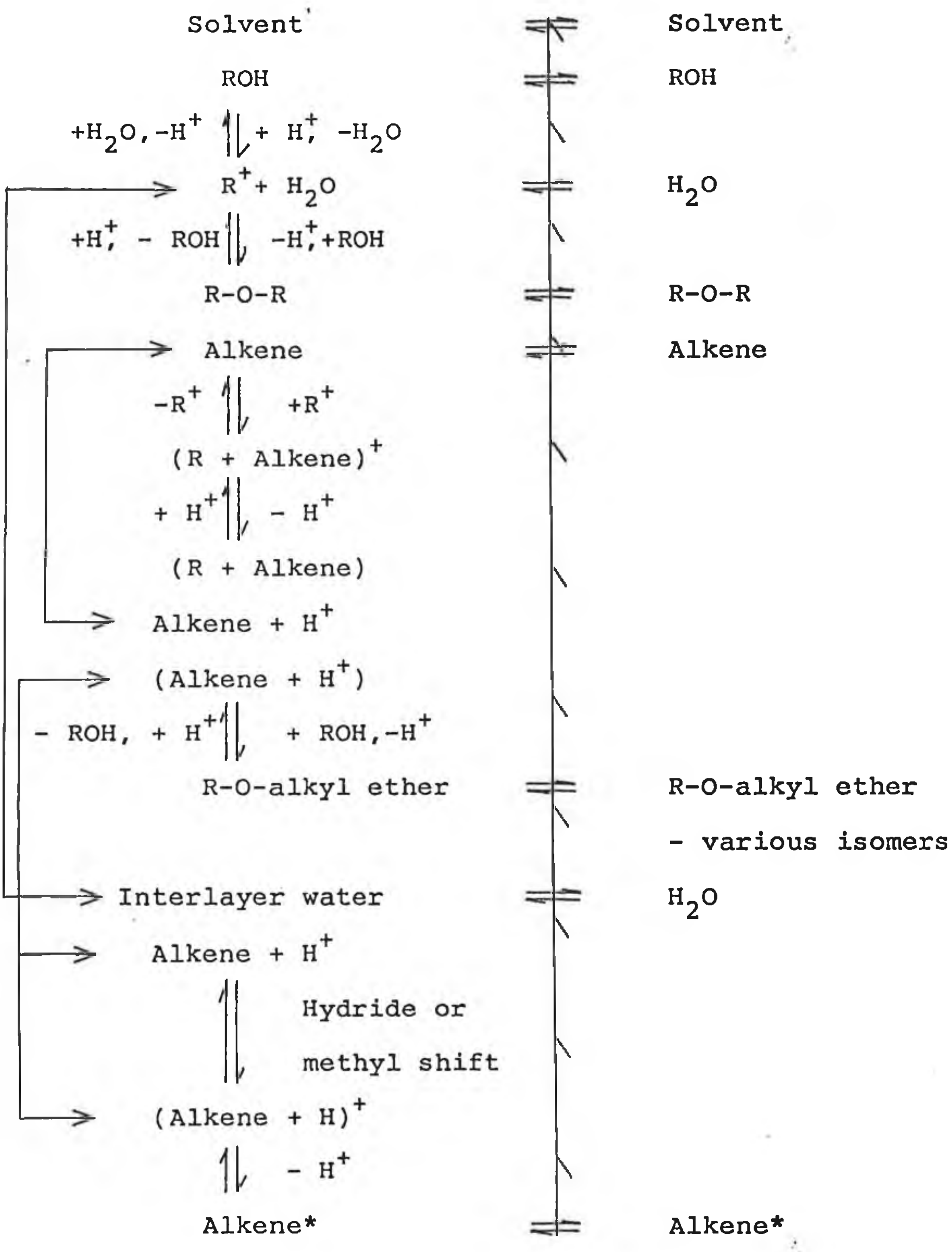
Reactions carried out at low temperatures (~60° C) are usually performed when the solvents and reactants are in the liquid phase. As in any heterogeneous catalytic system the efficiency of the catalyst is not necessarily governed by its own intrinsic activity and in the liquid phase other possible controlling factors such as distribution of reactants, solvents and products between the bulk phase and the adsorbed phase where reaction occurs may be present. As in the vapour phase sorption studies, the two types of organic molecules used for the liquid phase studies were methanol, and the cyclic ethers, 1,4- dioxan, tetrahydropyran and tetrahydrofuran over Cr(III)- and Al-exchanged montmorillonite. The effect of cation hydration state was monitored by ensuring that the samples contained different amount of preadsorbed water. Surface excess isotherms for adsorption from a two component cyclic ether/methanol mixture were used to identify the possible controlling factors of the clay catalysed organic reaction. The isotherm type was dominated by the binary mixture whereas the amplitude which follows the sequence DIOX > THP > THF, was further influenced by the exchange cation, Al > Cr(III), and the water content of the clay. The sorption of DIOX and THP from methanol exhibited a type IV isotherm in the Schay-Nagy classification on both cation - exchanged forms, whilst that of THF from methanol was a type I and THF was the preferred adsorbate. The azeotropic point for the type IV isotherms is near to 0.5 or 1:1 mole ratio for the samples of low preadsorbed water concentration but this shifts in favour of the cyclic ethers at higher levels of interlayer water indicating the preferred component is the DIOX or THP over a substantial portion of the composition range.

Isotherms of type I in the Schay-Nagy classification, such as those for the THF/methanol system, occur where there is a marked difference in the adsorption energies for the two components,[9] as stated earlier THF is the preferred adsorbate in both cation exchanged forms. In the presence of the increased water the uptake of THF is increased by ~ 50% in both forms. X-ray diffraction studies of the three solvent/methanol systems only the THF/methanol mixtures indicate that adsorption of the THF and methanol occur in separate layers by having 2 peaks in the diffraction profiles. The other two systems, 1,4- dioxan/methanol and THP/methanol both have only one peak in their profiles indicating a willingness of these two systems to remain mixed even after adsorption. It would seem that it is therefore more energetically rewarding for the THF/methanol system to fill individual interlayers with a particular component. This may help to explain why there was such a low yield of MTBE when THF was used as solvent.[1,7]

It has been found throughout these studies that caution must be exercised when interpreting any results involving the Fe(III)- exchanged form of the montmorillonite since there is evidence to suggest that some oxyhydroxy species is precipitated in the Fe(III)-exchange as a result of elevated temperatures.[10] However, this should not detract from the overall results showing the importance of many factors such as exchangeable cation and level of hydration, the size, geometry and polarity of the solvents and reactants. The final yields of the various products of the reactions catalysed by these types of exchanged montmorillonite depend not only on the above factors but also upon the distribution of products and reactants between the clay and the surrounding medium. The representation of the various equilibria in the clay/external medium system is relatively complex. An example of such a system is represented in Figure 7a, involving the reaction between an alcohol (ROH) and an alkene.[11] In the liquid phase this system is even more complicated if the various equilibria between the liquid medium surrounding the clay and vapour phase existing above the clay/liquid mixture are taken into account. Experimental distribution coefficients such as those obtained in this work are only now becoming available and the network of interconnecting equilibria are not, therefore, traceable at present.

Fig. 7a

A DIAGRAMMATIC REPRESENTATION OF THE PRODUCTION OF AN ALKYL ETHER FROM AN ALCOHOL OVER A CATION EXCHANGED CLAY.[X]



[X] After Adams, Clement and Graham.[11]

This work describes some of the interactions between solvents used in clay catalysed reactions and the clay catalysts themselves. It was found necessary to obtain information on both the type and strength of the surface acidity before any conclusions were drawn about such interactions. It has been presented that although the three cations are trivalent in nature the factors affecting their catalytic properties and indeed the importance of various interactions vary depending on the nature of the cation. Thereby leading to selective catalysis in one case.[11] These studies only represent the initial stages of the reactions occurring in clay catalysts as described in Fig. 7a and much further work would be needed to describe all the different interactions shown: the stability of the various species involved and also their mobility at the clay surfaces. Further studies involving other solvents and other reactions may yield more information about the clay surface itself and the availablity of the various sites involved in clay catalysis.

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