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INTERACTIONS OF HYDRAZINE AND OF HYDRAZINE DERIVATIVES WITH SOIL CONSTITUENTS AND WITH SOILS

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M.H.B. Hayes, P.J. Isaacson, K.Y. Chia, A.M. Lees
and T.B.R. Yormah,
Department of Chemistry,
The University of Birmingham,
Edgbaston,
Birmingham B15 2TT,
England.

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MATTHEW J. [illegible]
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The clay colloidal of soil can be predicted to have a large influence on the fate of hydrazines in the soil environment. Initial degradation microcalorimetric studies have shown that this influence arises mainly through the processes of sorption and degradation. Clay minerals can reversibly sorb hydrazine, and a certain amount of strong irreversibly sorption can also occur. The colloidal clay components catalyse the degradation of the hydrazine, and in some instances cause very rapid and vigorous degradation. The two main factors which influence hydrazine sorption and degradation are the pH values of the solutions, and the exchangeable metal cations held by the clay.

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1. INTRODUCTION

The overall aims of the research project were to establish the extents to which hydrazine and methylhydrazine compounds interact with soil colloidal constituents, and to understand the mechanisms of the interactions. This was done so that plausible recommendations could be made to minimize the possible impact of hydrazine compounds on the soil environment, and for the reclamation of contaminated soils.

The colloidal constituents are the active surfaces in soils in so far as sorption/desorption processes are concerned. These constituents are composed predominantly of soil clays, which are related structurally to the clay minerals, various hydrous oxides of iron and aluminium, and the amorphous, organic humus colloids. Each may have an independent existence in the soil, but more generally some or all are associated together to present a complex adsorbing surface which is often referred to as the conglomerate soil colloid.

It is important to know how the sorptives react with the well defined colloidal components in order to understand how they could interact with the more complex conglomerate colloids. This can be achieved by isolating the components, and studying the extents and mechanisms of interactions of the sorptives with the isolates. Because the compositions, structures, and properties of soil colloids can vary significantly from soil to soil, it has been considered appropriate initially to study the general types of reactions between hydrazine and well characterized preparations of clays from deposits, laboratory synthesized hydrous oxides of iron and aluminium, and fractionated humic colloids extracted from soils. It can be assumed that when interactions with such substances are understood it will be possible to explain interactions with soils where the compositions of the colloidal components are known.

Reactions involving hydrazines in aqueous solutions are most relevant to soil systems, where water is generally present. The major part of the work carried out involved studies in solution. However, hydrazines have significant vapour pressures at normal soil temperatures, and vapour phase/solid interactions are important, particularly where the concentration of hydrazine is high, and the amount of soil water is low. Some vapour phase adsorption and desorption experiments are described.

Results from our investigations of interactions of hydrazines with soil components have shown that these compounds can be unchanged and also transformed chemically in the sorption process. Dissolved oxygen extensively degrades hydrazines at high pH values (Ellis et al. 1960), and so sorption can be, to a large extent, distinguished from degradation under alkaline conditions by carrying out the experiments in the presence and in the absence of oxygen.

Many transition metals are known to catalyse the degradation of hydrazine (Cosser and Tompkins, 1971), and these can function in the absence of oxygen by acting as one- or two-electron acceptors (Bottomley, 1970). Except in the case of Cu(++) (Lurker, 1976) experiments with transition metals at their concentrations in natural waters, were found not to affect the degradation of hydrazine. However, their effective concentrations at the surfaces of soil colloids, with which they are commonly combined, will be much higher than in the bulk solution. Results from this project have shown that homoionic metal exchanged colloids give rise to significantly greater degradation of hydrazines than do the equivalent concentrations of metals in solution (Hayes et al. 1980 and 1981).

The model studies used organic colloids isolated from soils, clays from deposits and hydroxides of iron and aluminium synthesized in the laboratory. These studies have indicated the types of interactions which can occur between the hydrazine materials and the colloids and the mechanisms involved. A limited number of experiments were carried out with whole soils. A description of some of the materials and of the methods used have been given in previous reports (Hayes et al. 1980 and 1981), and only a brief description of these will be given here, but a more detailed description will be given of the more recent procedures used for studies with hydroxides of iron and aluminium.

2. MATERIALS

2.1 Clays

The <2 μm fractions of a montmorillonite (Camp Berteau, Morocco), a kaolinite (Oneal Pit, Georgia), an illite (Fithian) and a bentonite (Wyoming) were separated after NaOCl pretreatment to remove organic matter. The cation exchange capacity (CEC) of each sample was determined by isotope dilution using ^{22}Na as the tracer ion (see Section 3). In addition to the Na^+-exchanged forms, Al^{3+}-, Fe^{3+}-, Cu^{2+}-, Mn^{2+}-, Ca^{2+}-, Mg^{2+}-, and

K^+-montmorillonite and kaolinite clays were prepared by dispersing each clay (1 g) in 50 cm^3 of the metal chloride solution (1M), equilibrating by tumbling overnight, centrifuging, washing once with H_2O and then EtOH, and finally H_2O to remove chloride salts.

Humic Substances. Humic and fulvic acids were extracted in 0.5M aqueous NaOH in an atmosphere of dinitrogen gas. After centrifugation the supernatant was adjusted to pH 1.0 with HCl, and the precipitated humic acids were separated by centrifugation. The fulvic acids remained in solution. This solution was dialysed against distilled water and the fulvic retentates were freeze dried. The sedimented humic acids were first washed with distilled water, then dialysed against distilled water to remove salts and low molecular weight organic components, and the non-dialysable components were freeze dried.

2.2 Goethite (αFeOOH)

$Fe(NO_3)_3.6H_2O$ (0.125 moles) was dissolved in distilled water (225 cm^3), and sodium hydroxide (2.5M, 25 cm^3) was then added to the solution and the mixture was stirred vigorously. After flocs which formed on addition of alkali had redissolved a homogeneous dark red solution (pH 2.0) was obtained. This solution was allowed to age at room temperature for 50 hours. Then additional NaOH (2.5M, about 130 cm^3) was added to raise the pH to 11.85, and the total volume was brought to 500 cm^3 by adding distilled water. The mixture was aged at 50°C for five days before the supernatant was removed and the precipitate was dialysed until free from nitrate, and the retentates were freeze dried and stored in glass jars. The identity of the product was confirmed by comparison of the peaks in the X-ray diffractogram with those for the standard in the A.S.T.M. Powder Diffraction File.

2.3 Lepidocrocite (γFeOOH)

Lepidocrocite was prepared by oxidation of iron II chloride solutions using a procedure based on that of Taylor and Schwertmann (1978). Distilled water (350 cm^3) placed in a three-necked flask was degassed by bubbling with spot dinitrogen gas through. Any remaining oxygen in the gas had been removed by bubbling through alkaline pyrogallol, and traces of CO_2 were removed on passage through soda lime.

$FeCl_2$ (10.4 g) was added to give a 0.15M solution, and the pH was adjusted to 6.0 using an ammonia solution. HCl was produced throughout the oxidation, and the reaction mixture was maintained at pH 6.0 ± 0.2 by further addition of the ammonia solution using an automatic titrimeter. The O_2 was bubbled into the solution through a Pasteur pipette at a rate of 3-4 bubbles sec^{-1} (Figure 1).

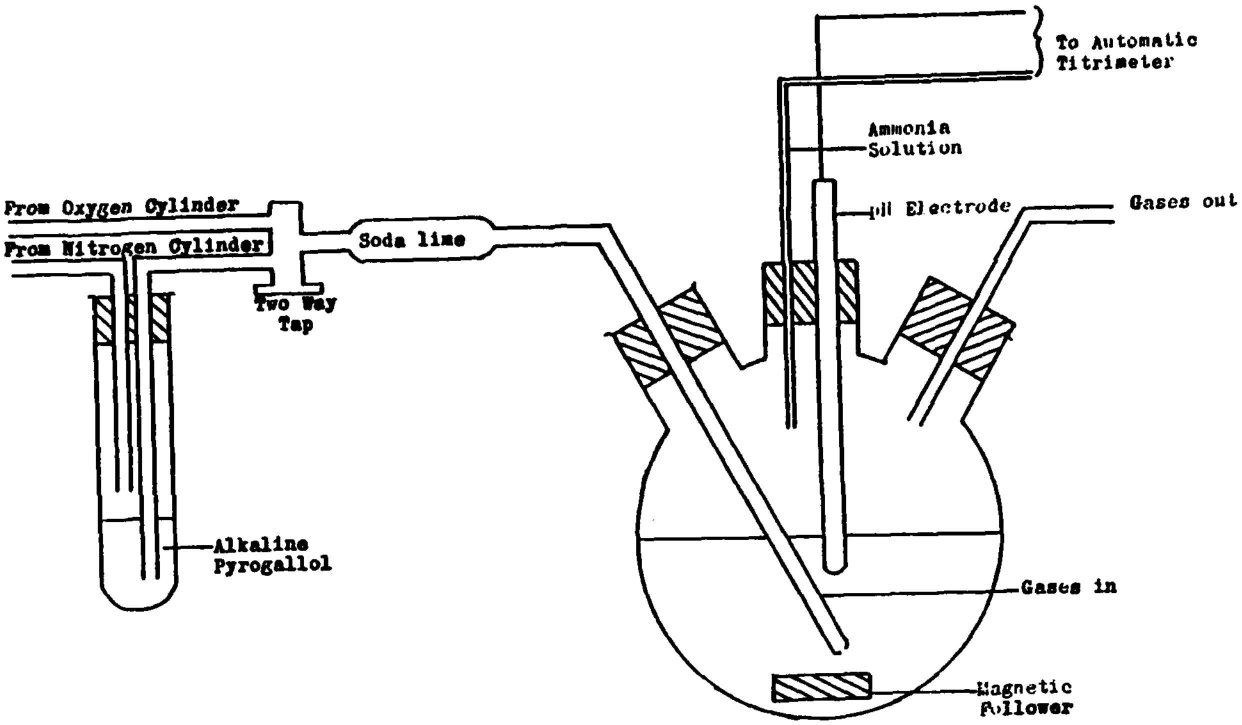


Figure 1. Apparatus for the synthesis of lepidocrocite

Initially a blue green precipitate was formed, but on further oxidation the yellowish brown final product was obtained. When oxidation was complete the precipitate was dialysed till the retentates were chloride free. The identity of the product was confirmed by comparison of the peak positions of the X-ray diffractogram with those of the standard in the A.S.T.M. Powder Diffraction File.

2.4 Aluminous Goethites

These were prepared by the methods described for lepidocrocite except that measured amounts of $AlCl_3$ were added to give solutions containing 5, 10, 15, 20, 25 and 30 mol per cent aluminium. The resulting solutions were treated as described for lepidocrocite. Characterization was by X-ray diffraction.

2.5 $Al(OH)_3$ Colloids-Iron Admixtures

Barnishel and Rich (1965) concluded that the nature of the aluminium hydroxide polymorph formed during a synthesis depends on the reaction conditions used. They found in general that gibbsite structures formed below pH 5.8 and that bayerite formed at higher pH values. They also found that the anion concentrations affected the rates of formation of the crystalline materials.

In an attempt to form aluminium hydroxide colloids with varying amounts of isomorphously substituted iron, three aqueous solutions, $AlCl_3$ (1M), $FeCl_3$ (1M), and $FeCl_2$ (1M) were prepared. The following mixtures were obtained using these solutions.

1. $AlCl_3$ (50 cm^3) + H_2O (150 cm^3);
2. $AlCl_3$ (45 cm^3) + $FeCl_3$ (5 cm^3) + H_2O (150 cm^3);
3. $AlCl_3$ (40 cm^3) + $FeCl_3$ (10 cm^3) + H_2O (150 cm^3);
4. $AlCl_3$ (40 cm^3) + $FeCl_2$ (10 cm^3) + H_2O (150 cm^3); and
5. $AlCl_3$ (45 cm^3) + $FeCl_2$ (5 cm^3) + H_2O (150 cm^3).

In all cases the pH values of the solution mixtures were adjusted to pH 5 by the addition of 1M NaOH, and the flasks were heated for 24 h at 60°C. At that time the pH had dropped to about 4 and sodium hydroxide solution was added to adjust the pH to 5. All flasks were maintained at pH 5 and at 60°C for three months. During this interval small samples of the precipitates were removed, dialysed, freeze dried, and subjected to X-ray analysis. These products were found to be amorphous in X-ray examination. Samples prepared using Fe(II) as the starting material were pale yellow (like goethite) in colour and those involving Fe(III) had a deep red-brown colour (like haematite).

$Al(OH)_3$ precipitates, formed by the addition of NaOH to 1M $AlCl_3$ solution, where the final pH was 6, when dialysed till chloride free, gave crystalline bayerite. When the mixture contained 5 and 10 mol % Fe(II) and was treated in the same way, an X-ray amorphous pale yellow product was obtained. The amount of iron in the sample from 5 mol % Fe(II) was determined as follows:

Reagents; 1% hydroquinone in water solution; 2,2'-bipyridyl (0.2 g in 10 cm^3 CH_3COOH, then diluted to 100 cm^3; 1M ammonium acetate; standard Fe(II) solution, 0.3511 g ammonium ferrous sulphate + 10 cm^3 H_2SO_4 (concentrated) diluted to 500 cm^3 with H_2O.

Procedure; 0.2838 g $Al/Fe(OH)_3$ product was dissolved in concd. HCl and diluted to 100 cm^3. To aliquots (1, 2, 3 to 10 cm^3) of stock solution were added 1 cm^3 of the hydraquinone solution, 2 cm^3 of the 2,2'-bipyridyl solution, and NH_4OH until the first trace of pink colour was obtained. Each sample was then made up to volume (100 cm^3) using the ammonium acetate solution. Absorbance values were measured at 522 nm, and the plot of Fe (mg dm^{-3}) versus absorbance was linear.

The composite formed from $Al(OH)_3$ + 5 mol % Fe(II) was found to contain 3.19% Fe by weight, and the Al to Fe ratio was 93.6:6.4.

When samples of this material in water were heated overnight at 190°C, and the resulting materials were examined by X-ray diffraction using CuK_α radiation, the peaks obtained corresponded to those for boehmite ($\gamma AlOOH$), and there were no peak shifts which might indicate isomorphous substitution with iron. When a sample was treated using a dithionite-citrate system buffered with sodium bicarbonate (Jackson and Mehra, 1960) to rmeove amorphous iron oxides, the resulting material was pure white, and had only traces of iron (bipyridyl test). The X-ray diffractogram of this material displayed large increases in peak intensities suggesting that the iron had been present as oxide impurities on the boehmite surface.

2.6 Hydroxy-Montmorillonite and Kaolinite Preparations

NaOH (0.105$\underline{M}$) solutions were added in 0.2 cm^3 increments, using a hypodermic syringe, to 0.5 per cent w/v or 1.0 per cent w/v of aluminium- or ferric-montmorillonite and kaolinite preparations. Base was added till the required pH values of 8.0 and 10.0 were reached. Suspensions were then left to equilibrate overnight while N_2 gas was bubbled slowly through.

2.7 Whole Soil

Sieved (3.38 mm) air-dried soil, 49.2% clay, 19.1% silt, 25.8% sand and 5.9% organic matter was used.

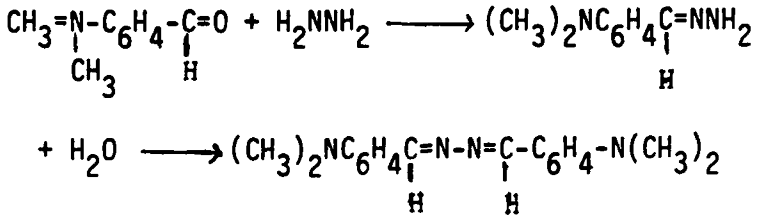
2.8 Hydrazine Compounds

Hydrazine hydrate ($N_2H_4.H_2O$) was purchased, pure, from Koch-Light Laboratories. Monomethylhydrazine CH_3NHNH_2 (98% purity) was purchased from the Aldrich Chemical Co. Ltd.

3. METHODS

3.1 Spectrophotometric Determination of Hydrazine and of Monomethylhydrazine

The method used a modification of that of Reynolds and Thomas (1965) in which p-dimethylaminobenzaldehyde was used to form a dimeric, coloured azine with the hydrazo group as follows:



$$CH_3{=}\underset{CH_3}{N}{-}C_6H_4{-}\underset{H}{C}{=}O + H_2NNH_2 \longrightarrow (CH_3)_2NC_6H_4\underset{H}{C}{=}NNH_2 \qquad (1)$$

$$+ H_2O \longrightarrow (CH_3)_2NC_6H_4\underset{H}{C}{=}N{-}N{=}\underset{H}{C}{-}C_6H_4{-}N(CH_3)_2$$

The modification used a 0.4% p-dimethylaminobenzaldehyde (DMBA) solution instead of the 4% solution used in the original procedure. The UV spectrum of the reaction solution showed that DMBA has a maximum absorbance at 398 nm and is larger than that of the coloured complex. This overshadowed the absorption at 470 nm of the DMBA-hydrazine complex. Hence the lower concentration DMBA solution (0.4%) was used. This modification caused a sharpening of the absorbance of the coloured complex and increased the overall sensitivity of the method.

A typical calibration curve for the determination of hydrazine was obtained as follows:

Hydrazine hydrate (25 µl) was injected into 5.0 cm^3 of deoxygenated distilled water in a glass vial with "sub-a-seal" stoppers. This solution (100 µl) was injected into 4.0 cm^3 of 8% w/v trichloroacetic acid solution (98% purity, from Fisons Scientific Apparatus). Aliquots of this solution in increments of 10 µl from 0 to 80 µl were placed in 5.0 cm^3 of 8% w/v TCA solution in a 10 cm^3 graduated flask. Aliquots (5.0 cm^3) of 0.4% w/v DMBA solution were then added to each of the flasks. At least 20 min was allowed for the colour to develop before measuring the absorbance at 470 nm. A calibration curve ranging from 0 to 10 µg of hydrazine was obtained. The addition of aqueous solutions to ethanoic solutions was volumetrically non additive, and so a different calibration curve was required for each experimental system.

A typical calibration curve for the determination of monomethylhydrazine (MMH) was obtained by injecting MMH (40 µl) into 10.0 cm^3 of deoxygenated water in a glass vial with "sub-a-seal" stoppers. An aliquot (100 µl) of this solution was then transferred into 3.0 cm^3 of the TCA (8% w/v) solution. Aliquots of this solution, in increments of 10 μl from 0 to 80 μl were placed in 10 cm^3 graduated flasks containing 5.0 cm^3 of the TCA (8% w/v) solution and 5.0 cm^3 aliquots of DMBA 0.4% w/v solution were then added to each of the flasks. At least one hour was allowed to lapse before absorbance was measured at 495 nm. A calibration curve was obtained covering the range from 0-10 μg MMH.

Determinations of hydrazine and of MMH in experimental samples used essentially the same procedures as described for the calibrations. Aliquots were adjusted such that the amounts of hydrazines assayed fell within the ranges of the calibration curves.

3.2 Degradations of Hydrazine and of Monomethylhydrazine (MMH)

3.2.1 In solution

Solutions of hydrazine or of MMH (5 cm^3), each of 10 and 7.0 meq dm^{-3}, respectively, were prepared in a 20 cm^3 glass vial with a "sub-a-seal" top, using distilled water as diluent. The concentrations of the hydrazine in solution were determined at hourly intervals beginning 15 minutes after the preparations were made.

3.2.2 In the presence of homoionically-exchanged clays

Suspensions of homoionically-exchanged clays (generally 0.5% w/v, and 5.0 cm^3 total volume), exchanged with Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, Mn^{2+}, and Cu^{2+} were contained in vials fitted with rubber seal tops and dispersed by ultrasonication (in a bath). Each suspension was dispersed using an ultrasonic bath, and hydrazine hydrate (2.5 μl) was injected into each of the bottles (equivalent to 1.6 mg, or 10.0 meq dm^{-3} of initial hydrazine concentration) and mixed on a vibrator. The concentration of hydrazine in the suspension and in the supernatant was determined after the mixture was centrifuged. The process was repeated at hourly intervals and then after 24 h.

To a suspension of Na^+-montmorillonite (0.5% w/v, 6.0 cm^3) MMH (1.3 μl equivalent to 1.8 mg or 7.0 meq dm^{-3} of initial MMH concentration) was injected and mixing was with a vibrator. The concentrations of MMH in the suspensions and supernatants were determined after fixed time intervals.

For determinations of hydrazines in the suspensions, aliquots of clay suspensions (1% w/v), but without hydrazines, were placed in the DMBA/TCA reagent to be used as blanks.

3.2.3 In the presence of the exchangeable cation as its chloride

The procedure described above was used except that instead of the clay, 320 ppm of the appropriate cation chloride solution was used. Changes with time in the concentrations of the hydrazines were determined.

3.3 Sorption/Desorption Studies

3.3.1 By the batch/slurry technique

Pure hydrazine solution (80 μl) was used to prepare 60 cm^3 of aqueous solutions of hydrazine at pH values of 4, 8, and 10. The desired pH was obtained after adjustments with 0.1M (for pH 8 or 10 solutions) or 1.0M (for pH 4 solutions) hydrochloric acid in 'sub-a-seal' stoppered glass vials. Deoxygenated distilled water was used and the vials were stoppered after flushing through with nitrogen. Fixed aliquots of the stock solution (in steps of 30 μl) were added to the stoppered vials of clay suspension. These were thoroughly mixed on a vortex stirrer, then equilibrated for 15 minutes, and centrifuged. The concentration of hydrazine in the supernatant in each vial was then determined.

Desorption isotherms. Successive volumes of supernatant were removed and replaced with deoxygenated distilled water at the pH of the clay suspensions. The suspensions were shaken up using a vibrator and centrifuged, and the supernatant concentration of hydrazine was then determined. Finally, as much supernatant as possible was removed by means of a syringe, and the same volume of deoxygenated distilled water was added. The contents were mixed with a vibrator and centrifuged. The amount of hydrazine in the supernatant was determined. Desorption was effected with 0.1M NaCl solution at the same pH as that of the centrifuged clay suspension, and by mixing and further centrifugation. The amount of hydrazine in the supernatant was determined. This process was repeated to check the total amount of sorbate desorbable by salt.

3.3.2 By the continuous flow stirred cell - automated colourimetric analysis technique (CFSC-ACA)

Examples of the application of the CFSC technique can be found for the adsorption of herbicides by soil colloids (Grice *et al*., 1973), the adsorption of poly(vinyl alcohol) by clay minerals (Burchill and Hayes, 1980) and the adsorption of heavy metals by humic materials (Hartmann, 1981). Hartmann (1981) has given a detailed account of the development of this technique from the basic concept of ultrafiltration. The theory behind the method has been described in some detail by Ryan and Hanna (1971), Smedley (1978), Hartmann (1981), Isaacson and Hayes (1984). Thus it suffices only to summarise the principles of CFSC, illustrating its potential in adsorption studies.

In the above applications of the CFSC technique, the determinations of the equilibrium concentrations were mostly carried out using collected fractions of the eluate. Scintillation techniques (Smedley, 1978), atomic absorption and radioisotopic labelling techniques (Hartmann, 1981), and refractive index measurements (Burchill and Hayes, 1980) are some of the common techniques used to measure the concentration of the adsorptive in the eluate fractions. Evaporation of solvent from the eluate samples has been one of the problems encountered where samples were collected. In this study, in particular, the determination of the hydrazine concentration at high pH values cannot allow the exposure of the droplets from the CFSC cell to the atmosphere because this would allow degradation of the hydrazine. This can be overcome by collecting the eluate under an atmosphere of nitrogen. However, in preference, a continuous method of determining the concentration of the eluate from the CFSC was developed and this eliminated the need for nitrogen enclosure and the problems of evaporation. The colourimetric method for determining hydrazine and monomethylhydrazine by Reynolds and Thomas (1965) was modified to suit the purposes of an automated system.

The continuous-flow system consists of a reservoir of the sorptive component in a solution of known concentration ($C_{\underline{i}}^{\mathrm{res}}$), connected to a cell of constant volume V (Figure 2). The cell contains a known mass of sorbent (m), retained in the cell by a membrane which is impermeable to the sorbent. The cell contents are continuously stirred, with the stirring device brought as close as possible to the membrane surface. Sorptive solution is introduced into the cell at a fixed rate; for every volume increment (δv) which enters the cell an equal volume must leave. The equilibrium solution concentration ($C_{\underline{i}}^{\ell}$) in the cell for each volume increment which enters it can only be determined with complete accuracy by taking samples from the cell, but this disturbs the system. This concentration can, however, be determined with sufficient accuracy by measuring the sorptive concentration in discrete fractions or in "plugs" of the cell eluate. The amount of $\underline{i}$ sorbed by the sorbent in the above system can be defined as the surface excess amount, ($n_{\underline{i}}^{s}$) which can be expressed as (IUPAC, 1972),

$$n_{\underline{i}}^{s} = n_{\underline{i}} - VC_{\underline{i}}^{l} \qquad (2)$$

where n_i is the total amount of component i in the cell.

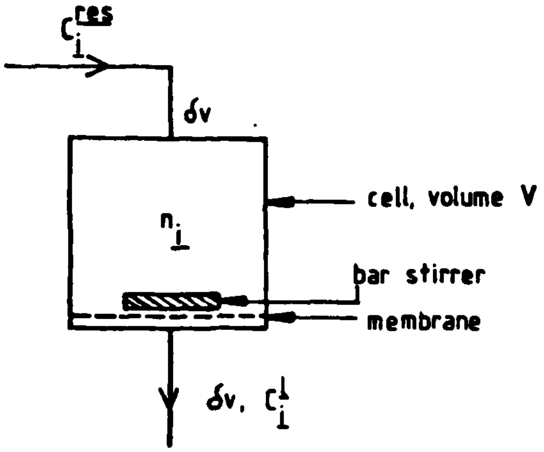


Figure 2. Schematic diagram showing the flow sequence of the sorptive i and the eluate out of the stirred cell

The total mass of sorptive in the whole system must be conserved. Hence, for a small value (dv) of reservoir solution introduced into the cell (and an equal volume eluted), the mass balance around the cell is given by

$$C_i^{res}dv - C_i^l dv = dn_i \tag{3}$$

The elution of the cell contents with a sorptive solution is known as a wash-in step, whilst elution with a desorbing solution is called a wash-out step. It is useful to consider first the sorptive concentration profiles to be expected on wash-in or wash-out in the case when no sorbent is present in the cell. The observed profiles in such cases will give ready indications of any interactions between the sorptive species and the ultrafiltration membrane employed.

Examination of the treatment by Isaacson and Hayes (1984) will show how the equations for wash-in and wash-out curves are obtained. Figure 3 shows typical wash-in and wash-out curves obtained when sorbent is absent (a and c) or present (b and d) in the cell. Curves a and c should follow the theoretical curves in each case. Failure to do this would mean that the sorptive is either adsorbed or rejected by the cell membrane.

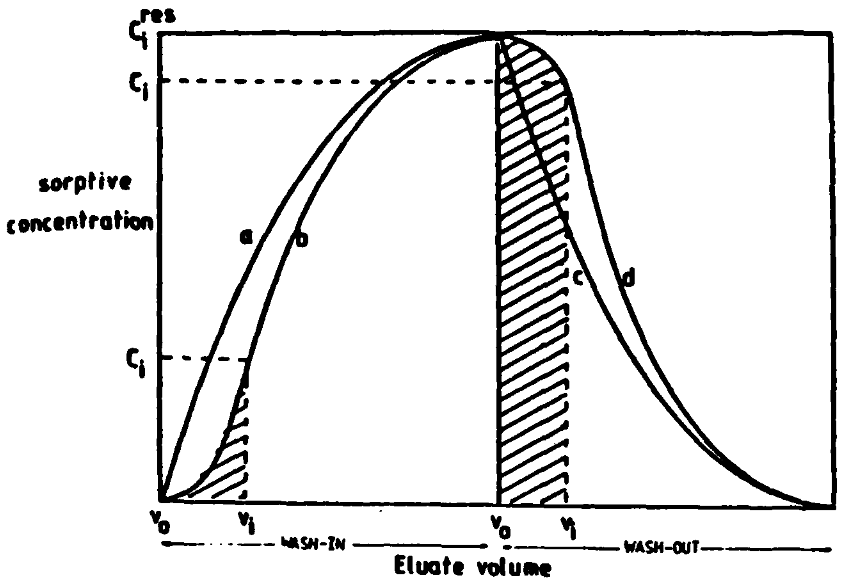


Figure 3. 'Wash-in' curve in the absence (a) and in the presence (b) of sorbent and the 'wash-out' curve in the absence (c) and presence (d) of sorbent

Isotherms for sorption or desorption of sorptive are readily obtained from plots of concentration vs. volume of eluate data, obtained when a sorbent suspension is contained in the continuous-flow cell. A typical wash-in curve obtained in the presence of sorbent is shown in Figure 3(b), where the sorptive concentration in the eluate is initially less than the no-sorbent case, and gradually approaches the latter as sorptive concentration approaches the reservoir concentration. It is assumed that the addition of sorbent causes a negligible change in the total volume (V) of the system. Equation (10) in Isaacson and Hayes (1984) states

$$n_{\underline{i}}^{s} = C_{\underline{i}}^{res}(v - v_0) - VC_{\underline{i}}^{l} - \int_{v_0}^{v} C_{\underline{i}}^{l} dv \qquad (4)$$

where v is the volume of solution from the reservoir entering the cell, v_0 is the voids volume, $C_{\underline{i}}^{res}$ is the concentration of i in the reservoir, and $C_{\underline{i}}^{l}$ is that of i in the eluate and V is the cell volume. The three terms on the right hand side of this equation can be easily calculated. The first term represents the amount of sorptive i that has entered the cell. The second term represents the amount of sorptive (at v = v) free in solution in the cell. The third term is the amount of sorptive which has been eluted from the cell, and this is equivalent to the shaded area under the experimental wash-in curve b in Figure 3.

A desorption isotherm is obtained when the reservoir solution is changed to one containing no sorptive. The mass balance around the cell for the elution of a small volume (dv) of the eluate is given by

$$dn_i^s = -V\,d\,C_i^l - C_i^l dv \qquad (5)$$

Integration of Equation (5) between the limits $n_i^s = n_i^{s(max)}$, $C_i^l = C_i^{max}$, $v = v_o$, and $n_i^s = n_i^s$, $C_i^l = C_i^l$, $v = v$ gives

$$n_i^s = (n_i^{s(max)} - VC_i^{max}) - VC_i^l - \int_{v_o}^{v} C_i^l dv \qquad (6)$$

The term in brackets on the right-hand side of Equation (6) is the total amount of sorbate and sorptive in the cell prior to elution with the desorbing solution. The second and third terms correspond to those in Equation (3), and the relevant amount of sorptive eluted from the cell is shown as the shaded area under curve d of Figure 3.

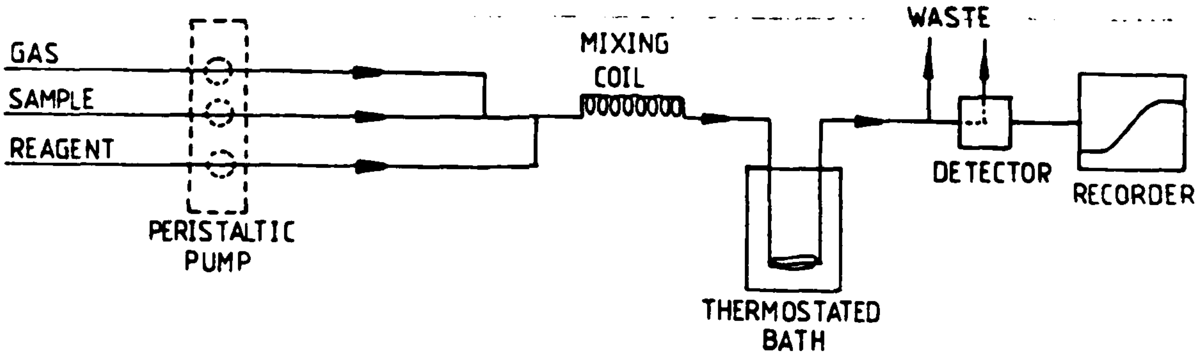


Figure 4. Schematic flow diagram of an Automated Colourimetric Analysis arrangement

Figure 4 illustrates the basic components of the automated colourimetric analysis system used. The principle of the method is as follows:

1. a continuously flowing stream of sample solution is segmented using a gas bubble (usually air or nitrogen). This process reduces laminar flow, and prevents interfacial mixing of one segment with the next;
2. local mixing of the sample and reagent within each segment is achieved as the "plugs" pass over each turn of a helical mixing coil with its

axis oriented horizontally. The contents of each liquid segment are thoroughly tumbled as it rises up on one side of the helix and descends upon the other side;

3. the reproducibility of the colour development and dtection, i.e. the colour of the complex, need not be developed to its maximum as long as the point at which the colour is measured is reproducible.

Dilution of the sample can also be achieved in the system by adding a diluent line. The diluent line is segmented instead of the sample and the latter is injected into the segments of diluent. These segments go through a mixing coil and are analysed by mixing with the reagent stream. If the segments are too large and intermixing occurs, the diluted stream can be debubbled and only a fraction of the diluted sample is used for subsequent analysis.

In order to achieve maximal colourimetric sensitivity, sharp and rapid responses of the detector to change with sample concentration as well as linearity of response with sample concentration are desired. Flow rates of the various streams can be readily selected so that they are in the optimum combination ot provide maximal colourimetric sensitivity. Also, an increase in the length of the light path allows for greater sensitivity, however, this usually affects the sharpness of response.

In the automated system for the CFSC technique, the eluate concentration was continuously changing. If the eluate stream is pictured as plugs of liquid, as the first plug of colour complex enters the flow through cell, the instantaneous response is an average of the total contents in the optical path length. Plug x_i gives an absorbance of a_i but its actual value is a_i' (Figure 5). As the next plug crosses the light path, the same averaging process occurs. Therefore, this process will affect the correlation between the concentration of a plug from the absorbance and the actual concentration of the sorptive solution in the CFSC. However, it does not significantly affect the actual adsorption isotherm as the sorptive concentration is calculated from differences in the absorbance. The change in concentration (δc_i) is gradual in the eluate stream and the transition time, t_t, is less than that in a calibration curve when concentration change is of a definite step change, i.e. as $\delta c_i^{\ell} \rightarrow 0$, $t_t \longrightarrow 0$.

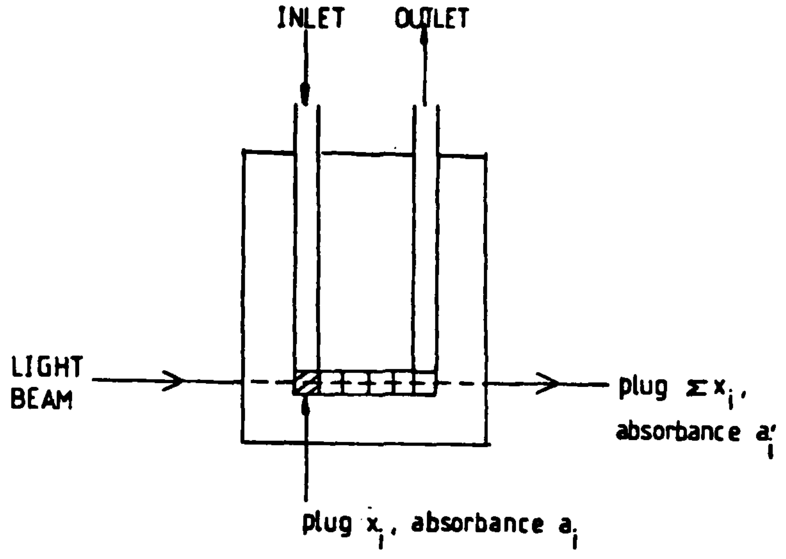


Figure 5. Plug flow of coloured complex in flow cell along the spectrophotometer light path

In the equations for the determination of the adsorption or desorption isotherms, void volume (v_0) data were considered. In this arrangement, void time (t_d and t_t) was considered instead.

A linear dependence of response upon concentration is desired in order to facilitate both the system calibration and the processing of the absorbance data by computer. Calibration using standards which cover the range of concentrations employed in an experiment is required to obtain the calibration factors, i.e. the slope and intercept of linear dependency.

The principal advantages of this automated continuous analysis over a manual method are:

1. the minimal handling of samples and reagents;
2. no evaporation effects as in the fraction collection method;
3. the continuous analysis of the eluate stream;
4. the short time required to determine the sorptive concentration.

Figure 6 provides an illustration of the stirred cell assembly and Figure 7 provides a schematic flow diagram of the combined continuous flow stirred cell automated colourimetric analysis arrangement.

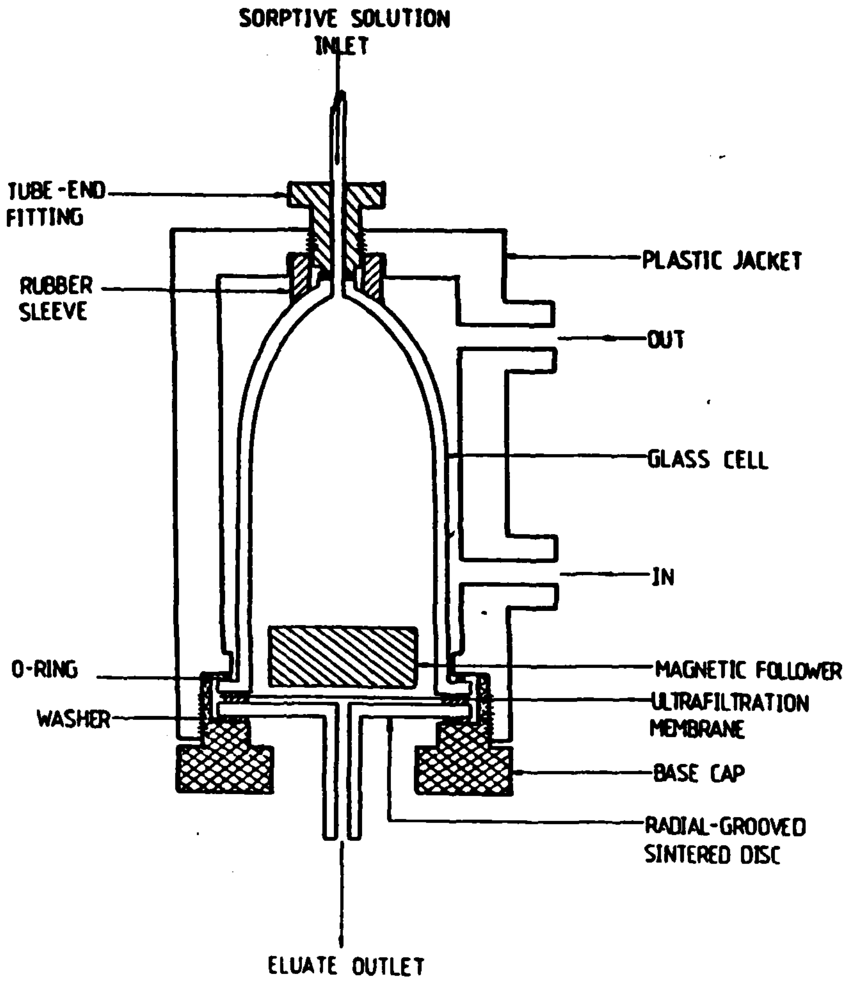


Figure 6. The ultrafiltration stirred cell assembly. The apparatus was laid flat, as indicated, when in use

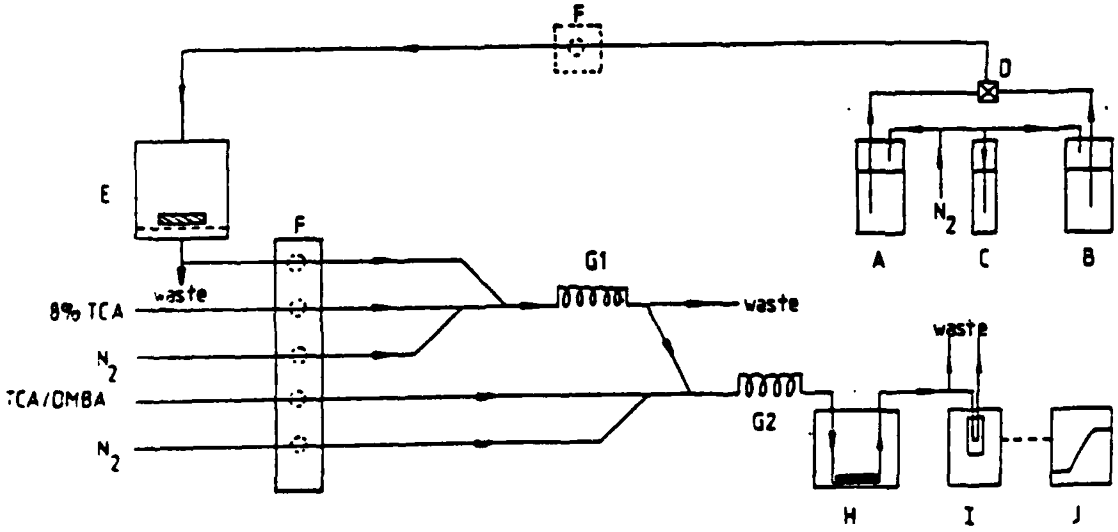


Figure 7. Schematic flow diagram showing the set-up of apparatus for the continuous flow stirred cell automated colourimetric analysis (CFSC-ACA). The lettered modes are described in the text

An Altex Derlin 4-way slider valve (D), with one port blanked off, allowed a switching from the adsorption mode to a desorption mode without introducing a break or air bubbles into the stirred cell (E). The eluate stream flowed out of the cell at the same rate as the inlet reservoir (A/B) stream. Part of the outlet stream was added into the nitrogen-segmented trichloroacetic acid diluent stream. The sample was mixed in the glass helix (G1) and debubbled. The debubbled stream was added to the nitrogen-segmented trichloroacetic acid and dimethylbenzaldehyde mixture reagent stream, and mixed (G2).

The coloured complex which developed was passed through a horizontal glass coil in the thermostated water bath (H) maintained at a temperature of 40 C ± 1 C. The segmented stream was debubbled before entering the flow-through cell in the spectrophotometer (I). A chart recorder (J), connected to the spectrophotometer, was used to give a continuous read out of absorbances of the eluate against time or volume of eluate.

The following describes the details of the major apparatus used in the arrangement.

Hydrazine was found to attack perspex. Therefore, a glass cell was used as the reaction vessel and this was housed inside a perspex jacket. Perspex cells were used by some workers (Hartmann, 1981 and Smedley, 1978) in the Group. A rubber sleeve was placed at the small opening at the glass cell, and an O-ring at the mouth. A 25 mm diameter radial grooved glass disc was seated into a plastic cap. The cap served as a support for the membrane (Sartorius PVC, 0.8 μm or Unipore Polycarbonate, 1.0 μm and 0.1 μm) which is held between rubber gaskets, which serve as a water seal. For the Unipore polycarbonate membranes, the smaller pore size membranes were placed near the glass disc and the larger pore size one was placed on top of it, in direct contact with the suspension. With this system, the adsorbent was held in the reaction vessel by the 1.0 μm membrane, and with its larger pore size, there was less danger of clogging. In the event of any smaller size clay colloid flowing through the membrane, the 0.1 μm membrane would serve to hold these back. This arrangement of the membranes has a greater resistance to tear against the knocking or rubbing of the stirrer in the reaction cell. The neck of the disc was in turn fitted into an 'Omnifit' connector with a PTFE tubing in a tube end fitting as the outlet. This was screwed tightly onto the top of the perspex jacket. Efficient mixing of the cell contents was achieved by a PTFE magnetic follower.

An Altex peristaltic pump with a fourteen channel manifold was used. An additional spring was placed on each side of the rocking platform to give a more regular pumping action especially when the manifold was almost fully loaded.

Various tubings used were obtained from L.K. Laboratory Supplies, U.K. The "accurate flow" manifold pump tubings were used for aqueous solutions. In the manual method of determination of hydrazine and monomethylhydrazine, the aliquot of sample was first added to 8% trichloroacetic acid (TCA) before the addition of the 0.4% DMBA in ethanol solution. However, pump tubings are easily attacked by organic solvents even using the silicon organic solvent-resistant tubings. Hence, a TCA/DMBA mixture of 7:3 proportion was used. Manual calibration curves for hydrazine and monomethylhydrazine obtained using this mixture were comparable to those obtained using the method of adding the reagents separately. Silicone tubing was used to transport this reagent.

In the development of this automated system, the optimum rate of flow of the diluent was 0.8 cm^3 min^{-1}. At the high concentration range, the reservoir concentrations of hydrazine and monomethylhydrazine were usually about 150 meq dm^{-3}. The minimum flow rate for the eluate and diluted eluate streams was 0.03 cm^3 min^{-1} even though there was a lower flow rate tubing of 0.015 cm^3 min^{-1} available. This type of tubing was not preferred because the narrow internal diameter often blocked after short periods of use. Thus, the need to increase dilution was limited by the optimal size and flow rate of the segments. A list of the pump tubings used is shown in Table 1.

Table 1. Manifold pump tubings used in the automated analysis

Stage	Stream	Colour Code	Flow Specification (cm^3 min^{-1})
Inlet to Stirred Cell	Reservoir Solutions	White-Orange	0.23
Outlet of Cell	Eluate	Orange-Red Orange-Blue	0.03 0.05
Dilution	8% TCA	Red	0.8
	Nitrogen	White	0.6
	Diluted Eluate	Orange-Blue Orange-Red	0.05 0.03
Colour Development	TCA/DMBA (7:3)	White (Silicon)	0.60
	Nitrogen	White	0.60
Output from Flow Cell	Waste Coloured Complex	Orange	0.42

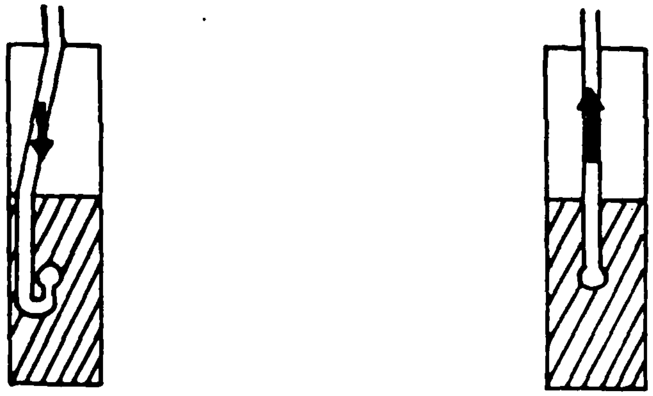
The flow rate of the waste line out of the flow-through cell was optimised in order to achieve a balance between fast flow through the cell and the avoidance of incorporating nitrogen bubbles in the light path.

PTFE tubings were used in connections where Omnifit tubing connectors (Biolab Ltd., Cambridge) were used, e.g. in lines into and out of CFSC.

Pump tubings were replaced regularly, depending on the frequency of their usage. When the arrangement was used daily, tubes had to be replaced every three weeks.

An MSE "Spectro Plus" spectrophotometer, with absorbance ranges of 0.1, 0.5 and 1.0, and output terminals to a "Servoscribe" chart recorder of variable range were used.

The dimensions of the ultra-micro continuous flow cell used are: height, 45 mm; width, 12.5 mm; light path, 10 mm; aperture, 3 mm; and chamber capacity, 0.08 cm^3. Figure 8 (a) and (b) show the construction of the flow cell with its inlet and outlet channels. The cell is placed on top of some rubber septa such that the aperture lies in the path of the light beam.



(a) (b)

Figure 8. Side-view of ultra-micro continuous flow cell

3.3.3 Procedure for sorption studies

Before each experiment, a calibration curve was determined with a range of standards which included the reservoir concentration. The flow rate into the cell and the void time were noted. The inlet line to the cell was fitted with the sorptive solution. The stirred cell was assembled and filled with the clay suspension (1% w/v) or with humic acid (1% w/v). PVC and Unipore Polycarbonate (Bio Rad Laboratories) of 1.0 and 0.1 μm pore sizes were used. A hypodermic syringe was used to transfer the suspensions into the assembled cell. Care was taken to remove any air bubbles by tapping the assembly gently.

The sorptive line was connected to the cell, plugs were removed, and the eluate line connected to the T-piece. The stirred cell assembly was placed horizontally, since this was found to prevent the clay and humic suspensions from blocking the membrane surfaces and clogging the pores. This orientation also minimised the contact between the magnetic follower and the membrane. Thus, a reduction of the incidence of membrane rupture was achieved. In selected experiments, fractions of the eluate were collected. These were used to determine pH and cation concentrations. In the cases of the humic acids the amounts of coloured materials lost were estimated by weighing the residues after evaporation and making corrections for chloride (Isaacson and Hayes, 1984).

The assembly was usually left to run till approximately four to six times the cell volume was eluted, or until a plateau was observed on the chart recorder. Care was taken to check sudden changes in response as small gas bubbles trapped in the light path caused changes in response with the recorder range. The slider valve was switched to the desorption solution, and the suspension was washed till a steady baseline was observed. After each experiment, distilled water was pumped through the entire system to flush the lines and the flow-through cell.

3.3.4 Examination of erros in the CFSC-ACA technique

The accurate estimation of sorption data from the sorption isotherms is dependent upon the erros involved in determining the parameters associated with the sorption equations. These are (a) the cell; (b) the void volume; (c) the eluate volume; (d) the mass of sorbent inside the stirred cell; and (e) the eluate concentration.

The first four parameters can be determined independently and are constant throughout a run. In the determination of these erros, particular attention was paid to effects which might be attributable to the ultrafiltration membranes and to make sure that errors were not caused by any properties involving the membranes.

(a) Determination of stirred cell volume. - The volume of the stirred cell can be determined by obtaining a wash-in and wash-out curve in the absence of sorbent material in the cell. For this the stirred cell is filled with water only. The eluate concentrations in the elution curve are then fed into a computer programme to calculate the cell volume. The cell volume was found to vary as a function of (i) changes in the reservoir concentration, (ii) repetitions of the experiment, and (iii) wash-in and wash-out curves. This is due to the fact that the cell volume was calculated from the reciprocal of the slope of a plot of the logarithm of a term involving reservoir concentration and eluate concentration against eluate volume. Thus, small changes in the slope cause significant differences in the estimates of the cell volumes. Table 2 below shows examples of some values of cell volume determined by wash-in and wash-out curves.

Table 2. Some values of cell volume used for sorption by clays as determined by wash-in and wash-out curves

Reservoir Concentration (meq dm^{-3})	Cell volume from Wash-in data (cm^3)	Cell volume from Wash-out data (cm^3)
10.21	6.1485	5.8849
10.21	6.4202	5.5599
9.78	7.1986	5.5899

A manual method of weighing the cell assembly when dried and full of water was preferred. This was repeated several times and the volume calculated was 5.98 ± 0.03 cm^{-3} for the cells used for sorption studies with clays. The volume of the cell used in humic acid studies was 13.59 cm^3.

(b) Determination of total void time. - To determine the total void time taken for the sensor to detect a response after connecting hte inlet hydrazine line to the cell was noted. This was compared with the time elapsed during calibration when the eluate line standard was introduced directly. The response time for the immediate detection of a change in concentration is the dead time. The variability of t_d was found to be 1%. The variability in the time required for the eluate to traverse the glass top and the short length of T-tubing connecting the stirred cell assembly to the eluate line is also about 1%.

In the case of the 5.98 cm^3 cell the transition time was found from the calibration curve to be an average of 3.8 minutes for the sensor to stabilise to a steady state from the immediate start of detection of the response, between a step change of 2.0 to 11.0 cm on the recorder scale. The variability of this term was found to be of the order of 0.9%. Hence, the total error in the determination of the void time or the start of an elution curve was within 1 to 2%. Subsequent absorbance readings were manually read off the elution curve at fixed time intervals after the void time.

(c) Measurement of eluate volume. - The measurement of eluate volume necessitated the determination of the flow rate of the solution into the cell. Absorbance readings were read off the curve corresponding to fixed time intervals and the eluate volume was calculated as the multiple of the flow rate and the time interval (usually taken as 5 minutes). The inlet flow rate was determined by weighing a definite volume of solution from the inlet stream into a weighed vial over a period of 5, 10 and 15 minutes. The variance in the flow rate was found to be 2%. This was checked against the outlet flow rate when the stirred cell contained only water and a clay suspension. The outlet flow rate was within the 2% variance of the inlet flow rate. A flow rate of about 0.23 cm^3 min^{-1} was employed for studies with clays and this gave a mean residence time for the sorptive in the cell of about 30 minutes. This was sufficient for equilibration as shown by the microcalorimetric studies. For studies with humic acids the flow rates ranged from 2.0 to 0.05 cm^3 min^{-1}, and the mean residence times were 7 to 270 min for the flow-rate range.

(d) Determination of the mass of sorbent in the stirred cell. - Errors accompanying the transfer of suspended materials to the stirred cell by a hypodermic syringe were minimised by shaking the suspension before and during transfer.

(e) Examination of the ultrafiltration membranes. - When estimating the different sources of errors, the reactivities of the membranes towards the sorptive molecules were examined. Reactivity of the membrane to certain sorptives was demonstrated by Hartmann (1981). In the determination of the stirred cell volume by running wash-in and wash-out curves without sorbent, the equilibrium sorptive concentrations in the experimental elution curves were comparable to the theoretical dilution curve. This behaviour was observed for PVC and polycarbonate membranes used. Thus, it was assumed that these membranes did not significantly interact with the sorptive molecules in the system.

Measurement of flow rates into and out of the stirred cell were comparable. In the membrane system used here, the inlet and outlet flow rates were measured at the beginning of a wash-in and at the end of a wash-out process, and the flow rates remained comparable to within 2% with and without sorbent suspensions in the stirred cells. Thus the membranes used caused no significant changes to the flow rate of the pump tubing throughout the experiments.

The clays and humic acids used were adequately held in the cell by these membranes. There was no evident loss of clay from the stirred cell, and small amounts of coloured materials, amounting to 2% of the total mass of humic adsorbents, were washed from the cells. These were washed in the water flush used before hydrazine was added to the system.

From the above, the membrane systems did not cause any significant errors to the determination of the amount of sorbate held.

3.4 Microcalorimetry Studies

An LKB 10700-2 Batch microcalorimeter was used. It consists of a rotatable calorimeter suspended in a thermostatic air bath and connected to an amplifier and chart recorder containing an integrator facility.

In order to investigate the interaction of homoionically-exchanged montmorillonite and humic acids with hydrazine, clay and humic acid suspensions were prepared such that the concentrations of sorbent in the microcalorimeter cells after mixing were the same as those used for the sorption studies. An aliquot (2.0 cm^3) of the suspension was transferred into the back compartment (the smaller of the two compartments) of the reaction cell. Hydrazine (4.0 cm^3 of appropriate concentration) solution was placed in the larger compartment. In the reference cell, 2.0 cm^3 of distilled water at the same pH as the adsorbent suspensions was transferred into the back compartment of the reaction cell and 4.0 cm^3 of the hydrazine solution was transferred into the front compartment. This was to compensate for any enthalpy changes due to neutralisation and dilution of the hydrazine solution. The heat of dilution of the adsorbent suspension was found to be negligible and therefore did not affect the determination.

The cell inlet ports were capped and the microcalorimeter was allowed to equilibrate until a steady baseline was obtained at the recorder (usually, the bath and cell contents attained a steady state after ca. 15 to 30 minutes). Temperature was adjusted by a thermostat control set at 28°C (±0.05°C). However, the actual temperature measured for each experiment could vary within 1.5°C of the set value. The appropriate response range was chosen (usually from 100 µV to 3 mV) depending on the sample. After a steady baseline was observed, the meter was set to zero point. Each run normally took 15 to 20 minutes.

For the experiments with the various homoionic-clays and metal chloride solutions, the drive motor that initiated mixing was also connected to a time switch. The time switch actuated the mixing unit drive motor at fixed intervals of 12 minutes. This process was used in order to examine if further reactions took place as a result of remixing the cell contents.

In order to detect the enthalpy of interaction in each experiment, the chart recorder was set at a particular voltage range. In the calibration run following each experiment, the same voltage range was employed, and a selected combination of calibration current and time of passage of this current was used to produce a response curve similar to that of the foregoing experiment. The heat evolved or absorbed per recorder unit was then calculated from the calibration curve.

The cell contents of the reaction vessel were removed by a syringe fitted with long hypodermic needles and the pH was measured. The cells were then cleaned by flushing with distilled water. The experiment was repeated interacting metal chloride solutions (960 ppm) with hydrazine (20 meq cm^{-3}), and separately with sodium hydroxide solutions of pH values of 12.

For studies of the heats of interactions of hydrazine, monomethylhydrazine with hydroxy-aluminium-montmorillonite, the 2% w/v clay suspensions of pH 8 were deoxygenated. Sorptive solutions of different concentrations were prepared and their concentrations determined prior to experimentation. The cells were flushed with nitrogen before the solutions (2.0 cm^3 each) were transferred into them. This served to reduce the decomposition of hydrazine due to the presence of oxygen in the solution or in the head space above the solutions. The distilled water at pH 8 in the reference cell was also prepared from deoxygenated water. Enthalpy changes caused by the dilution of the sorptive solution were therefore compensated. After the reaction had completed, the cell contents of the reaction vessel were removed to a plastic vial by means of a syringe with a hypodermic needle. The supernatant concentration of hydrazine was determined by the colourimetric method.

3.5 Determination of Exchangeable Aluminium in Aluminium-Exchanged Montmorillonite and Kaolinite Clays at pH 4 and pH 8

Two of possible mechanisms that contribute to the adsorption of hydrazine by aluminium-montmorillonite and -kaolinite preparations at pH 4 and pH 8 are:

(i) the exchange of hydrazinium ions for aluminium ions; and

(ii) the coordination of hydrazine to the aluminium ion.

The extent to which the ion-exchange mechanism (i) occurs during adsorption can be determined by examining the amount of aluminium exchanged on adsorption of hydrazine. The extent to which the coordination mechanism (ii) occurs can be determined by examining the amount of total hydrazine and aluminium desorbed by a 0.1M NaCl solution.

Prior to these determinations, the amounts of aluminium exchangeable under the pH conditions prevailing during adsorption (pH 4, 8 and 10), and under the conditions of desorption need to be determined. Al^{+++} ions are held by the clay with different tenacities under different pH conditions. Thus, firstly, the amounts of Al^{+++} in the supernatants of Al^{+++}-exchanged clay suspensions of pH values of 4, 8 and 10 were determined. Secondly, the amounts of Al^{+++} that can be desorbed by a 0.1M sodium chloride solution from the clays at the respective pH values were determined. Subsequent repeated desorptions by 1.0M sodium chloride solutions were carried out to determine the total amount of exchangeable aluminium. Lastly, 1.0M NaCl solutions in 0.1M HCl (acid) were used to extract the Al^{+++} ions that were fixed in the interlayers of the hydroxy-Al^{+++}-montmorillonite. The use of this strongly acidic NaCl solution also extracted aluminium from the clay structure, essentially 'dissolving' the clay. Hence, the total amount of Al^{+++} fixed in the Al^{+++}-clay suspensions under different pH conditions can be determined from these values.

Suspensions (7.0 cm^3 and 12.0 cm^3 of 2.0% w/v) of these aluminium-exchanged montmorillonite and kaolinite clays (pH 4.5) and hydroxy-aluminium-montmorillonite (pH 8.0 and 10.0) and kaolinite (pH 8.0) were prepared, respectively, in plastic vials. These were mixed thoroughly using a vortex stirrer, and then centrifuged. Suitable aliquots (200 μl and Al^{+++}-exchanged montmorillonite and 2.0 cm^3 for Al^{+++}-exchanged kaolinite) of the supernatant were used for the quantitative determination of aluminium. Sodium chloride was then added to the vials to give a final concentration of 0.1M NaCl solution. The vials were shaken, centrifuged and the amount of Al^{+++} in the supernatant was determined using the modified aluminon method (Hsu, 1963). Aliquots (4.0 cm^3) of the supernatant were removed from the vials and replaced by an equal volume of 1.0 M NaCl solution at the appropriate pH (4.0, 8.0 or 10.0). The vials were shaken, centrifuged, and each supernatant concentration of Al^{+++} was determined. This last step was repeated three times (or until Al^{+++} was undetected).

The supernatants were replaced by the same volume of 1.0M NaCl in 0.1M HCl acid and the supernatant concentrations of aluminium were determined. The use of an acid medium enables the exhaustive extraction of any aluminium that is fixed in the interlayers, and it causes the extraction of aluminium from the clay. This process was repeated four times for each sample (or until a negligible amount of Al^{+++} was detected in the supernatant in each case).

3.6 Determination of Aluminium Released during Adsorption and Desorption of Hydrazine by Al^{3+}-Montmorillonite (at pH 4.0 and 8.0), Hydroxy-Al^{3+}-Montmorillonite (pH 8.0) and Humic Acids (pH 4)

Two 2.0% w/v suspensions of aluminium-montmorillonite (samples A and B) and a 2.0% w/v suspension of hydroxy-Al^{3+}-montmorillonite (C) were prepared. The supernatant concentration of aluminium was determined for each sample. A suitable aliquot of hydrazine from prepared stocks at pH 4.0 and 8.0 was added to samples A and B, and of the pH 8.0 stock only to sample C. Each aliquot contained sufficient hydrazine to fully exchange the aluminium in the clay suspension, if this was possible. The supernatant concentrations of aluminium and hydrazine were again determined. Thus, any aluminium that was desorbed due to the adsorption of hydrazine on the clays should have increased the supernatant concentration of aluminium.

Supernatants of the samples were replaced by suitable aliquots of distilled water adjusted to the required pH. The supernatant concentration of aluminium was determined and then a definite weight of sodium chloride was added to each sample so that the concentration of salt in the suspension was 0.1M. The concentrations of aluminium and of hydrazine in the supernatants were determined.

Al^{3+} and Ca^{2+} in the equilibrium solutions of the hydrazine-humic acids systems were determined by atomic absorption.

3.7 Determinations of Cation-Exchange Capacity (CEC) Data Using the ^{22}Na Method

3.7.1 Determinations of CEC values of Al^{3+}-montmorillonite samples

Two 50 cm^3 aliquots of 1.0% w/v aluminium-exchanged montmorillonite suspension in plastic vials were centrifuged (using a MSE centrifuge), and the supernatants removed. Active 1.0M sodium chloride solution (5.0 cm^3) was added to each vial and the contents were vortex stirred, then centrifuged. The supernatant was removed and the process repeated three times. The clay was then washed three times with ethanol, to remove any excess active sodium chloride solution, and the vials were then placed under an infrared lamp. When the clay had dried, the vials were re-weighed. An average background radiation count was taken using an empty vial, and the radioactivity of the dried clay samples were measured. The average count was compared with the radioactivity of the 1.0M sodium chloride exchanging solution, to determine the exchange capacity of the clay. For example,

Average background count = x in T secs.
Average count for 1.0 cm^3 of active 1.0M NaCl solution = y in T secs.

Therefore, 1000 μeq of sodium, including ^{22}Na ions, in 1.0 cm^3 of solution gave y counts in T secs.

Average count for w g of dried clay = z

Therefore, exchange capacity of the clay $= \left(\frac{z-x}{y-x}\right) \times \frac{1000}{w}$

$= \mu$eq per g of clay

3.7.2 Determinations of CEC values of hydroxy-aluminium-montmorillonite preparations

^{22}Na-labelled hydroxy-aluminium-montmorillonite suspensions were centrifuged, then ethanol washed, before determining the radioactivity of the dried and weighed clay as before. Another two samples of this suspension were centrifuged and the supernatants of each were replaced by a solution of pH 8.0 hydrazine and monomethylhydrazine, respectively, and the contents were vortex stirred and centrifuged. The activity of the water washed and dried clays were also determined. By comparing the activities of the dried clay samples with that of a 1.0 cm^3 0.105M active sodium hydroxide solution, the amounts of sodium ions in these samples could be determined.

3.7.3 Determinations of exchange capacities of complexes of Al^{3+}-montmorillonites and of hydroxy-aluminium-montmorillonite hydrazines

One 5.0 cm^3 aliquot each of a 1.0% w/v suspension of aluminium- and of hydroxy-aluminium-montmorillonite was centrifuged, and the supernatant replaced by a hydrazine and a monomethylhydrazine solution, respectively, at pH 8.0. The suspensions were centrifuged and the supernatants replaced by 5.0 cm^3 aliquots of 0.01M active sodium chloride solution. The same process of washing, drying and weighing was also repeated using a 0.1M sodium chloride solution.

3.8 Investigations of Complexes Formed Between Hydrazines and Sorbent Species

3.8.1 X-Ray studies

X-ray diffraction analyses can be used to determine the approximate dimensions of the spaces occupied by intercalated molecules in the interlayers of montmorillonite, and the extents of hydroxy polymer formation in montmorillonite.

A Philips PW 1050/70 diffractometer was used employing CuK$_\alpha$ radiation ($\lambda = 1.541$ Å). The resolution slit was set at 0.2 mm and samples were scanned through 2θ from 3° to 30° at a rate of 1° min^{-1}. The output was recorded on a recorder as intensity vs. 2θ. The technique of sedimentation on a glass slide was used for sample preparation. The glass slides (3.5 x 2.5 cm and 2.0 x 2.5 cm) were covered with the sample. The uncovered section of the slide fitted into the clip holder of the sample chamber of the X-ray diffractometer.

Samples were prepared by the batch slurry technique. The clay suspension was sedimented on top of the glass slide at average area coverage of 3 mg cm^{-2}. Progressive analyses were carried out on the samples when paste-like, i.e. wet, after air-drying for 24 hours in an open-top dessicator, and after heating in the oven at 110°C for 4 hours. After heating, the slides were rapidly removed from the oven into a dessicator charged with phosphorous pentoxide, and X-ray analyses were carried out as soon as possible. The heated samples were placed in a dessicator over a dish of glycerol for 48 hours. This process was repeated using ethylene glycol. X-ray analyses were subsequently carried out. The samples analysed were:

(1), Al^{+++}-montmorillonite;

(2), Hydroxy-aluminium-montmorillonite of pH 8;

(3), Al^{+++}-montmorillonite interacted with hydrazine and monomethylhydrazine; and

(4), Hydroxy-aluminium-montmorillonite of pH 8 interacted with hydrazine and monomethylhydrazine.

3.8.2 Infra-red studies

Initial attempts to obtain infra-red spectra for the interacted complexes of hydrazines with clays and hydroxy-aluminium polymers were unsuccessful when samples were prepared in potassium bromide discs, because hydrazine absorptions were too weak. Sharper spectra were obtained by the use of self-supporting films prepared from clay suspensions. Infra-red studies were carried out on hydroxy-aluminium-montmorillonite preparations interacted with hydrazines from the aqueous and vapour phases.

Preparation of samples using uptake from the vapour phase. - Thin film samples of the pH 8 equilibrated hydroxy-aluminium-montmorillonite were made by using 20.0 cm^3 portions of 0.5% w/v suspensions. These suspensions, sufficient to give a 20 μm thick film, were poured, under suction, through a Sartorius SM 11318 0.01 μm cellulose nitrate membrane filter. The filters were then placed in an open oven to dry at low heat. When dry, a film of clay could be removed from the filter membrane. A piece of cardboard cut to shape was used to hold the film for the infra-red equipment (Perkin Elmer 180).

These films were then placed in separate desiccators above a dish of the liquid hydrazine or monomethylhydrazine, and were left standing overnight in a fume cupboard at a room temperature of 28°C. The films were placed in a dessicator until the time of analysis. After analysis, the sample was heated to 110°C for half an hour and then for two days. Subsequent heating for two hours each at 250°C and 350°C were carried out on the samples. After each heat treatment, infra-red spectra of the samples were recorded. All heating was carried out in a gas chromatographic oven in order to obtain precise temperature control.

Preparations using uptake from solution. - Aliquots (20.0 cm^3) of suspensions of equilibrated hydroxy-aluminium-montmorillonites were centrifuged at 8000 rpm for 10 minutes. Most of the supernatants were then removed from the samples with great care to avoid the loss of any material. Then 20.0 cm^3 aliquots of pH 8 hydrazine or monomethylhydrazine, each of 150 meq dm^3 concentration, were added to the samples, and the mixtures were thoroughly suspended and allowed to stand for fifteen minutes. These were centrifuged for the removal of the supernatant, and distilled water was added to remove excess hydrazine or monomethylhydrazine. The washing process was repeated thrice.

The washed suspensions of 20.0 cm^3 were used in the thin film preparations as described above. The above procedures were followed with an added step of washing with sodium chloride solution (0.1$\underline{M}$) for preparing the salt desorbed samples.

Preparations of hydrazine-humic complexes. - Infrared spectra of H^+-humic acid-hydrazine complexes (1-2 mg) made up in KBr discs (300 mg) were used.

3.8.3 Differential thermal analysis of hydrazines-Al^{3+}-montmorillonite complexes

A Stanton Redcroft 780 Simultaneous Thermal Analyser was used in this study. Alumina was used as a reference material. The same material and the amount was kept fixed throughout the study. A stream of dry nitrogen (flow rate ca. 60 cm^3 min^{-1}) was passed into the system to provide an inert atmosphere. The temperature programme was set to begin heating from 25°C to 800°C for the clay samples and from 25°C to 500°C for the hydrazine-clay complexes, at a rate of 10°C min^{-1}. After each sample was run the system was allowed to cool to room temperature before the following run was started. The chart recorder provided independent traces of temperature, weight, and the temperature differences between the two pans against time. Samples were run in duplicates.

In order to determine the heats of reaction of the hydrazines clay complexes, the system was calibrated using hydrated calcium sulphate ($CaSO_4.2H_2O$, A.R.) from 50 to 200°C, and silver nitrate ($AgNO_3$, A.R.) from 370 to 470°C. Definite weights (2, 5, 10 and 15 mg) of the standard materials were used, and the peak areas in each case were measured. A calibration curve of enthalpy against peak area was plotted.

The samples examined were:

(1) Al^{+++}-exchanged montmorillonite;
(2) Hydroxy-aluminium-montmorilloniate;
(3) Hydrazine (pH 8.0) and Al^{+++}-exchanged montmorillonite complex;
(4) Hydrazine (pH 8.0) and hydroxy-aluminium-montmorillonite complex;
(5) Monomethylhydrazine (pH 8.0) and Al^{+++}-exchanged montmorillonite complex; and
(6) Monomethylhydrazine (pH 8.0) and hydroxy-aluminium-montmorillonite complex.

3.9 Experimental Procedure for Vapour Phase Adsorption Studies

A modified McBain-Baker type apparatus was used to measure gravimetrically the quantity of gas adsorbed, using a helical silica spring. The apparatus used is shown schematically in Figure 9. The taps 1-4 were made of teflon, as supplied by Youngs Scientific, Acton, London. The joints in the system were made using O ring seals, and the system was pumped using a mercury diffusion pump, backed by an oil pump.

The helical silica spring was calibrated by measuring its extension for a series of weights. These weights were lengths of platinum wire which had been accurately weighed to 0.00001 g on a microbalance. The calibration points were fitted to a straight line, using a least squares linear regression analysis. The glass sample bucket was supported on a half pound breaking strain fishing line (Bayer, London).

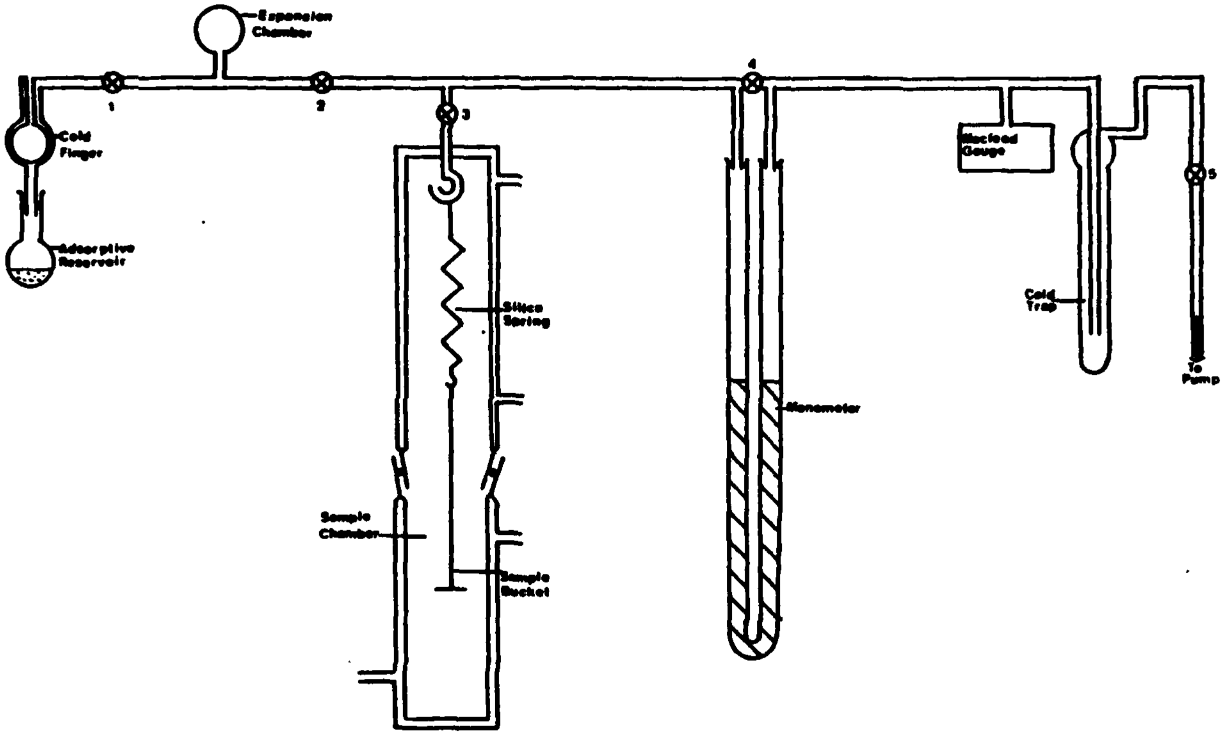


Figure 9. A schematic representation of the apparatus used to study adsorption from the vapour phase

At the beginning of each experiment the sample, which was placed in the sample bucket (Figure 9), was degassed by evacuating the system with all the taps except tap 1 open. Taps 2 and 4 were then closed, then tap 1 was opened to allow a very small quantity of the previously degassed adsorptive to enter the expansion chamber. Tap 1 was then shut and some of the gas from the expansion chamber was allowed into the system by opening tap 2. After the system had reached equilibrium, i.e. when no further weight change was observed in the sample, the gas pressure in the system was measured on the manometer, and the extension of the spring was noted. The pressure of the system was incremented in this fashion until the saturated vapour pressure of the sorptive was reached. All measurements were made using a cathetometer, to an accuracy of ±0.1 mm.

The apparatus was contained in a thermostatted fume cupboard, the temperature of which could be maintained to ±1.0°C. The sample itself was surrounded by a water jacket which could be maintained to ±0.02°C.

The desorption of the gas from the system was achieved by freezing the adsorptive in the reservoir using liquid air and adding liquid air to a cold finger. Tap 2 was closed and tap 1 opened, allowing the sorptive to condense on the cold finger. Tap 1 was then shut and tap 2 opened, the process was repeated until the required pressure was achieved, then the system was left to equilibrate.

The sample bucket was constructed in glass since this proved resistant to the chemicals used. The sample holders weighed about 50 mg which allowed a total weight of 50 mg of sample plus sorbate to be used, whilst still remaining within the 'Hookes Law' limit of the spring. During the experiments the samples were allowed to equilibrate for 1 hour, although no further weight changes could be detected after 20 minutes.

There was some movement of mercury vapour in the system from exposed mercury surface in the manometer, but no mercury appeared to condense in the sample chamber on the spring.

4. RESULTS AND DISCUSSION

4.1 Studies of Degradation of Aqueous Solutions of Hydrazine and of Monomethylhydrazine in the Presence and in the Absence of some Homoionically Exchanged Montmorillonites

Figure 10 shows the autoxidative degradation of hydrazine with respect to time in a 320 ppm solution at pH 12 (i), and of monomethylhydrazine in a 310 ppm solution at pH 9 (ii). The hydrazines in solution underwent an initial oxidation by the oxygen dissolved in solution; thereafter the concentrations of the hydrazine and of monomethylhydrazine remained constant. In the absence of clay, the concentration of hydrazine and of monomethylhydrazine which persisted in solution was about 90 and 85%, respectively, of that in the starting solution.

In the presence of a clay suspension, part of the original hydrazine and monomethylhydrazine added to the suspension was adsrobed by the homoionically-exchanged montmorillonite and part of the hydrazines were oxidised. The adsorption of the hydrazine and monomethylhydrazine by the clays was shown to be a rapid process in the microcalorimetric studies

Table 3. Extents of degradation and adsorption of hydrazines in the presence of 1% w/v suspensions of homoionic-montmorillonite at different pH values

Cation neutralising charge on clay	pH of suspension		% of unadsorbed hydrazine degraded after		Amount of sorbate held per g of clay
	Before	After	3 h	24 h	(ueq g^{-1})
Addition of hydrazine:					
K^+	6.4	9.6	30 ± 5%	40 ± 5%	-
Na^+	5.6	9.9	"	"	100
Ca^{++}	7.2	9.2	"	"	90
Mg^{++}	6.5	9.5	"	"	83
Cu^{++}	4.9	5.2	> 95%	> 95%	243
Mn^{++}	5.6	9.6	30 ± 5%	60 ± 5%	113
Al^{+++}	3.6	7.6	"	30 ± 5%	738
Fe^{+++}	2.8	7.6	"	50 ± 5%	819
Addition of monomethylhydrazine:					
Na^+	5.6	8.8	30 ± 5%	-	81

Table 4. Extents of degradation of hydrazine in the presence of metal chloride solutions (320 ppm of M^{n+}) at different pH values

Cation of metal chloride solution	pH of solution		% of total amount of hydrazine added degraded after	
	Before	After	3 h	24 h
Addition of hydrazine:				
K^+	5.4	8.4	⩽ 10	⩽ 10
Na^+	5.7	8.5	⩽ 10	⩽ 10
Ca^{++}	5.5	8.1	⩽ 10	20
Mg^{++}	5.2	8.4	⩽ 10	20
Cu^{++}	4.8	4.3	50	> 95
Mn^{++}	5.8	8.3	⩽ 10	75
Al^{+++}	3.6	3.6	⩽ 5	⩽ 5
Fe^{+++}	2.2	2.2	⩽ 5	20

which follow (Section 4.2). The amount of hydrazines adsorbed per gram of the dry cation-exchanged montmorillonite was estimated by the difference in the amount of hydrazine found in the suspension and in the supernatant as in curves (ii) and (iii), respectively, of Figures 10 a to h.
The extent of degradation of the unadsorbed hydrazine is calculated as follows:

$$\begin{array}{c}\text{Extent of degradation}\\ \text{of hydrazine in the}\\ \text{presence of a clay}\\ \text{suspension (1\% w/v)}\end{array} = \frac{\begin{array}{c}\text{Amount of hydrazine in the supernatant}\\ \text{after an interval of reaction}\end{array}}{\left[\begin{array}{c}\text{Amount of hydrazine}\\ \text{added at the start}\end{array}\right] - \left[\begin{array}{c}\text{Amount of hydrazine}\\ \text{adsorbed}\end{array}\right]}$$

The degradation of monomethylhydrazine in the presence of Na^{+}-exchanged montmorillonite (1% w/v suspension) is shown in Figure 10 (iii). After the first hour of reaction, the concentration of monomethylhydrazine in the suspension remained constant and the pH of the suspension was 8.8. The amount of monomethylhydrazine adsorbed per gram of Na^{+}-exchanged montmorillonite was only 81 μeq. The concentration of monomethylhydrazine that persisted in the solution had decreased to 65% of the starting solution after about 90 minutes. The pH of this suspension was similar to that of the solution in the absence of the clay (pH 9). The degradation of the monomethylhydrazine was apparently enhanced in the presence of the clay suspension.

Figures 10 a to h show the degradation of hydrazine with respect to time in the presence of various homoionically-exchanged montmorillonite preparations (curves ii and iii) and the respective metal chloride solutions (i). Table 3 shows the extent of the degradation of the hydrazine in the presence of the 1% w/v clay suspensions at different pH values. After the addition of 1600 μg of hydrazine hydrate to the 5.0 cm^{3} of the suspensions, the pH values of K^{+}-, Ne^{+}-, Ca^{++}-, Mg^{++}-, and Mn^{++}-exchanged montmorillonite preparations increased from 6.4, 5.6, 7.2, 6.5 and 4.8 to 9.6, 9.9, 9.2, 9.5, and 9.6, respectively. After three hours of interaction, the proportion of the total unadsorbed hydrazine that had degraded in solution was 30-35% (Figures 10 a to e (iii)). After 24 hours of interaction, only a small additional decrease in hydrazine concentration in the solutions was observed. Hence, additional degradation of hydrazine in the supernatant of the monovalent- and divalent-exchanged clay suspensions occurred slowly and to a small extent (less than 10% of the total unadsorbed hydrazine). However,

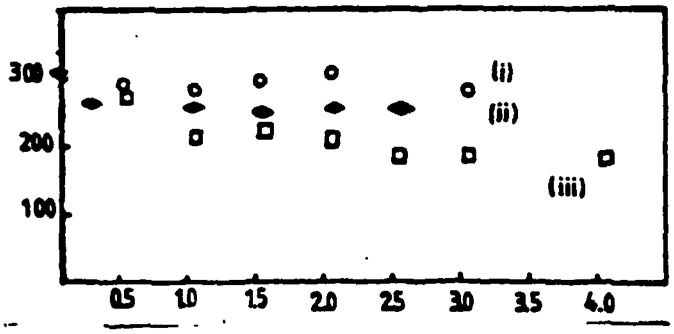


Figure 10. Degradation of hydrazine in solution at pH 12 (i), of monomethylhydrazine (MMH) in solution at pH 9.0 (ii), and of MMH in solution in the presence of 1% Na$^+$-montmorillonite

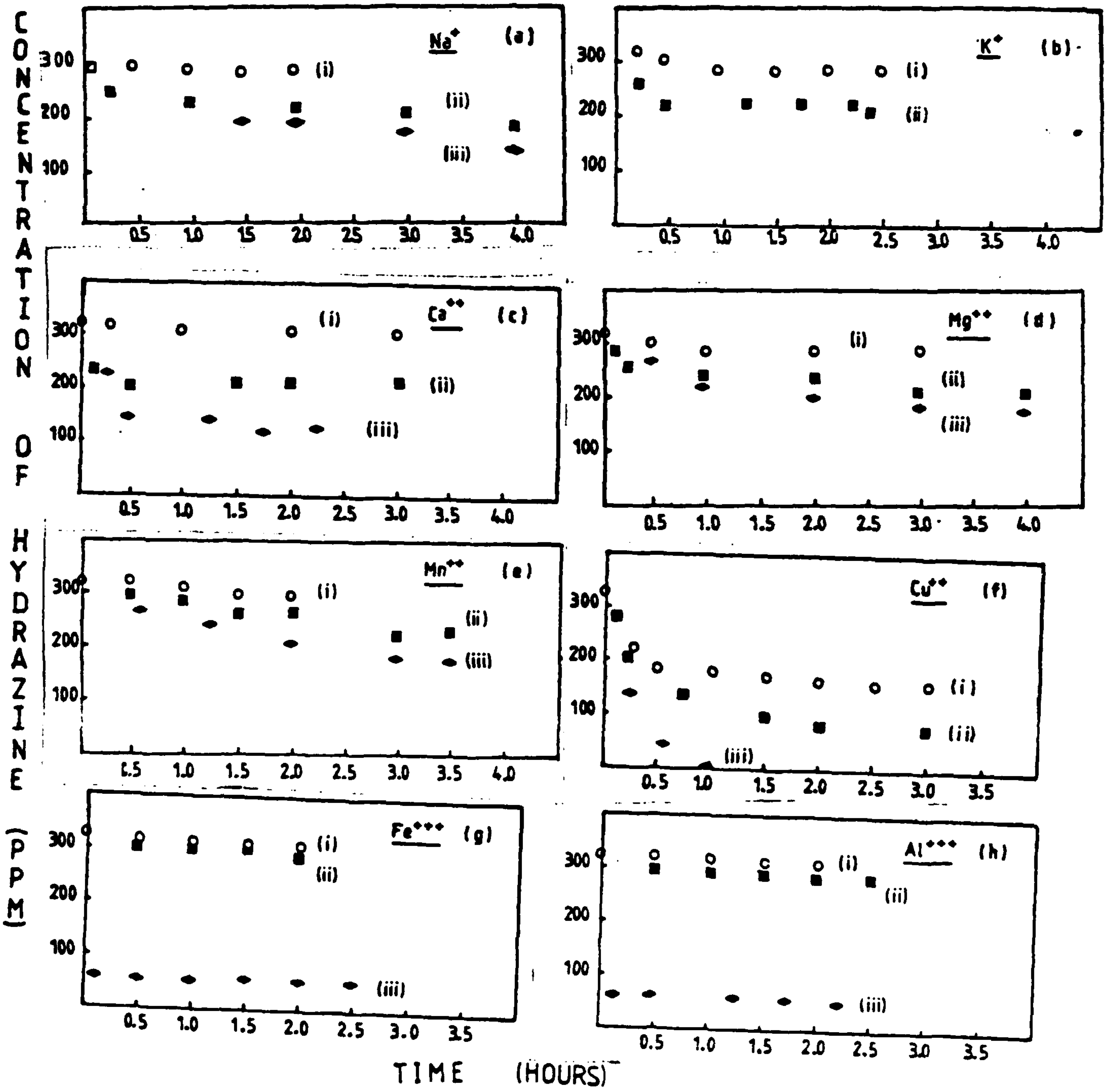


Figure 10 (continued). Degradation of hydrazine in Na$^+$ (a), K$^+$ (b), Ca^{2+} (c), Mg^{2+} (d), Mn^{2+} (e), Cu^{2+} (f), Fe^{3+} (g), Al^{3+} (h) chloride solutions (320 ppm of metal ion) in water (i), and in aqueous suspensions (1% w/v) of the cation-exchanged montmorillonite (ii), and (iii) in the supernatants from (ii).

in the Mn^{++}-exchanged system, the concentration of hydrazine which persisted in the supernatant after 24 hours was 40% of that of the starting solution.

When the clay suspensions had high pH values ranging from 9.2 to 9.9, the amount of hydrazine adsorbed by these monovalent- and divalent-exchanged clays was small. For K^{+}-montmorillonite, no detectable different in the hydrazine for Na^{+}-, Ca^{++}-, Mg^{++}- and Mn^{++}-montmorillonite, the adsorption was 100, 90, 83 and 113 eq of hydrazine g^{-1} of dry clay, respectively.

The pH of the trivalent Al^{+++}- and Fe^{+++}-exchanged montmorillonite suspensions was 7.6 after the addition of the hydrazine hydrate. The adsorption of hydrazine by these two clays was high compared to the other cation-exchanged clays. The adsorption was 738 and 819 μeq g^{-1} for the Al^{+++}- and Fe^{+++}-exchanged clays, respectively. After 3 hours of reaction, the amount of hydrazine in solution degraded to about 70% of the original hydrazine concentration in the supernatant.

The pH of the divalent Cu^{++}-exchanged montmorillonite suspension remained almost unchanged after the addition of the hydrazine hydrate at pH 5.2 (initial pH was 4.9). Vigorous effervescence was observed on addition of the hydrazine hydrate and the hydrazine in the supernatant was almost completely degraded (<1% remained) after an hour. The hydrazine that was adsorbed by the montmorillonite did not degrade further, as indicated by the fact that the hydrazine concentration remained constant in the suspension, as seen in curve (ii) of Figure 10 f.

Table 4 shows the extent of degradation of the hdyrazine in the presence of 320 ppm of cations in metal chloride solutions at different pH values. Each of the 5.0 cm^{3} metal chloride solutions had the same or larger amounts of metal ions than were present in the 5.0 cm^{3} of the 1% clay suspensions. After the addition of the hydrazine hydrate to the suspensions, the pH values of the K^{+}-, Na^{+}-, Ca^{++}-, Mg^{++}-, and Mn^{++}-chloride solutions increased from 5.4, 5.7, 5.5, 5.2 and 5.8 to 8.4, 8.5, 8.1, 8.4 and 8.3, respectively. The hydrazine in the solutions degraded to a small extent after three hours of reaction; the amount of hydrazine that degraded in the solutions was about 10% of that in the starting solutions (Figures 10 a to e (i)). The pH values of these metal chloride solutions were about one pH unit lower than those of the corresponding cation-exchanged montmorillonite. The degradation of the hydrazine was apparently much enhanced in the presence of the clay as the concentration of hydrazine that degraded in the solution was about 30 to 40% of that of the starting solution. After 24 hours of reaction, a significant additional amount of hydrazine was degraded in the manganous chloride solution since only 25% of the hydrazine concentration in the starting solution remained. Degradation of hydrazine in this solution also produced a light white gelatinous precipitate which rapidly darkened.

Both the pH values of the aluminium and ferric chloride solutions remained unchanged after the addition of the hydrazine hydrate (3.6 and 2.2, respectively). At this very low pH range, the hydrazine did not degrade and the hydrazine concentrations in the solutions remained constant (Figure 10 g and h (i)). An additional amount of hydrazine was apparently degraded in the ferric chloride solution after 24 hours and a gelatinous brown precipitate was formed in the solution.

This was not observed in the aluminium chloride solution and the hydrazine concentration remained constant even after 24 hours.

During the degradation of hydrazine in the cupric chloride solution, very vigorous effervescence was observed, and a grey precipitate was formed. However, the supernatant concentration of hydrazine remained apparently constant after 30 minutes of reaction (Figure 10 f (i)). Only 50% of the original amount of hydrazine in the solution remained. However, after 24 hours, the hydrazine in the solution had completely degraded.

4.1.1 Microcalorimetric studies of the interaction of hydrazine with homoionically-exchanged montmorillonite

The enthalpies of the interaction of hydrazine with preparations of montmorillonite that were homoionically-exchanged with ions of different valence are given in Table 5. The initial mixing of the hydrazine with the Na^+- and K^+-montmorillonite preparations produced enthalpies of 12.77 and 11.90 J g^{-1}, respectively. Subsequent mixings of the suspensions after twelve-minute intervals gave comparable responses with enthalpies of the order of 0.9 and 2.03 J g^{-1}, respectively. Mixing with Mg^{++}- and Ca^{++}-montmorillonite preparations produced a broad trace for the heat of reaction but the enthalpies of 3.12 and 4.83 J g^{-1}, respectively, were smaller than for the monovalent cations. The responses decreased for each subsequent mixing at twelve-minute intervals.

The interaction of hydrazine with Cu^{++}-montmorillonite was highly exothermic and produced an enthalpy of 86.3 J g^{-1}. Subsequent mixing produced peaks of rapidly decreasing energy outputs; after an overnight cycle of mixing repeated at twelve-minute intervals, the trace returned to baseline. Interaction with Mn^{++}-montmorillonite was less energetic, with an energy output of 9.73 J g^{-1}, and the subsequent mixing also produced peaks of decreasing energy, but these decreases were less than those for Cu^{++} system. The interaction with Al^{+++}-montmorillonite gave a sharp single response on initial mixing which peaked one minute after mixing and lasted only six minutes. Subsequent cycles did not provide additional outputs of energy.

Table 5. Enthalpies of the interactions of 10 meq dm^{-3} hydrazine with 1% w/v homoionic-montmorillonite at 28 ± 0.05°C

Type of homoionic-montmorillonite	pH of suspension <u>before</u> & <u>after</u> hydrazine interaction		Number of mixing	Enthalpy evolved per g of sorbent (J g^{-1} or J meq^{-1} cation)
K^+	5.3	8.5	1	11.90
			2	0.85
			3	0.95
Na^+	5.3	9.9	1	12.80
			2	2.06
			3	2.00
Mg^{++}	6.5	9.5	1	3.12
			2	1.01
			3	0.65
Ca^{++}	7.4	9.2	1	4.83
			2	1.85
			3	1.07
Cu^{++}	4.5	5.2	1	86.30
			2	23.30
			3	9.71
			4	5.99
			5	3.93
			6	2.00
Mn^{++}	6.1	9.6	1	9.73
			2	4.23
			3	3.88
Al^{+++}	3.6	6.8	1	11.70
Fe^{+++}	2.8	6.4	1	31.70
			2	5.20
			3	4.33

Table 6. Enthalpies of interactions of 10 meq dm^{-3} hydrazine with 320 ppm metal chloride solutions at 29 ± 0.05°C

Type of metal chloride solution	pH of suspension before & after hydrazine interaction		Number of mixing	Enthalpy evolved per meq of metal cation ($J\ meq^{-1}$)
K^+	5.8	8.6	-	N. D.*
Na^+	6.7	8.9	-	1.42
Mg^{++}	5.8	9.6	-	0.40
Ca^{++}	5.5	9.5	-	0.58
Cu^{++}	4.5	4.9	1	103.0
			2	16.68
			3	9.60
			4	8.96
			5	5.98
Mn^{++}	6.3	8.1	1	13.40
			2	8.46
			3	7.54
			4	4.50
			5	2.96
Al^{+++}	3.9	4.1	-	10.62
Fe^{+++}	2.5	2.8	-	69.00

Table 7. Enthalpies of interactions of sodium hydroxide solution (pH = 12.0) with 320 ppm metal chloride solutions at 28 ± 0.05°C

Type of metal chloride solution	pH of suspension before & after hydrazine interaction		Enthalpy evolved per meq of metal cation ($J\ meq^{-1}$)
Mn^{++}	6.3	6.8	13.00
Cu^{++}	4.9	5.5	33.48
Al^{+++}	3.9	4.2	6.67
Fe^{+++}	2.[illegible]	2.9	50.01

*[illegible]

The mixing of hydrazine with Fe^{3+}-clay produced a very sharp response like that of Al^{3+}-clay. The response was highly exothermic producing an enthalpy of 31.7 $J\ g^{-1}$. Subsequent mixing produced peaks with decreasing energy outputs. In all cases, the response was rapid on mixing, and in general the initial rise had peaked after five minutes, and after twenty minutes the trace had returned to baseline. These observations indicate that in all cases the interactions of hydrazine with the homoionic-montmorillonite preparations were rapid and equilibrium was attained in short periods of time.

The microcalorimetry of the interactions of hydrazine with the metal chloride solutions of Na^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Mn^{2+}, Al^{3+} and Fe^{3+} ions were also investigated. The results expressed as Joules per meq of metal ion are tabulated in Table 6. The interactions of hydrazine with the Na^+, Mg^{2+}, Ca^{2+}, Al^{3+} and Fe^{3+} salts gave a single exothermic peak and did not provide any additional peaks on subsequent mixing. In the cases of Cu^{2+}- and Mn^{2+}-chloride solutions, outputs of rapidly decreasing energies were produced on repeated mixing. The interaction with $CuCl_2$ was again highly exothermic (103 $J\ meq^{-1}$) and the values decreased in order for the various salts as follows: $FeCl_3$ (69.0 $J\ meq^{-1}$), $MnCl_2$ (13.4 $J\ meq^{-1}$), $AlCl_3$ (10.6 $J\ meq^{-1}$), and outputs for NaCl, $MgCl_2$ and $CaCl_2$ were very small.

The four metal cations which interacted most energetically with hydrazine were reacted with a sodium hydroxide solution (pH 12.0). The exothermic responses observed were in decreasing order as follows: Fe^{3+} (50.01 $J\ meq^{-1}$) > Cu^{2+} (33.48 $J\ meq^{-1}$) > Mn^{2+} (13.0 $J\ meq^{-1}$) > Al^{3+} (8.67 $J\ meq^{-1}$). The enthalpies involving the Fe^{3+}, Mn^{2+} and Al^{3+} ions were very similar to those of the cations with hydrazine. Subsequent mixing of these solutions did not provide any additional responses.

4.2 Summary of Results and Discussion of Degradations of Hydrazine and of Monomethylhydrazine in the Presence of Homoionically-Exchanged Montmorillonite

The factors that affect the interactions of hydrazine with the different homoionically-exchanged montmorillonite clay preparations were identified by examining the results obtained in the degradation and microcalorimetric investigations of the interactions of hydrazine with:

(a) aqueous suspensions of different homoionically-exchanged montmorillonite; and

(b) the corresponding metal chloride solutions containing equivalent amounts of metal cations.

4.2.1 Autoxidative degradation of hydrazine and monomethylhydrazine in aqueous solutions

In the autoxidative degradation of hydrazine and monomethylhydrazine in aqueous solutions, the initial concentration of hydrazine was 10 meq dm^{-3}, or 10^{-2}M, and the pH of the solutions were 12 and 9, respectively. The average oxygen content for a solution in equilibrium with air at 20 to 25°C is in the rnage of 2.7×10^{-4}M (Russell, 1973). Therefore, the concentration of hydrazines were about 100-fold in excess of the concentration of oxygen in the solutions. The concentration of both hydrazine and monomethylhydrazine decreased by about 2×10^{-3}M as they were oxidised by oxygen dissolved in the solutions. Thus, both hydrazine and monomethylhydrazine were unstable in the presence of air under conditions of high pH.

In the absence of oxygen, and with the pH value of the solution at 4, no degradation was observed in the solution. Therefore, under these conditions, the concentrations of hydrazine and monomethylhydrazine in aqueous solutions were found to be stable.

4.2.2 Interaction of aqueous suspensions of homoionically-exchanged montmorillonite preparations with hydrazine

Na^+-, K^+-, Mg^{2+}-, Ca^{2+}-exchanged montmorillonite. - The pH values of these cation-exchanged clay suspensions were in the range of 9.2 to 9.9 (Table 5). Degradation of hydrazine in these suspensions occurred to a greater extent than in the corresponding metal chloride solutions where the pH values ranged from 8.1 to 8.5 (Table 6). Thus, the higher pH value of the clay suspensions contributed to the enhanced degradation observed in these systems. However, the losses in the supernatant of the clay systems were already considerable (30% to 40% of total hydrazine added) in the presence of dissolved oxygen in these suspensions.

This observed enhancement in the degradation of hydrazine in the presence of these homoionically-exchanged montmorillonite suspensions suggests that the presence of montmorillonite as a heterogeneous component in the system catalysed the degradation of hydrazine. Degradation of monomethylhydrazine in aqueous solutions was also similarly enhanced by the presence of sodium-exchanged montmorillonite in spite of the fact that the pH values of both systems were similar (pH = 9). This was further substantiated by results obtained from the microcalorimetric studies of the interaction of hydrazine with these clay suspensions. The initial enthalpies evolved in the interaction of hydrazine with the Na^+-, K^+-, Mg^{2+}- and Ca^{2+}-

exchanged clays were 11.90, 12.80, 3.12, and 4.83 J g^{-1} of dry cation-exchanged clay, or J meq^{-1} of the cation (assuming that the CEC of the clays is 1 meq g^{-1} of dry clay). Additional low energy peaks (1 to 2 J g^{-1} dry clay) recorded in the subsequent mixing of the hydrazine interacted clay suspensions indicate that during each additional mixing cycle, additional amounts of hydrazine were slowly degraded in the presence of the clay. In contrast, no additional energies were recorded in the subsequent mixing of the metal chloride solutions of NaCl, $CaCl_2$, and $MgCl_2$. The enthalpies produced during the initla mixing of the hydrazine solutions (at pH 12) with metal chloride solution were negligible, only 0.6 to 1.4 J meq^{-1} of metal cation. Thus, it is clear that the presence of the homoionically-exchanged montmorillonite had a catalytic effect on the degradation of hydrazine. This result differs from a previous observation by MacNaughton _et al_. (1978) who noted that addition of oxide and clay solids did not change the rate of hydrazine oxidation in aqueous solutions.

Other work using such materials as Kieselguhr brick, and rust, had enhanced the degradation of hydrazine in aqueous solutions. Hayes _et al_. (1980, unpublished) reported the effects of the type of clay colloids on the degradation of hydrazine in the presence of oxygen at pH 8 to 9. They found that degradation decreased in the order of Na^+-illite ≈ Na^+-montmorillonite > Na^+-kaolinite, and the extent of the reactions in terms of heat evolved was Na^+-montmorillonite > Na^+-illite > Na^+-kaolinite. Subsequent mixes after initial mixing produced regular responses for Na^+-illite and Na^+-montmorillonite, but not for Na^+-kaolinite. Thus, illite and montmorillonite clays with their larger surface areas of 70 to 120 m^2 g^{-1} and 700 to 800 m^2 g^{-1}, respectively, compared to that of kaolinite of 30 to 40 m^2 g^{-1}, degraded hydrazine more effectively than kaolinite.

The enthalpies of reactions observed for the interactions of hydrazine with homoionically-exchanged montmorillonite were net heat outputs, i.e. resultants of the different heats of the different reactions that had occurred. Hydrazine was not adsorbed by K^+-montmorillonite under the final pH condition of 9.6. Sodium-exchanged montmorillonite adsorbed about 100 μeq g^{-1} of hydrazine, and of course some hydrazine was also degraded in the supernatant. For the interactions of Ca^{2+}- and Mg^{2+}-montmorillonite with hydrazine, the extents of degradation were similar to that of the Na^+-montmorillonite. It is interesting to note that the extent of adsorption of hydrazine by Na^+-, Ca^{2+}- and Mg^{2+}-montmorillonite was also similar, and that the enthalpy changes involved were exothermic, but significantly less exothermic in the cases of the alkali-earth than the alkali metals. The heat of hydration of the divalent cations is greater than that of the monovalent cations. Thus, during the adsorption of hydrazine by the exchanged clays, the energy required to replace the water molecules in the hydration shells of the divalent cations with hydrazine molecules would be greater than that of the monovalent cations. This was examined in the adsorption of hydrazine by Na^+- and Ca^{2+}-montmorillonite under different conditions of pH.

Al^{3+}- and Fe^{3+}-montmorillonite. - On adding hydrazine solutions of pH 8.0 to the suspensions of Al^{3+} and Fe^{3+}-montmorillonites, the pH values of the suspensions rose to 8.0. These values were higher than those for similarly treated Al^{3+} and Fe^{3+} chloride solutions (3.6 and 2.2 respectively). The amount of hydrazine degraded in the presence of these clay suspensions containing dissolved oxygen was 30% of the total hydrazine in the supernatant, whereas no detectable degradation was observed in the metal chloride solutions. Thus, in addition to the catalytic effects of the presence of the clay, the higher pH values of the clay suspensions, as compared with the metal chloride solutions, played a significant part in the enhanced degradation of the hydrazine. At low pH values, as in the metal chloride solutions, most of the hydrazine would exist at the $N_2H_5^+$ species and it would thus be significantly stabilized against oxidation.

The other possible mechanism by which hydrazine was degraded in the $FeCl_3$ solutions was through a reduction of the ferric ions to ferrous ions. However, under these experimental conditions, the predominant reaction was one of hydrolysis of the ferric ions since the hydrolysis of the first H^+ of $Fe(H_2O)_6^{3+}$ occurs at pH 2.9. Fine precipitates of ferric hydroxide were formed after twenty-four hours. The presence of these precipitates contributed to the subsequent very slow degradation of the hydrazine in this metal chloride solution (about 20% of total amount of hydrazine added) by providing heterogeneous surfaces which could facilitate degradation. However, reduction of ferric ions does occur in a large excess of hydrazine. Hayes et al. (1981, see Section 4.7.3) isolated a complex of ferrous-hydrazine chloride which was insoluble at pH 8 but soluble at low pH when excess hydrazine was interacted with geothite by washing hydrazine through a suspension of geothite in a CFSC experiment. The complex was suspected to be $Fe(N_2H_4)_2Cl_2$. (See pages 103 and 111)

The aluminium ions of aluminium chloride solutions are less acidic than the ferric ions of ferric chloride solutions. The loss of the first H^+ from $Al(H_2O)_6^{3+}$ occurs at pH 5. The hydrolysis of the second and third H^+ occurs at pH 5. The hydrolysis of the second and third H^+ occurs at slightly higher pH and is complicated by polymerisation of the hydrolysis products and the very slow precipitation of $Al(OH)_3$. Thus, no colloidal aluminium hydroxide was formed in the aluminium chloride solution of pH 3.6. No additional degradation of hydrazine occurred after prolonged standing in the $AlCl_3$ solution. A combination of factors, including low pH, absence of hydroxide precipitates at this pH, the inability of Al^{3+} ions to participate readily in a redox reaction, may all contribute to the relative stability of the hydrazine against degradation in this solution.

The microcalorimetric investigations showed that the hydrolysis of the ferric and aluminium ions was the main reaction when the solution of hydrazine at pH 12 was mixed with the metal chloride solutions. The enthalpies produced in the reaction between hydrazine and the metal chloride solutions ($AlCl_3$, 10.62 J meq^{-1} and $FeCl_3$, 69.00 J meq^{-1}) were comparable with those produced when a sodium hydroxide solution of pH 12 was added to the metal chloride solutions ($AlCl_3$, 8.67 J meq^{-1} and $FeCl_3$, 50.01 J meq^{-1}). This observation was consistent with the results from investigations of degradations which showed that insignificant amounts of hydrazine were degraded in the metal chloride solutions.

The enthalpies produced by mixing hydrazine with the Al^{3+}-montmorillonite and Fe^{3+}-montmorillonite suspensions were net enthalpies of the reactions of hydrazine involved in the processes of degradation and adsorption. Both Al^{3+}- and Fe^{3+}-montmorillonite adsorbed substantial amounts of hydrazine (738 and 819 μeq g^{-1}, respectively).

The initial enthalpy produced by mixing hydrazine and Al^{3+}-montmorillonite (9.73 J meq^{-1}) was comparable to that produced by the reaction between hydrazine and the metal chloride solutions (10.62 J meq^{-1}), and that produced by the reaction between sodium hydroxide solution of pH 12 and the metal chloride solution (8.67 J meq^{-1}). Unlike the other homoionically-exchanged montmorillonites examined, no subsequent heat was produced on additional mixing of the suspension. Thus, the remaining hydrazine seemed to remain stable in the presence of the hydrazine interacted Al^{3+}-montmorillonite.

The initial enthalpy produced by mixing hydrazine and Fe^{3+}-montmorillonite was 31.70 J meq^{-1}, and subsequent mixing produced significant additional energies which decreased with each subsequent cycle. Ferric ions and the adsorbed hydrazine were brought into close contact in the interlayer spaces of the montmorillonite. Under such circumstances of higher pH and concentration in the interlayer spaces, reduction of the ferric ions by hydrazine was encouraged. This may contribute to the enthalpy produced on subsequent mixing and to the additional degradation observed on prolonged standing. The enthalpies produced in the subsequent mixing cycles were also comparable to that produced by similar interactions of hydrazine with Mn^{2+}-montmorillonite.

The formation of hydroxides for both aluminium and ferric ions in the interlayers of the montmorillonite as well as the existing potential of the hydrazine to complex with Al^{3+}, Fe^{3+} and/or Fe^{2+} ions are factors which should be taken into account in considerations of the relative ease of adsorption of hydrazine by these clays, compared to the other homoionically-exchanged montmorillonite preparations. Accordingly, the adsorption of hydrazine by the Al^{3+}- and Fe^{3+}-montmorillonite was further examined in detail (Section 4.4.5-4.4.11).

Mn^{2+}-montmorillonite. - Degradation of hydrazine in the supernatant of the Mn^{2+}-montmorillonite suspension (30%) was greater than that in the metal chloride solution (10%). The pH of the first system rose from 5.6 to 9.6 on mixing with hydrazine, and the latter rose from 5.8 to 8.3. The enthalpies produced on this initial mixing of hydrazine with the Mn^{2+}-clay and $MnCl_2$ solution were 9.73 J g^{-1} of dry clay (or J meq^{-1} of metal ion) and 13.40 J meq^{-1} of metal ion, respectively.

In the above basic conditions, Mn^{2+} ions were readily hydrolysed to form the hydroxides which rapidly oxidized to the hydrous oxides; this was clearly observable in the metal chloride solution. In the initial mixing, adsorption of hydrazine by the Mn^{2+}-clay was 113 μeq g^{-1} in addition to the degradation of hydrazine in the supernatant. Thus, the net enthalpy produced in this initial mixing was a resultant of the heats of reactions involved in both the degradation and adsorption of the hydrazine. In the mixing of a sodium hydroxide solution of pH 12 with the $MnCl_2$ solution, hydrolysis of the Mn^{2+} produced an enthalpy of 13.0 J meq^{-1} of metal ion. This value was similar to that obtained for the addition of hydrazine to the manganous chloride solution. The enthalpy produced in the initial reaction of hydrazine with Mn^{2+}-montmorillonite was therefore largely due to the hydrolysis of the Mn^{2+} ions.

In subsequent mixing cycles of the hydrazine Mn^{2+}-clay suspension, further degradation of hydrazine produced enthalpies of 4 J g^{-1} of clay.

The concentration of hydrazine remaining after 24 hours of standing was only about 40% of the original. This demonstrates that the presence of Mn^{2+} as the exchange ion in the montmorillonite enhanced degradation of the hydrazine compared with that in the K^{+}-, Na^{+}-, Ca^{2+}-, and Mg^{2+}-montmorillonite systems. Further degradation of hydrazine was also observed in the subsequent mixing of the $MnCl_2$-hydrazine system. After each subsequent mixing additional decreasing amounts of energies were given off, and the further substantial degradation of hydrazine (about 75% of original) was observed on prolonged standing. However, in the $MnCl_2$-sodium hydroxide system, subsequent mixing did not produce additional energies of reaction. Thus, the ability of the Mn^{2+} to complex hydrazine and its ease of hydrolysis (pK_a of Mn^{2+} is 10.5) had resulted in a greater extent of interaction of hydrazine with Mn^{2+}-montmorillonite.

Cu^{2+}-montmorillonite. - Cupric ions in both Cu^{2+}-montmorillonite suspension and $CuCl_2$ solution actively degraded hydrazine producing the most energetic reactions (86 J meq^{-1} of exchangeable Cu^{2+} and 103 J meq^{-1} of Cu^{2+} in metal chloride solution) of all the interactions so far examined. The catalytic effect of Cu^{2+} in decomposing hydrazine has been well established. On mixing a cupric chloride solution (320 ppm) with a sodium hydroxide solution of pH 12, the heat of hydrolysis of the Cu^{2+} ions was 33.5 J meq^{-1} of Cu^{2+} ion. Thus, a major part of the heat produced in the above separate interactions between hydrazine and the Cu^{2+}-montmorillonite, and hydrazine and $CuCl_2$ solution, were due to the degradation reactions of the hydrazine.

Within one hour of mixing, all the hydrazine in the supernatant of the Cu^{2+}-montmorillonite suspension was degraded (initial pH 4.5 and final pH 5.2) while 50% of the hydrazine added was degraded in the metal chloride solutions (pH 4.3 to 4.5). In the reaction of hydrazine in the metal chloride solution, the initial rapid degradation of hydrazine was accompanied by the reduction of the cupric to cuprous ions. The complexation of Cu(I) by hydrazine stabilized the complexed hydrazine against degradation, thereby reducing the rate of degradation of the hydrazine in the solution.

In the presence of the clay, enhanced degradation of hydrazine could occur due to an increase in the effective Cu^{2+} concentration on the clay compared to that of the cupric chloride solution. Hydrazine was brought into closer contact with the exchangeable Cu^{2+} ions on the surfaces of the montmorillonite, resulting in a rapid degradation of hydrazine in the supernatant of the clay suspension. However, after the supernatant concentration of hydrazine was totally removed, hydrazine was still detected in the Cu^{2+}-montmorillonite. The adsorption of hydrazine by Cu^{2+}-montmorillonite was 240 eq g^{-1} of hydrazine. Microcalorimetric traces showed a continued production of heats of reaction on each mixing cycle of the Cu^{2+}-montmorillonite-hydrazine suspension over 24 hours. Hydrolysis or reduction of the exchangeable Cu^{2+} would cause an imbalance in the negative charges of the clay. Subsequently, this would be balanced by the adsorption of the hydrazinium ions. The adsorbed hydrazine was stabilized against very rapid degradation.

4.3 General Conclusions from Studies of Degradations

The main factors that affect the nature and extent of interactions of hydrazine with clays in aqueous environments are identified as follows:

(1) the pH of the system,
(2) the presence of oxygen,
(3) the presence of the clay, and
(4) the nature of the exchangeable cation on the clay.

Factors (1), (3), and (4) are in fact interdependent. In general, high pH and the presence of oxygen and of montmorillonite enhance the degradation of hydrazine. Both the degradation and adsorption of hydrazine take place in homoionically-exchanged montmorillonite systems. The presence of Cu^{2+} ions in montmorillonite causes the most rapid and vigorous degradation of hydrazine, and that of Mn^{2+} ions also causes extensive degradation of hydrazine, though at a slower rate. Al^{3+}- and Fe^{3+}-montmorillonites tend to adsorb the highest amounts of hydrazine at the pH values studied (about 8). K^{+}-, Na^{+}-, Ca^{2+}- and Mg^{2+}-montmorillonite degrade hydrazine slowly and the latter three clay preparations adsorb it to small extents.

The amounts of hydrazine that were adsorbed or degraded by the above cation-exchanged montmorillonites were determined by the different extents which each of the exchangeable cations could participate in hydrolytic, redox and/or complexation reactions. The degradation of hydrazine was enhanced in the presence of exchangeable cations, like Cu^{2+}, Mn^{2+} and Fe^{3+}. These cations readily reacted with dissolved oxygen and the hydrazine in solution giving rise to the catalytic oxidation of hydrazine. The hydrolysing power of the cations is directly related to their polarizing power.
The adsorption of hydrazine by each of the homoionically exchanged montmorillonite (Fe^{3+}-, Al^{3+}-, Cu^{2+}-, Mg^{2+}-, Ca^{2+}-, and Na^{+}-), was observed to increase in a similar order as the hydrolysing power of these cations as indicated by their pK_a values: Fe^{3+} (2.9) < Al^{3+} (5.01) < Cu^{2+} (7.6) < Mg^{2+} (12.0) < Ca^{2+} (12.5) < Na^{+} (14.6). If the exchangeable cation is

in the transition series, the greater complexing ability of the cation could also be expected to contribute to the adsorption of hydrazine by the particular cation-exchanged montmorillonite.

4.4 Studies of Adsorption, Under Different Conditions of pH, of Hydrazine and of Monomethylhydrazine by Some Homoionically (Na^+-, Ca^{2+}-, Fe^{3+}- and Al^{3+}-) Exchanged Montmorillonite and Kaolinite Clays

In the study of the adsorption of hydrazine by Na^+-, Ca^{2+}-, Fe^{3+}-, and Al^{3+}-exchanged montmorillonite and Na^+- and Al^{3+}-exchanged kaolinite, adsorption isotherms were obtained for each of these systems under different pH conditions. Desorptions, using water and sodium chloride solutions, were also carried out. The enthalpy changes that accompany the adsorption of hydrazine and monomethylhydrazine by hydroxy-aluminium-montmorillonite suspensions of pH 8.0 were obtained from microcalorimetric experiments. Further investigations into the adsorption mechanism involved in the adsorption of these hydrazines by the hydroxy-clay were carried out using ^{22}Na-labelled solutions of sodium hydroxide and chloride.

Some of the adsorption isotherms were initially obtained using both the batch slurry technique and continuous flow stirred cell (CFSC) method in order to test the reproducibility of the two. These adsorption isotherms were for the interactions of:

(1) Fe^{3+}-montmorillonite with a hydrazine solution of pH 8 (Figure 11);

(2) Al^{3+}-montmorillonite with a hydrazine solution of pH 4 and pH 8 (Figures 12 e and f); and

(3) hydroxy-aluminium-montmorillonite (pH 8.0) with a hydrazine solution of pH 8.0 (Figure 13 a).

The results of each of these isotherms obtained from the two techniques were within ±5% variability, which is within the experimental variation of the CFSC technique. The residence time of the adsorptive in the CFSC was about 25-30 minutes and this is regarded as sufficiently long for equilibrium conditions of adsorption to be established. This is substantiated by the microcalorimetric studies which indicated that the initial response of the interaction was complete within 20 minutes.

Several reservoir concentrations were used to obtain isotherms for the adsorption of hydrazine at pH 8.0 by hydroxy-aluminium-montmorillonite (pH 8.0). These concentrations were 8.58, 11.24 and 20.05 meq dm^{-3}. The isotherms given for adsorption from the different reservoir concentrations were calculated from elution data representing only up to 80% of the elution volume because values calculated from readings close to the reservoir concentration were inaccurate. Each isotherm was comparable within an acceptable ±5% variability. Adsorption of hydrazine at pH values of 4.0 and of monomethylhydrazine (pH 8.0) by Al^{3+}-exchanged montmorillonite (pH 10.0) was expected to be low; hence, reservoir concentrations of less than 20 meq dm^{-3} were used. In the case of interactions of hydrazines (pH 8.0) and of monomethylhydrazine (pH 8.0) with hydroxy-aluminium-montmorillonite (pH 8.0), where adsorption was expected to be high, a reservoir concentration of 150 meq dm^{-3} of adsorptive was used. Each run was repeated and the results represent the averages of two runs.

Figures 11, 12 and 13 show the interactions of hydrazine with Na^+-, Ca^{2+}-, Fe^{3+}- and Al^{3+}-exchanged montmorillonite under different conditions of pH. Na^+-montmorillonite adsorbed more hydrazine at pH 4 (660 μeq g^{-1}) than at pH 8 (100 μeq g^{-1}), whereas Ca^{2+}-, Fe^{3+}- and Al^{3+}-montmorillonite preparations gave the reverse trend. The same pattern of behaviour was observed for Na^+-kaolinite and hydroxy-aluminium-kaolinite (pH 8). At a suspension pH of 10 the adsorption of hydrazine by hydroxy-Fe^{3+}- and hydroxy-aluminium-montmorillonite was less than that at pH 8 (Figures 12 d and 13 c). Figures 14 a to c show the interactions of monomethylhydrazine solution of pH 8 with Al^{3+}-montmorillonite and hydroxy-aluminium-montmorillonite suspensions of pH 8. Figures 15 a and b show the enthalpy changes in the adsorption of hydrazine and monomethylhydrazine by the hydroxy-aluminium-montmorillonite at pH 8. Tables 7 and 8 provide data for the maximum adsorption obtained for these isotherms. Results of the amount of aluminium exchangeable during the adsorption and desorption of hydrazine in the exchange studies carried out using the ^{22}Na-labelled solutions are summarised in Tables 9 to 11.

4.4.1 Interactions of Na^+-montmorillonite with hydrazine solutions of pH 4.0 and 8.0 (Figure 11)

On addition of the prepared hydrazine solution (pH 4.0) to the Na^+-montmorillonite suspension of pH 5.7, the pH of the suspension decreased to 4.0. Adsorption approached a steady maximum value of 650 μeq g^{-1} at an equilibrium solution concentration of hydrazine of 6 meq dm^{-3}. Water washing of the complex removed only 200 μeq g^{-1} of adsorbate, whereas 340 μeq g^{-1} of hydrazine was desorbed using 0.1$\underline{M}$ NaCl solution. A total of 540 μeq g^{-1} of adsorbate was therefore desorbed from the clay and some 100 μeq g^{-1} remained on the clay.

Table 8. Maximum adsorption of hydrazine and monomethylhydrazine by montmorillonite preparations exchanged with cations of different valence

Exchangeable cation	pH of clay suspension	pH of hydrazines solution	Maximum adsorption (μeq g^{-1}) by clay of: N_2H_4	Maximum adsorption (μeq g^{-1}) by clay of: CH_3NHNH_2
Na^+	5.6	4.0	650^b	-
	5.6	8.0	100^b	-
Ca^{++}	4.0	4.0	70^b	-
	6.8	10.0	97^b	-
Al^{+++}	4.0	4.0	149^{b+c}	-
	4.0	10.0	900^{b+c}	1000^c
	8.0	8.0	1500^c	2000^c
	10.0	10.0	225^c	-
Fe^{+++}	2.8	8.0	900^c	-
	2.8	10.0	1100^b	-

b: batch slurry technique
c: CFSC technique
b+c: average of batch slurry and CFSC techniques

Table 9. Maximum adsorption of hydrazine by sodium- and aluminium-exchanged kaolinite preparations

Exchangeable cation	pH of clay suspension	pH of hydrazine solution	Maximum adsorption (μeq g^{-1}) by dry clay
Na^+	6.7	4.0	120
	6.7	8.0	75
Al^{+++}	4.5	4.0	42
	8.0	8.0	220

Addition of the pH 8.0 hydrazine solution to the Na^+-montmorillonite suspension increased the pH initially to 7.6, but the value was stabilised at 8.0 upon further additions. At the equilibrium solution concentration of 5 meq dm^{-3} of hydrazines, a steady maximum adsorption of only 100 μeq g^{-1} was obtained. This value was significantly less than the amount adsorbed at a suspension pH of 4. No desorption was carried out in this case as the amount adsorbed was low.

4.4.2 Interactions of Ca^{2+}-montmorillonite with hydrazine solutions of pH 4.0 and 8.0 (Figure 11)

The Ca^{2+}-montmorillonite suspension (1% w/v), having an initial pH of 6.8, was adjusted to 4.0 with 0.1$\underline{\underline{M}}$ hydrochloric acid. Adsorption approached a steady maximum value of 70 μeq g^{-1} at an equilibrium sorptive concentration of 6 meq dm^{-3}. When the supernatant was removed after centrifugation and replaced with distilled water, no desorption of hydrazine was measured. On using 0.1$\underline{\underline{M}}$ NaCl solution, all of the 70 μeq g^{-1} of sorbate was removed.

On addition of the first aliquot of the pH 8.0 hydrazine solution to the suspension at pH 6.8, the bulk suspension pH rose to 7.8, on adding further aliquots of hydrazine the pH value stabilized at pH 8. An an equilibrium concentration of 3.75 meq dm^{-3}, the pH value of the suspension was 7.8, and the adsorption was 96 μeq g^{-1} of hydrazine. Adsorption in this instance was slightly greater than that at pH 4.0. Washing with water did not desorb any significant amounts of adsorbate. When washed with 0.1$\underline{\underline{M}}$ NaCl solution, all of the sorbate was removed. Thus, in this system, where Ca^{2+} is the exchangeable cation on the clay, the pH of the suspension did not seem to significantly affect the amount of hydrazine adsorbed.

4.4.3 Interactions of Na^+-kaolinite with hydrazine solutions of pH 4.0 and 8.0 (Figure 12 a)

The CFSC technique was used for the determination of the adsorption isotherms at pH values of 4.0 and 8.0. The clay suspension (1% w/v) had an initial pH of 6.7. The maximum adsorption for interaction at pH 4 is higher than that at pH 8, and amounted to 120 and 75 μeq g^{-1}, respectively, for the two pH values. The reservoir sorptive concentrations used in each case were 7.01 and 9.60 meq dm^{-3} at pH 4.0 and 8.0, respectively.

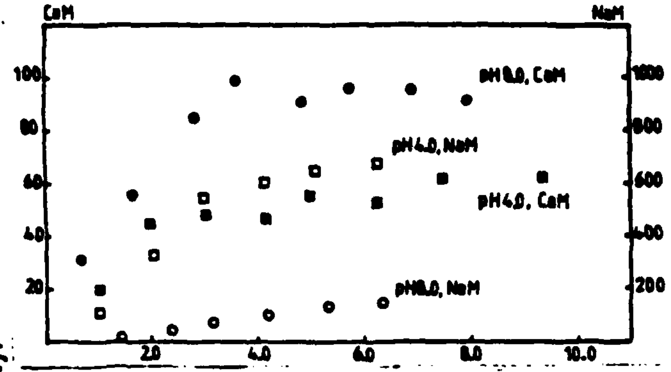


Figure 11. Isotherms (batch/slurry method) for adsorption of hydrazine, at pH 4.0 and 8.0, by Na^+-, and by Ca^{2+}-montmorillonites

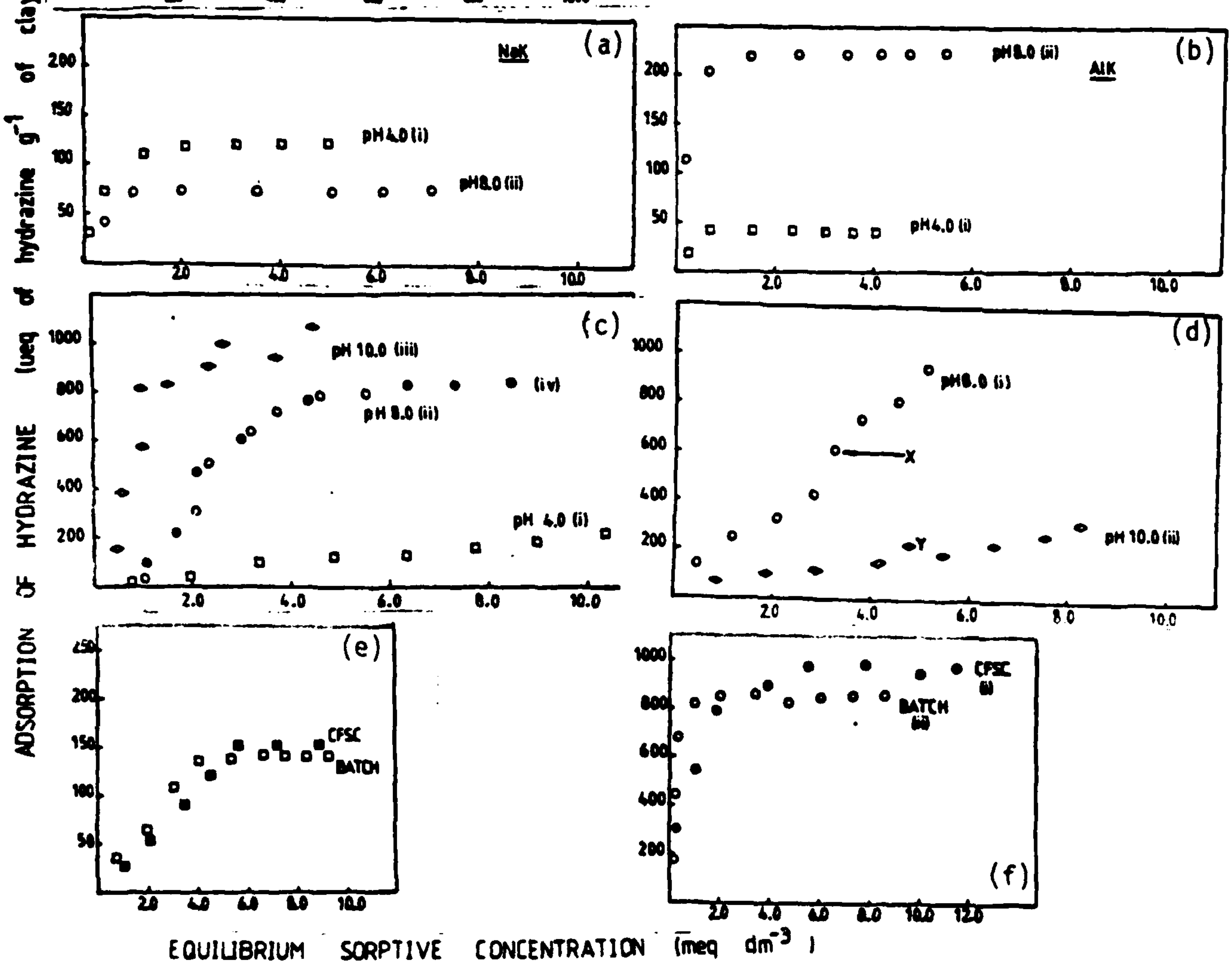


Figure 12. Isotherms for sorption of hydrazine by Na^+-kaolinite (a) and by Al^{3+}-kaolinite (b), pH 4.0 (i) and 8.0 (ii) using the CFSC method; by Fe^{3+}-montmorillonite (batch/slurry) at pH 4.0 (i), 8.0 (ii) and 10.0 (iii) and (CFSC) at pH 8.0 (iv) c , by hydroxy-Fe^{3+}-montmorillonite (batch/slurry) at pH 8.0 (i) and 10.0 (ii) d , (Desorption of hydrazine observed at point X when pH adjusted to 10, and point Y was obtained); by Al^{3+}-montmorillonite at pH 4.0 (e), 8 (f i), and 10 (f ii).

4.4.4 Interactions of Al^{3+}-kaolinite with hydrazine solution of pH 4.0 and of hydroxy-aluminium-kaolinite (pH 8.0) with hydrazine solution of pH 8.0 (Figure 12 b)

The CFSC technique was also used in these adsorption studies. The maximum adsorption for interaction at pH 4 was very minimal, only 42 μeq g^{-1}, and was markedly less than that for the Na^{+}-kaolinite case.

From the adsorption of hydrazine by the Al^{3+}-montmorillonite samples under different pH conditions, the maximum adsorption was found to be highest when the clay suspension was adjusted to pH 8.0 prior to any adsorption. Therefore, the Al^{3+}-kaolinite suspension (1% w/v) was adjusted to pH 8.0 with 0.105$\underline{M}$ NaOH solution in order to determine the maximum level of adsorption of hydrazine by this clay at pH 8. The molar ratio of hydroxide added to exchangeable Al^{3+} on the clay (i.e. the OH:Al ratio) was calculated to be 3.94. The maximum adsorption of hydrazine by this kaolinite preparation was found to be 220 μeq g^{-1} for an equilibrium sorptive concentration of 1 meq dm^{-3}. The sodium exchange capacity of Al^{3+}-kaolinite was 105 μeq g^{-1}; therefore, the amount of hydrazine adsorbed was about twice the exchange capacity of the clay.

Assuming that the area occupied by a hydrazine hydrate molecule lying with its N-N axis parallel to the surface of the clay was 23.1 $Å^{2}$, the total area occupied by the adsorbed hydrazine was 30.5 m^{2} g^{-1}. This coverage is in the range of the total specific surface area of Al^{3+}-kaolinite (29-44 m^{2} g^{-1}; Yormah, 1981).

4.4.5 Interactions of Fe^{3+}-montmorillonite with hydrazine solutions of pH 4.0, 8.0 and 10.0 (Figure 12 c)

The initial pH of the Fe^{3+}-montmorillonite suspension (1% w/v) was 2.8. Addition of the hydrazine solution of pH value 4.0 only increased the pH of the suspension to 2.9 for an equilibrium sorptive concentration of 10 meq dm^{-3}. The adsorption showed a linear rise with increasing equilibrium sorptive concentration within the concentration range examined. Hydrazine was not removed by water washing in the case of the Fe^{3+}-montmorillonite sample which had the highest amount of hydrazine adsorbed (198 μeq g^{-1}). When 0.1$\underline{M}$ NaCl solution was used, 111 μeq g^{-1} of adsorbate was removed; i.e. about 56% of the total hydrazine adsorbed.

On addition of successive aliquots of the pH 8.0 hydrazine solution, the pH of the suspension varied with the equilibrium solution concentration as follows:

Equilibrium sorptive concentration (meq dm^{-3})	pH value of suspension
1.21	3.7
2.19	4.0
2.25	4.8
3.65	4.9
3.75	5.9
5.47	7.0
5.63	7.1

Adsorption increased as the pH of the suspension increased, and finally the pH value reached a maximum of 8. For 6 meq dm^{-3} equilibrium sorptive concentration, an adsorption of 805 μeq g^{-1} was observed. The experiment was repeated using the CFSC technique and a reservoir sorptive concentration of 18.48 meq dm^{-3}. Samples were collected from the waste line of the stirred cell every quarter hour and the pH values of these samples increased from 5.6 to 7.4 as the equilibrium sorptive concentration increased from 4.0 to 11.2 meq dm^{-3}. The maximum adsorption for the equilibrium solution concentration of 10 meq dm^{-3} was 900 μeq g^{-1}. About 40% or 322 μeq g^{-1} of hydrazine was removed when the sample from the batch slurry experiments was washed with 0.1M NaCl solution. Desorption with the same salt solution using the CFSC technique removed 553 μeq g^{-1}, or about 61% of the total hydrazine adsorbed. This difference in the proportion of adsorbate desorbed by the two techniques could be due to some degradation of the desorbed hydrazine occurring in the batch slurry experiment.

The pH of the suspension for adsorption (batch slurry) of hydrazine solution of pH 10 varied as follows:

Equilibrium sorptive concentration (meq dm^{-3})	pH value of suspension
0.49	4.1
0.60	5.8
0.63	7.1
1.09	7.8
2.29	8.4
2.75	8.5
3.83	8.7
4.38	8.7

A very rapid increase in adsorption was observed as the pH values increased rapidly to about 8.9 at an equilibrium sorptive concentration of 2.29 meq dm^{-3}. The rate of adsorption then began to decrease as the rate of pH change of the equilibrium sorptive solution decreased. There was no distinct maximum adsorption of hydrazine by this clay suspension for the range of equilibrium sorptive concentrations studied. But, the decrease in the rate of adsorption beyond 4.0 meq dm^{-3} indicated that the maximum adsorption was in the range of 1000 μeq g^{-1}. Sodium chloride solution (0.1M) was added to each of the four water-washed samples from the batch slurry experiments having different adsorbate levels amounting to 385, 824, 986, and 1080 μeq g^{-1}. Desorption of 197, 468, 604, and 698 μeq g^{-1} of hydrazine (or about 51, 57, 61, and 65% of the total respective adsorbate) shows that the amount of hydrazine desorbed increased as the level of adsorption increased.

When the hydrazine sorptive solution added to the bulk clay suspension had a pH value of 8.0, the change in the resulting bulk suspension pH value with respect to the equilibrium sorptive concentration was slower than that when the hydrazine solution used had pH value of 10.0. Ath the same equilibrium hydrazine sorptive concentration of 2.2 to 2.3 meq dm^{-3}, the pH value of the bulk suspension was 4.0 in the first system with sorptive solution of pH 8, and 8.4 in the latter case with sorptive solution of pH 10. Consequently, the adsorption of hydrazine was only about 300 μeq g^{-1} in the first case compared to 800 μeq g^{-1} in the latter.

The adsorption results have shown that adsorption of hydrazine by Fe^{3+}-montmorillonite was critically dependent on the pH value of the hydrazine solution added to the clay, as was the resultant pH value of the clay suspension. As the pH value of the sorptive solution used increased from 4 to 10, the adsorption of hydrazine by Fe^{3+}-montmorillonite increased dramatically by nearly ten fold.

4.4.6 Interactions of hydroxy-ferric-montmorillonite of pH 8.0 and 10.0 with hydrazine solutions of pH 8.0 and 10.0, respectively (Figure 12 d)

Fe^{3+}-montmorillonite (1% w/v) preparations were adjusted to pH 8.0 and 10.0 by addition of 1.0M sodium hydroxide solution. The molar ratio of hydrazine added to exchangeable Fe^{3+} in each case was 3.15 and 4.2, respectively. In both cases, the amount of hydrazine adsorbed increased linearly as the equilibrium solution concentration of the hydrazine increased and no maximum adsorption was obtained for this range of equilibrium sorptive concentration (up to 10 meq dm^{-3}). However, the amount of hydrazine adsorbed by the hydroxy-ferric-montmorillonite at pH 8 was much greater than that at pH 10. A sample of the pH 8.0 clay suspension with 606 μeq g^{-1} of hydrazine adsorbed was also adjusted to pH 10.0, and then 268μeq g^{-1} of hydrazine was desorbed (i.e. from point X to Y in Figure 12 d).

Sodium chloride solution (0.1M) removed only 360 μeq g^{-1} of hydrazine from the hydroxy-ferric-montmorillonite of pH 8 containing a total of 950 μeq g^{-1} of adsorbate. No hydrazine was found in the supernatant when the hydroxy-ferric-montmorillonite sample of pH 10 containing 400 μeq g^{-1} of sorbed hydrazine was similarly washed with 0.1M sodium chloride solution.

4.4.7 Interactions of Al^{3+}-montmorillonite with hydrazine solutions of pH 4.0, 8.0, and 10.0 (Figures 12 e and f)

The initial pH values of the Al^{3+}-montmorillonite samples lay between 4.0 and 4.5. Adsorption of hydrazine by the clay suspension (1% w/v) was determined by both the batch slurry and CFSC techniques, and the reservoir sorptive concentration used in the case of CFSC was 11.53 meq dm^{-3}. The maximum adsorption measured, 148 and 150 μeq g^{-1}, respectively, was very similar for the two procedures. No detectable hydrazine was removed with distilled water and desorption with 0.1M NaCl solution resulted in the removal of 56 μeq g^{-1} of hydrazine. No further desorption of hydrazine was detected when the desorption process was repeated and even when the concentration of the sodium chloride solution was increased to 0.2M.

During adsorption using the batch slurry method, addition of the first aliquot of pH 10.0 solution of hydrazine raised the pH of the bulk suspension from 4.5 to 7.2. Successive additions of the solutions of hydrazine of pH 10 raised the pH of the suspension to 8.6. The maximum adsorption at this pH and for equilibrium sorptive concentration of 1.14 meq dm^{-3} was 840 μeq g^{-1}. During adsorption using the CFSC technique, a reservoir sorptive concentration of 19.5 meq dm^{-3} of pH value of 8.0 was used. The pH value of the first 3.0 cm^{3} of eluate collected was 7.8 and that of the subsequent fractions stabilised at 8.0, lower than the final pH value of the suspension obtained in the batch slurry technique. The maximum adsorption was 950 μeq g^{-1} for an equilibrium solution concentration of 4 meq dm^{-3}. The adsorption of hydrazine by Al^{3+}-montmorillonite was therefore markedly dependent on the pH value of the hydrazine solution used in the adsorption, as was the pH of the resultant suspension. The maximum adsorption was found to increase dramatically from 150 to 950 μeq g^{-1} when the pH value of the hydrazine solution used was raised from pH 4 to 8.

No hydrazine was desorbed with water, and on desorption using 0.1$\underline{M}$ sodium chloride solution 750 μeq g^{-1} of hydrazine was removed, i.e. about 78% of the total adsorbate. In the CFSC experiments, after maximum adsorption was obtained, the excess hydrazine in the equilibrium solution was removed with distilled water and then 0.1$\underline{M}$ NaCl solution as the eluent. A total of 646 μeq g^{-1} of hydrazine was calculated to be desorbed from measurements of the area under the peak. Thus, the adsorbed hydrazine was not desorbed with water, but about 70-78% was desorbed by 0.1$\underline{M}$ NaCl solution.

The eluate stream from the waste line that was not used in the colourimetric determination was also collected in three separate fractions, i.e. during washing with distilled water, 0.1$\underline{M}$ NaCl solution, and 0.1$\underline{M}$ hydrochloric acid. Aluminium was not detected in the water wash fraction nor in the 0.1$\underline{M}$ NaCl fractions. The 0.1$\underline{M}$ hydrochloric acid was subsequently used to wash out the remainder of the sorbed hydrazine that was strongly adsorbed by the clay. However, no significant amount of hydrazine was desorbed although 49 μeq g^{-1} of Al^{3+} was found in the acid fraction collected. This interaction of Al^{3+}-montmorillonite with a hydrazine solution of pH 8.0 had caused the exchangeable Al^{3+} to be fixed in the clay such that washing with 0.1$\underline{M}$ NaCl solution did not remove any Al^{3+}, and a slow removal of the Al^{3+} was effected only with acid washing. This was further investigated in Section using a labelled sodium chloride solution.

4.4.8 Interaction of hydroxy-aluminium-montmorillonite (pH 8.0) with a hydrazine solution of pH 8.0 (Figures 13 a and b)

The Al^{3+}-montmorillonite suspension of pH 4.0 was adjusted to pH 8.0 with 0.105$\underline{M}$ sodium hydroxide solution. The molar ratio of added hydroxide to exchangeable Al^{3+} in the clay was 4.0. Adsorption of pH 8.0 hydrazine solution by the hydroxy-aluminium-montmorillonite suspension (pH 8.0) was determined over two concentration ranges. In the low concentration range of up to 12 meq dm^{-3}, adsorption was carried out using both the batch slurry and CFSC techniques. An adsorption maximum was not obtained for this range of hydrazine concentrations. Nevertheless, a maximum adsorption of 1500 μeq g^{-1} was eventually obtained using a reservoir concentration of 130 μeq dm^{-3} with the CFSC technique. The eluate collected during the washing in of the sorptive solution to the stirred cell did not have any significant amount of Al^{3+} present.

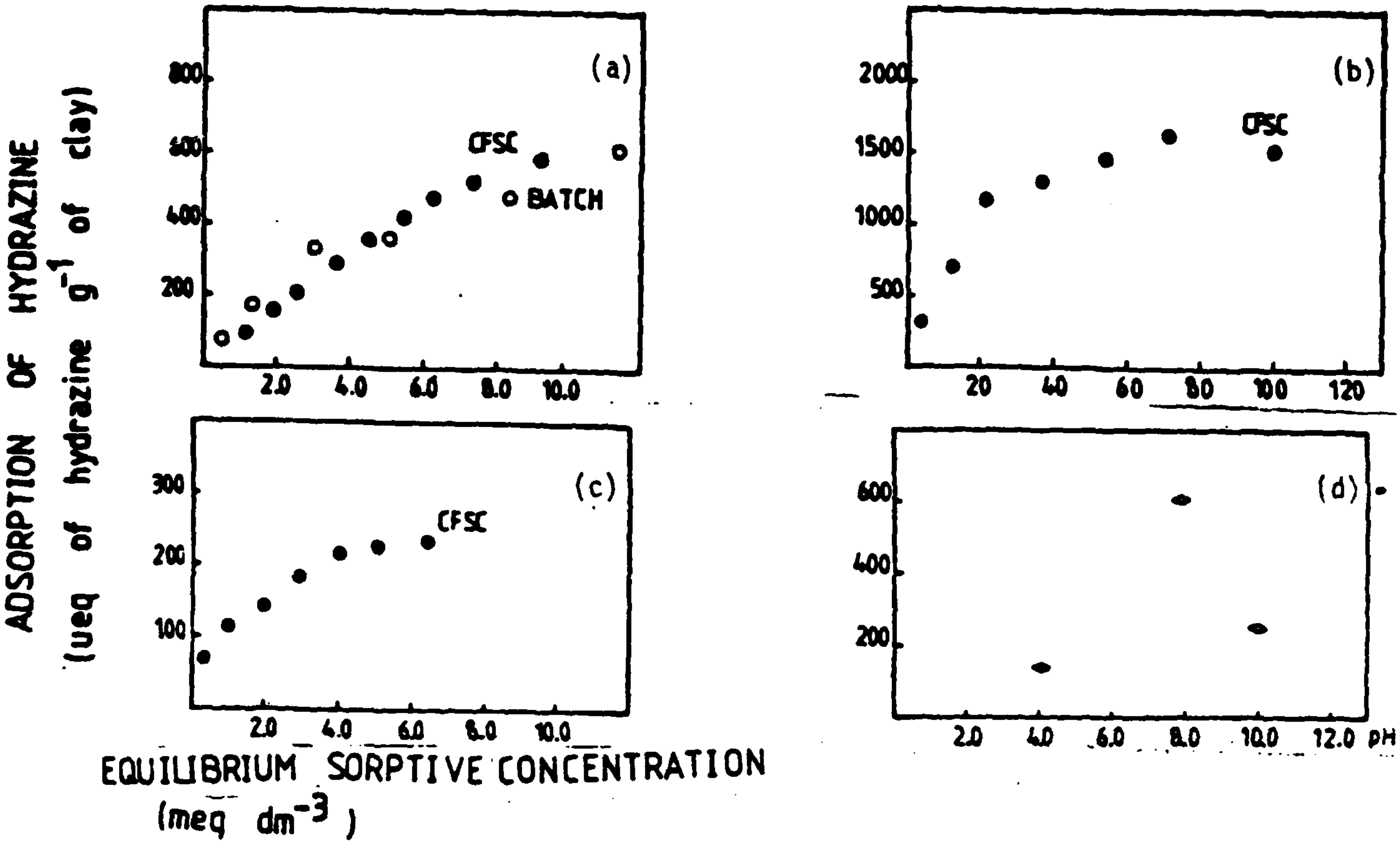
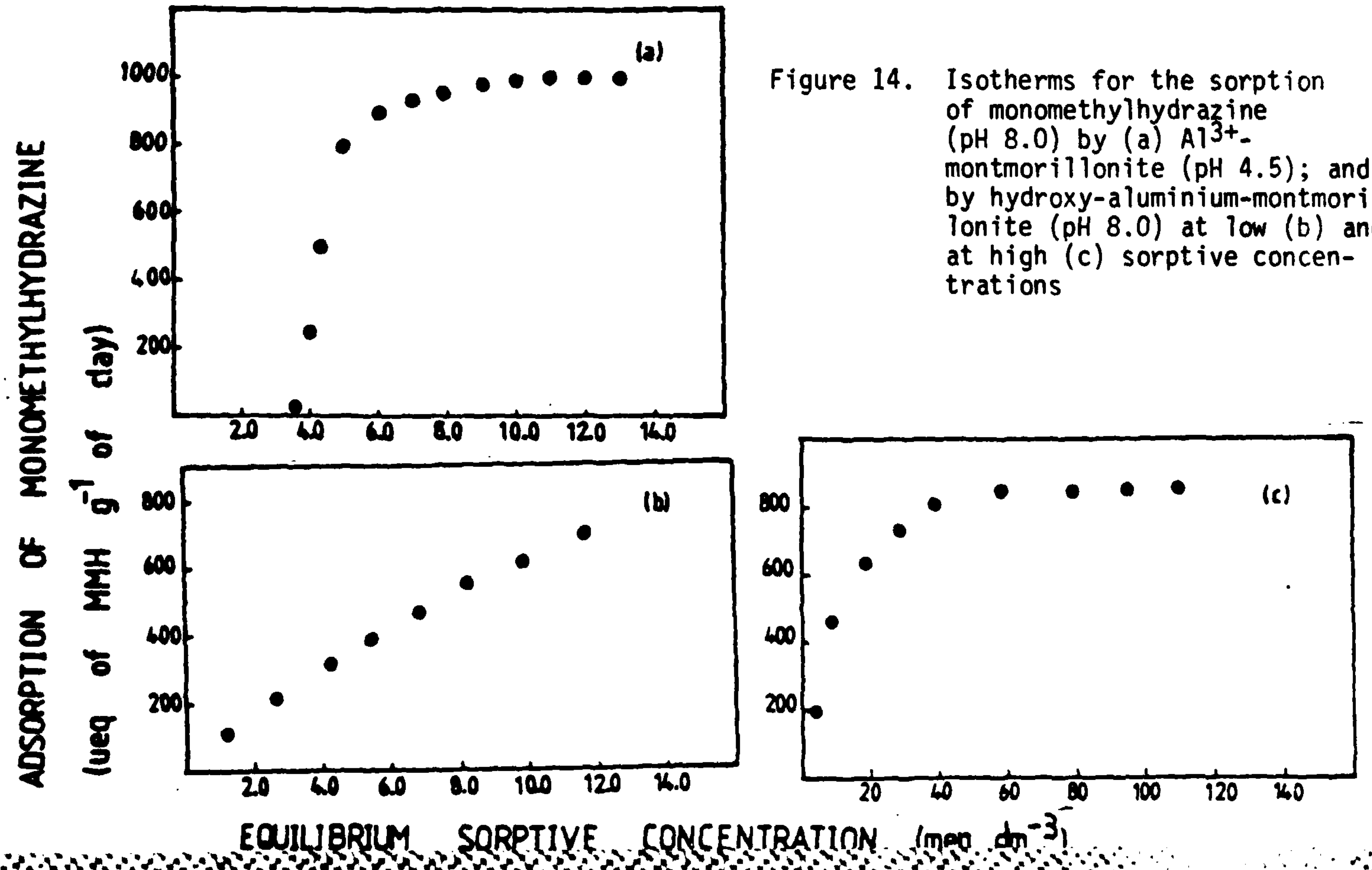


Figure 13. Isotherms for the adsorption of hydrazine by hydroxy-aluminium montmorillonite at low (a) and high (b) sorptive concentration, pH 8.0, and at pH 10.0 (c). Effects of the pH of the suspension on adsorption is shown in (d)

Figure 14. Isotherms for the sorption of monomethylhydrazine (pH 8.0) by (a) Al^{3+}-montmorillonite (pH 4.5); and by hydroxy-aluminium-montmorillonite (pH 8.0) at low (b) and at high (c) sorptive concentrations



The area covered by a hydrazine hydrate molecule lying with its N-N axis parallel to a horizontal surface is estimated to be 23.10 Å^2. The total surface area of the montmorillonite covered by the maximum amount of adsorbed hydrazine was therefore 416 m^2 g^{-1}. This coverage is therefore 57% of the specific surface area of the montmorillonite (725 m^2 g^{-1}). Water washing did not remove any significant amount of hydrazine from the adsorption complexes having 403, 510, and 648 μeq g^{-1} of adsorbate. Washing with 0.1M NaCl solution desorbed 290, 340 and 440 μeq g^{-1}, i.e. an average of about 70% of the amount adsorbed. Hence, at these levels of adsorption a definite proportion of the adsorbed hydrazine was desorbed. A similar proportion of adsorbate was desorbed from the complex obtained from the interaction of Al^{3+}-montmorillonite with a hydrazine solution of pH 8.

Table 10. The desorption of hydrazine and monomethylhydrazine and adsorption of Na^+ by hydrazine and monomethylhydrazine interacted Al^{3+}-montmorillonite and hydroxy-aluminium-montmorillonite complexes, using different concentrations of labelled NaCl solutions as the desorption media

Clay Preparations	Desorption medium (M NaCl solution)	Amount of hydrazine desorbed (μeq g^{-1})	Amount of sodium adsorbed (μeq g^{-1})
(a) Hydrazine interacted complexes			
Al^{+++}-montmorillonite (pH 4) interacted with hydrazine solution of pH 8	0.01	304	375
	0.1	642	572
Hydroxy-aluminium-montmorillonite hydrazine complex(pH 8)	0.01	466	472
	0.1	722	911
(b) Monomethylhydrazine interacted complexes			
Al^{+++}-montmorillonite (pH 4) interacted with monomethylhydrazine solution of pH 8	0.01	509	440
	0.1	1000	1520
Hydroxy-aluminium-montmorillonite monomethylhydrazine complex (pH 8)	0.01	658	408
	0.1	1130	1490

Washing of the adsorption complex with a maximum adsorption of 1500 μeq g^{-1} from the CFSC procedure, with 0.1M NaCl solution released a maximum of 722 μeq g^{-1} of hydrazine only (Table 10). This amount of hydrazine, when calculated as a proportion of the CEC of the clay, gave a value of 72%. This value was similar to the values obtained for the other adsorption complexes. These results indicate that some of the 1500 μeq g^{-1} of hydrazine adsorbed, the amount adsorbed up to the extent of the CEC, was adsorbed through a cation-exchange mechanism and a definite proportion of this amount of adsorbate was desorbed by 0.1M NaCl solution (70%).

4.4.9 Interaction of hydroxy-aluminium-montmorillonite of pH 10.0 with a hydrazine solution of pH 10.0 (Figure 13 c)

The Al^{3+}-montmorillonite suspension (1% w/v) was adjusted to pH 10.0 and the molar ratio of added hydroxide to exchangeable Al^{3+} on the clay was 4.7. A reservoir sorptive concentration of 9.5 meq dm^{-3} was used and the maximum adsorption was only 225 μeq g^{-1} of hydrazine. This is significantly lower than the amount adsorbed at suspension pH value of 8, and it is also lower than the CEC of the clay. The amount of Al^{3+} found in the eluate collected during the wash-in of the sorptive was 232 eq g^{-1}, i.e. about 23% of the original total exchangeable Al^{3+}. Washing the complex with 0.1M NaCl solution removed only a very small amount of hydrazine, about 20 to 30 μeq g^{-1}.

4.4.10 Interactions of Al^{3+}-montmorillonite and of hydroxy-aluminium-montmorillonite of pH 8.0 with a monomethylhydrazine solution of pH 8.0 (Figures 14 a to c)

During the adsorption by the CFSC technique of pH 8.0 monomethylhydrazine solution by Al^{3+}-montmorillonite, the pH values of the eluate fractions collected were determined. A sudden increase in adsorption to 1000 μeq g^{-1} occurred at pH 5.9, and the equilibrium sorptive concentration was about 4.0 meq dm^{-3}. This sudden change in adsorption was not observed in the adsorption isotherm of the interaction of Al^{3+}-montmorillonite with hydrazine solution of pH 8.0. The maximum adsorption of monomethylhydrazine by a suspension of hydroxy-aluminium-montmorillonite (pH 8.0) was 2200 μeq g^{-1} at equilibrium sorptive solution concentration of 60 meq dm^{-3} (Figure 14 c). No sudden change in adsorption was detected, as was observed for the Al^{3+}-montmorillonite system.

Assuming that the area covered by a monomethylhydrazine molecule lying with its N-N axis parallel to a horizontal surface is estimated to be 22.01 Å^{2}, the total surface area of the montmorillonite covered by the maximum amount of monomethylhydrazine adsorbed was calculated to be about 583 $m^2 g^{-1}$. This coverage is 80% of the specific surface area of montmorillonite (725 $m^2 g^{-1}$).

When 0.1$\underline{M}$ NaCl solution was used in the washing of the adsorption complex of Al^{3+}-montmorillonite and MMH, the total amount of MMH desorbed was calculated to be 1130 μeq g^{-1} (Table 10). Thus, the amount of monomethylhydrazine desorbed in each case was equivalent to the CEC of the clay.

4.4.11 Microcalorimetric studies of the adsorption of hydrazine and of monomethylhydrazine with hydroxy-aluminium-montmorillonite of pH 8

Figures 15 a and b show the changes in enthalpies which took place during the adsorption of hydrazine and of monomethylhydrazine by hydroxy-aluminium-montmorillonite. As adsorption proceeded, the exothermic interactions went through a maxima corresponding to the maximum amount of hydrazine and monomethylhydrazine desorbed from the respective hydrazines treated hydroxy-aluminium-montmorillonite. The adsorption of hydrazine was a more exothermic process than that for monomethylhydrazine. At the maxima, the enthalpies were around 14 and 6 J meq^{-1} respectively, and the differences in energies of adsorption at the maxima were about 8 J meq^{-1}. Subsequent adsorption beyond the maxima was less energetic, and the energy evolved decreased to a relatively constant value of 5.0 and 2.0 J meq^{-1} for hydrazine and monomethylhydrazine, respectively.

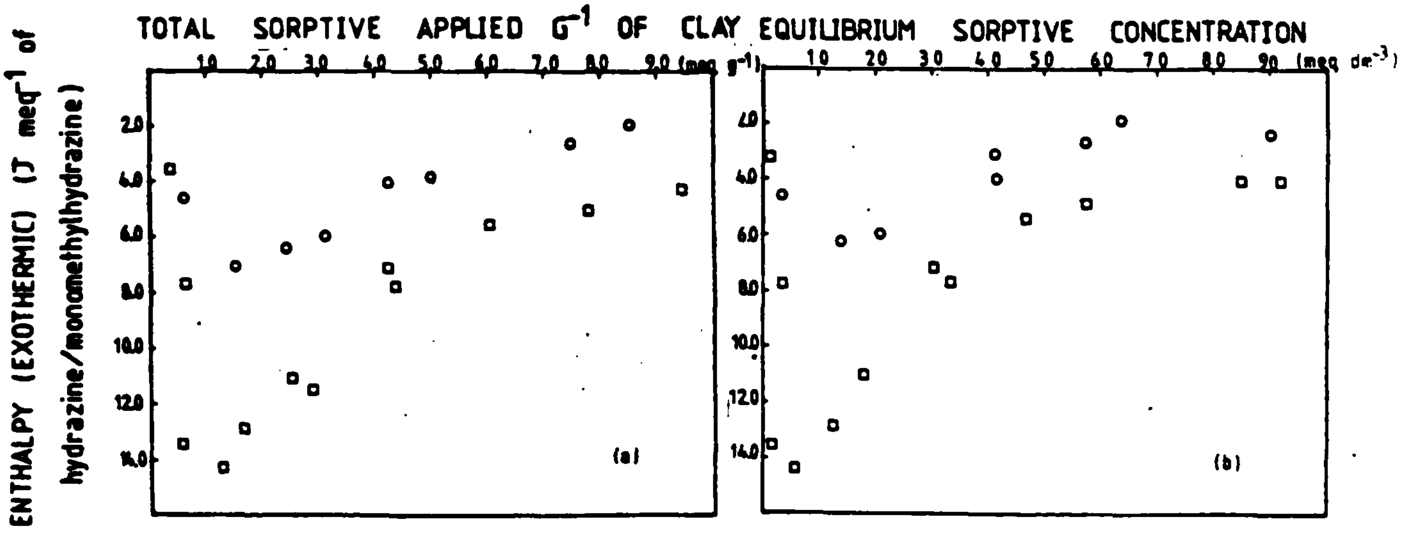


Figure 15. Enthalpy values for sorption of hydrazine and of MMH by hydroxy-aluminium-montmorillonite preparations

4.4.12 Studies of the exchangeability of aluminium in Al^{3+}-montmorillonite and -kaolinite at different pH values

The exchangeability of aluminium in Al^{3+}-montmorillonite preparations of different pH values was examined in order to understand the role of the cation in the exchange mechanisms involved during adsorption. The results are summarised in Table 9.

The Al^{3+}-montmorillonite suspension of pH 4.0 had a supernatant concentration of Al^{3+} of 70 μeq g^{-1}, and a further 148 μeq g^{-1} was desorbed by a 0.1$\underline{\underline{M}}$ NaCl solution. Following this, three washings using 1.0$\underline{\underline{M}}$ NaCl solution desorbed antoher 765 μeq g^{-1} of Al^{3+}. The amount of Al^{3+} desorbed totalled 983 μeq g^{-1}, equivalent to the sodium exchange capacity of the montmorillonite preparation. The sodium exchange capacity of this pH 4 suspension had been determined, using a ^{22}Na-labelled 1.0$\underline{\underline{M}}$ NaCl solution, to be 1060 μeq g^{-1}. Further repeated extractions, using 1.0$\underline{\underline{M}}$ NaCl solution in 1.0$\underline{\underline{M}}$ HCl acid resulted in the extraction of a total of 754 μeq g^{-1} of Al^{3+} from the clay lattice structure.

The hydroxy-aluminium-montmorillonite suspension of pH 8.0 had no detectable amount of Al^{3+} in the supernatant. Washing with water or 0.1$\underline{\underline{M}}$ NaCl solution did not desorb any Al^{3+}, and after three extractions using 0.1$\underline{\underline{M}}$ NaCl solution, only 58 μeq g^{-1} of Al^{3+} was desorbed. The Al^{3+} that was exchangeable had become fixed in the clay at this pH. The concentration of NaCl and the acidity of the extraction media were then raised to 1.0$\underline{\underline{M}}$ NaCl and 0.1$\underline{\underline{M}}$ HCl acid, and then 930 μeq g^{-1} of Al^{3+} was extracted immediately. Two additional separate washes using this acid sodium chloride solution extracted another 1270 μeq g^{-1}, and 1020 μeq g^{-1}, of Al^{3+} from the clay lattice structure.

The pH of the hydroxy-aluminium-montmorillonite was raised to 10.0 in another preparation. The amount of Al^{3+} in the supernatant of this suspension of pH 10 was 86 μeq g^{-1}. When washed with 0.1$\underline{\underline{M}}$ NaCl solution, this preparation immediately released another 871 μeq g^{-1} of Al^{3+}. A second extraction with 0.1$\underline{\underline{M}}$ NaCl solution released another 95 μeq g^{-1} of Al^{3+}. The total amount of Al^{3+} released from all these extractions was 1052 μeq g^{-1} of Al^{3+}, equivalent to the total exchangeable Al^{3+} in the Al^{3+}-montmorillonite.

The same effects of pH were also observed in the Al^{3+}-kaolinite suspensions. The Al^{3+}-kaolinite suspension of pH 4.0 had a supernatant Al^{3+} concentration of 31.4 μeq g^{-1}, and washing with a 0.1$\underline{\underline{M}}$ NaCl solution desorbed 25.7 μeq g^{-1} of Al^{3+}. Extracting three times with 1.0$\underline{\underline{M}}$ NaCl solution resulted in the desorption of antoher 47.9 μeq g^{-1} of Al^{3+}. Thus, the total amount of exchangeable Al^{3+} was 105 μeq g^{-1}. On extraction with 1.0M NaCl solution in 0.1M HCl acid, decreasing additional amounts of Al^{3+} were detected in the supernatants of successive washes. No detectable Al^{3+} was extracted from the hydroxy-aluminium-kaolinite suspension of pH 8.0 when the suspension was washed with 0.1M or 1.0M NaCl solutions. On washing with the acidified 0.1M NaCl solution, however, 130 μeq g^{-1} of Al^{3+} was extracted in the first wash and two subsequent washes again extracted successively less Al^{3+} from the clay lattice structure. These values were 60 μeq g^{-1} and 30 μeq g^{-1} for the first and second subsequent washes, respectively. The exchangeable Al^{3+} ions in the Al^{3+}-kaolinite suspension was also hydrolysed to hydroxy-aluminium polymers and fixed on the clay surfaces. These were only extracted with acidified sodium chloride solution.

4.4.13 Studies of the exchange mechanism in the adsorption of hydrazine and of monomethylhydrazine by Al^{3+}-montmorillonite and hydroxy-aluminium-montmorillonite at pH 8

Two approaches were used in these studies of the exchange mechanism involved in the adsorption of hydrazines by the Al^{3+}-montmorillonite suspensions of different pH values. In the first, the amounts of hydrazine adsorbed by the Al^{3+}-montmorillonite and the amounts of Al^{3+} desorbed were measured in order to determine whether the adsorption of hydrazine involved an exchange of Al^{3+} by hydrazine. In the second approach, labelled sodium hydroxide solution was used in the preparation of hydroxy-aluminium-montmorillonite suspensions of pH 8. Determination of the Na^+ left on the clay after the adsorption of hydrazine would indicate the extent of hydrazinium/Na^+ ion exchange during adsorption. Labelled NaCl solutions were also used to desorb the hydrazine from Al^{3+}-montmorillonite and hydroxy-aluminium-montmorillonite complexes when investigating the extent of hydrazinium/Na^+ ions exchange during desorption.

The Al^{3+}-montmorillonite suspension of pH 4 adsorbed 150 μeq g^{-1} of hydrazine, but the amount of aluminium in the supernatant was only 90 μeq g^{-1} (Table 11). Therefore, the adsorption of hydrazine under these conditions did not involve, to any significant extent, the exchange of Al^{3+} in the clay. Sodium chloride solution (0.1M) desorbed only 56 μeq g^{-1} of hydrazine and 130 μeq g^{-1} of Al^{3+}. This amount of desorbed Al^{3+} was the same as that found for an uninteracted Al^{3+} montmorillonite suspension at pH 4. Adsorption of hydrazine had caused the hydrolysis of some of the exchangeable Al^{3+}, but the amount of hydrazine sorbed was not sufficient to cause the fixation of all of the exchangeable Al^{3+} in the interlayer spaces of the clay.

Table 11. Amounts of hydrazine and aluminium exchanged during the adsorption and desorption of hydrazine by Al^{3+}-montmorillonite and hydroxy-aluminium-montmorillonite preparations

Clay Preparations	During adsorption of hydrazine		During desorption of hydrazine using 0.1 M NaCl solution	
	Amount of hydrazine adsorbed (μeq g^{-1})	Amount of Al^{+++} desorbed (μeq g^{-1})	Amount of hydrazine desorbed (μeq g^{-1})	Amount of Al^{++} desorbed (μeq g^{-1})
Al^{+++}-montmorillonite interacted with:				
pH 4 hydrazine	150	90	56	130
pH 8 hydrazine	753	N. D.	N. D.	N.D.
hydroxy-aluminium-montmorillonite of:				
pH 8	1500	N.D.	580	N.D.
pH 10	225	232	-	-

Table 12. Effects of different desorption media on the amounts of aluminium which can be removed from Al^{3+}-montmorillonite and -kaolinite (AlM and AlK) and hydroxy-aluminium-montmorillonite and -kaolinite (AlOHM and AlOHK) at different pH values

Desorption media	Amounts of Al^{+++} detected in the supernatants (μeq g^{-1})				
	AlM	AlOHM		AlK	AlOHK
	pH 4	pH 8	pH 10	pH 4	pH 8
Water	70	N. D.	86	31.4	N. D.
0.1 M NaCl	148	N. D.	-	25.7	N. D.
1.0 M NaCl	571	53	871	39.5	N. D.
	161	5	95	8.4	N. D.
	33	N. D.	N. D.	N. D.	N. D.
Total Al^{+++} extracted	983	58	1052	105	-
1.0 M NaCl in 0.1 M HCl	608	930	-	75	130
	146	1270	-	30	60
	N. D.	1020	-	20	30
	-	131	-	20	-

N. D.: non-detectable
- : not determined

No aluminium was exchanged during the adsorption of hydrazine by Al^{3+}- and hydroxy-aluminium-montmorillonite of pH 8, and none was removed on washing with 0.1M labelled NaCl solution (Table 12). Hydrolysis of the exchangeable Al^{3+} had rendered these ions non-exchangeable. Determination of the Na^{+}-exchange capacity of the hydroxy-aluminium-montmorillonite at pH 8, by using ^{22}Na-labelled 0.105M NaOH solution, gave a value of 1250 $\mu eq\ g^{-1}$ of Na^{+}. This value indicated an increase in the exchange capacity of the clay of about 200 $\mu eq\ g^{-1}$. The pH dependent charges of the hydroxy-aluminium polymers formed from the hydrolysis of the exchangeable Al^{3+} could have contributed to this increase in negative charges on the clay at this pH value.

Treatment of the Al^{3+}-montmorillonite that was interacted with a hydrazine solution of pH 8.0 with ^{22}Na-labelled 0.01M NaCl solution removed 304 $\mu eq\ g^{-1}$ of hydrazine, and 375 $\mu eq\ g^{-1}$ of Na^{+} was adsorbed by the clay. Washing of another sample of the clay-hydrazine complex with 0.1M NaCl solution (^{22}Na-labelled) desorbed a total of 698 $\mu eq\ g^{-1}$ of Na^{+} ions. The adsorbed hydrazine was displaced by the Na^{+} from the added labelled sodium chloride solution.

Adsorption of hydrazine by the hydroxy-aluminium montmorillonite of pH 8 caused the displacement of the Na^{+} ions already on the hydroxy-montmorillonite and only 50 $\mu eq\ g^{-1}$ of Na^{+} ions was left on the montmorillonite. Treatment of this hydrazine sorbed complex with labelled 0.01M NaCl solution raised the amount of Na^{+} on the clay to 472 $\mu eq\ g^{-1}$ and desorbed 466 eq g^{-1} of hydrazine. Thus, the desorption of hydrazine had involved an exchange mechanism in which the Na^{+} ions replaced the $N_2H_5^{+}$ ions. On using labelled 0.1M NaCl solution for washing, the total amount of hydrazine desorbed was 722 $\mu eq\ g^{-1}$ and the amount of Na^{+} adsorbed (900 $\mu eq\ g^{-1}$) was higher than the amount of hydrazine desorbed.

Treatment of the Al^{3+}-montmorillonite that was interacted with a monomethylhydrazine solution of pH 8.0 with labelled 0.01M NaCl solution resulted in the desorption of 509 $\mu eq\ g^{-1}$ of monomethylhydrazine from the complex and the adsorption of 440 $\mu eq\ g^{-1}$ of Na^{+}. Sodium chloride solution (^{22}Na-labelled) of a higher concentration (0.1M) was used in the washing of another sample of the clay-monomethylhydrazine complex, and a total of 1000 $\mu eq\ g^{-1}$ of sorbate was removed while 1520 $\mu eq\ g^{-1}$ of Na^{+} was left on the clay. Therefore, 1000 $\mu eq\ g^{-1}$ of monomethylhydrazine was displaced by Na^{+} and negative charges in excess of the exchange capacity of the Al^{3+}-montmorillonite (1000 $\mu eq\ g^{-1}$) were created on the clay on removal of the sorbate.

Washing of the hydroxy-aluminium-montmorillonite monomethylhydrazine complex of pH 8.0 with 0.01M NaCl solution removed 658 μeq g^{-1} of monomethylhydrazine and 440 μeq g^{-1} of Na^+ ions were adsorbed. On using labelled 0.1M NaCl solution for washing another sample of this complex, 1130 μeq g^{-1} of monomethylhydrazine was removed and 1490 μeq g^{-1} of Na^+ ions were adsorbed by the clay. In this instance, as in the case with monomethylhydrazine interacted Al^{3+}-montmorillonite, the sodium exchange capacity of the treated hydroxy-complex was 490 μeq g^{-1} greater than that of the original Al^{3+}-montmorillonite.

4.5 Discussion

4.5.1 Effect of pH on the adsorption of hydrazines by different valence cation-exchanged montmorillonites and kaolinites

The results of investigations described already demonstrate that the determining characteristics in hydrazine sorption by a particular clay are the pH values of the sorptive solution and the exchangeable cation held by the clay. The behaviour of the systems were examined at pH 4 and 8 since these are the extremes of pH that may normally be expected to be found in soils.

The exchangeable cations examined were the monovalent alkali Na^+ ion, the divalent alkali-earth Ca^{2+} ion, the trivalent metal Fe^{3+} ion, and the Al^{3+} ion. These represent a range of the types of the cations that are normally found in soil systems. Furthermore, the preliminary studies of the interactions between these systems and hydrazine had determined that, in the absence of oxygen, the principal interaction is one of adsorption rather than degradation.

More intensive investigations were carried out with homoionically-exchanged montmorillonites than with similar exchanged kaolinites because more hydrazine was sorbed per unit mass of the montmorillonite than by the kaolinite preparations. The responses of sorption to pH were found to be most pronounced when the exchangeable cations were the monovalent Na^+, trivalent Fe^{3+} and Al^{3+}, and the responses were not marked for Ca^{2+}. Thus, sorption isotherms were obtained for interactions between Na^+- and Al^{3+}-kaolinite preparations and hydrazine to examine if the same pattern of response to pH changes was obtained.

Adsorption at pH 4. - A sorptive solution at pH 4 consists of the hydrazinium ion ($N_2H_5^+$ or $CH_3NHNH_3^+$) since the pK_a of hydrazine and monomethylhydrazine are 8.10 and 7.85 at 20°C, respectively. The strength with which the exchangeable cations are held by the clay examined is in the increasing order of $Na^+ < Ca^{2+} < Al^{3+} < Fe^{3+}$. Consequently, at pH 4 the adsorption of hydrazine by Na^+-montmorillonite was highest amongst the systems examined because the adsorption involved a simple exchange of Na^+ ions for hydrazinium ions. In the cases of Ca^{2+}-, Fe^{3+}-, and Al^{3+}-montmorillonite, the replacement of the exchangeable ion is very difficult as it would involve two or three hydrazinium ions, depending on the valence of the cation. Therefore, the adsorption of hydrazine by the Ca^{2+}-, Fe^{3+}- and Al^{3+}-clays at pH 4 was significantly lower than that by Na^+-montmorillonite.

The polarizing and co-ordinating powers of the multivalent cations are greater than that of the monovalent Na^+ ion, and these powers are in the decreasing order of $Fe^{3+} > Al^{3+} > Ca^{2+} > Na^+$, as indicated by the pK_a in the increasing order of $2.7 < 5.01 < 12.7 < 14.6$. In the cases of the multivalent cations, there are other possible mechanisms of adsorption of hydrazine, such as through replacement of water by hydrazine in the hydration shell of the Ca^{2+}, Al^{3+} or Fe^{3+} ions, or the exchange of hydrazinium ions with a proton from a molecule of water of hydration around these polarizing ions. The adsorption of hydrazine by Al^{3+}-montmorillonite at pH 4 was 148 $\mu eq\ g^{-1}$, which is lower than that for Na^+- but higher than that for Ca^{2+}-montmorillonite (70 $\mu eq\ g^{-1}$) due to its higher polarizing power. Thus, an exchange reaction such as that which follows:

$$Al(H_2O)_6^{3+} + N_2H_5^+ \rightleftharpoons (Al(H_2O)_5(OH)^-(N_2H_5^+))^{3+} + H^+$$

could readily occur with Al^{3+}.

In the adsorption of hydrazine by Fe^{3+}-montmorillonite no maximum adsorption was observed at pH 4, even at an equilibrium concentration of 5.0 meq dm^{-3} or more, or the point at which maximum adsorption was observed for the other exchanged clays. The interaction of hydrazine with Fe^{3+}-montmorillonite was complicated by the fact that under anaerobic conditions, Fe^{3+} ions can be reduced to Fe^{2+} ions. In the interaction of geothite with hydrazine at pH 4, Fe^{2+} ions were eluted through the membrane of the stirred cell in a CFSC experiment (Section 4.7.3). The Fe^{2+} ion was found to form a soluble complex with hydrazine at this low pH. Thus, during the interaction of hydrazine with the ferric-clay, no maximum adsorption was obtained due to the possible "dissolution" of the Fe^{3+} ions as Fe^{2+} complex of hydrazine.

Cation exchange would also be the predominant mechanism in the adsorption of hydrazine by Na^+ -kaolinite at pH 4. The CEC of this kaolinite (100 μeq g^{-1}) preparation was about ten times less than that of Na^+ -montmorillonite, and its maximum adsorption was also less by the same order of magnitude. However, the amount of hydrazine adsorbed per meq of Na^+ was about twice as much for kaolinite (1200 μeq meq $^{-1}$) as for montmorillonite (650 μeq meq^{-1}). Many of the cation exchange sites of kaolinite are edge sites. These sites are therefore more accessible to the sorptive molecules than the exchange sites of montmorillonite which are mainly in the interlayer spaces of this expanding clay. The adsorption of hydrazine by Al^{3+} -kaolinite at this pH was very low, but again the amount of hydrazine adsorbed per meq of Al^{3+} was nearly thrice as much for kaolinite (420 μeq meq^{-1}) than for montmorillonite (150 $μeq^{-1}$) showing the significance of accessibility of the Al^{3+} ions in the adsorption of hydrazine at this pH.

Adsorption with sorptive solution of pH 8. When the pH value of the sorptive solution was raised from 4.0 to 8.0, the maximum adsorption of hydrazine resulting from the interaction of Na^+ -montmorillonite with hydrazine solution decreased significantly. At pH 8.0, the concentration of hydrazinium ions present in the sorptive solution would be the same as that of the hydrazine in the unprotonated form. Because cation exchange is the major mechanism of adsorption by the monovalent cation, a significant decrease in hydrazine sorption was observed as the pH was raised to 8. In the case of Ca^{2+} -montmorillonite, the maximum sorption of hydrazine at pH 8 (95 μeq g^{-1}) was in the same order as that at pH 4 (70 μeq g^{-1}). Thus, cation exchange was not the predominant adsorption mechanism in this instance and hydrolysis of and coordination to the cation increasingly contribute to the adsorption of the hydrazine.

In the cases of Fe^{3+} and Al^{3+} -montmorillonite, the ease of hydrolysis of the exchangeable cations contributed to the adsorption of the basic hydrazine sorptive. The supply of hydrazinium ions in a hydrazine solution of pH 8 is significant and this proportion will be even greater near the montmorillonite surface where the pH would be substantially lower than in the bulk solution due to partial dissociation of hydroxyl groups of the water molecules co-ordinated to these Fe^{3+} and Al^{3+} ions. Hence, the adsorption of these hydrazinium ions could involve an exchange with H^+ ions from the molecules of water of hydration around these highly polarising cations. The adsorption of hydrazine by these two exchanged clays was found to be similar to the CEC of these montmorillonites indicating that this is the predominant adsorption mechanism and the exchangeable cations were almost completely hydrolysed to the neutral hydroxides.

In the interactions of Al^{3+} -montmorillonite with hydrazine solutions of pH values of 8 and 10, similar values of maximum adsorption as those of Fe^{3+}clay were obtained. However, in both cases, the pH of the Al^{3+} -montmorillonite suspension rose rapidly to 8.0 even before the equilibrium sorptive concentration had reached 2.0 meq dm^{-3}, and the maximum adsorption was obtained. This more rapid rise with increasing equilibrium concentration in pH of the Al^{3+} -montmorillonite suspension, compared with that of the Fe^{3+} -montmorillonite suspension, reflected the greater acidity of the Fe^{3+} ion compared with the Al^{3+} ion. When excess hydrazine was present, such that all the exchangeable cations were hydrolyzed to the neutrally charged species, the final adsorption of hydrazine in both montmorillonites was found to be close to the CEC value of the clays.

Further investigations carried out with Al^{3+} -montmorillonite confirmed this mechanism of adsorption. No Al^{3+} was exchanged in the adsorption of hydrazine. The hydrolysis of the exchangeable Al^{3+} caused these to be fixed in the clay such that washing the adsorption complex with 0.1M sodium chloride solution did not result in any Al^{3+} being desorbed, though significant amounts of the sorbate, 700 μeq g^{-1}, was desorbed. The desorption of hydrazine using labelled sodium chloride solution (0.01M) showed that hydrazine was desorbed through replacement by the Na^{+} ions. On washing the complex with 0.1M sodium chloride solution (instead of 0.01M, the Ns^{+} ions replaced the hydrazine and the amount adsorbed was similar to the CEC of the clay. However, the amount of Na^{+} adsorbed was 20 μeq g^{-1} more than the hydrazine desorbed. The washing of the complex with sodium chloride solution of 0.1M had therefore further hydrolysed the Al^{3+}.

In the desorption of hydrazine from Al^{3+} -montmorillonite interacted with hydrazine solution of pH 8 or 10 with sodium chloride solution (0.1M), almost 80% of the sorbate was desorbed each time. However, in the case of the Fe^{+++} -montmorillonite, the proportion of sorbate desorbed was from 50 to 65%, depending on the amount of adsorption. The proportion desorbed was higher as the level of adsorption increased. Thus, the interaction of Fe^{3+} -montmorillonite with hydrazine at high pH might involve the reduction of a certain fraction of Fe^{3+} at the clay surface by the hydrazine. This reduction would involve the oxidation of the hydrazine and hence its degradation. Therefore, as more hydrazine was observed to have interacted with the clay, the ratio of the amount of hydrazine that was degraded to the total amount adsorbed would be less. Hence, as the amount of hydrazine that was interacted increased, the ratio of the amount of hydrazine desorbed to the total amount interacted would increase.

Further effects of pH studied were centred on clay systems in which the hydroxy polymers have already been formed. Thus, the Fe^{3+} - and Al^{3+} - montmorillonite and Al^{3+} -kaolinite studied were adjusted to pH 8 and 10 and equilibrated overnight prior to adsorption.

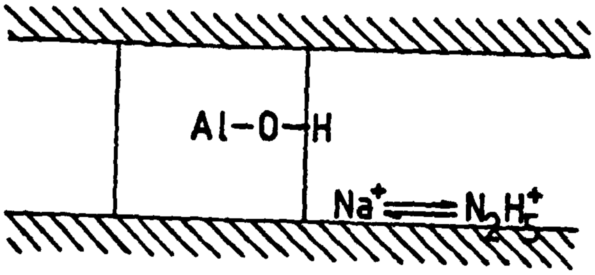
4.5.2 Adsorption of hydrazine and of monomethylydrazine by hydroxy-montmorillonite and -kaolinite preparations

The Fe^{3+} - and Al^{3+} - montmorillonite systems had shown a great propensity in forming insoluble hydrous oxides within a certain high pH range. These hydrous oxides can form either as discrete precipitates or as "films" on the clay surface. The formation of "films" will be favoured when the metal ions are already present on the colloid surfaces as the exchangeable cations. The results have shown that even more extensive sorption, beyond that of the CEC, occurred when the Fe^{3+} - or Al^{3+} - clays were equilibrated overnight.

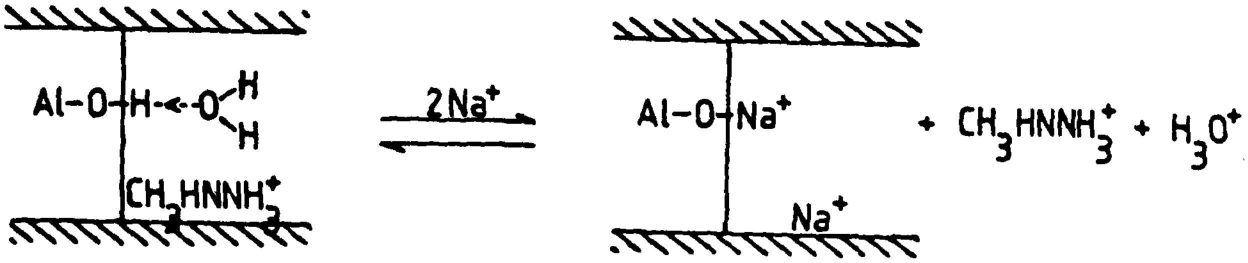
Maximum adsorption of hydrazine was obtained on the hydroxy-aluminium-montmorillonite preparations of pH 8 only when very high concentration sorptive solutions were used. As the CEC of the hydroxy-aluminium-kaolinite was lower than that of montmorillonite, the high concentration was not necessary, but sorption was also far above the CEC of the clay. The adsorption of hydrazine by the hydroxy-ferric-montmorillonite of pH 8, for an equilibrium sorptive solution concentration of 8.0 meq dm^{-3}, was already at the CEC value, though the adsorption isotherm did not have a plateau value for the range of sorptive concentration used. Further investigations into the mechanism of hydrazine sorption by hydroxymontmorillonite were carried out on the Al^{3+} - montmorillonite rather than the Fe^{3+} - montmorillonite. This was done because Al^{3+} ions do not catalyse the degradation of hydrazine while there is a possibility that the exchangeable Fe^{3+} ions do. Hence, the results obtained during the interactions of hydrazine with the clay cannot be simply assigned to adsorption process only.

Mechanisms of adsorption of hydrazine and monomethylhydrazine by hydroxy-aluminium-montmorillonite of pH 8 In a solution containing Al^{3+} ions with a molar ratio of hydroxide to Al^{3+} of 3.0 to 3.3, all of the Al^{3+} ions were found to be hydrolysed to neutrally charged $Al(OH)_{3n}$ species (Hsu and Bates, 1964). In the hydroxy-montmorillonite or -kaolinite preparations of pH 8, the molar ratio of added hydroxide to exchangeable Al^{3+} in the clay was 4.7 and 3.9, respectively. Hence, at the colloid surface, the exchangeable Al^{3+} would be hydrolysed to neutral hydroxy-aluminium species. Evidence from the exchange studies (and later X-ray results) showed that the hydrolysis of the Al^{3+} caused the Al^{3+} to become non-exchangeable when washed with $1.0\underline{\underline{M}}$ sodium chloride solution. The hydroxyl groups of the hydroxy complexes were also found to contribute to the negative charges on the clay when the hydroxy-montmorillonite was prepared by labelled sodium hydroxide solution and the Na^+ exchange capacity was 200 μeq g^{-1} in excess of the CEC of unhydrolysed clay (1000 μeq g^{-1}).

These results therefore confirmed that the exchange capacity of the hydroxy-aluminium-montmorillonite of pH 8 was balanced by Na^+ ions and the adsorption of hydrazine involved a replacement of these Na^+ ions by the hydrazinium ions to the extent of the exchange capacity. A schematic representation is shown below



The presence of the hydroxy-aluminium polymers had contributed to the enhanced adsorption of the hydrazine. Additional attraction between the lone pair electron of the hydrazine molecule and the polarized hydrogen atom of the hydroxyls on the aluminium hydroxide polymer could lead to stronger bonding of the hydrazine sorbate. This phenomenon was illustrated more clearly in the case of the adsorption of monomethylhydrazine by both Al^{3+} - exchanged montmorillonite and hydroxy-aluminium-montmorillonite at pH 8 where negative charges in excess of the exchange capacity were produced. The basicity of monomethylhydrazine in bulk solution was similar to that of hydrazine (pK_a of monomethylhydrazine is 7.85 at 25°C). However, its basicity would be enhanced when it was adsorbed in the interlayer spaces of montmorillonite. Due to its hydrophobic character, more molecules were displaced from the interlayer spaces causing the residual water to be more acidic. Consequently, the desorption of the monomethylhydrazine by labelled NaCl solution resulted in the further hydrolysis of some of the $Al(OH)_3$ causing more Na^+ ions (about 500 μeq g^{-1}) than the CEC to be adsorbed. This process is schematically represented below.



Assuming that the structure of the hydrolysed aluminium was that of gibbsite, the total area covered by the hydroxy polymer would be about 60 m^2 g^{-1} (calculated from crystallographic data of gibbsite structure). Thus, the total area covered by the maximum amount of adsorbed hydrazine and monomethylhydrazine, including that of the hydroxy species, was ca. 521 m^2 g^{-1}, and 643 m^2 g^{-1} respectively. A comparison of these values with the specific surface area of Na^+ - exchanged montmorillonite (725 m^2 g^{-1}), gave a total surface coverage of 72% and 90%, indicating that the adsorbed hydrazine and monomethylhydrazine molecules were lying as a single layer on the surface of the montmorillonite. This was further substantiated by X-ray diffractometry measurements of the c-spacing which showed no substantial increase of the c-spacing other than the possibility of the single layer sorbate (Section 4.61). Similarly, in hydroxy-aluminium-kaolinite, the coverage by the hydrazine molecules (30.5 m^2 g^{-1}) compared to the specific surface area of sodium- and ferric-exchanged kaolinite (29 and 44 m^2 g^{-1}), Yormah, 1981) indicated that the sorbate molecules were lying in a single layer on the clay surface.

The changes in the enthalpies during the adsorption of hydrazine and of monomethylhydrazine by this hydroxy-aluminium-montmorillonite of pH 8 showed that the enthalpy changes went through maxima of 14 J meq^{-1} and 6 J meq^{-1}, corresponding to an adsorption of 700 to 800 μeq g^{-1}, and 1000 μeq g^{-1} of hydrazine and monomethylhydrazine, respectively. Subsequent adsorption of both sorptives was less energetic and the enthalpies evolved decreased to a value of 5.05 and 2.0 J meq^{-1} for hydrazine and monomethylhydrazine sorption, respectively. The adsorption of monomethylhydrazine with its bulky group required more energy than hydrazine. The adsorption isotherm of monomethylhydrazine by Al^{3+} - montmorillonite showed that when the suspension had reached a certain alkalinity (about pH 6), sufficient hydrolysis of the exchangeable Al^{3+} had taken place leading to expansion of the interlayer spaces to an extent that a sudden increase in adsorption was observed. The adsorption of hydrazine did not require such an expansion as it was a smaller molecule and therefore had a greater ability to penetrate to the interlayer binding sites. The adsorption by hydroxy-aluminium-montmorillonite did not show such a sudden increase because the clay had already been equilibrated at pH 8 overnight. Thus, any expansion would have occurred prior to adsorption.

The predominant mechanism of adsorption of hydrazine and of monomethylhydrazine by hydroxy-aluminium-montmorillonite of pH 8, up to the extent of the CEC, was cation exchange of hydrazinium ions and Na^+ ions. Beyond the exchange capacity of the clay the mechanisms of adsorption of hydrazines are:

(1) the interaction of the strongly basic hydrazine with the hydroxide surface according to:

$$\text{Al-OH} + N_2H_4 \rightleftharpoons \text{Al-O}^- + N_2H_5^+ ,$$

(2) the action of Van der Waals forces between the sorbate and clay surface and that of the sorbate and sorbate molecules,

(3) hydrogen bonding between protonated and neutral species,

(4) the role of hydrazine or monomethylhydrazine as a monodentate, or bridging, ligand between aluminium sites on the gibbsite surface.

These complexes are further characterised by infra-red analysis and differential thermal analysis (Sections 4.6.2 and 4.6.4)

4.5.3 Effects of pH on the adsorption of hydrazine by hydroxy-montmorillonite

The results obtained when hydroxy-Fe^{3+} - and hydroxy- Al^{3+} - montmorillonite preparations of pH 10 were used in the adsorption of hydrazine of pH 10 demonstrate that the hydroxy-complexes are in fact only stable within a certain pH range. Thus, the pH of the system during adsorption is a determining factor in the amount of hydrazine adsorbed by the hydroxy-Fe^{3+} - and hydroxy-Al^{3+} - montmorillonite. Maximum adsorption occurred only when the pH of the bulk suspension was adjusted such that the extent of formation of neutral hydroxy species at the surface to the clay was maximum, and not when the pH was too high to cause the formation of negative hydroxy species of the exchangeable cation.

In the case of the hydroxy-ferric-montmorillonite suspension of pH value of 8, that was equilibrated overnight, complete hydrolysis of the exchangeable Fe^{3+} had occurred. Thus, a partial layer of hydrous ferric oxide was formed. The adsorption by the hydroxy-ferric-montmorillonite was therefore high and reached the CEC value, though within the 0 to 9 meq dm^{-3} sorptive concentration range adsorption did not reach a constant value. The formation of $Fe(OH)_4^-$ is significant only at pH values > 8.5; therefore the formation of this negatively charged species was still not significant when the pH of the hydroxy-montmorillonite was 8. But, when the pH of the hydroxy-ferric-montmorillonite suspension was 10, or in the case of adjusting the pH values of the suspension from 8 to 10, the alkalinity became sufficiently high such that the formation of the negative hydroxy species, $Fe(OH)_4^-$, caused the "dissolution" of the exchangeable Fe^{3+} from the clay. Thus, when the suspension of pH value 8 was adjusted to a pH value of 10, hydrazine was desorbed from the hydroxy-ferric-montmorillonite suspension. Also, the hydroxy-ferric-montmorillonite suspension of pH 10 adsorbed less hydrazine than that of pH 8 for the same equilibrium sorptive concentration.

The hydrazine solution of pH 10 would also consist essentially of the unprotonated species. When the hydroxy-aluminium-montmorillonite suspension was equilibrated at pH 10, the pH had risen to such an extent in the interlayer spaces that the exchangeable Al^{+++} would also form the negative hydroxy species, $Al(OH)_4^-$. This had also led to the great decrease in the amount of hydrazine adsorbed by the suspension of pH value of 10, Al^{+++} was also detected in the eluate fraction collected during the washing-in of the sorptive solution into the CFSC.

4.6. Characterisation of Hydroxy-Aluminium-Montmorillonite and of its Hydrazine and Monomethylhydrazine Sorption Complexes

4.6.1. X-Ray diffractometry

Table 13 summarises the results of the c-spacings from the X-ray diffractograms of the Al^{3+} -montmorillonite samples and their hydrazine and monomethylhydrazine complexes after different treatments. The wet hydroxy-aluminium-montmorillonite that had interacted with hydrazine solution had c-spacing of 2.025 nm, and the peak was very diffuse. That which interacted with monomethylhydrazine solution at pH 8 had a c-spacing of 1.76 nm despite the fact that a greater amount of monomethylhydrazine than hydrazine was adsorbed and that monomethylhydrazine is a larger molecule. The strong hydrophilic character of the hydrazine had led to more water being adsorbed by this complex than by the monomethylhydrazine complex.

Hydroxy-aluminium-montmorillonite can be considered as an intermediate between two extreme "end-members", smectite and chlorite. The similarities in X-ray diffractograms depend on the extent of interlayer formation. Laboratory preparations of hydroxy-aluminium-montmorillonite have thus been found to have a range of c-spacings from 1.23 to 1.67 nm, depending on the conditions of preparation. The hydrolysis of exchangeable Al^{3+}, up to the CEC, in Al^{3+}-montmorillonite by sodium hydroxide, hydrazine, and monomethylhydrazine at pH 8 did not result in a significant expansion of c-spacings. The c-spacings of Al^{3+}-montmorillonite and that interacted with the hydrazine and monomethylhydrazine solutions at pH 8, collapsed to 1.2 - 1.3 nm on air-drying.

The observed c-spacings for hydroxy-aluminium-montmorillonite complexes prepared at pH 7.5 and pH 9.0 by Keren, et al. (1977), were 1.38 and 1.31 nm, respectively. These values were higher than those obtained in this work, but Keren, et al., used 16000μeq g^{-1} of Al^{3+}, whereas only the exchangeable amount of cation was used in this work.

The response to heat treatment of potassium exchanged samples is the most useful X-ray diffraction criterion in recognising the presence of hydroxy interlayered montmorillonite (Barnishel, 1977). Changes in the c-spacing of these K^+-exchanged samples when heated from 25°C to 110°C, 300°C, and 500°C indicate the degree of stability of the hydroxy-aluminium polymers. The higher the temperature required to collapse or partially collapse the peak to 10 Å, the more stable are the interlayer polymers. The magnitude of the shift in the c-spacing of the (001) reflection upon potassium saturation and heating to 550°C is also a measure of the degree of filling of the interlayers, and small changes of the spacing will indicate a higher level of interlayer hydroxy-aluminium polymer formation.

In this study, K^+-exchange was not carried out because the changes in c-spacing were not significant on the hydroxy-aluminium samples. However, on oven-drying of the straight Al^{3+}-exchanged montmorillonite sample and that interacted with hydrazine solution at pH 8, the c-spacings collapsed to 1.1 - 1.13 nm. No significant changes in c-spacings were observed for the other hydroxy-aluminium samples that were prepared by equilibrating overnight at pH 8. Thus, the degrees of stabilities of any hydroxy-aluminium polymers present in the Al^{3+}-montmorillonite sample, and those formed from hydrolysis by hydrazine solution , pH 8, of the exchangeable Al^{3+} in the Al^{3+}-montmorillonite, were less than those that were allowed to equilibrate overnight at pH 8.

For a synthetic hydroxy-aluminium-montmorillonite, prepared from a solution of added hydroxide to Al^{3+}, molar ratio of 1.5, the extent of glycerol solvation in the samples depended on the extent of interlayer formation. With a high level of application of aluminium (more than 16000 μeq g^{-1} clay), a 2.3 nm c-spacing corresponding to two layers of glycerol was observed. With a lesser amount of aluminium per gram of clay applied, the c-spacing observed decreased. When 4000 ueq aluminium g^{-1} of clay was applied, a c-spacing of 1.9 nm was observed, and with no aluminium applied a c-spacing of 1.84 nm was seen on glycerol solvation. However, the presence of certain chloritic intergrades have also been found to impede the expansion of montmorillonite in glycerol. The vapour sorption of ethylene glycol by montmorillonite was not affected by intergrade formation and c-spacing swells to 1.7 nm.

The ethylene glycol solvation of the oven-dried hydroxy-aluminium complexes resulted in an expansion of c-spacing to 1.7 nm. When the same complex was interacted with monomethylhydrazine solution at pH 8, the c-spacing was only 1.61 nm. This decreased swelling could arise as the result of a more complete filling of the interlayer spaces by monomethylhydrazine (583 $m^2 g^{-1}$) than by the hydrazine (the coverage of hydrazine hydrate was only 461 m^2 g^{-1} for hydrazine). Hence, the replacement of water by ethylene glycol would be greater in the complex interacted with hydrazine solution than that with monomethylhydrazine solution at pH 8. However, in the case of the glycerol solvation, glycerol intercalated only in the case of the Al^{3+}-montmorillonite sample. Hydroxy polymers which were formed to some extent in all of the dried Al^{3+}-montmorillonite complexes will tend to hinder the movement of intercalating molecules in the interlayers. The larger size of the glycerol molecule probably further hindered its movement between the hydroxy polymers and thereby prevented its intercalation in most of these samples.

Table 13 Effects of various treatments on (001) spacings of Al^{3+}-montmorillonite (A1M) and the hydroxy complex (Al-OH-M); and their hydrazine and monomethylhydrazine (MMH) treated complexes

Clay Preparation	pH	Basal spacing (nm)				
		Wet	Air-dried	Oven-dried (110°C)	Exposed to	
					Ethylene Glycol	Glycerol
A1M	4	1.92	1.24	1.11	1.70	1.58
Hydrazine/A1M	4	1.92	1.26	1.13	1.70	1.29
Al-OH-M	8	1.84	1.22	1.24	1.70	1.29
Hydrazine/ Al-OH-M	8	2.05 (diffuse)	1.28	1.24	1.70	1.29
MMH/Al-OH-M	8	1.78	1.30	1.29	1.61	1.29

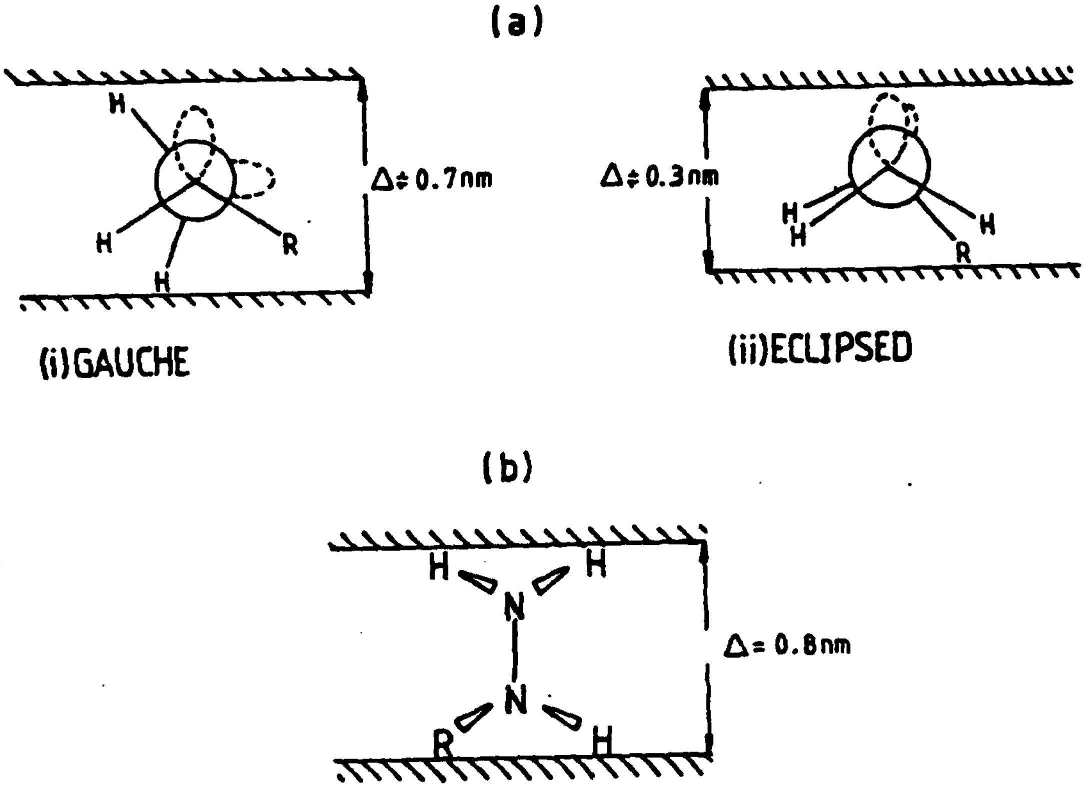


Figure 16 Hydrazine sorbate substances (R=H or CH$_3$) lying in interlayer spaces of Al^{3+}-montmorillonite (or the hydroxy complex) with:

(a) the N-N axis parallel to plane of the surface in gauche form (i) and in eclipsed form (ii); and

(b) the N-N axis perpendicular to plane of surface in gauche or eclipsed form.

Characterisation of the hydrazine and monomethylhydrazine solution phase adsorption complexes by XRD have shown that the c-spacings of the air-dried complexes of both Al^{3+}-montmorillonite and the hydroxy-clay were 1.2 - 1.3 nm. Assuming that the thickness of the clay interlayer when dried was 0.9 nm, the spacing occupied by the adsorbate was between 0.3 - 0.4 nm. The monomethylhydrazine molecule is a bulkier molecule than hydrazine and the Van der Waals radius of the methyl group is 0.2 nm. However, the methyl group can be keyed into the depressions on the surface of the clay once the monomethylhydrazine molecule has penetrated the interlayers. The c-spacing was therefore not significantly different from that of the hydrazine sorbed complexes. Using molecular models built to scale, the height of the hydrazine molecule lying with its N-N axis perpendicular to the plane of the surface or the clay in either gauche or eclipsed form would be 0.8 nm (Figure 16b). With the N-N axis parallel to the plane and its most favoured gauche conformation, the height of the molecule was 0.65 nm (Figure 16a (i)). However, in its eclipsed form (Figure 16a (ii)) the projected height of the molecule, using these Van der Waals radii, was 0.3 nm. Thus with the values for the air-dried complexes of 0.3 - 0.4 nm, most of the molecules would be lying with their N-N axes parallel to the plane and in the eclipsed conformation. The total surface coverages by the hydrazine and monomethylhydrazine molecules, calculated on the basis of the molecules lying with their N-N axes parallel to the surface, were 60 and 80 per cent, respectively. Many of the hydrazine molecules would lie end to end to each other with hydrogen bonding involving protonated and non-protonated hydrazines and water mlecules. Molecules of hydration, co-ordinated to the hydrazinium ions would also form a bridge between hydrazine and hydrazinium molecules.

4.6.2. Infra-red studies of hydroxy-aluminium-montmorillonite interacted with hydrazine and monomethylhydrazine

The adsorption of amines by various homoionically-exchanged montmorillonites have been extensively studied using infra-red analysis. The adsorption complexes have usually been obtained by:

(1) adding the amine as pure liquid to an air-dried montmorillonite film;

(2) interacting the amine in its vapour state with an air-dried montmorillonite film; and

(3) adding the amine as an aqueous solution to the montmorillonite suspension.

In the present studies the clay films were prepared from hydroxy-aluminium-montmorillonite suspensions of pH 8. Some of these films were exposed to hydrazine and monomethylhydrazine vapour, and some clay films were prepared directly from hydroxy-aluminium-montmorillonite suspensions that had interacted with aqueous solutions of hydrazine of pH 8.

Results have shown that the exchangeable aluminium in the hydroxy-aluminium-montmorillonite was held in uncharged, non-exchangeable hydroxy polymers, which would be distributed over the internal and external surfaces of the montmorillonite. The surface negative charges of this clay preparation were balanced by Na^+ ions which were almost fully exchangeable by the protonated forms of both hydrazines. The adsorption of hydrazine and of monomethylhydrazine were in excess over the CEC indicating that there were other binding mechanisms. The strongly nucleophilic character of the hydrazines will enable the molecules to interact with partially dissociated protons of the hydroxy-aluminium polymers and to participate in strongly held solvation shells around the exchangeable cations. Hydrogen bonding could also exist between th protonated and unprotonated forms of the sorbate.

Solvation of the exchangeable Na^+ ions may be the predominant mechanism by which hydrazines were sorbed from the vapour phase by the clay complex. In addition, hydrazines could also be held by weak Van der Waals forces and by hydrogen bonding to the clay. Infra-red spectra of these solutions and vapour phase hydrazine treated clay complexes would provide further evidence of the types of bonding that exist in these sorption complexes. Heating them to different temperatures for different lengths of time also provide information on the type of bonding involved and their thermal stabilities.

A number of distinct absorption bands were observed in the region 1000 - 4000 cm^{-1} of these infra-red spectra. The assignments of these bands were based mainly on spectral assignments for pure hydrazine and monomethylhydrazine; and for complexes of these in other sorbents. These are summarised and tabulated in Tables 14 to 17.

Table 14 IR spectra of hydrazine.(From Giguere and Liu 1952)

Absorption (cm^{-1})		Assignment
Vapour	Liquid	
3350	3338	N-H stretching
3325		"
3314		"
3280	3200	"
1628		N-H bending
1587		"
1493		"
1275	1280	"

Table 15 IR spectra of hydrazine adsorbed on kaolinite. (From Ledoux and White 1966)

Absorption (cm^{-1})	Assignment
3365	N-H stretching of monomeric N_2H_4
3310	N-H stretching of monomeric N_2H_4
2970	N-H stretching of N_2H_4 strongly hydrogen to hydroxylic surface of kaolinite

Table 16 IR spectra of hydrazine sorbed on irridium deposited alumina.(From Contour and Pannetier 1970)

Absorption (cm^{-1})	Assignment
1665	N-H bending of N-H adsorbed on Lewis acid sites
1620	N-H scissor
1460	NH_4^+ deformation
1270	NH_3 deformation

Table 17 IR spectra of monomethylhydrazine.(From Durig *et al.* 1966)

Absorption (cm^{-1})		Assignment
Vapour	Liquid	
3366		N-H stretching
3358		"
3314	3250	"
2967	2963	C-H stretching
2951	2937	"
2850	2858	"
2784	2784	"
1597	1608	NH_2 scissor
1479	1472	CH_3 deformation
1465	1438	"
1449	1411	"
1282	1295	NH_2 wag
1210	1194	CH_3 wag
1118	1120	N-H bending

Infra-red spectra of hydroxy-aluminium-montmorillonite

The infra-red spectra of hydroxy-aluminium-montmorillonite (Figure 17(i)) contained three regions of absorption:

at 3600, 3400 and 1600 cm^{-1}. These arose from the stretching vibrations of lattice hydroxyl groups and of weakly hydrogen bonded interlayer water, and from the hydroxyl bending vibrations, respectively. There was also a broad absorption from 2600 to 3300 cm^{-1} due to the acidic hydroxyl groups of the hydroxy-aluminium polymers in the interlayers.

On heating to 110°C for 24 hours, the 1630 and 3400 cm^{-1} absorption were considerably reduced as the weakly held interlayer water was removed. As dehydration occured, the residual acidic hydroxyl groups became even more dissociated and the development of the 2920 and 2840 cm^{-1} absorptions were observed. Washing of the hydroxy-aluminium-montmorillonite with NaCl solution (0.1 M) did not result in any significant changes in the original spectra.

Infra-red spectra of the complexes of hydroxy-aluminium-treated with hydrazine and monomethylhydrazine in aqueous solutions of pH 8.

The spectra of the complexes of both the hydrazine and monomethylhydrazine treated clay preparations were very similar to each other (Figures 17 (ii) and 17 (iii)) and differed in many ways from those of the original hydroxy clays.

OH stretching

In the stretching region of the spectrum, the position and intensity of the 3620 cm^{-1} lattice hydroxyl absorption were unchanged compared with the unreacted clay, but the broad 3400 cm^{-1} peak due to occluded water had moved to a higher frequency at 3420 cm^{-1} for the hydrazine hydrate- and at 3440 cm^{-1} for the monomethylhydrazine-clay complexes. This shift of the stretching vibration to higher absorption indicated a net reduction in the hydrogen bonding of the absorbed water due to the adsorption of these hydrazines. The monomethylhydrazine-clay complex had a slightly greater shift than the hydrazine-clay complex (20 cm^{-1}). This difference reflected the greater basic strength of the monomethylhydrazine by virtue of its greater hydrophobicity, compared to hydrazine when adsorbed in the montmorillonite. Thus, more water was displaced; as a result less hydrogen bonding would occur between the residual water molecules in the former complex than in the latter or in the original clay. In addition, because of the methyl substituent, the monomethylhydrazine molecule is the larger molecule and would therefore cause a greater disordering of the structure or the adsorbed water.

OH bending

Absorption in the deformation region of the spectrum was dominated by a strong, broad peak at 1630 cm^{-1}, which was partly due to OH_2 vibration of the occluded water. No obvious down-frequency shift of this vibration was observed compared to that of the original clay. This might be expected given the observed up-frequency shift of the OH stretching vibration at 3400 cm^{-1}. However, many other vibrational modes could give rise to absorptions in this region and the presence of these would account for the broadening of the observed peak.

NH bending

Vibrational modes that are likely to contribute to this 1630 cm^{-1} peak are:

(1) $-N^{+}-H--N$ asymmetric vibrations at 1640 cm^{-1};
(2) $-NH_3^+$ asymmetric vibrations at 1637 cm^{-1};
(3) $-NH_2$ scissors vibration at 1600 cm^{-1};
(4) $-NH_3^+$ deformation at 1600 cm^{-1}; and
(5) deformations of ammonia coordinated to Lewis acid sites at 1620 cm^{-1}.

The adsorption of the -NH bending frequency of 1530 cm^{-1} of the hydrazine hydrate-clay complex is good evidence for the presence of the hydrated hydrazinium species with hydrogen bonds between $-NH_3^+$ and H_2O species. Absorption at 1420 cm^{-1} is due to the -NH bending of the NH_4^+ showed that some degradation of the hydrazine had occured with subsequent sorption of the ammonium ions on the clay surfaces. The presence of both these absorptions was masked in the monomethylhydrazine-clay complex due to asymmetric $-CH_3$ (1460 cm^{-1}) and symmetric $-CH_3$ deformations (1350 cm^{-1}). Both these absorptions were at lower frequencies than might be expected (Table 15), which might reflect the strength of the hydrogen bonding in which the monomethylhydrazine molecules take part. The intensity of the $-CH_3$ deformation absorptions contrasted with the absence of discernible stretching frequencies for this group. This relative enhancement must result from a preferred orientation of the monomethylhydrazine molecules, relative to the partially orientated clay (001) planes in the plane of the self-supporting film, such that the dipole change of the deforming vibrations were less perpendicular to the 001 plane than dipole changes of the C-H stretching vibrations.

Washing of the hydrazine-clay complex with sodium chloride solutions (0.1 M) showed that most of the hydrazines were desorbed as the resultant spectra was similar to that of the uninteracted clay (Figure 17 (i)). However, the broad absorption due to the stretching vibrations of occluded water did not revert to its lower frequency and the presence of the low intensity -NH stretching absorptions indicated that there were still some residual hydrazines sorbed.

Effect of heat on the solution-phase adsorption complexes.

The infra-red spectra of the solution phase complexes showed marked changes when they were heated to 110°C for a half-hour interval and two-day interval, and then further heated at 250°C and 350°C for a two-hour interval at each temperature (Figures 17 (ii) and 17 (iii)).

Stretching region of the hydrazine-treated hydroxy-clay complex.

Absorptions in the stretching regions of the spectra for complexes with either of the hydrazines showed a drastic reduction in intensity of the OH vibration of occluded water even after heating to 110°C for only half an hour. The spectra of the hydrazine-hydrate-clay complex showed a strong development of an NH_4^+ absorption at 3280 cm^{-1} , and a broad absorption in the region 2700 to 3000 cm^{-1}. The absorption in the region 2100 to 2700 cm^{-1} was reduced. This absorption was assigned to OH vibrations of the more strongly acidic protons of hydroxy complexes, and to the most strongly hydrogen bonded hydroxyl and NH vibrations.

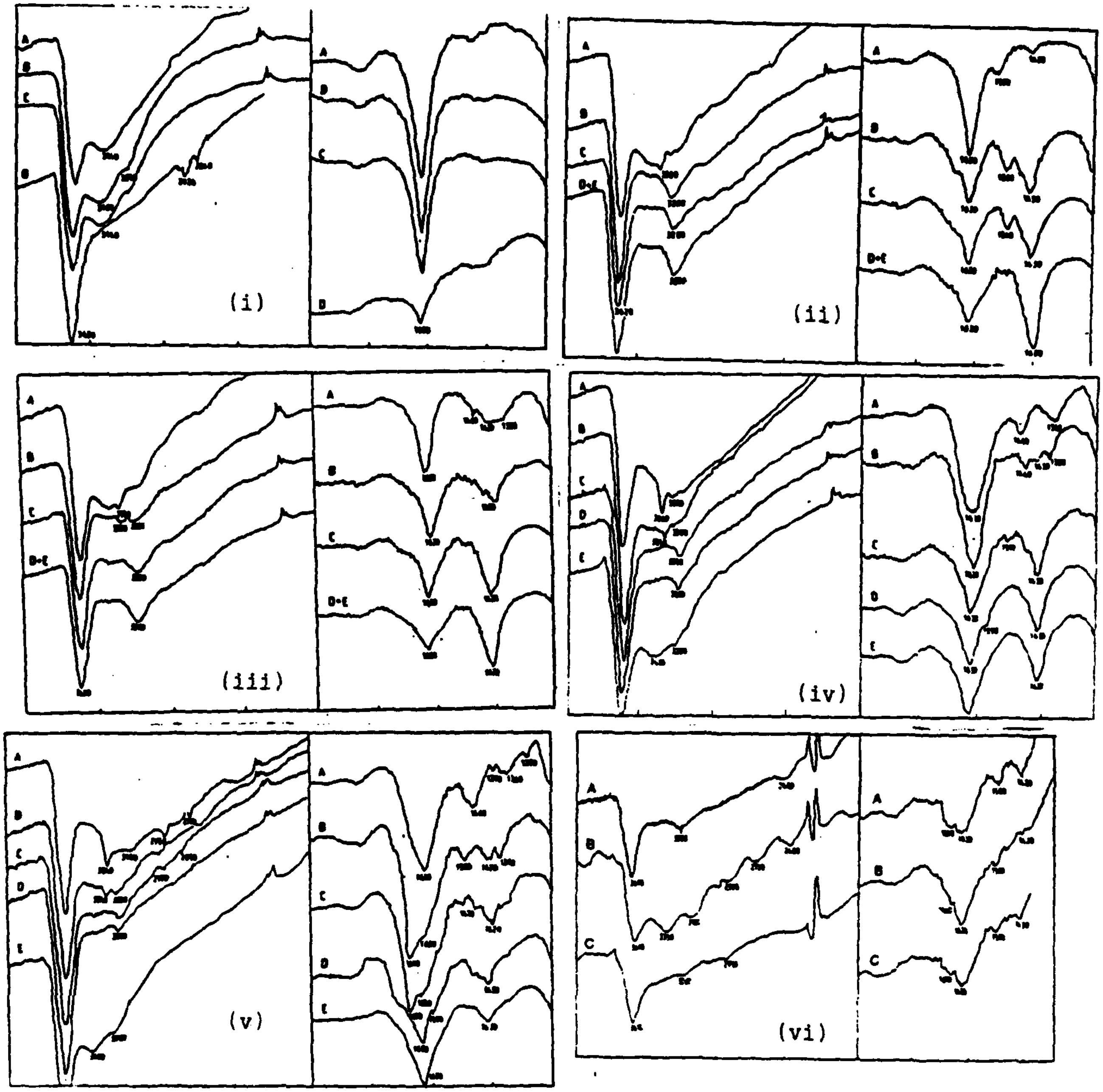


Figure 17. Infrared spectra of hydroxy-aluminium-montmorillonite (A), 0.1M NaCl-washed-hydrazine-clay complex (B), 0.1M NaCl-washed-monomethylhydrazine-clay complex (C), and the clay (A) heated at 110°C for 2 hours (D), curves (i); spectra of hydroxy-aluminium-montmorillonite treated with hydrazine solution of pH 8 (A), the complex heated at 110°C for 30 min (B), 110°C for 2 days (C), 250°C for 2 h (D), and 350°C for 2 h (E), curves (ii); same as (ii) except MMH was used instead of hydrazine (iii); same as (ii) except that adsorbent are treated with hydrazine vapour, (iv): same as (iv) except that MMH was used, (v); and spectra of hydroxy-aluminium-montmorillonite treated with MMH vapour and heated at 110°C for 2 h (A); then (A) was exposed to water vapour overnight (B); and (B) was heated at 110°C for 2 h, (C), curves (vi).

Stretching region of the monomethylhydrazine-treated hydroxy-clay complex.

The changes in the hydrazine-hydrate-clay complex occured upon heating to 110°C for half an hour, and were then only very litttle developed by further heating. By contrast, the spectrum of the monomethylhydrazine-clay complex when treated in a similar way, still included an absorption at 3350 cm^{-1} which assigned to NH_2 vibrations in non-hydrogen bonded molecules. This was only markedly reduced after prolonged heating at 110°C.

Bending of the hydrazine- and monomethylhydrazine-clay complex.

Absorption in the deformation region of the spectra for the monomethylhydrazine-clay complex were simplified after heating the complex, in that the methyl group vibrations were greatly reduced. The 1430 cm^{-1} absorption due to ammonium ions was enhanced progressively on longer and stronger heating, and the 1630 cm^{-1} absorption was gradually reduced.

The intensities of the 1430 and 1630 cm^{-1} absorptions changed in the same way in the spectra of the heated hydrazine-hydrate complex. But in addition, the 1530 cm^{-1} absorption shifted to 1510 cm^{-1} as dehydration of the hydrazinium ions occured at 110°C, and then it disappeared on heating the complex to 350°C. This shift to lower frequencies (from 1530 to 1510 cm^{-1}) in the spectra of the dehydrated or heated samples suggested that hydrogen bonds between the hydrazinium species, $-NH_3^+$ terminal, and $-NH_2$ were stronger than $-NH_3^+$ and H_2O. The reduction of the 1630 cm^{-1} peak on heating revealed a 1670 cm^{-1} absorption more clearly. This was assigned to a NH_2 deformation vibration by Ledoux and White (1966).

The behaviour of the spectra for heated clay complexes showed degradation of the sorbed hydrazines in clay complexes. It is clear from th results that monomethylhydrazine was much more readily degraded than hydrazine but that in both cases the ammonium ion degradation product was strongly sorbed by the hydroxy-aluminium-clay complex. This behaviour may be compared with the formation and sorption of ammonium ions as a decay product of ethylenediamine (EDA) sorbed on montmorillonite preparations, when these were heated beyond 160°C (Cloos and Laura, 1972). By contrast, Contour and Pannetier (1970) observed the disappearance of a 1460 cm^{-1} ammonium ion absorption when hydrazine was sorbed on an irridium-alumina catalyst and heated to 180°C.

The effects of dehydration on the absorptions of the hydrazine species can be seen clearly in the spectra of the hydrazine-hydrate complex where the hydrazine was not fully degraded by heating the complex at 110°C. The removal of a large part of the adsorbed water was accompanied by a partial dehydration of the hydrazinium ions. Some sorbed hydrazine would take over the role of solvating protonated species on the clay surface but the persistance of the 1670 cm^{-1} absorption on heating indicated that not all N-H bonds become strongly polarized.

The decrease in the overall extent of hydrogen bonding in the sorbed hydrazines, and the adsorption of the degradation product ammonia as ammonium ions meant that the proportion of the protonated hydrazine on the clay was reduced on heating and the resulting imbalance in the surface charge of the clay was balanced by the adsorption of the ammonium ions. Two possible processes of degradation of the sorbed hydrazines could be inferred from this observation; firstly, the protonated species was degraded in favour of the non-protonated species , or secondly, the deprotonation of the protonated species occured, followed by degradation of the non-protonated species on heating. Since the monomethylhydrazine sorbate in the monomethylhydrazine-clay complex was more heat resistant than that of the hydrazine-clay complex, the latter process seemed more likely as monomethylhydrazine is more difficult to deprotonate than hydrazine as it is stabilised by the methyl substituent.

Infra-red spectra of the complexes of hydroxy-aluminium-montmorillonite interacted with hydrazine and monomethylhydrazine in their vapour phases

The spectra in Figures 17 (iv) and 17 (v) of the complex formed between the clay hydroxy-aluminium material and either of the hydrazines from the vapour phase are again quite similar to each other but different from those obtained for the solution phase complexes.

Stretching region of the spectra.

The more marked differences in the stretching region of the spectra were:

(1) the very weak absorption due to OH vibrations of adsorbed water; and

(2) sharpened absorption at 3360 cm^{-1} and 3340 cm^{-1} due to a -NH vibration in monomeric weakly sorbed molecules for the hydrazine and monomethylhydrazine complex, respectively.

An absorption at 3280 cm^{-1} in the hydrazine-hydrate-clay complex spectrum indicated the presence of some ammonium ions; but this was not found for the monomethylhydrazine complex. Absorptions at 3180 - 3200 cm^{-1} in both cases indicate NH_2 or NH_3^+ vibrations, and a broad featureless absorption was again present in the range 3100 to 2500 cm^{-1}. However, some distinct absorption for the monomethylhydrazine-clay complex were superimposed on this at 2950, 2850 and 2790 cm^{-1}. These were assigned to the -CH vibrations of the $-CH_3$ group (Table 17).

Deformation region of the spectra.

The two spectra of hydrazine and monomethylhydrazine complexes were also quite similar to each other in the 1200 to 2000 cm^{-1} region. Both had very strong broad absorptions at 1630 cm^{-1} , but this was much less symmetrical for the monomethylhydrazine-clay complex than for the hydrazine-hydrate complex, which reflected the greater contribution of OH_2 deformation vibrations in the latter instance. The width of the absorption in both cases indicated a wide range of polarization of the contributing $-NH_2$ and $-NH_3^+{-}{-}{-}NH_2$ vibrations.

Absorption at 1470 cm^{-1} might, in both cases be due to molecules of hydrazine and monomethylhydrazine which are strongly coordinated to Na^+ ions on the clay surfaces, or to hydrazinium vibrations. However, the absorption was complicated in the monomethylhydrazine complex by a 1460 cm^{-1} peak assigned to the $-CH_3$ vibration. The presence of a strong, broad absorption at 1360 cm^{-1} in the hydrazine-hydrate-clay spectrum was quite surprising, as this molecule has no methyl group. It might, however, be due to a wagging $-NH_2$ vibration, to an -NH deformation in molecules very strongly coordinated to the surface cations which could cause the 1493 cm^{-1} NH bend to shift down frequency, or, it might also be due to bending of the hydroxyl group in the hydroxy-aluminium polymer. This absorption in the monmethylhydrazine-clay spectrum was complicated by other absorptions at 1390, 1350 and 1280 cm^{-1} which were assigned to $-CH_3$ groups involved in H-bonding to oxygen atoms on the clay surfaces, to the hydroxyl groups of the hydroxy complexes, and to a wagging $-NH_3$, or to a $-CH_3$ vibration.

The spectra showed the presence of sorbed hydrazinium molecules and hydrazine molecules with strongly polarized N-H bonds (and also C-H bonds in the case of monomethylhydrazine). Both hydrazines would readily displace water molecules in the outer spheres of coordination around the Na^+ ions at the cation exchange sites; these could also coordinate directly with the cations and perhaps form hydrogen bonds with the hydroxy-aluminium complexes on the clay surface. Further molecules of both hydrazines and water could them form hydrogen bonds with the co-ordinated molecules.

Effect of heat on the vapour-phase adsorption complexes.

The spectra of the two vapour-phase complexes (Figures 17 (ii) and 17 (v)) show that prolonged heating at 110°C was required to bring about maximum change in the complexes.

Stretching region.

The monomethylhydrazine-clay complex retained the 3340 cm^{-1} absorption, but the intensity was very much reduced after two days of heating at 110°C. Their intensity was reduced compared to the absorptions at 2950 and 2790 cm^{-1}. These absorptions at higher frequency for the methyl group might indicate that, on heating, the extent of hydrogen bonding in the remaining monomethylhydrazine were reduced.

The spectra of the hydrazine-clay complex showed a 3350 cm^{-1} absorption, slightly lower than the corresponding N-H strtch in the unheated sample (3360 cm^{-1}); this indicated that the more strongly hydrogen bonded and therefore more strongly held hydrazine sorbate was left on the heated clay. On prolonged heating for two days, these absorptions disappeared in both the complexes and a small NH_4^+ absorption at 3280 cm^{-1} developed which persisted even on heating at 250°C.

Deformation region.

Heating the hydrazine-hydrate-clay complex to 110°C for half an hour had its greatest effect on the 1360 cm^{-1} absorption in the deformation region of the spectrum. This absorption was reduced along with the 3360 cm^{-1} absorption and the broad 1630 cm^{-1} absorption was also narrowed on the high wave length side. This related reduction would imply a relationshil between the 1360 cm^{-1} absorption and the less strongly hydrogen bonded hydrazine molecules, which might show it to be a wagging $-NH_2$ vibration. The reduction in these absorptions was accompanied by a small development of the 1430 cm^{-1} NH_4^+ absorption, which is greatly enhanced on prolonged heating of the complex for two days. The development of the absorption at 1590 cm^{-1} was also observed. On heating these samples, partial deprotonation of the hydrazinium species could occur, producing unprotonated hydrazine molecules which were held on the clay by hydrogen bonding. This 1590 cm^{-1} absorption was probably due to NH_2 scissor deformation of these molecules. Both of these absorptions were lost on heating the complex further to 350°C; from such heating the only main absorptions which remained were the ammonium peak at 1430 cm^{-1}, and this was less intense than that for the solution phase adsorption complex.

The spectra of the monomethylhydrazine complex also showed a development of the 1430 cm^{-1} absorption, and a clear absorption at 1380 cm^{-1} , but there was a diminution of the 1460 and 1280 cm^{-1}absorptions. At 1500 cm^{-1} hydrazinium peak was present after heating for only half an hour. There was a striking development of a 1660 cm^{-1} absorption band, which persisted even after heating of the complex for two days. This absorption was interesting though not readily interpreted. It may be an $-NH_2$ deformation, as was noted by Ledoux and White (1966) in the spectra of a urea-kaolinite complex. It must be noted that all the NH stretching vibrations were greatly reduced at this stage, except for those assigned to the sorbed ammonium ions. Degradation of some of the monomethylhydrazine molecules on heating could lead to the formation of C=N or C=O bonds which would readily give rise to strong absorptions at this frequency.

Further heating to 250°C caused a sharp reduction in the 1670 cm^{-1} band, but it did not give further enhancement for the 3280 and 1430 cm^{-1} ammonium absorption. The development of the 1590 cm^{-1} peak of NH_2 scissoring vibration coincided with the decrease in the intensity of the 1470 and 1370 cm^{-1} absorptions. Hence, as most residual water and sorbed hydrazines were removed, deprotonation of the residual hydrazines could have occured giving rise to more free $-NH_2$ terminals and hence more intense $-NH_2$ vibrations. On heating to 350°C, the 1590 cm^{-1} absorption disappeared along with the other two 1470 and 1370 cm^{-1} absorptions.

Effects of sorbed water on the thermal degradation of the sorbed hydrazine and monomethylhydrazine.

The behaviour of the spectra of the hydrazine-hydrate-clay complex on heating resembled that of the solution phase complexes. At least ninety percent of the hydrazine hydrate molecules were still in the associated form in the vapour phase at this temperature (Altman and Adelman, 1952) so that a ready supply of both hydrazine and water molecules were available on the clay surface. The overall character of the complexes formed between the clay hydroxy-aluminium species and the hydrazine hydrate were therefore similar, whether the hydrazine was absorbed from the vapour- or the solution-phase.

In particular, the thermal stability of the sorbed hydrazine was similar and the product of decomposition (ammonia) was the same.

Very little water was present in the vapour phase monomethylhydrazine complex, and the thermal stability of the sorbate and the product of decomposition differed from the solution phase complex. The spectral evidence may point to a degradation mechanism in the vapour phase complex on the lines of a four centred concerted loss of ammonia (Golden <u>et al</u>., 1972):

$$CH_3NHNH_2 \longrightarrow CH_2{=}NH + NH_3$$

The methyleneimine so formed would be readily hydrolysed in the presence of interlayer water:

$$CH_2{=}NH \xrightarrow{H_2O} CH_2O + NH_3$$

and the formaldehyde so formed would be desorbed from the clay surfaces under mild heating conditions. A great reduction in the intensity of the 1670 cm^{-1} absorption relative to the 1630 cm^{-1} absorption was observed when the monomethylhydrazine vapour treated clay film heated at 110°C for two hours was exposed to water vapour overnight [Figure 17 (vi)]. On heating this sample at 110°C for another two hours, a reduction in the water deformation (1630 cm^{-1}) was observed and this coincided with a marked reduction in the intensity of the 1670 cm^{-1} band. The other deformation peaks of $-CH_3$ and $-NH_2$ at 1420, 1460 and 1500 cm^{-1} still persisted, but these were also reduced in intensity. Hence, the presence of water in the monomethylhydrazine-clay complex had caused the reduction of the 1670 cm^{-1} adsorption and the possible formation of the proposed $>C{=}N$ group. The adsorption complex from the vapour phase had different thermal decomposition pathways from that of the solution phase adsorption complex.

4.6.3 Mössbauer spectroscopic analysis

In order to detect any reduction of structural ferric iron by hydrazine during the interaction of aluminium-montmorillonite with hydrazine solution of pH 8, Mössbauer spectra of the Al^{3+}-montmorillonite and of the hydrazine interacted Al^{3+}-montmorillonite and that of hydroxy-aluminium-montmorillonite were obtained. Table 18 summarises the isomer shift and quadrupole splitting obtained from these spectra (Figures 18a to c).

All of the three spectra had a main peak at +0.35 mm s^{-1} and quadrupole splitting of 0.6 mm s^{-1} produced by ferric iron. This doublet corresponded to Fe^{3+} in Al^{3+} octahedra in the lattice structure of the montmorillonite.

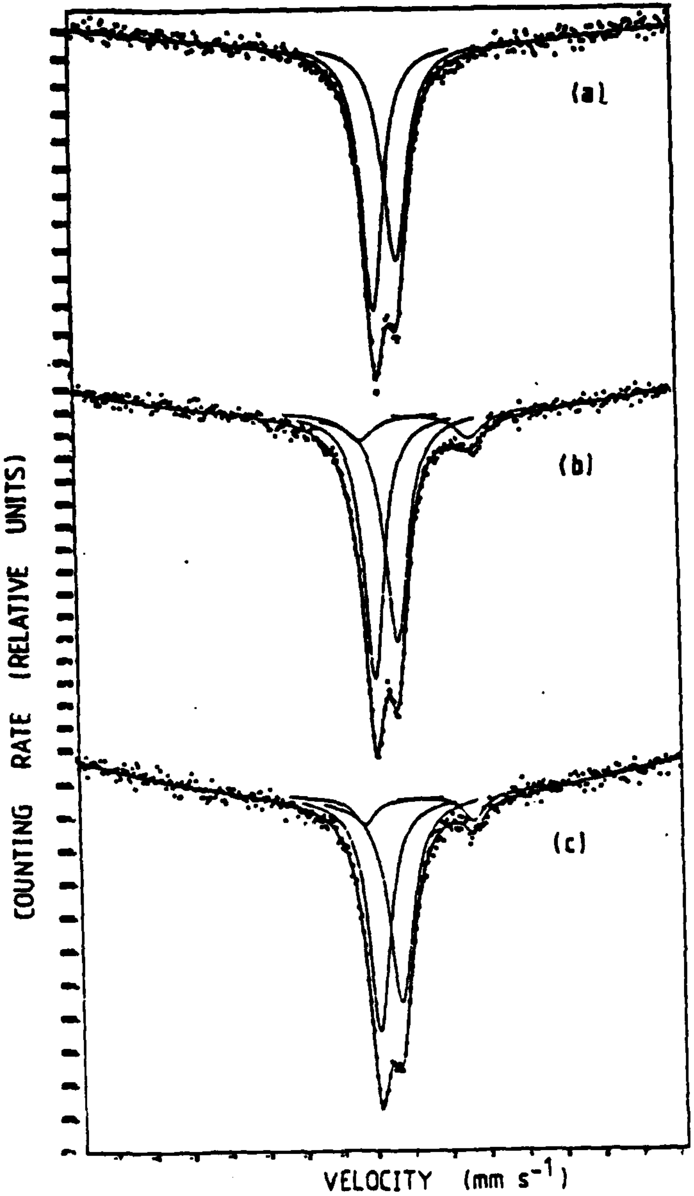


Figure 18

Fe.57 Mössbauer spectra at room temperature (293K) of Al^{3+} -montmorillonite (a); Al^{3+} -montmorillonite interacted with hydrazine solution at pH 8 (b); and hydroxy-aluminium -montmorillonite interacted with hydrazine solution at pH 8.

For the hydrazine interacted Al^{3+} -montmorillonite and hydroxy-aluminium-montmorillonite, additional peaks were observed at 1.156 and 1.451 mm s^{-1}, respectively, and a quadrupole splitting was observed at 2.9 mm s^{-1}. This smaller peak in the two spectra was produced by ferrous iron and these parameters are typical of ferrous iron in octahedral co-ordination, probably in a field of oxygen and hydroxyl ions (Weaver et al., 1967). The peak areas of the Fe^{2+} adsorption corresponded to 9.8 and 12.4% of the total amount of iron (both ferrous and ferric) in the clay for the Al^{3+} -montmorillonite and hydroxy-aluminium-montmorillonite samples, respectively.

However, the total amount of iron in this clay is actually very small (about 2.4% of the weight of the clay, Van Olphen and Fripiat, 1979); thus, the amount of hydrazine that was degraded due to the reduction of structural ferric iron would be very small in proportion to the total amount of hydrazine added in the sorption experiments. In any case, these results showed that on interaction with hydrazine, some of the ferric iron in the lattice of the Al^{3+}-montmorillonite was reduced by the hydrazine. The mechanism of reduction of the structural ferric ions involved tunnelling of a proton-electron pair from the interlayers into the structure.

Table 18 Mossbauer parameters determined for Al^{3+}-montmorillonite, and Al^{3+}-montmorillonite and hydroxy-aluminium-montmorillonite interacted with hydrazine solution of pH 8

Sample	Isomer Shift (δ) ($mm\ s^{-1}$)	Quadrupole Splittings (Δ) ($mm\ s^{-1}$)
Al^{+++}-montmorillonite	0.357 ± 0.01	0.605 ± 0.03
Hydrazine treated Al^{+++}-montmorillonite	1) 0.356 ± 0.01 2) 1.451 ± 0.06	0.604 ± 0.01 2.902 ± 0.12
Hydrazine treated hydroxy-aluminium-montmorillonite	1) 0.344 ± 0.01 2) 1.156 ± 0.06	0.581 ± 0.03 2.887 ± 0.12

4.6.4 Differential Thermal Analysis (DTA)

The two parameters derived from the DTA curves of this study were the peak temperatures and the enthalpies calculated from the areas under the thermal responses of the thermograms. These parameters were determined by the shapes of the curves, and these were in turn influenced by many factors connected with instrumental characteristics, the method of analysis, and the reference material employed. To ensure the reproducibility of the curves, all of the experiments were carried out on the same piece of Stanton-Redcroft thermal analyser, under similar conditions of analysis, and using alumina as the reference material. A slow flow of nitrogen during the experiments provided an inert atmosphere. The rate of heating was 10°C min^{-1}, and 10 to 20 mg of sample materials were used.

The DTA curve of the original Al^{3+} -montmorillonite sample has two endothermic peaks [Figure 19(i)]. The first peak, with temperature centered at 120°C, corresponded to the loss of interlayer water, and the next peak centered around 640°C, corresponds to a loss of lattice hydroxyls as water (or dehydroxylation). This DTA curve was very similar to that obtained for typical montmorillonite samples. The DTA curve of the hydroxy-aluminium-montmorillonite prepared at pH 8 [Figure 19(ii)] has, in addition to the dehydration peak temperatures of 87°C and 112°C and the dehydroxylation peak at 654°C, a third endothermic peak at 466°C which corresponded to the dehydroxylation of the hydroxy polymers in the interlayers.

On interaction with hydrazine and monomethylhydrazine, the DTA curves of these complexes showed two additional responses attributable to the thermal reactions of the adsorbed hydrazines. These were an exothermic response centered around 226°C and 237°C, and an endothermic response centered around 315°C and 350°C.

The DTA curve of the pH 8 hydrazine solution-treated Al^{3+} -montmorillonite had a sharp exothermic peak temperature at 237°C, followed by a broader endothermic peak temperature at 350°C. When the analysis was repeated in an atmosphere of air instead of nitrogen, the endothermic peak at 350°C became exothermic [Figure 19(iii)]. The DTA curve of a similarly treated hydroxy-aluminium-montmorillonite was very similar to that of the Al^{3+} -montmorillonite complex [Figure 19(iv)]. Using a slower chart speed of 100 mm h^{-1} rather than 200 mm h^{-1} caused the curve to spread along the temperature axis. The sharp exothermic response at 226°C was still observed and it was more clearly separated from the broad endothermic response observed at 350°C.

The DTA curves of the pH 8 monomethylhydrazine solution treated Al^{3+} -montmorillonite and that of hydroxy-aluminium-montmorillonite complexes had exothermic responses at 237°C and 232°C, respectively. These responses were not sharp, as in the hydrazine-interacted complexes, and seemed to be superimposed on a very broad exothermic response after the initial dehydration at 61 to 63°C. Following the exothermic responses, broader endothermic responses centred at 355°C and 315°C were observed for the Al^{+++} -montmorillonite and its hydroxy-clay complexes, respectively [Figures 19(v) and 19(vi)]. The peak temperatures of all the thermograms obtained are summarised in Table 19.

The area under the exothermic and endothermic responses were measured by calculating the area of triangles RST and T'UV, as shown in Figures 18(iii) to 18 (vi). The enthalpy changes thus calculated are summarised in Table 20.

Table 19 Peak temperatures on thermograms of Al^{3+}-montmorillonite (AlM) and hydroxy-aluminium-montmorillonite (Al-OH-M), and their hydrazine and monomethylhydrazine (MMH) solution phase sorption ion complexes

Clay Preparations	Peak Temperatures (T_m, ^oC) during					
	Dehydration		Hydrazine/MMH Decomposition		Dehydration	Dehydroxylation
AlM	-	120	-	-	-	641
Al-OH-M	87	112	-	-	466	654
Hydrazine/AlM	80	-	237	350	-	654
Hydrazine/Al-OH-M	66	-	226	350	-	654
MMH/AlM	66	-	237	355	-	654
MMH/Al-OH-M	63	-	232	315	-	654

Table 20 Heats of exothermic and endothermic reactions of hydrazine and monomethylhydrazine (MMH) treated Al^{+++}-montmorillonite (AlM) and hydroxy-aluminium-montmorillonite (Al-OH-M)

Clay Samples treated with:	Heats of Exothermic Reaction (kJ mol^{-1})		Heats of Endothermic Reaction (kJ mol^{-1})	
	Hydrazine	MMH	Hydrazine	MMH
AlM	236	243	107	157
Al-OH-M	216	310	116	188

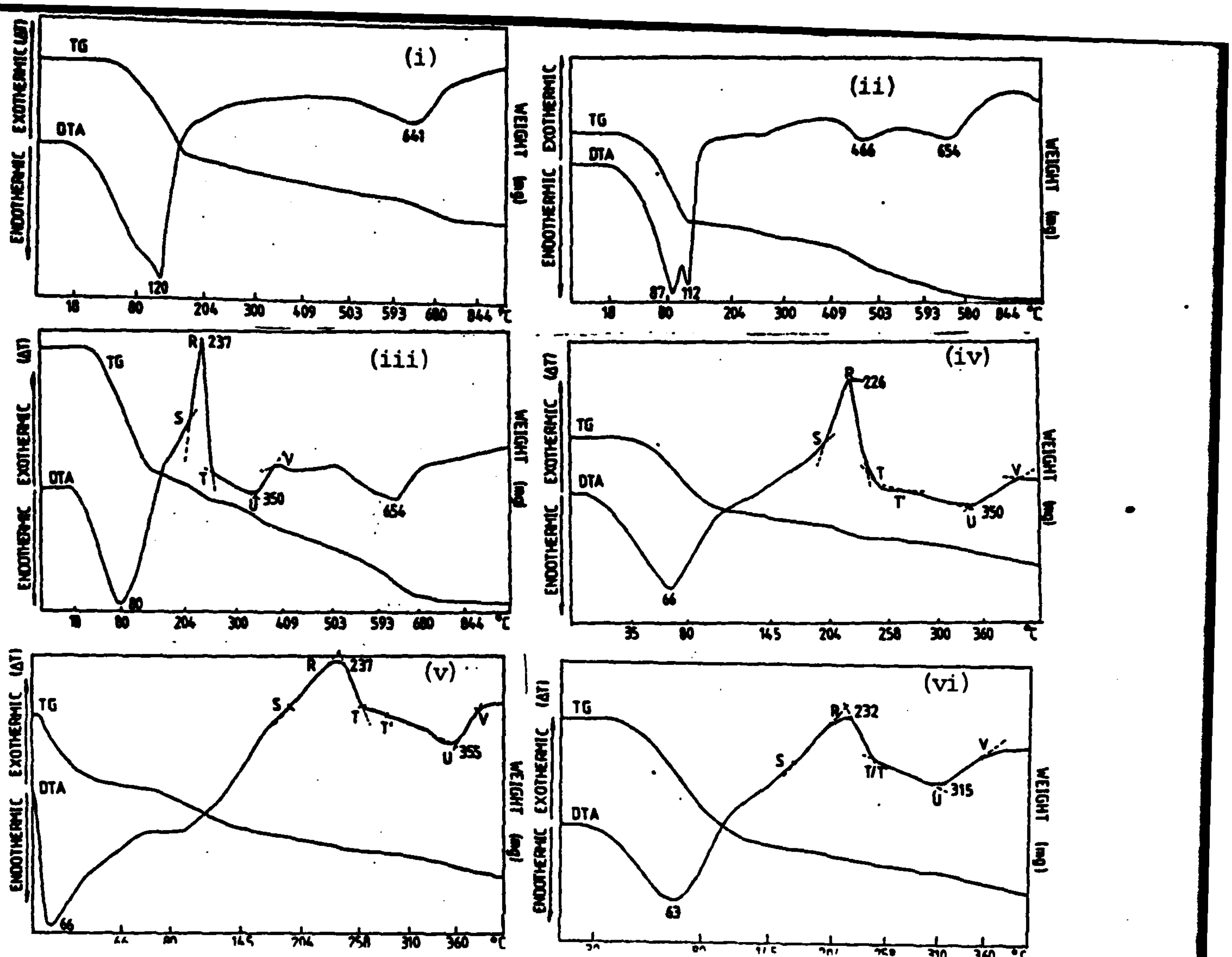


Figure 19. Differential thermogravimetric (TG) and differential thermal analysis (DTA) of Al^{3+} -montmorillonite (under N$_2$), (i); hydroxy-aluminium-montmorillonite, (ii); hydrazine sorbed Al^{3+} -montmorillonite (iii); hydrazine sorbed hydroxy-aluminium-montmorillonite, (iv); MMH-sorbed Al^{3+} -montmorillonite, (v); and MMH -sorbed hydroxy-aluminium montmorillonite.

Thermal degradation of hydrazine and monomethylhydrazine sorbed on Al^{3+} montmorillonite and the hydroxy preparations

The infra-red spectra of the solution-phase adsorption complexes formed between hydrazines and hydroxy-aluminium-montmorillonite have shown that thermal degradation of the sorbed hydrazines begins at or below 110°C, and that ammonia is a major product of this decomposition. A large endothermic response due to the dehydration of the clay preparation was observed within this range of temperature in the thermograms. This would mask any thermal response due to the degradation of hydrazine. The two additional responses at 260 and 350°C were observed even when the hydrazine-clay complexes were held at 120°C and 250°C for an extended period before further heating was continued.

The thermal decomposition of hydrazinium zeolite has been shown to occur by deprotonation of hydrazinium to yield hydrazine, which decomposed according to the overall equation:

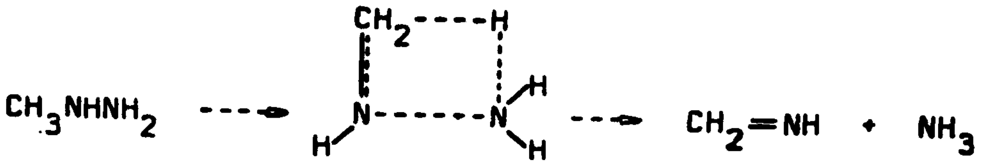
$$3N_2H_4 \longrightarrow 4NH_3 + N_2 \qquad (4.1)$$

and also by:

$$N_2H_4 \longrightarrow N_2 + 2H_2 \qquad (4.2)$$

to yield nitrogen and hydrogen. The first of these processes reached a maximum at 300°C after the latter had reached a maximum at 120°C. The first process has also been found to occur on fused silica in the 300 - 627°C temperature range, but it also has been observed to occur in this case heterogeneously above 60°C. With a catalyst such as iron, osmium, or ruthenium, the latter process was suppressed and the production of hydrogen was greatly reduced (Beyer<u>et al</u>., 1980).

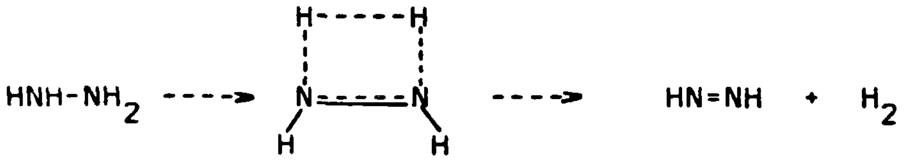
The thermal behaviour of hydrazine sorbed by hydroxy-aluminium-montmorillonite was rather different. Sorbate molecules were thermally destablised, such that they readily decomposed to yield ammonia at 110°C. The sorption of this ammonia as *ammonium* ions would imply that the degradation of the hydrazine sorbate involved the protonated species, and the subsequent imbalance in the surface charges of the clay was balanced by the ammonium ions. Some sorbate molecules were, however, resistant to decomposition at lower temperatures. The infra-red spectra of the solution-phase adsorption complexes at 250°C (Figures 17(ii) and 17(iii)) showed a slight increase in ammonium adsorption compared with that for the spectra heated at 110°C. Therefore, the exothermic decomposition reaction at 250°C could also involve the formation of ammonia. The molecules that were decomposing could be isolated from other hydrazine molecules, and so were unable to take part in the common multi-molecular reactions which begin at lower temperatures. Instead, they could decompose through a transition state involving a four-centered loss of ammonia, or through N-N homolysis. The heats of reaction for the response at 230°C in the thermograms were markedly higher than those reported for a four-centred loss of ammonia by monomethylhydrazine (27.17 kJ mol^{-1}. Equation 4.3) under low pressure pyrolysis conditions (Golden et al., 1972). However, these values were of the same magnitude as the N-N bond strengths of the two hydrazines, 293 and 276 kJ mol^{-1} for hydrazine and monomethylhydrazine, respectively (Shaw, 1975). Hence, if the four-centered loss of ammonia is the process for generation of the ammonia, then the sorption of ammonia considerably lowered the activation energy barriers for this process.



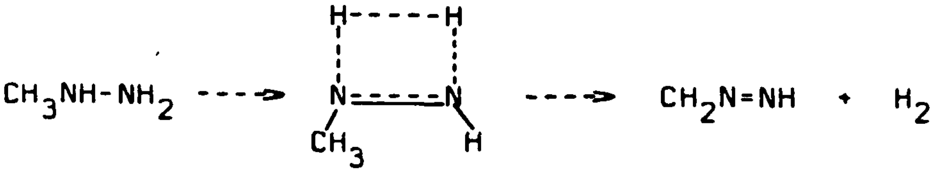
(4.3)

The endothermic reaction at 350°C became exothermic in the presence of air, suggesting that hydrogen was a product of this decomposition, and simultaneous reaction involving the formation of water in the oxygen-containing atmosphere could result.

The observed heats of reaction obtained for the endothermic response can be compared with those quoted for the four-centred concerted loss of molecular hydrogen for hydrazine and monomethylhydrazine (115 and 86 kJ mol^{-1}), for Equations 4.4 and 4.5 respectively).



(4.4)



(4.5)

The agreement was good for both the hydrazine- Al^{3+} -clay and the hydroxy-clay complexes (107 and 116 kJ mol^{-1}), respectively. Further descriptions of these decomposition reactions would require analysis of the very small amounts of products.

4.7 Studies of Sorption from Solution of Hydrazine by Goethite and Vapour Phase Sorption of Water and MMH by Hydrous Oxides and Clays

4.7.1 Synthetic samples of goethite, lepidocrocite, and aluminous goethites

Figure 20 presents x-ray diffractograms of the synthetic goethite (a) and lepidocrocite (g) samples prepared, and Table 21 presents the relevant x-ray diffraction data. It is seen that there is a good agreement between the d values obtained for the synthetic samples and those given in the standard A.S.T.M. Powder Diffraction File. Crystallinity was not good in the cases of the synthetic materials, as is evidenced by the lack of definition in the diffractograms. In the case of the aluminous goethites, it would appear that increasing the Al content of the medium improved the crystallinity of the product but it seemed that the definition of the traces was poorer than for goethite. Isomorphous substitution of aluminium for iron would be expected since Al^{3+} has a smaller ionic radius than Fe^{3+}, and hence diaspore (αAlOOH) has a smaller unit cell than that of goethite. The (111) spacing of goethites is known to decrease steadily with increasing aluminium contents. However, because of the low crystallinity of the synthetic samples prepared here a decrease in the (111) spacing could not be detected from the x-ray traces.

4.7.2 Isomorphous substitution of iron in Al(OH)$_3$ polymers

The attempted synthesis of such compounds is described in Section 2.5, and the data obtained indicated that isomorphous substitution was not achieved but instead amorphous iron oxides were formed which coated boehmite (γ AlOOH) synthesized from the AlCl$_3$ components of the mixtures.

4.7.3 Adsorption of hydrazine from solution by goethite

The CFSC-ACA technique (Section 3.3.2) was used to study the interactions of hydrazine with goethite at pH values of 8, 7 and 4. The isotherms obtained are shown in Figure 21. Isotherm (a) shows very large sorption of hydrazine (up to 6.4 m mol g^{-1}) at pH 8. The tendency of the isotherm to level off would indicate that deactivation of the surface towards further sorption of hydrazine occurred.

If it is assumed that only monolayer sorption of hydrazine took place and thatthe hydrazines were orientated with their N-N bond parallel to the surface, and that the area of the hydrazine molecule as $1.5 \times 10^{-19} m^2$, then a rough estimate of the surface area of the goethite covered would be $580 m^2$. [(6.4×10^{-3} mol g^{-1} hydrazine sorbed) $6.023 \times 10^{23} \times 1.5 \times 10^{-19}$]. This is well in excess of the values of 30 to 100 $m^2 g^{-1}$ usually quoted for goethite.

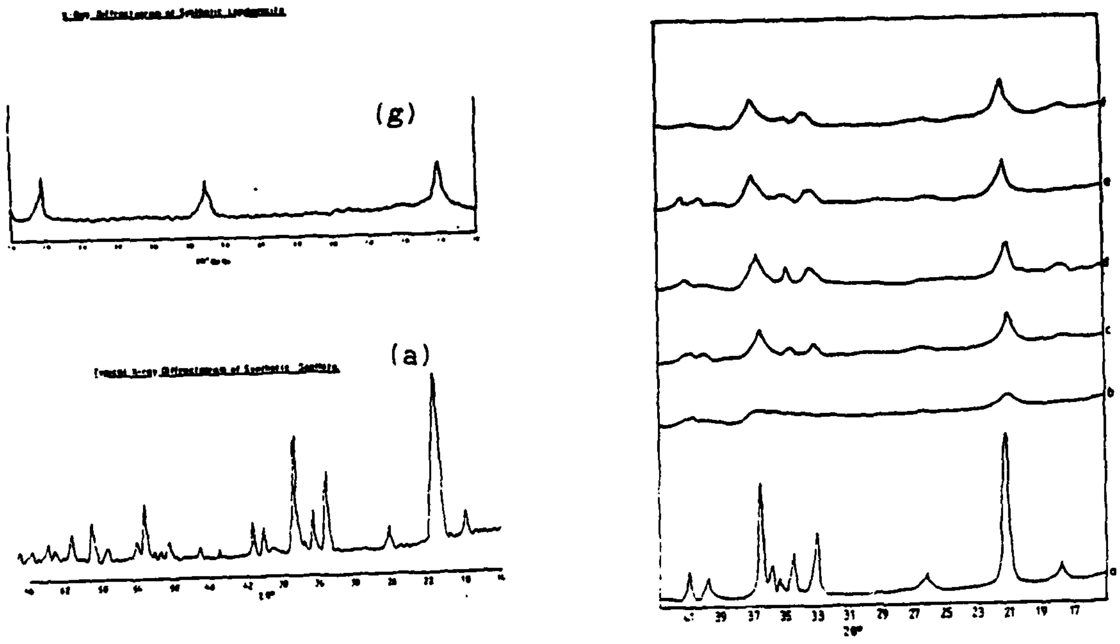


Figure 20. X-Ray diffractograms of synthetic goethite (a) lepidocrocite (g), and of aluminous goethites in which the synthesis medium contained 10% (b), 15% (c), 20% (d), 25% (e), and 30% (f) aluminium.

Table 21. X-Ray diffraction data for goethite and lepidocrocite samples.

2θ° for synthetic goethite	d value for peak Å	2θ° for standard goethite	d value for peak Å
17.80	4.98	17.81	4.98
21.25	4.18	21.24	4.18
26.44	3.37	26.34	3.38
33.25	2.67	33.27	2.69
34.70	2.58	34.73	2.58
35.50	2.53	35.52	2.52
36.00	2.49	36.10	2.49
36.62	2.45	36.68	2.45
39.95	2.25	40.02	2.25
41.15	2.19	41.22	2.19
44.60	2.03	45.08	2.01
47.30	1.92	47.34	1.92

synthetic lepidocrocite		standard values for lepidocrocite	
2θ°	dÅ	2θ°	dÅ
14.05	6.30	14.14	6.26
27.00	3.30	27.10	3.29
36.30	2.48	36.37	2.47
37.95	2.37	38.13	2.36
44.80	2.05	43.30	2.09
46.70	1.95	46.90	1.94
48.95	1.86	49.25	1.84

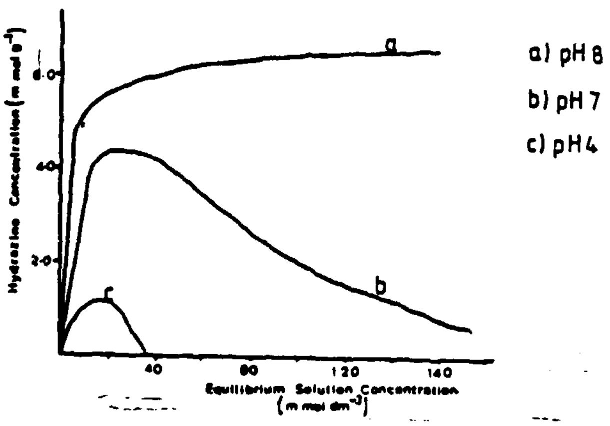


Figure 21. Isotherms for the interaction of goethite suspensions with hydrazine solutions at three pH values.

From these calculations, it is clear that a monolayer coverage of the goethite by hydrazine does not take place. The data do not preclude the formation of multilayers, but such is highly unlikely. Significantly more adsorbate would be held if the molecules were orientated end on to the surface, but the most likely explanation of the high so-called sorption is that hydrazine was degraded in the cell, aided by catalysis by the oxide surface.

The sorption isotherms at pH values of 4 and 7 both show an initial rise in the concentration of hydrazine sorbed, followed by an apparent decrease. This decrease, because of the nature of the CFSC method could represent a loss of hydrazine complex from the cell. Such would disturb the numerical analysis of the continous flow data. This behaviour was investigated by measuring the concentration of iron in the eluate using the standard thiocyanate complex colourimetric method. No iron (III) was detected in the eluate from the cell. By contrast, the release of iron II began as soon as the hydrazine entered the cell, and its concentration in the eluate rose to a maximum, 28.5 μgcm^{-3}, after a delay of a few minutes. The amount of iron II then slowly decreased to a steady value of 6.34 μgcm^{-3}.

The amount of iron washed out of the cell during 100 minutes of flow through was 376 µg or about 0.1% of the total iron present in the cell. Throughout the experiment there was a large excess of hydrazine over iron. The solubilization of iron was not due to the HCl used to decrease the pH of the hydrazine solution.

The rapid rise in concentration of iron in the eluate followed by its decrease to a constant concentration value could be due to factors such as:

(i) the rapid dissolution of the finer goethite crystalites, and the slower disolution of the coarser particles. (The goethite suspension is likely to contain materials of varying degrees of crystalinity);

(ii) the surface of the goethite may become deactivated after the reaction and then continue to react at a slower rate.

Whatever the reason, it can be stated that hydrazine reacted with goethite in suspension to produce iron II which then reacted to form a complex with additional hydrazine. The complex was soluble at low pH values and was eluted from the cell. (See page 43.)

No conclusive quantification of the results obtained from the continuous flow was possible since the numerical analysis relies on a mass balance round the cell, with all of the sorbent being retained in the cell. However, the following conclusions may be drawn:

(i) There is a large interaction between goethite and hydrazine solutions;

(ii) some form of interaction occurs at neutrality or in acidic conditions whereby the ion is solubilized, whether as iron (III) which is then reduced to iron (II) in solution, or directly in solution as iron (II) after reduction on the surface.

4.7.4 Vapour phase sorption of MMH by hydrous oxides and clays

The method outlined in Section 3.9 was used to study the adsorption of water vapur by goethite, Fe^{3+}-kaolinite and Na^{+} -kaolinite, and MMH by goethites, Na^{+} -kaolinite, Fe^{3+} -kaolinite, and Na^{+} -montmorillonite. The vapour pressure values and the weights of adsorptive measured for these systems were analysed using the BET equation and an estimation of the heat of adsorption of the monolayer for each system was made using the BET equation. Estimates were also made of the surface areas of the adsorbents, and the values obtained were compared with those found by other researchers. Details of the results are given in the publication by Hayes et al., (1984). A reprint is attached, and so the results are only summarized here.

H values for the extension of the spring were plotted against the weight added. The calibration obtained was linear, passing through the origin.

The values for the extension of the spring and for the vapour pressure of adsorptive were processed using a computer program. This program read in the data and converted each value of spring extension into a weight of gas sorbed. Knowing the mass of adsorbent present, these values were converted into the weight of adsorptive (g) g^{-1} of adsorbent. The vapour pressure of adsorptive was converted into partial pressure (P/P_0) values.

The slope and intercept of the line given by a plot of $P/X(P_0-P)$ against P/P_0 was calculated using a least squares linear regression analysis, and from this values of X_m and of C were calculated. From the constant C a value was obtained for ($E^1 - E^L$) and hence an estimate was obtained for the heat of sorption of the first layer.

The program was designed so that the calculations were first done for the initial three values. Then the process was continued for four values, five values etc. until all the values obtained were included in the calculations. In this way the effect of increasing partial pressures on the gradient and intercept of the plot of $P/X(P_O-P)$ against P/P_O was investigated.

<u>Water vapour sorption onto goethite</u> Figure 22a presents the isotherm for the sorption and desorption of water vapur on goethite. The isotherm shows no noticeable hysteresis and the initial and final weights of the sample were the same, indicating that the sorption of water on goethite is reversible.

Table 22 shows an analysis of the data obtained from the isotherm using the BET equation for data over different ranges of the isotherm. The specific cross-sectional area used for water was 10.8$\mathring{A}^2$ (12.5$\mathring{A}^2$ used in p.110)

<u>Sorption of monomethylhydrazine onto goethite</u> Figure 22b presents the isotherms for sorption of MMH vapour by and desorption from goethite. There is evidence for hysteresis below P/P_O values of 0.2 and the isotherm was not reversible. Even after exhaustive pumping about 7.5 μmol g^{-1} of sorbate was not removed. Table 23 shows the values obtained from the BET analysis of the isotherm. A value of 2.44 nm^2 was used in the calculations for the specific cross-sectional area of MMH.

The value of about 40 $m^2 g^{-1}$ found for the surface area of goethite from the vapour phase sorption of water and monomethyl-hydrazine is of the order of magnitude that would be expected for goethite. Aylmore (1974), reported BET surface areas of between 36 and 60 $m^2 g^{-1}$ for goethite, depending on the sorptive used. Argon gave the smallest surface area and carbon dioxide the largest. The estimates of the surface area of the goethite sample, using monomethylhydrzine are greater than those calculated using water as the adsorptive and this might suggest that the monomethylhydrazine is sorbed by hydrogen bonding to the hydroxyls on the surface of the goethite in a similar manner to that described for carbon dioxide by Russell <u>et. al</u>., (1975).

The values calculated for surface area and monolayer coverage are not affected to any great extent by the region of the isotherm studied. The values for the heat of adsorption of the first layer was greater than the latent heat of condensation of the water or monomethylhydrazine. Though the latent heat of condensation of water is greater than that of monomethylhydrazine the value of

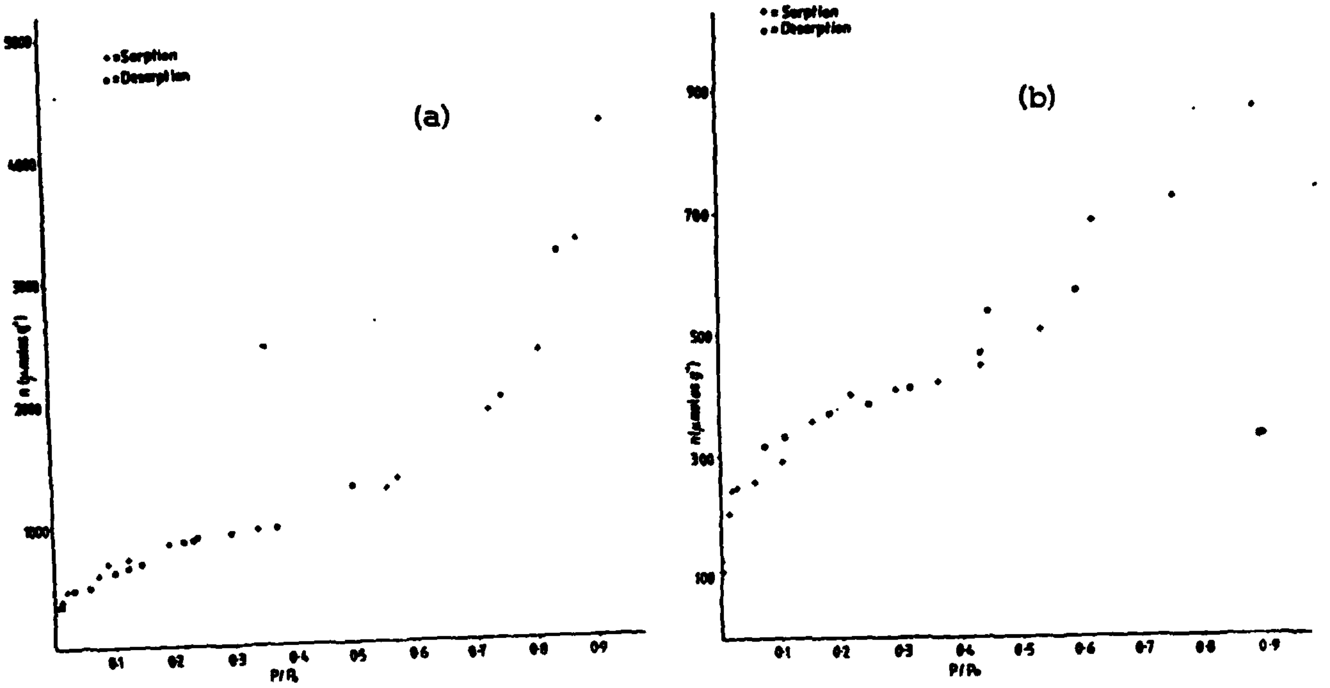


Figure 22. Isotherms for the sorption of water vapour at 301.2K (a) and MMH at 298.8K (b) by goethite.

Table 22. Isotherm analysis for sorption of water by goethite

P/P_0 range	n_{max} (μmol g^{-1})	H_{ads} (KJ mol^{-1})	surface area^a (m^2 g^{-1})	H^1 (KJ mol^{-1})
sorption (0.05-0.35)	620.0 ±40.0	11.55 ±3.0	40.37 ±5.0	-52.58 ±3.0
sorption (0.02-0.34)	602.0 ±50.0	11.75 ±3.0	39.17 ±5.0	-51.32 ±5.0
desorption (0.05-0.35)	626.0 ±90.0	10.29 ±3.0	40.71 ±5.0	-51.32 ±3.0
desorption (0.06-0.57)	623.0 ±90.0	10.54 ±3.0	40.50 ±5.0	-51.57 ±3.0

Table 23. Isotherm analysis for sorption of MMH lygoethide

P/P_0 range	H_{ads} (KJ mol^{-1})	n_{max} (μmol g^{-1})	surface area^a ($m^2 g^{-1}$)	H^1 (KJ mol^{-1})
sorption (0.05-0.35)	13.26 ±3.0	286.6 ±60.0	43.15 ±5.0	-53.88 ±3.0
sorption (0.01-0.37)	13.88 ±3.0	257.3 ±60.0	38.70 ±5.0	-54.26 ±3.0
desorption (0.07-0.32)	15.72 ±3.0	315.0 ±60.0	47.40 ±6.0	-56.09 ±3.0
desorption (0.07-0.45)	14.66 ±3.0	305.0 ±60.0	45.90 ±6.0	-55.03 ±3.0

H^1 for monomethylhydrazine was greater than that found for water. This suggests that there is a strong interaction between monomethylhydrazine and the goethite surface, as is further indicated by the fact that some of the adsorbate was not removed on evacuating the adsorbate adsorbent complex.

Sorption of Monomethylhydrazine vapours on NA$^+$ -montmorillonite. The isotherm for the sorption of MMH ny this clay was type II, but hysteresis was evident along the entire sorption-desorption path (Figure 23a). The loop shape is characteristic for sorption and desorption of polar vapors by montmorillonite and is attributable to the intercalation of the organi molecules between the expanding layers. X-Ray diffraction measurements gave a (001) spacing of 1.34 nm after desorption was complete, compared with a 0.97-nm spacing prior to the interaction, and this indicates that the residual MMH was held as a flattened monolayer between the clay layers.

Applications of BET and isosteric analyses are invalid in this system because of the irreversibility of the sorption process, but again these analyses were carried out for purposes of comparison. The specific surface area was estimated to be 725 m^2 g^{-1}, which is similar to that normally expected and the monolayer capacity to be 2.5 mmole g^{-1} (Table 4). Monolayer coverage would occur in the range of 2.4 to 3.7 $mmole^{-1}$ sorbate g^{-1} sorbent corresponding to an area of 722 to 1114 m^2g^{-1} of flattened sorbate molecules (for these estimates it is assumed that each MMH molecule touches two surfaces when flattened in the interlayer spaces. When the desportion process was terminated 2.7 mmole g^{-1} of sorptive remained on the clay corresponding to a surface coverage of 813 m^2 g^{-1}. This indicates again that the MMH, which was not desorbed, was held in the interlayer spaces of the clay, because the interlayer faces contribute almost all of the surface area of montmorillonite.

The pattern of the change in the values of the differential isosteric enthalpy of interaction as sorption increased was distinctly different from that for the Na^+ -K system (Figure 23d). Here the values increased from -80 kJ $mole^{-1}$ at low surface coverage and passed through a maximum of -130 kJ $mole^{-1}$ at monolayer coverage. The isosteric values then decreased rapidly as further sorption occurred. These values were derived from data taken at three temperatures and in this respect have limitations. They were, however, significantly greater than the net energy values (-15.1 kJ $mole^{-1}$) estimated from BET data. (Table 24).

Energy will have been required to separate the clay layers in order to allow access of the sorptive molecules to the interlayer sorption sites. The results show that binding to the sites, particularly through "hydrazination" of cations, was highly energetic, but the net isosteric enthalpy was influenced (lowered) by the expenditure needed to separate the layers. Although less energy was needed to expand the layers as sorption progressed some additional energy was then required to aid diffusion of the sorptive species through the narrow gaps to the more remote interior sites between the layers.

A small amount of residual water was associated with the clay, most likely with the exchangeable cations at the surface, as evidenced by the low surface area (460 m^2 g^{-1}, Table 24) calculated from data for sorption of water, and by comparison of the infrared spectra for the clay with and without interacted MMH.

A reduction in intensity of the broad infrared absorption bands centered at 3420 and at 1630 cm^{-1} due to occluded water indicated that the MMH competed well with these molecules. Energy will have been required to displace this water and this would also be reflected in a decreased net energy of sorption.

The infrared spectrum of the clay -MMH sorption complex also showed a small absorption band at 3340 cm^{-1} which may be assigned to N-H stretching of intercalated sorbate molecules. Deformation vibrations in a broad band from 1550 to 1720 cm^{-1} suggested a range of different polarizations of N-H bonds, but there was no evidence for the involvement of ion exchange in the binding process because there were no distinct absorption bands around 3200, 2000, and 1530 cm^{-1} to indicate the presence of protonated MMH species. The absence of bands at 3280 and 1420 cm^{-1} also suggested that ammonium ions which might result from degradation of the sorbate were not part of the sorbate. Bands at 1460 and 1370 cm^{-1} could be assigned to asymmetric and symmetric CH_3 deformation vibrations, respectively. Some iron (III), either within the crystal structure or at the surface was reduced to iron (II), as evidenced by the smaller absorption bands at 890 cm^{-1} in the MMH-clay complex as compared with the untreated clay.

The MMH to sodium ratio at monolayer at monolayer surface coverage was, to the nearest whole number, 3:1. A summation of the available evidence would suggest that the most likely sorption mechanisms would involve "hydrazination" of the exchangeable sodium cations in which the MMH molecules would coordinate in trigonal coplanar array with the interlayer cation. Such sorbate molecules could then weakly hydrogen bond to the siloxane surfaces on adjacent layers and this bridging effect would explain the difficulty in desorbing sorbate species from between the montmorillonite layers.

<u>Sorption of MMH on Na^+ -kaolinite</u>. Fig. 23b shows the reversibility of sorption of MMH by Na^+ -K, and the same trends were evident for the sorption and desorption of water vapor. The isotherms were type II or L-type, characteristic of physical sorption onto nonporous or macroporous sorbents with the formation of multilayers of sorbate.

Sorption isotherms were analyzed in the relative pressure (p/p_o) range of 0.05 to 0.35 using the BET equation, which enables calculation of the amount of vapor required to form a complete monolayer (X_m), and a constant (c) which is

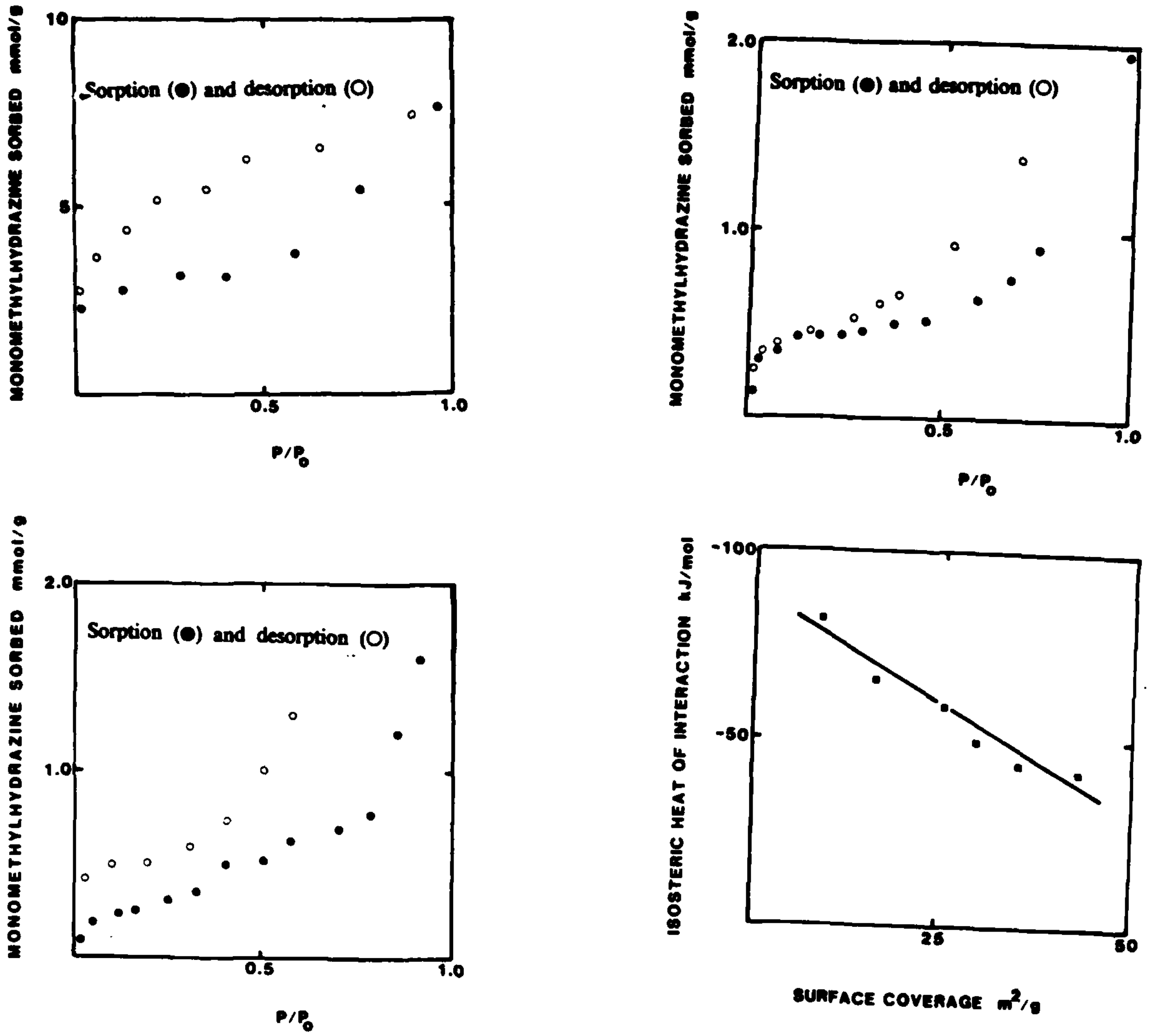


Figure 23. Isotherms for sorption and desorption of MMH by Na$^+$ -montmorillonite at 298K (a), by Na$^+$ - kaolinite at 298K (b), and by iron (III) kaolinite (c). Part (d) shows variation of isosteric enthalpy of MMH sorption with surface coverage for Na$^+$ - kaolinite.

exponentially related to the net energy of sorption (E_1 - L) by

$$E_1 - L = RT \ln \underline{c}$$

where E_1 is the average energy of sorption of the first layer of molecules, and L is the latent heat of condensation of the sorptive. The specific surface area (S) can also be calculated

$$\underline{S} = X_{\underline{m}} N A_{\underline{m}} 10^{-3}$$

where $X_{\underline{m}}$ is expressed in millimoles per gram, $A_{\underline{m}}$ is the molecular cross-sectional area of the sorbate, and N is Avogadro's constant.

Table 24 contains values for c, $X_{\underline{M}}$, net energy of sorption, and S for the sorption of MMH and of water vapor. The $\underline{S}$ value calculated for sorption of MMH (50 m^2 g^{-1}) where $A_{\underline{m}}$ = 25 Å^2, was larger than that for water vapor (29 m^{2}g^{-1};

Table 24. Values calculated from vapour phase sorption of MMH and water by kaolinite and montmorillonite preparations

BET Analysis	Monomethylhydrazine[a]			Water vapor[a]		
	Na^+-K	Fe^{3+}-K	Na^+-M	Na^+-K	Fe^{3+}-K	Na^+-M
C-constant	506	33	434	36	245	6.4
Specific surface area (m^2g^{-1})	50	32	725	29	15	460
Monolayer capacity (mmole g^{-1})	0.34	0.21	2.5	0.39	0.21	3.1
Net heat of sorption (kJ $mole^{-1}$)	−15.4	−8.6	−15.1	−8.9	−13.4	−4.6
Sorbate:exchangeable Ion	4:1	7:1	3:1	4:1	7:1	4:1

[a] Na^+-K, sodium-exchanged kaolinite; Fe^{3+}-K, iron(III)-exchanged kaolinite; Na^+-M, sodium-exchanged montmorillonite.

A_m = 12.5 $\AA^2$), and the net energy of sorption was approximately 50% greater at −13.2 kJ $mole^{-1}$ sorbed. Assuming that the latent heat of condensation of MMH is −40.4 kJ $mole^{-1}$ then the average energy of sorption of the first layer of molecules amounted to −53.6 kJ $mole^{-1}$.

Type II isotherms were also obtained for sorption of MMH at 308 and at 318 K. The differential isosteric enthalpy of interaction (q_{st}) was obtained from the slope of the plot of ln p versus 1/T, as given by

$$\ln p = \frac{q_{st}}{RT} \qquad (3)$$

where p is the pressure at which the same amount of sorption is measured at the different temperatures. Although a good linear plot was obtained (Fig. 23d), the limitations of data obtained from only three temperature values are recognized. Nevertheless Fig. 23d shows a linear decrease in q_{st} values from −80 kJ $mole^{-1}$ at low surface coverage to −45 kJ $mole^{-1}$ as monolayer coverage was approached. This latter value is approaching the average energy of sorption of the first layer estimated from BET parameters.

Figure 23d clearly indicates that the initial binding of MMH to sites on the Na^+-kaolinite was almost twice as energetic as later binding when sorption approached monolayer coverage. From the desorption isotherm (Fig. 23b) it is evident that, although some hysteresis occurred at the high relative pressure values, desorption followed sorption closely over the major portion of the isotherm. Only a very small amount of the MMH sorbate (0.01 mmole g^{-1}) resisted desorption. X-Ray diffraction indicated that no irreversible intercalation of the Na^+-kaolinite by MMH resulted from the reaction conditions employed.

On completion of monolayer coverage (as estimated by X_m, BET equation) the ratio of the number of MMH molecules adsorbed to the number of exchangeable sodium ions was, to the nearest whole number, 4:1 which was the same as the corresponding ratio for water molecules.

The mechanism of water vapor sorption involves hydration of the exchangeable sodium ions and probably some weak hydrogen bonding to the clay surfaces. MMH is a stronger nucleophile than water and could be expected to "hydrazinate" the exchangeable cations. Square coplanar coordination to the sodium ions is probable, but alternative trigonal coplanar with one molecule in four hydrogen bonded to coordinated molecules is also feasible. All molecules could be involved in intermolecular hydrogen bonding ($\Delta H^o = -1.75$ kJ $mole^{-1}$ is quoted for hydrogen-bond formation in the self-association of MMH), and it is probable that each molecule could be associated with the clay surface, most likely through hydrogen bonding. Unfortunately, it was not possible to obtain supportive data from infrared spectroscopy because the spectra obtained for MMH-Na^+-K complexes gave poor resolution.

Sorption of MMH on Fe^{3+}-kaolinite

Figure 23c gives isotherms for the sorption and desorption of MMH by Fe^{3+}-K. The sorption mode is a type II isotherm, but hysteresis is clearly evident in this instance, and 0.4 mmole g^{-1} was not removed when the sorption process was reversed. The retained sorbate was reduced to 0.04 mmole g^{-1} when the system was subjected to evacuation for 24 hr.

The limitations of BET analysis to the system described is recognized, but it was applied to the sorption mode for purposes of comparison. The specific surface area was estimated to be 32 m^2 g^{-1}, and the monolayer capacity of 0.21 mmole g^{-1} was the same as that for water vapor (Table 24). Thus the ratios of MMH and water molecules per Fe^{3+} ion were the same at 7:1. From BET measurements, the net energy of sorption was estimated at -8.6 kJ $mole^{-1}$, giving an E_1 value of -49 kJ $mole^{-1}$. This may be compared with the experimentally obtained monolayer coverage of -60 kJ $mole^{-1}$.

Sorption of MMH in the Fe^{3+}-K system is probably quite complex because the sorbate is capable of reducing Fe(III) to Fe(II) and complexes of the form $[Fe^{2+} (N_2H_4)_2 X_2]n$, where X = Cl, Br, J, CH_3, CO_2, or CNS, are known to form in aqueous systems with hydrazine as the bridging ligand.

4.8 Sorption of Hydrazine by Humic Acid Preparations

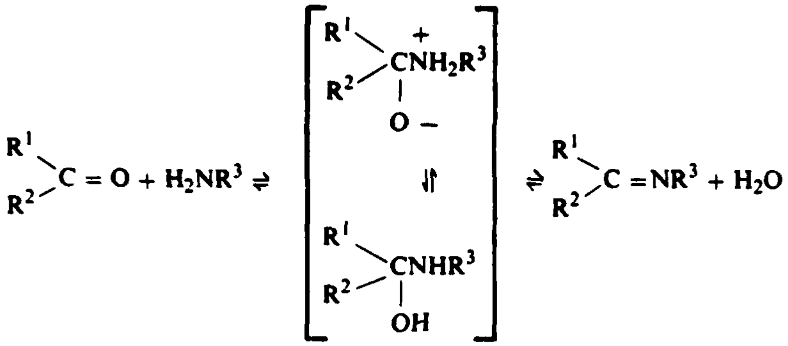
Humic acids (HA) were isolated as described in Section 2.1 from a humic histosol (Methwold, Norfolk, England). Ca^{2+} - and Al^{3+} - exchanged humates were prepared (see Isaacson and Hayes, 1984) by adjusting the pH of a 1% w/v suspension of H^{+} -HA to 5.5 and then adding excess Ca^{2+} or Al^{3+} ions as chloride salts. Sorption and desorption was measured by using the CFSC procedure (Section 3.3.2). Microcalorimetry used the LKB 10700-2 Batch Microcalorimeter.

Figure 24 (page 115) presents isotherms for sorption of hydrazine by H^{+}-HA, Ca^{2+} - humate, and Al^{3+} -humate, and the pH of the system was 4.0. Al^{3+} and Ca^{2+} displaced in the sorption processes were measured. The goodness of fit of the data to Freundlich, Langnuior, Temkin and Rothmund-Kornfeld equations were measured (see appended paper by Isaacson and Hayes, 1984). Data for the differential energies of sorption are given in Figure 25. The interactions were exothermic in every case, but the values recorded were different for the three preparations. Whereas the differential enthalpy decreased as more hydrazine was added to the H^{+} - HA and Al^{3+} - humate preparations, that for the Ca^{2+} -humate increased.

4.8.1 Mechanisms of sorption of hydrazine by humic acids in acid conditions

At pH 4 only 0.005 - 0.001% of the hydrazine in solution was not protonated; hence the hydrazinium ion species predominated in the interaction with the humic materials in these experiments. The involvement of ion exchange in the binding process indicated by the displacement from the adsorbents of protons and of calcium ions when hydrazine hydrate interacted with H^{+} -HA and Ca^{2+} -humate, respectively. The extent to which ion exchange was involved in the sorption processes may not be fully represented by the amounts of protons and of calcium ions (approximately 0.3 mol kg^{-1} sorbent) displaced from the sorbents by the hydrazine preparations. Hydrazine removal by acidified water (pH 4) and by 0.1$\underline{M}$ sodium chloride (pH 4) was similar for the three sorption systems, but it was greater than the estimates for protons and calcium ions removed by hydrazine hydrate at pH 4. It was assumed, for the calculations made, that sorption equilibrium was attained in the reaction cell. However, diffusion through sterically complex polymers is slow and it is possible that some of the exchanged cations might not have been released into the eluates from the cell. If so, hydrazinium and exchanged cation salts would be held in the polymer matrix.

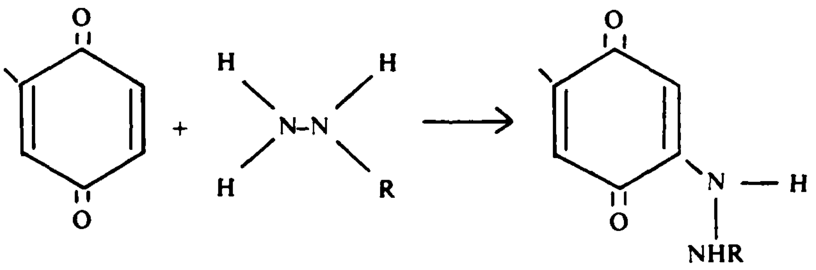
There is strong evidence to show that condensation reactions took place between hydrazine species and carbonyl groups on the humic structures, as indicated in reaction scheme (4.6)



(4.6)

where R^1 and R^2 are aliphatic or aromatic hydrocarbon groups and R^3 is NHX, in which X is H or an aliphatic or aromatic hydrocarbon substituent. The maximum rates for such reactions occur when the pH values of the media are close to the pK_a values of the hydrazine reactants. These principles are inherent in the reactions in which phenylhydrazine is used to estimate the carbonyl contents of the humic substances.

Hydrazine can also react at positions activated by carbonyl groups to form, for example, pyrazole derivatives in isoflavone structures. In a similar way, activation by carbonyl groups in quinone structures in humic compounds would provide substitution products as shown in scheme (4.7) (see Hayes and Swift, 1978).



(4.7)

Hydrazines incorporated in this way would be less susceptible to hydrolysis than products of condensation with carbonyl groups.

The changes in the infrared spectra of the interacted complexes are consistent with some replacement of C=O by C=N bonds and with an increase in the number of N-H bonds in the humate molecules. These spectral changes persisted after the complexes were washed with salt solution followed by acidified water to remove hydrazinium species held by ion exchange and by the less energetic binding forces.

If it is assumed that the hydrazine reacted with one carbonyl group only, half of the possible number of hydrazone derivatives were formed. However, if each hydrazine molecule condensed with two carbonyl groups, as is feasible, then nearly all of these groups were involved in condensation reactions in the cases of H^+ -HA and Ca^{2+} -humate systems.

Measurements of carbonyl contents were not made after interactions with the hydrazine species. Such measurements would provide information about the extent of the hydrazine-carbonyl condensations and allow better speculation about the extent to which substitution reactions occurred in the sorption processes.

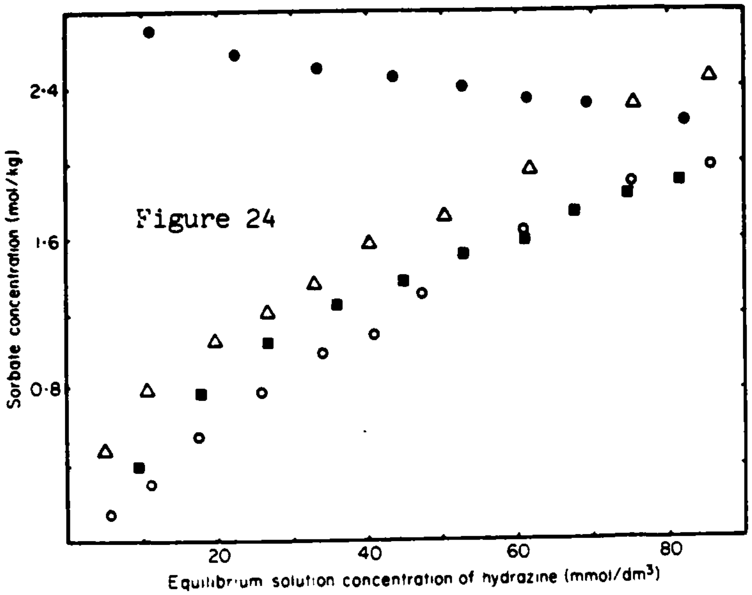
4.8.2 Conclusions from Studies of sorption of hydrazine by humic materials

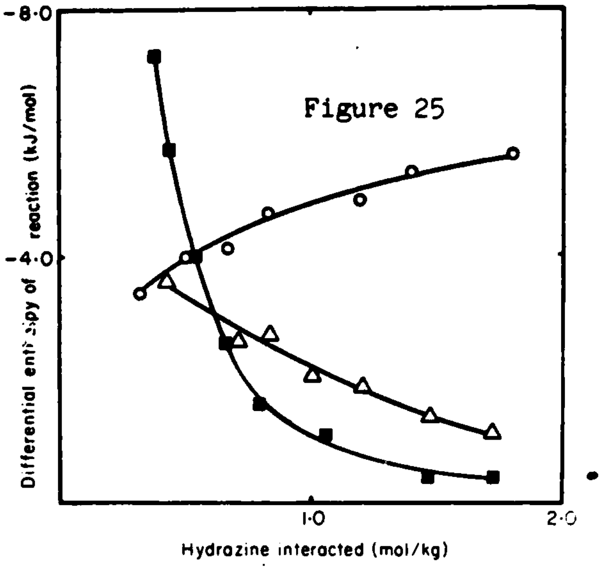
Isaacson and Hayes (1984) have discussed in detail the isotherms obtained for the H^+-, Ca^{2+} - and Al^{3+} -humic preparations, and the reader is referred to the appended paper by these authors. It is appropriate to comment here on the shape of the differential energy plot for sorption by the Ca^{2+} -humate. It is thought that the increase in enthalpy with sorption results from increased availability of internal sorption sites in the matrix as the macromolecular structure was expanded by replacement of Ca^{2+} -ions responsible for intermolecular bridging.

At pH 4 hydrated hydrazine compounds were more extensively held by H^+ - than by Ca^{2+} - or Al^{3+} -exchanged humic preparations. This reflects the greater ability of the ionized sorptive species to exchange with hydrogen rather than with calcium and aluminium ions on the exchange complex, and to disrupt hydrogen bonding rather than divalent- and polyvalent-cation bridges between the polymer strands.

The evidence provided by infrared spectroscopy points to the formation of condensation reaction chemisorption processes, even though the pH of the media were about four units lower than the optimum for such reactions.

The drying of humic substances gives rise to strong interstrand attractions and to conformations in which the more hydrophylic functional groups associate with each other in the interior of the macromolecular structure. Such arrangements present difficulties for the wetting of dry humic substances, and this phenomenon is well recognized. Although the pH used in this study was not highly relevant to most field conditions, it did not have a significant influence on the shapes and behaviour of the sorbent molecules. It did, however, ensure that the sorptive was primarily the hydrazinium ion species. It can be predicted that raising the pH would decrease the importance of ion exchange and increase the contribution of chemisorption to the binding processes.





(24) Isotherms for the sorption of hydrazine by: △, hydrogen-exchanged humic acid; ■, aluminium-exchanged humate; ○, calcium-exchanged humate; ●, isotherm for the desorption of calcium, by hydrazine, from calcium-exchanged humate.

(25) Differential enthalpy of reaction per mole of hydrazine sorbed per kg sorbent: △, hydrogen-exchanged humic acid; ■, aluminium-exchanged humate; ○, calcium-exchanged humate.

4.9 Experiments with Whole Soil

The objectives of USAF contract number AFOSR-80-0032 was to concentrate effort on studies of the mechanisms of interactions of hydrazine compounds with soil colloidal constituents. Hence only preliminary experiments were carried out to investigate reactions with whole soils.

A sieved (3.38 mm), air dry soil having 49.2% clay, 19.1% silt, 25.8% sand, and 5.9% organic matter, which had stable aggregates, was placed over a sintered disc in a 15 cm glass column (4 cm i.d.) and covered with glass wool. A three-port glass cap was fitted and sealed in place by an inert "O"-ring. The soil (ca. 200 cm^3) was first flushed with nitrogen, then washed with water by pumping into the input part (see Figure 26). Hydrazine and desorbing solutions were introduced in the same way. Attempts to introduce solution input to the top of the column failed because of gradual blockage of the sintered disc. The gas inlet and outlet parts of the cap allow an atmosphere of known composition to be maintained (nitrogen in initial experiments), and also allow collection of volatile products. The apparatus can be thermostatted by addition of a water jacket.

A schematic diagram of the apparatus used to study soil-hydrazine interactions is shown in Figure 26. Pure hydrazine hydrate (2.5 mol kg^{-1} soil) was washed into the soil and a vigorous interaction took place with some evolution of heat. The soil aggregates which were stable to water could be seen to break down, and bubbling (possibly from decomposition products of hydrazine) occurred in the pore spaces. Washing with water desorbed ca. 30% of the interacted

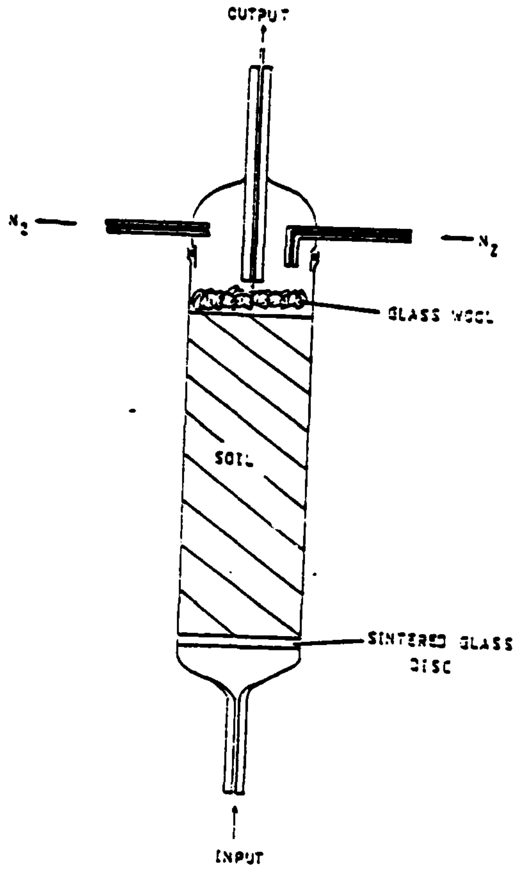


Figure 26. Schematic drawing of the set up used to observed hydrazines-whole soil interactions.

hydrazine, leaving a net interaction of ca. 1.7 mol Kg^{-1}. The eluate from the water washing contained some clay and silt (ca. 1% by weight of original soil) from the breakdown of soil aggregates, and was dark brown due to dissolved organic matter.

The results of this preliminary experiment show the very large potential of the soil used to interact with hydrazines. The breakdown of soil structure caused by swelling of clays and dissolution of organic matter will have important physical consequences on the fate of hydrazines. The drainage of hydrazines through such soils would be greatly impeded by such structure breakdown.

It can be concluded that the types of interactions observed in the laboratory for soil colloidal components will take place in the field, and it would appear that soils with appreciable amounts of clays and humic materials have a large capacity to degrade hydrazine.

5. SUMMARY AND GENERAL CONCLUSIONS

The clay colloidal component of soil can be predicted to have a large influence on the fate of hydrazines in the soil environment. Initial degradation and microalorimetric studies have shown that this influence arises mainly through the processes of sorption and degradation. Clay minerals can reversibly sorb hydrazines, and a certain amount of strong irreversible sorption can also occur. The colloidal clay component clay components catalyse the degradation of the hydrazines, and in some instances cause very rapid and vigorous degradation. The two main factors which influence hydrazine sorption and degradation are the pH values of the solutions, and the exchangeable metal cations held by the clay.

The degradation of hydrazine occurred in the presence of oxygen and the extent of degradation was shown to increase as the pH was increased because a greater proportion of unprotonated hydrazine species, N_2H_4 was present in the more alkaline solutions. In the presence of homoionic-exchanged montmorillonite, such as the K^+-, Na^+-, Mg^{++} - and Ca^{++} -clays, degradation was further enhanced due to the presence of heterogeneous surfaces provided by the clay particles. The Mn^{++} -, Cu^{++} -, and Fe^{+++} - exchanged montmorillonites were also found to catalyse the degradation of hydrazine in the presence of oxygen, due predominantly to the capacity of these cations to participate in redox reactions. They were first reduced by the hydrazine and then re-oxidised by oxygen present in the solution. Previous work has shown the effect of transition metal ions on the degradation of hydrazine in solution, but this study is first to show how the degradation is influenced when the metals are entrapped on the surfaces of clays and not 'free' in the bulk solution. In the presence of the Cu^{++} -montmorillonite, degradation of hydrazine on solution was very rapid and vigorous, whereas the degradation was much slower (than for the Al^{2+} clay) in Mn^2 - and Fe^{2+} - clay suspensions. The extents of degradation were greatly reduced in the absence of oxygen, but oxidation of hydrazine still took place. The cupric ions are readily reduced to Cu^+ ions and this is clearly observed in a solution containing cupric chloride. A small proportion, about 10 - 12%, of Fe^{3+} ions immobilised in the structure of the montmorillonite was found to be reduced to the ferrous (Fe^{2+}) state.

Microcalorimetric studies have shown that large enthalpy changes take place where strong interactions occur between hydrazine and the homoionic-montmorillonites. These interactions may involve the degradation and/or sorption of hydrazine. The sorption of various amines by montmorillonite has been extensively documented and researched and the nature of some of the complexes have been characterised. In this work, the effect of the pH value of the sorption media was found to greatly effect the sorption of the hydrazine, as an amine. The type of exchangeable cation in the homoionic-montmorillonite was found to be the other major factor in affecting the sorption of hydrazine. In the case of the monovalent Na^+ - montmorillonite, cation exchange between the Na^+ ions and hydrazinium ions is the main mechanism of adsorption; hence, at pH value of 4, the adsorption of hydrazine was five to six times greater than that at pH 8. As the polarizing power of cations increase they are more strongly bound by the clay surface and they are not readily replaced by the hydrazine sorptives. At low pH values, the protonated hydrazinium species can replace protons of water molecules co-ordinated to the cations, or at high pH values, hydrazine, as a base, can be protonated by protons of the more acidic co-ordinated water. For Ca^{2+} -montmorillonite, adsorption at pH 8 was only slightly greater than at pH 4 since both of the processes described at high and low pH values occurred to similar extents.

However, in the cases of Al^{3+} - and Fe^{3+} - montmorillonite, the adsorption was increased almost ten times when the pH of the sorptive solution was raised from 4 to 8. Under conditions of high pH, hydrazine can effectively act as a basic amine, causing the hydrolysis of the exchangeable Al^{3+} or Fe^{3+} to form hydroxides in the interlayers with simultaneous adsorption of the hydrazinium ions to balance the surface negative charges. The extent of interaction was further enhanced when the clay was adjusted to pH 8 by sodium hydroxide and equilibrated prior to sorption. The formation of interlayer hydroxide polymer fixed the exchangeable Al^{3+} rendering it non-exchangeable, as was observed during ion-exchange studies. The surface negative charge was balanced by Na^{+} ions which were readily replaced by the hydrazinium ions during hydrazine sorption. The amounts of hydrazine and monomethylhydrazine sorbed far exceeded the CEC value of the Al^{3+} - montmorillonite indicating that binding mechanisms other than ion exchange were in operation.

This sorption of excess hydrazines may be compared with the sorption of monoamines and diamines by homoionic exchanged montmorillonites in aqueous systems. The sorption of the excess amines has often been seen as a competition between sorbed water and the excess amine associated to the cation on the clay surface. Hence, experiments investigating the adsorption of amines on clays are often carried out in an environment where this competition from water is minimised; for example, under very low pressures at which monolayer water is present in the interlayers, or when the clay is suspended in a solution of the amine in an organic solvent. However, water is a better competitor for sorbed monoamines than for sorbed diamines. In their work with ethylenediamine in aqueous systems, Cloos and Laura (1972) found that the excess diamine was still adsorbed and the excess was not totally desorbed by water washing. In fact, Servias _et al_., (1962) and Fripiat _et al_. (1962) did find that washing the clay-amine complex with a non-polar solvent like benzene did not remove the excess diamines adsorbed, but it removed the excess monoamines. Hence, other factors like the stronger interaction between the diamine molecules through hydrogen bonding come into play when considering the adsorption of diamines in aqueous systems.

Therefore, in the case of sorption, of hydrazines by clay, the hydrazines (with their nitrogen atoms in the molecules) behave as diamines. Hydrogen bonding exists between the protonated amine and the unprotonated amine or water molecules, as shown in infra-red spectra studies, and as infrared from enthalpy changes from microcalorimetric studies. The sorbed hydrazine and monomethylhydrazine hydrogen bond with the hydroxy-aluminium polymer in the interlayer, providing greater stability for the sorbate in excess of the CEC value. Basal spacings from X-ray diffractometry indicated that the hydrazine and monomethylhydrazine sorbed lie in a single layer with its N-N axis parallel to the clay surface. In the case of the monomethylhydrazine sorbate, some "keying-in" of the methyl group into the surface occurs since the basal spacing of the dried complex was less than the Van der Waals diameter of the sorbate.

Heating of the hydrazines-hydroxy-aluminium-montmorillonite complexes caused the deprotonation and degradation to ammonia of the hydrazine and monomethylhydrazine sorbates. This principal decomposition product (NH_4^+ ions) was strongly held by the clay, (even at 350°C) as these cations balanced the surface negative charges. The sorbed water in the monomethylhydrazine-clay complex affected the other thermal decomposition products at 350°C. The diimine formed on elimination of hydrogen further reacted in the presence of water; when it was in a relatively dry environment it remained sorbed. Differential thermal analysis showed that some hydrazines are held in positions such that they are thermally degraded only at specific temperatures of 235°C and 350°C. Multimolecular decomposition normally occurs at lower temperatures, and it is likely that these hydrazines which degraded at higher temperatures underwent unimolecular decomposition through fourcentred loss of ammonia or hydrogen, or through N-N homolysis.

This work has highlighted the types of interactions of hydrazine and monomethylhydrazine with homoionic-montmorillonite preparations and factors affecting these interactions which can be extrapolated to other clay colloids, namely kaolinite. It has further elucidated the sorption mechanism of hydrazine and monomethylhydrazine by Al^{3+} -montmorillonite in aqueous systems. Further work on the thermal decomposition pathways of the sorbed hydrazines can be carried out on a gas-chromatograph-massspectrometer linked DTA apparatus, and using labelled methyl groups in the monomethylhydrazine sorptive. The interaction of hydrazine with Fe^{3+}-montmorillonite has many interesting aspects which can be further investigated; e.g., the oxidation and reduction of the hydrazine and Fe^{3+} ions; the contribution that the reduction of exchangeable Fe^{3+} ions to Fe^{2+} ions makes to the degradation and sorption of hydrazines; and the effect of hydrolysis on the fixation of the Fe^{3+} ions in the interlayer. Mossbauer spectroscopy offers a sensitive technique in determining the location of the reduced Fe^{2+} ions, e.g., in Al^{3+}-octahedra in the lattice of the clay structure, or at the edges of the clay, or in the interlayers.

Hydrous oxides are very important components of soils, and this study has shown that oxides and hydroxides of iron and aluminium are important for the binding and degradation of hydrazine structures. In studies of goethite in aqueous hydrazine media at pH values of 8, 7, and 4 there was clear evidence for the formation of soluble hydrazine-iron(II) complexes at pH 7 and especially at pH 4. Such complexes were not formed at pH 8.

Work is continuing to characterize more fully the nature of the complexes formed between hydrazine materials and oxides and hydrous oxides. These results will be presented at a later date as an APPENDIX to this report.

Detailed infrared spectra have been obtained for interactions of hydrazine, in solution and in the vapour phase, with goethite, and for goethite treated with monomethylhydrazine vapour. (These spectra will be included in the information to be appended.) The spectra for the goethite-hydrazine complexes confirm that there is a strong interaction between the materials, whether sorption is from the vapour or liquid phases. There was clear evidence for the N-N stretching mode in the composite spectrum at lower frequency than for hydrazine and there was clear evidence for hydrogen bonding of the adsorbate to the adsorbent.

In the case of MMH there was spectral evidence which suggested the presence of the $CH_2=NH$ species on the goethite surface. Again this would suggest degradation of the vapour phase complex based on a four centered concerted loss of ammonia (refer to Golden et al., 1972 and see page 93).

The results for the oxide-hydrous oxide materials indicate that in neutral and especially acidic conditions the iron oxides will form soluble complexes with hydrazine, and these complexes would be mobile in the soil profile.

Ion exchange was an important mechanism for the sorption of hydrazine by humic acid materials. There was evidence too for chemisorption processes, and plausible mechanisms would suggest the formation of Schiff base structures, and carbon to nitrogen bonds between quinone structures on the adsorbent and the amino group on the adsorbent. The results obtained have shown that the nature of the resident exchangeable cation in the humic matrix can influence the extents and the mechanisms of sorption.

From the standpoint of treating soils where hydrazine compound spillages have occurred the data which we have obtained suggest that the soil colloidal constituents will readily interact with the hydrazine compounds whether in solution or/and in the vapour phase. In some instances, especially under acidic conditions, soluble complexes will be formed with colloidal sesquioxides which could migrate into the drainage waters. Such complexes are not formed under alkaline conditions. An appropriate treatment for spills might be to lime the soils, or to treat with $CaCO_3$ to raise the pH to 8. Adsorption on the inorganic colloidal surfaces would hasten degradation of the hydrazine materials, and this degradation would be greatly accelerated by addition of Ca^{2+} salts.

APPENDIX

Although support for contract AFOSR-80-0032 has officially ended the senior author is continuing to work independently with aspects of the work. He will continue to submit data which may be added to this Appendix. These data will be concerned especially with mechanisms of binding of hydrazines to iron oxides. He feels too that it is important to investigate mechanisms of binding of hydrazine materials to humic substances at pH values relevant to most soils. Finally, he wishes to compare results for sorption of dimethylhydrazines with those for hydrazine and monomethylhydrazine.

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