THE SORPTIVE PROPERTIES
OF ORGANO-BENTONITES

by

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ABSTRACT

The sorptive properties of Wyoming bentonite and Ben-U-Gel, a commercial hectorite, containing α-ω alkyl diammonium ions have been investigated. The capacity of the derivatives towards sorbates incapable of swelling the clay was found to decrease, though not linearly, with increasing length of the alkyl chain of the ion. Comparison of theoretical and observed interlamellar areas revealed large discrepancies, reasons for which have been suggested. With acetonitrile as sorbate, the influence of the interlamellar ion was more complex. Ions having four, five or six carbon atoms in the alkyl chain gave rise to two-layer complexes, whilst both smaller and larger ions gave complexes of three interlamellar layers. Reasons for this behaviour have been proposed, and the orientation of the interlamellar ion in such cases has been discussed.

The differential heats and entropies of sorption of heptane and benzene on various derivatives have been calculated from isotherms measured at different temperatures. It was found that the heats decreased with increasing length of the alkyl chain of the interlamellar ion, the sorption becoming endothermic for chains of more than six carbon atoms. The endothermic sorption is attributed to the swelling of the clay and rearrangement of the interlamellar ions.

Hysteresis was observed in all the systems investigated, the hysteresis loops being of three types depending on the extent of swelling caused by the

sorbate. Theories of capillary condensation and swelling hysteresis have been discussed in relation to the observed behaviour.

Contrary to the findings of Weiss (1963), the clays containing small alkyldiammonium ions swelled beyond the limit expected if a "tie" effect was operative, but no sorbate was found which could swell the derivatives containing the larger ions up to this limit.

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INTRODUCTION

The properties of montmorillonites containing alkylammonium ions have been studied extensively in recent years, but relatively little work has been done on the alkyl-diammonium derivatives. It has been shown (Barrer and Reay, 1957) that small mono-alkylammonium ions act as "props" between the lamellae and thereby create a considerable intracrystalline porosity. By analogy it seemed that the interlamellar separation of the silicate layers could be varied systematically by changing the number of carbon atoms in the alkyl chain of the alkyldiammonium ions, and it should thus be possible to increase the sorptive capacity of the clay towards sorbates which were capable of swelling the clay to the maximum extent allowed by the alkyldiammonium ions crosslinking the silicate sheets. It is the purpose of the present work to investigate this possibility in a quantitative manner.

STRUCTURE OF MONTMORILLONITE

The structure of montmorillonite cannot be resolved by single crystal X-ray diffraction as the mineral occurs only in very small particles. It has been determined, not unequivocally however, by comparison with known structures of similar minerals, such as vermiculite, and from powder X-ray diffraction photographs.

The presently accepted structure is similar to the one proposed by Hofmann, Endell and Wilm (1933), who considered it to resemble pyrophilite (Pauling, 1930), but this was later modified by Marshall (1935) to account for the exchange capacity of the clay. He proposed the isomorphous replacement of some aluminium ions by magnesium or ferrous ions, and possibly of silicon by aluminium, the resulting negative charge being counterbalanced by ions between the sheets, which gave rise to the observed exchange capacity. The sheets consisted of a central aluminium layer, octahedrally co-ordinated to oxygen atoms and OH groups, sandwiched between two sheets of silica tetrahedra, their apices pointing inwards. The OH groups bonded to the aluminium ions lie in the same plane as the apical oxygen atoms, Fig. 1.1. The stacking of the sheets was investigated by Magdefrau and Hofmann (1937), who concluded that they were randomly superposed, though a more recent investigation by Longuet-Escard, Mering and Brindley (1960) questioned this turbostratic structure. Their X-ray diffraction patterns indicated a certain regular stacking of the sheets.

A rather different model was put forward by Edelman and Favejee (1940). They supposed that the silica tetrahedra were inverted, the apices pointing away from the layer, with a hydroxyl group at the apex instead of an oxygen atom. The ion-exchange properties were accounted for by assuming the hydrogen of the hydroxyl group to be replaceable. A review of the evidence for and against this structure was given by Reay (1956) and McEwan (1961), and will not be repeated here. The structure is incompatible with a Fourier synthesis (Brown, 1950), and is no longer considered as a probable one.

The unit cell dimensions for a and b axes are 5.17Å and 8.94Å respectively. The spacing in the c direction varies according to the cation present between the lamellae, and its state of hydration, but the thickness of the aluminosilicate layer is 9.4Å.

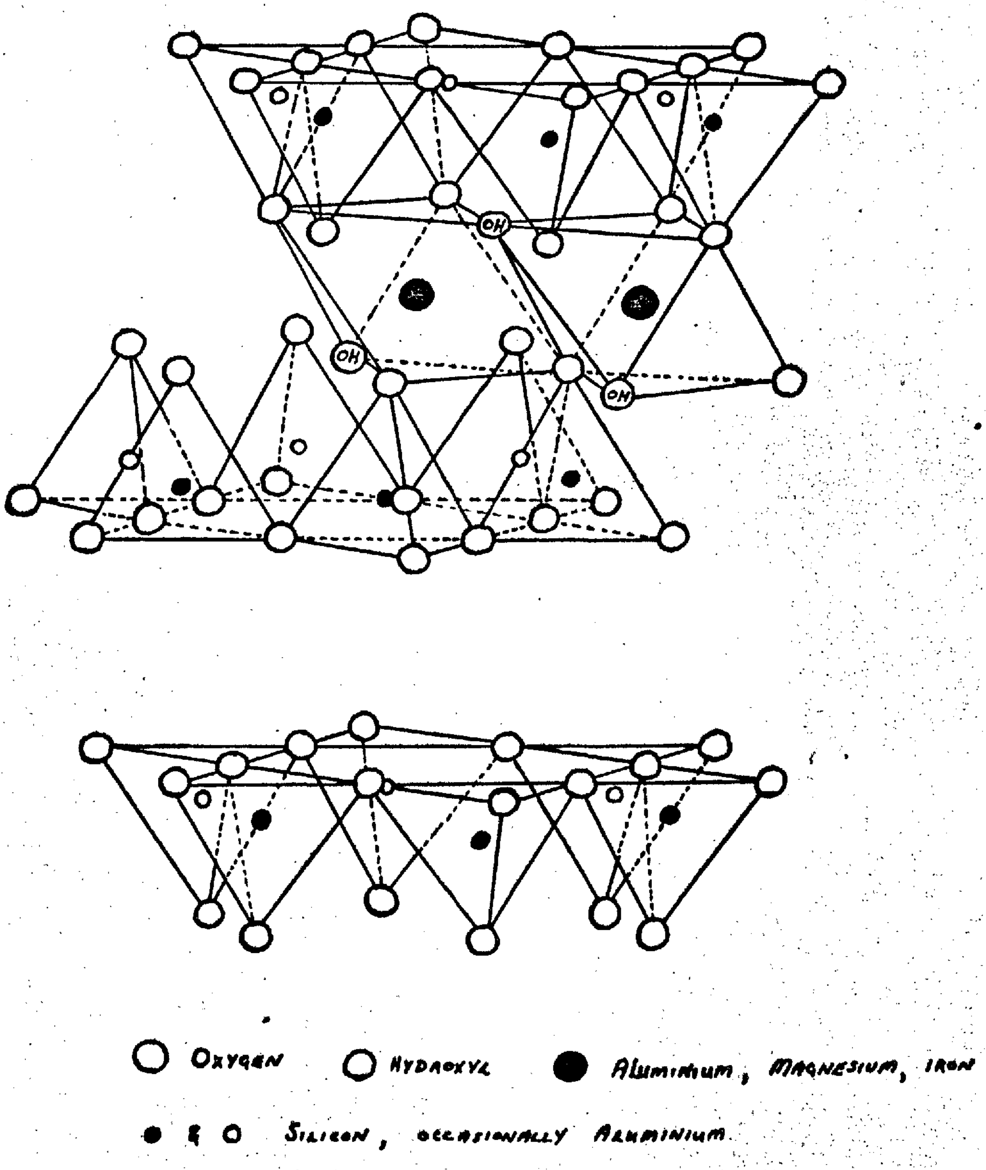

OH
OH
OH
Oxygen
Hydroxyl
Aluminium, Magnesium, Iron
● & ○ Silicon, occasionally Aluminium

Fig. 1.1

The chemical composition of the montmorillonites varies widely. The analyses of a large number of them by Ross and Hendricks (1945) led them to propose the general formula $[Si_8Al_{3.33}Mg_{0.67}O_{20}(OH)_4]X^+_{.67}$, X^+ being the interlamellar cation, though of course most samples deviate from this formula. It corresponds to a base exchange capacity of 91 meq per 100 g of clay, which is close to that of the Wyoming bentonite used in this work.

ION EXCHANGE

The exchangeable cations in the clay minerals arise in three ways. In the montmorillonite group, Grim (1953) estimated that the interlamellar ions required to neutralize the negative charge on the silicate layers accounted for over eighty per cent of the exchangeable ions. Broken bonds at the edges of the montmorillonite crystals account for most of the remaining ions. A third possibility, studied in detail by Weiss (1958b), is the replacement of the hydrogen of the $\equiv$ Si-O-H groups occurring at the end of the tetrahedral layer. This, however, does not provide a significant contribution to the cation exchange capacity of montmorillonite.

Numerous methods have been proposed for determining the cation exchange capacity of the clay minerals. Weiss (1958a) has shown that, provided suitable precautions are taken, preparation of the ammonium clay by suspension in ammonium chloride or acetate solution and subsequent analysis for the ammonium content gives good results. He criticises methods involving the preparation of acid montmorillonite, since his experiments showed that in all cases the clay was partially attacked by acid, even when using an ion exchange resin.

The use of manganese chloride was suggested by Bower and Truog (1940), the manganese being displaced from the clay using ammonium chloride solution, and estimated colorimetrically as MnO_4^-. Barium chloride was also found to give results in agreement with the ammonium acetate method, and the arsenate titration method devised by Jackson (1958) provides a rapid and accurate procedure for cation exchange capacity determination. Nevertheless, the ammonium acetate method remains the most widely used one.

ORGANIC COMPLEXES

As seen in the first section, natural montmorillonite possesses interlamellar cations, usually sodium, magnesium or calcium, which can be easily exchanged for other inorganic ions. In 1934 Smith prepared the first organic complexes of the clay, the work being extended by Gieseking (1939), who carried out the exchange with various alkyl ammonium ions and aromatic amine salts. He found that, unlike the inorganic derivatives, the tetra-alkyl ammonium clays did not swell in water, nor were the ions easily replaceable by hydrogen ions. Hendricks (1941) prepared further organic montmorillonites, and by comparing the observed interlamellar spacings with the dimensions of the organic ions, he was able to deduce the orientation of the ions between the lamellae. A series of primary n-alkyl ammonium montmorillonites was prepared by Jordan (1949), who found that the d001 spacing remained at 13.4Å for chains of up to ten carbon atoms, and was 17.4Å for those of twelve to eighteen carbon atoms. Since the van der Waals radius of a methylene group is about 4Å, he assumed that the organic ions with ten or less carbon atoms in the chain formed a monolayer, while those with more than ten carbon atoms a double layer. Calculations of the area occupied by an amine chain lying flat, and of the surface area of the clay available, supported this view. Though Cowan and White (1962) also obtained a d001 spacing of 17.6Å for their dodecylammonium montmorillonite and assumed a similar model, Weiss (1963) proposed that the alkyl chains were inclined to the silicate layer, and a one-dimensional Fourier synthesis confirmed this. On further investigation he found that the spacing could vary from 14.3Å to 22.1Å depending on the pretreatment of the clay, the analyses being identical in all cases, and also, by using a standard preparation procedure, that the spacing varied almost linearly with the surface charge density of the clay. Franzen (1955), investigating the structure of cetyltrimethylammonium montmorillonite, found that the ions formed a monolayer with the alkyl chain inclined to the silicate layer, and it would seem that this is a more likely model.

The nature of diammonium complexes was first examined by Hendricks (1941) using o and p phenylene diammine salts. He ascertained that both groups were effective and exhibited a 'tie' effect, the two groups being bound to adjacent layers. This effect has been investigated more recently by Weiss (1958a) using $\alpha\omega$ alkyl diammonium salts. On kaolinite, where exchange is possible only on the external surfaces, only one amine group is usually bound to the clay, unless two clay particles are held together. The first gives rise to equimolar exchange and the second to a value intermediate between equimolar and equivalent exchange. A third possibility, resulting in equivalent exchange, arises where the length of the amine chain is equal to the distance between sites of negative charge in the silicate layer, both ends of the chain being attached to the same sheet. He suggests that in montmorillonite and vermiculite, where most of the ions are interlamellar, only equivalent exchange is attained, the two amine groups being attached to adjacent layers. Further work by Weiss (1958b) seemed to confirm this theory, at least for vermiculite.

The orientation of the organic ions between the lamellae is of considerable interest. As already noted, normal alkylammonium ions with chain lengths between three and ten carbon atoms give an interlamellar spacing of 3.9Å, which is consistent with the chain lying flat between the lamellae, the plane of the carbon atoms being parallel to the layer. However, Greene-Kelly (1955a, 1956) observed that saturated ring compounds gave a similar spacing, while unsaturated rings, with all the carbon atoms lying in a plane, gave a smaller spacing, about 3.2Å, which would indicate that the zig-zag of the carbon chain in the alkyl ammonium clays is in fact perpendicular to the silicate layer. This theory received further support from Hofmann and Brindley (1960) on finding that sorption of molecules with strongly polar groups, such as ketones or esters, gave spacings of only 3.5Å, the zig-zag of the carbon chain presumably lying flat in this case.

If the sizes of the organic ions are calculated from van der Waals' radii, it is seen that there is an apparent contraction on intercalation, usually of the order of 0.6 to 0.7Å. Three theories have been proposed to account for this. McEwan (1948) and later Greene-Kelly (1956) supposed that it was due to hydrogen bonding between the methylene groups and the oxygen atoms of the silicate layers, but Hofmann and Brindley (1962) reject the idea on the grounds that the C-H stretching frequency of the methylene groups was unaltered. Greene-Kelly (1956) and van Olphen (1963) considered that the effect of adsorption forces on the bond lengths in the complexes may be sufficient to account for the contraction in some cases. After the suggestion of Glaeser (1951) and Barrer and Reay (1957) that it was due to the keying of the organic ion into the silicate sheets, Barrer and Kelsey (1961) calculated the possible extent of this penetration for different orientations of small alkyl ammonium ions, and obtained good agreement between theoretical and observed values. A detailed study of the orientation of methylammonium and ethylammonium ions in montmorillonite was made by Kinter and Diamond (1963) and by Rowland and Weiss (1963), who concluded that the ions assumed a vertical orientation, in contrast to the other members of the series, though the latter workers consider that the first ions to enter may be horizontal, reverting to a perpendicular position as the saturation exchange capacity is approached. The penetration into the sheets by longer chain molecules is discussed by Hofmann and Brindley (1962).

Similar configurations may be expected for the $\alpha\omega$ alkyl diammonium montmorillonites, though relatively little work has been carried out. Weiss (1958b) reported that these derivatives with up to twelve carbon atoms in the chain, assumed a flat orientation between the sheets in montmorillonite, giving a d001 spacing of 13.5Å, but much of his work was concerned with the more highly charged clays such as batavite, which cannot accommodate an alkylammonium ion with more than six carbon atoms in a flat orientation. Haase, Weiss and Steinfink (1963) determined the crystal structure of hexamethylene diammonium vermiculite and found that the chain was inclined at 32° to the silicate layer.

The thermodynamics of the exchange process were studied by Slabaugh (1954), using n-alkylammonium ions, and he found that the equilibrium constant increased rapidly with increasing length of the amine chain. These results were confirmed by Cowan and White (1958), who, however, found that the short chain amines, with less than seven carbon atoms, did not saturate the cation positions, whilst the longer chain amines were sorbed in excess of the base exchange capacity. Many workers have noted the physical adsorption of excess amine, but there seems to be some confusion as to the length of the amine chain required, and also as to the form of the physically sorbed amine. Cowan and White suggested that it was in the form of free amine, and put forward the following mechanism to explain it:

$$\text{Na}^{+}\ \text{mont} + \text{RNH}_3\text{Cl} \rightleftharpoons \overset{+}{\text{RNH}_3}\ \text{clay} + \text{NaCl}$$

$$\overset{+}{\text{RNH}_3}\ \text{clay} + \text{RNH}_3\text{Cl} \rightleftharpoons (\overset{+}{\text{RNH}_3}\ \text{clay})\text{RNH}_3\text{Cl} \overset{\text{H}_2\text{O}}{\rightleftharpoons} (\overset{+}{\text{RNH}_3}\ \text{clay})\text{RNH}_2 + \text{HCl}$$

though they neglected to measure any fall in pH of the solution. Grim, Alloway and Cuthbert (1947) also found that short chain amines were not sorbed in excess of the base exchange capacity, while dodecylammonium ions were, but analysis for halogen in the latter case showed that all the excess amine was present as undissociated salt. Support for this view was presented by Franzen (1955), whose Fourier synthesis from X-ray patterns showed the presence of the halogen, this being confirmed by analysis, and by Greenland and Quirk (1962) examining n-alkyl pyridinium derivatives of montmorillonite. Kinter and Diamond (1963) studied the exchange reaction with mono, di, and trialkyl ammonium salts, but their results were directly contrary to those of Cowan and White. They found that the lower amines, with one or two carbon atoms, were sorbed in excess of the base exchange capacity, those containing three to eight carbons in amounts equal to it, and those with nine or more carbon atoms in quantities less than the exchange capacity, presumably due to steric hindrance. As they did not detect a fall in pH of the exchange solution or the presence of halogen in the exchanged clay, they were unable to suggest in which form the excess amine existed. No evidence of excess sorption with methylammonium and ethylammonium ions was found by Barrer and his co-workers. The effect of steric hindrance with longer chain amines was noted by Slabaugh and Kupka (1958) and Uskov and Uskova (1961), who studied by a potentiometric method the intercalation of dodecylammonium ions. It was possible to titrate out the excess amine, which suggested that it was in the salt form.

The excess amine may generally be removed by washing with water or iso-propyl alcohol, though Cowan and White (1958) suggested that water may hydrolyse the lower amine clays according to the equation

$$\overset{+}{\mathrm{RNH}}_3\ \mathrm{clay} + \overset{+}{\mathrm{H}} + \mathrm{OH}' \rightleftharpoons \mathrm{H}^+\mathrm{clay} + \overset{+}{\mathrm{RNH}}_3 + \mathrm{OH}'.$$

No evidence of this was found, however, by Jordan (1949) or van Olphen (1963).

SORPTION AND SWELLING

The swelling of a vast number of inorganic and organic montmorillonites in various sorbates has been demonstrated over a period of years, but most of the work has been confined to the measurement of the interlamellar spacings of the clays. Barrer and his co-workers have, however, obtained considerable quantitative information on adsorption by clays containing small organic ions.

Much of the earlier work concerned the swelling of natural or inorganic montmorillonites in water (Brummer 1962, Reay 1956). The sorption of organic molecules on to sodium and calcium montmorillonites was investigated by Bradley (1945), who measured the d001 spacings for the sorption of various diamines, which formed a monolayer, and diols, the lower members of this series forming a double layer. The uptake of aliphatic diamines was studied more recently by Aragon, Cano Ruiz and MacEwan (1959), who found that the d001 spacing remained at 13.3Å, indicating a monolayer, up to octamethylene diamine, but increased to 25Å with decylmethylene diamine, the chain standing vertically. The monoamines were sorbed in a double layer, with most of the chain being vertical.

MacEwan (1948) measured the expansion caused by mono- and polyhydric alcohols, and concluded that alcohols with up to two carbon atoms per OH group formed a double layer, whilst the rest formed single layer complexes. Like Bradley (1945) he obtained complexes with benzene, 15.1Å, but it was later shown (Barrer and McLeod 1954) that dehydrated sodium montmorillonite did not form complexes with non-polar molecules. Similarly the three layer complexes with acetonitrile and nitromethane obtained by MacEwan and by Barshad (1952), were shown not to be formed on dehydration of the montmorillonite (Greene-Kelly, 1955a), while the addition of a trace of water initiated rapid formation of the complex. The influence of water on the sorption of other organic molecules has been investigated by van Olphen and Deeds (1962).

Bentonite adsorbed dry α-picoline to give a complex with spacing 15.9Å, but with the addition of increasing amounts of water it was possible to identify five discrete hydrates, all with different d001 spacings. Similarly pyridine, which when dry gives a complex with a spacing of 19.4Å, forms two hydrates of 23.3Å and 29.3Å, as was also observed by Greene Kelly (1955b). The latter suggested two water molecules and four pyridine molecules in octahedral co-ordination around the sodium ion, but van Olphen proposed that the water separated the two pyridine layers to form a layer in the centre.

Barrer and McLeod (1954) measured the sorption isotherms for permanent gases, water, ammonia, and several organic molecules on sodium montmorillonite. Only the polar molecules were sorbed into the interlamellar space, and those not until a certain threshold pressure had been attained. Water showed a step in both adsorption and desorption isotherms, corresponding to the formation and destruction of the second layer. Closer investigation by Zettlemoyer, Young and Chessick (1955) indicated that up to 0.7 relative humidity only a monolayer of water formed, between 0.7 and 0.9 there were two layers, and multilayer formation began above this value.

Intercalation by organo-clay derivatives was first studied by Jordan (1949) and Jordan, Hook and Finlayson (1950). They determined the gel volumes of n-alkyl-ammonium montmorillonites of varying chain length in a large range of organic liquids, and concluded that the most effective swelling agents were those having both highly polar and highly organophilic characteristics, since a toluene-methanol mixture was sorbed more strongly than either of the components separately. Nitrobenzene was the most effective single swelling agent. Also they found that a chain length of twelve or more carbon atoms was necessary for optimum swelling, and this was achieved when the exchange was exactly 100 per cent.

Considerable data on the swelling of alkylammonium and alkyldiammonium clays having different surface charge densities, has been obtained by Weiss and his co-workers. Weiss, Mehler and Hofmann (1956a,b) prepared a series of n-alkylammonium batavites and montmorillonites. The interlamellar spacing of the former varied according to the length of the carbon chain, and according to the orientation of the chain. On preparation they often assumed a vertical orientation, giving the maximum d001 spacing, but this could be reduced by the application of pressure, when the chain assumed a smaller inclination, preferentially at 56° which allowed maximum hydrogen bonding by the $-\overset{+}{N}H_3$ group, though inclination at lower angles was possible. The three montmorillonite derivatives studied had spacings of 13.4Å as expected (Jordan 1949). On intercalation of n-alcohols or alkylamines having a similar chain length to the organic ion in the clay, both the high and low charged clays swelled to the same extent, and from the measured spacing it was postulated that a double layer was formed, all the molecules and ions assuming a vertical orientation. Area calculations confirmed that this was the most likely arrangement. Weiss (1963) measured the swelling of n-dodecylammonium beidellite and montmorillonite in a large variety of organic liquids and found that in nearly all cases the clays swelled to give a d001 spacing of 28 to 30Å, which corresponds to the cation standing normally to the sheets. The layer charge appeared to have little effect on this, and in no case was any swelling detected with saturated hydrocarbons.

Clays containing α-ω alkyl diammonium ions were also shown to swell in most organic liquids, but the hydrogen bonding of the $-\overset{+}{N}H_3$ groups to the oxygens in the silicate layers was found to impose further restrictions on swelling (Weiss 1958c). The clays with an odd number of carbon atoms in the alkyl chain of the organic ion did swell until the chain was vertical, the expected "tie" effect preventing further swelling. However, the clays in which the alkyl chain had an even number of carbon atoms showed a smaller swelling than would have been expected for a vertical orientation of the chain, and Weiss calculated that the chains were inclined at 56° to the lamellae. This would allow maximum hydrogen bonding for the $-\overset{+}{N}H_3$ groups, and it appeared that sorption forces were insufficient to break these bonds.

Sorption isotherms on $\overset{+}{N}(CH_3)_4$ and $\overset{+}{N}(C_2H_5)_4$ montmorillonites (Barrer and McLeod 1955) showed profound changes from their counterparts on sodium montmorillonite. Non-polar as well as polar molecules were sorbed into the interlamellar space, a threshold pressure no longer being in evidence. As might be expected, the $\overset{+}{N}(C_2H_5)_4$ clay, which had only a slightly higher interlamellar spacing than the $\overset{+}{N}(CH_3)_4$ montmorillonite, sorbed less than the latter. It was suggested that while polar molecules tend to form clusters around the organic ion, the non-polar molecules are sorbed generally over the silicate sheet.

Following up this work, Barrer and Reay (1957) attempted to improve the sorptive capacity by using smaller organic ions, such as $CH_3\overset{+}{N}H_3$, which would occupy less of the surface. The uptake was increased for sorbates which were capable of swelling the clay, such as benzene, but for larger molecules like iso-octane and other branched chain hydrocarbons, the energy required to swell the methylammonium clay sufficiently to accommodate them was greater than the free energy of sorption, and consequently sorption was decreased. They attempted to separate the isotherms representing interlamellar and external sorption, but calculation of surface areas from experimental isotherms did not correlate very well with the theoretically derived area. The problem was investigated more closely by Barrer and Perry (1961), who made detailed calculations as to the effect of the lateral extent of organic ions on sorption, and were able to explain many of the differences in sorption by $\overset{+}{N}H_3CH_3$ and $\overset{+}{N}(CH_3)_4$ montmorillonites. They made the further suggestion that partial exchange should create greater spaces between the organic ions and thus considerably improve the sorptive capacity, but when this was investigated by Barrer and Brummer (1963) a directly contrary effect was noted, the sorption increasing linearly with the percentage exchange. This was attributed to interstratification of the clay, some layers containing only organic ions and others only inorganic ions.

The sorption of organic vapours on $\overset{+}{N}H_3CH_3$ and $\overset{+}{N}(CH_3)_4$ montmorillonites was found to be exothermic (Barrer and Kelsey 1961), but with a large organic cation, dimethyldioctadecylammonium, which completely filled the interlamellar space, they found that endothermic sorption resulted, there being a large positive entropy of sorption. These results were confirmed by Slabaugh (1963). The main factor governing intercalation appeared to be the cohesive energy density, steric factors being no longer of importance. White (1964) questioned this conclusion, since sorption varied with the method of preparation of the derivative, and proposed that the sorption was governed by the structure of the derivative, though no evidence of structural differences was given.

Cowan and White (1962) studied the uptake of phenol from aqueous solutions on to a range of alkylammonium montmorillonites, and plotted Freundlich isotherms. They proposed that the sorption forces were of two main types; hydrogen bonding by the hydroxyl group to the silicate sheet and van der Waals bonding of the aromatic ring to the organic ions, maximum sorption being obtained where there was a balance between hydrophilic and organophilic surface. This was found to occur with dodecylammonium bentonite. Street and White (1963), in a similar investigation, proposed that with quaternary ammonium ions where the nitrogen atom is more basic, this may act as the hydrophilic agent rather than the silicate surface. Differences in the uptake of phenol into dodecylammonium and tetradecylammonium montmorillonites were observed by Cowan (1963). While the heat of sorption on the dodecylammonium clay was always negative, the initial sorption on the tetradecylammonium derivative was endothermic. He concluded that this was because swelling was necessary in the latter case, but it is difficult to see why he assumes that the dodecylammonium ion gives a double layer complex with a spacing of 8Å while the larger tetradecylammonium ion gives only a single layer complex with a spacing of 4Å. This is contrary to the observations of Jordan (1949).

THEORETICAL SORPTION ISOTHERMS

The object of a theoretical isotherm equation is that it should describe not only the shape of the experimental isotherm, which can usually be done fairly readily by varying the equation parameters, but also be able to predict the entropy changes or temperature dependence of the system, and be based on a reasonable physical model of the system. Of the many isotherms proposed a few relevant ones are discussed briefly below.

An early attempt to devise an isotherm equation was made by Freundlich (1906), but his equation,

$$x = kp^{1/n}$$

where $n>1$, was purely empirical, k and n being arbitrary constants. While fitting many experimental isotherms at low pressures, it was unable to account for saturation of the sorbent at higher pressures.

In 1918 Langmuir, considering that molecules sorbed on to a surface formed only a monolayer, derived an isotherm equation kinetically, the rates of condensation and evaporation of the sorbate molecules to and from the surface being equal at equilibrium. He obtained the equation

$$\theta = \frac{bp}{1+bp},$$

θ being the fraction of the surface covered, and b a constant depending on the factors involved in the condensation-evaporation equilibrium. A similar equation has been derived statistically by Fowler (1935).

Unfortunately the basic assumptions on which this model is based, viz:

(i) that sorption is restricted to a monolayer

(ii) that the surface is homogeneous, all sites being of equal energy

(iii) that the sorbed molecules are localised

(iv) that there is no lateral interaction between the adsorbed molecules,

are seldom tenable, and in recent years numerous isotherm equations have been proposed in an attempt to rectify these drawbacks.

Though surfaces are usually heterogeneous, the differential heats of sorption do not always decrease with coverage as would be expected, since the decreasing energy of sorbate-sorbent interactions is often counterbalanced by increasing lateral sorbate-sorbate interactions. Thus even on non-uniform surfaces there is occasionally apparent conformation to the Langmuir equation. Attempts have been made to treat non-uniform surfaces by considering them to be composed of small patches, each in itself uniform and obeying the Langmuir equation. Further progress is impeded since the distribution of the patches is unknown, though Tomkins (1950) and Halsey and Taylor (1947) were able to derive a Freundlich-type isotherm by assuming an exponential distribution of sites. Other attempts to treat heterogeneous surfaces have been reviewed by Young and Crowell (1962).

Two approximations have been proposed to take account of lateral interactions between sorbed molecules in localised adsorption. The Bragg-Williams approximation (1934) assumed that the sorbed molecules are distributed randomly over the available sites, and the number of nearest neighbour interactions were then determined. Fowler (1936), applying this approximation, derived the isotherm equation

$$bp = \frac{\theta}{1-\theta}\, e^{\frac{\theta z w}{kT}}$$

where w is the energy of interaction of a pair of sorbate molecules, and z the number of nearest neighbours.

Using a second approximation which takes into account the variation in energy of the sites due to interactions with molecules adsorbed on to neighbouring sites, Fowler derived a more complicated equation

$$bp = \frac{\theta}{1-\theta}\left(\frac{2-2\theta}{\beta+1-2\theta}\right)^{z}$$

where $\beta = \left[1-4\theta(1-\theta)(1-e^{w/kT})\right]^{\frac{1}{2}}$.

Hill (1939) calculated that the energy barriers between sorption sites were normally less than one kcal per mole, and so, except at very low temperatures, on a homogeneous surface the adsorbed layer will be mobile. In this case the adsorbed film may be treated as a two-dimensional fluid, and isotherm equations may be derived via the Gibbs adsorption equation from the appropriate equation of state. For a mobile film with lateral interaction between molecules, a two-dimensional van der Waals type equation of state has been applied and this leads to an isotherm

$$p = K\,\frac{\theta}{1-\theta}\,\exp\left(\frac{\theta}{1-\theta} - \frac{2\alpha\theta}{kT\beta}\right) .$$

Hill (1946) related the two-dimensional constants α and β to their counterparts a and b in the three-dimensional van der Waals equation, and also derived a value of K. This, and similar equations, do not usually describe experimental observations very closely, however, though Ross and Winkler (1955) obtained some measure of agreement at low pressures.

Despite these objections to the theoretical basis of the Langmuir equation, it has proved a useful one in practice.

MULTILAYER SORPTION

One of the chief drawbacks of the Langmuir isotherm was that it was unable to explain the large increase in sorption at high relative vapour pressures, and it was to overcome this difficulty that Brunauer, Emmett and Teller (1938) propounded their multilayer theory. It was based on the same assumptions as the Langmuir theory, with the exception that sorption was no longer restricted to a monolayer, and with the further assumption that the energy of sorption of the second and higher layers was equal to the heat of liquefaction of the sorbate. Assuming that an infinite number of layers may be formed, the isotherm equation is

$$\frac{p}{V_{(p_o-p)}} = \frac{1}{V_m c} + \frac{c-1}{V_m c}\, {}^{p}/_{p_o}$$

where V is the volume sorbed at pressure p, v_m the volume sorbed in a completed monolayer, and c a constant depending on factors involved in the condensation-evaporation equilibrium. It is given by

$$c = \frac{a_1 b_2}{a_2 b_1} \exp - \frac{(E_1 - E_L)}{RT}$$

Further, assuming a_1b_2/a_2b_1 is approximately unity (Barrer and Riley, 1950), then the heat of sorption may be calculated from a single isotherm.

For porous sorbents the adsorption may be restricted by the size of the pores, and an isotherm for a maximum of n layers, which, in view of the third variable n, often fits experimental results more closely, was proposed by Brunauer, Deming, Deming, and Teller (1940) as

$$\frac{V}{V_m} = \frac{p/p_o \, c}{(1-p/p_o)}\left[\frac{1-(n+1)(p/p_o)^n + n(p/p_o)^{n+1}}{1+(c-1)p/p_o - c(p/p_o)^{n+1}}\right]$$

all the symbols having their usual significance.

However, as p/p_o approaches unity in this equation, V/V_m tends to $cn(n+1)/2(n+1)$, or approximately $n+1/2$, and not to n. Recently a more simple equation has been derived by Dellyes (1963), who considered that the rates of condensation and evaporation from the n^{th} layer will be very small, and not as for all other layers as assumed in the derivation of Brunauer et al. He obtained the equation

$$\frac{V}{V_m} = \frac{c_{p/p_o}(1-(p/p_o)^n)}{(1-p/p_o)(1+(c-1)p/p_o)}$$

and showed that the sorption of nitrogen on palygorskite obeyed this equation over the total pressure range.

The B.E.T. model has been modified to take into account lateral interactions (by Hill, 1947) using the Bragg-Williams approximation, and his isotherm approximated more closely to the experimental one, especially at higher relative pressures where the B.E.T. isotherm fails. Kiselev (1961) also derived an equation taking into account lateral interactions, but his interaction constants were difficult to evaluate.

It was pointed out by Halsey (1948) that sorption of a molecule on to an isolated molecule, as is assumed possible in the B.E.T. model, is most unlikely, and suggested that a triangular array of molecules is a necessary condition for sorption of a molecule into the second layer. There would, therefore, on a uniform surface, be very little sorption into the second layer until the first layer was at least half completed. Further modifications to allow for decreasing interaction energy in successive layers were made by McMillan and Teller (1951), Cook (1948), and Barrer, Mackenzie and MacLeod (1953).

The majority of these modifications introduce extra constants, and make their application to experimental isotherms correspondingly more difficult. Nevertheless, the B.E.T. isotherm remains a useful semiquantitative model, especially for the determination of surface areas.

HEATS AND ENTROPIES OF SORPTION

The thermodynamic approaches to sorption have been discussed fully by Hill (1952) and by Young and Crowell (1963).

Applying solution thermodynamics to the sorbed phase, where $\mu_s = f(P,T,n_s)$ for a given mass of sorbent

$$d\mu_s = -\bar{S}_s dT + \bar{V}_s dP + \left(\frac{\partial\mu}{\partial n_s}\right) dn_s$$

the symbols having their usual significance, and subscript s referring to the sorbed phase. Since at equilibrium $\mu_s = \mu_g$, then for a constant amount sorbed we may derive the equation

$$\left(\frac{\partial \ln P}{\partial T}\right)_{n_s} = -\frac{\Delta\bar{H}}{RT^2} ,$$

$\Delta\bar{H}$ being the differential heat of sorption.

The heats of sorption are usually expressed with respect to the liquid state of the sorbate, and so the latent heat of vaporisation of the sorbate must be subtracted. The Clapeyron-Clausius equation then takes the form

$$\Delta\bar{H} = \bar{H}_s - \tilde{H}_L = RT^2\left(\frac{\partial \ln p/p_o}{\partial T}\right)_{n_s}$$

The differential entropy of sorption with respect to the liquid state is given by

$$\Delta\bar{S} = \bar{S}_s - \tilde{S}_L = \frac{1}{T}\left[\Delta\bar{H} - RT\ln p/p_o\right]$$

These equations will not be exact when applied to systems exhibiting hysteresis, since either the adsorption or desorption process will be irreversible, though the error involved is probably not great. Everett and Whitton (1955), studying the adsorption of benzene on charcoal, found a difference of only two per cent between calorimetrically determined and Clapeyron heats, though a larger discrepancy was found by Gregg and Wheatley (1956) for the sorption of benzene on alumina.

Slabaugh and Kennedy (1963) measured the heats of sorption of methanol and water on organo bentonites and obtained good agreement between calorimetric and Clapeyron heats. A recent investigation by Kington and Smith (1964) into the adsorption of argon on to porous glass, showed that the heat of adsorption determined from the Clapeyron-Clausius equation was in accordance with the calorimetric heat, but the heat of desorption was greater than the calorimetric heat, which suggests that the desorption process is the irreversible one in this system. The difference in heats was not large however. Thus the inaccuracies arising from applying the Clapeyron-Clausius equation to systems exhibiting hysteresis in the present work will probably be less than the experimental error.

HYSTERESIS

Though hysteresis loops in sorption isotherms were obtained as early as 1896 these were later shown to be due to impurities in the sorbent, and it was thought for many years that hysteresis was a spurious effect. The work of Foster (1932, 1934) and later of Rao (1941) finally established hysteresis as a distinct phenomenon. Of the many theories put forward to explain it, the capillary condensation theory has been the one most discussed. The equation relating the vapour pressure over a curved surface to the radii of curvature of the meniscus, r_1 and r_2, and the contact angle θ,

$$RT\ln p/p_o = -\overline{V}\sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\cos\theta$$

where $\overline{V}$ is the molar volume of the liquid and σ its surface tension, was derived by Kelvin. Condensation thus occurs over a concave surface at a lower pressure, p, than over a plane surface, p_o.

Zsigmondy (1911) suggested that the contact angle might be greater on sorption than desorption, which applying Kelvin's equation, would lead to desorption from a capillary at a lower pressure than adsorption. Later experiments show, however, that one or two molecular layers of sorbate are adsorbed on to the walls before condensation commences, and it is therefore unlikely that the contact angle will differ in the two processes. Indeed it is usually taken as zero.

In 1932, Foster, considering open-ended cylindrical pores, put forward the "delayed meniscus" theory. He proposed that on adsorption successive layers of adsorbate molecules formed on the walls of the pore, but condensation could not occur until a meniscus had formed, that is until the layers had merged at the narrowest point of the pore. On commencing desorption, however, the pore was full of liquid and desorption from the spherical meniscus was governed by the Kelvin equation

$$RT\ell n\, p/p_0 = -\frac{2V\sigma}{r}\ .$$

Cohan (1938), while maintaining that desorption took place according to the Kelvin equation, derived an equation for the adsorption part of the isotherm. He considered that a monolayer of sorbate formed on the walls of the capillaries, thus forming a cylindrical meniscus of radius r-D, where r is the pore radius and D is the thickness of the adsorbed layer. The vapour pressure above the cylindrical meniscus is then given by

$$RT\ell n\, p/p_0 = -\frac{\sigma\bar{V}}{(r-D)}$$

since $r_2 = \infty$, and condensation takes place in accordance with this equation. Hysteresis will then occur so long as $r > 2D$. Though Cohan obtained some measure of agreement between theoretical values of D and those calculated from the point of closure of the hysteresis loop, the pore distributions calculated from adsorption and desorption parts of the isotherm often differ. The model is too simple to give quantitative results.

An alternative model which would give rise to hysteresis was proposed by Kraemer (1931) and McBain (1935). They suggested that the main body of the pore was only accessible through a narrow neck, and two filling mechanisms are then possible.

Where $R > 2(r-D)$ condensation begins in the neck of the pore according to the Cohan equation and proceeds until a meniscus of radius R has formed, when the main body of the pore may fill in accordance with the Kelvin equation. When $R < 2(r-D)$ the body of the pore fills first at a pressure corresponding to R in the Kelvin equation. Evaporation from both types of pores is governed by the neck radius, desorption occurring at a pressure corresponding to r in the Kelvin equation. The work of Rao (1941) supported this theory. He determined the adsorption and desorption scanning curves for water adsorption on various sorbents, and concluded that while the desorption scanning curves always joined the main desorption curve, the path of the adsorption scanning curve was dependent on the previous history of the system, and could either join the main adsorption curve or go to the vertex of the hysteresis loop.

In a detailed theoretical analysis Katz (1949) classified the adsorption scanning curves as Type I and Type III, and the desorption curves as Type II and Type IV, Figures 1.2a,b,c,d respectively. Systems exhibiting type I sorption curves would give only type IV desorption curves, and similarly type III sorption curves were accompanied by type II desorption curves. Further he considered that the former would be obtained where ink-bottle type pores predominate, while the latter are consistent with a system containing only open-ended pores. Though this work was at variance with Rao's results, Katz suggested that had Rao taken more points on the desorption scanning curves, then the curves would have continued to the lower closing point of the hysteresis loop.

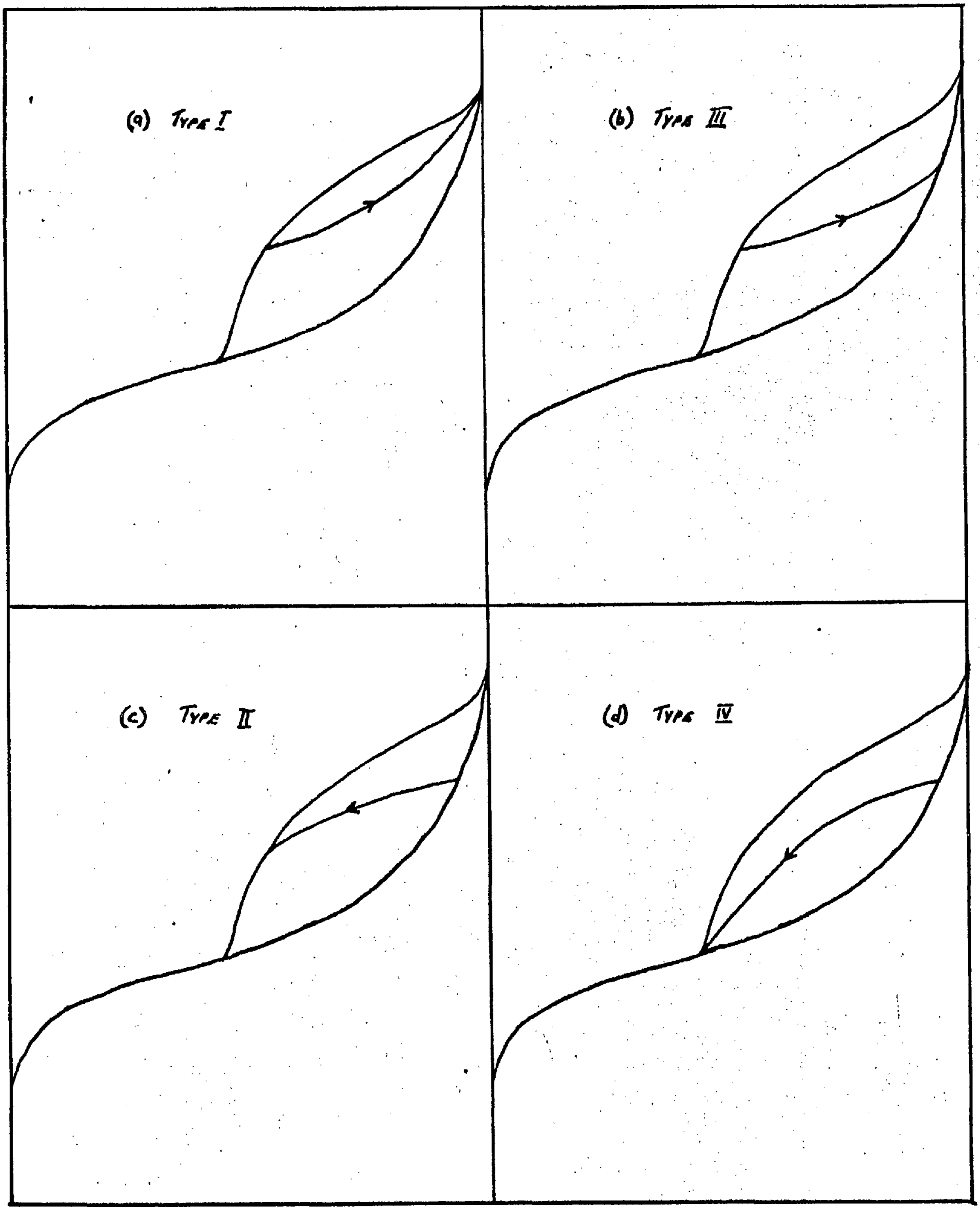


Fig. 1.2.

De Boer (1958) has considered the various hysteresis loops obtained and suggested different types of pores which would give rise to them, whilst Barrer, McKenzie and Reay (1956) have calculated the isotherms expected from ink-bottle and trough-shaped capillaries and spherical cavities.

Though the Kelvin equation has been widely used in calculation of pore size distributions it is necessary to bear in mind the considerable approximations involved. Firstly the thickness of the adsorbed layer is usually unknown, though it is often taken to be two molecular diameters (Foster 1948). Secondly, the liquid condensed in capillaries may not have the same surface tension and molar volume as the bulk liquid, though the experiments of Cohan and Meyer (1940) show that there is little deviation in capillaries down to 100 Å diameter. Carman (1952) and Barrer (1954) found normal values in capillaries of 20-30 Å diameter.

Though capillary condensation probably accounts for the majority of cases of hysteresis observed at higher relative vapour pressures, it does not explain hysteresis which persists to zero pressure. Several proposals have been made, but the one put forward by Hirst (1948) is probably the most relevant to the low pressure hysteresis observed in this work. He proposed that in certain cases the sorbent behaves as an elastic material, and as the pressure of the sorbate vapour increased the attractive forces between two sorbent surfaces were gradually overcome and the material swelled. On desorbing again to the pressure at which swelling commenced the sorbent surfaces are still widely separated, and the attractive forces between them are much lower than when this pressure was reached on the adsorption branch. Only when more sorbate is removed by further reducing the pressure will the two surfaces approach once more, thus giving rise to a hysteresis loop in the isotherm. Barrer and McLeod (1954) considered that this would explain the low pressure hysteresis found in sorption on organo montmorillonites. Brooks (1965), on the other hand, suggested that the clay platelets took up a different orientation giving rise to a differing pore structure. At such low relative pressures, however, the pores would require diameters of only one or two molecular diameters, and condensation phenomena would cease to have any meaning.

Barrer, Drake and Whittam (1953) proposed that hysteresis may be explained by a nucleation process. When a germ-nucleus of a new phase is formed in the existing phase additional free energy terms for interfacial surface tension and strain associated with the nucleus must be added to the normal free energy of formation of the new phase. Since these terms are positive the nucleus will not grow until the sorbate pressure is in excess of the pressure at the point of true thermodynamic equilibrium. By a similar argument the reversal to the original phase on desorption is delayed beyond the thermodynamic equilibrium point, and so hysteresis results.

In an attempt to correlate the behaviour of all systems involving hysteresis, Everett and Whitton (1952) put forward the domain theory, which was later expanded upon by Everett and Smith (1954) and Everett (1954, 1955). They considered that a system existed as a large number of independent domains, each of which could exist in two states, I and II, the change being brought about by altering some external variable x. For hysteresis to occur the value of x for state I changing to state II must be greater than for the reverse process. The domains themselves often have geometrical boundaries, and in the present context would coincide with the capillaries. In order to be able to predict the behaviour of a system a knowledge of the distribution functions for the values of x at which the domains change states is required. They may be obtained approximately from families of scanning curves. On the basis of this theory Everett and his co-workers were able to derive seven theorems concerning the behaviour of systems exhibiting hysteresis. Two of these were identical to Katz's rules discussed earlier, while a third postulated that the slope of a scanning curve was always less than the slope of the main curve. Enderby (1955, 1956) considered the case when a domain could interact with its nearest neighbours, and concluded that when the interaction was such that it aided transitions five of Everett's theorems were valid, but the one relating to the slopes of scanning curves and main curves no longer held. In the investigation of adsorption of butane on porous glass Quinn and McIntosh (1957) found that in certain regions the slopes of scanning curves were in fact greater than that of the main desorption curve, and concluded that this behaviour was due to the interdependence of "ink-bottle" pores.

It appears therefore that there are several causes of hysteresis, and since two or more of these may apply to any one system simultaneously, theoretical analysis becomes very difficult.

EXPERIMENTAL

PREPARATION OF SORBENTS

A series of α-ω alkyldiammonium montmorillonites was prepared, using the method employed by Brummer (1962) for the preparation of organobentonites.

The alkyl diamines were obtained from Fluka, and were guaranteed to have a melting point within 2°C of the literature value. These were neutralised using a slight excess of AnalaR hydrochloric acid, the alkyl diammonium salts crystallised out, and their melting points determined.

About 6 g samples of a natural Wyoming bentonite provided by Fullers Earth Union Ltd. were suspended in 250 ml of a normal solution of the appropriate diammine salt, and the mixture heated to 50°C for one hour. After allowing to stand overnight, the supernatant liquid was poured off, and the clay was washed with a further 100 ml of the normal solution of the diammine hydrochloride. The clay was filtered off and washed with ethanol until the washings showed no trace of chloride ion, but it was subsequently found that the clay still contained excess diammonium salt, and all further samples were subject to a Soxhlet extraction with water for four hours, which was sufficient to remove all traces of chloride ions.

A second sample was extracted for 50 hours with iso-propyl alcohol (Cowan-White, 1958), but the clay was found still to contain chloride ion.

After drying at 60°C the organic montmorillonites were ground to pass a 200-mesh sieve, and were analysed for nitrogen content by the Dumas method in the Analytical Laboratory.

A similar series of α-ω alkyldiammonium clays was prepared from Ben-u-gel, a hectorite provided by Berks Ltd.

For comparison a series of n-alkylammonium montmorillonites was also prepared by a similar process, except that for the longer chain amines the exchange reactions were carried out in alcoholic solution, the amine salts being almost insoluble in water. The Soxhlet extraction was also performed using ethanol or iso-propyl alcohol.

CATION EXCHANGE CAPACITY

The base exchange capacities of the natural Wyoming bentonite and the Ben-u-gel were determined using ammonium acetate solution, as suggested by Kelley (1948).

A sample of the clay was dispersed in a normal solution of ammonium acetate, heated to 50°C for thirty minutes, and allowed to stand for several hours. The supernatant liquid was poured off, and the clay again dispersed in more ammonium acetate solution to ensure complete exchange. The clay was filtered off, washed several times with small quantities of aqueous alcohol to remove excess ammonium acetate, and then dried at 60°C. Samples of this clay were analysed for ammonia by the Kjeldahl method and nitrogen by the Dumas method, and thus the base exchange capacity of the air-dried clay determined.

In order to compare different clay samples it is better to express the base-exchange capacity in terms of the dry weight of the clay, and so the loss in weight of the ammonium clay on outgassing at 50°C and 10^{-6} mm pressure was measured, and the base exchange capacity corrected accordingly. Tables I, II and III give the nitrogen contents of the various organo-clay derivatives, calculated on the basis of 1 gram of outgassed sodium clay.

TABLE I

α-ω Alkyl diammonium montmorillonites

No. of C atoms in chain	Nitrogen content %
NH_4	1.16
2	1.20
3	1.20
4	1.22
5	1.13
6	1.16
7	1.15
8	1.18
9	1.21
10	1.25
12	1.17

TABLE II

Alkyl ammonium montmorillonites

1	1.12
2	1.12
3	1.21
5	1.19
6	1.13
12	1.13

TABLE III

Alkyl diammonium hectorites

NH_4	1.24
2	1.26
3	1.27
4	1.32
5	1.32
9	1.28
12	1.28

SORBATES

Gases for the volumetric system

Helium, argon, nitrogen, and oxygen, were obtained from British Oxygen Company, and were spectrally pure. They were supplied in break-seal one-litre bulbs, which were joined directly to the vacuum system.

Vapours for the gravimetric system

AnalaR benzene was once distilled in air and then twice in vacuo in the apparatus, the middle fraction being retained each time.

Heptane, of International Petroleum Testing Standard obtained from BDH, acetonitrile, of at least 99.5% purity from Fluka, and α-ω diamino propane, from Fluka, were twice distilled in the apparatus under vacuum, once over quicklime to ensure the absence of water vapour.

The vapour pressure curves of all the sorbates were identical with those given in the literature.

APPARATUS

Pumping system

The high vacuum system, illustrated in figure 2.1, was similar to the one used by previous workers in this field, and full details are given by Reay (1956). An Edwards "Speedivac" rotary pump, capable of reducing the pressure to 10^{-3} cm of Hg, was backed by a mercury diffusion pump giving a vacuum of 10^{-6} cm of mercury. A cold trap surrounded by liquid oxygen was included to prevent condensible vapours reaching the pumps, and the

PUMPING SYSTEM

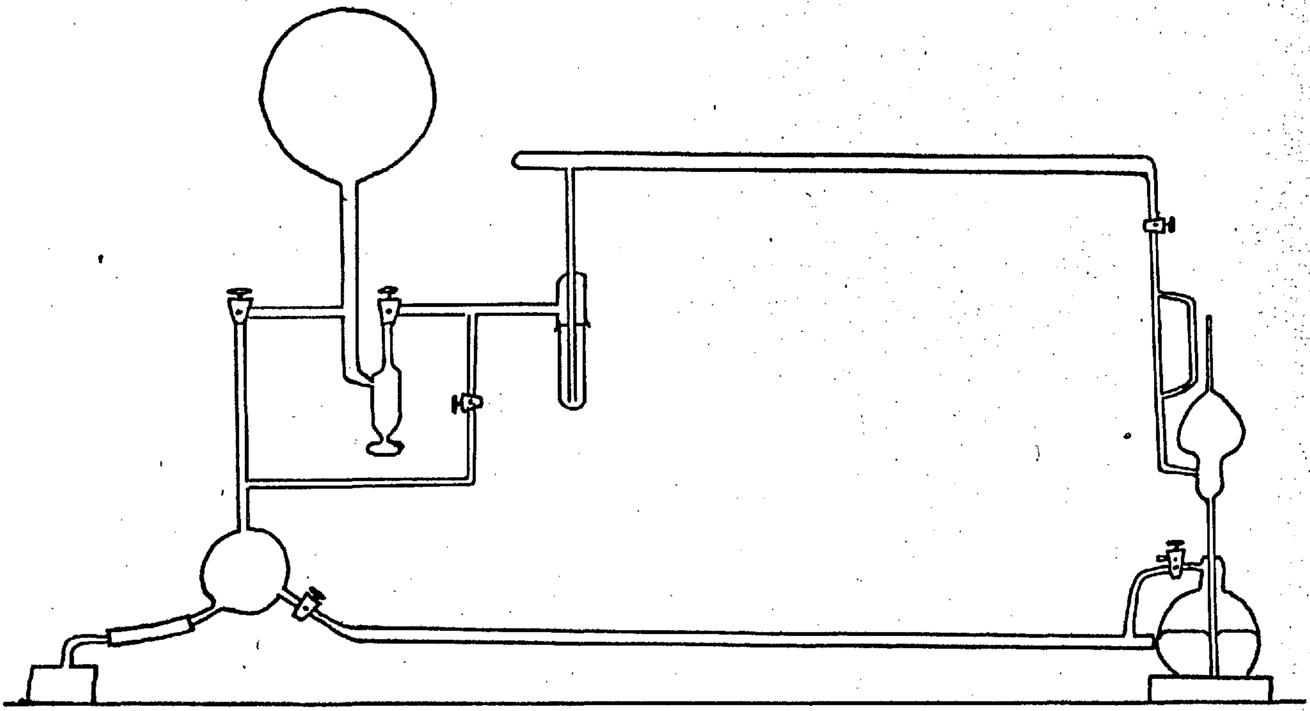


FIG. 2.1

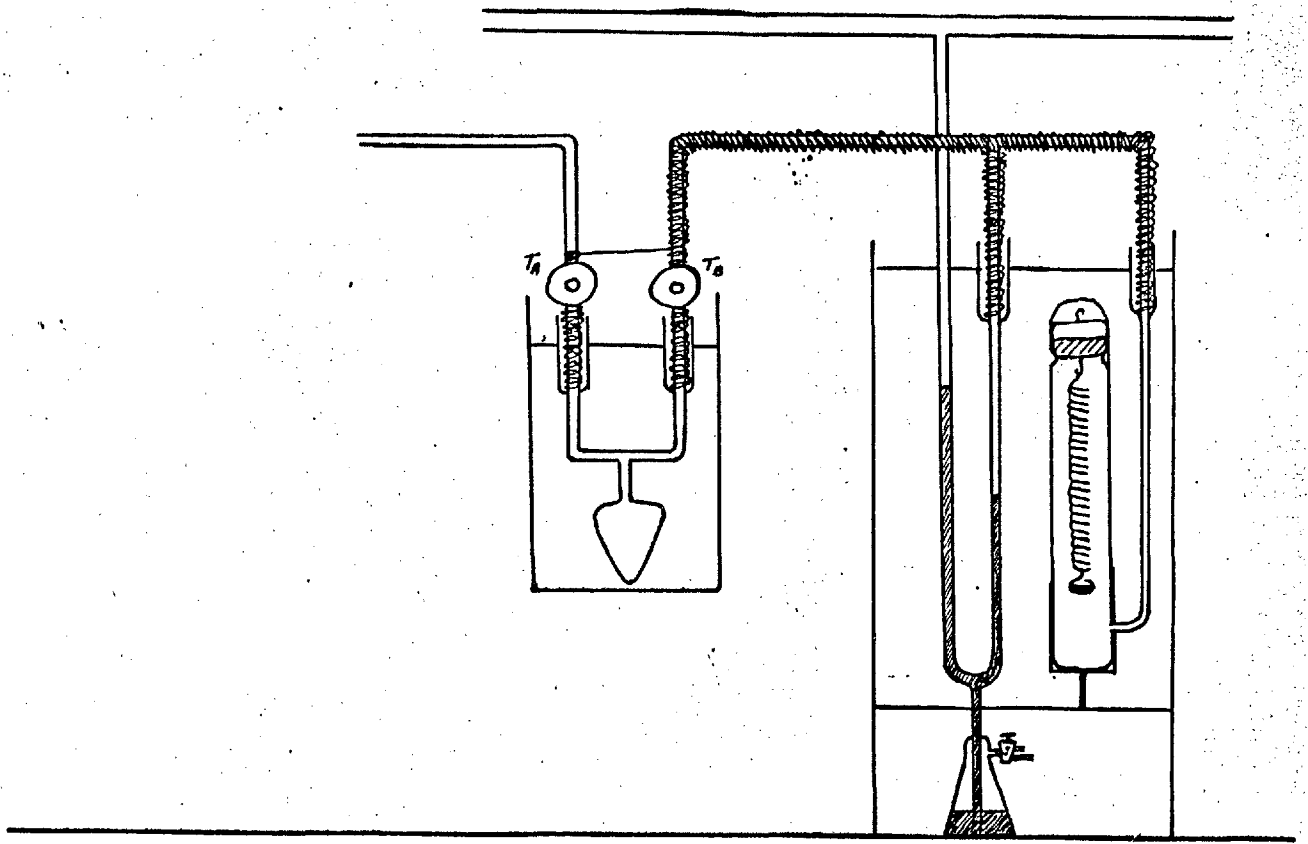


FIG. 2.3

inclusion of a large buffer volume allowed the mercury pump to operate whilst the high vacuum line was isolated from the rotary pump.

VOLUMETRIC SYSTEM

A volumetric technique was employed in determining the sorption isotherms of the permanent gases, the apparatus for which is shown in Figure 2.2. The sample was contained in a small bulb blown on the end of 3mm Pyrex tubing, and was attached via a cone and socket to the doser system, which in turn was connected via tap T5 to the gas supply line. The manometer was constructed from standard 1 cm tubing, to minimise capillary depression corrections.

Calibration

(i) Doser system

The volume per cm of the manometer tubing, the volumes of each of the bulbs of the gas burette, and the volume between tap T_3 and the first bulb were determined by mercury calibration before assembling the apparatus. The dead volume enclosed by taps T_2, T_3, T_4, T_5, and a fixed mark (X) on the manometer was measured by helium calibration, the volume of the whole system being varied by successively filling each of the bulbs of the gas burette, the pressure being measured each time. The dead volume (V) is then given by the relationship

$$P_1(V+V_{D_1}+V_{m_1}) = P_2(V+V_{D_2}+V_{m_2})$$

where P_1 and P_2 are the initial and final pressures respectively, V_{D_1} and V_{D_2} the initial and final volumes of gas in the burette, and V_{m_1} and V_{m_2} initial and final

VOLUMETRIC SYSTEM

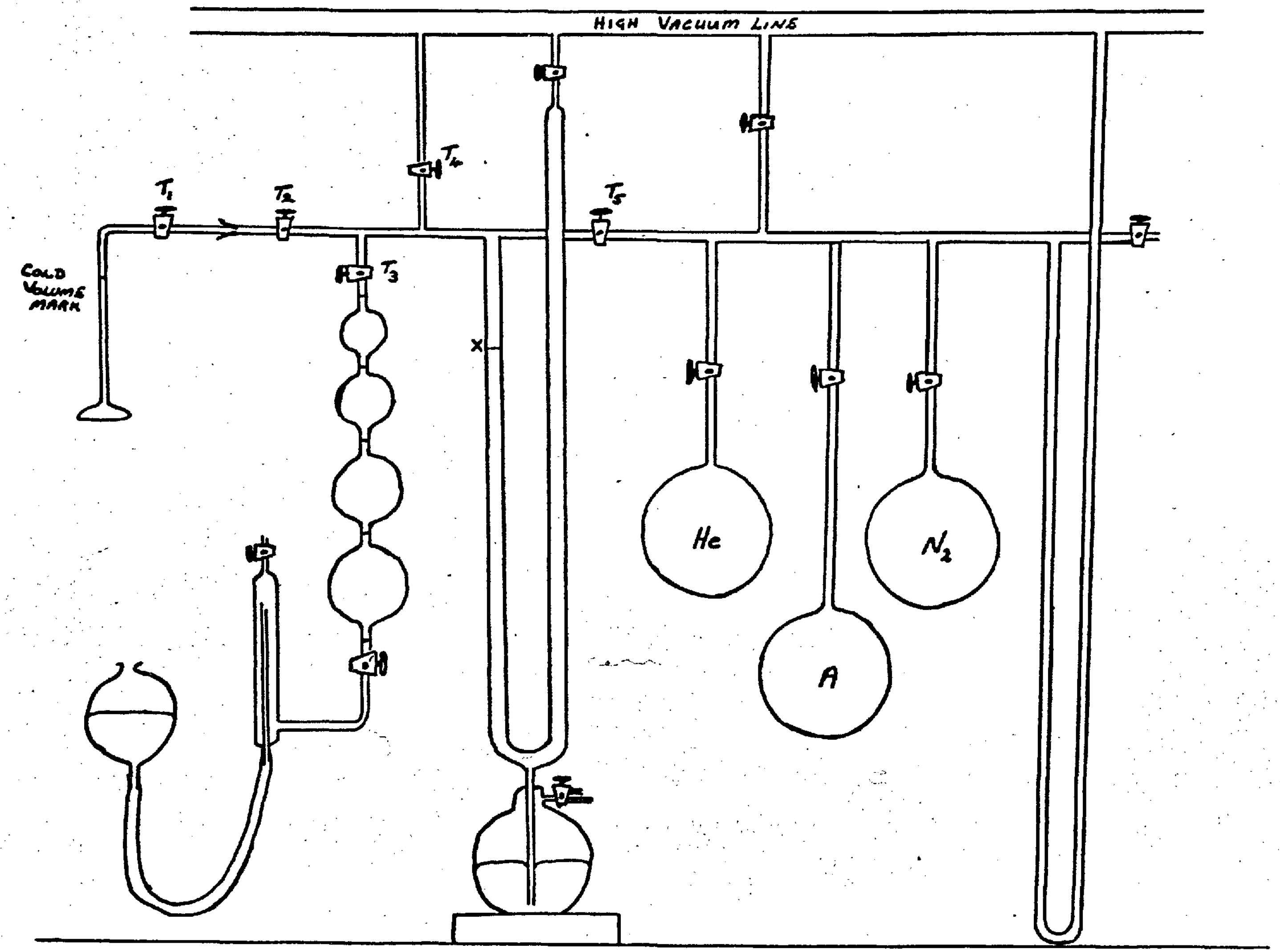


FIG. 2.2

volumes of gas in the manometer. The ten values of V this obtained differed by not more than 0.1 ml, giving a maximum error of 0.5%.

(ii) Cold volume

The volume of the sorption tube up to the cold volume mark was found by mercury calibration, but from this the volume of clay sample and glass wool plug, used to prevent the sorbent escaping from the tube, had to be subtracted.

In order to determine the weight of the outgassed clay, the assembly consisting of sample tube, tap T_1, and cone, was weighed and then attached to the system and evacuated at 60°C. At intervals it was disconnected, all the grease removed from the cone, and weighed again, the process being repeated till constant weight was attained. Usually there was no change after 12 hours.

The density of the organo-clay derivative was calculated assuming the Ross-Hendricks formula for the montmorillonite, and the volume occupied by the dry clay sample was thus determined.

Finally the volume between tap T_2 and the cold volume mark was found by helium calibration, with the sample immersed up to the cold volume mark in liquid nitrogen.

This volume will vary slightly according to the thermostatting liquid, since there is no sharp change at the cold volume mark from the temperature of the thermostatting liquid to ambient temperature. It is important therefore that this volume is determined for each thermostatting liquid used.

Measurement of isotherms

After outgassing the sample, taps T_2 and T_4 were closed, and gas admitted to the doser volume via tap T_5. Its temperature and pressure were recorded, and the initial volume at N.T.P. thus calculated. The sample was immersed up to the cold volume mark in the refrigerant liquid, usually liquid nitrogen, though some isotherms were measured at a higher temperature using solid carbon dioxide in petroleum ether as refrigerant. Tap T_2 was opened and the system was allowed to reach equilibrium before the temperature and pressure were again recorded. Most of the gas was adsorbed in the first minute or two, and there was no further detectable change after $\frac{3}{4}$ hour, so this period of time was subsequently allowed for equilibration. The volume of gas remaining in the system may be calculated, and the volume sorbed is therefore the difference between the initial and final volumes. The pressure may be increased in two ways; firstly by closing tap T_2 and admitting more gas into the doser volume, or more easily by reducing the volume of the gas burette. Full details of the method of calculation are given by Reay (1956).

GRAVIMETRIC SYSTEM

In 1926 McBain and Bakr developed a technique of measuring sorption isotherms using a silica helical spring, the extension of which is directly proportional to the load it carries. The system used here employed four such springs, each having a sensitivity of about 25 cm per g, and a maximum load of one gram. A cathetometer reading to .001 cm was used to measure the lengths of the springs, the cross wires of the telescope being focussed on the tangents to the hooks rather than their tips, as this was found to be more accurate (Milligan et al, 1951).

The springs were calibrated at four temperatures, 30, 40, 50 and 60°C, and the two spring constants, the initial length and the sensitivity per gram, were calculated by the method of least squares at each temperature. The extension was found to vary linearly with load over the whole range at each temperature, but the sensitivity decreased with increasing temperature. The decreasing sensitivity varied linearly, however, with temperature over the range considered.

Each spring, carrying a small pyrex bucket containing about 0.4 g of clay, was suspended in a balance case constructed from 4 cm pyrex tubing, which in turn was immersed in a thermostat tank (figure 23).

These two thermostat tanks were 30x15x12" in size, with plate glass front and rear to enable the springs to be seen distinctly through a telescope. The main heating was provided by a one k.w. heater at the base of the tank, whilst the temperature was controlled by a Sunvic bimetallic strip regulator activating a relay connected to a 250 watt immersion heater. Each tank was provided with two stirring rods carrying a number of paddles, which proved sufficient to maintain the temperature at any point in the tank to within ±0.05°C of the required temperature.

One of the tanks also contained two mercury manometers, one limb of each being connected to the high vacuum line and one to the sorbate bulb and balance cases. A cut-off was included in the latter to prevent mercury jumping over into the balance cases in case of accident. All the tubes connecting the balance cases and manometers to the sorbate bulb were wrapped with asbestos covered heating wire, which passed below the water level in the thermostat tanks protected by a glass seal. This was maintained at about 80°C and prevented condensation of the vapour in the tubes when the temperature of the sorbate bulb was raised above ambient temperature.

Measurement of isotherms

The sorbate was introduced into the apparatus, evacuated, and twice distilled as was described in a previous section. Finally it was distilled into the sorbate storage bulb, which was isolated from the rest of the apparatus by two greaseless taps. These had a Neoprene diaphragm, and were found to be much superior to the mercury cut-offs used in the early experiments. Greased taps are unsuitable since most of the sorbates used in this work dissolve apiezon grease.

In all cases the clay samples were outgassed at 70°C to constant weight. The initial outgassing usually took 24 hours, but up to three days were sometimes necessary after hydrocarbons had been sorbed on to the sample. It proved impossible to remove all the acetonitrile sorbed on to the clays by outgassing, even at 150°C, and it was concluded that a certain amount was chemisorbed. It was therefore necessary to change the samples after acetonitrile sorption, before a different sorbate could be used.

For the initial measurement the sorbate was frozen in liquid nitrogen and then allowed to warm up slowly with tap T_B open until the required pressure was reached, the tap then being closed. The system was left to equilibrate, two hours being sufficient for all sorbates at relative pressures below 0.3. The pressure in the system could then be increased simply by opening and closing tap T_B. For vapour pressures above that possible at ambient temperature, the sorbate bulb was surrounded by a subsidiary thermostat, which consisted of a five litre beaker containing water, the temperature of which was controlled by a Sunvic bimetallic regulator in conjunction with a 250-watt immersion heater. For vapour pressures corresponding to temperatures below ambient on desorption the bulb was cooled in liquid nitrogen.

The time required to attain equilibrium varied with the sorbate used and the relative vapour pressure. With the hydrocarbons equilibrium was usually reached within two hours at all vapour pressures, but with those sorbates which caused the clay to swell considerably several days often elapsed before equilibrium was attained, especially at relative vapour pressures above 0.7. The graph of uptake against $\sqrt{\text{time}}$ was almost a straight line, suggesting that the process was diffusion controlled.

Since hysteresis was present in all these systems certain precautions were necessary. It was important during the adsorption isotherm that the pressure was not allowed to fall at any time and similarly on the desorption isotherm it was not allowed to rise, otherwise scanning curves rather than the limiting sorption and desorption curves would have resulted.

ACCURACY OF RESULTS

Two manometers were incorporated into the gravimetric system, and so the mean pressure value was taken, though the two values rarely differed by more than 0.01 cm. Since saturated vapour pressures were normally in excess of 10 cm of mercury, the error in the relative pressure value was not greater than ±.001.

The cathetometer could be read to ±.002 cm, giving a maximum error in reading the length of the spring of ±.004 cm, whilst the initial spring extension for the more weakly sorbed substances was of the order .150 cm. Thus there may be an error of up to 4% in the measured amount sorbed in certain cases, but in most cases the error will not exceed 1%.

Buoyancy corrections were sometimes necessary at higher relative pressures, detailed calculations of which were given by Kelsey (1959).

X-RAY DIFFRACTION

The samples of powdered clay under investigation were placed in capillary tubes drawn from 6 mm pyrex glass tubing, which could then be attached to the high vacuum line for outgassing and equilibration with the sorbate. The samples were X-rayed using a Newton Victor Raymax 60 or a Hilger and Watts Microfocus X-ray set, giving copper Kα X-radiation of wavelength 1.542Å. The photograph was taken on a flat plate placed 9 cm from the specimen, and the d001 spacing was estimated from the diameter of the first order diffraction ring.

In certain cases orientated films were prepared by subjecting the powdered clay to a high pressure. These were mounted on a glass fibre and X-rayed as above. Several attempts were made to obtain an X-ray pattern from an orientated flake mounted in a capillary tube, since this would have made it possible to outgas the sample, but diffraction from the walls of the capillary tube obscured any line given by the specimen.

RESULTS AND DISCUSSION

INTRODUCTION

The sorption isotherms for nitrogen, argon and several organic compounds on a range of alkylmonoammonium and alkyldiammonium montmorillonites have been determined. The results are tabulated in Appendix I.

In general the reproducibility of the isotherms was good, except when using acetonitrile and 1:3 propyldiamine as sorbates. A chemical reaction appeared to have taken place in both cases. All of the isotherms were sigmoidal in shape corresponding to type II in Brunauer's classification, and all showed hysteresis on desorption, though only where swelling of the clay had taken place did the hysteresis persist below a relative pressure of 0.3. The shapes and sizes of the hysteresis loops differed considerably, depending upon the extent of the swelling which had taken place, and in several cases scanning curves were determined.

Concurrent X-ray diffraction studies to determine the d001 spacings, gave information as to the orientation of the interlamellar molecules.

INTERLAMELLAR STRUCTURE

The d001 spacings for the various alkylmonoammonium and alkyldiammonium clays, outgassed at 60°C and 10^{-6} mm Hg pressure, are given in Table 3.I.

In accordance with the results of previous workers, (Jordan 1949, Weiss 1963), the spacing was found to be constant at approximately 13.3 Å for all complexes

TABLE 3.I

Alkyl diammonium montmorillonites

$\overset{+}{N}H_3(CH_2)_x\overset{+}{N}H_3$	d001 (Å)
$\overset{+}{N}H_3\overset{+}{N}H_3$	10.7
$\overset{+}{N}H_3(CH_2)_2\overset{+}{N}H_3$	12.2
$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$	12.9
$\overset{+}{N}H_3(CH_2)_4\overset{+}{N}H_3$	13.4
$\overset{+}{N}H_3(CH_2)_5\overset{+}{N}H_3$	13.3
$\overset{+}{N}H_3(CH_2)_6\overset{+}{N}H_3$	13.2
$\overset{+}{N}H_3(CH_2)_7\overset{+}{N}H_3$	13.3
$\overset{+}{N}H_3(CH_2)_8\overset{+}{N}H_3$	13.3
$\overset{+}{N}H_3(CH_2)_9\overset{+}{N}H_3$	13.3
$\overset{+}{N}H_3(CH_2)_{10}\overset{+}{N}H_3$	13.3
$\overset{+}{N}H_3(CH_2)_{12}\overset{+}{N}H_3$	13.4

Alkyl monoammonium montmorillonites

$\overset{+}{N}H_3C_xH_{2x-1}$	d001 (Å)
NH_4	10.5
$\overset{+}{N}H_3CH_3$	11.6
$\overset{+}{N}H_3C_2H_5$	12.8
$\overset{+}{N}H_3C_3H_7$	13.1
$\overset{+}{N}H_3C_4H_9$	13.3
$\overset{+}{N}H_3C_5H_{11}$	13.4
$\overset{+}{N}H_3C_6H_{13}$	13.4
$\overset{+}{N}H_3C_{12}H_{25}$	14.6

Alkyl diammonium hectorite

$\overset{+}{N}H_3(CH_2)_x\overset{+}{N}H_3$	d001 (Å)
$\overset{+}{N}H_3(CH_2)_2\overset{++}{N}H_3$	12.2
$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$	13.0
$\overset{+}{N}H_3(CH_2)_5\overset{+}{N}H_3$	13.3
$\overset{+}{N}H_3(CH_2)_9\overset{+}{N}H_3$	13.3

having three or more carbon atoms in the alkyl chain. The one exception to this is the dodecylammonium montmorillonite, which will be discussed later. If the thickness of the silicate layer is taken to be 9.4 Å the interlamellar spacing is approximately 4 Å, which suggests that all the alkylammonium chains lie with their axes parallel to the silicate layers. Two possible orientations remain, however; one with the zigzag of the carbon chain perpendicular to the silicate sheet, and one with the zigzag parallel, usually denoted as α_I and α_{II} configurations respectively. As noted in an introductory section, it was at first assumed that the chains were in an α_{II} configuration, since the diameter of a methyl group, 4Å, corresponded to the interlamellar spacing, but no allowance was made for possible keying of the organic molecules into holes in the silicate layers. If each of the methylene groups in an alkyl chain lies in a hollow between two adjacent oxygen atoms, the extent of penetration into the sheet is about 0.4Å, (Hoffmann and Brindley 1962), and if this occurs at two adjacent surfaces the total shortening of the contact distances is about 0.8Å, which is sufficient to allow an α_I configuration with the interlamellar spacing remaining at 4Å. In a more recent investigation, Fripiat and his co-workers (1962) studied the change in d001 spacing during the adsorption of n-alkylamines and n-alkyldiamines into "acid" montmorillonites. With the alkylamines the spacing attained a maximum of 12.8Å, when the amount sorbed corresponded to the exchange capacity of the clay, whilst with the alkyldiamines present in quantities equivalent to the exchange capacity of the clay, the spacing was only 12.2Å . On sorption of excess diamine the d001 spacing increased until equal to that of the alkylammonium clays, the following reaction taking place:

$$\overset{+}{N}H_3(CH_2)_x\overset{+}{N}H_3 \text{ mont.} + NH_2(CH_2)_xNH_2 \rightarrow 2\overset{+}{N}H_3(CH_2)_xNH_2 \text{ mont.}$$

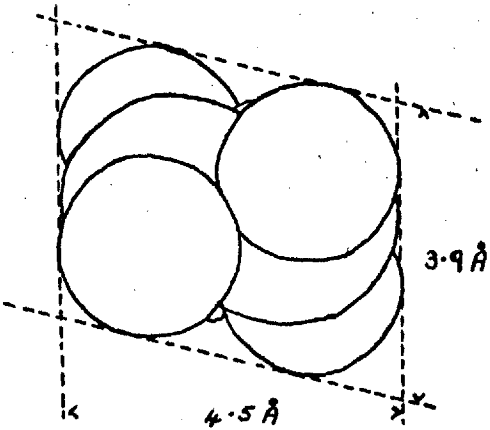
They proposed, therefore, that the alkylammonium ions assume an α_I configuration whilst the alkyldiammonium ions take up an α_{II} configuration. In the present investigation, where all the complexes have been prepared by exchange with the alkylammonium or alkyldiammonium salts, all the clays have a similar spacing of 13.3Å, and it seems probable, therefore, that all the complexes containing three or more carbon atoms in the alkyl chain have an α_I configuration.

The dodecylammonium montmorillonite had a d001 spacing of 14.6Å. This is at variance with the results of Jordan (1949) and Cowan and White (1958), who prepared a sample having a spacing of 17.6Å, which they assumed to be a two-layer complex, and of Greene Kelly (1955b) whose sample had a spacing of only 13.4Å. More recently Weiss (1963) found a variation from 14.2 to 22.1Å depending upon the method of preparation of the sample and subsequent treatment.

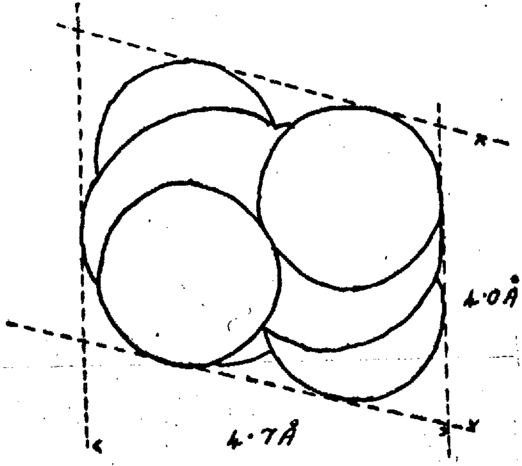
The possibility that an interstratified complex had been obtained was considered, but since the nitrogen analysis indicated complete exchange, and an orientated flake gave a rational series of higher order lines in the X-ray diffraction pattern, this explanation was discounted. Comparison of the area occupied by the dodecylammonium ions with the interlamellar area available to them shows that it is not possible for the ions to lie horizontally between the sheets. It seems probable that they are inclined at a small angle, the spacing indicates 5°, to the silicate layer.

Since the dimensions of the hydrazinium and monomethylammonium ions are very similar, the two clay derivatives might reasonably be expected to have similar interlamellar separations. However, the hydrazinium complex was found to have a spacing of only 10.7Å, almost 1Å less than that of the methylammonium derivative, and since the ion has a minimum height of 3.9Å, it must penetrate a considerable distance into the silicate sheets. Scale drawings of the hydrazinium and methylammonium ions, calculated from bond length data and van der Waals atomic radii (Pauling1960, Bondi 1964), are shown in Figs. 3.I and 3.2.

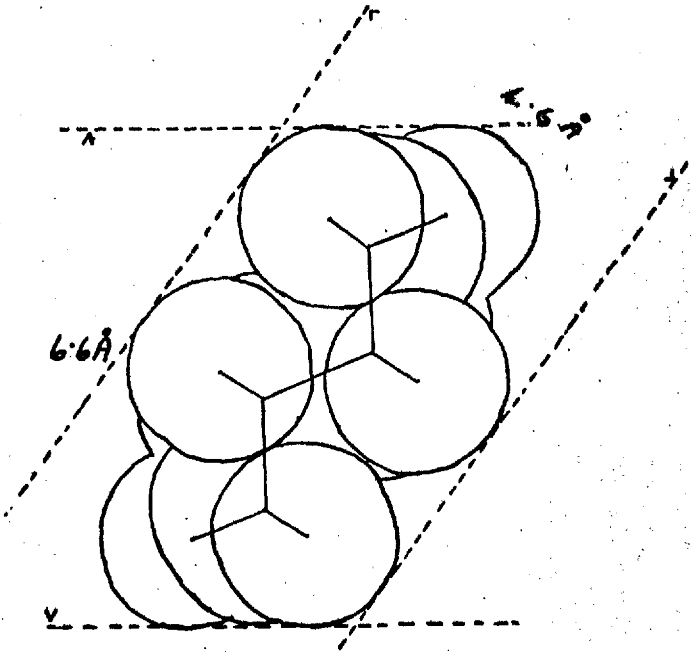
Assuming that the oxygen atoms at the base of the silica tetrahedra have a van der Waals radius of 1.4Å (Pauling 1960), the diameter of the cavity formed by these hexagonally arrayed oxygen atoms will be 2.8Å, which would allow the hydrazinium ion to penetrate only 1Å at each contact (Fig. 3.3), assuming the axis of the molecule to be perpendicular to the silicate sheet. This would result in an interlamellar spacing of 11.9Å. For a spacing of only 10.7Å, the ion must embed itself into the layer to the extent of 1.6Å per contact, and this obviously necessitates a reduction of about 0.8Å in the apparent diameter of the molecule. Strong hydrogen bonding between the oxygen atoms of the silicate sheets and the hydrogen atoms of the $-\overset{+}{N}H_3$ groups, as observed by Weiss (1958c), may account for this. This contraction due to hydrogen bonding has been noted by several workers, and Greene-Kelly (1955a) suggested that hydrogen bonding was responsible for almost all



$\overset{+}{N}H_3$ $\overset{+}{N}H_3$ Fig. 3. I



$CH_3\overset{+}{N}H_3$ Fig. 3. 2



$\overset{+}{N}H_3\,(CH_2)_2\,\overset{+}{N}H_3$

Fig. 3. 4

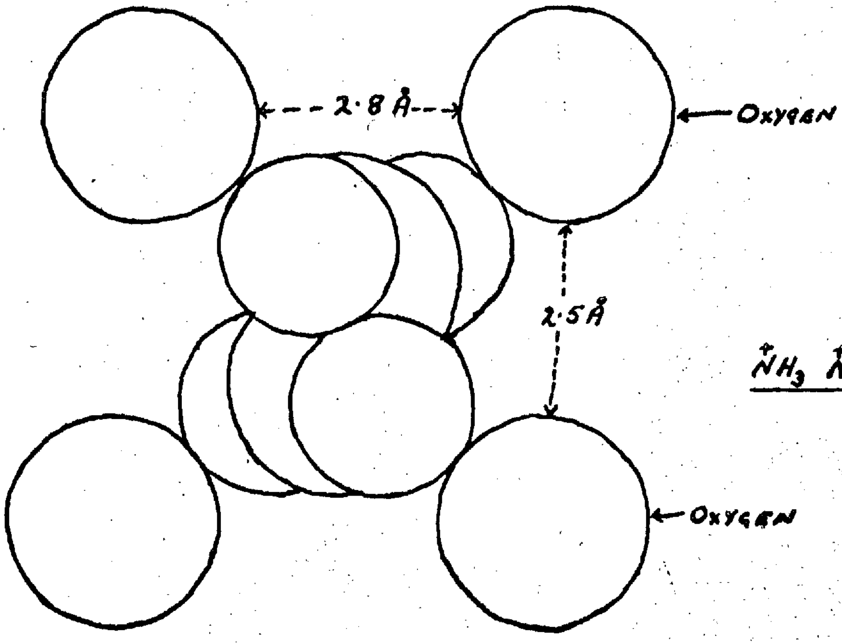


Fig. 3. 3

$\overset{+}{N}H_3\,\overset{+}{N}H_3$

apparent molecular contractions. A further factor favouring this penetration into the lamellae is that the positively charged nitrogen atom is brought nearer to the seat of negative charge in the octahedral layer, thus increasing the strength of the electrostatic bond. Haase, Weiss and Steinfink (1963), in studying the crystal structure of hexamethylene diamine vermiculite, measured a nitrogen-oxygen distance of 2.68Å, which would be in accordance with the above hypothesis.

As the mean distance between negative charges in the silicate layer is 10Å, assuming an even distribution (Fripiat et al. 1962), the shorter chain diamines are unable to satisfy two charges in the same layer, but may satisfy charges in adjacent layers, as is the case for the hydrazine model discussed above. With alkyldiammonium ions containing six or more carbon atoms it becomes possible to satisfy charges in the same layer.

The structure of methylammonium montmorillonite has been the subject of a number of investigations, the most recent of which (Rowland and Weiss 1963) proposed that the axis of the molecule was parallel to the clay surface until the exchange capacity of the clay was attained, but on sorption of excess amine the ions became perpendicular. The latter view was confirmed by the work of Kinter and Diamond (1963) in their experiments on glycerol retention. The former orientation allows one hydrogen atom of the methyl group and one of the $-NH_3$ group to sink into the hexagonal cavities of adjacent layers giving a spacing of 11.6Å (Rowland and Weiss 1963), whilst when the molecule is perpendicular the spacing rises to 12.6Å. This assumed that the $-NH_3$ did not contract as appeared to be the case with the hydrazinium complex. If the amine head can embed itself in the cavity as in the above case, then a spacing of 11.6Å may be obtained with the axis of the molecule perpendicular to the silicate layer. The available evidence is insufficient to decide which model is correct.

The d001 spacing of the ethylene diamine derivatives is rather less than the calculated value, even allowing for the amine groups to embed themselves completely in the cavities in the silicate layer. The height of the molecule is 6.6Å (Fig. 3.4) which, even with a total interlamellar penetration of 3.2Å, would correspond to a d001 spacing of 12.8Å. It is probable that the molecule is inclined at 56° to the silicate layer, i.e., with the C-N bonds perpendicular to the lamellae, since this allows maximum hydrogen bonding, and also represents the position of closest approach of the positive and negative charges. Weiss (1963), considering the more highly charged alkyldiammonium vermiculites, found that the ions with an even number of carbon atoms in the alkyl chain were always inclined at 56° to the lamellae, though a Fourier analysis by Haase, Weiss and Steinfink (1963) of hexamethylene diammonium vermiculite showed the angle to be somewhat lower.

If the ion were orientated with its axis parallel to the silicate layer the extent of penetration into the layer should not be more than 0.4Å per contact, and since the height of the ion is 4.6Å, the calculated d001 spacing would be over 13Å.

These calculations are based on bond lengths and van der Waals radii given by Pauling (1960) and Bondi (1964). Whilst the values for bond lengths are probably quite accurate, the van der Waals radii are subject to some uncertainty, since they may change with environment.

SWELLING

As noted in the introduction, it was thought possible to prepare a variety of alkyldiammonium clays whose swelling ability would be controlled in the limit by the length of the alkyl chain of the interlamellar ion. Thus a preliminary X-ray diffraction investigation was undertaken to determine which sorbates would cause appreciable swelling of the clay. Previous experience (Jordan 1949, Weiss 1963) had shown that sorbates having both highly polar and organophilic characteristics were most effective.

Two procedures were adopted: in the first, the clay derivative was outgassed, usually at 60°C though other temperatures were used, and was then allowed to equilibrate with the sorbate at room temperature; while in the second, the clay was not outgassed before equilibration. In general the two methods gave identical results, though differences were noted in three cases with acetonitrile as sorbate. Occasionally spacings were measured when the sorbate was at a pressure less than the saturated vapour pressure, but these results will be discussed later in conjunction with the sorption isotherms.

In view of the results obtained by Weiss and his co-workers (1958c, 1963) the results of this investigation were a little surprising. Of the many sorbates tried, only acetonitrile caused the alkyl diammonium derivatives to swell more than 2Å. The aromatic compounds such as benzene, dioxan and cyanobenzene, gave d001 spacings between 14.6 and 15.1Å, which probably corresponds to a single layer standing with the plane of the ring perpendicular to the silicate sheet (Reay 1956).

The hydrocarbons, such as heptane, produced only very slight expansion, 0.1 to 0.2Å, when sorbed on to any of the clays, whilst normal primary amines and alcohols did not produce any swelling with the alkyl diammonium derivatives, even after heating at 80°C for three days. Some swelling was obtained when they were sorbed on to the longer chain alkylammonium derivatives, but the alkyl diammonium derivatives were the prime interest in this investigation.

Though acetonitrile induced appreciable swelling in all the clay derivatives, the ethyl and propyl cyanides were not sorbed beyond a monolayer, since no spacing exceeded 13.6Å after three days' equilibration at 80°C. The spacings attained with acetonitrile under various conditions are tabulated below, (Table 3.II).

The alkyl diammonium clays with more than seven carbon atoms give a spacing of 19.6 to 20.6Å under all conditions, whilst the spacings of ones with four to six carbon atoms are in the region of 16.3Å. The spacing obtained with the lower members of the series is dependent upon the outgassing temperature, the spacing decreasing with increasing temperature.

A spacing of 19.6Å was found by McEwan (1948) in studying the sorption of acetonitrile on sodium montmorillonite. He postulated the formation of a three layer complex, which allows about 3.4Å per layer. If

TABLE 3.II

No. of C atoms	Treatment		
	Not outgassed	Outgassed 60°C	Outgassed 110°C
(1) Diammonium montmorillonites			
0	20.0		16.1
2	19.6	19.6	16.4
3	19.7	15.9	15.9
4	16.2	16.4	
5	16.4	16.3	
6	16.9	16.8	
7	19.8		
8	19.6	19.8	
9		19.8	19.7
10		20.0	
12	20.6	20.4	20.4
(2) Monoammonium montmorillonites			
1	16.4		
2	16.3		
3	20.6		
4			
5			
6	21.0		
12	16.3		
(3) Diammonium hectorites			
2	19.7	19.6	
3	19.4		
4	16.2		
5	16.3		
9	19.5	19.7	
12	19.9	19.9	

this is accepted it seems reasonable to assume that the 16.3Å spacing corresponds to a two-layer complex.

1:3 diamino propane produced a d001 spacing of 14.3Å with each of the samples considered. This is consistent with a molecule standing perpendicular to the layer, since the N-N distance is 4.9Å, which is also the interlamellar separation, but further evidence as to the orientation must be adduced from sorption isotherms.

On the basis of these results sorption isotherms for heptane, which causes little swelling, benzene and propane diamine, which result in slight swelling, and acetonitrile as the sorbate which produces the largest swelling, were studied in detail.

SORPTION ISOTHERMS

(i) Volumetric

The sorption of nitrogen on each of the organo-clay derivatives at 78°K was determined, and the results are summarised in Figs. 3.5, 3.6 and 3.7. It is seen that the uptake varies little with carbon chain length up to six carbon atoms for the alkyl diammonium clays, but decreases rapidly with longer alkyl chains, becoming equal to that of the sodium clay when there are ten carbon atoms in the chain. The alkyl monoammonium clays behave rather differently, however, the uptake falling almost linearly with chain length. The difference in uptake of nitrogen between the montmorillonite and hectorite derivatives is probably due to a difference in particle size, since the clays have a similar exchange capacity. In certain cases the sorption

KEY TO GRAPHS

No.	Symbol	
Na^+	◇	Na^+ or $\overset{+}{N}H_3CH_3$
2	+	$\overset{+}{N}H_3(CH_2)_2\overset{+}{N}H_3$ or $\overset{+}{N}H_3C_2H_5$
3	○	$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$ or $\overset{+}{N}H_3C_3H_7$
4	x	$\overset{+}{N}H_3(CH_2)_4\overset{+}{N}H_3$ or $\overset{+}{N}H_3C_4H_9$
5	△	$\overset{+}{N}H_3(CH_2)_5\overset{+}{N}H_3$ or $\overset{+}{N}H_3C_5H_{11}$
6	⧄	$\overset{+}{N}H_3(CH_2)_6\overset{+}{N}H_3$ or $\overset{+}{N}H_3C_6H_{13}$
7	▽	$\overset{+}{N}H_3(CH_2)_7\overset{+}{N}H_3$ or $\overset{+}{N}H_3C_7H_{15}$
8	■	$\overset{+}{N}H_3(CH_2)_8\overset{+}{N}H_3$ or $\overset{+}{N}H_3C_8H_{17}$
9	◐	$\overset{+}{N}H_3(CH_2)_9\overset{+}{N}H_3$ or $\overset{+}{N}H_3C_9H_{19}$
10	□	$\overset{+}{N}H_3(CH_2)_{10}\overset{+}{N}H_3$ or $\overset{+}{N}H_3C_{10}H_{21}$
12	⊗	$\overset{+}{N}H_3(CH_2)_{12}\overset{+}{N}H_3$ or $\overset{+}{N}H_3C_{12}H_{25}$

All amounts sorbed refer to 1 gm of outgassed sorbent.

NITROGEN ON MONTMORILLONITES AT 78°K.

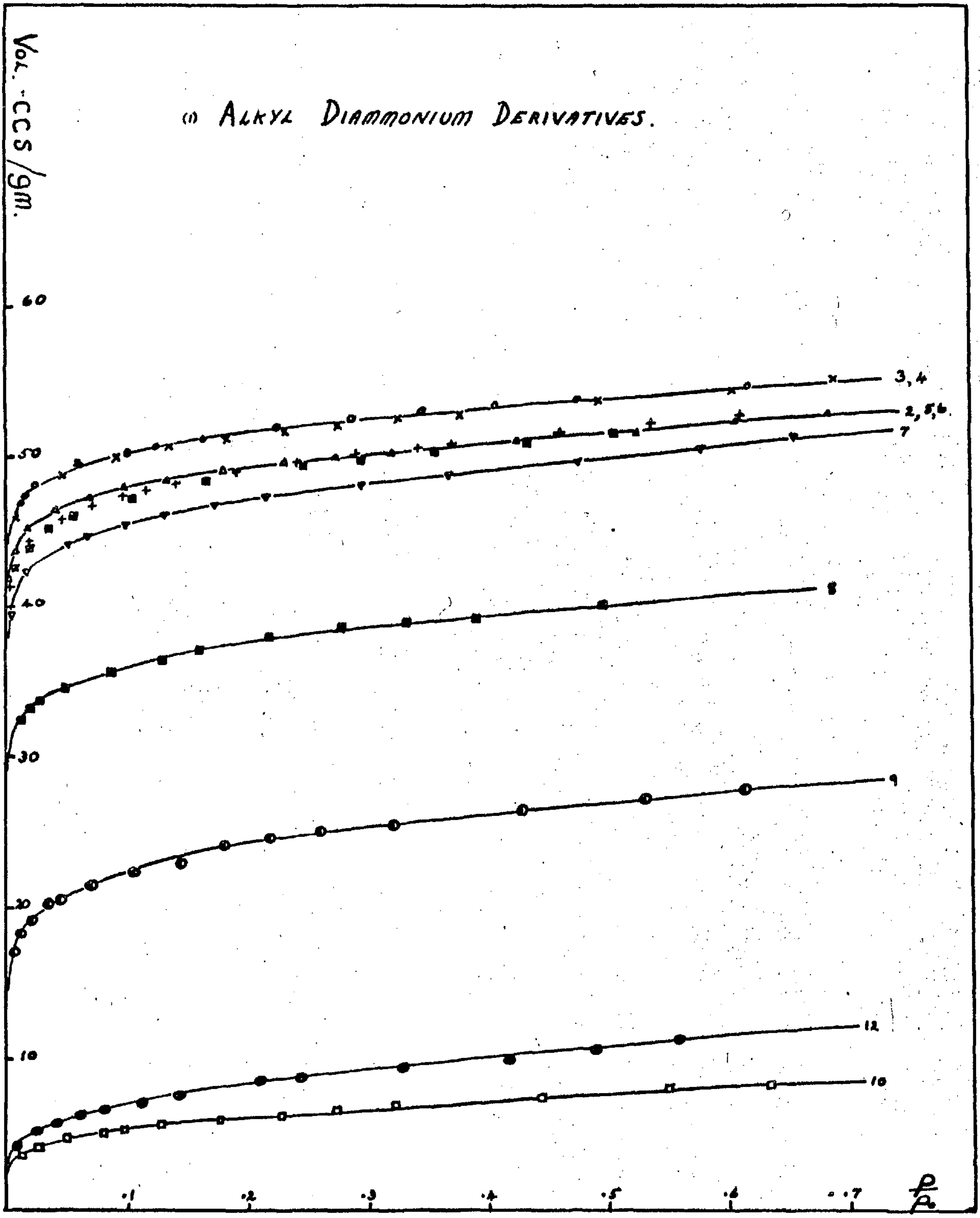


Fig. 3.5

B.E.T. PLOT FOR SORPTION OF NITROGEN ON MONTMORILLONITES.

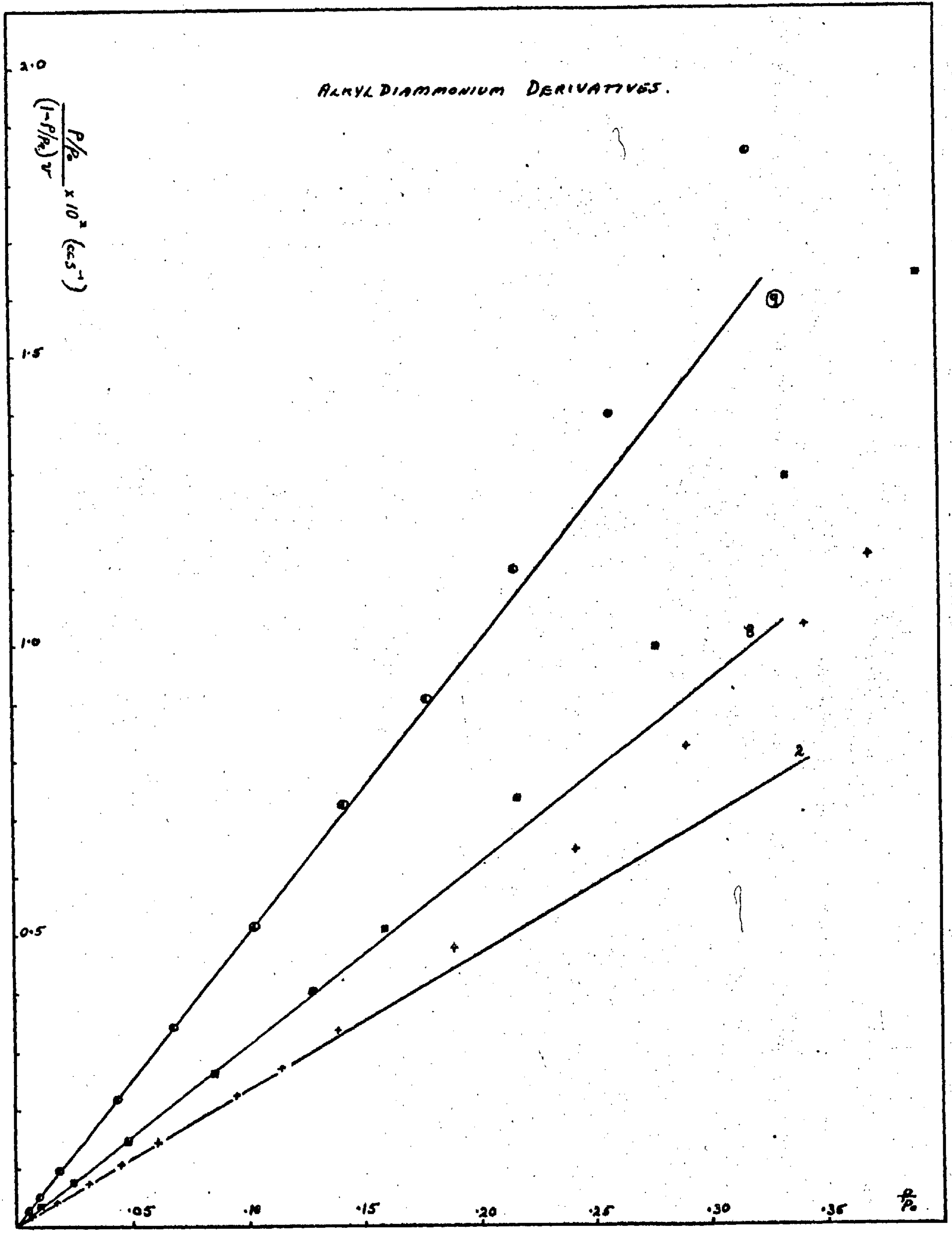


FIG. 3.6(a)

NITROGEN ON MONTMORILLONITES AT 78°K

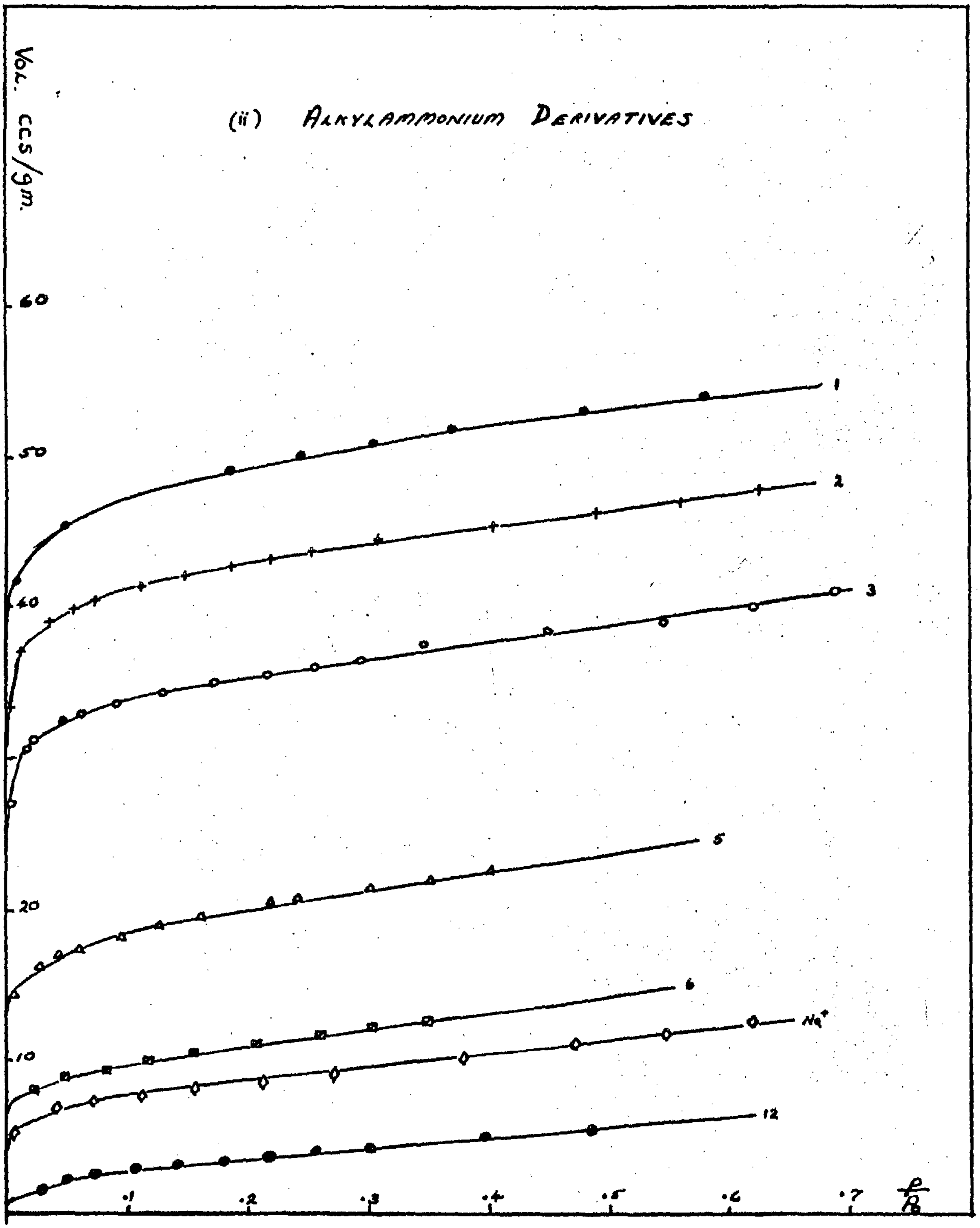


Fig. 3.6

NITROGEN ON HECTORITES AT 78°K.

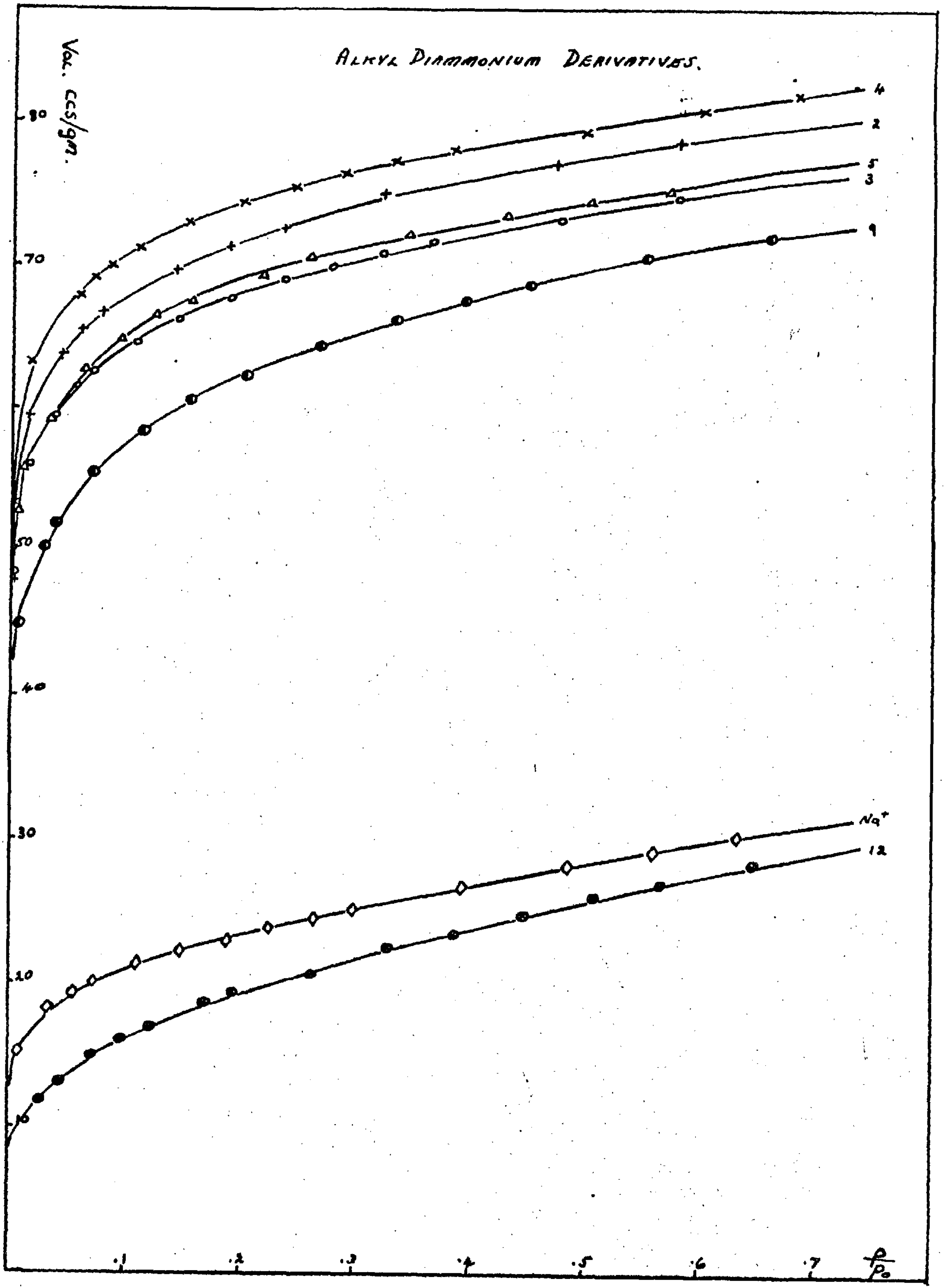


FIG. 3.7

isotherm was extended to saturated vapour pressure and the desorption isotherm determined (Fig. 3.8). All the samples studied gave a hysteresis loop of similar shape which closed at approximately 0.5 p/p_0.

The sorption and desorption isotherms for argon on a number of samples at 78°K were measured (Figs. 3.9, 3.10 and 3.11). They closely resemble those for nitrogen, though the amount sorbed is slightly higher, and the loops do not close until 0.3 p/p_0 is reached. In certain cases scanning curves were also determined. The two oxygen isotherms measured are also of type II (Brunauer classification), the hysteresis loop closing at 0.3 p/p_0 (Fig. 3.8).

The volume of gas required to complete a monolayer was calculated in each case from the appropriate B.E.T. isotherm. The results are listed in Table 3.III. A few values were calculated from the Huttig isotherm but they did not usually differ by more than 3 per cent. The B.E.T. plots were somewhat unusual in being linear down to almost zero pressure (Fig. 3.6a), though they often deviated above 0.2 p/p_0. This corresponds to a high 'c' constant and indicates that the monolayer is complete at a low relative pressure, as would be expected from the rectangular shape of the sorption isotherm.

(ii) Gravimetric

As stated in the previous section, the sorption isotherms for heptane, benzene, 1:3 diamino propane, and acetonitrile on a range of alkyl diammonium montmorillonites and hectorites were also studied. The adsorption isotherms are plotted in Figs. 3.12 to 3.21.

TABLE 3.III

V_m and w_m values.

No. C atoms	N_2	A	O_2	n-C_7H_{16}	C_6H_6	CH_3CN	$NH_2(CH_2)_3NH_2$
(1) Alkyl diammonium montmorillonites							
2	43.1					.0559	
3	44.6	43.6		.0498	.1059	.0508	.0738
4	44.2					.0524	
5	43.0	45.5				.0472	
6	42.4	44.8	50.5	.0500	.0889	.0471	.0714
7	40.6						
8	32.9		40.0	.0402	.0730	.0323	.0730
9	20.0					.0337	
10	4.95	6.85		.0270	.0427		.0690
12	6.85					.0249	
(2) Alkylammonium montmorillonites							
Na^+	6.8						
1	41.7						
2	36.1				.1064		
3	30.4				.1095		
5	16.4						
6	9.1				.0898		
12	3.3				.0087		
(3) Alkyl diammonium hectorites							
Na^+	18.8	27.3					
2	61.5						
3	57.5	61.7			.125	.0816	
4	62.5						
5	58.2	64.1			.115	.0727	
9	51.9	56.8				.0678	
12	16.8				.0377	.0352	

V_m for N_2, A, O_2 in cc at s.t.p./g.

w_m for C_7H_{16}, C_6H_6, CH_3CN, $NH_2(CH_2)_3NH_2$ in g/g.

SORPTION ON MONTMORILLONITES AT 78°K.

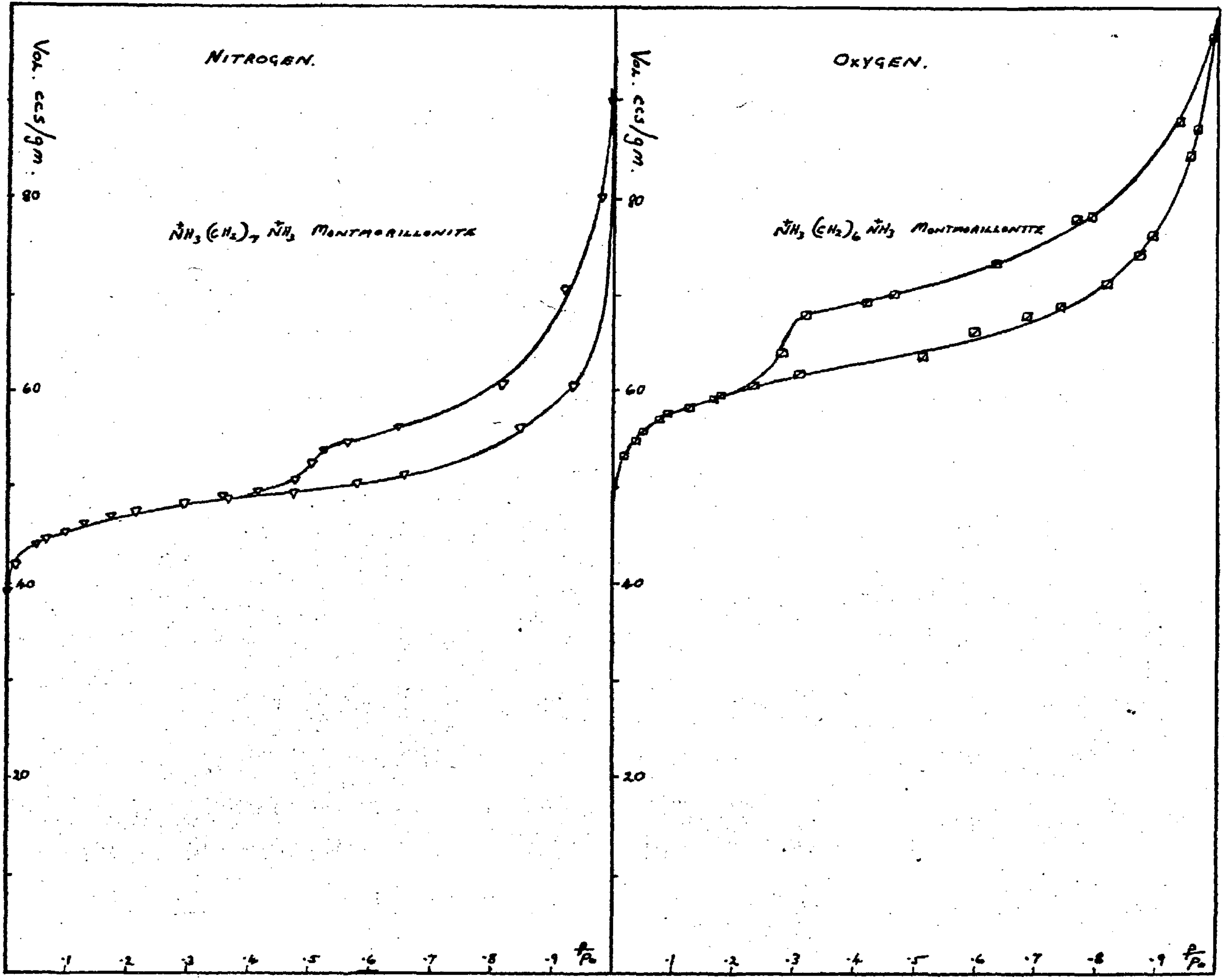


FIG. 3.8

ARGON ON MONTMORILLONITES AT 78°K.

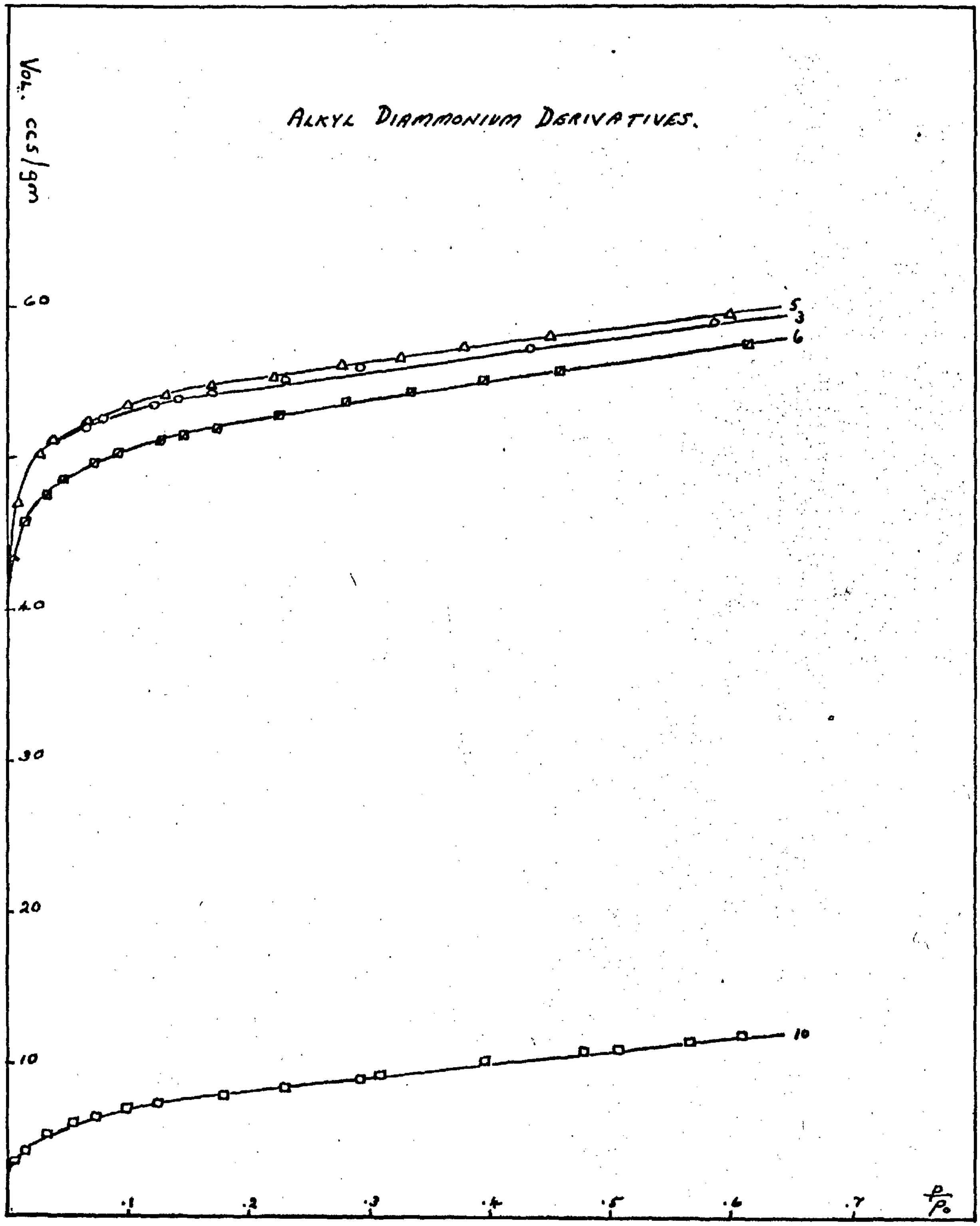


FIG. 3.9

ARGON ON HECTORITES AT 78°K

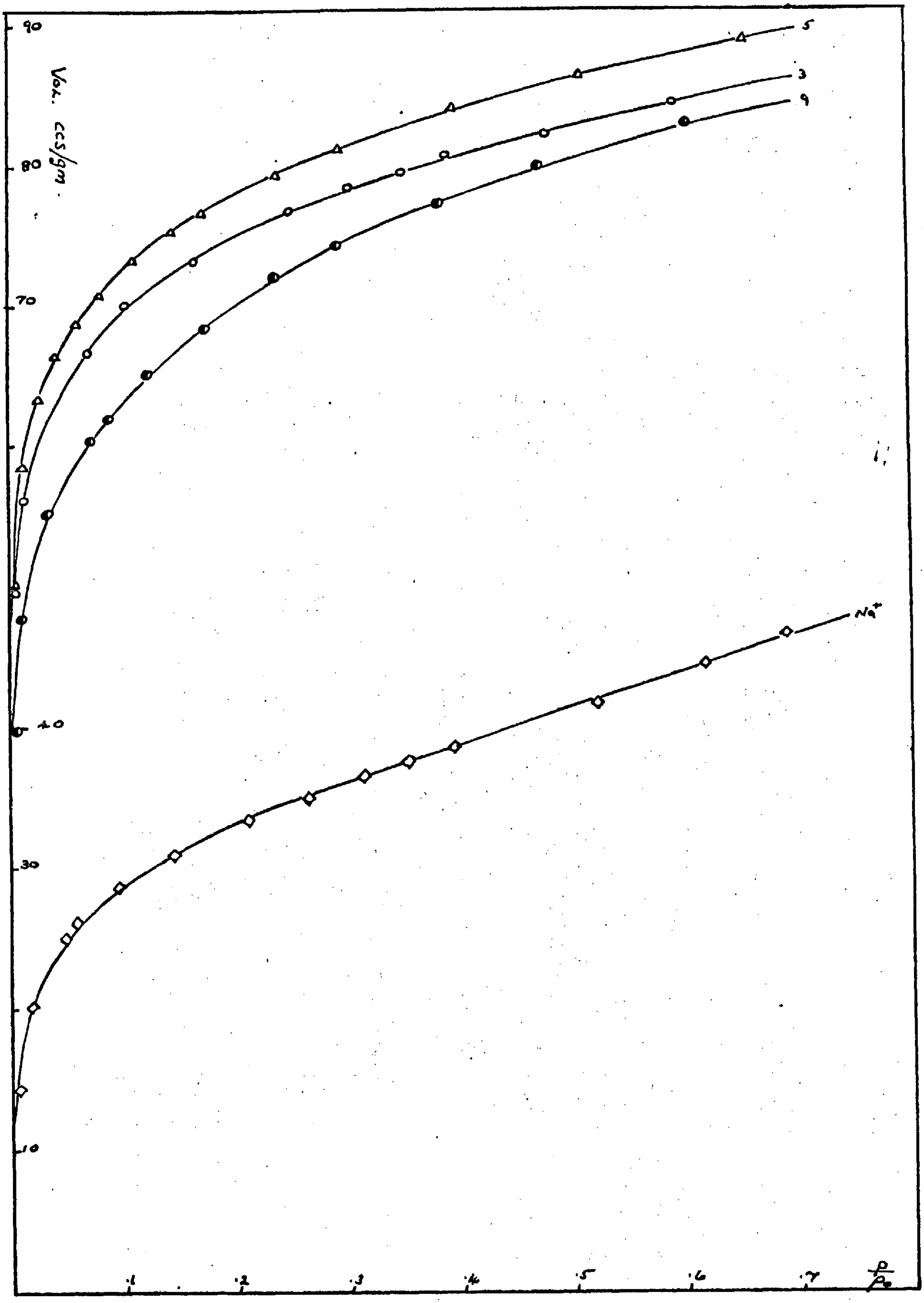


FIG. 3.10

ARGON SORPTION AT 78°K.

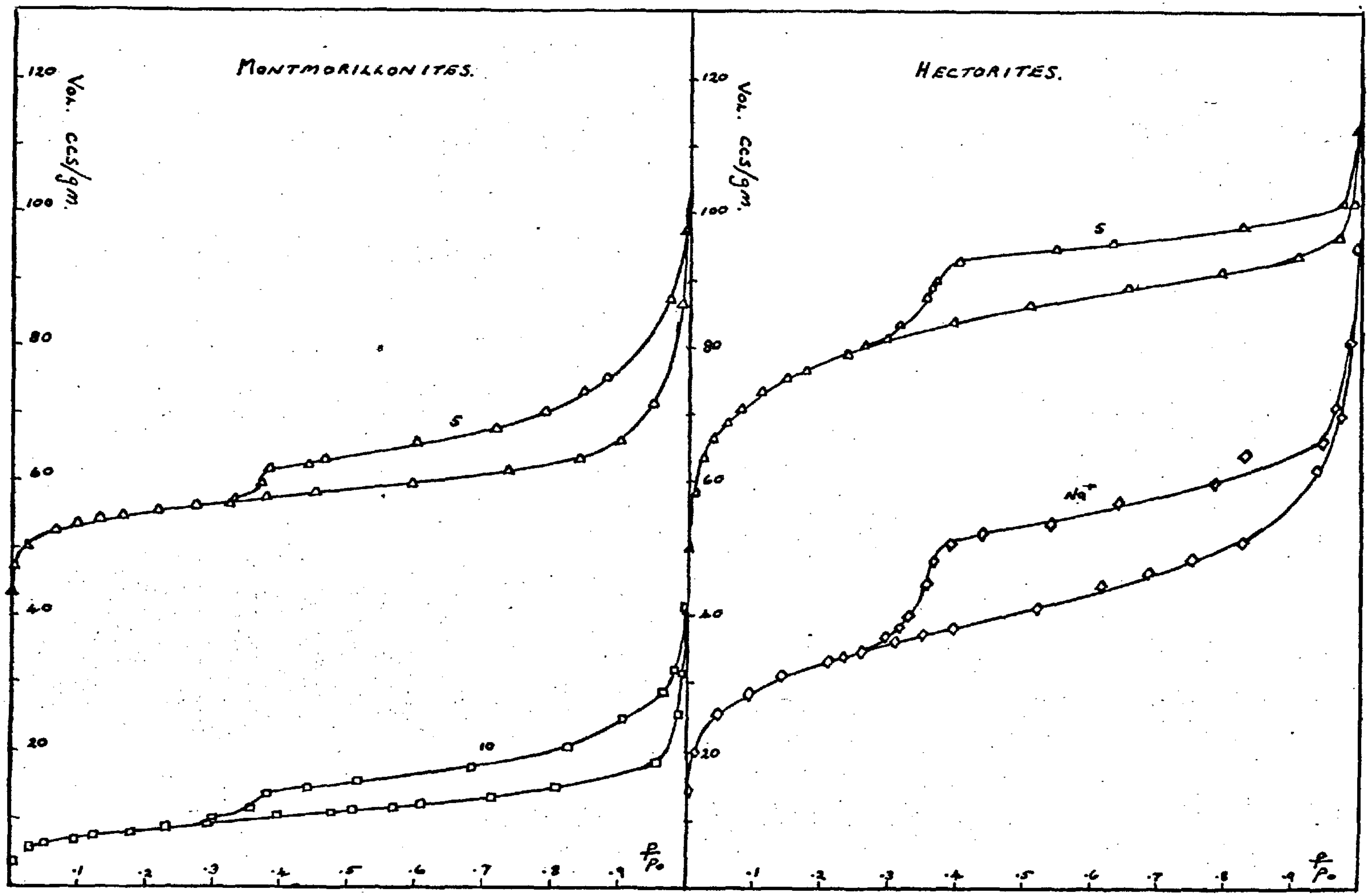


FIG. 3.11

BENZENE ON MONTMORILLONITES AT 40°C.

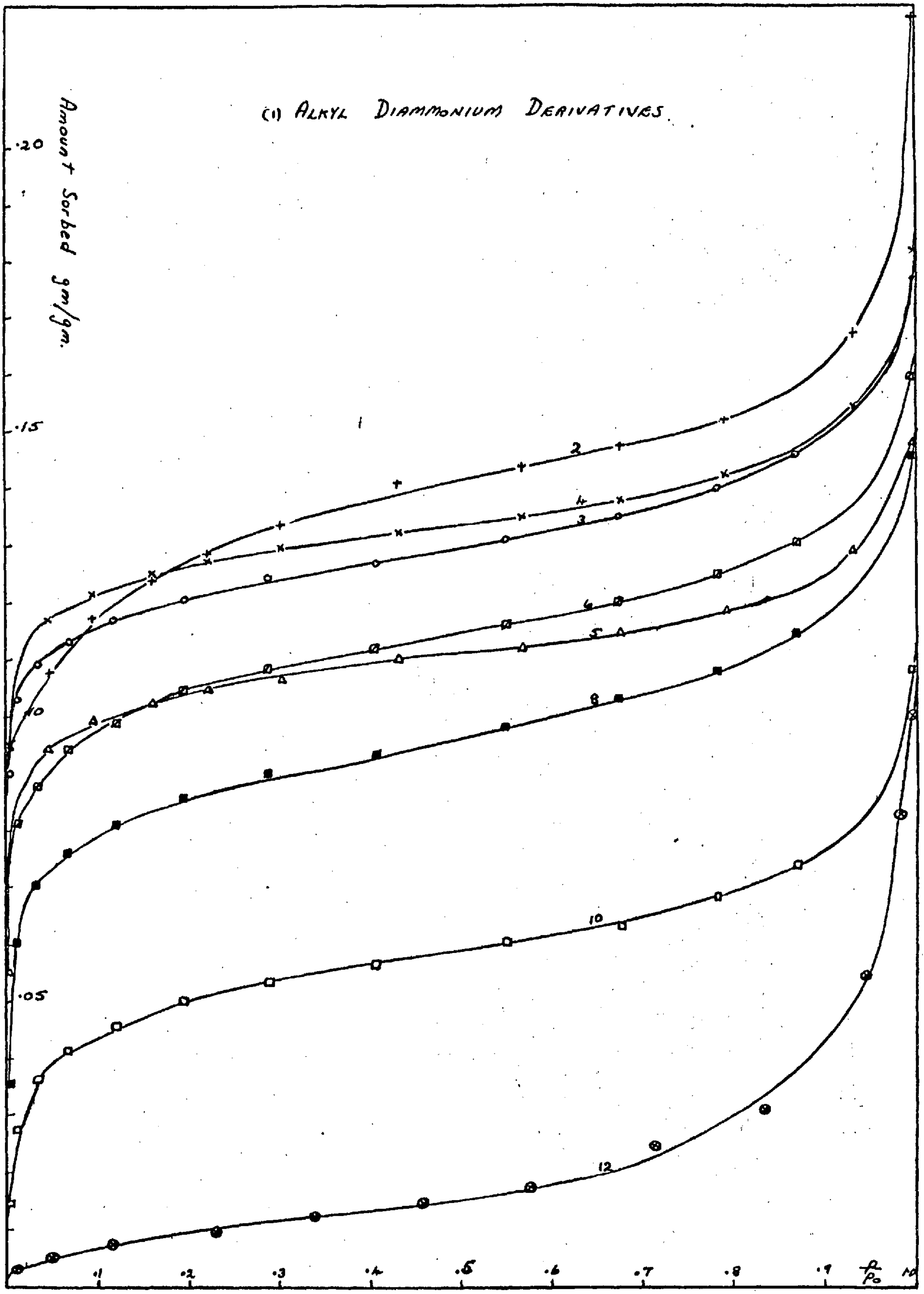


FIG. 3.12

BENZENE ON MONTMORILLONITES AT 50°C.

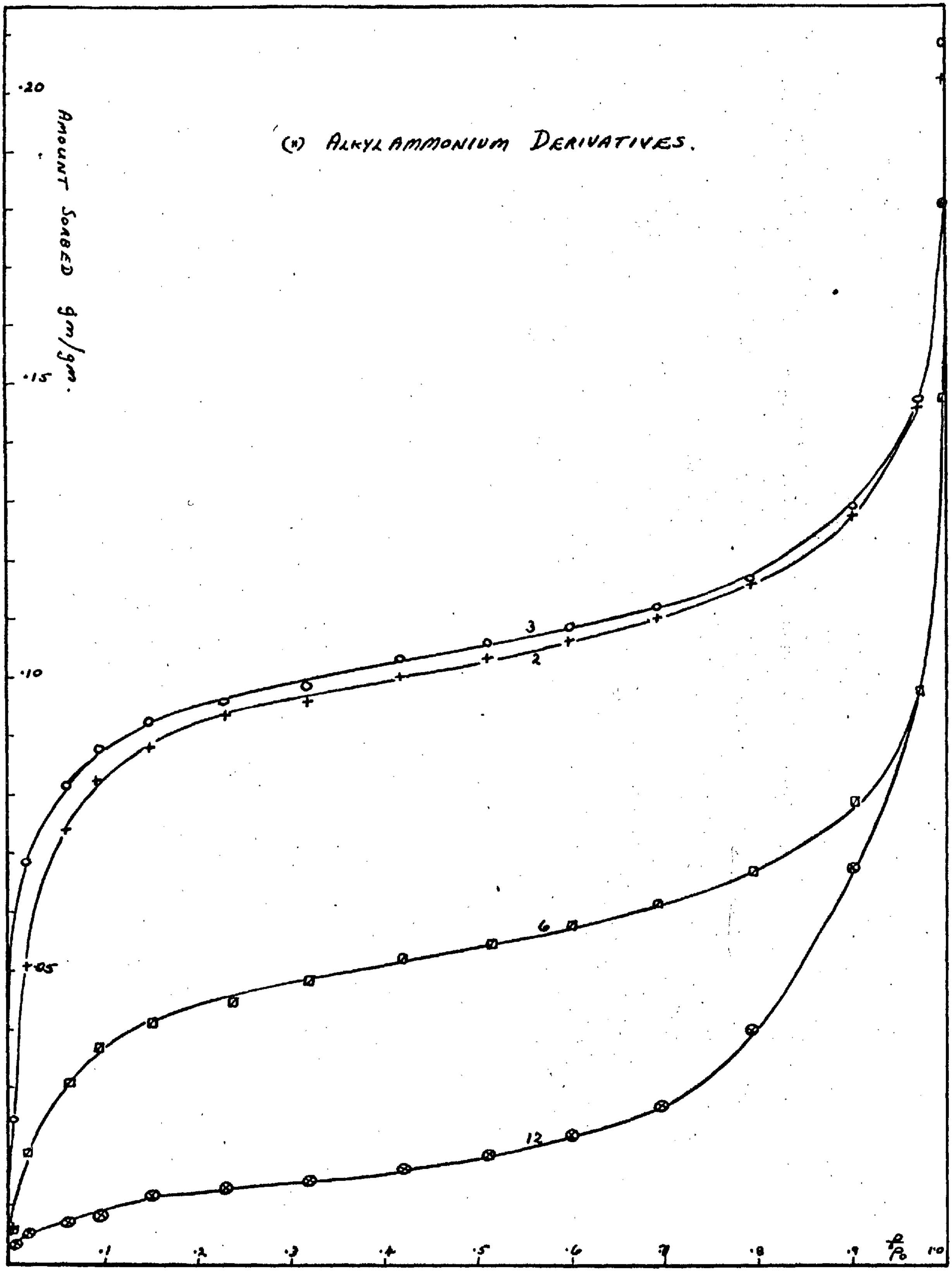


FIG. 3.13

BENZENE ON HECTORITES AT 40°C.

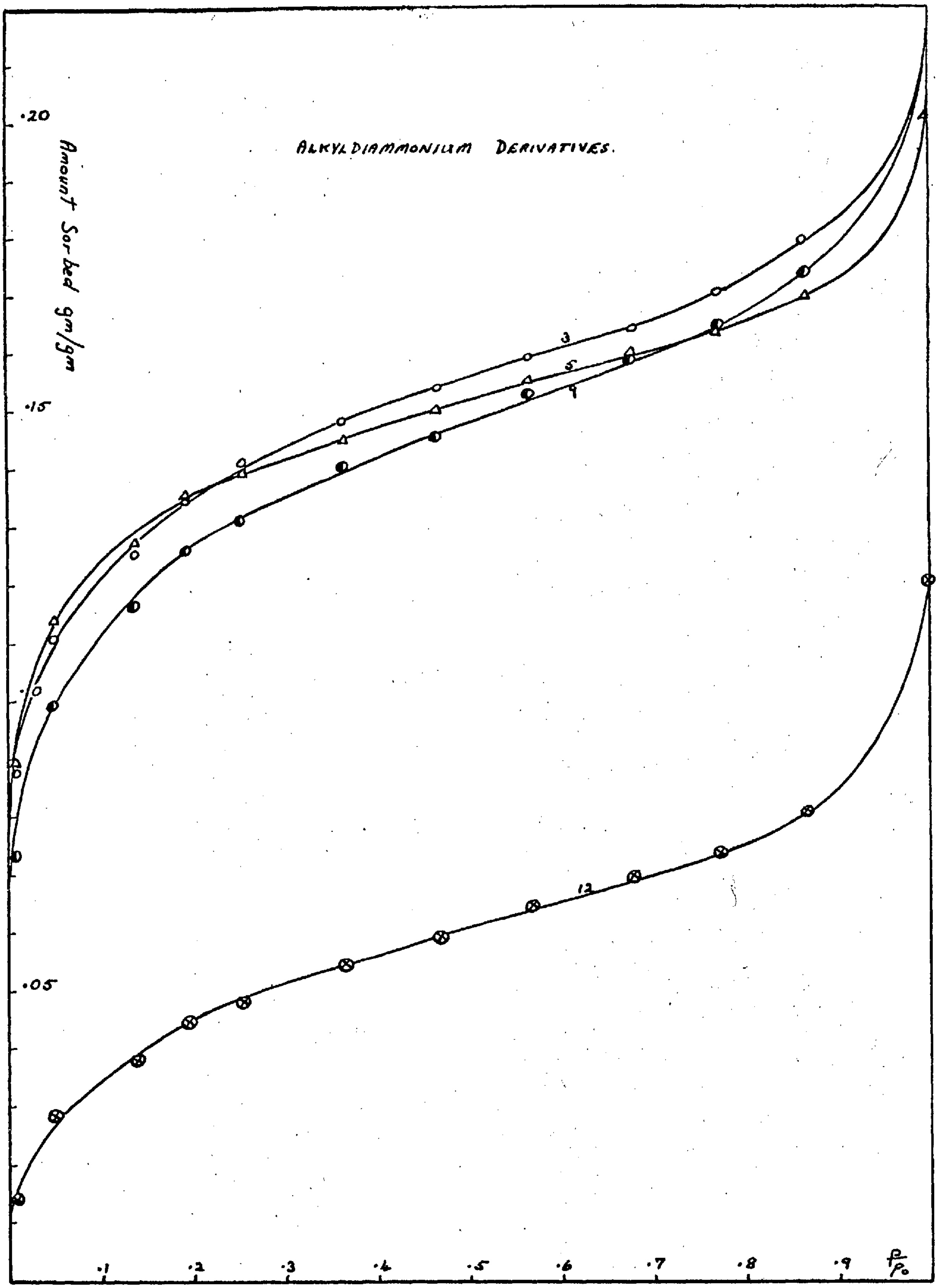


FIG. 3.14.

HEPTANE ON MONTMORILLONITES AT 40°C.

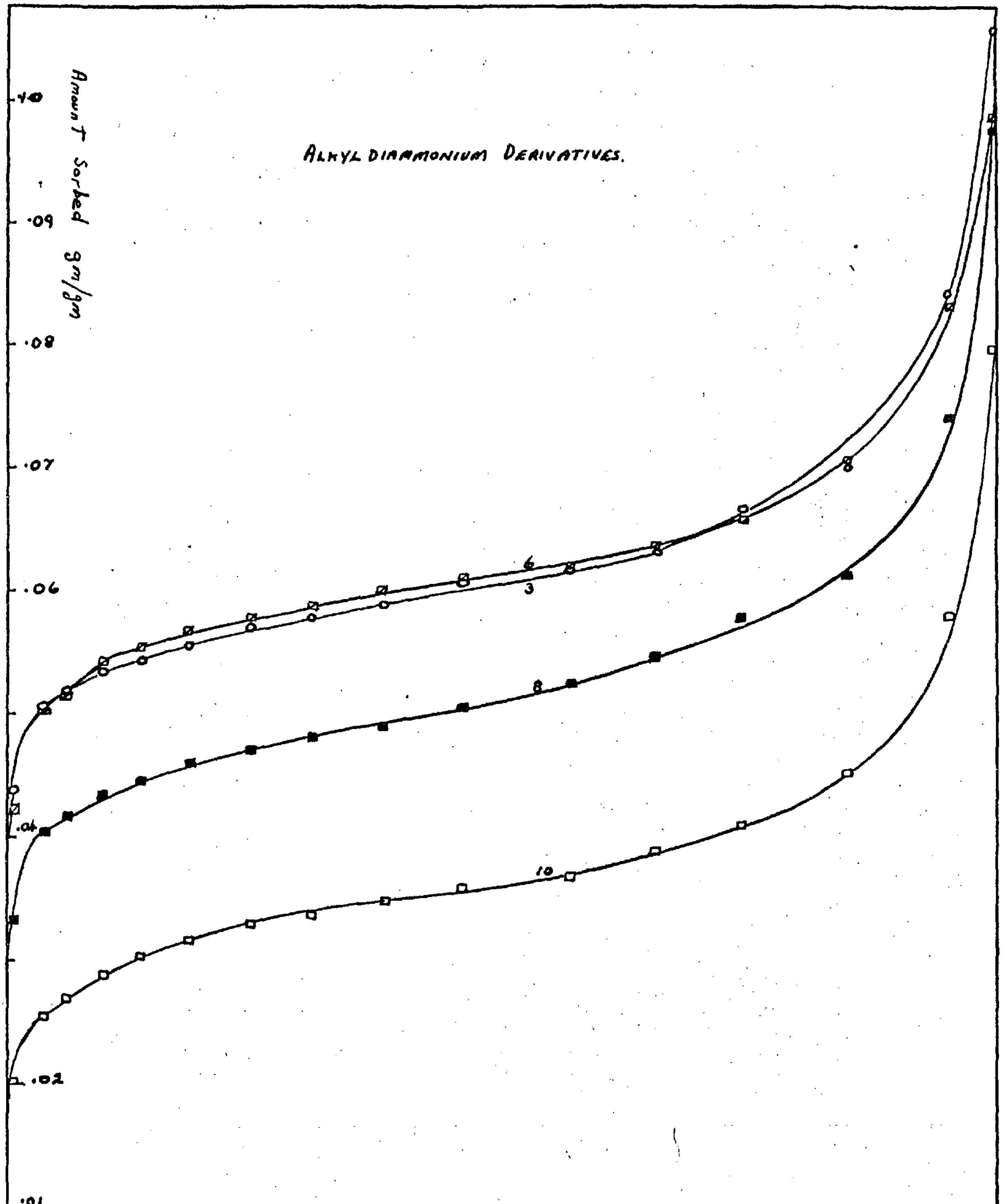


FIG. 3.15

SORPTION ON MONTMORILLONITES AT 40°C

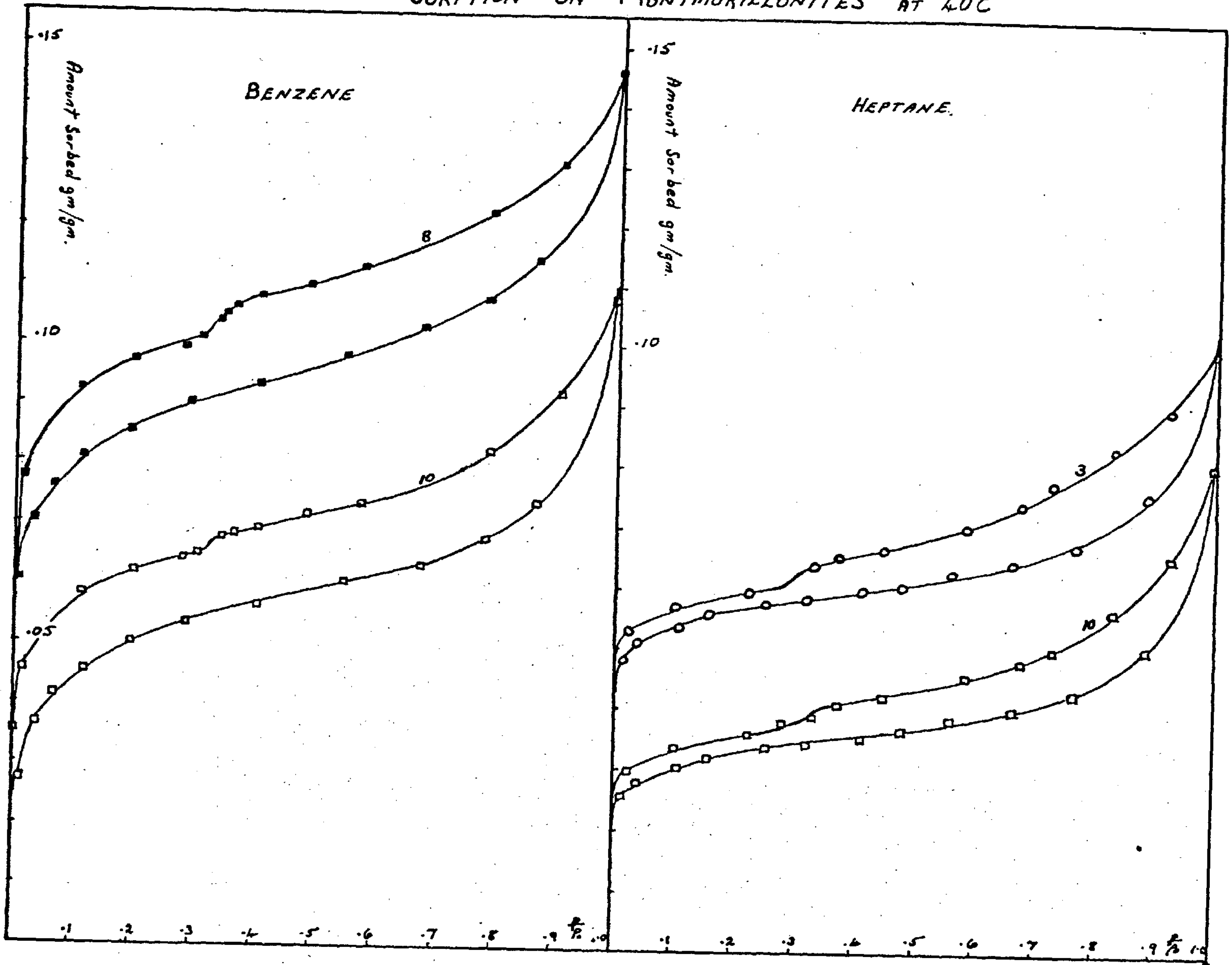


FIG. 3.16

ACETONITRILE ON MONTMORILLONITES AT 50°C.

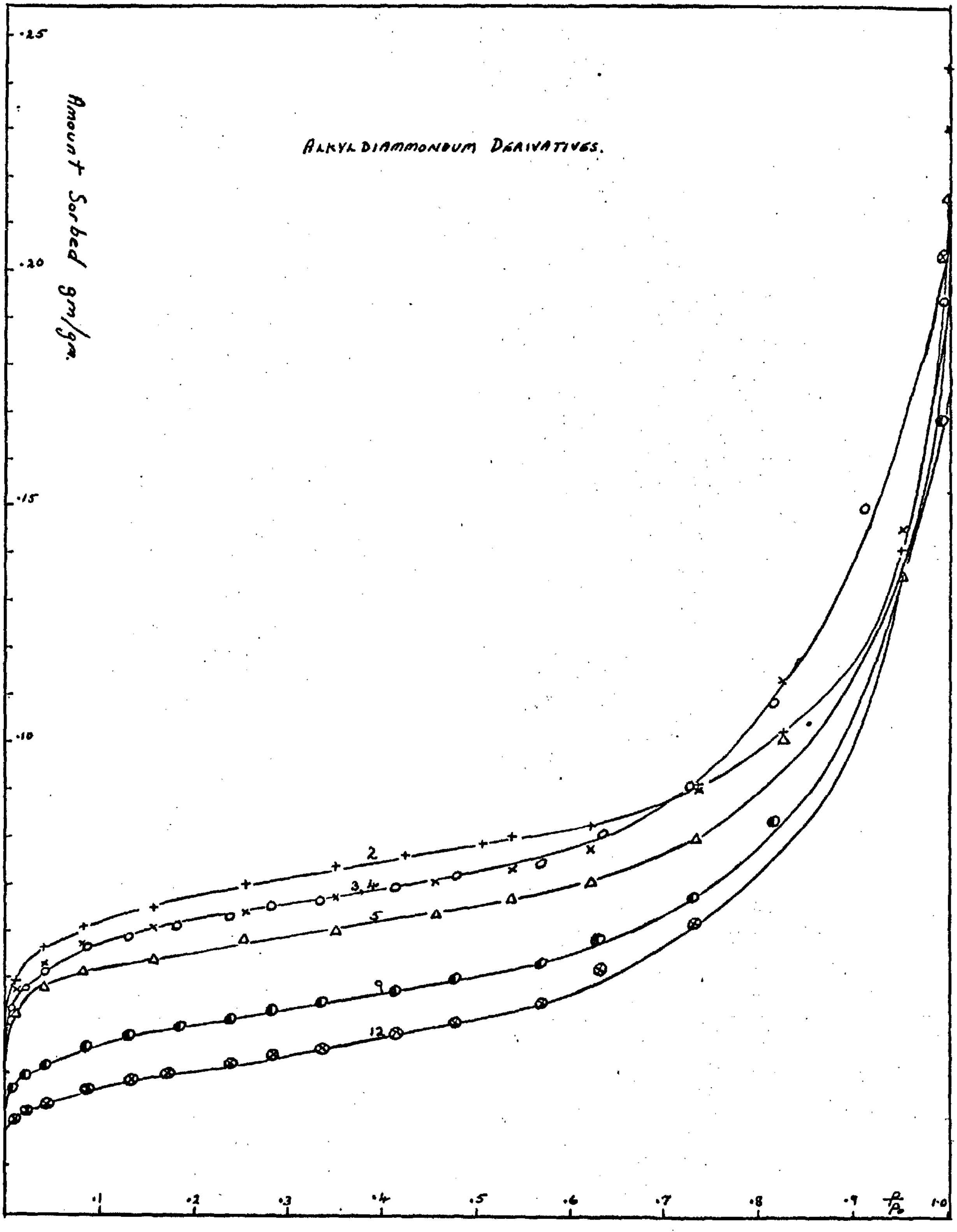


FIG. 3.17

ACETONITRILE ON HECTORITES AT 60°C.

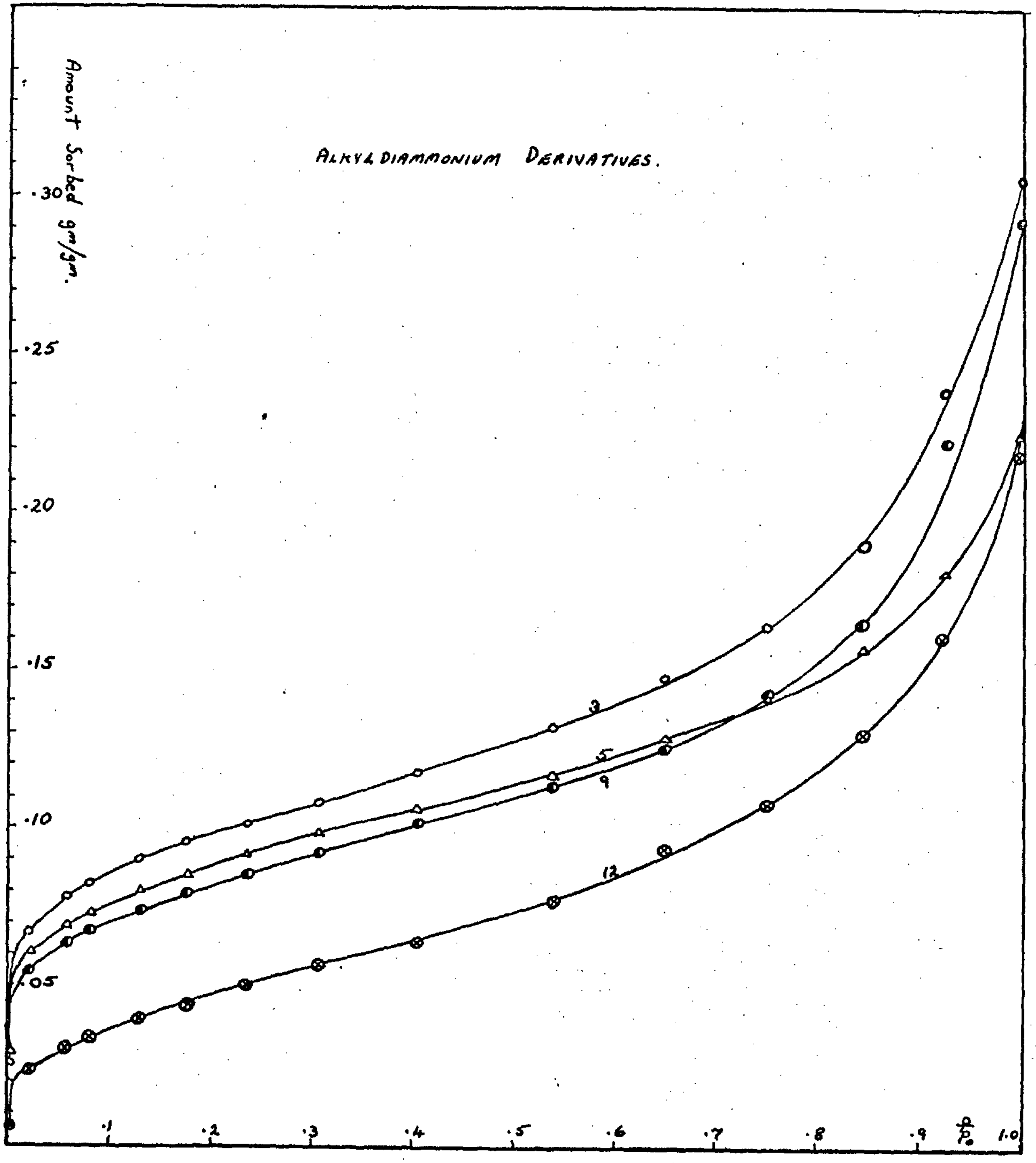


FIG. 3.18

ACETONITRILE ON MONTMORILLONITES AT 50°C.

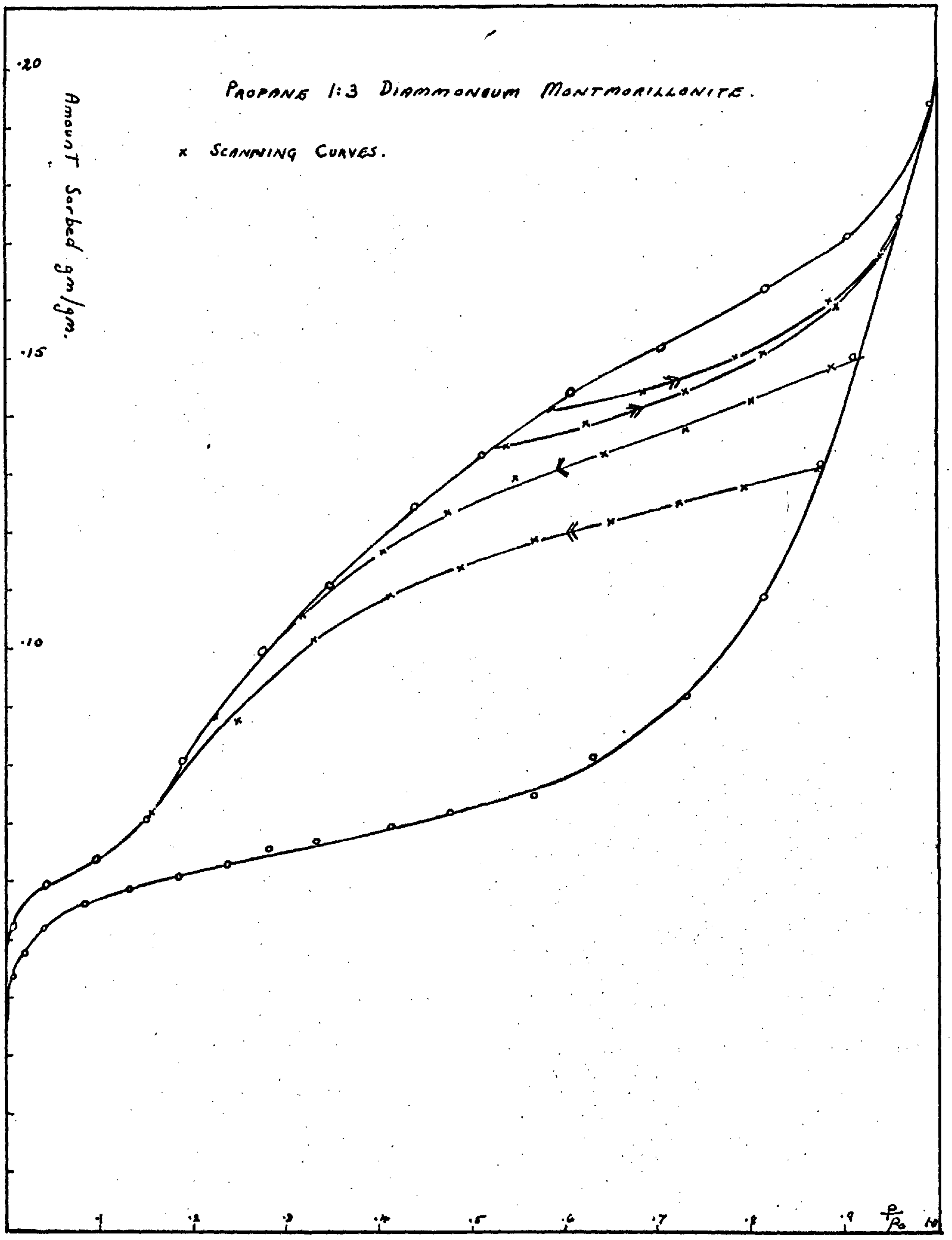


FIG. 3.19

1:3 DIAMINO PROPANE ON MONTMORILLONITES AT 40°C.

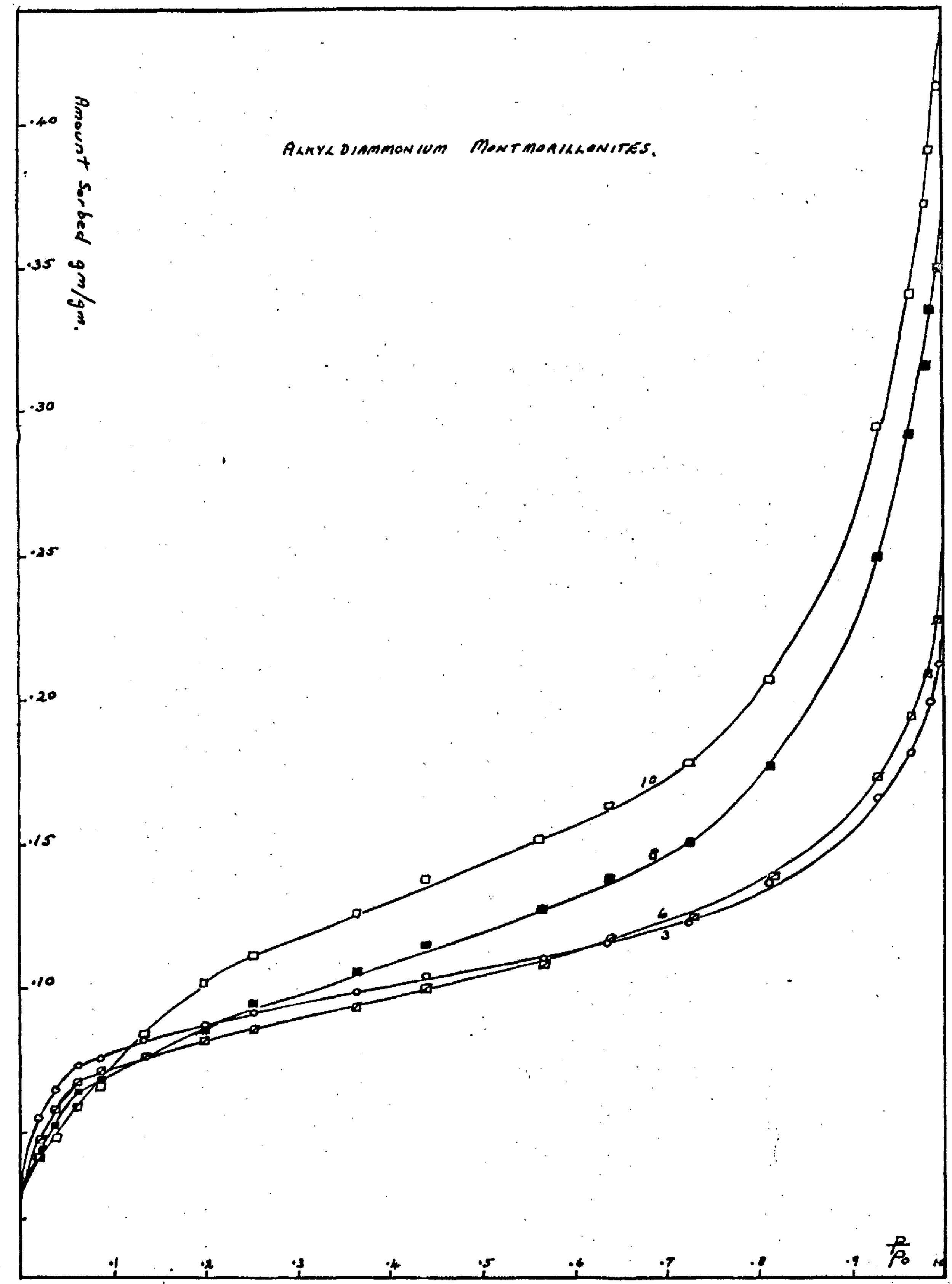


FIG. 3.20

1:3 DIAMINO PROPANE ON MONTMORILLONITES AT 40°C.

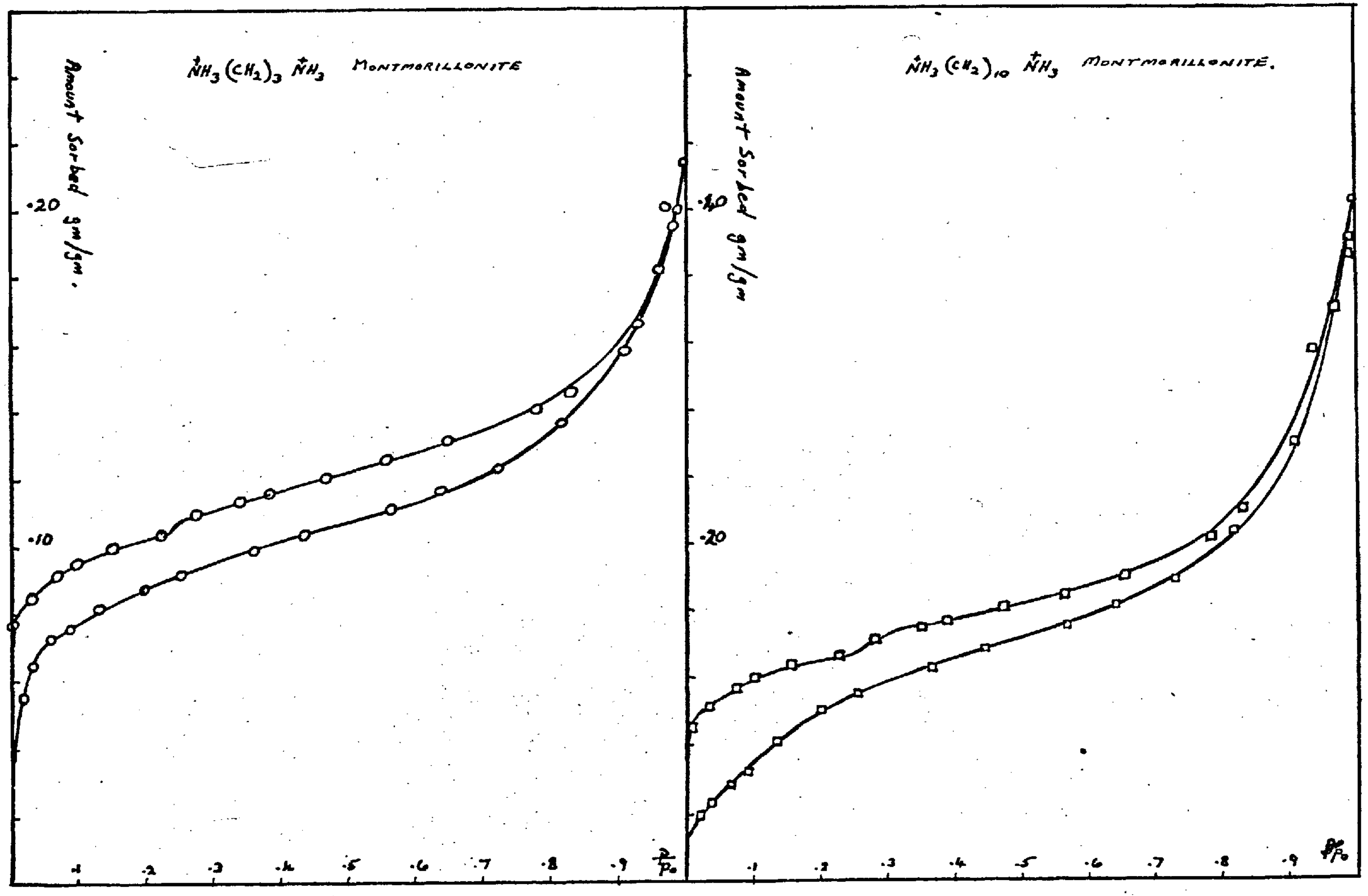


FIG. 3.21.

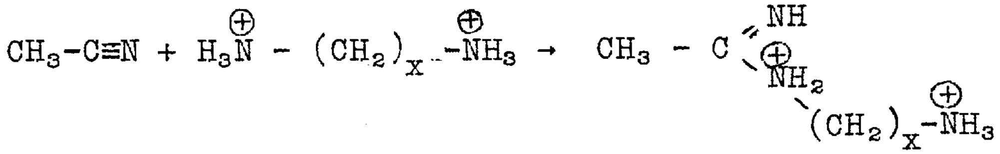
It is seen that at low relative pressures benzene is sorbed to a greater extent than the other three sorbates, which might be expected since the clay was shown by X-ray measurements to have swollen to 15.0Å when equilibrated with benzene at a relative pressure of 0.1, whilst no swelling was recorded when the relative pressure of acetonitrile was below 0.5. The 1:3 diamino propane isotherms are exceptional in that though they commence in the order expected, they rapidly change over so that the longer chain derivatives are sorbing more than the shorter chain ones, even at a relative pressure of 0.2. Since all the derivatives swell to 14.3Å when the 1:3 diamino propane is at its saturated vapour pressure, the above results indicate that in this case the ease with which swelling takes place increases with increasing length of the alkyl chain of the interlamellar ion.

X-ray measurements showed that the clays were fully swollen when the relative vapour pressure of acetonitrile reached 0.85, and again crossing of the sorption isotherms in this region reflects the ease and extent of swelling of the clays with different alkyl chain lengths, though the pattern here is not so clear as with the 1:3 diamino propane isotherms. The effect is partially obscured by the onset of capillary condensation in this region.

Though all the sorbates gave a hysteresis loop persisting to almost zero pressure, the size and shape of the loops varied considerably, as will be seen from Figs. 3.16, 3.19 and 3.21. The desorption isotherms for heptane, benzene, and propane diamine show the characteristic shoulder (Barrer and McLeod 1955, Barrer and Reay

1956) at approximately 0.3 p/p_0, which probably corresponds to the final evaporation of capillary condensate. Acetonitrile gives a much broader loop with no apparent shoulder, and it appears therefore that the desorption is a much more gradual process than with the other sorbates. A number of scanning curves were determined for this system, but these and the phenomenon of hysteresis will be discussed in a later section.

It was not possible to outgas the organo-clay derivatives to their original weight after sorption of acetonitrile or 1:3 diaminopropane, though benzene and heptane were removed quite easily, and gave reproducible isotherms on readsorption. After completion of the acetonitrile isotherm one of the samples was removed from the apparatus, and its surface area determined by nitrogen sorption after outgassing at steadily increasing temperatures. The results are shown in Fig. 3.22. A temperature in excess of 150°C was not used since there is a danger that the organic ion will decompose above this temperature (Reay 1956). The surface area is only slightly greater than that of the sodium clay. It seems that the acetonitrile and 1:3 diamino propane are chemisorbed. Acetonitrile may undergo the following reaction



The nitrogen analysis before and after sorption, the results of which are given below, indicated that between 30 and 60 per cent of the $-\overset{\oplus}{N}H_3$ groups might have reacted in this manner.

NITROGEN ON $\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$ MONTMORILLONITE AFTER CH_3CN SORPTION.

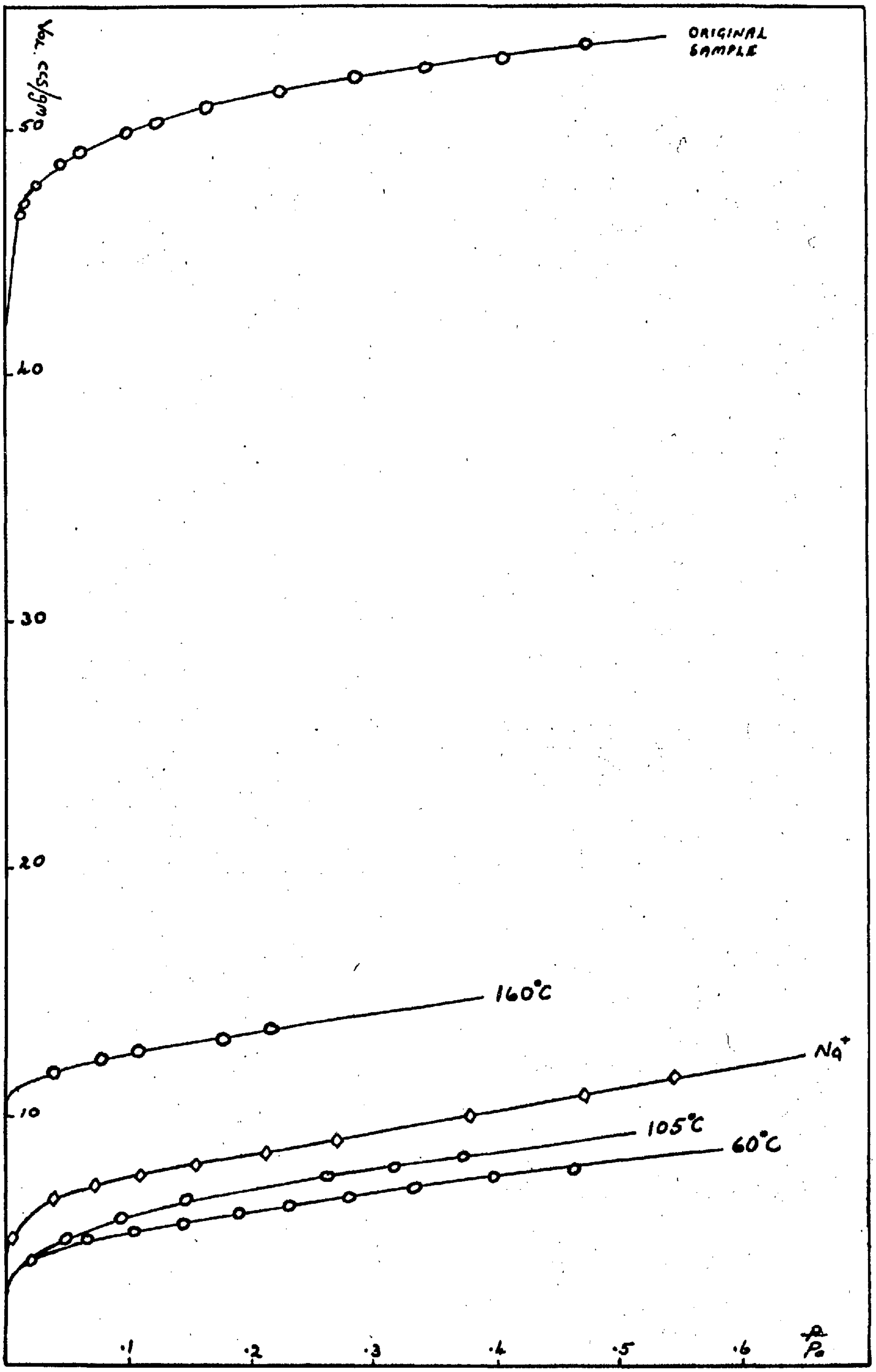


FIG. 3.22

Derivative	N % before CH_3CN sorption	N % after CH_3CN sorption
$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$ hectorite	1.25	1.98
$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$ hectorite	1.28	1.67
$\overset{+}{N}H_3(CH_2)_9\overset{+}{N}H_3$ hectorite	1.22	1.61
$\overset{+}{N}H_3(CH_2)_{12}\overset{+}{N}H_3$ hectorite	1.26	1.74

1:3 diamino propane probably undergoes the following reaction, as proposed by Fripiat et al (1962).

$$\overset{\oplus}{N}H_3-(CH_2)_x-\overset{+}{N}H_3 + NH_2(CH_2)_3NH_2 \rightarrow \overset{+}{N}H_3(CH_2)_xNH_2 + \overset{+}{N}H_3(CH_2)_3NH_2$$

The monolayer coverages were again calculated from B.E.T. plots, and the values are given in Table 3.III. Most of the plots resembled those for the permanent gases, being straight from very low pressures to about .25 p/p_0. The lines passed through or very close to the origin in nearly all cases. Several values were estimated from Huttig plots, but since these isotherms were not linear over a larger pressure range than the B.E.T. ones and gave values differing by not more than three per cent, only a few were calculated.

The sorption of heptane at 30, 40, 50 and 60°C, and benzene at two different temperatures was studied to obtain thermodynamic data for the sorption of these compounds. Such data were not obtained for acetonitrile and 1:3 diamino propane since the hysteresis loops were large and because of the attendant chemisorption.

THEORETICAL AND MEASURED SORBENT AREAS

In order to make a valid comparison of the sorbing capacities of the various organo-clay derivatives, all the results given in the previous section were based on the amount sorbed for a number of unit cells equal to the number contained in 1 gram of original but outgassed sodium clay. These values are easily calculated from the gram unit cell weights of the clays, i.e. the weight of an Avagadro number of unit cells, which are listed in Table 3.V1. The Ross-Hendricks (1945) formula

$$[Si_8Al_{3.33}Mg_{0.67}O_{20}(OH)_4]Na_{0.67}$$

for the composition of the unit cell of Wyoming bentonite has been used in these calculations. Though this is a general formula for montmorillonites, its use was thought to be justified, since the exchange capacity of the bentonite was 88 meq/100 grams of clay compared to the Ross-Hendricks requirement of 90 meq/100 grams.

An approximate unit cell formula for the hectorite, Ben-U-Gel, has been calculated from a knowledge of its composition and exchange capacity of 90 meq/100 grams, as

$$[Si_{7.76}Mg_{5.30}Al_{.03}K_{.02}Na_{0.78}Li_{0.61}Ca_{0.41}O_{20}(OH)_4]$$

The total surface area of a gram unit cell of either clay may then be calculated from the a and b dimensions of the unit cell. Wyoming bentonite, having a = 5.18Å and b=8.94Å (Deer, Howie and Zussman 1962) will have an area of 56×10^4 square metres per gram unit cell, and the hectorite, with a=9.16 and b=5.2, an area of 57.3×10^4 m^2 per g.u.c., assuming the clay to exist as single sheets.

In practice, however, the crystals are an aggregate of particles several sheets in thickness, and the total surface area may then be divided into external and interlamellar areas. Table 3.IV gives the relationship between the mean number of sheets per particle and the ratio of external to interlamellar area.

TABLE 3.IV

No. of sheets per particle	External area m^2/g.u.c.x10^3	Internal area m^2/g.u.c.x10^3
1	560	0
2	280	140
3	187	187
4	140	210
6	93	234
10	56	252
20	28	266
26	21.6	269
32	17.5	272
∞	0	280

The area available to the sorbate molecules will be equal to the total area minus the area occupied by the organic ions. The latter cannot, however, be calculated with any certainty. Numerous methods have been proposed for estimating molecular sizes, but the results from different approaches are not usually consistent. The areas of small, approximately spherical molecules have been estimated from their liquid or solid densities, but this implies a similar packing in the monolayer as in the liquid or solid state, which is not necessarily true. Estimates from molecular models are subject to the uncertainty in the values taken for the van der Waals radii of the atoms. A third method which has been widely employed, is to compare the v_m value for the sorbate under consideration to that of nitrogen on the same sorbent, and then assuming that the nitrogen molecule has an area of 16.2Å at 78°K, the area of the sorbate molecule may be calculated. This procedure generally yields values somewhat greater than the methods outlined above, but it has two chief drawbacks. Firstly, it is necessary to assign an area to the nitrogen molecule which is not unequivocal (Livingston 1944), and secondly, in any further calculations it must be assumed that the molecule has the same orientation on the surface.

Since the intercalation of a number of long chain aliphatic ions has been studied, the procedure adopted in calculating their areas was to take the product of length and thickness of the molecules, neglecting any possible penetration of one alkyl chain into another. Using bond lengths and van der Waals radii given by Pauling (1960) and Bondi (1964), the lengths of the diammonium ions are calculated from the equation

$$1.26(n-1) + 2\times1.2 + 3.8$$

where n is the number of carbon atoms in the chain. Similarly, an equation for monoammonium ions is

$$1.26(n-1) + 1.2 + 3.9$$

These equations are in accord with the value of just less than 13Å recorded by Steinfink et al (1963) by X-ray analysis for the hexamethylene diammonium ion.

The thickness of the alkyl chain is rather more difficult to assess. Catalin models give values of 3.8 or 4.2Å depending on whether the zigzag of the carbon chain is perpendicular or parallel to the surface, whilst calculations from bond lengths and van der Waals radii give values of 3.9 and 4.7Å respectively. The cross-sectional area of an alkyl chain has been estimated at about 20Å^2, which corresponds to a thickness of 4.46Å for square packing and 4.16Å for hexagonal packing. From X-ray diffraction measurements Steinfink estimated the area of the hexamethylene diammonium ion in vermiculite to be 58Å, which corresponds to a thickness of about 4.6Å. This value is in accordance with that used by Smith, Pierce and Cordes (1950), who found that the areas of certain molecules calculated on this basis agreed with those determined by comparison with the nitrogen surface area. Finally, Müller (1933) determined that the nearest distance of approach of two hydrocarbon chains was 4.7Å.

In view of these results the width of the hydrocarbon chain is here taken to be 4.6Å. The area of the methylammonium ion was estimated by Reay (1956) to be 21Å^2 when lying parallel to the sheet, and 14Å when perpendicular to the surface. Columns three and four of Table 3.V give the lengths and areas of the various ions used, and columns five and six show respectively the total area covered by the ions and the free interlamellar area per gram unit cell. In calculation of the latter values it has been assumed that the number of ions on the external surface is related to the ratio of external surface, as estimated by nitrogen sorption of the sodium clay, to the total theoretical surface available. This is only 4 per cent in the case of Wyoming bentonite, but amounts to 12 per cent for the hectorite. It is implicit in this assumption that the external area of the organo-clay derivatives is similar to that of the sodium clay, but other work (Reay 1956, White and Street 1964) has shown that the area may change appreciably when another small inorganic ion is substituted for the sodium ions. Greene-Kelly (1964) suggested that intercrystalline areas may be inaccessible to nitrogen molecules in sorption on montmorillonite aggregates. Figures 3.5 to 3.7 on the other hand show that nitrogen sorption on the derivatives with large alkylammonium and alkyldiammonium ions is similar or slightly less than on the sodium clay. Dicks (1965) obtained similar results with tetrabutylammonium clays. It is thought therefore that this approximation is justified. Reay (1956) and Kelsey (1959) attempted to measure the external area of the organo-clay derivatives by first destroying the organic molecule at 400°C, and values obtained were much higher than for sodium clay It is possible, however, that heating to 400°C would rupture the clay particles, and also that any carbon granules formed from decomposition of the organic ions would sorb a certain amount of nitrogen, both of which would contribute to these high values.

Taking the generally accepted values of 16.2Å^2 for nitrogen and 13.8Å^2 for oxygen molecules at 78°K, the monolayer areas may be calculated from the v_m values given previously. The area of the argon molecule is usually taken as 13.8Å^2, this value being derived from liquid density measurements, but higher values have been used (14.6Å^2 Hsieh 1964), since use of the lower area often leads to surface area measurements inferior to those determined by nitrogen sorption (Rouquerol et al 1964). Estimations of the area of a heptane molecule vary from 43 to 64Å^2, whilst benzene has an area of 25Å^2 when perpendicular and 41Å^{2}when lying flat. Calculations

TABLE 3.V

No. of C atoms in alkyl chain	Gram unit cell weight	Length of ion (Å)	Area of ion (Å^2)	Area of ions per g.u.c. $m^2 x10^{-3}$	Free area per g.u.c. $m^2 x10^{-3}$
Na^+	735				
(i) Alkyl diammonium montmorillonites					
2	746	7.6	34.8	68	204
3	750	8.8	40.6	79	193
4	755	10.1	46.4	91	182
5	759	11.3	52.2	102	171
6	764	12.6	58.0	113	161
7	769	13.9	63.7	124	150
8	773	15.1	69.5	135	139
9	778	16.4	75.3	147	128
10	783	17.6	81.2	158	117
12	792	20.2	92.5	181	86
(ii) Alkylammonium montmorillonites					
1	746	4.7	21.6	84	188
2	755	6.5	29.8	116	157
3	765	7.7	35.6	139	126
4	774	9.0	41.4	162	114
5	783	10.2	47.1	184	92
6	792	11.5	52.9	206	71
12	848	19.1	87.6	352	0
(iii) Alkyl diammonium hectorites					
Na^+	770				
2	777	7.6	34.8	72	189
3	781	8.8	40.6	84	179
4	786	11.3	46.4	96	168
5	791	12.6	52.2	108	157
9	811	16.4	75.3	156	114
12	825	20.2	92.5	192	83

TABLE 3.VI

Surface area from sorption isotherms (areas in $m^2 x 10^{-3}$ per gram unit cell)

No. of C atoms	N_2	A	O_2	C_6H_6	C_7H_{16}	CH_3CN	$NH_2(CH_2)_3NH_2$ $\perp$ orient	$\parallel$ orient
(i) Alkyl diammonium montmorillonites								
Na^+	21.8							
2	138			149		145		
3	143	119		148	141	132	88.0	179
4	141			155		136		
5	138	124		127		122		
6	135	122	137	126	141	122	85.0	174
7	130							
8	105		108	103	113	83.5	88.2	176
9	64					87.5		
10	15.8	18.7		60.5	76.5		83.5	170
12	21.8			12.3		64.5		
(ii) Alkylammonium montmorillonites								
1	133							
2	115			116				
3	97.4			118				
5	52.5							
6	29.2			54.5				
12	10.4			10.0				
(iii) Alkyl diammonium hectorites								
Na^+	63.0	77.0						
2	206							
3	193	177		185		222		
4	210							
5	195	176		171		197		
9	174	162				184		
12	56.4			55.9		95.5		

from density measurements yield an area of 22Å^2 for the acetonitrile molecule, which is in reasonable agreement with the value of 24Å^2 derived from a scale model. The sorbent areas obtained for monolayer coverages determined by the B.E.T. method are compared in Table 3.VI.

It is seen that the areas of the clay derivatives derived from the various sorbates, with the exception of 1:3 diamino propane, are consistent, when one considers the approximations involved. As stated previously, the B.E.T. plots for the sorption of 1:3 diamino propane were poor, and the surface areas derived from them show correspondingly poor agreement with areas from other sorbates. One possible explanation is that the molecules change their orientation at a relatively low pressure. The first molecules imbibed probably have the axis of the carbon chain parallel to the lamellae, whilst as more is sorbed the chain becomes perpendicular, this change occurring more readily the longer the chain of the interlamellar diammonium ion, as suggested in a previous section. The observed monolayer areas may then be explained by assuming that in the case of the decyldiammonium montmorillonite the sorbed amine is orientated with its carbon chain perpendicular to the layers at very low pressures, while the angle of orientation is lower for the clays containing shorter alkyl diammonium ions.

The interlamellar area covered by the sorbate in the various derivatives may be obtained approximately by subtracting the area of the appropriate sodium clay from the total monolayer areas. In the case of benzene a smaller area, $13.3 \times 10^{+3}$ m^2 per g.u.c., is deducted since the benzene molecule probably lies flat on the external surface, whereas the above calculations were based on a perpendicular orientation of the benzene molecule. Similar considerations apply for the perpendicular orientation of the 1:3 diamino propane molecules, 9×10^3 m^2 per g.u.c. being subtracted from the total area.

Comparison of theoretical and observed interlamellar areas show large discrepancies. The permanent gases cover only 60 to 70% of the theoretically available area in the alkyldiammonium montmorillonites, and the agreement is worse for chains exceeding eight carbon atoms in length. The organic sorbates show a similar coverage of 60 to 70% of the available interlamellar surface, and this extends to the longer alkyl chain derivatives also. Better agreement is obtained with alkyl diammonium hectorites, up to 85% of the theoretical areas being attained, but again correspondence is worse for the longer alkyl diammonium ion derivatives. It is thought that the results for the nonyldiammonium hectorite may be anomalous, since some difficulty was experienced in its preparation. In two attempts at the preparation, an amorphous powder was obtained, and the sample finally used appeared to be a much finer aggregate than the other derivatives, which probably accounts for the high surface areas obtained with this complex.

The alkylammonium montmorillonites exhibit similar characteristics, though agreement between theoretical and observed values becomes progressively worse as the number of carbon atoms in the alkyl chain increases beyond three.

Because of this poor agreement between theoretical and observed values, a second approach to the calculation of observed areas was tried. If the isotherm for a sorbate on sodium clay is subtracted from the isotherm for that sorbate on the organo-clay derivative, the resulting isotherm should be of Type I (Brunauer classification), corresponding only to the interlamellar sorption. Unfortunately isotherms of only nitrogen and argon on the sodium clays were determined in this investigation. The results of Brummer (1962) for the adsorption of heptane on a similar sample of sodium montmorillonite have been used in the calculation of the interlamellar sorption of that sorbate. Figures 3.23 and 3.24 illustrate the type of isotherms obtained. It appears that the interlamellar monolayer is not complete below a relative pressure of 0.25, and the monolayer area values derived from B.E.T. plots are probably too low. The interlamellar area obtained in the two approaches together with the theoretical area, are compared in Table 3.VII.

Though the agreement is improved the calculated values are still considerably below the theoretical values. Several factors probably contribute to this discrepancy. The Ross-Hendricks formula has been assumed for the unit cell structure, but it does not represent the true composition of the unit cell. It is unlikely, however, that the error attributable to this source is greater than 5%. The greatest uncertainty is in the area attributed to the ions and sorbed molecules, which may be as great as 25%. Thirdly, all the available area is not necessarily accessible to the sorbate molecules, and the rapid decrease in nitrogen sorption when the carbon chain length of the interlamellar diammonium ions exceeds seven, (Fig. 3. 5), would support this view. It is unlikely that the

INTERLAMELLAR SORPTION OF NITROGEN ON MONTMORILLONITES.

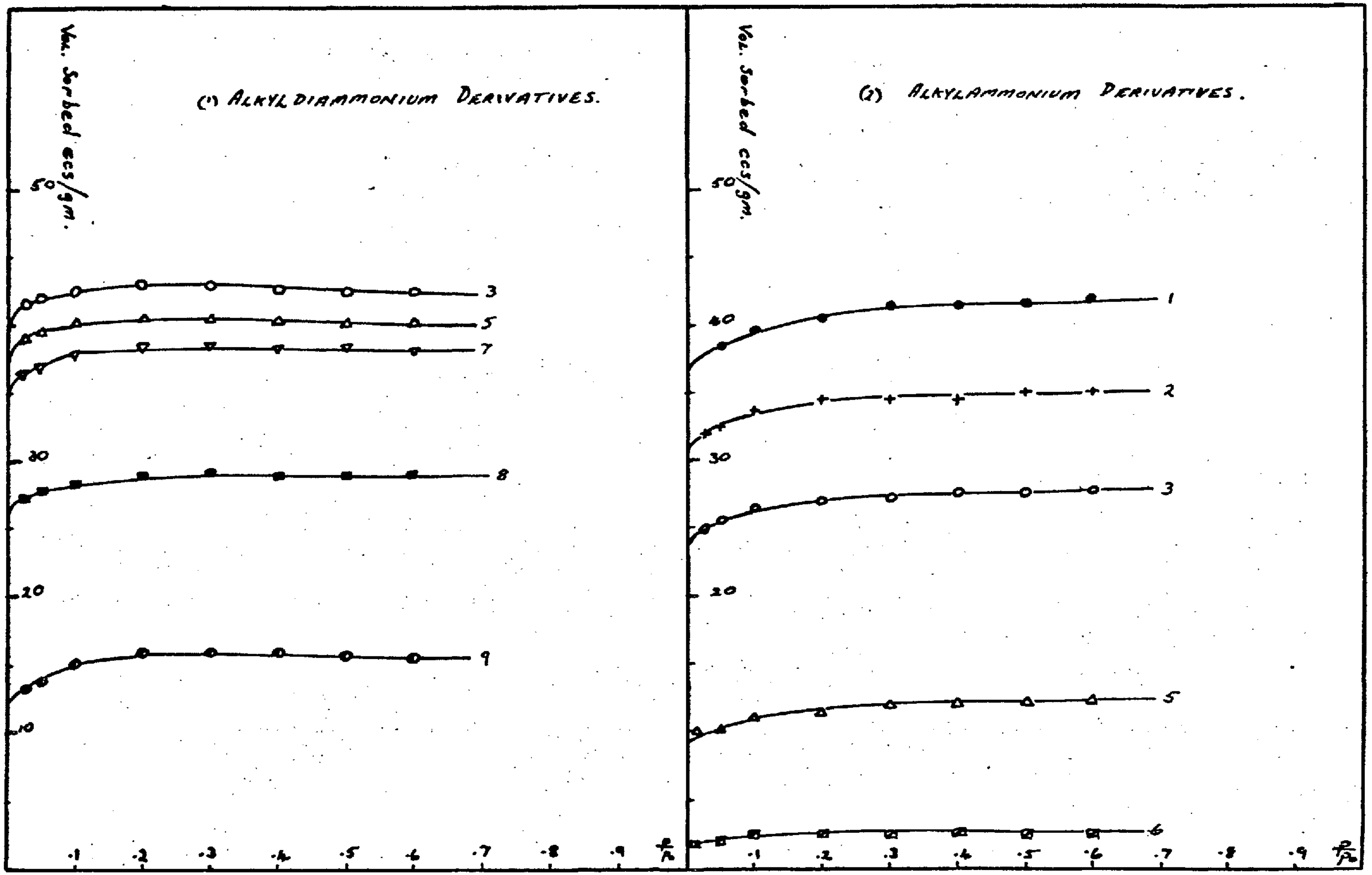


FIG. 3.23

INTERLAMELLAR SORPTION ON ALKYLDIAMMONIUM HECTORITES.

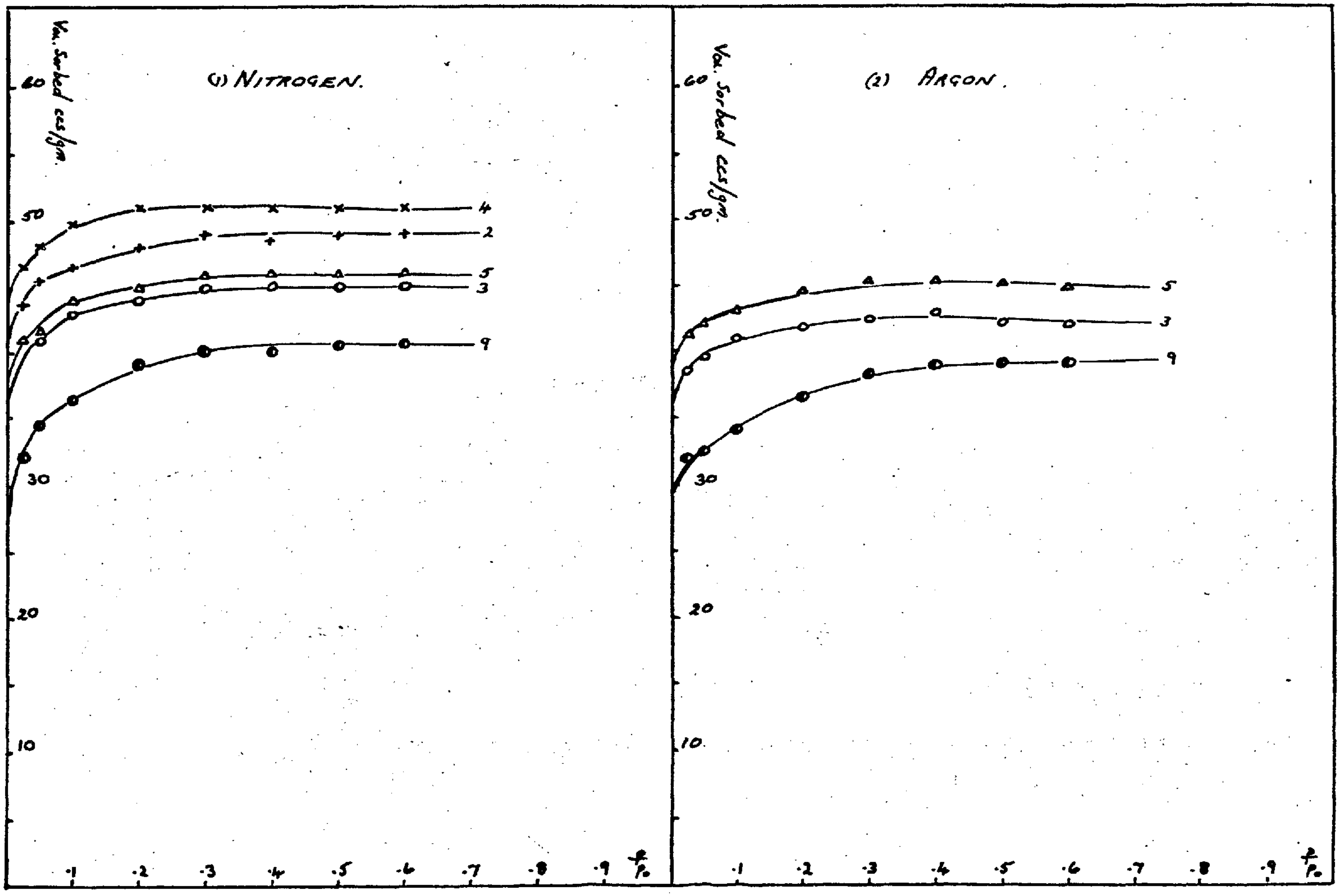


FIG. 3.24

TABLE 3.VII

Comparison of interlamellar areas

No. of C atoms	From N_2 sorption $m^2 x 10^{-3}$/g.u.c.		From heptane sorption $m^2 x 10^{-3}$/g.u.c.		Theoretical area $m^2 x 10^{-3}$/guc
	B.E.T.	Subtraction of isotherms	B.E.T.	Subtraction of isotherms	
(i) Alkyl diammonium montmorillonites					
2	116	130			204
3	121	136	119	138	193
4	119	136			182
5	116	129			171
6	113	128	119	139	161
7	108	123			150
8	83.2	92.6	91	109	139
9	42.0	50.8			128
10	0	0	55.0	70.5	117
12	0	0			86
(ii) Alkyl ammonium montmorillonites					
1	111	133			188
2	93.2	110			157
3	75.6	87.5			126
5	30.7	38.2			92
6	7.4	8.0			71
12	0	0			0

the interlamellar ions are mobile at liquid nitrogen temperature, and the channel separating two alkyl chains may be too narrow to admit a nitrogen molecule. The tendency to encompass a certain area of sorbate surface, and so make it inaccessible to nitrogen molecules, will increase with increasing length of the alkyl chain of the ion. In the case of the alkylammonium derivatives, where there is twice the number of interlamellar ions, the decrease in sorbing power is much more rapid, almost no interlamellar sorption of nitrogen taking place on hexylammonium montmorillonite.

At the higher temperatures at which the organic sorbates are imbibed the ions will have a degree of mobility, and may rearrange to admit appreciable quantities of sorbate, as in the case of benzene and heptane on decyldiammonium and hexylammonium montmorillonites. The ions will not be completely mobile, however, as the amine heads are electrostatically bound to the centres of negative charge in the silicate sheet. Thus, even at these higher temperatures, a certain area of the silicate sheet may be inaccessible to the sorbate molecules. Dodecylammonium montmorillonite, in which the ions completely fill the interlamellar space, does not imbibe benzene.

The apparent anomalies in the tables, such as propyl diammonium montmorillonite sorbing more nitrogen than the ethyl derivative, are attributable to slight differences in composition and particle size of the organo-clays. Though a standard method of preparation was adhered to as closely as possible certain differences may still arise. The ions themselves may influence the particle size, as was found to be the case for small inorganic ions. Dodecylammonium montmorillonite, for example, sorbs less than the sodium clay, which suggests that this large ion gives rise to larger particles. However, since the interlamellar area varies little with particles comprising more than 15 sheets, the differences are not very significant. The uptake of nitrogen on sodium montmorillonite indicates a mean particle thickness of 26 sheets, whilst sodium hectorite has a mean thickness of only 9 sheets.

INTERLAMELLAR SORPTION BEYOND A MONOLAYER

X-ray measurements indicated that only the acetonitrile was imbibed to form more than a monolayer in the interlamellar space, and it was thought it might be of interest to compare the observed and theoretical amounts of interlamellar sorption at high pressures. This might indicate at which pressures the second and possibly third layers are completed, since the isotherm does not show distinct steps as found with the isotherm for the sorption of water on sodium montmorillonite. The free interlamellar volumes corresponding to various d001 spacings were calculated, and are given in Table 3.VIII. Column VII of this table gives the volume which would be available if the carbon chain of the interlamellar ion were standing perpendicularly to the silicate layer, and the final column the volume available when the ions of even numbered carbon chains are at 56° to the layer as suggested by Weiss (1963). Table 3.IX shows the maximum possible uptake of the sorbate into the interlamellar region corresponding to the measured spacing, and these values may then be compared with the observed uptake, Figs. 3.12 to 3.20.

Some allowance must be made for external sorption, but only the sorption of heptane on sodium montmorillonite has been determined. Very approximate values, though sufficiently accurate for this discussion, may be calculated for other sorbates from a comparison of their molecular areas.

In the case of benzene and heptane sorption it is seen that, after allowing for external sorption, the amount sorbed does not exceed the theoretical maximum below saturated vapour pressure, and indeed is often much lower, especially for the longer chain derivatives of the clay. This was also found to be the case when comparing theoretical and observed areas in the previous section. These data thus support the contention that only a monolayer of heptane and benzene is sorbed into the interlamellar region. The position of the interlamellar ion is discussed later.

Acetonitrile sorption is a little more complex since two sets of spacings were obtained from X-ray data, one set at ~16.3Å corresponding to a two-layer complex and the other, ~19.7Å, to a three-layer complex. In no case does the sorption reach the possible maximum for a three-layer complex, and in most cases the volume required to complete two molecular layers of acetonitrile is only attained very near saturated vapour pressure. While it is not expected that the acetonitrile molecules will pack as efficiently as in the bulk liquid, this sorbate is a comparatively small molecule and steric considerations should not greatly reduce the volume sorbed below the theoretical amount. Since X-ray measurements showed that a swelling to ~19.7Å had occurred at a relative pressure of 0.85, it appears that a third layer may develop before the second is complete. This is probably true of the first and second layers too, and explains why no steps are observed in the sorption isotherm.

Similar calculations for the sorption of 1:3 diamino propane yield rather unexpected results. X-ray data indicated that the organo-clays swelled to only 14.3Å in this sorbate, but the theoretical uptakes corresponding to this spacing are very much less than the observed quantities, the ratios ranging from about 0.5 in the case of propyldiammonium montmorillonite to 0.2 for decyldiammonium montmorillonite of the observed values (Fig. 3.20). These discrepancies are far too large to be accounted for by surface sorption, and the very slow uptake at higher pressures, which was also observed for acetonitrile, suggested sorption beyond a monolayer. The amounts sorbed at relative pressures of 0.75, 0.85 and 0.95 are given in the table below, together with the necessary interlamellar spacing, allowance being made for external sorption.

No. of C atoms per ion	Relative pressure = 0.75		p/p_o = 0.85		p/p_o = 0.95	
	Amount sorbed gm/gm	Spacing Å	Amount sorbed gm/gm	Spacing Å	Amount sorbed gm/gm	Spacing Å
3	.1100	4.4	.1230	4.8	.1420	5.4
6	.1100	5.0	.1260	5.5	.1500	6.2
8	.1400	6.3	.1740	7.4	.2360	9.3
10	.1680	7.6	.2040	8.7	.2860	11.3

These spacings are the minimum requirement, and will probably be greater to allow for steric restrictions on the sorption of the molecules.

TABLE 3.VIII
Free interlamellar volumes

No. of C atoms /ion	Ion Vol. per guc $Å^3 x 10^{-23}$	Free vol. per g.u.c. $Å^3 x 10^{-23}$					
		14.3Å	15.0Å	16.3Å	19.7Å	Fully extended chain	Chain at 56°
(i) Alkyl diammonium montmorillonites							
0	132	1188	1377	1671*	2718*		
2	208	1112	1301	1672*	2532*	1272	612
3	262	1058	1247	1488*	2508*	1568	
4	314	1006	1195	1546*	2458	1856	1066
5	366	954	1143	1494*	2406	2144	
6	419	901	1090	1571*	2353	2431	1521
7	473	847	1036	1384	2327*	2717	
8	525	795	984	1332	2245*	3005	1975
9	578	742	931	1279	2222*	3292	
10	632	688	877	1225	2218*	3578	2438
12	736	584	773	1121	2224*	4154	2894
(ii) Alkylammonium montmorillonites							
2	411		1098			789	
3	516		993			1024	
6	815		694			1745	
12	1440					3140	
(iii) Alkyldiammonium hectorites							
2	198		1220	1550	2402*	1207	568
3	250		1168	1498	2280*	1474	
5	350		1068	1395*	2255	2010	
9	552		866	1196	2008*	3078	
12	705		713	1043	1975*	3885	2705

* These values are calculated from observed d001 spacings.

TABLE 3.IX

Theoretical interlamellar sorption

No. of C atom/ion	Amount sorbed gm/gm				
	Aceto-nitrile ~19.7Å	Aceto-nitrile ~16.3Å	1:3 Diamino propane	Benzene	Heptane
(i) Alkyldiammonium montmorillonites					
2	.2625	.1735	.1331	.1523	.0830
3	.2600	.1543	.1265	.1460	.0790
4	.2544	.1602	.1203	.1400	.0733
5	.2495	.1550	.1141	.1340	.0684
6	.2440	.1630	.1080	.1277	.0635
7	.2415	.1437	.1012	.1212	.0585
8	.2330	.1381	.0950	.1150	.0536
9	.2305	.1325	.0888	.1090	.0486
10	.2300	.1270	.0823	.1028	.0436
12	.2310	.1162	.0699	.0950	.0340
(ii) Alkylammonium montmorillonites					
2				.1285	
3				.1160	
6				.0812	
12					
(iii) Alkyldiammonium hectorites					
2	.2380	.1535		.1362	
3	.2260	.1483		.1305	
5	.2230	.1382		.1193	
9	.1990	.1185		.0968	
12	.1960	.1033		.0796	

No explanation for this disparity between X-ray and isotherm results is apparent. The isotherms were quite reproducible, and several samples swollen in the sorbate were X-rayed, the d001 spacing being 14.3Å in each case. Though the X-ray photographs were taken at 25°C and the isotherms measured at 40°C, it is not thought that this would account for the difference, especially as the organo-clay was equilibrated with the sorbate in certain cases at 80°C previous to X-ray exposure. The sorbate used in the X-ray measurements was not rigorously dried, as was that used for the sorption, and this may have some effect.

As the length of the 1:3 diamino propane molecule is about 8.3Å and its width 4 to 5Å depending upon orientation, several orientations of the interlamellar molecules are possible. For the propyl and hexyl diammonium clays a monolayer of 1:3 diamino propane with its chain perpendicular to the silicate sheet or two layers lying parallel to the sheet would suffice to account for the calculated spacings at $p/p_o = 0.95$). However, the montmorillonites containing larger ions require at least two molecules of 1:3 diamino propane standing at an angle, but not necessarily perpendicular, to the clay surface, or at least three layers lying parallel. There is no evidence as to which of these orientations is correct, but the possibility of a greater degree of hydrogen bonding of the $-NH_2$ or $-\overset{+}{N}H_3$ group to the oxygen atoms of the silicate sheet would favour inclination of the ions.

The position of the organic ion in these swollen complexes is of interest, since the original intention was to provide a series of sorbents whose swelling would be limited by the size of the ion. This is clearly not the case since the hydrazinium, ethylene diammonium, and propyl diammonium clays all swell to about 19.8Å in acetonitrile, whereas their lengths would allow swelling to only 11.3, 14.2 and 15.4Å respectively if they exhibited a "tie" effect. The other ions would allow swelling to the observed maximum. As the average distance between negative charges in one layer is about 10Å, these small ions are unable to satisfy two charges simultaneously. It is, however, possible that the sheets are very heterogeneous, the centres of negative charge occurring in patches, which may bring the charges sufficiently close for the two ends of the organic ions to be accounted for. A second possibility is that the ions are completely divorced from the silicate sheet, forming a central layer between two layers of acetonitrile molecules, as happens with small inorganic ions (McEwan 1948). There is some evidence for this occurring for alkylammonium ions in vermiculite on the sorption of water (Garrett and Walker 1962). This separation of electrostatic charges would require considerable energy, but the acetonitrile molecules, being highly polar, would gain energy from interaction with the area of silicate sheets thus exposed, and the energy of solvation of the cation would be higher than if it remained in contact with the sheet. An alternative arrangement would have one amine head in contact with the layer as close as possible to a centre of negative charge, and the other either lying on the silicate surface or free in the interlamellar space. A fourth possibility is that the ion lies flat on the surface with its two positive ends equidistant from centres of charge. The fact that the clays containing ions with four, five or six carbon atoms would swell only to about 16.4Å, indicating a two-layer complex, is interesting. It is possible that these ions are of approximately the correct length to bring the $-\overset{+}{N}H_3$ groups into close contact with two centres of negative charge in the same layer, and thus in order to form a three-layer complex, in which the ion forms a central layer, requires breaking two strong electrostatic bonds instead of one as in the case of the smaller ions. This would be sufficient to prevent formation of a three-layer complex. These ions are also of the correct length to allow formation of a two-layer complex but not a three-layer one if they exhibit a tie effect, but it is difficult to see why these ions should do so and not the smaller ones.

The longer ions with seven or more carbon atoms may lie flat on the silicate surface with each $-\overset{+}{N}H_3$ group near a negative centre, though in view of the above evidence this is unlikely. Alternatively, they could be inclined to the layer, the heads satisfying charges in adjacent layers, or exist as a central layer. The former is probably the more energetically feasible of these two suggestions.

In the sorption of 1:3 diamino propane it was postulated that there was an exchange of charges, the sorbed molecule and the interlamellar ion each attaining a single charge, thus obviating the necessity of satisfying two charges in one ion.

Since the ease of swelling should increase with decreasing layer charge, it was thought that derivatives of a clay with a lower base exchange capacity might swell in sorbates other than acetonitrile. It was not found possible to procure such a clay. The sample of Hector 34, which had a widely reported exchange capacity of 60 meq/100 gms, was found to contain approximately 40 per cent calcite, and on purification the base exchange capacity increased to 86 meq/100 gms.

HEATS AND ENTROPIES OF SORPTION

The differential heats of adsorption of heptane and benzene on four alkyl diammonium montmorillonites have been calculated using the Clapeyron-Clausius equation. In the case of heptane, where isotherms were measured at four different temperatures, the heats were estimated from plots of -log p/p_0 against $1/T$, whilst with benzene, when only two temperatures were used, the differential heats have been calculated from plots of -log p/p_0 against amount sorbed. The results are summarised in Figures 3.25 and 3.26, and the corresponding entropies of sorption are given in Figures 3.27 and 3.28.

Since the isotherms were not always perfectly reproducible, especially with the longer carbon chain derivatives, the quantitative values for heats of sorption and desorption must be regarded with some reservation. This is especially true where the amount sorbed is small as the highly rectangular nature of the isotherm makes it difficult to get accurate data at low pressures. Nevertheless the general trends exhibited are probably correct.

The sorption of heptane on the propyl diammonium montmorillonite, the smallest ion derivative investigated, is exothermic at all coverages, ranging from 9kcals per

HEATS OF ADSORPTION OF HEPTANE ON ALKYLDIAMMONIUM MONTMORILLONITES.

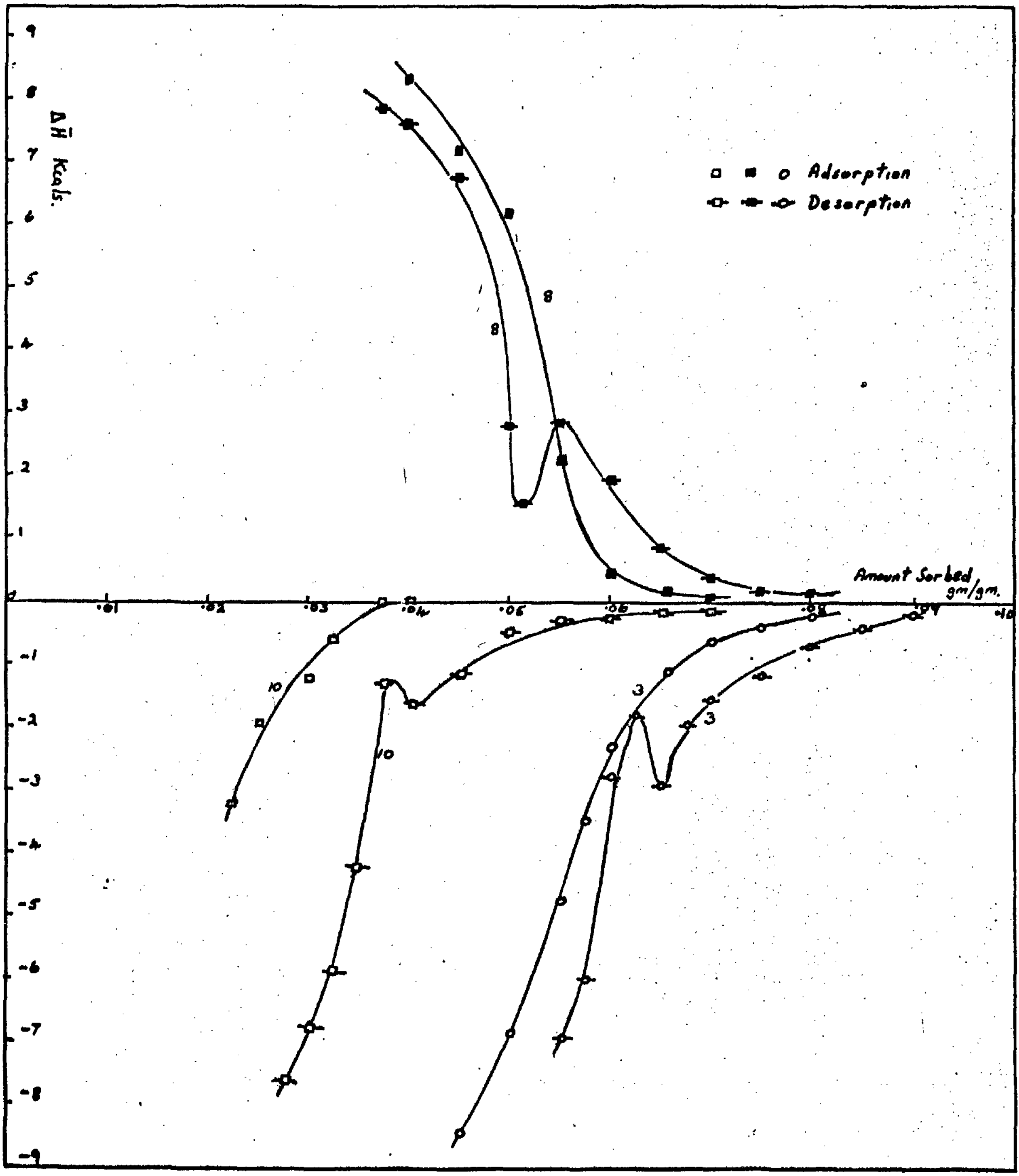


FIG. 3.25

HEATS OF ADSORPTION OF BENZENE ON ALKYLDIAMMONIUM MONTMORILLONITES.

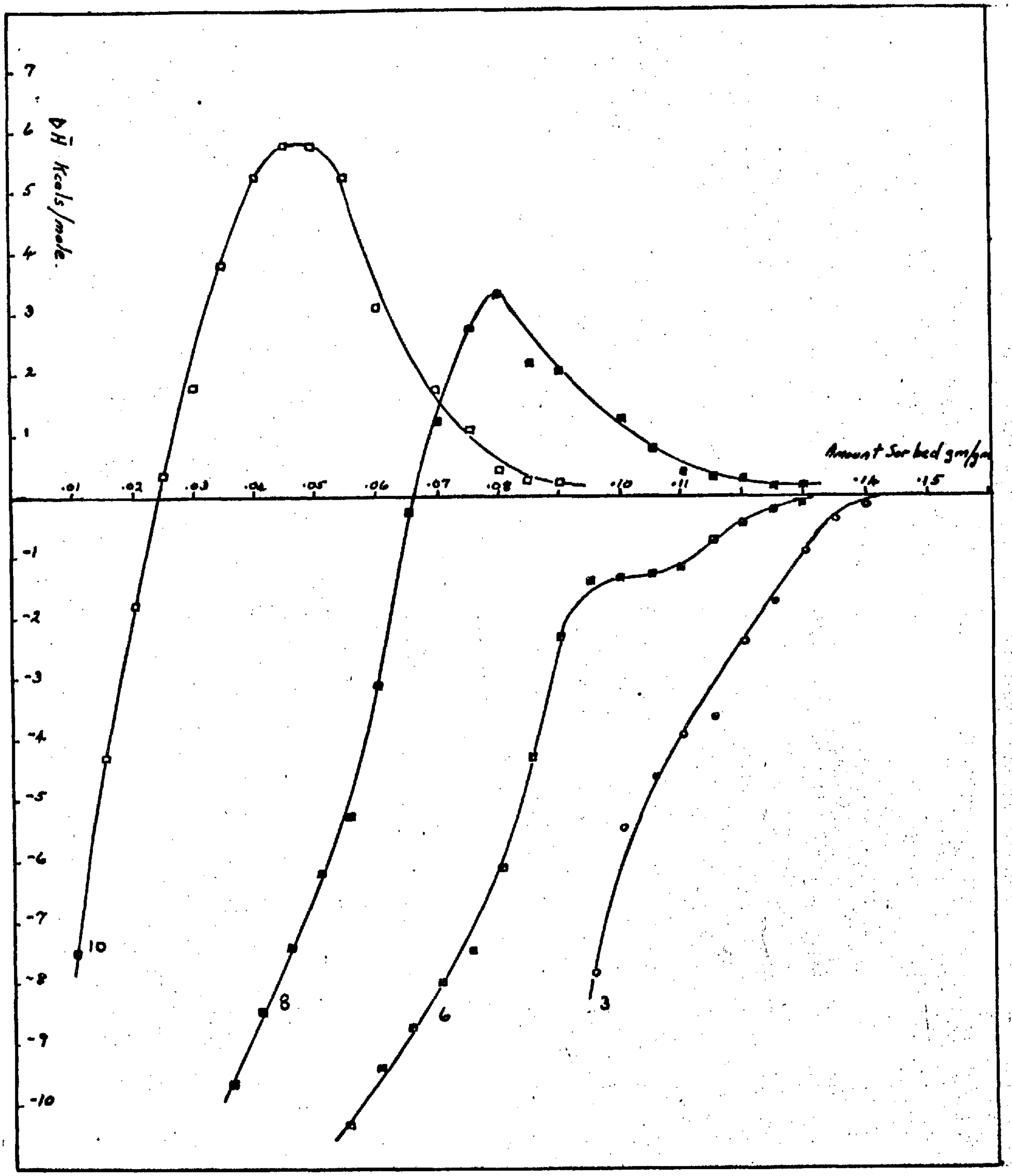


FIG. 3.26

ENTROPY OF SORPTION OF HEPTANE ON ALKYLDIAMMONIUM MONTMORILLONITES.

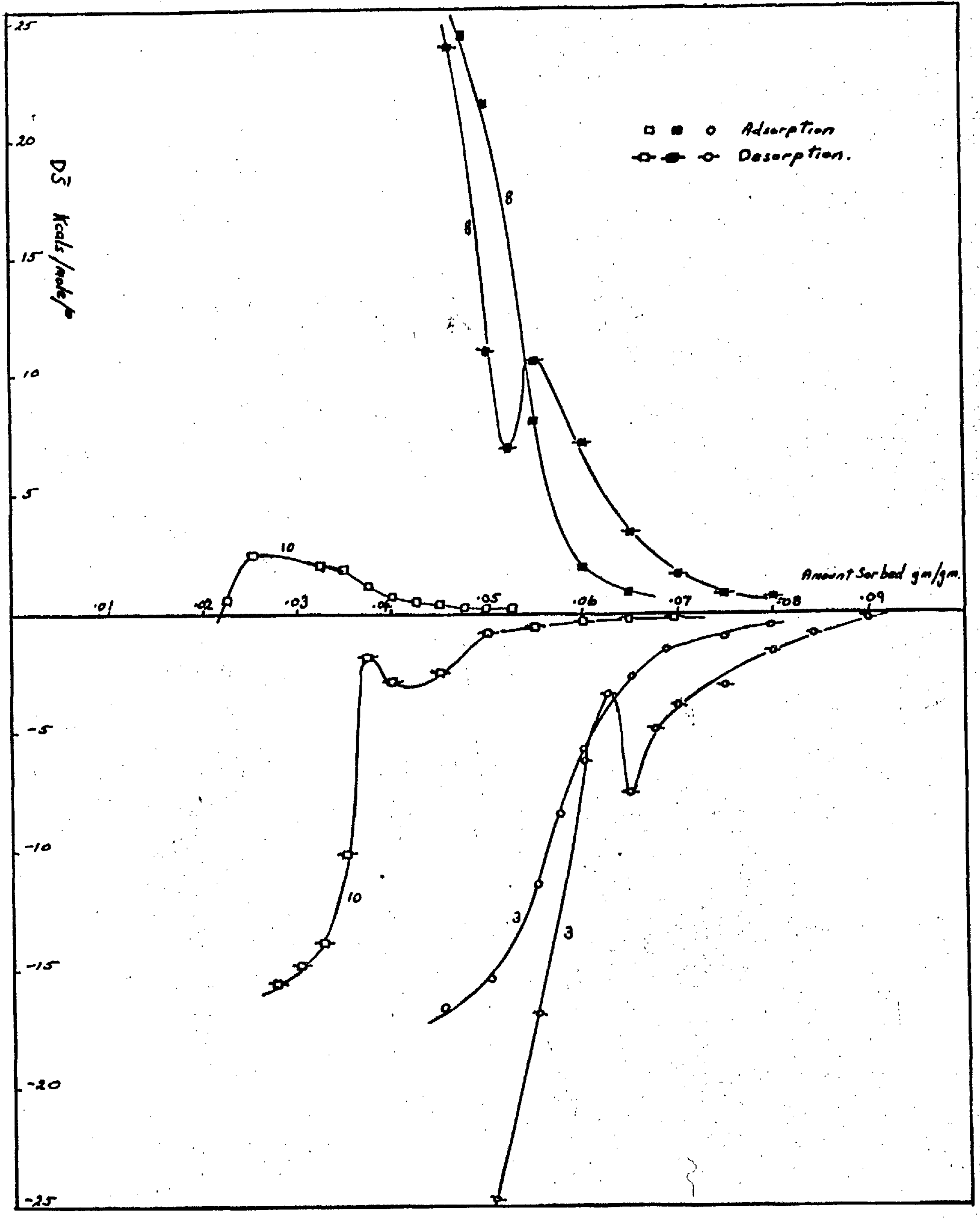


FIG. 3.27

ENTROPY OF SORPTION OF BENZENE ON ALKYLDIAMMONIUM MONTMORILLONITES.

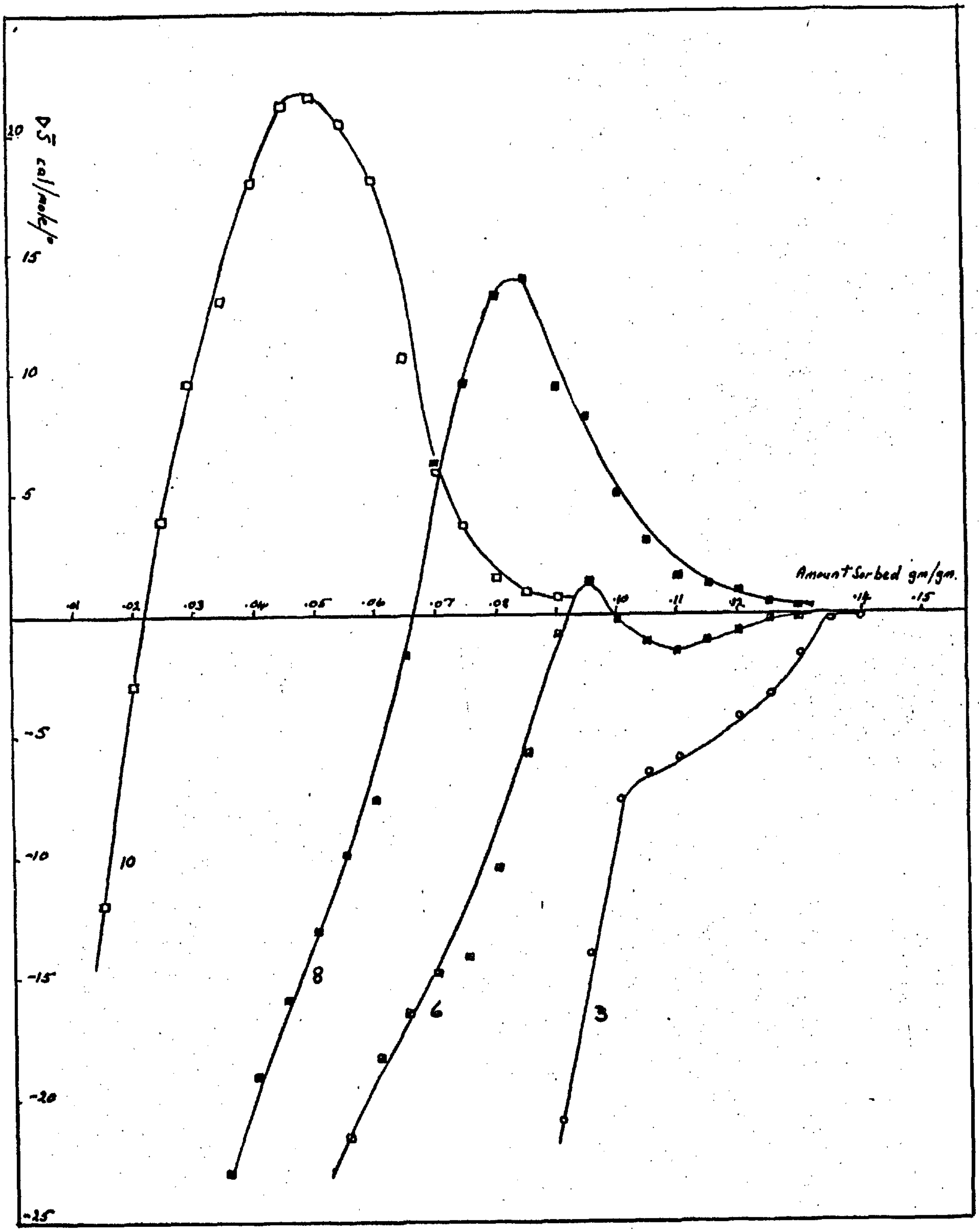


Fig. 3.28

mole at low coverage to a very low value where capillary condensation is occurring. This behaviour is closely analogous to the sorption of heptane on methyl and tetramethylammonium montmorillonites investigated by Brummer (1962) and Kelsey (1959). As the size of the interlamellar ion increases the heat of adsorption rapidly decreases, being zero throughout the range of coverage considered for the hexyldiammonium montmorillonite, and indeed positive for the octyldiammonium clay. The trend then appears to be reversed, however, sorption on decyldiammonium montmorillonite being slightly exothermic. The heats of desorption follow a somewhat similar pattern, though the heat is usually greater for a given coverage. This again is in general agreement with the findings of Brummer and Kelsey. A similar trend is noted in the heats of adsorption of benzene on the four clays, except that there is no apparent reversal for the decyldiammonium derivative, and all the differential heats at the lowest coverages observed are exothermic. It seems probable that had data been available for the sorption of heptane on octyldiammonium montmorillonite at very low pressures, this also would have shown a negative heat of sorption.

In the sorption of molecules into montmorillonite containing small organic ions most of the energy of sorption arises from interaction between the sorbate molecules and the silicate sheet. Though some energy is requiredto increase the interlamellar spacing to incorporate the sorbate molecules, probably little energy is required to rearrange the small organic ions to allow maximum sorption. On balance, therefore, the sorption is strongly exothermic. As the size of the organic ions increases they may have to undergo considerable rearrangement to allow penetration of the sorbate molecules, a process which will be endothermic. In addition there is less silicate surface available to the sorbate molecules, and they interact increasingly with the interlamellar organic ions, which would lead to a reduction in the adsorption energy. Thus the energy required for swelling and rearrangment of the cations may exceed the heat of sorption. There is in this case a large positive entropy of mixing of sorbate molecules and organic ions. For the small ion derivatives the entropy of sorption is negative, being as much as -25 cals/°/mole at low coverages for benzene and heptane. The sorbed molecules may lose one or two translational degrees of freedom and also rotational freedom.

The minima observed in the heats of desorption curves correspond to the shoulder in the desorption isotherm, which is considered to be the point at which most of the remaining capillary condensate evaporates. The sharp fall in the differential heat at this point is in accord with this view, since the heat should tend to the heat of vaporisation of the sorbate at that pressure.

The initial heats and entropies of sorption of benzene on all the derivatives are strongly negative. This is expected since the surface of the clay is heterogeneous and there will be certain sorption sites giving rise to highly exothermic sorption. When approximately .06 gm/gm of benzene has been adsorbed on to the octyldiammonium montmorillonite the sorption becomes endothermic and this change is presumably associated with lattice swelling. This amount of benzene is greater than the possible external sorption, and it appears therefore, that a considerable amount of benzene is sorbed into the interlamellar region at a very low pressure with the plane of the benzene ring lying parallel to the lamellae. Only at a higher pressure, though still below $p/p_0 = 0.1$ according to X-ray measurements (see Section on Swelling, p. 53), do the benzene molecules assume a perpendicular orientation.

Brummer (1962) attempted to calculate the heat of interlamellar sorption, assuming that the heat of external sorption on sodium montmorillonite was equal to that on the methylammonium clay. This may be justified for the small methylammonium ion, but will not be valid where larger organic ions are present on the external surface, and therefore no such calculation will be attempted here.

HYSTERESIS

Hysteresis was found to occur in all the isotherms determined in this work, but the loops were of three types. The permanent gases gave hysteresis loops which closed at some pressure greater than 0.25 p/p_0, whilst the loops for heptane, benzene and propane diamine, though of similar shape, remained open to zero pressure. The latter set of isotherms exhibited a shoulder on the desorption curve at about 0.3 p/p_0. Acetonitrile gave much broader hysteresis loops which remained open to zero pressure, but gave no shoulder in the isotherm, nor any apparent steps which might correspond to loss of third and second layers of adsorbate. These types will be discussed separately.

The hysteresis observed in the sorption of the permanent gases is probably due entirely to capillary condensation. If it is assumed that the hysteresis is due to condensation between parallel plates, then the pressure at which the condensate evaporates is related to the distance between the plates, assuming the dimensions of the plates are large compared with the distance between them, by

$$RT\ln p/p_0 = -\frac{\sigma V}{r_K}$$

where r_K is equal to half the distance separating the plates minus the thickness of the adsorbed layers. The pore size distributions of the heptyl diammonium montmorillonite and butyl diammonium hectorite have been calculated from the nitrogen desorption isotherms, employing the method of Dollimore and Heal (1964). Their equations have been modified slightly since condensation occurs between parallel plates and not in a tubular capillary. It is apparent from Figure 3.30 that one size of pore predominates, and this appears to be independent of the organic ion present or even the type of clay. In both cases there is a sharp peak at 15Å, corresponding to an interplate distance of 30Å. This includes an allowance for the thickness of the adsorbed layer. As might be expected it also corresponds to the point at which the shoulder appears on the isotherm, and consequntly, since the isotherms for argon and oxygen sorption are very similar in shape, complete pore size distributions have not been determined for these sorbates, but only the Kelvin radius corresponding to the shoulder in each case. As with nitrogen this distance is independent of the organic ion or type of clay (Table 3.X). To obtain the true

ADSORPTION OF NITROGEN AT 78°K.

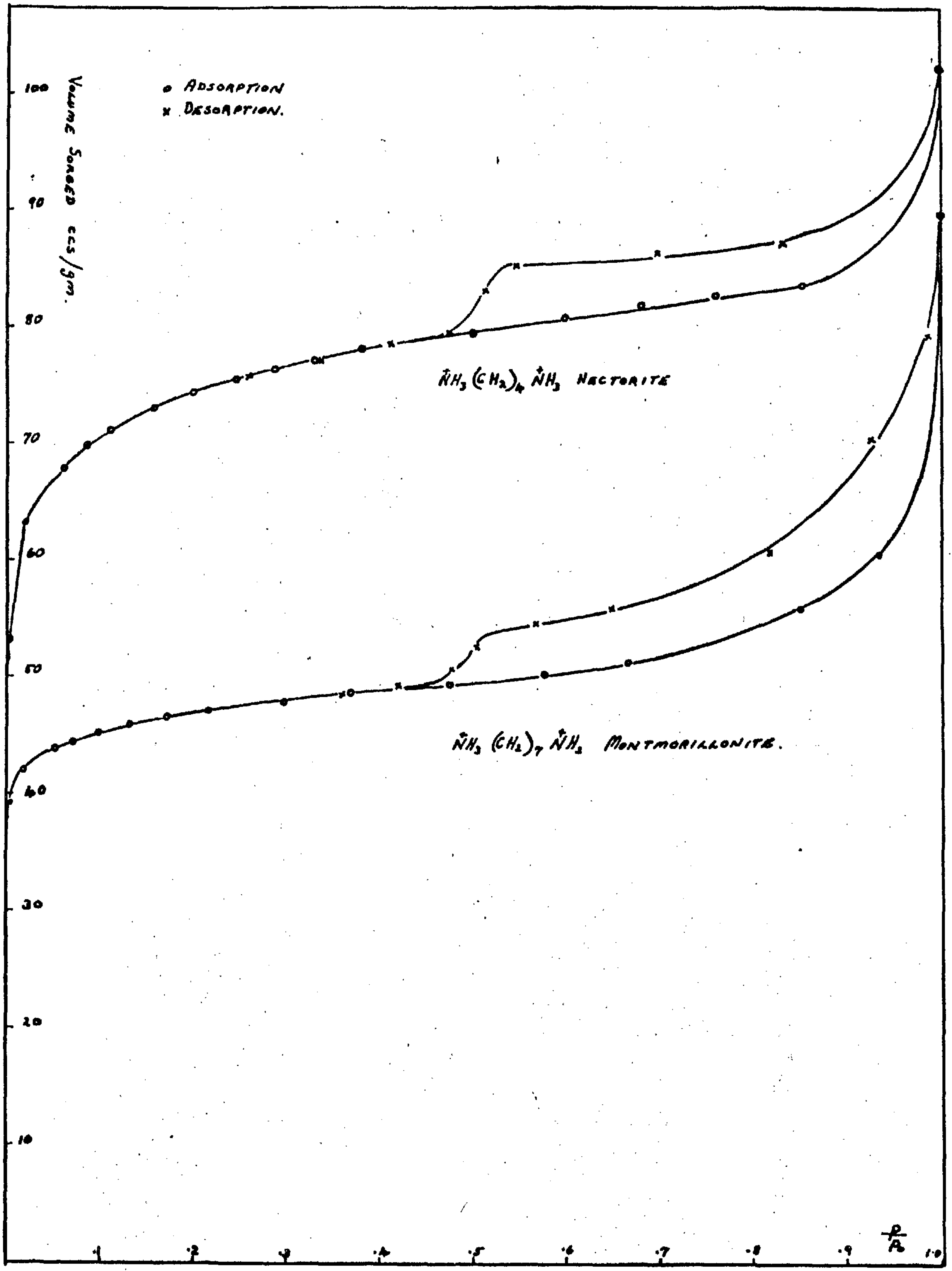
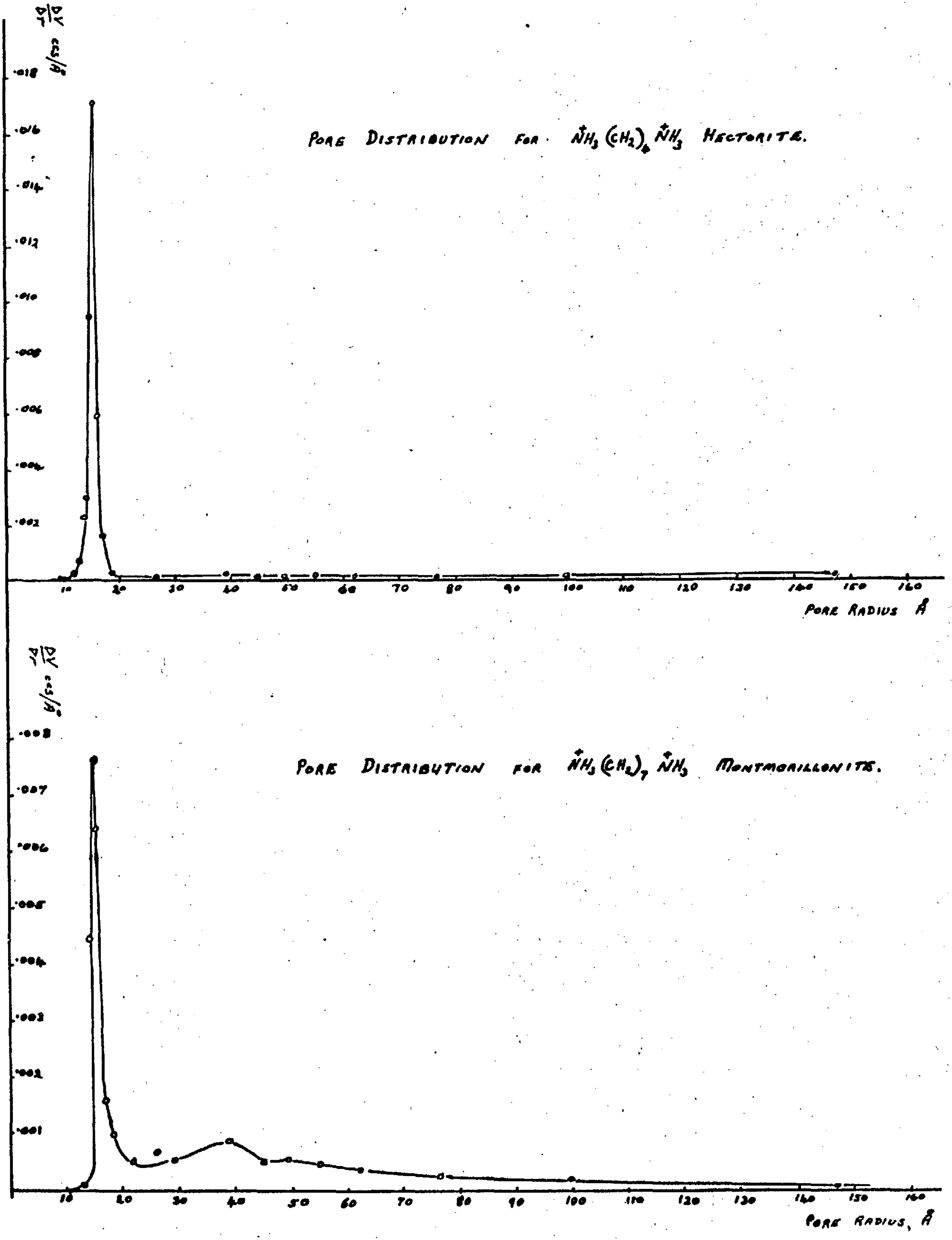


FIG. 3. 29



PORE DISTRIBUTION FOR $\overset{+}{N}H_3(CH_2)_6\overset{+}{N}H_3$ HECTORITE.

PORE DISTRIBUTION FOR $\overset{+}{N}H_3(CH_2)_7\overset{+}{N}H_3$ MONTMORILLONITE.

FIG. 3. 30

TABLE 3.X

Pore radii at shoulder

No. of C atoms/ion	Pore radius r_K in Å			
	Nitrogen	Argon	Benzene	Heptane
(i) Alkyldiammonium montmorillonites				
2			8.4	
3		6.6	8.2	10.6
4			8.5	
5		6.6	8.6	
6		6.5	8.4	11.0
7	6.9			
8			8.4	10.6
9				
10		6.4	8.3	10.7
12				
(ii) Alkyldiammonium hectorites				
Na		6.4		
3			8.4	
4	7.0	6.4		
5		6.5	8.4	
12			8.5	

distance between the sheets the thickness of the adsorbed layer must be added, but this is not known with any certainty. Foster (1948) has suggested a distance of two molecular diameters. Similar calculations for the shoulder observed on the desorption of the organic sorbates confirm that the interplate distance is a function only of the sorbate (Table 3.X), and from the calculated Kelvin radii it is seen that the capillary condensate is four to five molecules in thickness for each of the sorbates, assuming a flat orientation for the organic molecules. The shoulder moves to higher relative pressures as the temperature increases but this can be attributed to the decreasing surface tension of the sorbate, the calculated Kelvin radius remaining approximately constant. This lends support to Barrer and McLeod's theory (1954) that the platelet-shaped particles of montmorillonite are drawn into a thixotropic structure at high relative vapour pressures, which will only disintegrate again when the pressure falls sufficiently for the condensate to evaporate. A similar proposal was considered by Aylmore and Quirk (1962), who suggested a domain structure, each domain consisting of crystallites in parallel orientation as envisaged by Barrer and McLeod, but the domains themselves being randomly arranged. In determining the pore size distribution they found two peaks, and considered that the larger corresponded to interdomanial spacings, though this is hardly consistent with a random array of domains. In the present work only one peak was found, and the gradual slope of the isotherms down to the shoulder would indeed be consistent with evaporation from a wide range of interdomanial pores.

One adsorption scanning curve and one desorption scanning curve were also determined for the sorption of argon on two organo-montmorillonites, Fig. 3.31. In each case the scanning curve crossed the loop to join the main curve, which is in accordance with Katz's rule, though since a change in pore shape at high pressures was postulated, the rule may no longer have any significance. The proposed sorption mechanism accounts quite

SORPTION OF ARGON AT 78°K.

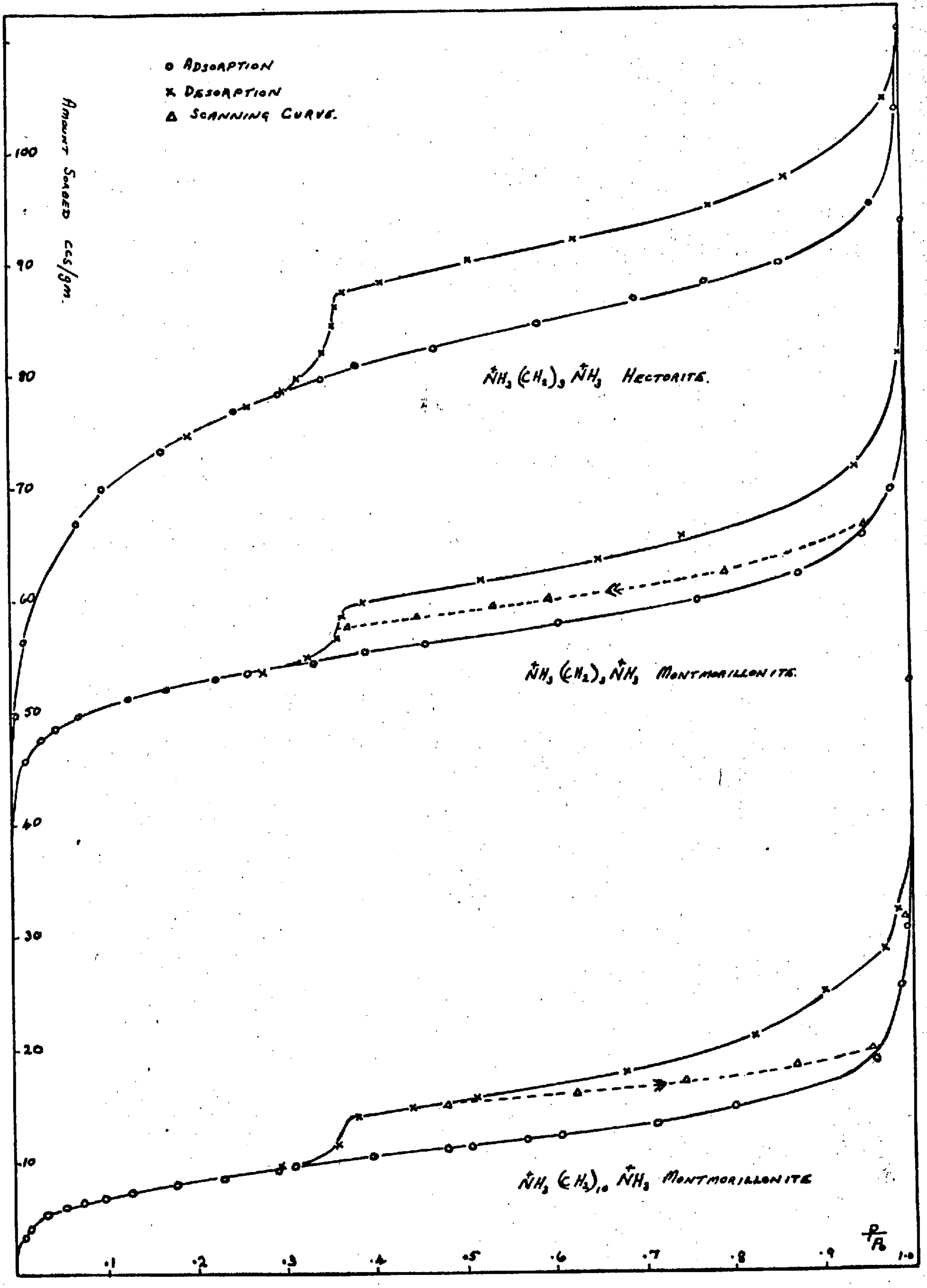


FIG. 3.31

simply for the desorption scanning curve, but the path of the adsorption scanning curve is difficult to predict. During the initial adsorption condensation may occur between particles and in wedge-shaped crevices which probably exist in a system of this type. As the wedge-shaped pores fill with condensed sorbate the surface tension forces may pull the walls into a parallel alignment giving the ordered structure envisaged above, the number of crevices undergoing this change increasing with pressure. Thus, if desorption is commenced at 0.95 p/p_o, where there is a partly ordered structure, evaporation of the interdomanial condensate proceeds as on the main desorption curve, but the condensate between the parallel lamellae remains until the shoulder is reached. Thus the desorption scanning curve meets the near-vertical portion of the shoulder. If the adsorption scanning curve is begun at a point just above the shoulder (Fig. 3.31) most of the interdomanial condensate will have evaporated, but the intordomanial portion remains, so it might be expected that the adsorption scanning curve would remain above the main adsorption curve to the apex of the loop. However, the nature of the interdomanial pores is complex and the effect on them of a certain ordering of the structure cannot be predicted. In practice it appears that the amount of condensation is reduced so that the scanning curve joins the main curve. It may be noted here that the intradomanical condensate accounts for only about 20 per cent of the total condensed sorbate.

The occurrence of low pressure hysteresis has been ascribed to interlamellar expansion of the clays (Barrer and McLeod 1954), and though this is almost certainly a contributory cause, it does not appear to be a fully satisfactory explanation, since little hysteresis would be expected with heptane which causes a swelling of only 0.1 to 0.2Å. Similarly benzene, which was shown to have expanded the clay at a relative pressure of less than 0.1, would not be expected to give such a large hysteresis loop (Figure 3.32) between 0.1 and 0.3 p/p_0. The hysteresis is certainly connected with the interlamellar region since no low pressure hysteresis is observed on natural montmorillonite where the non-polar organic sorbates do not penetrate. It seems probable that the hysteresis is also due to rearrangement of the cations at higher vapour pressures to make more sites available to the sorbate. Evidence for this rearrangement was given in the section on "Sorption isotherms". The permanent gases do not show this because rearrangement is not possible at liquid nitrogen temperature. However, this might be expected to lead to greater low pressure hysteresis the larger the alkyl chain of the cation, but this is not observed.

A much broader hysteresis loop is obtained on sorption of acetonitrile and Hirst's swelling theory (1948) seems applicable in this case, the third and second layers of acetonitrile being retained to a pressure lower than that at which they were formed. From the possible theoretical amounts sorbed, Table 3.IX, it appears that the third layer, where it is formed, evaporates just below saturated vapour pressure, but the second layer disappears much more gradually, the evaporation being complete only at the point where the desorption curve becomes convex to the pressure axis (Fig. 3.19 and 3.34), usually at relative pressures of 0.2 to 0.25. The amount sorbed at this point corres-

ADSORPTION OF BENZENE AT 40°C.

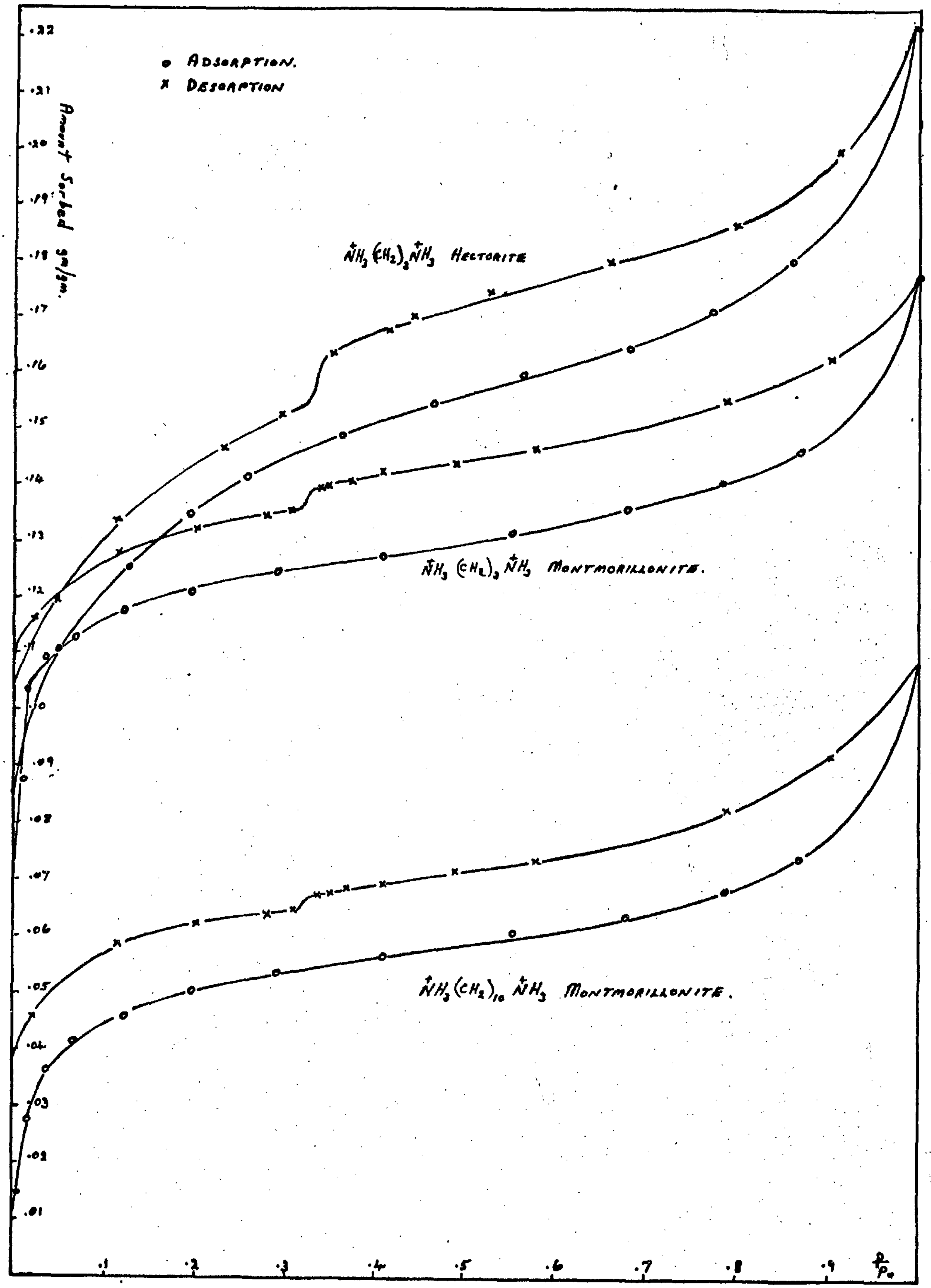


Fig. 3.32.

ADSORPTION OF HEPTANE AT 40°C.

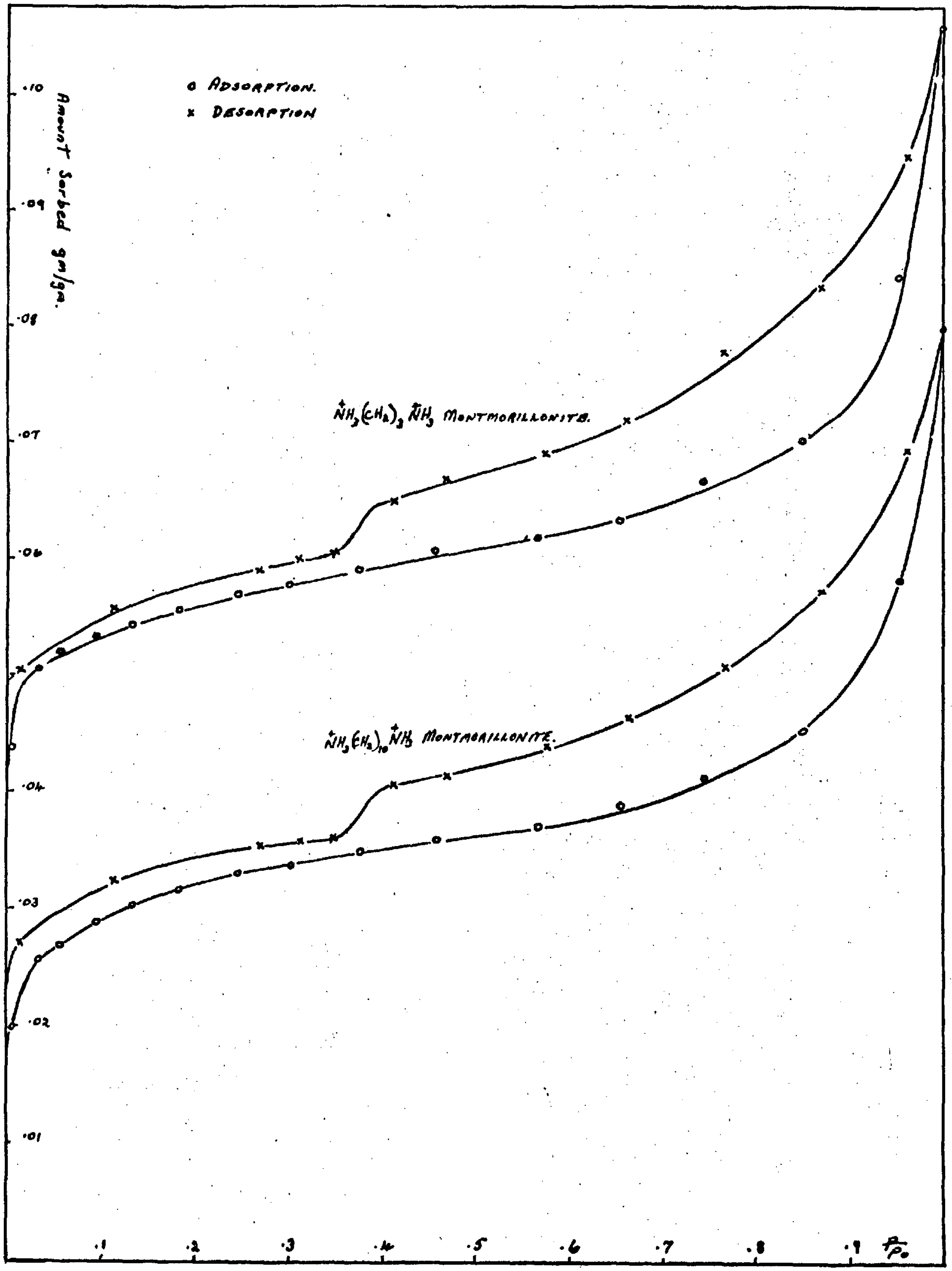


Fig. 3. 33

ADSORPTION OF ACETONITRILE AT 50°C.

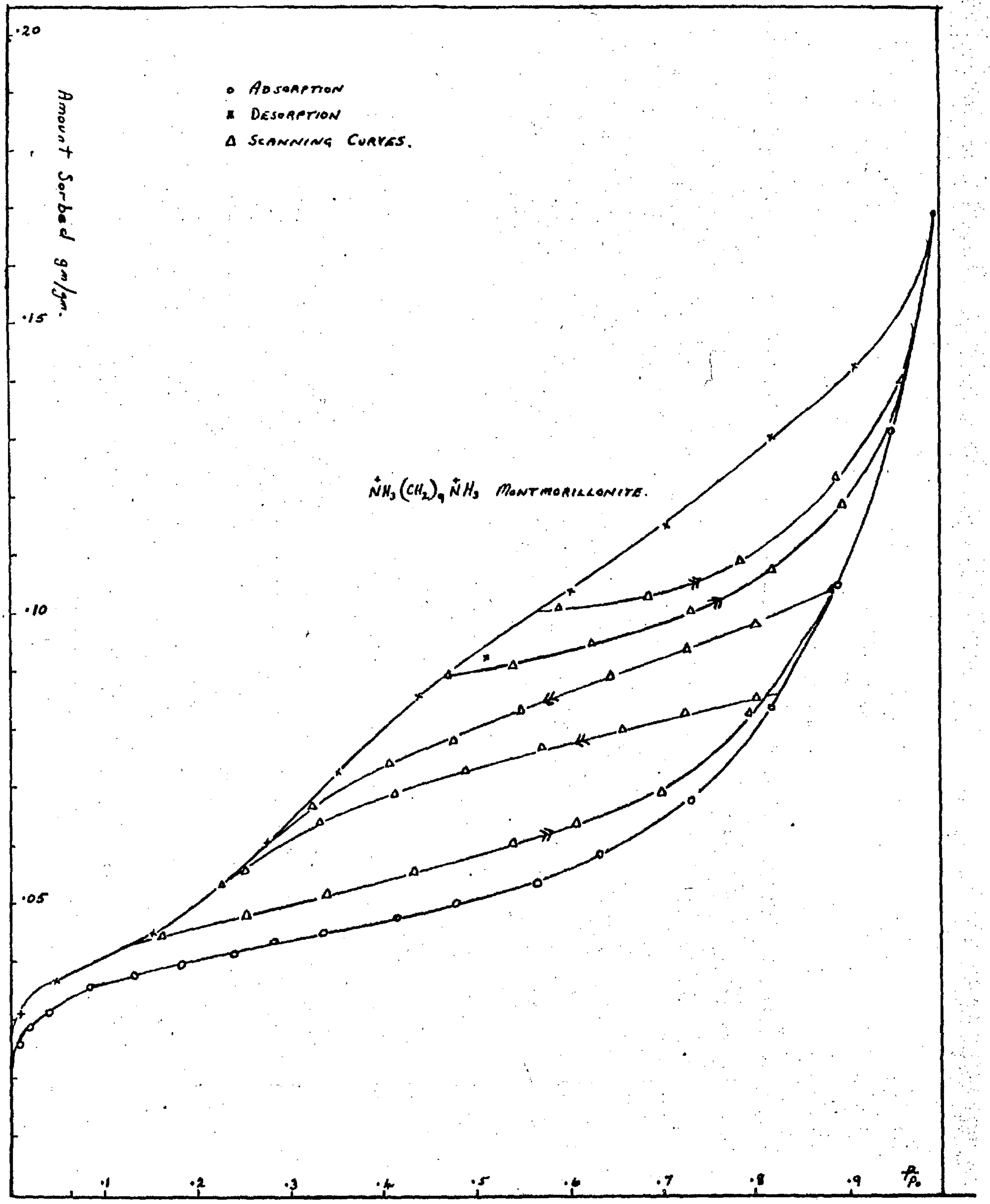


FIG. 3.34.

ponds to a completed monolayer in all cases, neglecting external sorption which will be very small at this pressure. There is no significant difference in the isotherms for clays containing ions with four, five or six carbon atoms, which adsorb a maximum of two layers.

Whether the scanning curves join the main curves or approach them asymptotically is not clear from the experimental points determined (Figs. 3.9 and 3.34), but the latter seems more likely. Starting from a point on the adsorption curve, where the second layer of sorbate will be only partially formed, the desorption scanning curve should remain below the main curve which represents desorption from a fully completed second layer. Similarly for the adsorption scanning curve, the clay at any given pressure will be more swollen at a point on the desorption curve than on the main adsorption curve, and may remain so throughout the subsequent adsorption. Since there are no steps in the adsorption isotherm it must be assumed that different layers expand at different relative pressures and it seems reasonable to suppose that the higher the relative pressure required to bring about expansion the sooner the layers will contract on desorption. This would explain why the adsorption scanning curves do not run parallel to the main curve. Interparticulate condensation will also influence the curves but below a relative pressure of about 0.9 the hysteresis due to swelling is much more important.

The low pressure hysteresis is probably due to the causes discussed previously, though it may also be due in part to chemisorption (see Sorption Isotherms, p. 79).

SUMMARY AND CONCLUSION

The change in the sorptive capacities on replacing the small inorganic ions in Wyoming bentonite and a commercial hectorite, Ben-U-Gel, by α-ω alkyl diammonium ions has been investigated. A few alkylammonium clays were prepared for comparison.

The probable orientations and extent of penetration of the interlamellar organic ions into the silicate layer have been predicted by comparison of calculated ion dimensions and observed d001 spacings for the outgassed sorbents. The extent of penetration of small alkyl-diammonium ions appears to be greater than for similar alkylammonium ions.

Contrary to the findings of Weiss (1958c,1963) X-ray measurements showed that only acetonitrile caused appreciable swelling, though sorption data indicated that 1:3 diamino propane may also do so. Benzene and heptane formed only a monolayer, benzene taking up a perpendicular orientation, even at low pressures, and heptane a parallel one, as was found for methyl and tetramethyl ammonium clays (Barrer et al.). The isotherms for acetonitrile and 1:3 propane diamine were smooth indicating gradual formation or destruction of second and third layers. The crossing of the isotherms of the various derivatives, especially noticeable in the case of the latter sorbate, indicated that the longer alkyl chain derivatives swell more easily than do those with small organic ions.

A discrepancy of up to 35 per cent was found between the theoretical and measured interlamellar areas, and proposals were put forward to explain this. It was noted that the discrepancy increased the longer the alkyl chain of the interlamellar ion, especially in considering the sorption of the permanent gases. Better agreement was observed for the organic sorbates and it was suggested that this was due to ion rearrangement. The B.E.T. isotherms were unusual in being linear from zero to 0.2 p/p_0 in most cases, but the estimated B.E.T. areas for interlamellar sorption were smaller than those determined by making an allowance for external sorption and assuming an interlamellar monolayer. Good type I isotherms (Brunauer classification) were obtained for the estimated interlamellar sorption. The difference in uptake between the montmorillonite and hectorite derivatives was attributed to differences in crystallite thickness, montmorillonite crystals having an average thickness of 26 sheets, and those of hectorite about 10 sheets.

The position occupied by the alkyldiammonium ions in the swollen complexes has been discussed, but the evidence was insufficient to draw any definite conclusions. The small alkyl chain ions, having less than three carbon atoms, probably form a centre layer sandwiched between two layers of acetonitrile molecules, whilst the longer ions may have both amine groups in contact with a silicate sheet.

The sorption of hydrocarbons on montmorillonites containing small alkyldiammonium ions was shown to be strongly exothermic and exo-entropic, but became endothermic and endo-entropic for clays containing the larger ions. Reasons for this behaviour have been proposed. The endo-entropic sorption appears consistent with a mixing process for ions and sorbate molecules.

Hysteresis has been observed in all the systems studied and may be explained by three different mechanisms. At high relative vapour pressures it is due almost entirely to capillary condensation, except in the case of acetonitrile where hysteresis due to swelling is also important. At low pressures swelling of the sorbent and rearrangement of the cations are thought to be responsible. The shoulders on the desorption curves are adequately explained by the theory of Barrer and McLeod, and the observed scanning curves are also consistent with this theory.

In conclusion it appears that the small alky l diammonium ions at least do not exhibit a "tie" effect as had been expected. Unfortunately no sorbate was found which could swell the clay sufficiently to determine the effect of the longer alkyl chains in this capacity. The limited swelling of the butyl, amyl, and hexyl diammonium montmorillonites could be attributed to a "tie" effect, but an alternative explanation was suggested. A clay with a lower layer charge should swell more readily, and this might yield more decisive results.

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APPENDIX I

ISOTHERM DATA:

p = pressure cm of Hg

p/p_o = relative vapour pressure

V = volume sorbed in cc/gm of Na^+ clay

x = amount sorbed gm/gm of Na^+ clay

MONTMORILLONITE DERIVATIVES

NITROGEN ISOTHERMS

Na^+	78°K
p/p_o	V
.004	5.22
.039	6.79
.071	7.28
.108	7.68
.154	8.10
.211	8.59
.270	9.14
.377	10.13
.470	11.03
.545	11.76
.617	12.57

$\overset{+}{N}H_3(CH_2)_2\overset{+}{N}H_3$	78°K
p/p_o	V
.005	41.86
.017	43.96
.031	45.01
.045	45.70
.061	46.31
.095	47.18
.114	47.64
.139	48.01
.189	48.83
.242	49.50
.291	49.97
.342	50.42
.369	50.73
.460	51.43
.536	52.05
.611	52.51

Na^+	195°K
p	V
0.415	.023
1.058	.047
2.469	.075
3.656	.098
5.161	.124
6.824	.156
9.000	.182
11.547	.223
16.465	.299
21.937	

$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$	78°K
.010	46.63
.022	47.72
.043	48.62
.060	49.14
.099	49.94
.122	50.31
.163	50.89
.224	51.59
.286	52.19
.344	52.60
.406	52.99
.475	53.54
.617	54.43
.747	55.24

$\overset{+}{N}H_3(CH_2)_4\overset{+}{N}H_3$ 78°K

p/p_o	V
.005	45.61
.043	48.55
.058	49.00
.089	49.72
.133	50.39
.181	50.92
.231	51.45
.276	51.86
.325	52.21
.375	52.53
.493	53.37
.602	54.04
.687	54.92
.765	55.86
.879	58.27
.944	62.65
.969	65.25
.901	60.71
.803	58.27
.665	56.55
.520	53.59
.476	53.35
.407	52.93
.338	52.43
.261	51.83
.188	51.09

$\overset{+}{N}H_3(CH_2)_5\overset{+}{N}H_3$ 78°K

p/p_o	V
.001	41.67
.005	43.54
.015	44.98
.038	46.21
.066	47.00
.096	47.68
.131	48.21
.178	48.85
.228	49.30
.273	49.73
.320	50.06
.425	50.85
.525	51.46
.605	52.10
.682	52.65

$\overset{+}{N}H_3(CH_2)_5\overset{+}{N}H_3$ 195°K

p	V
0.194	0.39
0.312	0.72
0.421	0.95
0.605	1.33
0.724	1.61
0.981	2.11
1.439	2.95
1.817	3.54
2.489	4.53
3.189	5.46
3.880	6.30
4.486	6.96
5.160	7.60
7.997	9.91
10.020	11.36
12.116	12.28
14.395	13.29
6.027	8.39

$\overset{+}{N}H_3(CH_2)_6\overset{+}{N}H_3$	78°K
p/po	V
.005	42.35
.016	43.94
.032	45.01
.055	45.91
.103	47.07
.163	48.20
.248	49.14
.296	49.57
.356	50.28
.432	50.91
.504	51.36

$\overset{+}{N}H_3(CH_2)_7\overset{+}{N}H_3$	78°K
p/po	V
.002	39.26
.015	42.05
.050	43.91
.066	44.39
.098	45.17
.129	45.91
.171	46.55
.215	47.05
.296	47.88
.367	48.57
.476	49.35
.578	50.25
.654	51.23
.848	55.97
.933	60.55
.955	77.71
1.005	90.10
.985	79.03
.923	70.41
.818	60.70
.649	55.90
.563	54.49
.503	52.63
.477	50.82
.416	49.72
.358	49.30
.219	48.01

$\overset{+}{N}H_3(CH_2)_7\overset{+}{N}H_3$	90°K
p	V
.451	36.88
2.711	40.08
6.213	41.33
8.710	41.98
11.791	42.49
15.010	42.90
17.923	43.23
22.755	43.83
30.134	44.32
37.151	44.67
42.880	44.94
47.808	46.05

$\overset{+}{N}H_3(CH_2)_8\overset{+}{N}H_3$	78°K
p/po	V
.011	32.37
.018	33.17
.048	34.67
.086	35.60
.128	36.35
.159	37.07
.218	37.89
.278	38.63
.334	38.93
.391	39.12

$\overset{+}{N}H_3(CH_2)_9\overset{+}{N}H_3$ 78°K

p/po	V
.004	17.09
.009	18.26
.018	19.08
.032	20.09
.043	20.65
.068	21.39
.103	22.26
.142	22.85
.179	24.10
.217	24.57
.259	25.02
.321	25.53
.428	26.37
.530	27.18
.713	27.86

$\overset{+}{N}H_3(CH_2)_{10}\overset{+}{N}H_3$ 78°K

p/po	V
.010	3.63
.023	4.08
.047	4.61
.077	5.02
.095	5.22
.126	5.55
.174	5.87
.226	6.22
.272	6.58
.321	7.01
.444	7.36
.549	7.98
.635	8.22

$\overset{+}{N}H_3(CH_2)_{12}\overset{+}{N}H_3$ 78°K

p/po	V
.005	4.13
.022	5.15
.058	6.13
.078	6.62
.109	7.07
.141	7.59
.207	8.45
.242	8.74
.327	9.51
.415	9.87
.487	10.52
.558	11.16

$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$ after acetonitrile sorption 78°K

Outgas 67°C

p/po	V
.064	5.04
.102	5.34
.143	5.71
.188	6.08
.231	6.46
.278	6.74
.331	7.19
.396	7.60
.462	7.86

Outgas 106°C

p/po	V
.048	4.90
.092	5.83
.145	6.55
.261	7.52
.316	7.96
.372	8.45

Outgas 160°C

p/po	V
.036	11.81
.076	12.33
.107	12.69
.176	13.20
.214	13.70

$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$ after acetonitrile sorption — 195°K

p	V
.782	1.07
1.413	1.65
2.164	2.23
3.062	2.69
5.832	3.97
9.389	5.05
11.228	5.51
15.835	6.31
20.945	6.88

$\overset{+}{N}H_3CH_3$ — 78°K

p/po	V
.048	45.50
.184	49.00
.244	50.01
.304	50.80
.370	51.75
.479	52.96
.579	53.99

$\overset{+}{N}H_3C_2H_5$ — 78°K

.001	33.41
.010	36.97
.034	38.92
.072	40.41
.111	41.37
.148	42.11
.185	42.74
.218	43.23
.252	43.73
.309	44.47
.403	45.43
.490	46.33
.560	46.97
.625	47.75

$\overset{+}{N}H_3C_3H_7$ — 78°K

p/po	V
.001	26.89
.014	30.64
.046	32.39
.091	33.62
.128	34.32
.171	35.01
.215	35.57
.254	36.01
.293	36.52
.344	37.65
.449	38.53
.546	39.09
.620	40.11
.688	41.05

$\overset{+}{N}H_3C_5H_{11}$ — 78°K

p/po	V
.003	14.41
.025	16.29
.041	16.93
.093	18.25
.125	18.87
.158	19.50
.217	20.63
.239	20.73
.299	21.39
.351	21.96
.401	22.63

$\overset{+}{N}H_3C_6H_{13}$ — 78°K

p/po	V
.020	8.04
.046	8.83
.079	9.57
.114	10.07
.152	10.59
.203	11.28
.257	11.69
.301	12.18
.347	12.76

NITROGEN ON MONTMORILLONITE

$C_{12}H_{25}\overset{+}{N}H_3$	78°K
p/p_o	V
.028	1.57
.048	2.09
.069	2.49
.103	2.81
.139	3.14
.178	3.43
.215	3.76
.253	4.00
.300	4.31
.395	4.91
.485	5.43

OXYGEN

MMONTMORILLONITE DERIVATIVES

$\overset{+}{N}H_3(CH_2)_8\overset{+}{N}H_3$ 78°K

p/po	V		
.012	39.22	.740	68.74
.014	39.72	.816	71.22
.033	41.76	.875	74.19
.049	42.93	.897	76.07
.091	44.62	.957	84.48
.142	45.91	.967	87.00
.180	46.96	.990	96.91
.262	48.45	.939	87.96
.343	50.00	.795	78.51
.430	51.19	.769	77.71
.507	52.24	.636	73.34
.587	53.44	.465	70.26
.662	54.79	.420	69.46
.824	59.95	.318	67.63
.904	66.90	.281	63.88
.931	72.57	.173	59.54
		.090	57 .46

$\overset{+}{N}H_3(CH_2)_6\overset{+}{N}H_3$ 78°K

.019	53.22
.024	53.66
.037	54.92
.049	55.76
.078	56.92
.127	58.35
.167	59.37
.230	60.57
.308	61.86
.514	64.82
.599	65.94
.684	67.45

ARGON ISOTHERMS

$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$ 78°K

p/p_o	V
.065	52.09
.097	53.34
.120	53.58
.168	54.42
.227	55.29
.290	56.14
.433	57.40
.585	59.15
.736	61.01
.846	63.51
.915	67.19
.937	69.26
.979	80.83
1.000	95.42
.990	89.01
.956	81.95
.874	73.16
.701	67.00
.616	63.96
.526	64.04
.447	62.69
.371	60.36

$\overset{+}{N}H_3(CH_2)_5\overset{+}{N}H_3$ 78°K

p/p_o	V
.001	43.23
.006	47.09
.024	50.30
.066	52.54
.099	53.49
.130	54.11
.167	54.76
.220	55.54
.276	56.19
.326	56.79
.378	57.41
.449	58.23
.597	59.63
.735	61.33
.840	63.13
.902	65.98
.949	71.27
.993	86.38
1.000	97.39
.975	87.20
.883	75.41
.849	73.26
.795	70.42
.719	67.94
.601	65.50
.467	63.18
.442	62.60
.383	61.87
.371	59.63
.329	57.29
.252	56.09

$\overset{+}{N}H_3(CH_2)_6\overset{+}{N}H_3$ 78°K

p/p_o	V
.013	45.77
.030	47.69
.070	49.70
.126	51.20
.145	51.58
.168	52.00
.224	52.87
.280	53.78
.334	54.49
.392	55.27
.458	55.92
.612	57.69
.764	59.57
.875	61.93
.950	65.18
.983	69.34
1.000	94.71
.994	81.28
.946	71.21
.751	65.26
.650	63.33
.525	61.42
.395	59.54
.368	58.36
.359	56.44
.326	54.82
.263	53.66

Scanning curves

.400	55.33
.469	56.20
.823	60.88
.950	66.11
.800	62.05
.602	59.81
.536	59.11
.452	58.27
.375	57.52
.330	54.90

$\overset{+}{N}H_3(CH_2)_{10}\overset{+}{N}H_3$ 78°K

p/p₀	V
.005	3.64
.017	4.44
.052	6.10
.097	6.95
.123	7.35
.178	7.99
.227	8.56
.291	9.07
.394	10.29
.476	10.99
.506	11.12
.566	11.72
.607	12.03
.711	13.11
.802	14.47
.956	18.53
.989	25.12
.991	31.29
1.000	52.36
.984	31.68
.967	28.41
.932	24.63
.826	20.69
.682	17.63
.514	15.48
.440	14.67
.380	13.71
.358	11.44
.295	9.86

Scanning curves

.536	11.98
1.000	48.74
.883	21.62
.483	14.86
.625	15.68
.746	16.70
.866	18.10
.952	19.63
.986	30.33

$\overset{+}{N}H_3(CH_2)_5\overset{+}{N}H_3$ 195°K

p	V
1.142	1.02
1.552	1.29
1.968	1.61
2.358	1.89
2.678	2.28
4.337	3.44
5.754	4.61
7.257	5.69
8.724	6.51
10.240	7.46
12.474	8.97
16.779	10.90
21.310	12.53
25.397	13.75
29.694	14.89

ACETONITRILE ISOTHERMS

First run 40°C

p/p_o	$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$ x	$\overset{+}{N}H_3(CH_2)_8\overset{+}{N}H_3$ x	$\overset{+}{N}H_3(CH_2)_9\overset{+}{N}H_3$ x	$\overset{+}{N}H_3(CH_2)_{12}\overset{+}{N}H_3$ x
.006	.0328	.0186	.0185	.0098
.012	.0360	.0209	.0205	.0119
.027	.0395	.0235	.0233	.0141
.053	.0428	.0261	.0256	.0165
.094	.0461	.0290	.0287	.0184
.145	.0493	.0315	.0310	.0216
.209	.0521	.0349	.0332	.0233
.298	.0543	.0363	.0360	.0265
.373	.0579	.0387	.0385	.0289
.458	.0617	.0414	.0414	.0328
.529	.0669	.0440	.0442	.0376
.591	.0726	.0465	.0473	.0430
.656	.0800	.0483	.0506	.0518
.729	.0957	.0556	.0651	.0749
.808	.1068	.0631	.0777	.0889
.873	.1213	.0801	.1009	.1121
.941	.1471	.1116	.1369	.1592
.996	.1692	.1426	.1635	.2057

Second run 50°C

.006	.0437	.0251	.0261	.0200
.018	.0477	.0281	.0289	.0219
.039	.0519	.0303	.0314	.0234
.085	.0563	.0347	.0358	.0267
.131	.0587	.0365	.0379	.0284
.184	.0608	.0384	.0396	.0297
.236	.0628	.0402	.0416	.0320
.281	.0655	.0419	.0436	.0338
.333	.0669	.0432	.0450	.0350
.414	.0692	.0452	.0475	.0381
.478	.0718	.0473	.0502	.0412
.566	.0746	.0505	.0533	.0452
.630	.0811	.0545	.0586	.0526
.730	.0916	.0619	.0675	.0620
.815	.1086		.0840	
.910	.1500			
.995	.1936	.1609	.1685	.2054
.907	.1705	.1368	.1424	.1608
.817	.1616	.1265	.1300	.1458
.707	.1516	.1136	.1151	.1268

.609	.1440	.1022	.1035	.1134
.512	.1330	.0893	.0920	.0981
.438	.1242	.0810	.0857	.0857
.347	.1107	.0620	.0728	.0712
.275	.0994	.0565	.0610	.0617
.190	.0806	.0471	.0490	.0515
.149	.0704	.0429	.0449	.0441
.042	.0592	.0358	.0368	.0318
.005	.0521	.0302	.0313	.0276

<u>Scanning curves</u>

.797	.1275	.0822	.0855	.0948
.723	.1246	.0805	.0829	.0911
.652	.1217	.0770	.0803	.0871
.569	.1185	.0748	.0770	.0813
.490	.1138	.0704	.0729	.0727
.413	.1090	.0664	.0688	.0670
.332	.1015	.0612	.0644	.0623
.248	.0876	.0525	.0557	.0554
.889	.1486	.0985	.1039	.1277
.802	.1420	.0934	.0981	.1195
.728	.1374	.0898	.0939	.1124
.644	.1332	.0860	.0891	.1019
.550	.1292	.0815	.0834	.0889
.471	.1230	.0762	.0776	.0796
.407	.1168	.0710	.0740	.0738
.318	.1057	.0631	.0671	.0668
.224	.0882	.0528	.0540	.0544
.153	.0720	.0443	.0442	.0432
.249		.0468	.0480	.0472
.335		.0512	.0518	.0511
.430		.0525	.0554	.0547
.530		.0592	.0604	.0625
.608		.0622	.0641	.0684
.699		.0683	.0692	.0761
.786		.0799	.0834	.1008
.888		.0989	.1047	.1290
1.000		.2736	.1993	.2572
.591	.1409	.0967	.1008	.1138
.689	.1440	.0996	.1030	.1199
.788	.1498	.1050	.1090	.1317
.888	.1592	.1143	.1237	.1566
.925		.1197		
.963	.1742	.1286	.1405	.1762
.473	.1333	.0861	.0895	.0940
.539	.1348	.0879	.0910	.0964
.625	.1384	.0906	.0945	.1020
.732	.1439	.0954	.1008	.1154
.816	.1505	.1020	.1072	.1327
.895	.1588	.1111	.1189	.1513
.942	.1678	.1212	.1314	.1674

	$\overset{+}{N}H_3(CH_2)_2\overset{+}{N}H_3$	$\overset{+}{N}H_3(CH_2)_4\overset{+}{N}H_3$	$\overset{+}{N}H_3(CH_2)_5\overset{+}{N}H_3$
p/p_o	x	x	x
First run 60°C			
.005	.0406	.0394	.0366
.028	.0487	.0448	.0424
.051	.0524	.0479	.0451
.096	.0571	.0497	.0475
.154	.0608	.0528	.0496
.235	.0645	.0563	.0528
.315	.0677	.0584	.0550
.410	.0698	.0607	.0567
.508	.0729	.0644	.0602
.608	.0766	.0693	.0645
.711	.0812	.0775	.0701
.801	.0874	.0946	.0829
.926	.1056	.1242	.1118
.980	.1376	.1462	.1349
1.003	.1773	.1692	.1492
.974	.1441	.1540	.1419
.889	.1220	.1401	.1305
.823	.1133	.1340	.1246
.716	.1032	.1259	.1180
.592	.0928	.1192	.1106
.485	.0793	.1104	.1012
.397	.0738	.1006	.0893
,355	.0726	.0907	.0807
.306	.0702	.0804	.0705
.232	.0673	.0606	.0591
.150	.0632	.0580	.0528
.052	.0568	.0519	.0470
.020	.0507	.0481	.0433

Second Run 50°C

p/po	$\overset{+}{N}H_3(CH_2)_2\overset{+}{N}H_3$ x	$\overset{+}{N}H_3(CH_2)_4\overset{+}{N}H_3$ x	$\overset{+}{N}H_3(CH_2)_5\overset{+}{N}H_3$ x	$\overset{+}{N}H_3(CH_2)_6\overset{+}{N}H_3$ x
.001	.0267	.0298	.0304	.0300
.010	.0483	.0475	.0423	.0419
.040	.0560	.0530	.0480	.0468
.083	.0609	.0568	.0516	.0510
.155	.0655	.0603	.0541	.0541
.253	.0700	.0636	.0583	.0589
.349	.0743	.0671	.0600	.0613
.455	.0779	.0703	.0637	.0646
.536	.0803	.0733	.0674	.0685
.622	.0828	.0774	.0704	.0704
.733	.0913	.0904	.0797	.0821
.825	.1026	.1137	.1012	.1026
.947	.1411	.1459	.1357	.1522
1.001	.2436	.2309	.2161	.2704
.989	.2138	.1972	.1793	.2509
.946	.1504	.1680	.1601	.1618
.865	.1475	.1528	.1446	.1589
.739	.1323	.1412	.1357	.1407
.677	.1254	.1362	.1303	.1339
.589	.1147	.1316	.1256	.1248
.549	.1084	.1283	.1218	.1191
.467	.0926	.1221	.1151	.1016
.371	.0809	.1134	.1015	.0757
.290	.0757	.0967	.0799	.0632
.195	.0715	.0688	.0614	.0596
.052	.0607	.0577	.0527	.0522

BENZENE ISOTHERMS

40°C

	$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$	$\overset{+}{N}H_3(CH_2)_6\overset{+}{N}H_3$	$\overset{+}{N}H_3(CH_2)_8\overset{+}{N}H_3$	$\overset{+}{N}H_3(CH_2)_{10}\overset{+}{N}H_3$
p/p_0	x	x	x	x
.002	.0901	.0545	.0355	.0147
.011	.1034	.0806	.0608	.0277
.032	.1092	.0890	.0705	.0363
.063	.1131	.0942	.0761	.0414
.117	.1173	.0996	.0810	.0458
.194	.1207	.1046	.0855	.0502
.289	.1245	.1086	.0902	.0536
.406	.1272	.1120	.0932	.0565
.550	.1314	.1163	.0982	.0608
.677	.1355	.1205	.1035	.0636
.785	.1402	.1252	.1081	.0682
.866	.1461	.1308	.1146	.0739
1.000	.1772	.1599	.1462	.1083
.902	.1627	.1473	.1307	.0922
.789	.1551	.1391	.1226	.0826
.576	.1467	.1281	.1131	.0735
.488	.1438	.1248	.1100	.0718
.406	.1422	.1218	.1081	.0693
.365	.1404	.1208	.1063	.0684
.347	.1398	.1203	.1050	.0678
.336	.1393	.1193	.1039	.0678
.307	.1357	.1155	.1012	.0652
.279	.1344	.1145	.0997	.0642
.200	.1319	.1120	.0977	.0623
.111	.1276	.1074	.0927	.0586
.017	.1162	.0939	.0778	.0457
60°C				
.004	.0839	.0356	.0229	.0124
.010	.0987	.0703	.0501	.0257
.038	.1082	.0884	.0727	.0404
.078	.1126	.0955	.0797	.0474
.157	.1174	.1015	.0868	.0526
.268	.1218	.1064	.0915	.0579
.358	.1243	.1093	.0950	.0611
.453	.1271	.1122	.0979	.0636
.540	.1298	.1144	.1004	.0652
.647	.1332	.1178	.1039	.0686
.759	.1387	.1229	.1093	.0745
.869	.1426	.1279	.1177	.0799
1.000	.1698	.1568	.1520	.1098

MONTMORILLONITE DERIVATIVES

HEPTANE 30°C

	$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$	$\overset{+}{N}H_3(CH_2)_6\overset{+}{N}H_3$	$\overset{+}{N}H_3(CH_2)_8\overset{+}{N}H_3$	$\overset{+}{N}H_3(CH_2)_{10}\overset{+}{N}H_3$
p/p_o	x	x	x	x
.015	.0485	.0461	.0339	.0257
.038	.0513	.0491	.0379	.0280
.107	.0539	.0523	.0402	.0306
.154	.0560	.0542	.0421	.0321
.250	.0578	.0558	.0466	.0339
.318	.0586	.0569	.0452	.0347
.409	.0600	.0584	.0468	.0357
.476	.0610	.0597	.0480	.0369
.559	.0633	.0613	.0501	.0389
.660	.0649	.0634	.0515	.0404
.763	.0679	.0661	.0543	.0433
.884	.0765	.0739	.0621	.0508
.998	.1004	.0987	.0859	.0811
.922	.0908	.0871	.0742	.0661
.829	.0841	.0806	.0683	.0571
.728	.0781	.0749	.0622	.0505
.672	.0746	.0718	.0575	.0483
.582	.0706	.0686	.0557	.0460
.442	.0669	.0648	.0521	.0428
.371	.0659	.0620	.0511	.0415
.331	.0644	.0596	.0490	.0390
.223	.0596	.0563	.0448	.0360
.100	.0571	.0536	.0424	.0338
.022	.0531	.0485	.0372	.0299
40°C				
.002	.0439	.0421	.0334	.0201
.032	.0506	.0500	.0404	.0257
.053	.0519	.0514	.0418	.0270
.093	.0535	.0533	.0436	.0290
.132	.0543	.0543	.0447	.0305
.182	.0556	.0554	.0461	.0319
.243	.0571	.0569	.0472	.0331
.299	.0578	.0578	.0484	.0338
.375	.0590	.0588	.0491	.0349
.457	.0607	.0601	.0507	.0360
.565	.0619	.0620	.0526	.0370
.654	.0634	.0638	.0548	.0391
.743	.0667	.0662	.0580	.0413
.849	.0702	.0709	.0616	.0454
.949	.0843	.0833	.0742	.0582
.996	.1059	.0988	.0988	.0799
.960	.0947	.0911	.0832	.0692
.862	.0834	.0829	.0727	.0572
.766	.0778	.0772	.0669	.0508

contd

40°C (contd.)				
.663	.0718	.0724	.0618	.0465
.576	.0690	.0692	.0594	.0441
.470	.0659	.0664	.0572	.0415
.410	.0649	.0651	.0555	.0407
.301	.0599	.0588	.0496	.0358
.271	.0591	.0585	.0492	.0355
.111	.0557	.0547	.0453	.0324
.010	.0503	.0469	.0380	.0273
50°C				
.007	.0451	.0431	.0360	.0233
.023	.0491	.0476	.0404	.0267
.066	.0517	.0515	.0440	.0297
.136	.0537	.0535	.0455	.0315
.211	.0548	.0553	.0475	.0327
.264	.0565	.0565	.0487	.0333
.360	.0575	.0577	.0499	.0345
.441	.0587	.0589	.0513	.0352
.538	.0605	.0605	.0531	.0371
.646	.0622	.0625	.0551	.0389
.750	.0648	.0647	.0582	.0406
.848	.0684	.0683	.0613	.0439
.950	.0824	.1769	.0741	.0526
1.000	.1040	.0875	.0969	.0658
60°C				
.006	.0430	.0434	.0379	.0224
.026	.0471	.0481	.0423	.0263
.078	.0503	.0519	.0457	.0292
.125	.0524	.0537	.0472	.0306
.189	.0536	.0554	.0499	.0322
.269	.0556	.0568	.0507	.0332
.373	.0571	.0588	.0523	.0349
.463	.0586	.0598	.0537	.0362
.542	.0596	.0610	.0553	.0368
.629	.0608	.0630	.0570	.0381
.713	.0635	.0646	.0592	.0401
.812	.0656	.0679	.0612	.0426
.912	.0725	.0753	.0683	.0499
.999	.0979	.1066	.0917	.0938
.910	.0885	.0851	.0770	.0614
.818	.0761	.0787	.0711	.0530
.715	.0700	.0729	.0658	.0472
.620	.0671	.0689	.0630	.0437
.523	.0652	.0662	.0607	.0422
.422	.0633	.0636	.0577	.0398
.359	.0590	.0596	.0545	.0359
.348	.0585	.0593	.0533	.0359
.292	.0578	.0580	.0511	.0347
.203	.0561	.0562	.0501	.0334
.092	.0536	.0533	.0468	.0314
.026	.0492	.0485	.0416	.0276

MONTMORILLONITE DERIVATIVES

1:3 Propane diamine. 40°C

	$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$	$\overset{+}{N}H_3(CH_2)_6\overset{+}{N}H_3$	$\overset{+}{N}H_3(CH_2)_8\overset{+}{N}H_3$	$\overset{+}{N}H_3(CH_2)_{10}\overset{+}{N}H_3$
p/p_o	x	x	x	x
.020	.0548	.0472	.0438	.0417
.035	.0644	.0584	.0524	.0477
.061	.0731	.0675	.0645	.0589
.089	.0757	.0707	.0686	.0659
.133	.0816	.0764	.0770	.0837
.199	.0870	.0821	.0867	.1014
.254	.0914	.0862	.0946	.1115
.363	.0990	.0935	.1060	.1261
.440	.1040	.1003	.1150	.1379
.566	.1105	.1086	.1274	.1514
.638	.1162	.1152	.1379	.1632
.727	.1232	.1235	.1510	.1781
.815	.1366	.1374	.1772	.2073
.931	.1660	.1735	.2499	.2949
.964	.1824	.1941	.2920	.3406
.984	.1955	.2096	.3156	.3718
.987	.1999	.2181	.3359	.3911
.998	.2132	.2282	.3492	.4136
.973	.2011	.2137	.3469	.4046
.910	.1580	.1570	.2028	.2573
.832	.1454	.1428	.1718	.2172
.780	.1401	.1379	.1588	.2015
.651	.1313	.1290	.1446	.1810
.558	.1258	.1232	.1363	.1689
.470	.1205	.1175	.1290	.1608
.385	.1162	.1124	.1224	.1528
.347	.1136	.1096	.1189	.1483
.277	.1099	.1053	.1138	.1420
.226	.1035	.0989	.1059	.1332
.152	.1000	.0948	.0986	.1266
.099	.0952	.0902	.0918	.1204
.071	.0914	.0856	.0842	.1134
.032	.$_8$51	.0781	.0751	.1042
.003	.0768	.0713	.0654	.0904

BEN-U-GEL DERIVATIVES

Nitrogen isotherms

Na^+	78°K
p/p_0	v
.001	10.90
.006	15.16
.032	18.16
.052	19.16
.071	19.94
.109	21.31
.148	22.17
.88	23.03
.224	23.75
.265	24.46
.298	25.11
.393	26.73
.485	28.16
.560	29.25
.632	30.26

$\overset{+}{N}H_3(CH_2)_2\overset{+}{N}H_3$	78°K
.014	59.41
.042	63.66
.061	65.37
.077	66.62
.143	69.67
.189	71.21
.238	72.57
.325	74.95
.475	77.09
.582	78.62
.667	80.08
.744	81.50
.927	88.39
.950	90.37
.994	99.72

$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$	78°K
.001	48.42
.012	55.90
.034	59.41
.055	61.40
.070	62.46
.108	64.49
.144	66.21
.190	67.67
.237	68.92
.279	69.86
.322	70.77
.366	71.60
.478	73.28
.581	74.75
.767	77.96
.853	80.36
.907	82.43
.969	91.13
1.000	101.07
.953	93.12
.858	88.94
.715	85.92
.545	83.69
.501	79.36
.473	74.69
.405	72.55
.317	70.98
.219	68.81

$\overset{+}{N}H_3(CH_2)_4\overset{+}{N}H_3$	78°K
.001	53.22
.016	63.12
.057	67.79
.071	68.96
.085	69.83
.110	71.13
.152	72.79
.200	74.25
.247	75.44
.289	76.32
.332	77.14
.384	78.03
.500	79.21
.602	80.76
.683	81.86
.761	82.68
.854	83.54
1.000	102.25
.832	87.14
.698	86.33
.544	85.45
.512	83.02
.474	79.69
.413	78.49
.338	76.99
.257	75.71

$\overset{+}{N}H_3(CH_2)_5\overset{+}{N}H_3$	78°K	$\overset{+}{N}H_3(CH_2)_{12}\overset{+}{N}H_3$	78°K
.001	47.88	.026	11.92
.004	52.69	.041	13.03
.011	55.93	.070	15.08
.032	59.67	.094	16.10
.062	62.61	.120	17.07
.094	64.75	.168	18.72
.124	66.33	.192	19.45
.155	67.52	.260	20.73
.217	69.29	.326	22.55
.260	70.35	.385	23.55
.346	72.03	.446	24.78
.431	73.41	.506	26.01
.503	74.32	.564	27.08
.573	75.21	.647	28.44
.713	76.82	.728	29.56

$\overset{+}{N}H_3(CH_2)_9\overset{+}{N}H_3$	78°K
.005	44.86
.026	50.28
.037	51.94
.047	53.02
.070	55.58
.114	58.38
.155	60.47
.202	62.23
.269	64.46
.336	66.11
.394	67.41
.453	68.57
.554	70.39
.633	71.80

ARGON

Ben-u-Gel Derivatives

Na^+	78°K	$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$	78°K
.005	14.34	.001	44.50
.015	20.20	.003	49.74
.046	25.19	.011	56.28
.056	26.22	.069	66.75
.093	28.76	.103	70.03
.143	31.05	.165	73.29
.210	33.45	.250	76.82
.262	35.07	.303	78.43
.312	36.46	.351	79.50
.353	37.57	.389	80.75
.394	38.63	.479	82.19
.522	41.69	.593	84.43
.617	44.53	.703	86.36
.689	46.66	.783	87.91
.752	48.84	.862	89.41
.827	51.51	.963	94.84
.937	62.11	.996	103.32
.969	70.16	1.000	111.16
.984	76.17	.983	104.24
.993	81.03	.868	97.24
1.000	95.54	.788	94.79
.949	75.16	.634	91.84
.829	65.94	.518	90.14
.788	64.34	.418	88.18
.642	59.93	.373	87.24
.543	57.32	.366	86.03
.439	53.81	.363	84.44
.394	52.52	.353	81.99
.372	50.99	.326	79.68
.369	48.63	.305	78.57
.358	45.06	.266	77.21
.331	40.28	.198	74.78
.318	38.68		
.298	37.51		
.231	34.62		

$\overset{+}{N}H_3(CH_2)_5\overset{+}{N}H_3$	78°K
.001	41.38
.003	50.22
.010	58.48
.025	63.43
.040	66.36
.059	68.72
.080	70.78
.110	73.21
.146	75.33
.172	76.61
.239	79.33
.296	81.20
.397	84.01
.509	86.41
.656	89.05
.797	91.42
.904	93.67
.968	96.79
.996	101.36
1.000	112.88
.980	101.76
.828	98.10
.631	95.83
.547	94.93
.401	93.06
.370	90.06
.367	89.51
.355	87.94
.313	83.46
.262	80.89
Repeat	
.944	95.60
.998	111.51
.628	94.65
.402	92.05
.368	90.44
.350	87.19
.311	84.29
.260	80.77
.205	78.60

$\overset{+}{N}H_3(CH_2)_9\overset{+}{N}H_3$	78°K
.002	39.83
.008	47.96
.031	55.22
.069	60.50
.086	62.13
.122	65.18
.174	68.53
.237	72.00
.291	74.20
.382	77.32
.473	79.86
.604	82.88
.728	85.48
.832	87.61
.928	89.76
.984	91.87
.999	109.49
1.000	127.85
.961	93.45
.882	91.94
.769	90.65
.657	89.25
.516	88.12
.388	86.54
.374	85.39
.359	83.73
.350	81.50
.327	78.49
.278	75.32
.256	73.33

ACETONITRILE ON BEN-U-GEL

	$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$	$\overset{+}{N}H_3(CH_2)_5\overset{+}{N}H_3$	$\overset{+}{N}H_3(CH_2)_9\overset{+}{N}H_3$	$\overset{+}{N}H_3(CH_2)_{12}\overset{+}{N}H_3$
p/p_o	x	x	x	x
.001	.0258	.0295	.0286	.0054
.019	.0671	.0604	.0547	.0232
.053	.0776	.0688	.0638	.0300
.079	.0822	.0729	.0674	.0334
.127	.0898	.0798	.0738	.0390
.176	.0953	.0855	.0792	.0436
.234	.1012	.0921	.0860	.0500
.305	.1083	.0990	.0925	.0566
.404	.1181	.1067	.1018	.0640
.535	.1325	.1178	.1138	.0774
.646	.1480	.1291	.1261	.0936
.749	.1646	.1409	.1409	.1083
.842	.1904	.1574	.1660	.1303
.922	.2386	.1810	.2234	.1611
1.000	.2954	.2245	.2936	.2189
,948	.2598	.2136	.2466	.1988
.841	.2295	.1937	.2140	.1698
.732	.2079	.1788	.1910	.1452
.619	.1899	.1664	.1702	.1254
.519	.1716	.1493	.1480	.1034
.406	.1519	.1328	.1243	.0872
.297	.1289	.1133	.1013	.0713
.211	.1100	.1002	.0874	.0597
,096	.0904	.0828	.0711	.0449
.026	.0742	.0685	.0587	.0328

BENZENE

Ben-U-Gel Derivatives

60°C

p/p_0	$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$ x	$\overset{+}{N}H_3(CH_2)_5\overset{+}{N}H_3$ x	$\overset{+}{N}H_3(CH_2)_9\overset{+}{N}H_3$ x	$\overset{+}{N}H_3(CH_2)_{12}\overset{+}{N}H_3$ x
.001	.0288	.0162	.0168	.0041
.011	.0933	.0852	.0692	.0130
.026	.1074	.1010	.0845	.0192
.048	.1184	.1107	.0952	.0254
.113	.339	.1258	.1096	.0356
.183	.1423	.1330	.1177	.0409
.244	.1482	.1378	.1245	.0451
.333	.1559	.1438	.1316	.0505
.358	.1567	.1438	.1317	.0506
.456	.1633	.1491	.1390	.0559
.572	.1698	.1546	.1462	.0611
.677	.1751	.1603	.1532	.0675
.778	.1813	.1650	.1594	.0726
.878	.1887	.1714	.1670	.0804
.961	.2003	.1782	.1763	.0900
.995	.2153	.1861	.2014	.1022
.899	.2046	.1818	.1796	.0976
.842	.2005	.1801	.1764	.0954
.772	.1961	.1780	.1722	.0929
.690	.1922	.1747	.1682	.0899
.576	.1856	.1715	.1619	.0863
.464	.1790	.1662	.1554	.0812
.386	.1696	.1545	.1436	.0635
.367	.1668	.1534	.1412	.0616
.318	.1623	.1494	.1374	.0586
.282	.1592	.1468	.1342	.0560
.205	.1536	.1424	.1271	.0520
.065	.1314	.1263	.1077	.0391

40°C

.009	.0878	.0891	.0732	.0142
.047	.1107	.1140	.0994	.0283
.124	.1252.	.1275	.1162	.0380
.195	.1345	.1353	.1257	.0444
.255	.1410	.1397	.1308	.0480
.363	.1485	.1455	.1403	.0547
.467	.1541	.1505	.1458	.0595
.565	.1596	.1556	.1533	.0648
.683	.1643	.1601	.1593	.0699
.773	.1709	.1640	.1650	.0740
.867	.1799	.1699	.1742	.0808
1.0000	.2547	.2013	.2579	.1213
.912	.1994	.1796	.1895	.0970
.798	.1863	.1768	.1778	.0938
.659	.1797	.1739	.1723	.0906
.528	.1743	.1716	.1670	.0871
.444	.1701	.1687	.1626	.0843
.411	.1673	.1662	.1596	.0818
.399	.1654	.1647	.1576	.0806
.352	.1631	.1627	.1548	.0769
.292	.1523	.1515	.1429	.0605
.229	.1464	.1462	.1355	.0560
.110	.1336	.1345	.1213	.0464
.045	.1192	.1233	.1072	.0385

50°C

.001	.0488	.0183		.0047
.004	.0904	.0606		.0090
.009	.1080	.0818		.0130
.021	.1216	.0989		.0189
.041	.1267	.1094		.0248
.070	.1353	.1181		.0301
.126	.1458	.1278		.0364
.179	.1527	.1340		.0406
.214	.1576	.1381		.0450
.276	.1611	.1419		.0482
.343	.1659	.1450		.0515
.414	.1722	.1507		.0572
.518	.1783	.1566		.0626
.597	.1819	.1600		.0662
.712	.1886	.1652		.0718
.827	.1956	.1713		.0776
.922	.2066	.1801		.0866
.948	.2106	.1829		.0907
.953	.2128	.1849		.0929
.999	.2249	.1913		.1022