180. *Sorption of Mixtures, and Selectivity in Alkylammonium Montmorillonites. Part II.*[1] *Tetramethylammonium Montmorillonite.*

By R. M. Barrer and G. S. Perry.

The sorption of various mixtures of pairs of hydrocarbons of different structural types has been examined in tetramethylammonium montmorillonite. Selectivities vary with the total amount sorbed, the composition of the feed mixtures, and the temperature, and for hydrocarbon pairs of appropriate type can become very large. The affinity decreases in the sequence benzene > n-heptane, n-hexane > cyclohexane > iso-octane. The influence has been studied of varying amounts of these hydrocarbons upon the *c*-spacing of the clay. All the hydrocarbons are intercalated, and in order to explain the selectivities, sorption capacities of the clay and orientations of interlamellar sorbate, not only the intersheet spacing and molecular configuration, but also the distances between the interlamellar organic ions must be taken into account.

Two previous investigations have been made of the intercalation of single sorbates by tetramethylammonium montmorillonite. They have indicated that this sorbent exhibits pronounced selectivities,[2,3] and in consequence excellent separations of various mixtures of organic molecules have been demonstrated.[4] In the present research sorption of mixtures has been investigated to correlate the separations with equilibrium studies, and to determine and interpret selectivities. Steric factors involving interlayer separation in the sorbent, and molecular size and configuration in the sorbate, play important rôles in the ability of the clay to occlude various species. A comparison of these with corresponding factors observed in Part I[1] for monomethylammonium montmorillonite is of particular interest. In the latter sorbent true molecular sieve separations were observed for several categories of mixture, the differences in selectivity depending upon the exclusion of one component from the interlamellar pore space of the sorbent.

Experimental.—The apparatus, sorbates, and *X*-ray procedures have been described in Part I.[1] The tetramethylammonium montmorillonite was taken from a sample previously employed.[4] The parent clay was a Wyoming bentonite.

Results and Discussion

c-*Spacings.*—The basal spacing of outgassed NMe_4^+-montmorillonite was 13·6 Å, increasing to 13·9 Å in the presence of saturated water vapour, corresponding to intersheet distances of 4·2 and 4·5 Å, respectively. Figs. 1*a* and *b* give the *c*-spacings for the clay crystals equilibrated at various relative pressures and amounts sorbed, for benzene, cyclohexane, n-heptane, iso-octane, and n-perfluoroheptane.

Benzene expands the *c*-spacing to 14·6 Å even at relative pressures as low as 0·05, the spacing being thereafter unchanged up to saturation.[3] There is no evidence that a threshold pressure must be exceeded before penetration occurs, as was the case with $CH_3{\cdot}NH_3^+$-montmorillonite (Part I). Once penetration occurs the spacing for the monomethylammonium clay approaches, with increasing sorption, the slightly larger spacing of 15·0 Å. The intersheet distances in the two sorbents are thus 5·2 and 5·6 Å, respectively, and in both sorbents are considered to be associated with vertically oriented benzene monolayers between the aluminosilicate layers.[3] The intersheet distance reflects the

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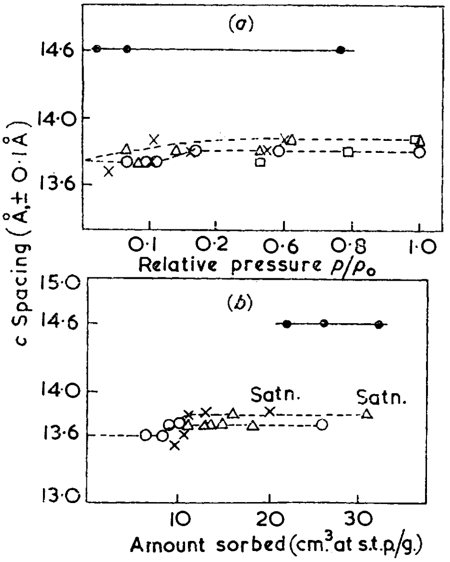
[1] Part I, Barrer and Perry, preceding paper.
[2] Barrer and MacLeod, *Trans. Faraday Soc.*, 1955, **51**, 1290.
[3] Barrer and Reay, *Trans. Faraday Soc.*, 1957, **53**, 1253.
[4] Barrer and Hampton, *Trans. Faraday Soc.*, 1957, **53**, 1462.

apparent contraction in over-all van der Waals dimensions of intercalated molecules,[3, 5-7] associated with keying of atoms of the molecule into the rather open hexagonal networks of the aluminosilicate sheets, or with some compression of the sorbed molecules[3] (see also below).

n-Heptane expands the *c*-spacing of tetramethylammonium montmorillonite from 13·6 to 13·8 Å, the intersheet distance then being 4·4 Å. This contrasts with the behaviour of the monomethylammonium clay, which expanded only to 13·0 Å (Part I), the intersheet distance being 3·6 Å. Two inter-lamellar arrangements of n-alkane chains are possible, which are shown schematically in Figs. 2*a* and *b*. In the first the zig-zag of the n-alkane chain lies parallel to the aluminosilicate layers, the chain thickness normal to the plane of the zig-zag being ~4·0 Å.[8] In the second arrangement this zig-zag lies in a plane normal to the lamellæ, and the chain thickness is 4·9 Å (Figs. 2*b* and *c*). These two orientations are compatible with the spacings found in the monomethylammonium and tetramethylammonium forms of the clay respectively. The contractions from 4·0 to 3·6 Å and from 4·9 to 4·4 Å in the two sorbents are in line with the apparent contractions in van der Waals dimensions referred to.

FIG. 1.

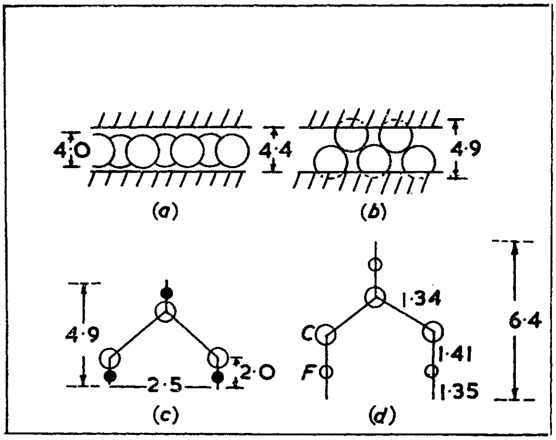


(*a*) c-*Spacings at room temperature for sorbates at various equilibrium relative pressures.*

(*b*) c-*Spacings at room temperature for sorbates as functions of amounts sorbed.*

● *Benzene*; ○ *iso-octane*; × *heptane*; △ *cyclohexane*; □ *perfluoroheptane.*

FIG. 2.



(*a*) *and* (*b*) *The flat and vertical orientations of the zig-zag of n-alkane chains in relation to the free distance between sheets in* NMe_4*-montmorillonite.*

(*c*) *and* (*d*) *Dimensions of the zig-zag in a n-alkane and a n-perfluorocarbon respectively.*

The minimum height of the tetramethylammonium ion is 4·9 Å, and the actual intersheet distance in the corresponding ion-exchanged clay (13·6 Å) gives 4·2 Å as intersheet distance, the contraction due to keying of hydrogen atoms into the aluminosilicate sheets or to compression being then 0·7 Å. The chair model of cyclohexane also has a minimum height of 4·9 Å, while that of iso-octane (2,2,4-trimethylpentane) is 5·0 Å. Accordingly, both these sorbates might be expected to produce little expansion when intercalated by

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[5] Bradley, *J. Amer. Chem. Soc.*, 1945, **67**, 975.

[6] Greene-Kelly, *Trans. Faraday Soc.*, 1955, **51**, 412.

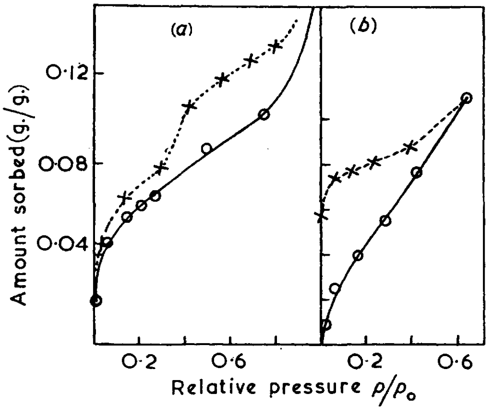
[7] Talibudeen, *Trans. Faraday Soc.*, 1955, **51**, 582.

[8] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 1941, p. 189.

the tetramethylammonium clay. Indeed, Figs. 1*a* and *b* show that this is the case, the expansion being if anything less than for n-heptane. The thickness of the cyclohexene molecule is ~4·6 Å, and it was also observed that a sample of the clay saturated with this sorbate gave *c*-spacings of 13·7 Å, the intersheet distance being ~4·3 Å. This small expansion, together with the substantial sorption (Fig. 3*a*), is evidence of penetration between the aluminosilicate layers. Like benzene, other hydrocarbons such as n-heptane and cyclohexane give, on the above evidence, variously oriented monolayers within the clay, and in admixture with the organic ions.

n-Perfluoroheptane was the only one of the sorbates investigated here which failed to penetrate. The height of the zig-zag of the n-perfluoroheptane chain in the interlamellar orientation of Fig. 2*b* would be 6·4 Å (Fig. 2*d*). In the orientation of Fig. 2*a* this height would be 5·5 Å. In long-chain n-perfluorocarbons, however, the simple zig-zag may, for steric reasons, be replaced by a helix which could have a considerable diameter [9] (~5·9 Å). In any case a substantial expansion of the clay would be necessary if intercalation occurred, which is certainly not observed (Fig. 1*a*). This, coupled with the small sorption (Table 1), indicates negligible interlamellar penetration. Some of this sorption may be due to impurities in the n-perfluoroheptane, accounting for the slight expansion at high relative pressures.

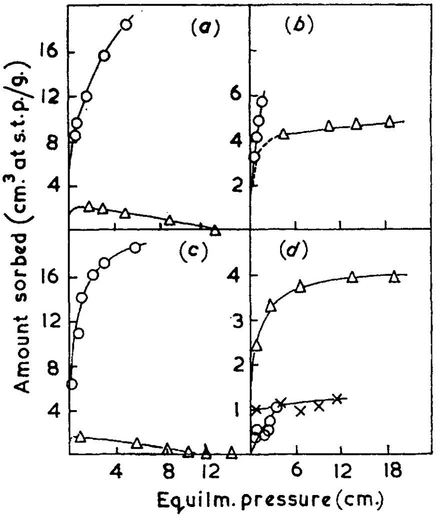
FIG. 3.



Isotherms at 60° *for cyclohexene on* (*a*) NMe_4-*montmorillonite and* (*b*) *the parent* Ca-*clay from which the alkylammonium clay was prepared.*

○ = *Adsorption,* × = *desorption.*

FIG. 4.



(*a*) *and* (*b*) *Isotherms for benzene* (○) *and heptane* (△) *from two mixtures;* (*a*) 0·67, (*b*) 0·30 *mol. fraction of benzene.*

(*c*) *Isotherms for benzene* (○) *and cyclohexane* (△) *from a mixture;* 0·67 *mol. fraction of benzene.*

(*d*) *Cyclohexane isotherms from several mixtures with n-heptane; mol. fraction of n-heptane:* ○ 0·85, × 0·56, △ 0·16.

(*All isotherms refer to* 80°.)

Isotherms of Single Sorbates.—The isotherms of most single sorbates may be considered, when necessary, in connection with the isotherms of their binary mixtures (see below). The B.E.T. monolayer equivalents, v_m, are summarised in Table 1 as obtained in the

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[9] Bunn, *Nature*, 1954, **174**, 549.

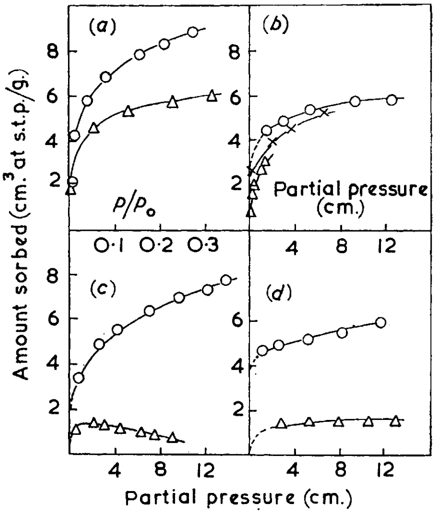
TABLE 1. *Monolayer equivalents (cm.^{3} at s.t.p./g. outgassed weight).*

Sorbate	v_m values This work	 Ref. 10	Area of sorbate molecule * (Å^2)	Equiv. monolayer area (m.^{2}/g.) (this work)
Benzene	21·2	25·0	25	143
Cyclohexane	6·8	11·3 [11]	46	84
Cyclohexene	7·7	—	43	89
n-Heptane	6·4	9·2	51	88
n-Hexane	6·7	—	44	79
Iso-octane	4·7	6·9	52	65
n-Perfluoroheptane	2·6	—	78 †	54

* Estimated from Courtauld models. † Calc. for zig-zag chain form.

present and in earlier work.[10,11] The B.E.T. method, for sorption which is partly interlamellar and partly associated with uptake upon external surfaces, has substantial limitations,[3] and the molecular areas are also approximate. The most accurate v_m value and equivalent monolayer area are those for benzene, but the above uncertainties make the actual isotherms the best measure of the considerable capacity of the sorbent.

FIG. 5.



(*a*) *Cyclohexane* (○) *and n-heptane* (△) *isotherms for each pure sorbate.*

(*b*) *n-Heptane isotherms from several mixtures with cyclohexane*; *mol. fractions of n-heptane*: ○ 0·85, × 0·56, △ 0·16.

(*c*) *Isotherms for cyclohexane* (○) *and iso-octane* (△) *in a mixture*; 0·70 *mol. fraction of cyclohexane.*

(*d*) *Isotherms for n-hexane* (○) *and iso-octane* (△) *in a mixture*; 0·55 *mol. fraction of hexane.*

(*All isotherms refer to* 80°.)

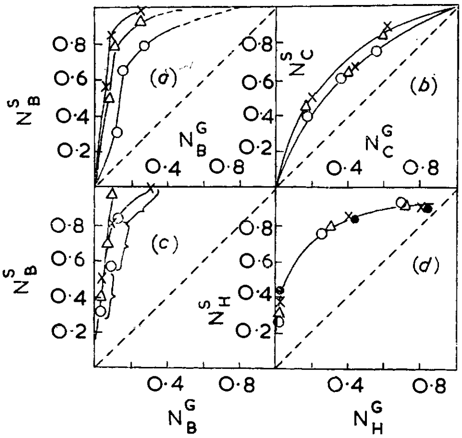


FIG. 6. *Equilibrium composition diagrams for* 80° *at various total pressures for* (*a*) *benzene in mixtures with n-heptane,* (*b*) *cyclohexane in mixtures with iso-octane,* (*c*) *benzene in mixtures with cyclohexane, and* (*d*) *heptane in mixtures with cyclohexane.*

Total pressures (cm.): (*a*) ○ 2·5, △ 10·0, × 15·0; (*b*) ○ 2·5, △ 10·0, × 20·0; (*c*) ○ 2·5, △ 10, × 20; (*d*) ○ 2·5, △ 5·0, × 10·0, ● 20·0.

For individual points on the curves, mol. fractions of the first-named constituents in the initial mixtures were, reading upwards: (*a*) 0·30, 0·50, 0·67; (*b*) 0·30, 0·52, 0·70; (*c*; *in triads*) 0·16, 0·47, 0·67; (*d*; *in groups of four*) 0·16, 0·56, 0·85.

The uptake of cyclohexene (Fig. 3*a*) was free from the chemical side-reaction noted with the methylammonium clay, but was associated with an extended hysteresis involving lattice expansion. The isotherm is closer to that of cyclohexane than of benzene. The sample of tetramethylammonium montmorillonite was prepared from a Ca-montmorillonite * having a substantially larger external surface area than the Wyoming bentonite

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* Kindly supplied by Fuller's Earth Union, Redhill.

[10] MacLeod, Ph.D. Thesis, Aberdeen, 1955.

[11] Reay, Ph.D. Thesis, London, 1956.

used as parent material for all other alkylammonium clays of this paper and of Part I. An augmented uptake of cyclohexene gave an equivalent monolayer area of ~205 m.^{2}/g. The parent clay gave the unusual isotherm of Fig. 3*b*, where however a chemical reaction may be occurring (cf. Part I). v_m for cyclohexene in Table 1 refers to an isotherm at 80° on NMe_4-montmorillonite derived from the Wyoming bentonite, and by which cyclohexene was less copiously sorbed.

Mixture Isotherms.—Isotherms of mixtures were measured at 80° C over a range of compositions for the following systems: Benzene–n-heptane (0·67, 0·50, 0·30), benzene–cyclohexane (0·67, 0·47, 0·24), n-heptane–cyclohexane (0·85, 0·56, 0·16), cyclohexane–iso-octane (0·70, 0·52, 0·30), n-hexane–iso-octane (0·70, 0·55, 0·23). The figures in parentheses refer to the constant mol. fraction of the first-mentioned component in the feed mixture. In addition, the benzene–n-heptane mixture having a mol. fraction of benzene of 0·67 was studied at 85°, 90°, and 95°. In Figs. 4 and 5 are presented some of the partial isotherms obtained at 80°.

(a) *Benzene–n-heptane.* Benzene is selectively sorbed for all the compositions of feed mixtures studied, and as the sorption of benzene increases, n-heptane is progressively displaced from the sorbent, until a position is reached in certain mixtures in which the sorbed phase is virtually pure benzene (*e.g.*, Fig. 4*a*). Similar but less complete displacements have also been reported for binary mixtures of permanent and noble gases occluded by zeolites.[12] In tetramethylammonium montmorillonite the enrichment factor can be extremely large under certain conditions. There is no evidence of the formation of the " adsorption azeotrope " observed for this mixture in the monomethylammonium clay (Part I), in comparison with which the selectivity towards benzene is much enhanced.

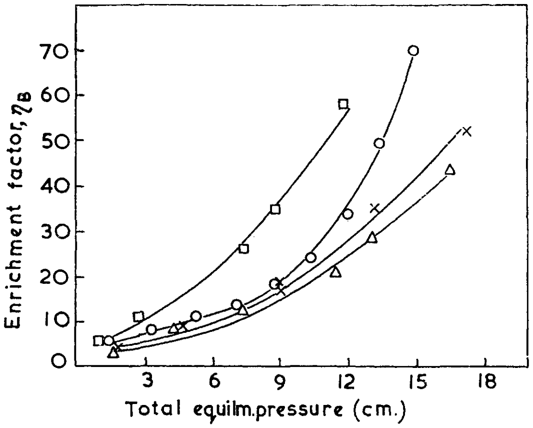


FIG. 7. *Enrichment factors as functions of pressure and temperature for benzene in a benzene–n-heptane mixture.*

□, 80°; ○ 85°; × 90; △ 95° c.

(b) *Benzene-cyclohexane.* This pair behaves very similarly to the benzene–n-heptane mixtures, the cyclohexane being, under appropriate conditions and for appropriate compositions, completely displaced from the sorbent (Fig. 4*c*), so that then the enrichment factor for benzene becomes as before indefinitely large. High selectivities to benzene were observed also with the monomethylammonium clay (Part I).

(c) *n-Heptane–cyclohexane.* The isotherms of the pure single sorbates (Fig. 5*a*) show that more cyclohexane than n-heptane is taken up at a given relative pressure. Nevertheless, the affinity of the n-heptane for the clay is superior to that of cyclohexane, as is demonstrated by the partial isotherms of each species shown in Figs. 4*d* and 5*b*. In competitive sorption, the uptake of n-heptane is affected much less by presence of cyclohexane than conversely, and the adsorbed phase is much enriched in n-heptane. The separation is again in the direction observed for the monomethylammonium clay (Part I).

[12] Barrer and Robins, *Trans. Faraday Soc.*, 1953, **49**, 929.

(d) *n-Hexane–iso-octane and cyclohexane–iso-octane.* In both these mixtures the first-mentioned component was always selectively sorbed (*e.g.*, Figs. 5*c* and 5*d*). The good separation of hexane from iso-octane [4] is reflected in the enrichment factor, which varied from 9·5 to 4·7 for the feed mixture having a mole fraction of 0·55 of n-hexane.

Selectivity.—The mixture isotherms can be further interpreted in terms of enrichment factors (or selectivity coefficients), η, defined for component A in a mixture of A and B by (Part I):

$$\eta_{\mathrm{A}} = \frac{N_{\mathrm{A}}^{\mathrm{S}}}{N_{\mathrm{B}}^{\mathrm{S}}} \cdot \frac{N_{\mathrm{A}}^{\mathrm{G}}}{N_{\mathrm{B}}^{\mathrm{G}}} = \frac{N_{\mathrm{A}}^{\mathrm{S}}}{N_{\mathrm{B}}^{\mathrm{S}}} \cdot \frac{p_{\mathrm{A}}}{p_{\mathrm{B}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where N's denote mol. fractions and the superscripts " S " and " G " denote " sorbed phase " and " gas (or vapour) phase " respectively. The enrichments for component A can be usefully presented in the form of curves of $N_{\mathrm{A}}^{\mathrm{S}}$ *vs* $N_{\mathrm{A}}^{\mathrm{G}}$, as in Fig. 6. In this Figure the subscripts " B," " C," and " H " denote respectively benzene, cyclohexane, and n-heptane. The results of the preceding section and Fig. 6, and corresponding data for the monomethylammonium clay (Part I), may now be compared. First, in the tetramethylammonium clay the affinity sequence can be written as:

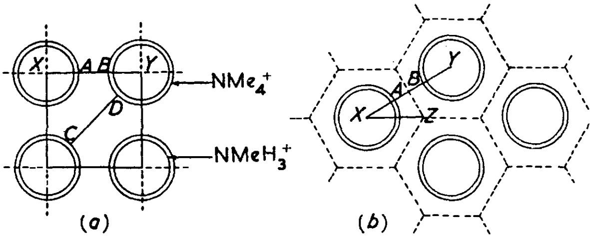


FIG. 8. (*a*) *and* (*b*) *The square and hexagonal arrays of alkylammonium ions considered in relation to inter-ion spacing, showing free distances of importance.*

benzene > n-heptane, n-hexane > cyclohexane > iso-octane

which to some extent can no doubt be regarded as representative of the corresponding classes of hydrocarbon. For separations of simple aromatic compounds from n-alkanes this sorbent is to be preferred to the monomethylammonium clay. In separations of aromatic compounds from simple naphthenes both sorbents should be effective, but the tetramethylammonium form can give larger coefficients, η_{B}, under appropriate conditions. In separations of n-alkanes such as heptane or hexane from simple cycloalkanes both sorbents can be effective and the evidence is that the monomethylammonium clay might be especially good. For separating straight- from branched-chain paraffins (*e.g.*, n-heptane or n-hexane from iso-octane) both sorbents could be effective, but for the cyclohexane–iso-octane pair only the tetramethylammonium clay offers a reasonable enrichment combined with moderate sorptive capacity.

Inspection of Figs. 6 and 7 shows that the enrichment factors can depend strongly on the total pressures, and so on amount sorbed, as well as on the composition of the feed mixture, so that choice of the correct range of physical operating conditions can be important. Enrichments also depend upon temperature, as is shown for benzene–heptane mixtures in Fig. 7. Better enrichments are here clearly obtained at lower temperatures, and also for higher pressures or larger amounts sorbed (excluding the region where capillary condensation in spaces between clay crystallites can occur). The temperature-dependence of the enrichment factors is in accord with the results of other workers,[13,14] and could be anticipated from simple theories of the adsorption process.

Interlamellar Cations.—(a) *Complete ion exchange.* The interplay of steric and other factors determining selective sorption by expanded montmorillonites has been discussed

[13] Reeds and Kammermeyer, *Ind. Eng. Chem.*, 1959, **51**, 1707.

[14] Benedek and Szepesy, *Acta Chim. Acad. Sci. Hungary*, 1958, **14**, 31.

with considerable success in terms of intersheet spacing and molecular shape and dimensions,[2,3,4,15,16] but less attention has been given to the importance of lateral distances between the organic ions located between the aluminosilicate layers. Thus, for a series of hydrocarbon molecules all of which can penetrate into the interlamellar spaces we have demonstrated that profound differences in selectivity are still found. The question arises as to whether such differences do not originate at least in part from *lateral* interionic spacings.

That ion size can largely determine the interlamellar sorptive capacity of a given expanded clay sorbent has been very well shown in the case of tetramethyl- and tetraethyl-ammonium montmorillonite.[2] The capacity for sorbing benzene is about three times as large for the former as for the latter, although after imbibing this molecule each clay should show practically the same intersheet distance. The more bulky NEt_4^+ ion fills much more of the intersheet pore volume than does the NMe_4^+ ion. Calculations were then made of the extent of the available intersheet areas when organic ions of different dimensions replace completely the small inorganic ions of the parent clay.[3,15] Although this approach gave qualitative agreement with experiment, the observed intersheet areas were normally less than those calculated. We therefore now propose to consider the actual free distances between organic ions in relation to the molecular dimensions of sorbates.

FIG. 9*a*. *Possible orientations of non-rotating tetramethylammonium ions in a regular array on the hexagonal oxygen network of the clay, showing resultant variable free distances between ions.*

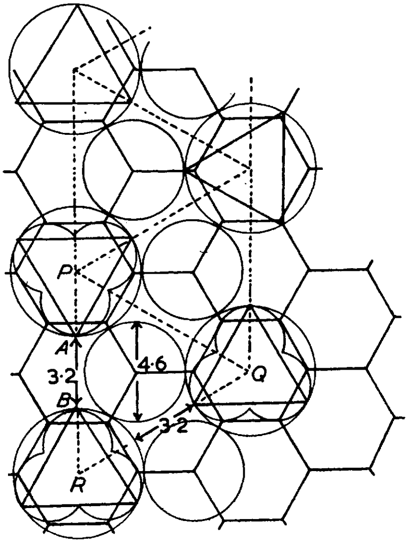
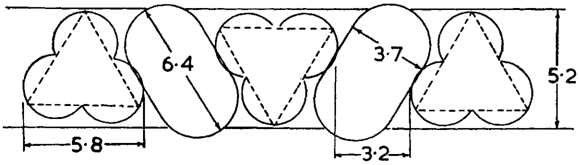


FIG. 9*b*. *Interlamellar orientation suggested for benzene molecules between tetrahedral* NMe_4^+ *ions.*



Square and hexagonal arrays of interlamellar cations were considered (Fig. 8). In the square array two free distances *AB* and *CD* can be considered, and one distance *XY* between ionic centres. In the hexagonal array one free distance *AB* and one distance *XY* are required. We accept for the calculations Ross and Hendricks's idealised formula[17] for the unit cell content of outgassed montmorillonite: $[Si_8Al_{3\cdot33}Mg_{0\cdot67}O_{20}(OH)_4]M_{0\cdot67}^+$ where M^+ denotes the exchangeable ion and in which the "*a*" and "*b*" dimensions of

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[15] Barrer and Reay, 2nd Internat. Congress on Surface Activity, Butterworths, London, 1957, p. 79.

[16] Barrer and MacLeod, *Trans. Faraday Soc.*, 1954, **50**, 980.

[17] Ross and Hendricks, U.S. Geol. Survey, Prof. Paper 205B, 1945.

the unit cell are 9·0 and 5·2 Å. In absence of any cations, the surface area per g. unit cell consisting of a single sheet with two surfaces would be 560×10^3 m.^{2}. This area represents only external area. When the crystal is two sheets thick, there are 280×10^3 m.^{2} of external area and 140×10^3 m.^{2} of internal area per g. unit cell, because in general only a monolayer of ions or of sorbate is present between a pair of sheets. Similarly in a pile consisting of n aluminosilicate sheets the internal area is $[(n - 1)/2n] \times 560 \times 10^3$ m.^{2}/g.u.c. and the external area is $[2/2n] \times 560 \times 10^3$ m.^{2}/g.u.c. When n is large enough, the internal area is thus 280×10^3 m.^{2}/g.u.c. Such areas are not developed in actual expanded clay crystals because, *inter alia*, part of the intersheet area is occupied by cations.

In a square array, with only the intersheet areas considered, each cation, of which there are $0{\cdot}67 \times 6{\cdot}02 \times 10^{23}$ per g.u.c., is shared with four squares of which therefore there is an equal number each of area $280 \times 10^{23}/0{\cdot}67 \times 6{\cdot}02 \times 10^{23} = 70$ Å^2. Thus the square edge (XY in Fig. 8*a*) is 8·4 Å. Correspondingly in a hexagonal array each cation is shared by six triangles of area 35 Å^2 and edge XY (Fig. 8*b*) of 9·0 Å. The shortened intersheet distances of the alkylammonium montmorillonites as compared with the van der Waals diameters of the ions (this paper and ref. 3) indicate keying of the ions into the six-membered rings of the aluminosilicate sheets. This is not possible for the square array with $XY = 8{\cdot}4$ Å which therefore need not be considered further, but is exactly possible for the hexagonal array with $XY = 9{\cdot}0$ Å, there being one alkylammonium ion above the centre of each alternate hexagon of oxygen atoms of diameter 5·2 Å and free diameter ($5{\cdot}2 - 2 \times$ radius of O) $= 2{\cdot}4$ Å (Fig. 9*a*). This free diameter determines the extent of any keying of the organic ions into the oxygen network.

For a hexagonal network of the organic ions NMe_4^+ and NH_3Me^+, rotating about axes normal to the aluminosilicate sheets, Barrer and Reay [3,15] estimated areas of about 26 and 17 Å^2, respectively, corresponding to radii of $\sim$2·9 and 2·4 Å. In the hexagonal array the free inter-ion distances are 3·2 Å for the NMe_4^+-clay and 4·2 Å for the NH_3Me^+-clay, while the corresponding diameters of the largest circles which can be inscribed in the hexagonal array to touch each of three ions are respectively 4·6 and 5·6 Å. If the alkylammonium ions cease to rotate, then according to their mutual orientations towards each other, some or all of the above dimensions will increase to a certain extent. This is shown in Fig. 9*a* for NMe_4^+ ions having their triangular bases parallel to the aluminosilicate sheets. Some of these bases may be adhering to the upper lamella, and some to the lower, and this may further modify the free inter-ion distances. The latter situation does not arise for the dumb-bell-shaped NH_3Me^+ ion. The intersheet distance being only 2·2 A (Part I) these ions probably lie with their long axes parallel with the sheets, with keying of H atoms into upper and lower sheets of anionic oxygens. This is the orientation considered by Barrer and Reay [3] in estimating the area. If the lattice expands sufficiently on intercalating the sorbate (*e.g.*, in presence of benzene) the NH_3Me^+ ions could reorient with their long axes normal to the aluminosilicate sheets, and this would also augment the free inter-ion distances AB. We thus see that the distances given above tend to be lower linits, characteristic only of rotating states of the interlamellar ions.

With this qualification in mind, for hexagonal arrays of rotating ions the following comments may be made:

(i) From the dimensions of benzene considerable compression would be necessary if this molecule were intercalated by either NMe_4^+- or NH_3Me^+-clay with the benzene nucleus parallel to the aluminosilicate sheets. This situation would be eased only in part if rotation of organic ions ceased, because while some of the gaps between ions are rather large some are still small (Fig. 9*a*). On the other hand, with non-rotating ions and the more economical packing associated with vertical orientation of the benzene rings all the interionic space could be available.

With the triangular bases of alternate NMe_4^+ ions adhering respectively to the upper and the lower aluminosilicate sheets, a tilted stacking of benzene molecules is required, as shown in Fig. 9*b*. On the other hand, for NH_3Me^+-montmorillonite the stacking can be vertical. This observation may reasonably explain the greater intersheet distance (5·6 Å) reached with the $CH_3{\cdot}NH_3^+$-clay than with the NMe_4^+-clay (5·2 Å).

(ii) The intersheet distances for cyclohexane and cyclohexene complexes with NMe_4^+-montmorillonite are too small for vertical orientation of these species, but the molecules have considerable lateral dimensions. It is suggested therefore that these two compounds, and also the bulky iso-octane molecule, occupy only the larger gaps associated with non-rotating states of the tetramethylammonium ions (Fig. 9*a*). In this event the capacity of the sorbent will be much reduced as compared with that for benzene. Comparison of the equivalent monolayer values, v_m, of Table 1, or direct comparison of the sorption isotherms, shows that the predicted difference in capacity exists.

(iii) The intersheet distances of the n-alkane complexes of NH_3Me^+- and NMe_4^+-montmorillonite (Section 3) suggest respectively horizontal and vertical orientations of the plane of the zig-zag of the carbon chain. The greater free distance between NH_3Me^+-ions may be decisive in allowing the horizontal arrangement in the NH_3Me^+-clay.

(b) *Partial ion exchange.* The partial exchange of small Na^+ or Ca^{2+} ions by alkylammonium ions raises interesting but so far unexplored problems. The small inorganic ions can be sunk into the six-membered rings of the aluminosilicate sheets.[18] They may therefore play little part in excluding sorbate molecules from the dehydrated crystals, and are partly screened by ambient negatively charged oxygen atoms. If the large organic ions are located over the remainder of the sites in the hexagonal array of Fig. 9*a*, this array will have a statistically distributed series of gaps, and the average distance between nearest neighbour pairs of organic ions must increase as the amount of exchange decreases and with it the available intersheet porosity and monolayer equivalent areas must rise. It should indeed be possible to approach more nearly the maximum interlamellar sorptive capacity of the clay of 280 × 10^3 m.^{2}/g.u.c. Some average free inter-ion distances (*AB* of Fig. 8*b*) are given in Table 2.

TABLE 2. *Average free distances* AB (*Fig.* 8) *between organic ions in partially ion-exchanged montmorillonites.*

Ions in hexagonal array	Average free distances in Å for % exchange				
	100	80	60	40	20
NMe_4^+	3·2	4·4	5·9	8·4	14·3
NH_3Me^+	4·2	5·4	6·9	9·4	15·3

Conclusion.—The considerations of the previous section indicate that distributions and orientations of, and distances between, the organic interlamellar cations introduce steric factors into the sorption phenomena comparable in importance with intersheet distances and molecular configuration in determining the sorption capacities and strong selectivities shown by expanded clay sorbents. Only by considering all three factors together can one attempt to interpret the selectivity, or the orientation of the interlamellar monolayers of sorbate. No quantitative theory of the observed enrichment factors is possible, because the sorption equilibria do not follow any simple isotherm equation, and because both interlamellar and external surfaces of the crystallites are simultaneously involved and may vary in proportions between specimens. Nevertheless, it has been possible to measure enrichment factors quantitatively and to demonstrate the way in which they depend upon amount sorbed, composition of feed material, and temperature. In utilising to the best advantage the selectivity of expanded clay sorbents as separation media, reliable information of this kind must be obtained and interpreted.

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IMPERIAL COLLEGE, LONDON, S.W.7.

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[18] Barrer and Reay, *J.*, 1958, 3824.