179. *Sorption of Mixtures, and Selectivity in Alkylammonium Montmorillonites. Part I. Monomethylammonium Bentonite.*

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

A study has been made of the sorption of single and of binary mixtures of hydrocarbons by methylammonium montmorillonite. This has been combined with *X*-ray measurements of the *c*-spacing in presence of various amounts of sorbed hydrocarbons, which have demonstrated interlamellar sorption for benzene and n-heptane, but its absence for cyclohexane or iso-octane (2,2,4-trimethylpentane). Three kinds of mixture were then examined: one having both components intercalated; three having one component intercalated; and one having neither component intercalated. The middle group shows true molecular-sieve behaviour, modified by some competitive adsorption on external crystallite surfaces.

Interlamellar sorption of benzene by the clay derivative occurs only above a threshold pressure, and some phenomena akin to nucleation of a new phase can be observed. Such behaviour was not found for n-alkanes. Monomethylammonium montmorillonite sorbs cyclohexene irreversibly and appears to catalyse its polymerisation.

It has been shown, by using a bentonite * having a B.E.T. area to nitrogen of about 21·7 m.^{2}/g., that a very great increase in the effective area of the sorbent may be achieved simply by replacing the inorganic ions by $Me{\cdot}NH_3^+$, $Me_2NH_2^+$, Me_3NH^+, Me_4N^+, and Et_4N^+. As a result the outgassed clay copiously sorbed atmospheric gases, and also many hydrocarbons which were not sorbed to any extent before ion-exchange.[1,2,3] The clays have developed a permanent interlamellar porosity which is responsible for these effects. They may be very effective in resolving molecular mixtures,[4] the components of which penetrate with different selectivities into the interlamellar spaces. In the present paper an account is given of these selectivities through the study of equilibria between binary mixtures of vapours in the vapour phase in and on porous-clay crystals having methylammonium as the interlamellar ion. In this way quantitative understanding of molecular-sieve behaviour may be obtained, and thus means for predicting the selectivity towards other mixtures. This information can be correlated with similar information reported in the following paper for a tetramethylammonium bentonite, which has different porosity characteristics; and with the behaviour of dimethyl dioctadecylammonium bentonite (Bentone-34), useful in gas chromatography [5,6] and possessing some interesting properties as a sorbent.[7]

Adsorption isotherms of mixtures cannot in general be predicted from those of the individual pure components.[8,9] Accordingly selectivity and its causes can be adequately established only by studying sorption equilibria of mixtures. Compared with the information available on the uptake of single species, mixture sorption is a rather neglected field, of which understanding has so far been limited. Accordingly, there is need for various studies of the kind now reported.

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* The term " bentonite " can be used to describe montmorillonite clays that may not be completely pure.

[1] Barrer and MacLeod, *Trans. Faraday Soc.*, 1955, **51**, 1290.

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

[3] Barrer and Reay, *Trans. Faraday Soc.*, 1957, **53**, 1253.

[4] Barrer and Hampton, *Trans. Faraday Soc.*, 1957, **53**, 1462.

[5] White, *Nature*, 1957, **179**, 1075.

[6] White and Cowan, *Trans. Faraday Soc.*, 1958, **54**, 557.

[7] Barrer and Kelsey, unpublished work.

[8] Lewis, Gilliland, *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 1153, 1157, 1160.

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

EXPERIMENTAL

The apparatus for measuring the sorption and intercalation of vapour mixtures has been described elsewhere.[4] It was, however, modified by connecting the freezing-out bulb F_2[4] to the doser volume through a mercury cut-off. This allowed isolation of the added hydrocarbon, required to restore the original composition of the vapour mixture. When a further dose of the mixture is added the possibility of diluting the source mixture is thereby avoided.

The sorbates studied in this and in the following paper, their quality, and some physical characteristics of importance for this work, are recorded in Table 1.[10] The methylammonium bentonite was that used earlier.[4] In general, analysis of binary mixtures was readily effected by refractometry. For n-hexane–iso-octane * mixtures, however, gas–liquid partition chromatography was employed, the areas under the curves for the separated components being determined as suggested by Keulemans,[11] and the instrument calibrated by means of the pure n-hexane and iso-octane.

c-Spacings of the crystals of sorbent were measured from powder photographs obtained at 24° with a Hilger and Watts HRX *X*-ray unit and filtered Cu-K_α radiation. A flat plate camera was employed, and the specimen-to-film distance was 10 or 11 cm. Measurements were made on samples contained in Pyrex capillaries.[3] Before introduction of sorbate, the clay was outgassed at 100° for 8—10 hr. under a high vacuum, a condition known to remove virtually all sorbed water.[1] After equilibration with the required pressure of sorbate vapour the capillaries were sealed and were ready for *X*-ray-diffraction studies.

TABLE 1. *Characteristics of the sorbates.*

Compound	Origin and quality	B. p.	n_D	Latent heat of vaporisation (kcal./mole)	Saturation v. p. at 80° (cm.)
Benzene	" AnalaR "	80·1°	1·5011	7·36 (80°)	75·5
Cyclohexane	For spectroscopy (B.D.H.)	80·8	1·4263	7·89 (25°)	74·3
Cyclohexene	Reagent (B.D.H.)	82·9	1·4467	—	68
n-Heptane	Engine standard	98·4	1·3876	7·71 (90°)	42·7
n-Hexane	N.C.L., Teddington	68·7	1·3751	6·92 (60°)	106·2
Iso-octane	Engine standard	99·2	1·3916	8·39 (25°)	50·5
n-Perfluoroheptane	Some impurities (Minnesota Mining and Mfg. Co.)	82·5	—	—	—

TABLE 2. B.E.T. *monolayer values,* v_m.

Sorbate	Mol. area (Å^2) of sorbate	v_m value (cm.^{3} at s.t.p./g.*) This work	Ref. 13
Benzene	25	23·3	27·3
n-Heptane	51	7·6	10·9
n-Hexane	44	8·7	—
Cyclohexane	46	3·5	5·0
Iso-octane	52	1·9	2·1

* All sorptions refer to 1 g. of outgassed sorbent.

X-*Ray Measurements*.—The *c*-spacing of outgassed monomethylammonium bentonite was 11·6 ± 0·1 Å, and was confirmed on samples derived both from Na- and Ca-rich parent clays. In air the *c*-spacing rose to 12·2 Å, and at saturation with water vapour the value was 12·8 Å. The last value agrees with those reported elsewhere [12,13] and it seems probable that the value of 12·0 Å found by Barrer and Reay [2,3] refers to a sample containing some sorbed water. The figure of 11·6 Å gives a free distance of 2·2 ± 0·1 Å between surfaces of adjacent aluminosilicate lamellæ.

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* The material described, for brevity, by its commercial name " iso-octane " is 2,2,4-trimethylpentane.

[10] Timmermans, " Physico-chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

[11] Keulemans, " Gas Chromatography," Reinhold Publ. Corp., New York, 1957.

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

[13] Greene-Kelly, *Trans. Faraday Soc.*, 1956, **52**, 1281.

Interesting variations in the *c*-spacings of the lattice in presence of several sorbates are shown as a function of relative pressure in Fig. 1*a* and of amount sorbed in Fig. 1*b*. The amount sorbed was interpolated from previous data [3] by assuming that it was a function only of relative pressure, p/p_0, the temperature coefficients of sorption in terms of p/p_0 being small. The figures show a progressive increase in *c*-spacing in presence both of benzene and of n-heptane, demonstrating clearly the interlamellar uptake. On the other hand, there is a little swelling only at high relative pressure (in the region of capillary condensation) for cyclohexane, and none at all for iso-octane. Since the dimensions of each molecule are such that intercalation would cause substantial lattice expansion, for neither sorbate when alone is the interlamellar porosity appreciably accessible. Although a molecular-sieve effect is thus demonstrated quite conclusively for the pure sorbates, it is possible that when lattice expansion has occurred in presence of benzene or heptane, cyclohexane or iso-octane might now have some access to the interlamellar pores. This can be considered only by study of actual mixtures.

Sorption of Mixtures.—Isotherms of the following mixtures, over a range of compositions, have been measured at 80°, the figures quoted giving the compositions of the mixtures in terms of the mole fractions of the first-named component: Benzene–n-heptane 0·89, 0·67, 0·50, 0·30, 0·16. Benzene–cyclohexane 0·80, 0·50, 0·20. n-Heptane–cyclohexane 0·64, 0·50, 0·21. Cyclohexane–iso-octane 0·69, 0·25. n-Hexane–iso-octane 0·71, 0·53, 0·36.

FIG. 1.

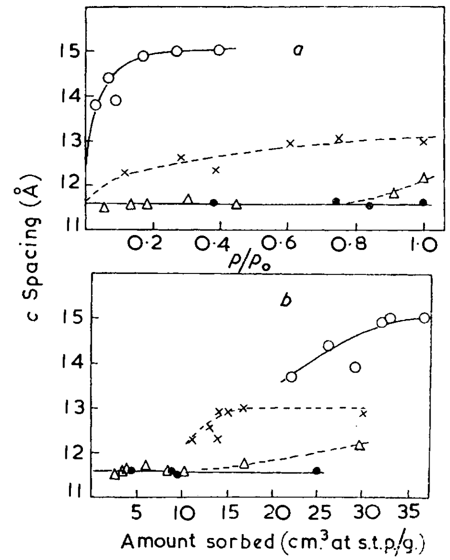

FIG. 2.

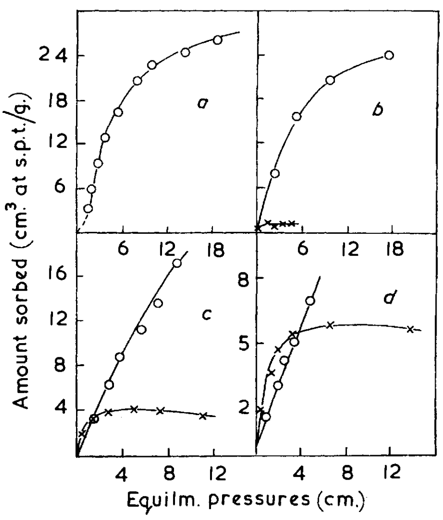

FIG. 1. (*a*) *c-Spacings at room temperature as a function of relative pressures of sorbates with which the complexes are in equilibrium.*

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

○, *Benzene*; ×, *n-heptane*; △, *cyclohexane*; ●, *iso-octane.*

FIG. 2. (*a*) *The benzene isotherm showing evidence of a threshold pressure for small amounts sorbed.*

(*b*), (*c*), (*d*) *Isotherms for benzene* (○) *and n-heptane* (×) *from mixtures of initial compositions* (*b*) 0·89, (*c*) 0·67, *and* (*d*) 0·50 *mol. fraction of benzene.*

The sorption isotherms of each pure component were measured in addition, and equivalent B.E.T. monolayer values, v_m, recorded in Table 2, are, in view of uncertainties in the method, and differences in the samples of sorbent used, in reasonable agreement with values obtained by Reay.[14] The low v_m values for cyclohexane and iso-octane support the *X*-ray evidence that these sorbates are not appreciably intercalated. Benzene gives, as observed previously, much the largest v_m value, compatible with its vertical orientation between lamellæ.[2,3]

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

Figs. 2*b*—5*c* show the isotherms at equilibrium of each component for some of the mixtures listed above. The mixtures chosen are of three kinds: (i) those in which both pure components undergo interlamellar sorption (benzene–n-heptane); (ii) those in which only one pure component undergoes interlamellar sorption (benzene–cyclohexane; n-heptane–cyclohexane; n-hexane–iso-octane); (iii) those in which neither pure component undergoes inter-lamellar sorption (cyclohexane–iso-octane). The characteristics of the isotherms, and the selectivities, can be discussed with this behaviour in mind.

DISCUSSION OF ISOTHERMS.

(a) *Benzene–n-Heptane.*—Unusual features are shown by the benzene–heptane mixtures sorbed by the methyl ammonium clay. The change-over in order of selectivity observed by Barrer and Hampton[4] is confirmed (Figs. 2*c* and *d*), as is the curious, nearly linear form of the benzene isotherms when the feed mixtures contained 0·33 and 0·50 mol. of n-heptane. The isotherm of pure benzene (Fig. 2*a*) approaches type V in Brunauer's classification,[15] a shape also given by ammonia in natural clay.[1,16]. In the latter case it was suggested that the first additions of sorbate are restricted to external surfaces of the crystals, and that only after a threshold pressure of sorbate vapour has been reached is there penetration between the lamellæ.[1] This explanation can now be applied to the uptake of benzene by the

FIG. 3.

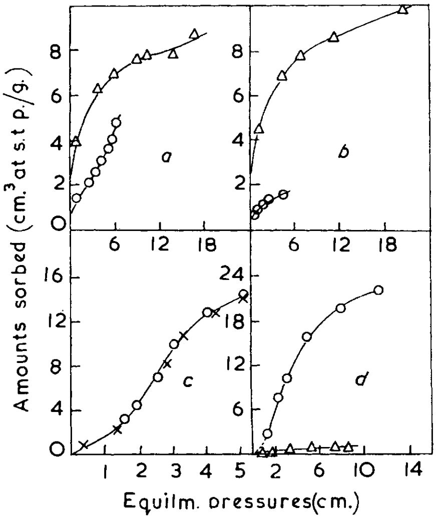

FIG. 3. (*a*), (*b*) *Isotherms for benzene* (○) *and n-heptane* (△) *from mixtures poor in benzene* [*mol. fraction* (*a*) 0·30, (*b*) 0·16].

(*c*) *Reproducibility of isotherm for benzene in a benzene–cyclohexane mixture* (*benzene mol. fraction* 0·5), *showing tendency to a threshold pressure for benzene.* ○ 1*st*, × 2*nd run.*

(*d*) *Isotherms for benzene and cyclohexane, showing selectivity to benzene* (*benzene mol. fraction* 0·80).

○ *Benzene;* △ *cyclohexane.*

FIG. 4.

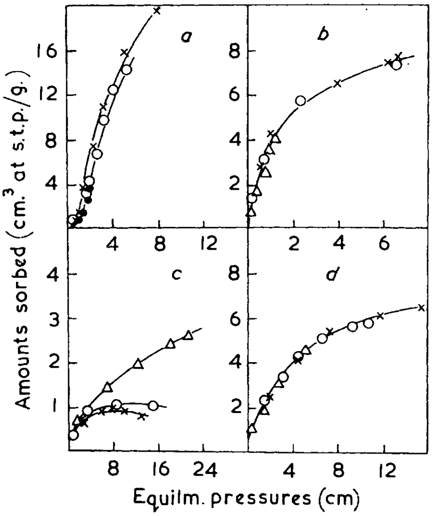

FIG. 4. (*a*) *The isotherms for benzene from mixtures with cyclohexane, showing that the benzene sorption is little affected by presence of cyclohexane. Benzene mol. fraction*: × 0·80; ○ 0·50, ● 0·20.

(*b*) *and* (*d*) *Behaviour similar to that shown in Fig.* 4 (*a*), *for* (*b*) *n-heptane in mixtures with cyclohexane, and* (*d*) *for n-hexane in mixtures with iso-octane.* (*b*) *n-Heptane mol. fraction*: × 0·64, △ 0·54, △ 0·2. (*d*) *n-Hexane mol. fraction*: × 0·71, ○ 0·53, △ 0·36.

(*c*) *The isotherms of cyclohexane in mixtures with n-heptane, strongly modified by the latter. Cyclohexane mol. fraction*: △ 0·77, ○ 0·50, × 0·36.

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[15] Brunauer, " The Adsorption of Gases and Vapours," Oxford Univ. Press, 1945, p. 150.

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

methylammonium clay. On the other hand, isotherms of n-heptane do not show a threshold pressure, and n-heptane must be presumed to penetrate between lamellæ from the lowest pressures. When it is intercalated, benzene expands the lattice considerably more than n-heptane (Figs. 1*a* and *b*) (the energy requirement for which may account for its initial exclusion), and its intercalation then takes place copiously and the order of selectivity between benzene and n-heptane is reversed. Benzene uptake thus involves phenomena akin to the nucleation of a new phase in a matrix of the old.

At points where the isotherms cross (Figs. 2*c* and *d*), neither component is selectively sorbed, and this composition has been called the " adsorption azeotrope " (Reeds and Kammermeyer[17]). The adsorption azeotropic compositions occur at different pressures

FIG. 5.

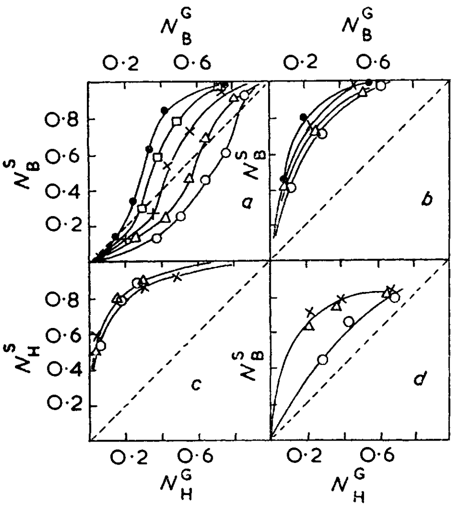

FIG. 6.

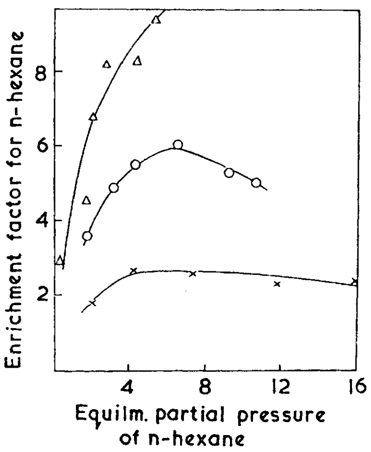

FIG. 5. *Mol. fractions of first-named constituent in sorbed phases as a function of mol. fraction in the gas phases, at equilibrium.*

(*a*) *Benzene–n-heptane.* (*b*) *Benzene–cyclohexane.* (*c*) *n-Heptane–cyclohexane.* (*d*) *n-Hexane–iso-octane.*

Individual curves refer to total equilibrium pressures as follows: ○ 2·5, △ 5·0, × 10, □ 15, ● 20 cm. *For individual points on the curves, mol. fractions of the first-mentioned constituent in the initial mixtures were, reading upwards*: (*a*) 0·16, 0·30, 0·50, 0·67, 0·89; (*b*) 0·21, 0·50, 0·64, 0·80; (*c*) 0·20, 0·50, 0·80; (*d*) 0·31, 0·53, 0·71.

FIG. 6. *Enrichment factors at* 80° *as functions of partial pressure of n-hexane in mixtures with iso-octane. Mol. fractions of n-hexane in the original mixtures*: × 0·71, ○ 0·53, △ 0·36.

of benzene and n-heptane for different initial compositions. For mixtures both richer and poorer in benzene (Fig. 2*b*; and Figs. 3*a* and 3*b* respectively) adsorption azeotropic compositions cannot readily be located if they occur at all.

(b) *Benzene–Cyclohexane.*—In this mixture, only benzene is intercalated in the pure state (see above). The important question arises whether, when the lattice has once been expanded by the benzene, the cyclohexane will also be able to penetrate between lamellæ. A rather good adsorption-chromatographic separation of this pair by the methylammonium clay was reported;[4] some mixture isotherms are shown in Fig. 3*c* and *d* and Fig. 4*a*. The very great selectivity towards benzene is apparent from Fig. 3*d*, and the type V character of the isotherms of benzene in the mixtures is seen clearly in Fig. 3*c*.

When the isotherms for benzene in three different mixtures with cyclohexane are plotted on the same diagram (Fig. 4*a*), all three are seen to be nearly superposable. Cyclohexane, whether at mol. fraction 0·80, 0·50, or 0·20, offers little competition for sorption sites.

[17] Reeds and Kammermeyer, *Ind. Eng. Chem.*, 1959, **51**, 707.

It thus appears that even when benzene has entered and expanded the lattice of the clay crystals there is little or no tendency for cyclohexane also to enter.

(c) *n-Heptane–Cyclohexane; n-Hexane–Iso-octane.*—In both these mixtures it is only the n-alkane which, in the pure state, undergoes interlamellar sorption (see above). For the first mixture the isotherms of n-heptane are seen to be almost superposable in three mixtures for which the mol. fractions of cyclohexane are 0·36, 0·50, and 0·79 respectively (Fig. 4*b*). Thus, cyclohexane does not effectively compete with n-heptane for sorption sites between the lamellæ. On the other hand, as the n-heptane content increases the already small sorption of cyclohexane is progressively decreased (Fig. 4*c*). It can be seen that both molecular species are in competition for the small external surface of the clay crystals, and that only n-heptane has access to the much more numerous interlamellar sorption sites. A similar situation is found for hexane–iso-octane mixtures, the hexane isotherms being independent of varying mol. fractions of iso-octane (Fig. 4*d*).

(d) *Cyclohexane–Iso-octane.* For this mixture neither component has appreciable access to the interlamellar pores (see above), and there can be competition for the external surfaces of the crystallites only. For neither component are the partial isotherms independent of varying proportions of the other, and the crystals show no marked preference for either. The isotherms of the two pure hydrocarbons also cross at ~10 cm. pressure. Good separations of this pair would not be possible by adsorption chromatography on the methylammonium clay.

ENRICHMENT FACTORS

In a sorption equilibrium involving species A and B at mol. fractions N_A^G and N_B^G in the gas phase and N_A^S, N_B^S in the sorbed phase, the enrichment factor for A can be defined as

$$\eta_A = N_A^S N_B^G / N_A^G N_B^S = N_A^S p_B / N_B^S p_A \qquad \text{. . . . . (1)}$$

where p_B and p_A are equilibrium partial pressures in the gas phase. In defining N_A^S and N_B the sorbed phase is regarded as a binary mixture of A and B, just as is the gas phase. A convenient way to express enrichment factors is to plot N_A^S against N_A^G, by analogy with similar diagrams for vapour–liquid mixtures. Fig. 5*a*, *b*, *c*, and *d* show such plots for some of the mixtures which have been studied. A completely non-selective sorption is represented by the diagonal broken lines in the figures. Good enrichments in the intercalated component are seen for each of the three pairs, benzene–cyclohexane, n-heptane–cyclohexane, and hexane–iso-octane, of which the first mentioned component only is intercalated. The more complex behaviour described above, and the change-over in selectivity for the benzene–n-heptane pair are well shown in Fig. 5*a*. Good enrichment factors for either component can occur under appropriately selected conditions.

When, as in the present system, the sorbent provides two distinct sorbing regions, an interlamellar surface and an external surface, there is advantage in considering the selectivities for each region separately:

$$\left.\begin{aligned} \eta_A^i &= \frac{p_B}{p_A} \cdot \frac{N_A^i}{N_B^i} = \frac{p_B}{p_A} \cdot \frac{n_A^i}{n_B^i} \\ \eta_B^a &= \frac{p_B}{p_A} \cdot \frac{N_A^a}{N_B^a} = \frac{p_B}{p_A} \cdot \frac{n_A^a}{n_B^a} \end{aligned}\right\} \qquad \text{. . . . . (2)}$$

where the superscripts " i " and " a " denote " intercalated " and " adsorbed externally " respectively and *n*'s denote actual numbers of moles of A and B intercalated or adsorbed externally. Then for the total numbers of moles of A and B sorbed we have:

$$\left.\begin{aligned} n_A^s &= n_A^i + n_A^a \\ n_B^s &= n_B^i + n_B^a \end{aligned}\right\} \qquad \text{. . . . . (3)}$$

From eqn. 1 we obtain for the measured selectivity:

$$\eta_A = \frac{p_B(n_A^i + n_A^a)}{p_A(n_B^i + n_B^a)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

On rearranging and making use of eqns. 2, we have:

$$n_B^s \eta_A = n_B^i \eta_A^i + n_B^a \eta_A^a \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

which gives the general relation between the measured enrichment factor, η_A, and those for interlamellar sorption and for adsorption on external surfaces, respectively η_A^i and η_A^a. Eqn. 5 is applicable to the benzene–n-heptane system, after the threshold pressure when intercalation of benzene has commenced.

For the special case when component A is intercalated but not component B, we have $n_B^i = 0$ and, from eqn. 4:

$$\eta_A = \eta_A^a\left(1 + \frac{n_A^i}{n_A^a}\right) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

so that $\eta_A \longrightarrow \infty$ as required, when $n_A^i/n_A^a \longrightarrow \infty$. Eqn. 6 is then appropriate for n-heptane–cyclohexane, benzene–cyclohexane, and hexane–iso-octane mixtures, and also for the molecular-sieve zeolites. Thus, for chabazite or Linde sieve 5A, the component A could be a n-alkane, and B could be an isoalkane, naphthene, or aromatic hydrocarbon. For these and other zeolites the external surface is very small compared with the internal surface so that n_A^i/n_A^a is very large indeed. The porous clay sorbent considered here differs, for the three mixtures referred to, only in that the ratio of internal to external surface is smaller. This difference arises on account of the small size of clay crystallites. The best molecular-sieve alkylammonium montmorillonites or bentonites will be those having the best developed crystallites, and so the smallest external area. The external areas can be estimated from those of the original Na- or Ca-clay before ion-exchange, or by the method of Barrer and Reay.[3]

When the enrichment factor for n-hexane in admixture with iso-octane is plotted as a function of the partial pressure of n-hexane, it is seen (Fig. 6) that at a given partial pressure of the n-alkane the enrichment factor is *greater* the *poorer* the mixtures are in n-hexane. This situation is the converse of that normally observed when tetramethylammonium montmorillonite is the sorbent (Part II, following paper), but is understandable in terms of eqn. 6. Thus, at fixed partial pressure of A, n_A^i can, if anything, only decrease as the mixture is made richer in B. However, Fig. 4*d* shows that for the mixtures in question n_A^i is virtually unchanged. Consequently the term $(1 + n_A^i/n_A^a)$ increases. η_A^a may, of course, increase or decrease, but the over-all effect can easily be an increase in η_A as the mixtures become poorer in A.

APPENDIX. CATALYTIC ACTIVITY OF METHYLAMMONIUM CLAY.

In several clay–sorbate systems evidence has now been obtained of irreversible sorption processes and of catalytic activity, which may greatly modify their molecular-sieve activity and selectivity. Thus, pyridine could not be desorbed completely from a natural montmorillonite [16,19] or from tetramethylammonium montmorillonite.[14] t-Butyl alcohol was reversibly sorbed by the tetramethylammonium clay,[1] but it was in part dehydrated and the isobutene was polymerised by the monomethylammonium clay.[3] There was also some evidence of dehydration of cyclohexanol by tetramethylammonium montmorillonite.[4] There appears to be no report of sorption of alkenes or alkynes by montmorillonite or its derivatives, and in connection with the mixture isotherms examined in this paper the behaviour of cyclohexene, as an intermediate between benzene and cyclohexane, had been examined.

It was soon apparent that in the monomethylammonium clay irreversible sorption occurred (Fig. 7), although sorption by the tetramethylammonium clay was reversible (see Part II).

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

[19] Greene-Kelly, *Trans. Faraday Soc.*, 1955, **51**, 425.

The cyclohexene could not be desorbed, about 5 cm.^{3} at s.t.p. per g. of " cyclohexene " remaining after outgassing. A second isotherm now lay below the first and diverged from it (Fig. 7), and two desorption points showed negligible hysteresis. The results are compatible with polymerisation of cyclohexene to a non-volatile substance which remained trapped in or on the clay crystallites. This polymerised material then acts as a high-boiling liquid and dissolves some cyclohexene, to give the linear second isotherm. After outgassing at 100° the clay gave a *c*-spacing of 11·7 Å, equal to that of the outgassed parent material. A fresh sample of the sorbent saturated with cyclohexene gave a *c*-spacing of ~14·4 Å.

In a further experiment 3 g. of the sorbent, outgassed at 80° for 24 hr., were heated in a sealed tube with excess of cyclohexene at 80°. After removal of the cyclohexene the clay was dark grey-green, but after outgassing the *c*-spacing was 11·6 Å, a figure which rose to ~15 Å at saturation with benzene. A sample of the clay, treated as above with cyclohexene, was extracted in a Soxhlet apparatus with hot benzene; the original colour of the clay was thereby restored. Evaporation of the extract gave a small amount of an oil, the infrared spectrum of which did not contain the 3000 cm.$^{-1}$ band of the original cyclohexene. A test for nitrogen was negative. Samples of clay subjected to the action of cyclohexene were then analysed for carbon and hydrogen, with the results shown in Table 3.

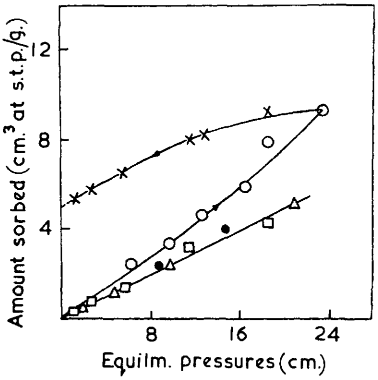

FIG. 7. *Irreversible sorption of cyclohexene at* 80°. *Run* 1: ○ *Adsorption;* × *desorption. Run* 2: △ *Adsorption;* ● *desorption.* □ *Calc. desorption.*

TABLE 3.

	Found (%)		Compn. (% by wt.) of sorbed organic material *	
Treatment of methylammonium clay	C	H †	C	H
Specimen A	1·12	1·73	—	—
Specimen B [7]	1·04	1·60	—	—
Sample of A after treatment with cyclohexene (2 days at 80°)	6·40	2·13	93	7
Same sample of A after benzene-extraction	2·03	1·87	86	14
Sample of A used in sorption measurements after outgassing	3·08	1·83	95	5
Pure cyclohexene	—	—	90	10

* *I.e.*, excluding methylammonium ions.

† The figure for H includes any hydrogen present as sorbed H_2O or as OH.

The figures given in the last two columns of Table 3 give, as averages C 91% and H 9%, which are fairly close to the composition of cyclohexene or its polymers. This molecule is known to undergo thermal decomposition, dehydrogenation, and polymerisation.[20] Polymers ranging from dimer to heptamer have been prepared by the action of hydrogen fluoride on cyclohexene.[21] The polymerisation by the clay may be associated with the hydrogen atoms attached to nitrogen in the $Me{\cdot}NH_3^+$ ions, since the tetramethylammonium clay was not catalytically active under our conditions.

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