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SHAPE-SELECTIVE SORBENTS BASED ON CLAY MINERALS: A REVIEW[1]

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Abstract—A review is presented of work carried out over the last 40 years on non-porous sorbents and on microporous shape-selective sorbents derived from palygorskite, smectite, and vermiculite. Among such materials four kinds of behavior were observed. In some systems uptake was restricted to external surfaces; in others, intercalation also occurred but only above threshold pressures. If the interlayer region was completely filled by long-chain organic cations, imbibition was possible, but in amounts which were very strongly dependent upon the cohesive energy density of the sorbate. Finally, in certain permanently expanded derivatives of layer silicates intercalation proceeded without any threshold pressure, just as in zeolites.

In this latter group, micropores existed which sometimes resulted in shape-selective sorption and molecule sieving. The micropores in clay minerals were modified by varying the size and shape of the interlayer cations, their charge, and the charge density of the siliceous layers. The interplay of these factors was investigated and the micropore sorbents were shown to be highly effective in the separation of mixtures.

Key Words—Adsorption, Imbibition, Intercalation, Palygorskite, Porosity, Shape-selective, Smectite, Vermiculite.

INTRODUCTION

Over the course of the last 40 years, clay minerals have been studied extensively by the author and coworkers in the Departments of Chemistry, first in the University of Aberdeen and then in the Imperial College in London. The work has consisted of two programs: one on the synthesis and hydrothermal reactions of clay minerals and one on the behavior of clay minerals and their derivatives as sorbents. For reasons of space, this account will deal only with certain parts of the work on sorbents.

ASPECTS OF SORPTION BY CLAY MINERALS

The parent clay materials, their cation-exchange capacities, external surface areas, and the cationic forms studied are given in Table 1. Four kinds of behavior have been observed:

1. Outgassed smectites containing only small inorganic interlayer cations did not intercalate non-polar molecules, nor did these molecules penetrate the intracrystalline channels present in palygorskite and sepiolite (Barrer and MacLeod, 1954; Barrer and Mackenzie, 1954; Barrer *et al.*, 1954; Barrer and Reay 1957). Sorption isotherms for the external surfaces were of the sigmoid type-2 form (Brunauer, 1944), as illustrated for the attapulgite variety of palygorskite in Figure 1. Hysteresis loops were observed between sorption and desorption branches, which in smectites closed at relative pressures in the range 0.27 to 0.47, according to the sorbate and the temperature.
2. In confirmation of work done elsewhere, outgassed smectites containing only small inorganic interlayer cations intercalated polar molecules. Intercalation occurred only after a threshold pressure was reached, the theoretical basis for which was recently given by Barrer (1984). Isotherms showed one or more steps, and here hysteresis between sorption and desorption branches characteristically persisted to very low relative pressures (Barrer and MacLeod, 1954). These features are illustrated for pyridine and water in Figure 2.
3. Dimethyldioctadecylammonium-montmorillonite (Bentone 34) behaved differently from materials in either of the above categories. Here, the interlayer cations swelled the clay and filled all the interlayer space. The long chains were closely packed and were steeply oriented to the surface. This organoclay imbibed certain molecules with further swelling to give isotherms which in shape resembled type 3 isotherms, like those of benzene in rubber, as seen in Figure 3 (Barrer and Kelsey, 1961b). The extent of imbibition appeared to be controlled by the cohesive energy density (C.E.D.) of the sorbate, as shown by the correlation in Table 2. Maximum uptake should occur if the C.E.D. of the sorbate and of the organic interlayer region, modified by the siliceous layers, most closely matched. That imbibition can be very selective is seen from the relative uptakes of paraffins, aromatics, and heterocycles. The extraction of aromatics and heterocycles from petro-

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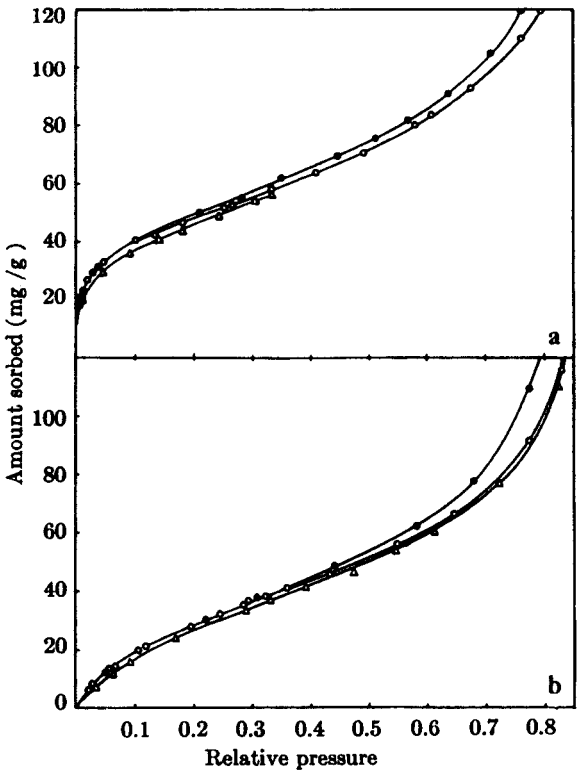


Figure 1. Type-2 sorption isotherms of (a) n-heptane and (b) iso-octane on attapulgite variety of palygorskite outgassed at 70°C, ⊙. ○, △, sorption at 50°C; ●, desorption at 50°C (Barrer and Mackenzie, 1954).

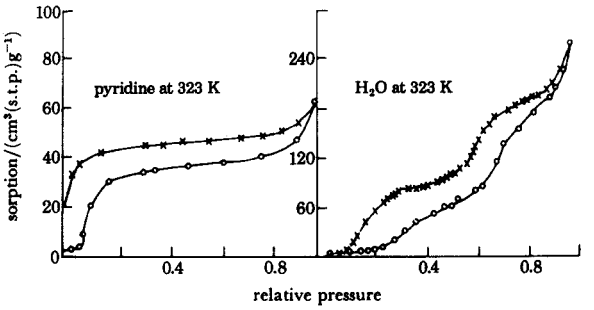


Figure 2. Isotherms at 50°C of pyridine (left) and water (right) on Na-rich montmorillonite, showing steps and hysteresis. ○, sorption; ×, desorption (Barrer and MacLeod, 1954).

leum using Bentone 34 or analogous organo-smectites merits further attention.

4. If layer silicates were exchanged with ions large enough to hold the layers permanently apart without filling all the interlayer space, a notable range of shape-selective microporous sorbents was obtained, to which the rest of this account will be devoted. Microporosity was first demonstrated in 1955 with Me_4N^+ and Et_4N^+ as the interlayer cations (Barrer and MacLeod, 1955). The reasoning is seen in Figure 4 (Barrer, 1986). It is d_1 and d_3, each of molecular dimensions, which control access to the interlayer regions of the crystal. In the Me_4N- and Et_4N-montmorillonites, d_1 was, respectively, 4.1 and 4.5(5) Å. The expanded crystals freely intercalated many permanent gases and non-polar molecules, that were not intercalated in the parent montmorillonite. As a result, the sorption capacity was greatly enhanced and, as with zeolites, intracrystalline sorption required no threshold pressures.

INTERLAYER POROSITIES OF SMECTITE MOLECULAR SIEVES

Total micropore volumes were evaluated in some of the sorbate-free outgassed smectites. The total interlamellar area was evaluated for the average number of sheets in the parent crystals. From this, the area occupied by the interlamellar cations was subtracted (with allowance for the fraction of these on external basal surfaces). To obtain the porosity, the net interlamellar area was then multiplied by the free distance between sheets, d_1. The results, in cm^3/g, are given in Table 3.

Table 1. Clay minerals and exchange forms studied.

Mineral	External area (m^2/g)	CEC[1] (meq/100 g)	Cationic forms[2]
FH150[3]	8	150	Na, Cs, $MeNH_3$, Me_4N, $NH_3(CH_2)_2NH_3$, Co(III)(en)$_3$
FH90[3]	11	90	
Montmorillonite (as Bentone 34)	14.8	—	$Me_2N(C_{18}H_{37})_2$
Montmorillonite A (Na-rich)	21.7	91	Na, NH_4, Cs, $MeNH_3$, Me_2NH_2, Me_3NH, Me_4N, Et_4N, n-$C_nH_{2n+1}NH_3$ (n = 2, 3, 4, 5, 12), NH_3NH_3, $NH_3(CH_2)_nNH_3$ (n = 2 to 10, and 12)
Hectorite (as Ben-a-Gel)	81.4	90	NH_4, $NH_3(CH_2)_nNH_3$ (n = 2, 3, 4, 5AA, 9, 12)
Montmorillonite B (Ca-rich)	85.4	102	Ca, $MeNH_3$, Me_4N
Palygorskite, variety attapulgite	195 (max.)	—	natural

[1] Cation-exchange capacity.
[2] Me = methyl; Et = ethyl; en = ethylenediamine.
[3] FH150 and FH90 = fluorhectorites having CECs of 150 and 90 meq/100 g, respectively (see Barrer and Jones, 1970).

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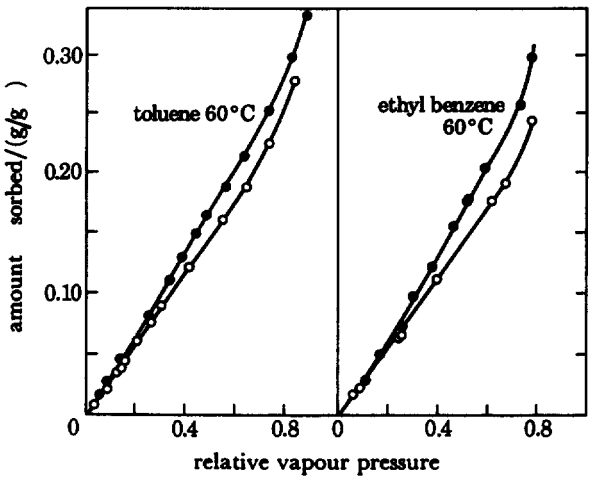


Figure 3. Isotherms at 60°C of toluene and ethylbenzene in extracted, outgassed Bentone 34, showing the type-3 isotherm contours. O, sorption; ●, desorption (Barrer and Kelsey, 1961b).

The micropore volumes are considerable, although somewhat less than those in most zeolites.

The free distance, d_1, between sheets sometimes expanded further if guest molecules were intercalated. An evaluation of microporosity was therefore also made, this time for fluorhectorite-90 and -150 filled with guest molecules. The BET value of the saturation uptake, v_m, was corrected for adsorption on the external surface, and it was next found what volume of liquid sorbate the corrected v_m would represent. This was taken as the pore volume, the results being given in Table 4 (Barrer and Jones, 1971).

The micropore volumes were readily accessible for molecules of appropriate shape and size, and the resultant selectivities made these microporous smectites of very considerable interest. Various large molecules, such as n-octane (Figure 5), were rapidly intercalated

Table 2. Cohesive energy densities (C.E.D.) and total uptake at relative pressure 0.2 in Bentone 34 (Barrer and Kelsey, 1961b).

Sorbate	$(C.E.D.)^{½}$ $(cal/cm^3)^{½}$	Temp. (°C)	Uptake (mmole/g)	d(001)[1] (Å)
iso-C_4H_{10}	6.25	−30	0.06_2	—
n-C_4H_{10}	6.7	−30	0.07_7	—
iso-C_8H_{18}	6.85	45	0.11	23.2
n-C_7H_{16}	7.45	45	0.11	23.2
cyclo-C_6H_{12}	8.20	45	0.16	23.2
ethylbenzene	8.8	60	0.52	—
toluene	8.90	45	0.65	27.2
benzene	9.15	45	0.81	27.2
dioxane	10.0	60	0.92	—
pyridine	10.7	60	1.79	—
nitromethane	12.6	45	1.38	—

[1] d(001) of the parent material extracted with alcohol was ~23.2 Å.

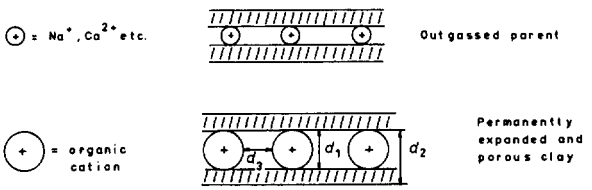


Figure 4. Representation of an unexpanded and a permanently expanded layer silicate, showing the important free distances d_1 and d_3 (Barrer, 1986).

in ethylenediammonium fluorhectorites-90 and -150 (Barrer and Jones, 1971). To minimize external adsorption, the external areas should be as small as possible. These areas for the fluorhectorite samples were only 11 and 8 m^2/g of parent material (Table 1).

MODIFYING THE MICROPORES

Ways in which the micropores were modified involved changing d_1 and d_3 of Figure 4 and were explored by: (1) varying the size and shape of the ionic interlayer props; (2) increasing the charge and therefore decreasing the number of the interlayer cations; and (3) altering the composition of the siliceous layers and therefore their anionic charge.

Table 3. Calculated interlayer free areas and porosities of some organomontmorillonites and organohectorites (Barrer and Millington, 1967).

Cation	g.u.c. wt.[1]	Ion co-area (Å²)	d_1[2] (Å)	Free area (m^2/g)	Porosity (cm^3/g)
Alkylammonium montmorillonites (CEC = 85 meq/100 g)					
$CH_3NH_3^+$	746	21.6	2.2	294	0.065
$C_2H_5NH_3^+$	755	29.8	3.4	214	0.073
n-$C_3H_7NH_3^+$	765	35.6	3.7	184	0.068
n-$C_4H_9NH_3^+$	774	41.4	3.9	155	0.060
n-$C_5H_{11}NH_3^+$	783	47.1	4.0	126	0.050
n-$C_6H_{13}NH_3^+$	792	52.9	4.0	98	0.039
α, ω-alkyldiammonium montmorillonites (CEC = 85 meq/100 g)					
$^+NH_3(CH_2)_2NH_3^+$	746	34.8	2.8	278	0.078
$^+NH_3(CH_2)_3NH_3^+$	750	40.6	3.5	262	0.092
$^+NH_3(CH_2)_4NH_3^+$	755	46.4	4.0	246	0.098
$^+NH_3(CH_2)_5NH_3^+$	759	52.2	3.9	231	0.090
$^+NH_3(CH_2)_6NH_3^+$	764	58.0	3.8	216	0.082
$^+NH_3(CH_2)_7NH_3^+$	769	63.7	3.9	201	0.078
$^+NH_3(CH_2)_8NH_3^+$	773	69.5	3.9	187	0.073
$^+NH_3(CH_2)_9NH_3^+$	778	75.3	3.9	172	0.067
α, ω-alkyldiammonium hectorites (CEC = 91 meq/100 g)					
$^+NH_3(CH_2)_2NH_3^+$	769	34.8	2.8	240	0.067
$^+NH_3(CH_2)_3NH_3^+$	774	40.6	3.6	224	0.080
$^+NH_3(CH_2)_4NH_3^+$	779	46.4	[3.9]	208	[0.081]
$^+NH_3(CH_2)_5NH_3^+$	783	52.2	3.9	192	0.075
$^+NH_3(CH_2)_9NH_3^+$	802	75.3	3.9	128	0.050

CEC = cation-exchange capacity.
[1] g.u.c. = gram unit cell.
[2] d_1 = the free distance between adjacent siliceous layers (see Figure 4).

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Table 4. Pore volumes in Co(III) $(en)_3$-fluorhectorites-90 and -150[1] estimated from monolayer saturation capacities, v_m (Barrer and Craven, 1987).

Sorbate	Temp. (K)	v_m (cm^3 at stp./g)	Volume at T (cm^3/mole)	cm^3 (liq) per g of sorbent
Co(III)$(en)_3$-FH90				
O_2	77.3	67. (8)	26.5	0.08 (0)
O_2	90.2	66. (5)	27.9	0.08 (3)
N_2	77.3	51. (3)	34.7	0.07 (9)
N_2	90.2	45. (7)	37.4	0.07 (6)
Ar	77.3	65. (6)	27.4	0.08 (0)
Ar	90.2	63. (7)	29.1	0.08 (3)
CH_4	90.2	50. (0)	38.7	0.08 (6)
iso-C_4H_{10}	273.2	19. (2)	100.1	0.08 (6)
neo-C_5H_{12}	273.2	23. (7)	117.4	0.12 (4)
CO_2	273.2	31. (4)	47.4	0.06 (6)
Co(III)$(en)_3$-FH150				
O_2	77.3	51. (7)	26.5	0.06 (1)
O_2	90.2	49. (3)	27.9	0.06 (1)
CO_2	273.2	21. (4)	47.4	0.04 (5)

[1] See terminology explained in footnote in Table 1.

Intercalation modified by cation shape and size

Examples of molecules intercalated or excluded in $MeNH_3$-, Me_2NH_2-, Me_3NH-, Me_4N-, and Et_4N-montmorillonite A are given in Table 5 together with values of d(001) and d_i for the outgassed sorbents, the external areas, A_e, and the free interlamellar areas, A_i (Barrer and MacLeod, 1955; Barrer and Reay, 1957). Whether or not intercalation occurred was often very dependent upon temperature, indicating activated diffusion ($D = D_0\exp(-E/RT)$). As an example from Table 5, O_2 and N_2 were intercalated in the Et_4N-montmorillonite A at 78 K, but the uptake of Ar and CH_4 was slight. The approximate van der Waals dimensions of the molecules are: O_2, 2.8 × 3.9 Å; Ar, 3.8$_3$ Å; N_2, 3.0 × 4.1 Å; CH_4, ~ 4 Å. Another example of fine tuning to molecular dimensions at low temperatures is illustrated in Figure 6 for uptakes of O_2 and N_2 in Co(III)$(en)_3$-fluorhectorite-150. At 77.3 K O_2 was copiously sorbed, but on the time scale of the experiment, N_2 was not (Craven, 1976; Barrer, 1978; Barrer and Craven, 1987).

At 323 K Me_4N- and Et_4N-montmorillonite intercalated some rather bulky molecules including neopentane (Table 5). In contrast, the $MeNH_3$-form at 323 K did not intercalate iso-C_5H_{12}, iso-C_8H_{18}, or cyclohexane, although it freely intercalated n-paraffins, cyclopentane, and aromatics.

As already noted, intercalation was sometimes accompanied by further significant increases in d(001). For example, n-paraffins increased d(001) from 11.6 to 13 Å in $MeNH_3$-montmorillonite and benzene increased d(001) to 15 Å in this form. Benzene also increased d(001) from 13.5 to 14.6 Å in the Me_4N-form. The d(001) values of 15 and 14.6 Å corresponded to benzene molecules stacked on edge between the cations (Barrer and Perry, 1961a, 1961b).

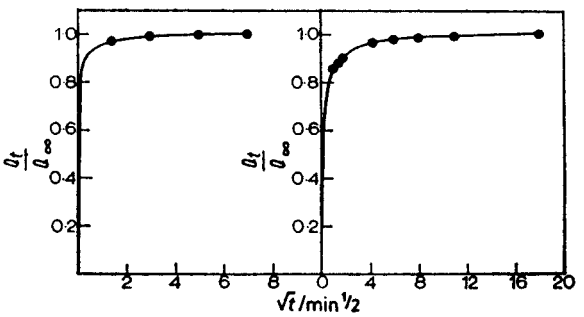


Figure 5. Rates of intercalation at 50°C of n-octane in ed-fluorhectorite-90 (left) and ed-fluorhectorite-150 (right) (ed = ethylenediammonium). Q_t denotes amount sorbed at time t, and Q_∞ is this amount at equilibrium (Barrer and Jones, 1971).

The small interlayer free area, A_i, of the Et_4N-montmorillonite and the d_i of only 4.5(5) Å (d(001) = 13.95 Å) require a flattened conformation of the organic ion, which can be seen with a model (Barrer and MacLeod, 1955). The flattened form covers more of the interlayer area than the other cations. The free areas, A_i, of Me_4N- and Et_4N-montmorillonite are compared for some guest molecules in Table 6. At 323 K the ratio of A_i for the largest molecules is nearly independent of molecular shape and size.

Cation chain length and intercalation

Figure 7 shows isotherms for N_2 at 78 K in a series of alkylammonium and α-, ω-alkyldiammonium forms of montmorillonite and hectorite (Barrer and Millington, 1967). The numbers on the curves are the carbon numbers of the cations. At $p/p_0 < 0.6$, the isotherms are all of type 1. The illustration shows that the uptakes in the alkylammonium-montmorillonite samples decreased with chain length much more rapidly than in

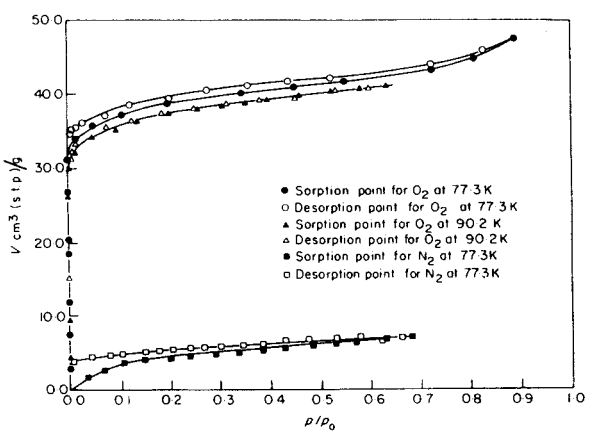


Figure 6. Isotherms for O_2 at 77.3 and 90.2 K and N_2 at 77.3 K in Co(III)$(en)_3$-fluorhectorite-150, showing the large differences in uptake (Barrer, 1978).

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Table 5. Comparison of some alkylammonium montmorillonites.

Cationic form	$MeNH_3^+$	$Me_2NH_2^+$	Me_3NH^+	Me_4N^+	Et_4N^+
g.u.c. wt.	740	749	759	768	806
d(001) (Å)	12	12.2	13.0	13.5	13.9 (5)
d_i (Å)	2.6	2.8	3.6	4.1	4.5 (5)
A_e (m^2/g)	21.5	21.2	21.0	20.7	19.7
A_i (m^2/g)	140	127	105	121	68
Temp. (K)	Some molecules intercalated at the temperature in column 1				
78	N_2				
90	O_2, N_2, Ar	O_2, N_2, Ar	O_2, N_2, Ar	O_2, N_2, Ar	O_2, N_2
90	CH_4	CH_4	CH_4	CH_4	
273	n-C_4, iso-C_4	n-C_4, iso-C_4	n-C_4, iso-C_4	n-C_4, iso-C_4	
323	n-C_5, n-C_6			n-C_5, n-C_6	n-C_5, n-C_7
323	cyclo-C_5			cyclo-C_5	iso-C_8
323	benzene			iso-C_5, iso-C_8	neo-C_5
323	toluene			neo-C_5	benzene
323	o-xylene			benzene	methanol
323	p-xylene			toluene	t-butanol
323				o-, p-xylene	
323				methanol	
323				t-butanol	
Temp. (K)	Molecules showing little intercalation at the temperature in column 1				
78					Ar, CH_4
323	cyclo-C_6				
323	iso-C_5, iso-C_8				
323	neo-C_5				

g.u.c. = gram unit cell.

the alkyldiammonium-montmorillonite samples. For example, n-$C_5H_{11}NH_3^+$ and $^+NH_3(CH_2)_4NH_3^+$ have about the same length, but the N_2 uptakes were much larger for the $NH_3(CH_2)_4NH_3$-form. One reason for this is that the number of the divalent ions was only half the number of the monovalent ions in each homoionic form. Therefore, more free interlayer area was present with the divalent ions.

Intercalation modified by cationic and by lamellar charge

The importance of cationic charge has already been illustrated in Figure 7, if N_2 isotherms in the alkylammonium and alkyldiammonium series of montmorillonites are compared. The importance of layer charge on the siliceous sheets is illustrated by comparing the synthetic fluorhectorite samples listed in Table 1. These fluorhectorite samples, after correcting for impurities, had cation-exchange capacities of 90 and 150 meq/100 g, and were therefore termed FH90 and FH150. They were examined in their non-porous Na-forms and in their microporous $MeNH_3$-, Me_4N-, $NH_3(CH_2)_2NH_3$-, and Co(III)$(en)_3$-forms.

In the non-porous Na-forms the external surfaces were small (11 and 8 m^2/g). Accordingly, isotherms of the microporous forms were little affected by this small external surface except as p/p_0 approached unity and, as in zeolites, isotherms were of type 1. This is seen in Figure 8 for n-octane at 50°C in each of the ethylenediammonium (ed) forms (Barrer and Jones, 1971). The smaller saturation capacity of the ed-FH150 sample was a consequence of the large layer charge and therefore an increased number of ethylenediammonium ions per unit of interlayer area. Sample FH150 appears to be a vermiculite, rather than a smectite.

Table 7 gives examples, among the guest molecules

Table 6. Comparison of interlayer free areas, A_i, in Me_4N- and Et_4N-montmorillonites.

Guest	Temp. (K)	δ[1] (Å)^2	A_i/m^2/g in: Me_4N-form	ET_4N-form	Ratio of A_i values
O_2	78	13.6	143	68	2.1 (0)
O_2	90	14.1	142	77	1.8 (4)
N_2	78	16.2	149	40[3]	3.7 (3)
CH_3OH	323	17.7	131	50	2.6 (2)
C_6H_6	323	25[2]	143	42	3.4 (0)
$(CH_3)_3COH$	323	32.4	129	33. (3)	3.8 (7)
n-C_5H_{12}	323	47.9	130	34. (0)	3.8 (2)
n-C_7H_{16}	323	64	132	32. (4)	4.0 (7)
iso-C_8H_{18}	323	67	109	28. (7)	3.8 (0)

[1] δ denotes the molecular co-area.
[2] Cross-sectional area for C_6H_6 on edge.
[3] This low value at 78 K may be due to non-equilibrium.

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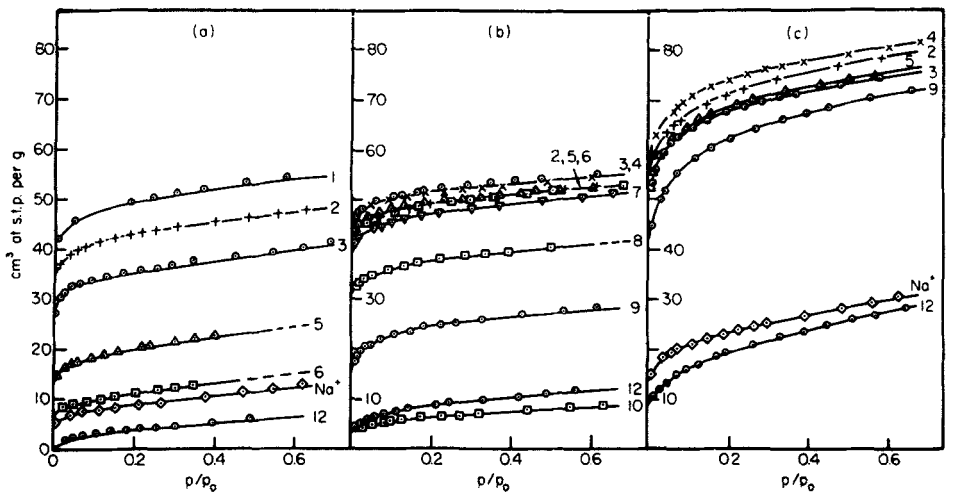


Figure 7. Sorption of N_2 at 78 K by (a) alkylammonium montmorillonites, (b) alkyldiammonium montmorillonites, and (c) alkyldiammonium hectorites. The number on each curve gives the carbon number of the cation. Isotherms in the parent Na-form are also shown (Barrer and Millington, 1967).

actually studied, of intercalation in and exclusion from the exchange forms of samples FH90 and FH150. Especially in the Co(III)(en)$_3$-FH150 sample, intercalation was, as already seen in Figure 6 for O_2 and N_2, very sensitive to molecular dimensions and temperature. Figure 9 further illustrates this sensitivity in the dramatic differences in rates of uptake in the Co(III)(en)$_3$-FH150 sample for H_2, D_2, Ne, and O_2 (very fast at 77.3 and 90.2 K) and N_2, Ar, and CH_4 (very slow at 77.3 and 90.2 K).

The virtual exclusion of O_2, N_2, and Ar from the micropores of the $MeNH_3$-forms of samples FH90 and FH150 at 78 K is noteworthy, because these gases were all intercalated at similar temperatures by $MeNH_3$-montmorillonite. The cation-exchange capacities of sample FH90 and the montmorillonite were nearly the same (90 and 91 meq/100 g (Table 1)). Therefore, the interlamellar free distance between adjacent cations (d_3 of Figure 4) was almost the same, and so was the vertical free distance, d_1, between sheets (~2.2 Å).

This difference in behavior represents another significant variable, which was considered to have arisen from differences in the size and perfection of the crystallites. Thus, sample FH90 and the Na-rich montmorillonite used had respectively about 85 and 26 lamellae per average crystal, and the crystals of sample FH90 were much larger. For penetration of O_2, N_2, or Ar into the $MeNH_3$-forms expansion in d_1 was needed, involving nucleation of the expanded phase at crystal edges. At 78 K this nucleation, as the prerequisite for penetration, occurred only in the $MeNH_3$-montmorillonite, in which the smaller flake size and number of lamellae per crystal were more favorable for nucleation.

Differences between a given cationic form of sample FH90 and the corresponding form of sample FH150 could not have arisen from d_1, because d_1 was the same. The differences must have arisen primarily from d_3, estimates of which are given below (Barrer and Jones, 1971):

Cation	d_3 FH90(Å)	d_3 FH150(Å)	d_1(Å)
Me_4N^+	~2.7	~0.8	4.0
$[NH_3(CH_2)_2NH_3]^{2+}$	~4.9 to 7.5*	~3.8 to 5.3*	2.8
$Co(en)_3^{3+}$	6.7	3.4	4.2

where * means according to the mutual pair orientation. As was observed experimentally, on the basis of the above estimates, the failure of Me_4N-fluorhectorite-150 to intercalate N_2 at 78 K was to be expected.

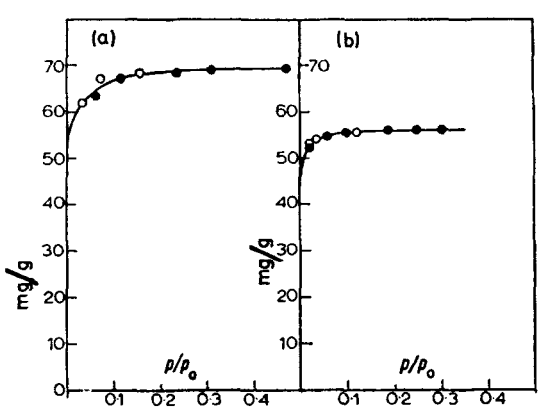


Figure 8. Sorption isotherms of n-octane at 323 K, in (a) ed-fluorhectorite-90 and (b) ed-fluorhectorite-150. ●, sorption; ○, desorption; ed = ethylenediammonium (Barrer and Jones, 1971).

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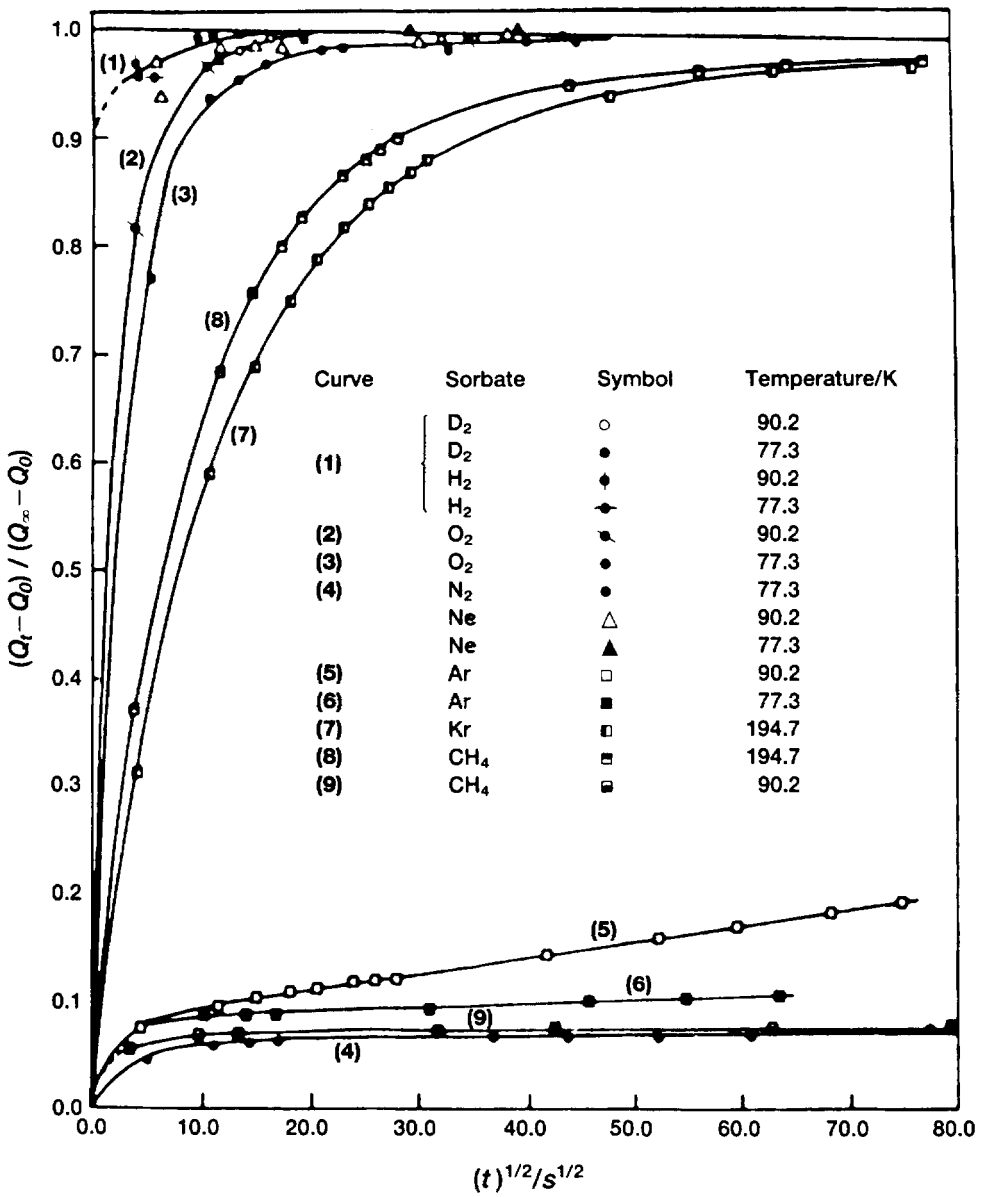


Figure 9. Sorption rates for H_2, D_2, O_2, N_2, Ne, Ar, Kr, and CH_4 in Co(III)$(en)_3$-fluorhectorite-150. At 77.3 and 90.2 K the group He, D_2, O_2, and Ne, which are all intercalated very rapidly, are strongly differentiated from the group N_2, Ar, and CH_4, which are intercalated very slowly, if at all (Barrer, 1978).

PARTIAL EXCHANGE AND SORPTION CAPACITY

A series of partially exchanged (Na, $MeNH_3$)- and (Na, Me_4N)-montmorillonite samples was investigated to see whether partial exchange could enhance the sorption capacity. An enhancement was to be expected if Na^+ and an organic cation were randomly mixed in each interlayer region. The free interlamellar area, however, was found to be almost exactly proportional to the equivalent cation fraction of the interlayer organic ion. The only explanation is that the partially exchanged crystals contained a mixture of interstratified cation layers, some containing only organic cations and the rest only Na^+ (Barrer and Brummer, 1963).

Incomplete exchange is thus an important variable if sorption capacities are compared, either among different cationic forms or for the same cationic form prepared in different laboratories.

THERMAL STABILITY

The thermal stability of smectite molecular sieves is determined by that of the interlamellar cations, if these

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Table 7. Examples of intercalation and exclusion in fluorhectorite-90 and -150 (FH90 and FH150).[1]

Cationic form	d(001) (Å)	d_1 (Å)	Temp. (K)	Intercalation in FH90		Intercalation in FH150	
				Yes	No	Yes	No
$MeNH_3^+$	11.6	2.2	78		O_2, N_2, Ar		O_2, N_2 Ar
Me_4N^+	13.4	4.0	78	O_2, N_2, Ar			N_2
			90	O_2, N_2, Ar, CH_4			
$^+NH_3(CH_2)_2NH_3^+$	12.2	2.8	78	O_2, N_2, Ar		O_2, N_2, Ar	
			273	n-C_4, iso-C_4		n-C_4, iso-C_4	
			323	n-C_8		n-C_8	
			323	2,3-di-Me-C_4	2,3-di-Me-C_4	2,3-di-Me-C_4	2,2-di-Me-C_4
			323	cyclo-C_5	neo-C_5	cyclo-C_5	neo-C_5
			323	cyclo-C_6	2,2,4-tri-Me-C_5	benzene	cyclo-C_6
			323	benzene			2,2,4-tri-Me-C_5
			323	toluene			
			323	m-xylene			toluene, m-xylene
			323	mesitylene			mesitylene
$Co(en)_3^{3+}$	13.6	4.2	77.3	H_2, D_2, Ne, Ar		H_2, D_2, Ne, O_2	N_2, Ar
			77.3	O_2, N_2			
			90.2	H_2, D_2, Ne, Ar		O_2	CH_4, Ar
			90.2	O_2, N_2, CH_4			
			194.7	Kr, CH_4		Kr, CH_4	
			273.2	Kr, CO_2			
			273.2	iso-C_4			
			273.2	neo-C_5			

[1] See explanation of terminology in footnote in Table 1.

are alkylammonium ions or $Co(en)_3^{3+}$. For the latter ion, a thermogravimetric analysis in air indicated negligible decomposition at <100°C up to complete decomposition at 250°C (Barrer and Jones, 1971). Several alkylammonium forms of montmorillonite A were also examined by outgassing each of them at a series of increasing temperatures and comparing the BET monolayer equivalent areas with that of the same form outgassed at 50°C. Figure 10 shows that all forms were stable to outgassing to ~150°C, and that the $MeNH_3$-form was least stable and the Me_4N-form most stable (Barrer and Reay, 1957).

SEPARATION

Factors which make permanently expanded clay minerals attractive for separations include the following: (1) Clear selectivity sequences are common for molecules of different structural types, such as aromatics and n-, iso-, neo-, and cycloparaffins, and are enhanced for certain of these by molecule sieving. (2) High rates of sorption are found near room temperature (cf. Figure 5), and the intercalated molecules can be rather easily desorbed. (3) Intercalation capacities are satisfactory. Thus, in $NH_3(CH_2)_2NH_3$-fluorhectorite-90 and -150 (respectively, termed ed-FH90 and ed-FH150, where ed = $NH_3(CH_2)_2NH_3$) observed uptakes of typical hydrocarbons in wt. % were (Barrer and Jones, 1971):

Sorbate	wt. % in: ed-FH90	ed-FH150
n-hexane	—	6.7
n-octane	6.9	6.4
2,3-dimethylbutane	5.1	4.5
cyclopentane	7.2	7.6
cyclohexane	5.9	not intercalated
benzene	12.9	8.1
toluene	9.6	not intercalated
m-xylene	5.6	not intercalated
mesitylene	5.4	not intercalated

Isotherms were determined at 349.8 or 353 K for the following binary mixtures with feed mixtures of constant composition for each mixture isotherm, but changing these compositions over a given series of isotherms (Barrer and Hampton, 1957; Barrer and Perry, 1961a, 1961b):

Mixture	Cationic form of montmorillonite Et_4N-	Me_4N-	$MeNH_3$-
C_6H_6 + n-C_7H_{16}	+	+	+
n-C_7H_{16} + cyclo-C_6H_{12}	−	+	+
n-C_6H_4 + iso-C_8H_{18}	−	+	+
cyclo-C_6H_{12} + iso-C_8H_{18}	−	+	+
C_6H_6 + CH_3OH	−	+	+
C_6H_6 + cyclo-C_6H_{12}	−	−	+
CH_3OH + CCl_4	−	+	−

where + or − denote systems for which mixture isotherms were or were not determined. Figure 11 compares the mixture isotherms for the pairs benzene + methanol and benzene + n-heptane in the Me_4N- and $MeNH_3$-montmorillonite samples. The illustration shows the selectivity to be the opposite in the two sorbents for benzene + methanol and that a cross-over in selectivity exists in the $MeNH_3$-form for benzene +

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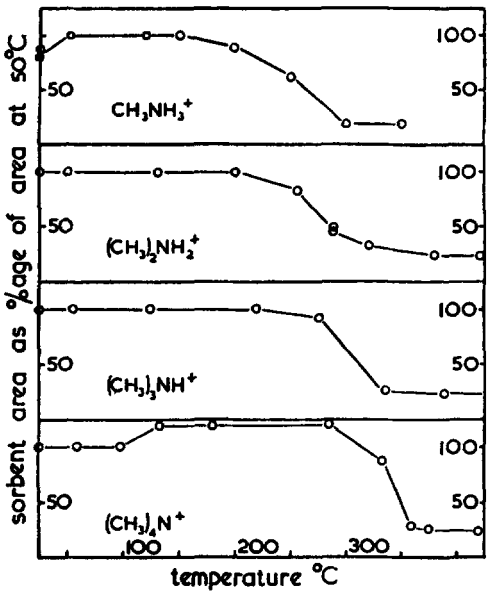


Figure 10. The BET monolayer equivalent areas, measured by N_2 sorption as functions of outgassing temperature for $MeNH_3$-, Me_2NH_2-, Me_3NH-, and Me_4N-montmorillonite samples. The areas are expressed as percentage of the area obtained on outgassing at 50°C (Barrer and Reay, 1957).

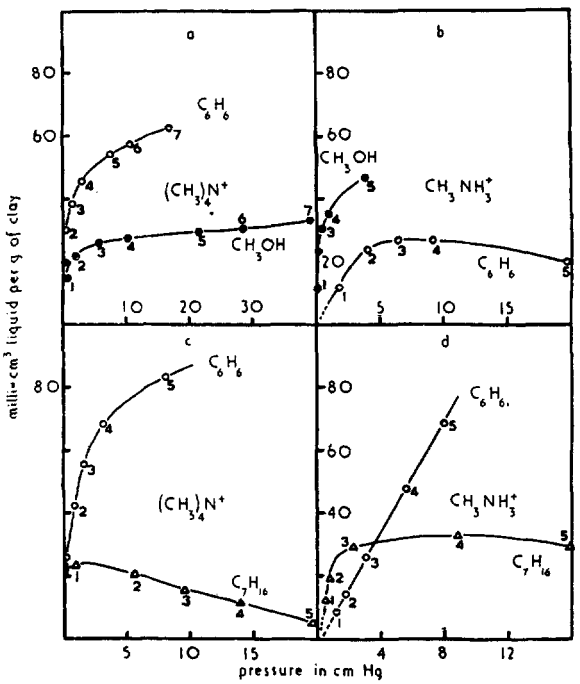


Figure 11. Comparison of isotherms at 76.8°C for binary mixtures on Me_4N- and $MeNH_3$-montmorillonites. The numbers allow corresponding points on each isotherm to be identified. The mole fractions of benzene in the feeds were (a) 0.37, (b) 0.40, (c) 0.60, and (d) 0.59 (Barrer and Hampton, 1957).

n-heptane. These selectivity data illustrate the strong influence of the exchange ion on separation factors.

Separation factors are defined for component A in a mixture of A + B as

$$\eta_A = n_A^S\, n_B^G / n_B^S\, n_A^G = n_A^S p_B / n_B^S p_A, \qquad (1)$$

where n denotes mole and p is partial pressure. The superscripts "S" and "G" denote sorbed and gaseous, respectively, and the subscripts "A" and "B" denote the two components. If the sorbent provides two distinct sorbing regions (external and interlamellar), the separation factors for each are η_A^a and η_A^i, respectively, where,

$$\left.\begin{aligned} \eta_A^a &= n_A^a p_B / n_B^a p_A \\ \eta_A^i &= n_A^i p_B / n_B^i p_A \end{aligned}\right\} \qquad (2)$$

and where superscripts "a" and "i" denote adsorbed and interlamellar. Also

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

If Eq. (3) is substituted in Eq. (1) and the result rearranged, using Eq. (2), one obtains the general result (Barrer and Perry, 1961a):

$$n_B^S \eta_A = n_B^i \eta_A^i + n_B^a \eta_A^a, \qquad (4)$$

for the influence of η_A^i and η_A^a upon the overall separation factor, η_A. For the special but important case in which component A is intercalated but B is not,

$$\eta_A = \eta_A^a (1 + n_A^i / n_A^a). \qquad (5)$$

Eq. (5) applies, for example, if one component is a n-paraffin and the other is iso-octane or cyclohexane and the sorbent is $MeNH_3$-montmorillonite-A of Table 1.

Figure 12 shows for Me_4N-montmorillonite the separation factors for benzene + n-heptane (where both

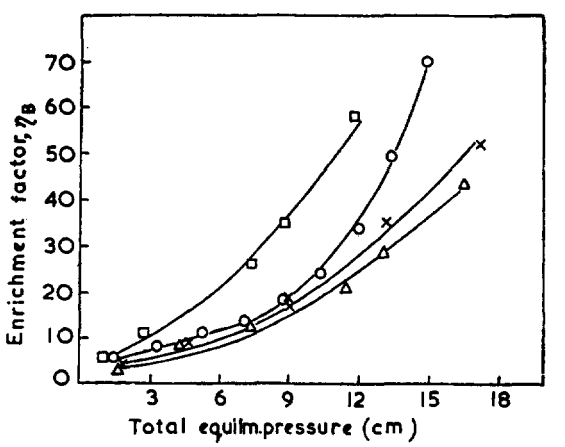


Figure 12. Separation factors as functions of total equilibrium pressure and of temperature for benzene in a benzene + n-heptane mixture. The sorbent was Me_4N-montmorillonite, and the feed mixture always contained 0.67 mole fraction of benzene. □, 80°C; ○, 85°C; ×, 90°C; and △, 95°C (Barrer and Perry, 1961b).

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Table 8. Composition changes of equilibrium liquid effected with Me_4N-montmorillonite (Barrer and Hampton, 1957).

Wt. of sorbent (g)	Mixture A + B	mole fraction A	Volume of liquid (cm^3)	Volume recovered (cm^3)	Composition of liquid recovered
7.5	C_6H_6 + iso-C_8H_{18}	0.5	1.5	0.2	~100% iso-C_8H_{18}
	C_6H_6 + iso-C_8H_{18}	0.5	2.0	0.3	96% iso-C_8H_{18}
6.5	cyclo-C_6H_{12} + C_6H_6 (m.f. 0.1) + thiophene (m.f. 0.1) + toluene (m.f. 0.1)	0.7	2.0	0.6	97% cyclo-C_6H_{12}
8.5	CH_3OH + CCl_4	0.4	1.5	0.25	99% CCl_4
7.5	C_6H_6 + n-C_7H_{16}	0.6	1.7	0.2	98% n-C_7H_{16}
7	n-C_7H_{16} + iso-C_8H_{18}	0.67	1.5	0.2	75–80% iso-C_8H_{18}
6	C_6H_6 + cyclo-C_6H_{12}	0.25	4.5	1.0	92% cyclo-C_6H_{12}

are intercalated) as a function of the total pressure and temperature. $\eta_{C_6H_6}$ increases with pressure and decreases with rising temperature (Barrer and Perry, 1961b).

In a second approach to separations, liquid mixtures were equilibrated with the sorbent, some of the non-sorbed liquid was centrifuged off, and its composition was compared with that of the initial mixture. The more weakly sorbed component was highly enriched in the liquid recovered, as the results in Table 8 show.

In a third approach, chromatography was used. A volume of liquid of known composition was injected into a stream of dry N_2 passing through a column of sorbent. At 77°C, using the Me_4N-montmorillonite, separations were achieved for the following pairs (Barrer and Hampton, 1957):

benzene/cyclohexane	cyclo-hexane/cyclo-hexanol
toluene/cyclohexane	n-heptane/methanol
benzene/n-heptane	n-hexane/cyclo-hexane
benzene/carbon tetrachloride	n-heptane/iso-octane
benzene/toluene	n-heptane/cyclo-hexane
methanol/carbon tetrachloride	thiophene/benzene

The sorbent is notable for the selectivity shown for the aromatics and for thiophene and for its preference for n-paraffins compared with cyclo- and branched-chain paraffins.

With $MeNH_3$-montmorillonite separations were effected for the mixtures: benzene/cyclo-hexane, benzene/iso-octane, methanol/toluene, benzene/toluene, n-heptane/methanol. In this sorbent the selectivity for aromatics over n-paraffins was reduced and at low loadings may have been reversed. Aromatics were preferred over cyclo- and branched chain paraffins.

CONCLUDING REMARKS

This summary of part of our work on microporous clay minerals illustrates their potential as sorbents. In recent years, with a view to obtaining larger pores and increased thermal and hydrothermal stability, others have used various oligomeric inorganic oxycations of Al, (Al, Si), Si, Ti, Zr, Cr, and Fe as props to separate the sheets (cf. Vaughan, 1988). The products usually have greater interlayer free distances than organoclays and are providing a new chapter in the story of porous layer silicates. They may prove to be sorbents and catalysts significant in the wider saga of porous crystals, comprising zeolites, porosils, AlPOs, microporous organoclays, and certain Werner complexes and clathrates. These so-called pillared clays (PILCs) provide meso- as well as micropores, and require more detailed characterization.

REFERENCES

Barrer, R. M. (1978) *Zeolites and Clay Minerals as Sorbents and Molecular Sieves:* Academic Press, New York, pp. 474, 476.

Barrer, R. M. (1984) Sorption and molecular sieve properties of clays and their importance as catalysts: *Phil. Trans. Roy. Soc. London A* **311,** 333–352.

Barrer, R. M. (1986) Expanded clay minerals: A major class of molecular sieves: *J. Inclusion Phenomena* **4,** 109–119.

Barrer, R. M. and Brummer, K. (1963) Relations between partial ion exchange and interlamellar sorption in alkylammonium montmorillonites: *Trans. Faraday Soc.* **59,** 959–968.

Barrer, R. M. and Craven, R. J. B. (1987) Smectite molecular sieves. Part II. Expanded fluorhectorite sorbents: *J. Chem. Soc. Faraday Trans. I* **83,** 779–787.

Barrer, R. M. and Hampton, M. G. (1957) Gas chromatography and mixture isotherms in alkylammonium bentonites: *Trans. Faraday Soc.* **53,** 1462–1475.

Barrer, R. M. and Jones, D. L. (1970) Chemistry of soil minerals. Part VIII. Synthesis and properties of fluorhectorites: *J. Chem. Soc. A,* 1531–1537.

Barrer, R. M. and Jones, D. L. (1971) Chemistry of soil minerals. Part X. Shape-selective sorbents derived from fluorhectorites: *J. Chem. Soc. A,* 2594–2603.

Barrer, R. M. and Kelsey, K. E. (1961a) Thermodynamics of interlamellar complexes. Part I. Hydrocarbons in methylammonium montmorillonites: *Trans. Faraday Soc.* **57,** 452–462.

Barrer, R. M. and Kelsey, K. M. (1961b) Thermodynamics of interlamellar complexes. Part II. Hydrocarbons in dimethyldioctadecylammonium bentonite: *Trans. Faraday Soc.* **57,** 625–640.

Barrer, R. M. and Mackenzie, N. (1954) Sorption by atta-

https://doi.org/10.1346/CCMN.1989.0370501 Published online by Cambridge University Press

pulgite. Part I. Availability of intracrystalline channels: *J. Phys. Chem.* **58,** 560–568.

Barrer, R. M., Mackenzie, N., and (in part) MacLeod, D. M. (1954) Sorption by attapulgite. Part II. Selectivity shown by attapulgite, sepiolite and montmorillonite for n-paraffins: *J. Phys. Chem.* **58,** 568–572.

Barrer, R. M. and MacLeod, D. M. (1954) Intercalation and sorption by montmorillonite: *Trans. Faraday Soc.* **50,** 980–989.

Barrer, R. M. and MacLeod, D. M. (1955) Activation of montmorillonite by ion exchange and sorption complexes of tetra-alkylammonium montmorillonites: *Trans. Faraday Soc.* **51,** 1290–1300.

Barrer, R. M. and Millington, A. D. (1967) Sorption and intracrystalline porosity in organoclays: *J. Coll. Interface Sci.* **25,** 359–372.

Barrer, R. M. and Perry, G. S. (1961a) Sorption of mixtures and selectivity in alkylammonium montmorillonites. Part I. Monomethylammonium bentonite: *J. Chem. Soc.,* 842–849.

Barrer, R. M. and Perry, G. S. (1961b) Sorption of mixtures and selectivity in alkylammonium montmorillonites. Part II. Tetramethylammonium montmorillonite: *J. Chem. Soc.,* 850–858.

Barrer, R. M. and Reay, J. S. S. (1957) Sorption and intercalation by methylammonium montmorillonites: *Trans. Faraday Soc.* **53,** 1253–1261.

Brunauer, S. (1944) *The Physical Adsorption of Gases and Vapours:* Oxford Univ. Press, Oxford, United Kingdom, p. 150.

Craven, R. J. B. (1976) Sorption and separation by ion-exchanged synthetic fluorhectorites: Ph.D. thesis, London University, pp. 164, 231.

Vaughan, D. E. W. (1988) Recent developments in pillared interlayered clays: Preprint from *Perspectives in Molecular Sieve Science,* W. H. Flank and T. E. Whyte, Jr., eds., Amer. Chem. Soc. Symposium, Toronto, 1988.

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