

GAS CHROMATOGRAPHIC SEPARATION OF LINEAR HYDROCARBONS ON MICROPOROUS ORGANO-SMECTITES

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Abstract—A series of organo-montmorillonites and organo-hectorites was prepared by complete ion-exchange from the pure sodium form of the parent smectites. The organic cations were tetramethylammonium, trimethylated quaternary ammonium derivatives of the lysine and of the ornithine methyl esters, quaternarized polyammonium cations, or tetraphenylphosphonium (TPP). These organo-smectites were used as packing material for gas chromatography columns. Mixtures of light hydrocarbons (methane to n-butane; "C₁" to "C₄") could be separated. The degree of separation depends on the presence of micropores or of organophilic mesopores. The BET surface area, the micropore and mesopore volumes, as well as the size distribution of micropores and mesopores were measured for several systems. As a general trend, the retention times of the light hydrocarbons decrease with an increase of the micropore volume. In the case of TPP-montmorillonite, characterized by a large mesopore volume but for which no microporosity could be detected, separation of longer linear hydrocarbons (n-pentane to n-octane) could also be achieved.

Key Words—Gas chromatography, Gas separation, Hectorite, Hydrocarbons, Mesoporosity, Microporosity, Montmorillonite, Organo-clays, Smectites.

INTRODUCTION

Organo-clays are prepared by exchanging with organic cations the interlayer, charge-compensating, natural cations of clays such as those of the smectite family. Some organo-clays have been used as selective gas chromatographic adsorbents (White, 1957; Barrer and Hampton, 1957; Mortimer and Gent, 1963; Cowan and Hartwell, 1962; Fuchs, 1972; Knust and Schüller, 1975; Datar and Ramanathan, 1975). For example, montmorillonite exchanged with alkylammonium cations exhibited selective retentions of aromatics relative to paraffins and naphthenes (White, 1957). A smectite exchanged with methylbenzylidodecylammonium and containing an amide additive has been shown to have selective adsorption properties for organics such as alcohols, esters, ketones and hydrocarbons (Chuckwunenye and McAtee, 1987).

The intercalation of organic cations into the interlamellar spaces of smectites can open up galleries of molecular dimensions, producing zeolite-like materials with molecular sieve properties (Barrer, 1978). This type of material should be particularly well adapted to the separation of small molecules. However, only a limited amount of data on the applications of organo-clays for the separations of gases and hydrocarbons has been reported in the literature (Thielmann and McAtee, 1975; Thielmann, 1978; McAtee and Harris, 1977). A series of organo-clays was used recently as chromatographic adsorbents for the separation of air/methane/carbon dioxide (Lao *et al.*, 1991). At about the same time, the separations of air, C₆H₆/C₆H₁₄, CH₄/CO₂ and C₈ aromatic isomers were reported in a pil-

lared zirconyl-clay column (Yang and Baksh, 1991; Baksh and Yang, 1991).

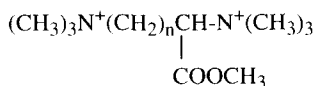
The development of efficient methods of separation of the lower hydrocarbons is an important issue for the petro-chemical industry, since the consumption of energy is rather high in the cryogenic separation processes which are still mainly used. In contrast, adsorption and membrane separation processes look quite promising for this purpose (Ilinitich *et al.*, 1992; Yang, 1987). In our earlier studies it was demonstrated that both the interlamellar spacings and the microporosity of the organo-clays were the most important factors controlling the separation of methane/carbon dioxide gaseous mixtures (Lao *et al.*, 1991).

In this paper we report the chromatographic separation of light hydrocarbons on microporous organo-smectites. The retention parameters of the hydrocarbons are correlated to the organo-clay micropore structure which was characterized by low-pressure nitrogen adsorption and desorption isotherms.

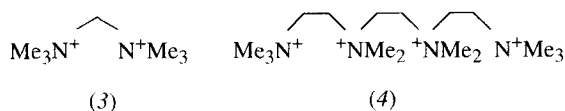
EXPERIMENTAL METHODS

The clay materials, SWy-1 and SHCa-1, were obtained from the Source Clay Repository, University of Missouri. The purification of the clays was done by standard gravitation procedures (Villemure *et al.*, 1985). Particle size analysis revealed that more than 90% of the sample was <0.2 μm esd in the case of montmorillonite and <2 μm esd in the case of hectorite. The homoionic Na⁺ montmorillonite (Na-M) and hectorite (Na-H) were prepared, purified by dialysis, and freeze-dried.

The organic cations used in this study included tetramethylammonium (TMA^+), tetraphenylphosphonium (TPP^+), the trimethylated quaternary ammonium derivatives of the lysine and of the ornithine methyl esters (LYS-Me^{2+} (1), ORN-Me^{2+} (2) and the quaternarized polyammonium cations MMDA^{2+} (3) and MTETA^{4+} (4) (Lao *et al.*, 1991).



(1) $n = 4$; (2) $n = 3$.



These quaternarized ammonium derivatives were incorporated into the interlamellar spaces of homoionic Na-montmorillonite and Na-hectorite at full cationic exchange capacity. The respective measured CEC values of 93 ± 8 and 90 ± 8 mequiv/100 g of clay are in good agreement with the theoretical values of 87 and 89 mequiv/100 g of clay (Jaynes and Bigham, 1987; Villemure, 1990). The CEC values were determined both by measuring the quantity of sodium released (ion-selective electrodes) and the quantity of organic cation absorbed by the clays (colorimetry) (Latiueu, 1991).

The organo-clays were dried under vacuum at 60°C overnight and particles of size 60–120 mesh were selected as packing material for the chromatographic columns (9 in. \times 1/8 in. o.d. and 3 ft \times 1/8 in. o.d.). Columns were equilibrated for eight hours prior to the experiment, at 90°C , with a flow of the carrier gas helium.

A Philips PW 1050/81 X-Ray diffractometer was used for X-ray diffraction studies using $\text{CuK}\alpha$ radiation. The GC instrument used was a GOW-MAC model 69-550P with a thermal conductivity detector and a SP4270 chromatography integrator. Retention times were measured in minute from the point of injection to the maximum peak height. Samples studied included gaseous light hydrocarbons ($\text{C}_1\text{--C}_4$) and liquid hydrocarbons ($\text{C}_5\text{--C}_8$). The BET measurements were performed at 77 K in an OMNISORP 100 sorptometer using nitrogen as the adsorbate. The N_2 adsorption data were used for the calculation of BET surface area, micropore volume and micropore size distribution. Desorption data were used for the calculation of mesopore volume, size and size distribution (Gregg and Sing, 1982).

In the cases where micropore volumes were not directly measured from BET methods, they were calculated from the theoretical surface area, based on the unit cell area (Villemure, 1990), from which the cross-sectional area of the organic cation was subtracted (Lao

et al., 1991). This value was then multiplied by the interlamellar distance, as measured by X-ray diffraction [$d(001) = 9.6 \text{ \AA}$]. When a comparison between the calculated and the BET measured value was possible, such as in the case of MMDA-H, the two values agreed fairly well (calculated: $77 \text{ mm}^3/\text{g}$; measured: $63 \text{ mm}^3/\text{g}$).

RESULTS AND DISCUSSION

The interlamellar spacings of the organo-clays were obtained by subtracting the thickness of the clay layer (9.6 \AA) from the experimentally determined basal spacings ($d(001)$). They are given in Table 1. The intercalation of the organic cations increased the interlamellar distances from 2.8 \AA [sodium-montmorillonite (Na-M)] to generally 4–5 \AA and 9.2 \AA in the case of tetraphenylphosphonium (TPP) incorporated into montmorillonite (TPP-M). A distance of 4–5 \AA corresponds to the height of a trimethylated quaternarized ammonium group keyed into the macrorings of the silicate surfaces. So, in all the cases, the $^+\text{NMe}_3$ moiety determines the interlamellar distance and the rest of the organic cation must lie approximately parallel to the clay layers. If the cross-sectional area per charge of the organic cation is smaller than half the area per charge of each layer, microporosity should be created. The size of the cavities will be determined by the distance between each organic cation, acting as pillars, in such a way that a higher charge density on a cation will produce larger cavities. One can expect the larger cavities to be obtained in the case of polyammonium cations, such as 4, or in the case of the smaller cations, such as TMA^+ or 3. The interlamellar distances in the organo-hectorites were systematically larger than that in the corresponding organo-montmorillonites.

The recent development of low-pressure sorption instruments has helped in the analysis of micropores. This was demonstrated in particular for zeolites (Cotterman *et al.*, 1991; Gregg and Sing, 1982; Webb and Conner, 1991) and for a class of Zr-pillared clays (Yang and Baksh, 1991). The N_2 adsorption isotherms at 77 K were measured for a series of organo-clays down to pressures in the range 10^{-6} to 10^{-7} atm. The results are shown on Figure 1 for the system MMDA-M. Similar isotherms were obtained for the other organo-clays, except in the case of TPP, for which no microporosity was detected. The isotherms are of type I in the low pressure region, with the superposition of an isotherm of type IV in the high pressure region, diagnostic of meso/macroporosity (Gregg and Sing, 1982).

The total surface areas (BET surface areas), micropore volumes and mesopore volumes of the organo-clays which were calculated from the N_2 adsorption and desorption data are summarized in Table 2. A correlation of the BET surface area, the micropore volume and the mesopore volume with the cation size could be seen in Table 2. With an increase of the cation

Table 1. Interlamellar spacings ($d_{001} - 9.6$) (Å) and retention times of hydrocarbons (C_1-C_4) on chromatographic columns filled with organo-smectite particles at 140°C and under an He flow of 35 ml/min. The abbreviations of the organic intercalates are described in the Experimental Part; M: montmorillonite; H: hectorite.

Organo-clay	Inter-layer spacing	Retention time (min)			
		C_1	C_2	C_3	C_4
Na-M	2.8	0.10	0.10	0.10	0.10
TMA-M	4.3	1.64	5.15	—	—
TPP-M*	9.2	0.54	1.10	2.50	7.50
LYS-Me-M	4.6	0.66	2.63	8.30	32.08
ORN-Me-M	4.5	0.35	1.94	6.14	29.31
MMDA-M	4.3	0.33	2.35	6.54	24.94
MTETA-H	5.1	0.28	1.58	5.23	24.30
TMA-H	4.6	0.29	2.06	6.14	22.80
LYS-Me-H	5.0	0.47	2.24	8.38	34.19
ORN-Me-H	4.8	0.30	1.83	6.88	32.48
MMDA-H	4.7	0.29	1.94	5.87	21.82
MTETA-H	5.0	0.17	1.14	4.46	20.38

* Column temperature: 30°C.

size, both the BET surface area and the micropore volume decreased correspondingly. For example, the micropore volume in the MMDA-montmorillonite is tenfold larger than that in the LYS-Me-montmorillonite. In the case of TPP-M, the TPP⁺ cations covered almost all the clay surfaces such that no micropore volume was obtained. However, a large mesopore volume was measured. Presumably, the mesopores resulted from some delamination of the layers during the sample preparation (Ocelli *et al.*, 1984; Ocelli and Finseth, 1986). Micropore size and mesopore (macropore) size distribution were also calculated from the N₂ adsorption and desorption data. The micropore size distribution analysis showed that a sharp micropore distribution centered on an equivalent spherical diameter of 5 Å was found in the samples of TMA-M, MMDA-M and MMDA-H. This corresponds to the height of the micropores measured by X-ray diffrac-

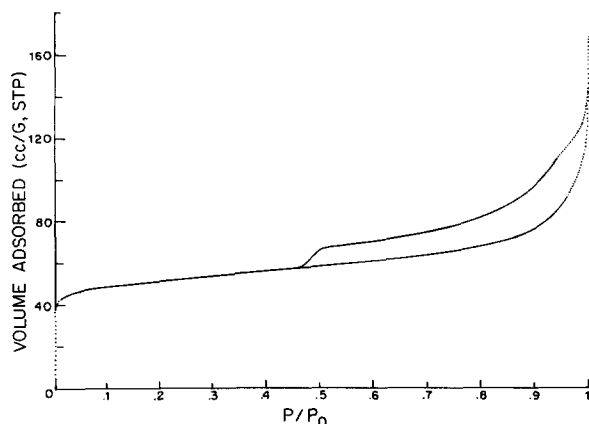


Figure 1. Nitrogen adsorption and desorption isotherms of the organo-montmorillonite MMDA-M.

Table 2. Cross-sectional area per unit charge of the organic cation (obtained from CPK models), and BET surface area, micropore volume and mesopore volume of some organo-smectites used in this study. Abbreviations: M: montmorillonite; H: hectorite; organic cation: see Experimental Part.

Organo-clay	Size of cation (Å/charge)	BET surface (m ² /g)	Micropore vol. (cm ³ /g)	Mesopore vol. (cm ³ /g)
TMA-M	29	210.3	0.071	0.048
MMDA-M	23	194.1	0.065	0.051
MMDA-H	23	219.2	0.068	0.074
LYS-Me-M	47	56.6	0.007	0.018
TPP-M	106	55.9	0	0.467

tion. The LYS-Me-M sample had a broad micropore size distribution. All the organo-clays had a sharp mesopore distribution centered on a diameter of 40 Å with the exception of TPP-M which had both mesopores at 40 Å and at 200 Å in equivalent spherical diameters.

The retention times of C_1-C_4 hydrocarbons (methane-butane) on gas chromatography columns filled with various organo-montmorillonite and organo-hectorite particles are shown in Table 1. The retention times of the hydrocarbons on the organo-clay columns were larger than that on the Na-montmorillonite column. The retention times increased with an increase of the number of carbons of the hydrocarbons. This result is comparable to the results for chloroalkylammonium-smectites (McAtee and Harris, 1977; Thielmann, 1978). No measurable separation of hydrocarbons could be observed on a Na-montmorillonite (Na-M) column. In this latter case, the most plausible interpretation is that not only are the interlamellar spaces hydrophilic, but also the interlamellar distance (2.8 Å) is too small to allow inclusion of the hydrocarbon molecules between the aluminosilicate layers. As a result the only allowed chromatographic path of the hydrocarbons is in the spaces between the clay particles; and, as a result, the

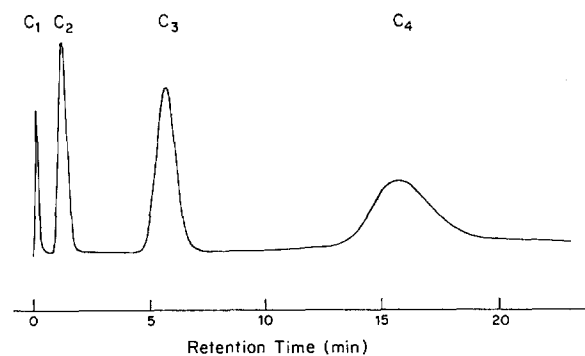


Figure 2. Chromatographic separation of C_1-C_4 hydrocarbons by a MMDA-montmorillonite column: column: 9 in. \times 1/8 in. o.d. carrier gas: He at 50 ml/min column temperature: 70°C hold 4 min, then to 90°C at 10°C/min.

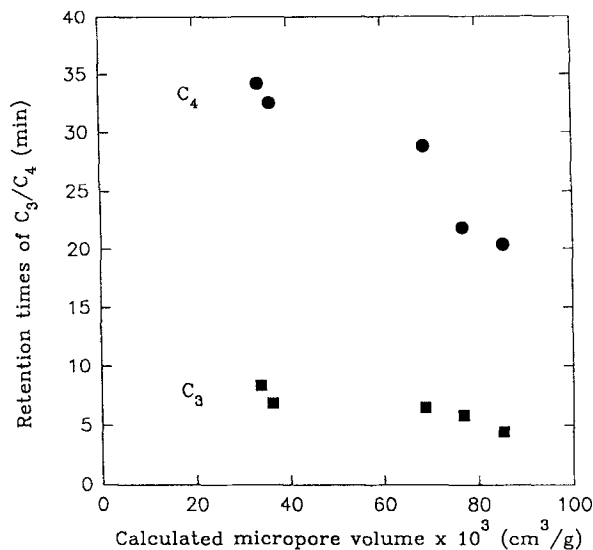


Figure 3. Correlation between the retention times of hydrocarbons (C_3/C_4) and the calculated micropore volume of the organo-clays.

differences in the various diffusion rates cannot be large enough to allow separation. The intercalation of organic cations into the interlamellar spaces of the clays, however, increased the interlayer distance such that the interlamellar spaces became available for adsorption of hydrocarbons. The longer retention times of hydrocarbons on the organo-clays, compared to that on Na-M, can be attributed to the adsorptions of hydrocarbons in the micropores of the organo-clays. Figure 2 shows an example of the type of separation that can be achieved on a very short MMDA-M column.

The retention times of the hydrocarbons could generally be correlated to the dimensions of the micropores in the organo-clays. The correlation between the retention times of propane and n-butane in the organo-clays and the micropore volumes is shown in Figure 3. One can note that the retention times decrease as the micropore volume in the organo-clays increases. This finding is in agreement with the fact that not only diffusion rates of hydrocarbons in large micropores are expected to be larger than in smaller ones, but also that the desorption rates are expected to be faster. Short retention times of hydrocarbons were observed in the TPP-M column in which large amounts of mesoporosity were found (Table 2). This is attributed to the higher diffusion rates of hydrocarbons in the organophilic mesopores of this sample. Therefore, a complete separation of hydrocarbons could be achieved at room temperature on a TPP-M column (Table 1), while in all the other systems the separations were achieved at higher temperatures. In addition, the mesoporous TPP-M material could be used for the separation of hydrocarbons with higher molecular weight (C_5 – C_8 ; n-pentane–n-octane), as shown on Figure 4.

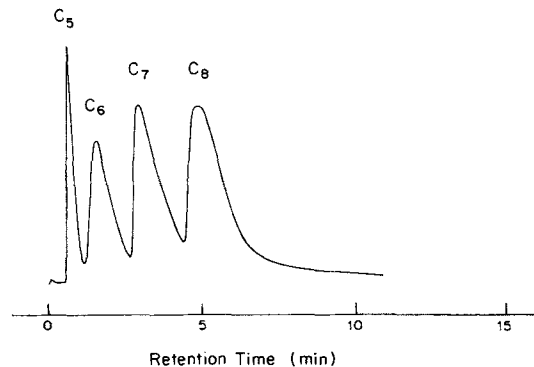


Figure 4. Chromatographic separation of C_5 – C_8 hydrocarbons by a TPP-montmorillonite column: column: 3 ft \times $\frac{1}{8}$ in. o.d. carrier gas He: at 45 ml/min column temperature: 90°C hold 1 min, then to 170°C at 20°C/min.

CONCLUSIONS

The separation of light hydrocarbons could be achieved on a chromatographic support consisting of organo-smectite particles. The separation depends on the presence of micropores or of organophilic mesopores in the organo-clay. The gas chromatography results reported above demonstrate that organo-clays, which can be prepared with a large variety of pore sizes and shapes, can provide a large degree of flexibility in controlling separation processes.

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