GAS CHROMATOGRAPHIC SEPARATION OF CRESOLS BY VARIOUS QUATERNARY AMMONIUM SUBSTITUTED MONTMORILLONITES

Key Words—Cresol, Dispersion, Gas chromatography, Montmorillonite, RNH_3-montmorillonite.

Over the past two decades, the utilization of organo-clays as chromatographic stationary phases has received much attention. White (1957), who first described the use of an organo-clay in this capacity, exchanged the natural cations of montmorillonite with several alkylquaternary ammonium ions and determined the selective retention of aromatic hydrocarbons relative to paraffins and naphthenes. He postulated that the aromatic hydrocarbons followed adsorption chromatography while partition chromatography occurred with the paraffins. Barrer and Hampton (1957), using aklylammonium montmorillonites as stationary phases, obtained a sharp separation of paraffins (C_6 or larger). They discussed selectivity of the paraffins in terms of microsieving abilities of the clays.

Mortimer and Gent (1963), using commercially available dimethyldioctadecyl ammonium montmorillonites found that interlamellar distances played only a minor part in the separation of xylene isomers. Cowan and White (1962) proposed that the electronic transitions occurring within the sorbate molecules governed the extent of adsorption. In the separation of aromatic hydrocarbons relative to paraffins, it generally has been accepted that adsorption plays the greater role. As a result, aromatic hydrocarbon separation has received much attention (Mortimer and Gent, 1963; Datar *et al.,* 1975; Cowan and Hartwell, 1962; Van Rysselberge and Van der Stricht, 1962; Kiselev *et al.,* 1972; Fuchs, 1972; Chitour and Vergnaud, 1974; Carringer *et al.,* 1975; Vasofsky and Slabough, 1976).

The present study deals with chromatographic behavior of quaternary ammonium substituted montmorillonite and quaternary amine salts coated onto a stationary phase. A number of straight chain amines and aromatic amines were chosen so that a variety of clay-complexes could be examined.

EXPERIMENTAL

Centrifuged, spray-dried Wyoming montmorillonite obtained from Baroid Division, NL Industries, was weighed and added in small increments to 2 liters of distilled water in a three-speed Waring Blendor and stirred for 15 min. The amine salts were weighed and dissolved in 250 ml of distilled water and added in small aliquots to the clay dispersion over a 5-min dispersion time. The dispersion was allowed to stand for 24 hr before it was filtered and washed with distilled water until free of chloride ion using the silver nitrate test. The resulting organo-clay was dried at 100°C. All samples were prepared on the basis of 1 meq organic cation per 1 g of dry clay. The column packing material was prepared by dispersing the organo-clay in a mixed solvent of 90% toluene-10% methanol and adding it to a weighed amount of Chromosorb W. The solvent was removed by drying at 100°C in an oven. The amine salts used were tetramethylammonium (TM) chloride, dimethyldioctadecyammonium (DMDO) chloride, benzyloctadecyldimethylammonium (BODM) chloride, and dibenzyldioctadecylammonium (DBDO) chloride.

Columns were prepared using aluminum tubing with a 2.4-mm inner diameter and a 2-m length. One end of the tubing was plugged with a piece of glass wool, the tube was suspended with a short thistle tube attached to the open end, and the sample packing was poured into the column while it was vibrated at 60 c/s with an Electrograver tool. After filling, the column was plugged with glass wool and Swagelok fittings placed on both ends of the tubing. The finished columns were then bent into a coil by wrapping the tubing around a cylindrical form, 6.5 cm in diameter.

Gas chromatographic data were obtained using an Areograph Model 204 gas chromatograph. The detector for the chromatograph consisted of a hydrogen-flame ionization detector operated at 190 V dc. Helium was used as the carrier gas with a flow rate of 40 ml/min, and each column was conditioned at 150°C for one day with a small helium flow. Samples for separation were injected with a Hamilton number 19 syringe. Retention times were measured in arbitrary units of 24 sec/unit from point of injection to maximum peak height.

Surface area measurements were obtained with a Perkin Elmer Model 212C Sorptometer. The desorption curve was used for the calculation of the surface area as described by Thomas and Bohor (1968).

RESULTS AND DISCUSSION

In addition to the organo-clay packed columns, columns of centrifuged Na-exchanged Wyoming bentonite and of Chro-

Table 1. Isomer retention times and R values of amine chlorides on organo-montmorillonites.

Amine salt[3]	Retention time[1] cresol			R values cresol[2]			
	meta	ortho	para	Rop	Rom	Rpm	ΣR
TM chloride	1	1	1	0	0	0	0
DMDO chloride	4.5	3.5	4.5	0.5	0.4	0	0.9
DBDO chloride	3.0	2.8	3.0	0.1	0.1	0	0.2
BODM chloride	1.5	1.1	1.5	0.4	0.4	0	0.8
Chromosorb W	2.0	1.4	2.0	0.7	0.7	0	1.4

[1] Retention time in arbitrary units of 24 sec/unit from point of injection to maximum peak height.

[2] Resolution between any two peaks calculated from $R_{xy} = 2d/(y_1 - x_1)$, where d is the distance between maxima of peaks and x and y and x_1 and y_1 are the width of the baseline cut by the two tangents for each peak. R_{op} = resolution between ortha and para; R_{om} = resolution between ortha and meta; R_{pm} = resolution between para and meta; ΣR = an arbitrary value used to compare overall separating ability of the columns.

[3] TM = tetramethylammonium; DMDO = dimethyldioctadecylammonium; DBDO = dibenzyldioctadecylammonium; BODM = benzyloctadecyldimethylammonium.
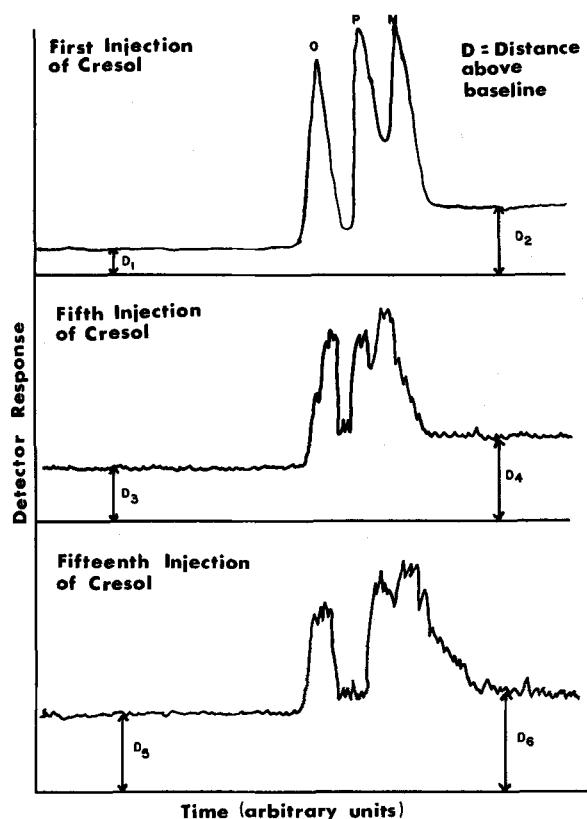
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Figure 1. Effect of number of cresol injections on peak resolution and background of chromatograph runs.

Figure 2. Effect of the addition of acetone on peak resolution of cresols of chromatograph runs.

mosorb W were prepared. When cresol mixtures were injected, the sodium-clay column simply adsorbed the cresol, whereas the Chromosorb W column gave a two peaks with no separation of the meta and para isomers. Columns were also prepared containing Chromosorb W coated with each of the amine salts. The chromatograph peaks obtained were very sharp, but the separation was not great. The retention times and R values (resolution between any two peaks) for each of these columns are shown in Table 1.

The columns containing organo-clay coated onto Chromosorb W were prepared at a concentration of 10% by weight of the organo-clay. Surface areas of these packing materials were found to be about 1 m²/g, except for the tetramethylammonium montmorillonite which had a area of 186 m²/g. As a general rule, the lower the surface area, the less likely will the isomers be separated by a microsieving process. R values of these columns are shown in Table 2. The column that gave the poorest separation was the tetramethylammonium-clay column, apparently due to adsorption of the cresol on the clay surface. The column that gave the best separation for the cresol isomers was the one that contained dibenzyldioctadecylammonium montmorillonite on Chromosorb W. From a consideration of the size of the tetramethylammonium ion it can be shown that this ion has the ability to separate the clay platelets but that it will not fully cover the surface. Thus, the nitrogen gas used in the specific surface area determination has access to the clay surface and therefore yields the relatively high value. For a clay such as dibenzyldioctodecylammonium montmorillonite, however, the surfaces between clay platelets are fully occupied by bulky organic groups which results in a low mea-
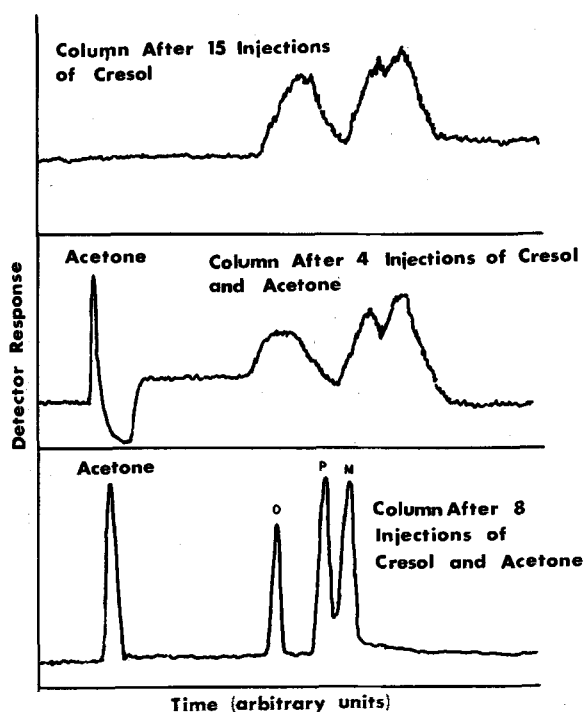
sured surface area and no available clay surface for cresol adsorption.

A column was prepared by first adding 5% dibenzyldioctadecylammonium chloride and then 5% dibenzyldioctadecylammonium montmorillonite to Chromosorb W (R values shown in Table 2) to determine if the resulting organophilic Chromosorb W surface might enhance the separating ability of the organo-clay. As shown, this column performed the same as the dibenzyldioctadecylammonium montmorillonite column.

It was noted with all columns that repeated injections of cresol gave a decrease in column resolution as illustrated in Figure 1. This was probably due to the retention of cresol onto the column as indicated by an increase in background with increasing number of injections. Using the column that contained 5% DBDO amine chloride and 5% DBDO montmorillonite as an example, it was shown that cresol dissolved in acetone or injections of acetone restored the resolution of the

Table 2. R valves for isomer 10% organo-clay columns.

Quaternary ammonium montmorillonites[1]	Cresol[1]			
	Rop	Rom	Rpm	ΣR
TM montmorillonite	0.36	0	0.36	0.72
DMDO montmorillonite	0.4	0.7	0.5	1.6
DBDO montmorillonite	1.7	1.8	0.5	4.0
BODM montmorillonite	1.1	0.8	0.3	2.2
5% DBDO montmorillonite/ 5% DBDO chloride	1.4	1.9	0.7	4.0

[1] See Table 1 for abbreviations.

Before Dispersant is Added

Organic Layer - - - -
Dispersant ⊂⊃

After Dispersant is Added
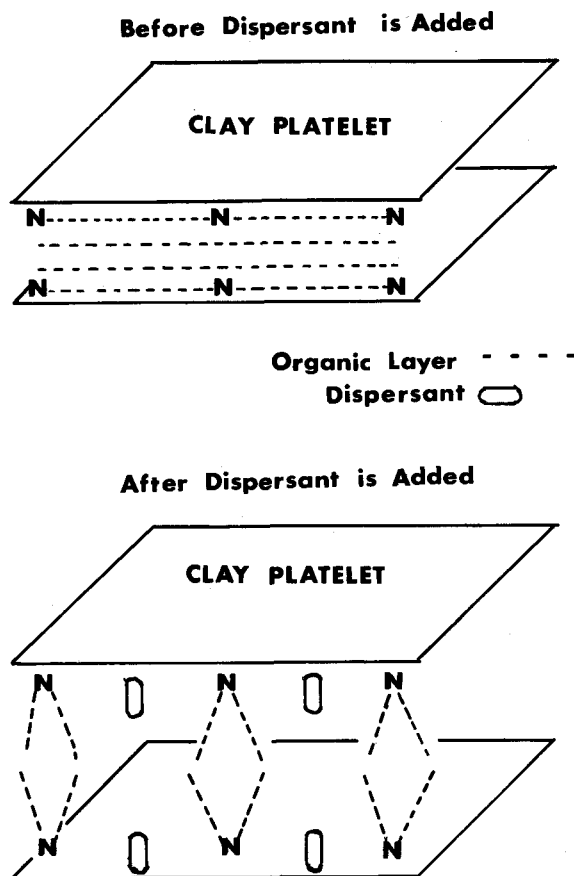
Figure 3.   Schematic representation of the effect of a dispersant on organo-clays.

Organic Layer - - - - - - - -
Silicate Layer ═══════
Acetone ⊂⊃

Before Acetone

After Acetone

Figure 4.   Schematic representation of the effect of acetone dispersant on organo-clay sorbed to Chromosorb W.

column (Figure 2). This cycle of cresol retention and acetone-induced recovery of resolution could be repeated several times indicating no permanent change in the column itself. No known reaction takes place between acetone and cresol, and thus the effect is apparently due to acetone alone and not to a complex formed between the cresol and acetone.

To explain the action of the acetone on the chromatograph columns, it should be considered that a large cation such as DBDO would completely cover the clay surface (Jordon, 1949). Furthermore, in the preparation of lubricating greases by the gelation of oil with a compound such as DBDO-clay, polar organic substances such as acetone are effective in increasing the dispersion of the colloid (Finlayson and Mc-Carthy, 1950; Fariss, 1957; Damerell and Milbergh, 1956). Granquist and McAtee (1963) envisioned that the polar solvent dispersants were attracted to clay surfaces, forcing the free ends of the organic chains of the quaternary ammonium molecules from the clay surface and thus aiding the separation and dispersion of the clay platelets (see Figure 3).

The dispersant action of acetone on organo-clays can explain the behavior of the 5% DBDO chloride-5% DBDO montmorillonite column. After the column was conditioned for 24 hr with helium (very low rate of flow), most of the volatile material was probably expelled from the surface of the organo-clay, and the aggregates collapsed. With this helium flow, the baseline of the recorder was at its minimum value. As mixtures of cresol were injected, the isomers of cresol were separated,
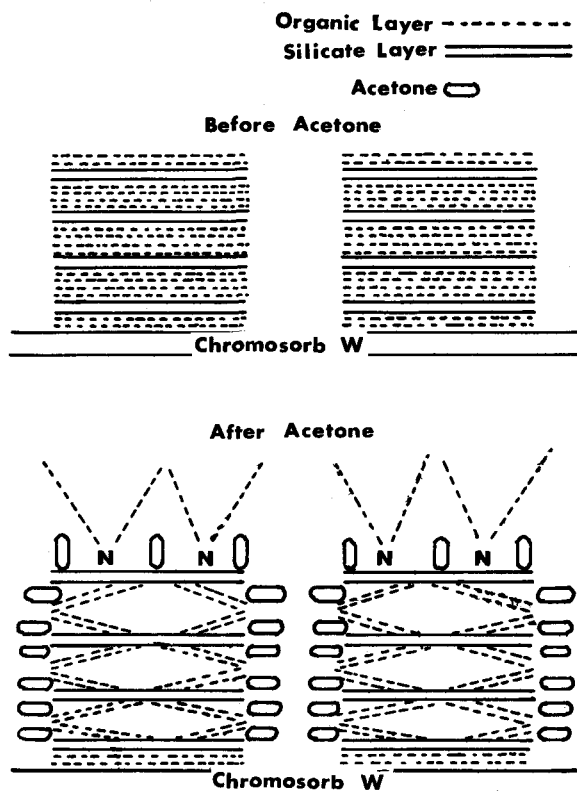
but some of the cresol was apparently adsorbed to the clay surface. As this cresol was slowly released over a long period of time, a high recorder background was observed. When acetone was injected into the column (5–19 injections of 10 μl each) the background noise on the recorder returned to its original value. It is proposed that the acetone caused a slight swelling of the clay platelet aggregates much in the same manner as that in grease systems (Figure 4) and in so doing released the trapped cresol. Since cresol is much less polar than acetone and thus less strongly adsorbed to the clay surface, the acetone displaced the cresol. The column temperature of 150°C was much higher than the boiling point of acetone (85°C); therefore, most of the acetone held by ion–dipole interaction with the exchange cation was quickly expelled from the column, although some may have been retained due to the strong adsorption forces between the acetone and clay. It also was found that when small amounts of acetone were mixed with the cresols, an increase in peak resolution occurred.

Amounts of acetone too small to cause a general expansion of clay aggregates might have been sufficient to expand organic molecules on the uppermost surface of each aggregate. These clay platelets with their organic ligands extended could then be of prime importance in the separation of cresol isomers. Peak resolution did not change abruptly after stopping the acetone injections, but degraded slowly, indicating that all of the acetone did not desorb immediately but was released slowly from the clay surface. It is proposed that the efficiency of separation of cresol isomers is mainly a function of the organic ligands extended from the clay surface. As the ligands collapse to the clay surface, the cresol is trapped resulting in loss of resolution and high background.

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