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CROSS-LINKED HYDROXY-Al-MONTMORILLONITE AS A STATIONARY PHASE IN LIQUID CHROMATOGRAPHY

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Abstract—Quasi-spherical particles (7-μm mean diameter) were prepared from cross-linked hydroxy-Al-montmorillonite (basal spacing = 15.3 and 18.6 Å) by spray-drying. These particles (SP-CLM) were used as a packing material for columns in high-pressure liquid chromatography (HPLC). Aromatic phosphate esters, chlorosubstituted phenyl-ureas, monosubstituted benzenes, and the o-, m-, and p-isomers of disubstituted benzenes were separated on the columns, using isopropanol and hexane. Alkyl and alkoxy groups in the solute molecules sterically hindered the interaction of these molecules with the solid phase. The retention of the isomers of disubstituted benzenes that possess one electronegative (or dipolar) and one nonpolar substituent increased in the order: o- < m- < p-. In contrast, for all investigated disubstituted benzenes containing two electronegative (or dipolar) substituents, the o-isomer was retained on the 18.6-Å SP-CLM more strongly than the m- and p-isomers. The chromatographic data suggest that the strength of the interaction of phenolic groups with the solid phase increased with the acidity of these groups. The o-isomers of phenols that contained an additional electronegative (or dipolar) substituent displayed an exceptionally strong adsorption. The capacity of the o-isomers of disubstituted benzenes containing two electronegative (or dipolar) substituents to form chelates with Al probably was responsible for the strong retention of such o-isomers compared with the retention of the corresponding m- and p-isomers.

Cross-linked hydroxy-Al-montmorillonite acted as a strong and selective adsorbent for many families of organic compounds. It was used successfully as the solid phase in HPLC separations with eluents ranging from nonpolar (e.g., hexane) to highly polar (e.g., water).

Key Words—Adsorption, Chelation, Cross-linked smectite, Disubstituted benzene, High-pressure liquid chromatography, Hydroxy-Al, Monosubstituted benzene, Phenyl-urea, Phosphate esters.

INTRODUCTION

The use of spray-dried, quasi-spherical particles of montmorillonite (SP-bentonite) as a packing material for high-pressure liquid chromatography (HPLC) columns was reported by Mingelgrin and Tsvetkov (1985) and by Tsvetkov and Mingelgrin (1987). The spray-dried particles were composed of clay platelets, the orientation of which relative to each other within the particle closely resembled their orientation in the suspension used to generate the SP-bentonite. This orientation contrasts with the parallel, face-to-face arrangement of platelets typical of bentonite powder. Chromatographic separations by SP-bentonite columns have been used to study the interaction of many organic monomers with montmorillonite (Mingelgrin and Tsvetkov, 1985; Tsvetkov, 1985; Tsvetkov and Mingelgrin, 1987). Cross-linked hydroxy-Al-montmorillonite (Al-CLM), developed by Lahav *et al.* (1978), made available a new adsorbent having a rigid, well-defined structure. Such cross-linked montmorillonite products can be prepared with different c-spacings. The c-spacing is determined by the nature and organization of the polycationic hydroxy-Al species intercalated with the negatively charged montmorillonite platelets (Shabtai *et al.*, 1984; Lahav and Shani, 1978). Size-selective separations can thus be achieved by preparing Al-CLM products having the desired basal spacing. The Al in the intercalated polycations is an acidic site, which may serve as a central cation in complexes with numerous molecules and ions.

In the present study, the interaction of Al-CLM with some aromatic adsorbates was investigated. The following aspects of that interaction were examined: (1) the role of the intercalated Al species in the adsorption process; (2) the effect of variations in the c-spacing on the chromatographic behavior of Al-CLM; (3) the dependence of the interaction between substituted benzenes and Al-CLM (or other aluminosilicate systems) on the nature of the substituents and on their relative position around the aromatic ring; and (4) the potential use of cross-linked hydroxy-Al-montmorillonite for chromatographic separations of aromatic molecules. Results obtained in the present study may make it possible to predict the order of elution of the ortho-, meta-, and para- isomers of many environmentally and economically important disubstituted benzenes if the eluent is nonaqueous.

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EXPERIMENTAL

Aqueous suspensions of Al-CLM were spray dried, and the resulting particles (SP-CLM) were used as the solid phase in HPLC columns. SP-CLM has a low swelling capacity; hence, it can be used with solvents of practically any polarity. Preheating, which was required to stabilize SP-bentonite if it was used with polar solvents, was not necessary for SP-CLM for most applications, even if water was used as the mobile phase.

Preparation of the Al-CLM

Homoionic Na-clay was prepared by washing crude Fisher bentonite (B-235, Fisher Scientific Co., Fairlawn, New Jersey) four times with a 1 M NaCl solution, followed by the removal of the excess electrolytes by dialysis. The suspension was then centrifuged and freeze-dried. The <2-μm fraction was separated by sedimentation. Hydroxy-Al suspensions were prepared by dropwise addition of a 0.2 M NaOH solution in deionized water to a 0.2 M $AlCl_3$ solution up to an OH/Al ratio of 2.3. The resulting aluminum hydroxide suspension was aged at 35°C for 20 days.

The cross-linking was carried out by a procedure described by Lahav and Shani (1978), using a 0.2% (w/v) clay suspension. Al-CLM having Al/clay ratios of 2 and 4 mmole/g were prepared.

Spray drying

A 0.7% (w/v) suspension of Al-CLM in deionized water was fed into a spray drier (Laboratory Spray Drier, Niro Atomizer, Copenhagen, Denmark). The inlet and outlet temperatures were 350° and 110°C, respectively, and the feeding rate was 6.9 liter/hr. Because the suspension was sprayed from the atomizer into a very hot (350°C) air stream, the drops evaporated at such a high rate that the suspended Al-CLM tactoids had insufficient time during the drying process to significantly modify their orientation relative to each other. Consequently, the Al-CLM tactoids retained a relative orientation in the dried particles similar to that in the suspended state, resulting in a poorly ordered arrangement of the tactoids within the SP-CLM particles (Mingelgrin and Tsvetkov, 1985).

Preparation of the HPLC columns

The spray-dried material (SP-CLM) was washed three times with a 40% isopropanol solution in doubly distilled water and twice with pure isopropanol to remove the excess of NaCl. A slurry of the washed material in degassed isopropanol was then prepared. A stainless steel column (16 × 0.46 cm) was filled with the suspended SP-CLM with the aid of a precolumn (30 × 0.46 cm). The packing was performed by first using low vacuum and then a high-pressure Tracor 955 LC pump at 4000 psi with n-hexane as the eluent.

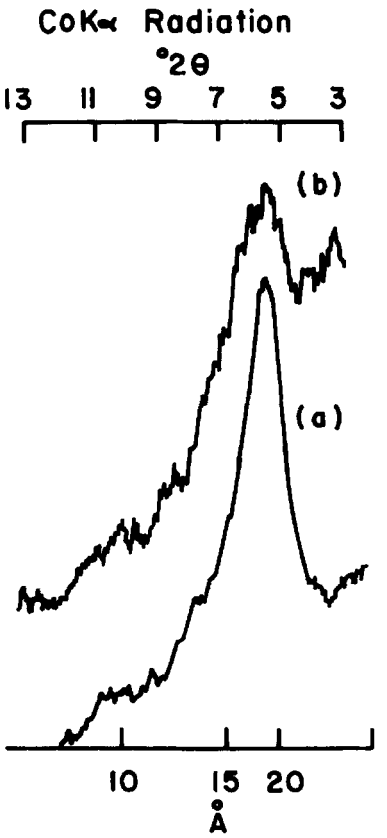


Figure 1. Small-angle X-ray powder diffractograms of wide-spaced hydroxy-Al-montmorillonite. (a) Before spray-drying (Al-cross-linked montmorillonite). (b) After spray-drying (SP-cross-linked montmorillonite). CoKα radiation.

Analytical procedures

Scanning electron micrographs (SEMs) of SP-CLM samples were obtained using a Cambridge S-180 electron microscope. X-ray powder diffraction (XRD) analysis was performed using a Philips X-ray diffractometer type 1030 and Co radiation. HPLC chromatograms were made on a Tracor HPLC system equipped with a variable-wavelength UV detector model 970A. Solvents of HPLC grade (E. Merck, Darmstadt) were used in all experiments. The eluents used were n-hexane, isopropanol, and various mixtures of these two solvents.

RESULTS

The d-values of the various cross-linked montmorillonite products were determined by XRD to be 15.3 and 18.6 Å for the Al-CLM prepared with 2 and 4 mmole Al per g clay, respectively. In the following, the cross-linked montmorillonite having a d-value of 18.6 Å will be referred to as wide spaced (ws) and that with a d-value of 15.3 Å will be referred to as narrow spaced (ns). The d-value of the spray-dried SP-CLM (ws) was

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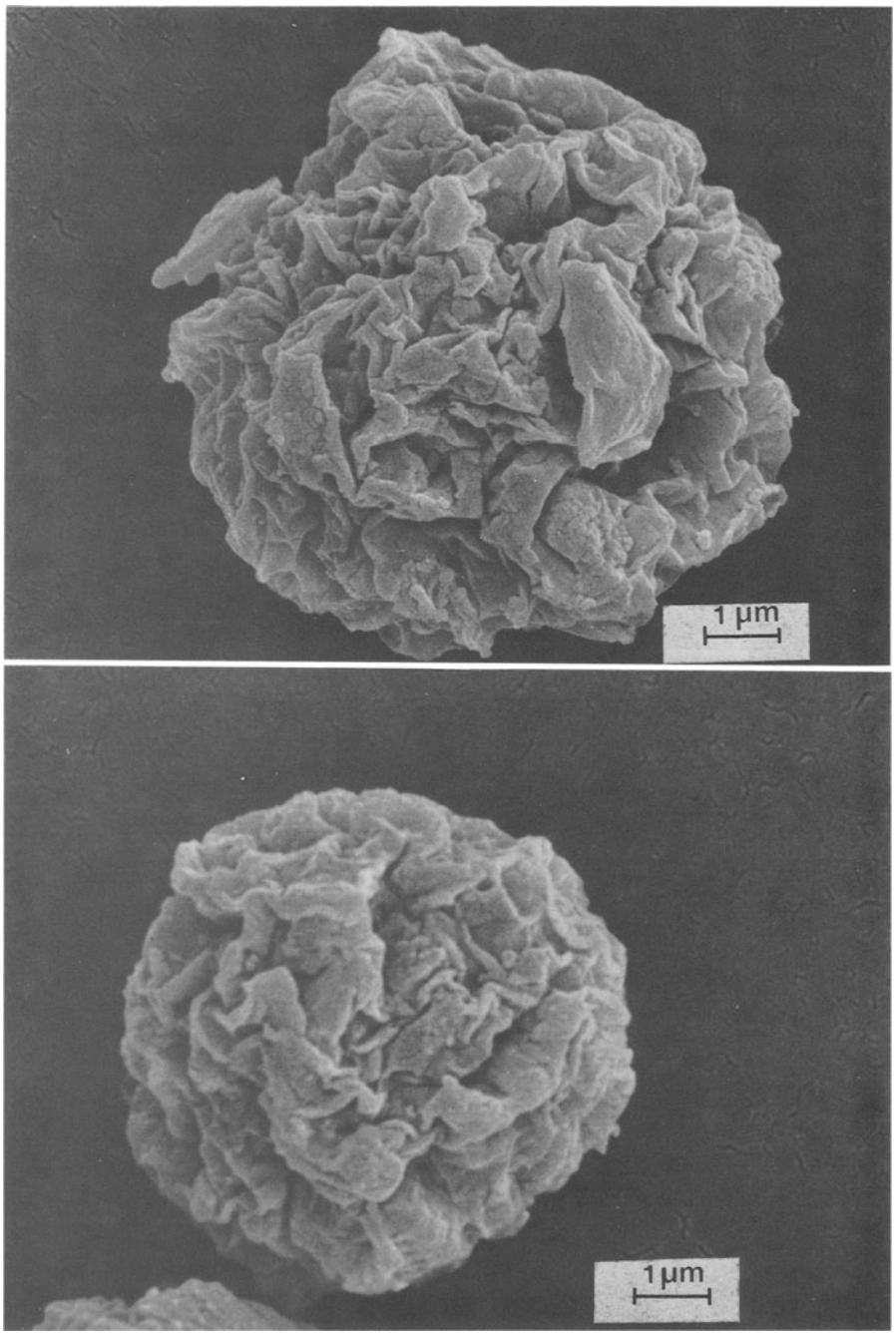


Figure 2. Scanning electron micrographs of spray-dried wide-spaced hydroxy-Al-montmorillonite.

18.6 Å, the same as that of the Al-CLM from which it was prepared (Figure 1). The poorly resolved XRD pattern in Figure 1b at $<5°2\theta$ is in agreement with the suggested poorly ordered arrangement of the hydroxy-Al-montmorillonite tactoids in the SP-CLM particles (Mingelgrin and Tsvetkov, 1985; see also the Experimental section of the present paper). The XRD peak corresponding to the 001 spacing broadened if the Al-CLM was spray dried to form SP-CLM (Figure 1). This broadening suggests some deformation in the cross-linked product during the spray-drying process. SEMs of SP-CLM particles are presented in Figure 2. The quasi-spherical particles had a mean diameter of 7 μm.

The adsorption on Al-CLM of nitrophenyl-organophosphate esters and of chlorosubstituted phenylureas was investigated. The pesticides parathion (0,0-di-

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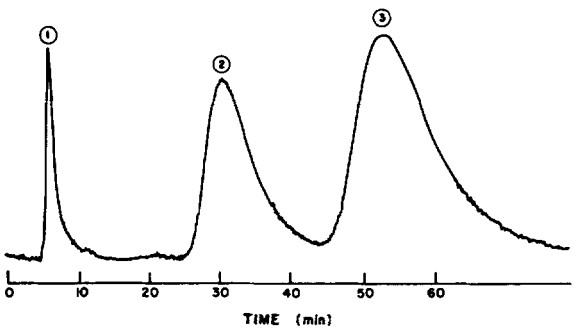


Figure 3. Separation of p-nitrophenol (1), parathion (2), and methyl parathion (3) on a wide-spaced, spray-dried, cross-linked montmorillonite column (16 × 0.46 cm); eluent = isopropanol; flow rate = 0.28 ml/min; detection UV, λ = 250 nm. Paraoxon was eluted after 140 min.

Table 1. Retention of some substituted phenyl pesticides on spray-dried, cross-linked montmorillonite columns (eluent = isopropanol).

Compound	Melting point[1] (°C)	Solubility in water[1] (mg/liter)	d-value 15.3 Å Capacity ratio (k')[2]	d-value 18.6 Å Capacity ratio (k')[2]
Parathion	6	24	0.7	4.2
Methyl parathion	35–36	55–60	0.6	8.1
Paraoxon	—	104	0.8	22.3
Linuron	93–94	81	0.1	0.5
Diuron	158–159	42	0.5	2.5
Monuron	174–175	230	2.6	3.6

[1] Worthing (1983).

[2] The capacity ratio (k') is defined as: $(t_r - t_0)/t_0$, where t_r is the retention time of the compound of interest, and t_0 is the retention time of non-interacting molecules that are eluted through the column at the rate of flow of the eluent.

ethyl-0-4-nitrophenyl phosphorothionate) and methyl parathion (0,0-dimethyl-0-4-nitrophenyl phosphorothionate) and their metabolites paraoxon (0,0-diethyl-0-4-nitrophenyl phosphate) and p-nitrophenol were well separated on SP-CLM (ws) columns (Figure 3 and Table 1). The strength of adsorption of the organophosphate esters on SP-CLM (ws) increased in the order: parathion < methyl parathion < paraoxon. The same order was observed for the retention of these esters on spray-dried montmorillonite (SP-bentonite) columns (Tsvetkov, 1985). This order is in agreement with the mechanism proposed by Mingelgrin and Saltzman (1979) for the adsorption of organophosphate esters, according to which the phosphate (or thiophosphate) group interacts with cations at the solid surface or with the hydration shells of the cations. Thus, paraoxon may have adsorbed more strongly than parathion and methyl parathion because the P=O bond is more polar than the P=S bond. Whereas the dipole moment of paraoxon is 5.30 debye, that of parathion is 4.98 debye (Ketelaar *et al.*, 1958). Methyl parathion adsorbed more strongly than parathion, probably because the methoxy groups of methyl parathion hindered the approach of the thiophosphate moiety to the interacting site at the surface to a lesser extent than did the more bulky ethoxy groups of parathion.

The retention of all three organophosphate esters by the narrow spaced SP-CLM (d = 15.3 Å) was rather weak (Table 1), possibly because of the inaccessibility of the adsorption sites in the interlayer spaces of SP-CLM (ns). Both the methoxy and ethoxy groups were apparently bulky enough to retard the penetration of the adsorbate molecules into the interlayer spaces of the narrow spaced, pillared CLM product (Lahav *et al.*, 1978).

Figure 4 presents the separation of three chlorosubstituted phenylureas (urons) on SP-CLM (ws) columns. The investigated urons were: linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea], diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea], and monuron [3-(4-chlorophenyl)-1,1-dimethylurea]. The retention of the urons was in the order: linuron < diuron < monuron (Figure 4 and Table 1).

The k' values (defined in footnote to Table 1) of linuron and diuron on SP-CLM (ns) were five-fold smaller than the k' values on the wide-spaced SP-CLM. The k' value of monuron on the narrow-spaced SP-CLM was, however, only less than 1.4 times smaller than on the wide-spaced cross-linked product (Table 1).

Table 2 presents the capacity ratios (k') of different monosubstituted benzenes eluted with hexane or with a hexane-isopropanol mixture from an SP-CLM (ws) column. Electronegative or dipolar substituents increased the retention, and hydrocarbon substituents decreased the retention. Whereas phenol, nitrobenzene, and aryl halides were retained by SP-CLM (ws)

Table 2. Retention of some monosubstituted benzenes by spray-dried, cross-linked montmorillonite (wide spaced).

Compound	Dipole moment[1] (debye)	Melting point[1] (°C)	Capacity ratio (k')[2] Hexane	Capacity ratio (k')[2] 40% hexane-60% isopropanol
Isopropylbenzene	—	−96	0.00	—
Ethylbenzene	0.59	−95	0.00	—
Toluene	0.36	−95	0.02	0.05
Benzene	0.0	5.5	0.17	0.13
Bromobenzene	1.70	−30.8	0.29	0.13
Chlorobenzene	1.69	−45.6	0.31	0.13
Fluorobenzene	1.60	−41.2	0.45	0.17
Phenol	1.45	43	—	0.40
Nitrobenzene	4.22	5.7	—	1.3

[1] Weast (1973).

[2] k' is defined in Table 1.

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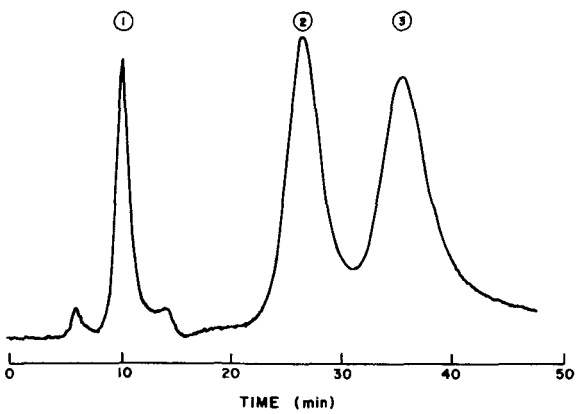


Figure 4. Separation of linuron (1), diuron (2), and monuron (3) on a wide-spaced, spray-dried, cross-linked montmorillonite column (16 × 0.46 cm); eluent = isopropanol; flow rate = 0.2 ml/min; detection UV, λ = 237 nm.

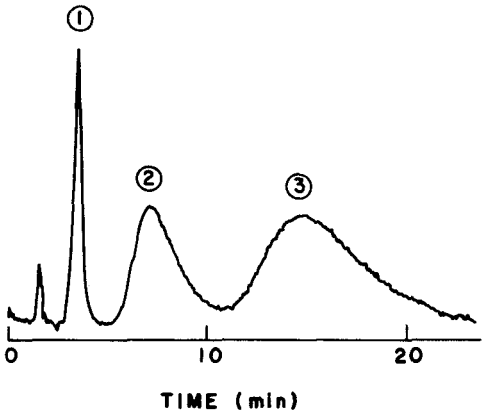


Figure 5. Separation of p- (1), m- (2), and o- (3) bromophenol on a wide-spaced spray-dried cross-linked montmorillonite column (16 × 0.46 cm); eluent = 7% isopropanol in hexane; flow rate = 1 ml/min; detection UV, λ = 281 nm.

more strongly than benzene, isopropylbenzene, ethylbenzene, and toluene adsorbed more weakly. The data therefore suggest that the extent of adsorption of the monosubstituted benzenes was controlled by the strength of the electrostatic interactions between the adsorbate molecule and the intercalated clay (e.g., the interaction between the polar substituents and the cationic species of Al).

The retention by SP-CLM (ws) of the three isomers of some disubstituted benzenes was studied and the determined capacity ratios and selectivity constants (see definition in footnote to Table 3) are presented in Table 3. Some of the chromatograms obtained are given in Figures 5 and 6. The investigated disubstituted benzenes may be divided into two groups according to whether their o-isomer was eluted before or after their m- and p-isomers. The first group, designated below as group I, included all the molecules containing one electronegative (or dipolar) and one nonpolar substituent (cresols, nitrotoluenes, bromotoluenes). All molecules containing two electronegative (or dipolar) substituents (dicholorobenzenes, dibromobenzenes, chloronitrobenzenes, bromonitrobenzenes, bromophenols, nitrophenols, dihydroxybenzenes) belonged to group II.

The retention of the isomers of the compounds in group I increased in the order: o- < m- ≤ p-. The o-isomers of all the members of group II displayed, on the other hand, a stronger retention than the m- and p-isomers. The retention of the isomers of the nonphenolic compounds of group II was in the order: o- > m- > p-. Both substituents of the disubstituted benzenes belonging to group II were able to interact electrostatically with positive sites on the stationary phase due to the electronegative or dipolar nature of all the substituents of the investigated group-II compounds (Table 3). As discussed below, the capacity of both substituents to participate simultaneously in the adsorption process was probably the main reason for the relatively strong retention of the o-isomers of the group-II compounds on the wide-spaced CLM product.

The retention of the isomers of bromophenol was determined on both SP-CLM (ns) and SP-CLM (ws). As opposed to the order of retention on the wide-spaced CLM product (Table 3), the order on the narrow-spaced product was o- < m- < p-.

Every isomer of the phenols of group II was retained by SP-CLM (ws) more strongly than the equivalent isomer of the nonphenolic group-II compounds (see, e.g., Table 3). This difference in retention suggests a stronger interaction of the stationary phase with the phenolic group than with any other of the substituents studied. As for all other members of group II, the o-isomers of the phenols in this group displayed a stronger retention than the m- or p-isomers. The order of elution of the m- and p-isomers varied, however, from phenol to phenol, with the less acidic isomer being eluted first (Table 3).

DISCUSSION

The OH:Al ratio used in the preparation of the Al-CLM suggests that the intercalated species was a cationic Al oxyhydroxide. According to Bottero *et al.* (1980), the dominant Al species formed under conditions similar to those employed in the present study for the preparation of the intercalated hydroxy-Al may be $Al_{13}O_4(OH)_{28}(H_2O)_8^{3+}$. The nature of the intercalated Al species is, however, likely to be strongly dependent on the conditions under which the cross-linked product was prepared. Hydroxy-Al oligomers ranging in size from Al_6 to Al_{13} and having a positive charge of as much as 7 were proposed as the dominant Al species in several intercalated clays (e.g., Pinnavaia, 1983).

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Table 3. Retention of disubstituted benzenes by a wide-spaced, spray-dried, cross-linked montmorillonite.[1]

Compound	Dipole moment (debye)	Acidity constant[7] (pK_a)	Eluent: Hexane k′	Hexane α	1% isopropanol in hexane k′	1% isopropanol in hexane α	10% isopropanol in hexane k′	10% isopropanol in hexane α	60% isopropanol in hexane k′	60% isopropanol in hexane α
Group I[2]										
o-	1.44[3]		0.09	0.75						
m-Bromo-	1.75[3]		0.12	1.00						
p-toluene	1.93–2.15[3]		0.16	1.33						
o-	3.66[6]		6.40	0.62			0.88	0.88		
m-Nitro-	4.14[6]		10.4	1.00			1.00	1.00		
p-toluene	4.42[6]		13.1	1.26			1.12	1.12		
o-	1.44[6]	10.33			2.90	0.55	0.81	0.62		
m-Cresol	1.60[6]	10.10			5.30	1.00	1.31	1.00		
p-	1.64[6]	10.28			5.90	1.11	1.31	1.00		
Group II[2]										
o-	1.67–1.87[4]		0.20	1.05						
m-Dibromo-	1.22[4]		0.19	1.00						
p-benzene	0.0		0.01	0.05						
o-	2.50[5]		0.42	1.91						
m-Dichloro-	1.72[5]		0.22	1.00						
p-benzene	0.0		0.03	0.14						
o-Bromo-	4.00[6]				2.51	2.76	2.31	2.85		
m-nitro-	3.17–3.41[3]				0.91	1.00	0.81	1.00		
p-benzene	2.45[6]				0.51	0.56	0.38	0.47		
o-Chloro-	4.64[5]				2.67	2.87	2.62	2.78		
m-nitro-	3.73[5]				0.93	1.00	0.94	1.00		
p-benzene	2.83[5]				0.50	0.54	0.38	0.41		
o-	1.36[6]	8.45					4.31	1.81		
m-Bromo-	—	9.03					2.38	1.00		
p-phenol	2.80[6]	9.34					1.81	0.76		
o-	2.58[6]	9.48					—		>16	>7
m-Diol	1.53[6]	9.44					—		2.67	1.00
p-	0.0	10.0					3.80		1.60	0.60
o-	3.11[6]	7.23							>16	>7
m-Nitro-	3.90[6]	8.36							2.23	1.00
p-phenol	5.05[6]	7.16							3.97	1.78

[1] The retention is expressed in terms of k′, the capacity ratio, which is defined in a footnote to Table 1. The selectivity constant (α) is relative to the m-isomer: $\alpha = k'/k'_m$ where k'_m is the capacity ratio of the meta isomer.
[2] Criteria for classifying a disubstituted benzene as a member of either group I or group II are given in the text.
[3] Boit (1964).
[4] Richter (1943).
[5] Weast (1973).
[6] Kiselev *et al.* (1980).
[7] Rochester (1971).

The intercalation of montmorillonite with hydroxy-Al substantially reduced the capacity of the clay to swell. As a result, the HPLC runs could be made at relatively low pressures. A flow rate of 1 ml/min in the 16-cm columns used required pressures of <500 psi with hexane as the liquid phase and <1500 psi with isopropanol.

Although the eluents used possessed a relatively wide range of polarities, none approached the polarity of water. The analysis and interpretation of the results may not, therefore, always apply to aqueous systems in which effects such as competition with solvent molecules for adsorption sites may dominate the behavior of the eluted compounds in the chromatographic system of interest.

Retention of substituted phenyl pesticides

Both the nitrophenyl-organophosphate esters and the chlorosubstituted phenylureas display a relatively strong affinity to montmorillonite (e.g., Van Bladel and Moreale, 1974; Bowman and Sans, 1977). The interaction of these compounds with Al-CLM may therefore be relevant to the potential use of montmorillonite-based products in the controlled release of these biocides and in their chromatographic separation.

The striking reduction in the retention of the phos-

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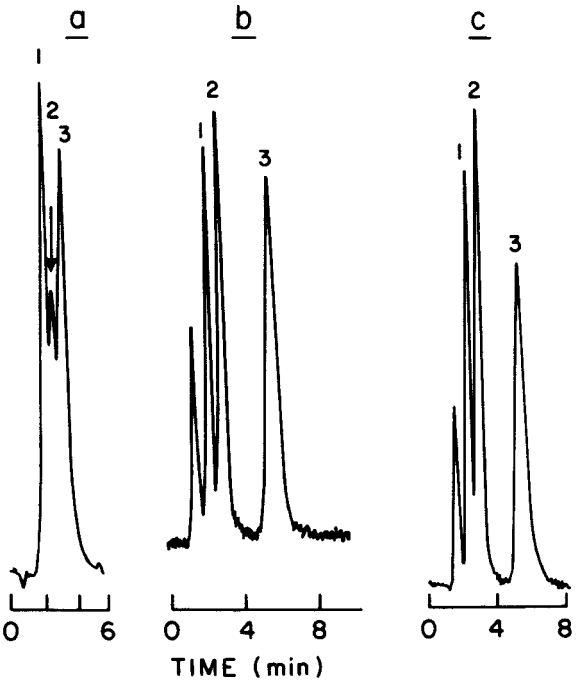


Figure 6. Separation of the isomers of some disubstituted benzenes on a wide-spaced, spray-dried, cross-linked montmorillonite column (16 × 0.46 cm). (a) o- (1), m- (2), and p- (3) nitrotoluene; eluent = 3% isopropanol in hexane; flow rate = 1 ml/min; detection UV, λ = 265 nm. (b) p- (1), m- (2), and o- (3) chloronitrobenzene; eluent = 1% isopropanol in hexane; flow rate = 1 ml/min; detection UV, λ = 270 nm. (c) p- (1), m- (2), and o- (3) bromonitrobenzene; eluent, flow rate, and detection as for chloronitrobenzene.

phate esters if the d-value was decreased from 18.6 to 15.3 Å (Table 1) suggests the feasibility of using Al-CLM in chromatographic and catalytic size-selective processes. Whereas the laminar structure of smectites allows a relatively free motion of both exchangeable cations and adsorbate molecules inside the interlayer spaces in the plane parallel to the clay platelets, the rigid pillared structure of the CLM hindered such motion. The pillared structure was thus a barrier to penetration into the interlayer spaces in two dimensions, whereas a laminar structure blocks penetration in only one dimension. Accordingly, a pillared structure should be more efficient in size segregation than a laminar structure.

The retention of the urons increased with their melting point, but did not correlate well with their solubility in water (Table 1). Crystal packing and consequently melting point are strongly affected by steric considerations. Similarly, the strength of interaction of adsorbate molecules with the surface is a sensitive function of the extent of steric hindrance to the approach of interacting groups in the adsorbate molecule to the surface. Steric effects may thus have influenced in a similar way, both the order of elution of the related urons and their melting points. In contrast, the order of aqueous solubilities of the urons is more likely to be controlled by the strength of interaction between the various moieties in the solute molecules and the small and mobile water molecules than by steric hindrance.

Linuron, which had the lowest k′ value of the three urons tested (Table 1), also contains the bulkiest (methoxy) group in its urea moiety. This moiety is the most polar part of the uron molecule and, hence, the likeliest site of the strongest interaction between the uron and the hydrophilic solid phase in the presence of the relatively weakly polar eluents used. A bulky substituent in the urea moiety may thus have caused an appreciable steric hindrance to the interaction of the uron with a surface. Linuron's methoxy group is replaced in the other two urons by the smaller methyl group. Accordingly, both the k′ values and melting points of diuron and monuron were higher than those of linuron. As expected, the replacement of a methoxy group by a methyl group did not affect the aqueous solubility of the urons in the same clear cut fashion that it affected their retention and melting point (Table 1). Although the bulkier methoxy group increased the steric hindrance to the access of the active urea group to the surface, it did not significantly decrease the accessibility of the urea moiety to water molecules in the aqueous solution. Furthermore, the methoxy oxygen atom probably enhanced the polarization of the uron and acted as an additional site for H-bonding with water.

Monuron was retained more strongly than diuron (Table 1). Adding an electronegative substituent such as a Cl atom in the aromatic ring weakens the basic character of the O and N atoms of the urea moiety by decreasing the electron density about them. Inasmuch as the urea group acts as a base in its interactions with clays and related systems (e.g., Theng, 1974), the observed reduction in the retention of the urons upon the addition of a Cl is in agreement with the suggested dominant role of the urea moiety in the interaction of the urons with the stationary phase. Chlorobenzene had a lower k′ value than o-dichlorobenzene (Tables 2 and 3). Accordingly, the addition of a second Cl atom in an ortho position to the existing Cl should have increased the retention of the urons if their dominant interaction with the surface was through the chlorinated ring moiety, unless that addition appreciably reduced the penetrability of the uron even into the interlayer spaces of the wide spaced SP-CLM. The addition of the Cl atom, however, decreased the retention of the urons. All three urons were retained by the SP-CLM (ws) more strongly than either chlorobenzene or o-dichlorobenzene, suggesting that the urea moiety and not the chlorinated ring made the dominant contribution to the interaction of the urons with the stationary phase.

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The urons as well as the organophosphate esters, adsorbed on SP-CLM (ws) more strongly than on SP-bentonite (Tsvetkov, 1985). Inasmuch as the urea moiety interacted with the surface as a base, the counter cations (which are Lewis acids) may have played an important role in the adsorption of the urons on both solids (e.g., Mortland, 1970), as they most likely did in the adsorption of the organophosphate esters (e.g., Mingelgrin and Saltzman, 1979). Regardless of whether the urons and the organophosphate esters interact directly with the cation or indirectly through a water bridge, the Al-CLM, with its high content of cationic Al species, should have thus been a stronger adsorbent for the substituted phenyls than SP-bentonite, the dominant counter ion of which is Na^+ (Mingelgrin and Tsvetkov, 1985).

Both diuron and linuron are dichlorosubstituted and were apparently too bulky to display significant penetration into the interlayer spaces of the narrow-spaced Al-CLM. The ortho position of the two Cl atoms in both these urons increased the hindering effect of the substituents on the penetration into the pillared structure of the cross-linked montmorillonite. The relatively small difference between the k′ values of monuron on Al-CLM (ns) and on Al-CLM (ws) (Table 1), suggests that the capacity of this mono-chlorosubstituted phenylurea to penetrate into the interlayer spaces of the narrow-spaced cross-linked product was considerably greater than the penetrating capacity of the dichlorosubstituted urons. The decrease of the d-value caused a similar (five-fold) reduction in the k′ values of linuron and diuron (Table 1), in agreement with the suggestion presented above that the strong impact of the methoxy-methyl substitution on the retention of the urons on SP-CLM resulted mostly from the effect of the substitution on the distance of closest approach between the active urea moiety and the site on the solid surface with which it interacted. The influence of this substitution on the capacity of the uron to penetrate into the interlayer spaces was likely rather small compared with the effect of the addition of a Cl atom in an ortho position to another Cl, especially due to the fact that Cl^- has a considerably larger ionic radius than O^{2-}.

The improvement in the separation between monuron and diuron, obtained by replacing SP-CLM (ws) with SP-CLM (ns) (Table 1), illustrates the potential for size-selective chromatographic and catalytic processes inherent in solid phases formed by cross-linking hydroxy-Al and montmorillonite.

Retention of monosubstituted benzenes

The order of retention of the aryl halides was inversely related to their dipole moments (Table 2). If a polar molecule can be well approximated by a point dipole, the intrinsic molecular property that determines the strength of its electrostatic interactions is the dipole moment. The aryl halides cannot be well approximated by point dipoles in their interaction with the stationary phase, because the distance between the centers of negative and positive charge in these molecules will likely be larger than, or at least similar to, the distance between the interacting site on the surface and the interacting site in the molecule. Consequently, the substituent's electronegativity should become more important and the dipole moment less important in determining the strength of retention of the aryl halides. Indeed, in the present study, the retention of the halo-substituted benzenes increased with the electronegativity of the halide substituents. The order of retention was: bromobenzene (2.8) < chlorobenzene (3.0) < fluorobenzene (4.0), the figures in parentheses being the electronegativities of the halide atoms (Cotton and Wilkinson, 1966). The radii of the halide ions are inversely related to their electronegativities. Because the dipole moment increases with the distance of charge separation, the difference between the electronegativities was apparently small enough and the difference between the ionic radii large enough to reverse the order of the dipole moments (Table 2), compared with the order of the electronegativities. The retention of the aryl halides decreased accordingly as their dipole moments increased. The above discussion dealt with the permanent charge separation (or permanent dipole moment). The interaction energy with the surface is actually dependent on the instantaneous charge separation (or the sum of the permanent and induced dipole moments), which is affected by the polarizability of the interacting molecule. Inasmuch as the polarizability of bromobenzene should be higher than that of chloro- or fluorobenzene (e.g., Hirschfelder *et al.,* 1954), the inverse relation between the dipole moment and k′ of the aryl halides cannot be attributed to the difference in polarizability between these compounds.

The capacity ratio of nitrobenzene was much larger than that of the aryl halides (Table 2), probably due to the relatively high electron density of the nitro group. The dipole moment of nitrobenzene, which is more than twice that of the aryl halides, reflects this high electron density.

H-bond formation possibly plays an important role in the adsorption of monosubstituted benzenes. The halide substituents may form H-bonds with hydration water molecules or with the hydroxyl groups of the hydroxy-Al species. Phenol, which has a smaller dipole moment than any of the aryl halides, adsorbed significantly more strongly (Table 2). Both the phenolic H and O atoms can form H-bonds with hydrated, oxygenated, and hydroxylated species at the Al-CLM surface. Because phenols are acids (albeit very weak), they can, in addition to forming H-bonds, dissociate at the surface and strongly interact as phenolate anions with the positively charged sites (e.g., the cationic Al species) in the stationary phase.

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The net contribution of the apolar hydrocarbon substituents to the observed adsorption of the monosubstituted benzenes was probably negative, because such substituents may have sterically hindered the interaction (e.g., Sahay and Low, 1974) between the aromatic ring and the surface. Benzene had a higher k′ value than any of the investigated monosubstituted benzenes containing a hydrocarbon substituent. The fast elution of these substituted benzenes compared with the elution of benzene (Table 2) is an agreement with the dominant role suggested for steric hindrance in determining the strength of interaction between the monosubstituted benzenes with a weakly polar substituent and the solid phase.

Retention of disubstituted benzenes

As was suggested for the monosubstituted benzenes (Table 2), the nonpolar substituent of the group-I disubstituted benzenes (see definition of groups I and II in the Results section) probably affected the retention mainly through the extent to which this substituent sterically hindered the electrostatic interaction between the eluted molecule and the surface. The closer the nonpolar substituent is to the polar one, the stronger should be the steric hindrance to the interaction of the polar moiety with hydrophilic sites at the surface. Accordingly, the ortho isomers of the disubstituted benzenes of group I had lower k′ values than the meta and para isomers (Table 3).

The retention of the o-isomers of all the investigated group-II compounds was stronger than that of the corresponding m- and p-isomers. If the two polar substituents of a group-II compound were bulky enough, however, an ortho position could have produced an electrostatic repulsion between the substituents, which in turn would have reduced the electron charge density in the substituents and with it both the dipole moment of the molecule and the strength of its electrostatic interaction with the surface. Although the dipole moment of o-dichlorobenzene was, as expected, considerably larger than that of chlorobenzene, the dipole moment of o-dibromobenzene was similar to that of bromobenzene. Likewise, the dipole moment of o-chloronitrobenzene was larger, and the dipole moment of o-bromonitrobenzene smaller, than the dipole moment of nitrobenzene (Tables 2 and 3). Accordingly, the k′ value of o-dibromobenzene was only slightly larger than that of m-dibromobenzene, whereas the k′ value of o-dichlorobenzene was almost double that of m-dichlorobenzene. The k′ values of the m-isomers of dibromo- and dichlorobenzene were similar (Table 3). The relative magnitudes of the dipole moments and of the k′ values pointed out above suggest that repulsion between two sufficiently bulky substituents (e.g., Br atoms) in an ortho position may have indeed reduced the charge separation in the disubstituted benzene and, hence, both the molecule's dipole moment and the strength of its electrostatic interaction with the stationary phase.

No correlation between the dipole moment and the strength of retention was found for the phenolic members of group II. For some nonphenolic group-II substances (e.g., halonitrobenzenes), the retention of the o-isomers was too strong compared with the retention of the m- and p-isomers to have resulted from the adsorbate molecules acting simply as point dipoles having the measured molecular dipole moments (Table 3). Inasmuch as the substituents of the investigated group-II compounds were electronegative, (or dipolar), the strong retention of the o-isomers may have arisen from the capacity of two substituents in the ortho position to form a chelate with the Al in the cationic hydroxy-Al species. The effectiveness of the o-isomers of the nonphenolic substances in group II as bidentate ligands was a function of the electronegativity of their substituents and, if the substituents were sufficiently bulky, of the substituents' size (e.g., dibromobenzene, Table 3). The strong retention of the group-II phenols and, in particular, their o-isomers (Table 3) suggests an interaction between Al and the dissociated phenolate (RO^-). Polarization by the electric field emanating from the charged sites in the stationary phase may have substantially increased the tendency of the weakly acidic phenolic groups to dissociate. By extension of the mechanism proposed above for the retention of the o-isomers, interaction between polar substituents and sites of opposite charge on the surface was probably the dominant mechanism of adsorption of the investigated disubstituted benzenes on Al-CLM.

The correlation between the retention of the m- and p-isomers of the group-II phenols and acidity (Table 3) supports the suggestion that the phenol group might have interacted with positively charged sites at the surface predominantly as a phenolate anion. The outstanding affinity of the o-isomers of the group-II phenols to the stationary phase regardless of the relative acidity of the o-, m-, and p-isomers probably resulted from the aforementioned capacity of disubstituted benzenes containing two sufficiently small, electronegative (or dipolar) substituents in an o-position to interact with the surface as bidentate ligands.

The order of elution of the isomers of the disubstituted benzenes of group II through SP-CLM (ws) cannot be explained by the relative ease of penetration of the isomers into the interlayer spaces. Although the o-isomers should probably have encountered the strongest hindrance to penetration into the pillared structure, group-II o-isomers had higher k′ values than the m- or p-isomers (Table 3). The molecular sizes of the investigated disubstituted benzenes were probably small enough to prevent steric hindrance to the penetration into the interlayer spaces of the wide-spaced CLM (d = 18.6 Å) from affecting the order of elution of the isomers.

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At sufficiently narrow basal spacings (or if the substituents were sufficiently bulky), however, differences in the ease of penetration into the interlayer spaces may have a strong influence on the relative retention of the isomers of disubstituted benzenes. As pointed out above, the pillared structure of Al-CLM should cause its interlayer spaces to be less accessible to penetration by the o-isomers than by the m- and, especially, the p-isomers. Accordingly, attaching a Cl atom to the benzene ring in an ortho position to another Cl seemed to have resulted in a strong decrease in the penetration of the urons into the interlayer spaces of the SP-CLM (ns). The effect on penetration into the interlayer spaces should have been even stronger if the bulkier Br atom were added in an ortho position instead of the Cl atom. Thus, the order of elution of the isomers of bromophenol from the narrow-spaced SP-CLM was opposite to that from the wide-spaced SP-CLM (Results section). The enhancement in retention of the o-isomers of disubstituted benzenes containing two electronegative (or dipolar) substituents brought about by the capacity of these isomers to act as bidentate ligands was apparently nullified in the case of bromophenol retention on SP-CLM (ns) by the restricted penetrability of o-bromophenol into the interlayer spaces. Differences in penetrability may have actually reversed the order of elution of the isomers of bromophenol from the order that would have existed if access of all the isomers into the interlayer spaces were free and the retention was controlled by the strength of interaction between the adsorbate molecules and the attractive sites at the surface alone.

The role of Al in the retention of the group-II disubstituted benzenes on Al-CLM may be surmised from a comparison between Al-CLM and hydroxylated silica gel as solid phases in HPLC separations of these benzene derivatives. Kiselev *et al.* (1980) reported that o-bromonitrobenzene adsorbed on the hydroxylated silica gel from nonpolar solvents more strongly than the p-isomer. On the other hand, the order of retention on the hydroxylated silica gel of the isomers of phenols which were classified in the present study as belonging to group II was in all cases: o- < m- < p-. Thus, the exceptionally strong retention of the o-isomers of group-II phenols observed on Al-CLM was not observed if these phenols were eluted from the hydroxylated silica gel. Strong electron attracting sites (such as cationic Al species) were not present at the silica surface, but that surface may have contained acidic protons (e.g., Unger, 1979). One such proton can form H-bonds simultaneously with both substituents of a group-II ortho-disubstituted benzene. This bidentate interaction may explain the above mentioned observation that the o-isomer of bromonitrobenzene adsorbed on the hydroxylated silica gel more strongly than the p-isomer. Kiselev *et al.* (1980) suggested, however, that an intramolecular H-bond probably exists between the phenolic hydroxyl and the second substituent in the ortho-isomers of the group-II phenols. This bond had to be broken to enable the simultaneous interaction between both substituents and a surface proton. The energy of interaction between the two substituents and the surface proton may not have been much greater than the intramolecular H-bond energy. Consequently, the tendency of the intramolecular H-bond to be replaced by a bidentate interaction with a surface proton should have been relatively small, in agreement with the fast elution from the hydroxylated silica gel of the o-isomers of the phenols containing an additional electronegative (or dipolar) substituent compared with the elution of the m- or p-isomers. The bidentate interaction of two adjacent electronegative or dipolar substituents with an Al ion should be considerably stronger than the internal H-bond; accordingly, for all the phenols in group II (as for all other group-II compounds), the o-isomer had a higher k′ value on the Al-rich SP-CLM (ws) than the m- and p-isomers. The above discussion suggests that chelation with Al was the reason for the strong retention of the o-isomers of the group-II disubstituted benzenes which was observed on SP-CLM (ws).

SUMMARY AND CONCLUSIONS

Spray-dried Al-CLM (SP-CLM) was used successfully in many chromatographic separations. Al-CLM samples having different basal spacings were prepared by making small changes in the preparation procedure of the cross-linked product. The optimization of the chromatographic process for various separations based on molecular size and shape was thus possible. The cationic Al species present in Al-CLM displayed, most likely, a strong interaction with negative or polar moieties in the adsorbate molecules. Inasmuch as the distance of charge separation in the investigated substituted benzenes was sufficiently large, the strength of interaction was determined mainly by the charge density at the site (or sites) in the adsorbate molecule with which the Al actually interacted (rather than by the molecule's dipole moment), as well as by steric considerations. Steric factors had a dominant effect on the strength of interaction of many of the investigated compounds with the solid phase. The o-isomers of the disubstituted benzenes that were designated in the present study as members of 'group II' displayed a singularly strong retention on SP-CLM, apparently due to the capacity of these isomers to form bidentate electrostatic complexes with Al.

The limited swelling capacity of Al-CLM makes it suitable for use as a solid phase in liquid chromatography even with polar eluents. Some of the chromatographic separations achieved with this solid phase, such as the separation of the ortho isomers of halonitrobenzenes from the m- and p-isomers, may be applicable to a number of industrial processes.

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