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POTASSIUM HALIDE-TREATED MONTMORILLONITE (KTM) AS A SOLID PHASE IN LIQUID CHROMATOGRAPHY

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Abstract—Columns for high pressure liquid chromatography were prepared from spray dried samples of montmorillonite that were heated with potassium halides (KTM) to increase both the cation density on the clay surfaces and the expandability of the interlayers. Some of the clay samples were exchanged with Cu before and/or after the potassium halide treatment.

Retention of nitrobenzene and its chloro and methyl derivatives, of methyl substituted phenols and of nitrophenols on these columns was studied, using eluents ranging in polarity from hexane to isopropanol. The retention of the aromatic molecules depends on their specific interaction with active sites on the clay surfaces and on steric effects which limit access to the clay interlayers. Both penetrability and surface interaction are controlled by the composition and method of preparation of the solid phase and by the polarity of the mobile phase. Very strong adsorption of some eluates and efficient chromatographic separations between related substituted benzenes were achieved. Mixtures of the three isomers of cresol, chloronitrobenzene, nitrotoluene or nitrophenol were completely resolved by a judicious combination of solid phase and eluent.

Key Words—Disubstituted benzenes, HPLC, Montmorillonite, Potassium halides.

INTRODUCTION

High pressure liquid chromatography (HPLC) has been used to investigate the interaction of a wide variety of aromatic compounds and amino acids with montmorillonite (Mingelgrin and Tsvetkov, 1985; Tsvetkov and Mingelgrin, 1987) and with cross-linked hydroxy-aluminum-montmorillonite (Al-CLM) (Tsvetkov *et al.*, 1990). The purpose of the present study is to use HPLC to probe the interaction of substituted benzenes with potassium halide treated montmorillonites (KTM) as a function of the method of preparation of the KTM and the nature of its exchangeable cation.

Heating montmorillonite with a potassium halide leads to sorption of interlayer cations in excess of the exchange capacity of the original clay. Charge balance is maintained by loss of structural protons, which causes changes in the properties of clay. While still possessing a high surface area, the KTM acquires a more rigid structure and a higher concentration of interlayer cations compared with untreated clay (Heller-Kallai, 1975a, 1975b). Such modifications may convert the treated clay into a more stable and efficient adsorbent and improve its suitability to serve as a solid phase in filters for organic contaminants and in preparative and analytical separations.

Retention of some monosubstituted benzenes and of the three isomers of several disubstituted benzenes on various KTMs was studied. Different substituents including methyl, chloro, nitro, and hydroxy groups were investigated in an attempt to elucidate the effect of the nature of the substituents and their relative positions around the aromatic ring on the adsorption process. Understanding the mechanism of adsorption could help in choosing the appropriate adsorbent and eluent for chromatographic or clean-up systems, as well as in assessing the suitability of a KTM as a heterogeneous catalyst for any given reaction. The relatively narrow basal spacings of the KTMs coupled with their ability to swell may enable the design of KTM-eluent combinations suitable for size selective separations.

MATERIALS AND METHODS

The potassium halide treated montmorillonites (KTMs) were prepared from Wyoming montmorillonite (Ward Natural Science Establishment, Rochester, N.Y.) following the procedure described by Heller-Kallai (1975a). Samples were heated with excess KBr or KCl (montmorillonite : halide 1:7) at 540°C for various periods of time. As was previously shown (Heller-Kallai, 1975a), KBr and KCl are, in effect, interchangeable. Aliquots were subsequently cation-exchanged with Cu^{2+}. Experiments were also carried out with Cu montmorillonite, which was heated with KBr, as described, and was then re-exchanged with Cu^{2+}. The nomenclature used to designate the KTM systems is defined in Table 1.

Solid phases for the HPLC columns were prepared by spray drying the ground KTMs from aqueous suspension using a laboratory spray dryer (Nyro atomizer)

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Table 1. Nomenclature and selected characteristics of the clay systems.

Column	Sample[1]	Basal spacing [Å]		meq Cation/100 g Clay		
		Air dried	Glycolated	K	Cu	K + Cu
[K1]	SP-(M-KCl[1])	12.1	16.7	105	—	**[2]
[CuO]	SP-(M-Cu)	9.5	9.5	5	100	105
[Cu1][3]	SP-(M-KCl[1]-Cu)	9.5	17; 9.4	13	120	133
[Cu2][3]	SP-(M-KCl[5]-Cu)	9.6	17; 9.6	13	120	133
[Cu3]	SP-(Cu-KBr[1]-Cu)[24]	9.8	17; 9.4	54	220	274
	M-Cu-KBr[1]	12.3	17	82	115	197

[1] The clay systems are defined by the formula SP-(N-XY[a]-Nf)[b], where SP is spray-dried, N is the countercation before the potassium halide treatment, M indicates that the sample was not exchanged before the treatment, XY is the potassium halide used, a is the heating time (hours) at 540°C in the presence of excess salt, Nf is the cation introduced after salt treatment, and b is the heating time in hours of the final product before spray-drying. All the samples were heated at 510°C for 20 hr after spray-drying.

[2] Total interlayer cations (Na + Ca + K) = 134 meq/100 g.

[3] Loss on ignition: SP-(M-KCl[1]-Cu) 5.6%; SP-(M-KCl[5]-Cu) 4.9%.

with a peristaltic pump to feed the suspension. The experimental conditions were as follows: columns [K1], [Cu0], [Cu1] and [Cu2]—concentration of suspension 0.8%, flow rate 5.5 l/hr, inlet–outlet temperature 360°/110°C; column [Cu3]—concentration of suspension 0.2%, flow rate 3 l/hr; inlet–outlet temperature 350°/110°C. The lower concentration of the solid phase in the suspension used to prepare column [Cu3] was adopted because the sample did not disperse in water as well as the other preparates. In order to stabilize the solid phase, the spray-dried (SP) montmorillonites were heated at 500°–520°C for 20 hr.

Size selection of the spray-dried particles (mean diameter 5 μm) was achieved by sedimentation in an isopropanol–hexane mixture (3:7 v/v). Apparent diameters were estimated from the sedimentation rate according to Stoke's law and verified by scanning electron microscopy (Figure 1). The scanning electron micrographs demonstrated that the size distribution of the SP-(M-KCl[1]-Cu) and SP-(M-KCl[5]-Cu) systems was such that they could have been used as a solid phase even without undergoing the size separation procedure (e.g., Figures 1b and 1c).

After size selection, the particles were packed from hexane into stainless steel columns of 0.46 cm i.d., ranging in length from 6 to 16 cm. HPLC chromatograms were obtained on a Tracor HPLC system equipped with a variable wavelength UV detector model 970A.

XRD traces of sedimented aqueous suspensions of the samples were recorded in the air-dried state and after glycolation to determine the expandability of the interlayer space. The samples were glycolated by heating at 60°C for 1 hr in ethylene glycol vapour and equilibrating at room temperature for several days. When expansion was incomplete, the treatment was repeated to attain maximum expansion. IR spectra of KBr discs of the solid phases were recorded on a Nicolet 740 FTIR spectrometer.

The samples were analyzed chemically to establish their Cu and K content, which was normalized to the amount of Al present. Al was used in preference to Si because the sample contained quartz, which may not have been homogeneously distributed. Chemical analyses were carried out at the Geological Survey of Israel, using inductively coupled plasma spectrometry and atomic absorption. In addition, the samples were examined in an electron microprobe to ascertain that no halide remained and to check whether a separate Cu-containing phase was formed in the course of the various pretreatments.

RESULTS

The stationary phase

The chemical analyses showed that, following cation exchange of sample M-KCl[1] by Cu, most of the K was exchanged (Table 1). The potassium halide treatment enhanced the expandability of the clay. Even after drastic heating, all the Cu-containing KTMs were expanded on glycolation, while the spray-dried Cu-montmorillonite [Cu0] was not (Table 1).

Some representative IR spectra are shown in Figure 2. The spectrum of sample SP-(M-KCl[1]) (Figure 2a) is similar to the spectra of KTMs previously described (Heller-Kallai, 1975a). The dominant Si-O absorption appeared at 1036 cm^{-1}; the Al-OH-Fe libration at 878 cm^{-1} became very weak, whereas the Al-OH-Mg libration at 847 cm^{-1} persisted. The OH stretching band appeared at 3634 cm^{-1}. The spectrum of the heated copper exchanged clay SP-(M-Cu), without potassium halide treatment (Figure 2b), is characteristic of montmorillonite saturated with small interlayer cations and subsequently heated (Calvet and Prost, 1971; Heller-Kallai, 1975a). The frequency of the dominant Si-O absorption was increased, and two OH librations occurred at 932 and 875 cm^{-1}. The OH stretching band occurred at 3644 cm^{-1}.

The IR spectra of samples SP-(M-KCl[1]-Cu) and SP-

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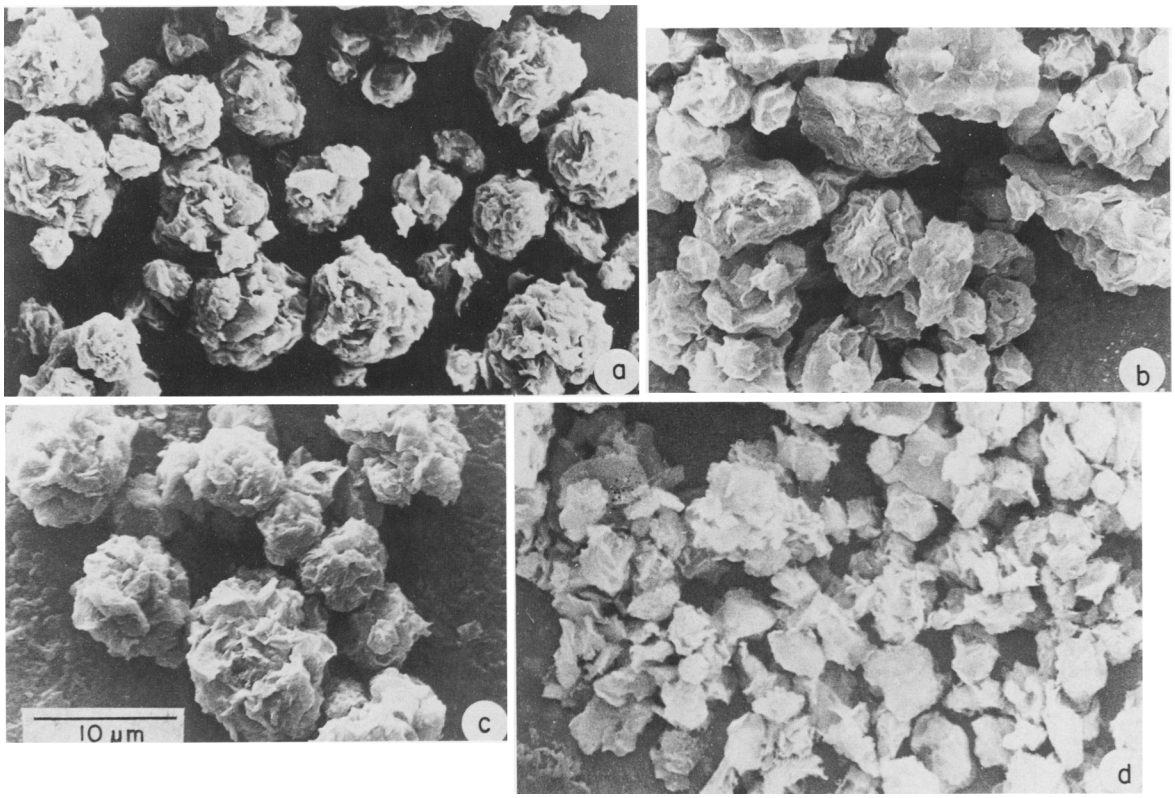


Figure 1. Scanning electron micrographs of spray-dried (SP) montmorillonites: a) SP-(M-Cu) after size separation; b) SP-(M-KCl^5-Cu) before size separation; c) SP-(M-KCl^5-Cu) after size separation; d) SP-(Cu-KBr^1-Cu)^{24} after size separation. For nomenclature see Table 1.

(M-KCl^5-Cu) (Figure 2c) resembled the spectrum of SP-(M-Cu), except for the OH stretching band, which appeared at a somewhat lower frequency (3638 cm^{-1}). The chemical analyses and IR spectra of SP-(M-KCl^1-Cu) and SP-(M-KCl^5-Cu) were very similar despite the fact that more prolonged KCl treatment of the original clay did cause additional changes. Apparently, these changes were partly reversed by the subsequent exchange with Cu ions. The greater loss on ignition of sample SP-(M-KCl^1-Cu) compared with that of SP-(M-KCl^5-Cu) (Table 1) suggests that SP-(M-KCl^5-Cu) was slightly more dehydroxylated.

Sample Sp-(Cu-KBr^1-Cu)^{24} shows a very high total K + Cu content (274 meq/100 g). This sum was considerably lower for sample Cu-KBr^1 (197 meq/100 g) from which sample SP-(Cu-KBr^1-Cu)^{24} was derived by cation exchange. The K was only partly displaced, but microprobe analysis showed that no discrete Cu-containing phase had formed (in contrast to a sample of Cu-KBr^5, for example, where such a phase was detected). It appears, therefore, that some Cu hydroxide was precipitated in the clay interlayers. The IR spectrum established that the sample was largely dehydroxylated, but several weak bands appeared in the OH stretching region, which were not present in any of the other spectra. These may be due to interlayer hydroxide complexes. The dominant Si-O absorption was broad, with a maximum at 1029 cm^{-1}, characteristic of KTMs.

Effect of spray drying

In general, spray-drying results in the formation of quasi-spherical particles suitable for use in chromatography and filtering. Scanning electron micrographs showed that most particles of the spray-dried KTMs from which columns [K1], [Cu0], [Cu1], and [Cu2] were prepared were, indeed, quasi-spherical. Only the sample used for column [Cu 3], which was heated for 24 hr at 540°C before spray drying, did not disperse in the spray-dried suspension. Consequently, it consisted of particles of irregular shape with a wide range of sizes (Figure 1).

Solvent effect

A wide range of isopropanol-hexane mixtures was used as the mobile phase (Tables 2–5). In general, an inverse correlation was observed between the retention time and the isopropanol content. An important exception is pure hexane. With the more extensively heated solid phases (e.g., [Cu2] and [Cu3]), it produced a

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Table 2. Capacity ratios of some nitrobenzene derivatives on different clay columns.

Compound	Dipole moment (Debye)[2]	Eluent	Capacity ratio (k') on columns[1]: [K1]	[Cu0]	[Cu1]	[Cu2]	[Cu3]	Al-CLM[3]
Nitrobenzene	4.22	A	6.2	1.2		4.5	0.1	
		B				7.9		
		C	2.8	1.3	2.0	1.4	0.2	
o-chloronitrobenzene	4.64	A	4.9	1.4				
		C	1.7	0.8	1.5	0.8		2.7
		D				0.3		
m-chloronitrobenzene	3.73	A	8.5	2.7				
		C	4.3	2.0	3.3	2.0		0.9
		D				0.5		
p-chloronitrobenzene	2.83	A	13.1	3.5				
		C	6.9	2.5	6.2	3.5		0.5
		D				0.8		
o-nitrotoluene	3.66	A	6.0				0.3	6.4
		C	2.0	1.3	1.5	1.3		
		D					0.7	0.9
m-nitrotoluene	4.14	A	9.9	2.7			0.2	10.4
		C	6.3	3.6	6.3	4.5		
		D				0.9	0.7	1.0
p-nitrotoluene	4.42	A	13.6	6.2			0.9	13.1
		C	13.0	6.1	8.9	9.5		
		D				1.4	1.2	1.1

Mobile phase: A) hexane, B) 0.1% isopropanol in hexane, C) 1% isopropanol in hexane, D) 10% isopropanol in hexane.

[1] The capacity ratio, k', is experimentally defined as $k' = (V_R - V_0)/V_0$, where V_0 is the void volume (the interstitial volume of the mobile phase), $V_R = t_R x$, where t_R is the retention time and x is the flow rate.

[2] Kiselev *et al.* (1980) and Weast (1973).

[3] Al-CLM: cross-linked hydroxy-Al-montmorillonite, basal spacing 18.6 Å (Tsvetkov *et al.*, 1990).

faster elution of the investigated eluates than did mobile phases with a finite but sufficiently low isopropanol content (Tables 2 and 3).

Chromatographic separations

Monosubstituted benzenes. The capacity ratios (see definition in footnote of Table 2) of benzene, toluene, bromobenzene, and nitrobenzene on the various columns indicate that nitrobenzene was retained strongly on all the columns investigated except on [Cu3] (Table 2), whereas the other monosubstituted benzenes investigated displayed only weak retention.

Substituted nitrobenzenes. All the isomers of nitrotoluene adsorbed more strongly than the corresponding isomers of chloronitrobenzene on the solid phases investigated (Table 2). For both substituted nitrobenzenes the order of retention was o < m < p. The efficient resolution achieved with selected KTMs is ex-

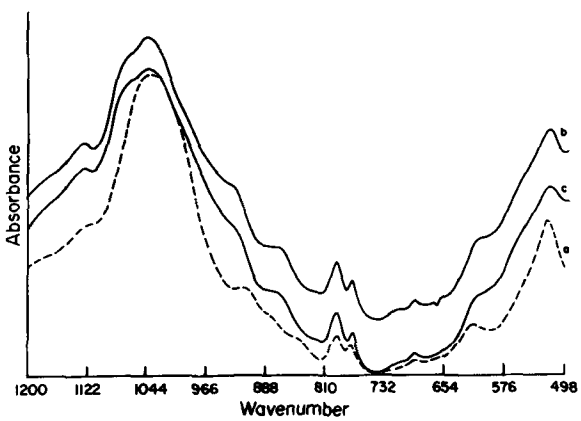


Figure 2. IR spectra of KBr discs of a) SP-(M-KCl[1]); b) SP-(M-Cu); c) SP-(M-KCl[5]-Cu). The spectra are offset vertically for clarity.

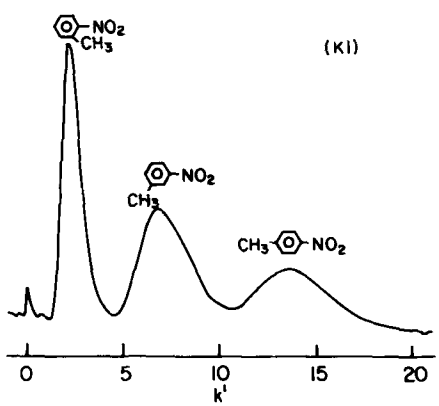


Figure 3. Separation of o-, m- and p-nitrotoluenes on column [K1], flow, 1.5 ml/min; mobile phase, 1% isopropanol in hexane; detection, UV, 260 nm.

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Table 3. Capacity ratios of some methyl-substituted phenols on different clay columns.

Compound	Acidity constant[1]	Eluent	Capacity ratio (k') on columns: [K1]	[Cu0]	[Cu1]	[Cu2]	[Cu3]	Al-CLM[2]
		A	0.9	0.5	5.8			
2,3,5-trimethylphenol	10.59	B	0.1		0.6			
		C	0.1		0.0	0.0		
		A	3.7	1.1	3.2	2.4		
o-cresol	10.33	B	2.7		1.4	2.7		
		C	1.2		0.4	0.4	0.1	2.9
		A	10.6	1.0	7.3	5.7		
p-cresol	10.28	B	4.6		3.4	6.7		
		C	2.6		0.7	0.7	0.2	5.9
		A	10.6	2.2	9.7			
3,5-dimethylphenol	10.2	B	4.9		3.0			
		C	2.0		0.5	0.6		
		A	10.8	1.4	8.4	5.5		
m-cresol	10.10	B	7.1		3.1	6.7		
		C	2.8		0.7	0.7	0.3	5.3

Mobile phase: A) hexane, B) 0.1% isopropanol in hexane, C) 1% isopropanol in hexane.
[1] Rochester (1971).
[2] See footnote to Table 2.

emplified by the chromatograms presented in Figures 3–5.

The [K1] column showed the strongest adsorption for all the nitro compounds investigated (Table 2). The affinity of Cu saturated montmorillonite ([Cu0]) toward substituted nitrobenzenes was enhanced by pretreatment with potassium halide. In general, 1 hr of pretreatment ([Cu1]) resulted in stronger adsorption than 5 hr ([Cu2]).

Substituted phenols. Table 3 presents capacity ratios of some methyl substituted phenols. The retention of these phenols on the investigated solid phases was generally correlated with the acidity of the eluate (Table 3). Accordingly, o-cresol was both the weakest acid and the fastest eluting of the three cresol isomers, but its retention was considerably lower than that expected from the relative magnitude of the isomers' acidity constants alone. A number of deviations were observed from the correlation between acidity and retention, indicating that factors other than the tendency of the eluate to interact with the surface through the phenolate group affected retention.

Adsorption of the methyl substituted phenols on [Cu0] was small relative to that on the KTMs and column [K1] (without Cu) retained most of these eluates more effectively than the Cu-containing solid phases (Table 3). A notable exception is 2,3,5-trimethylphenol, which was retained more strongly on [Cu1] than on [K1]. Pinnavaia and Mortland (1971) have shown that the substitution of an aromatic ring with methyl groups increased the tendency of the adsorbate to form a π complex with Cu^{+2} cations. Such a complex is not likely to be formed with K^+ cations, accounting for the widely different effect the addition of a third methyl group in the 2- position (namely adjacent to the active OH group and thus sterically hindering its interaction with the surface) had on the adsorption of the phenols on [K1] and on [Cu1].

A chromatogram of o- and p-cresol on column [Cu2] is presented in Figure 6. The separation ratio (k'_p/k'_o) with 0.1% isopropanol in hexane as eluent was as high as 2.5.

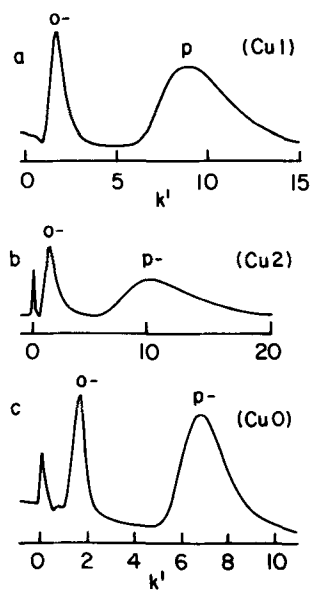


Figure 4. Separation of o- and p-nitrotoluenes on column a) [Cu1] and b) [Cu2], flow, 2.5 ml/min; c) [Cu0], flow, 0.2 ml/min. Mobile phase, 1% isopropanol in hexane; detection, UV, 260 nm.

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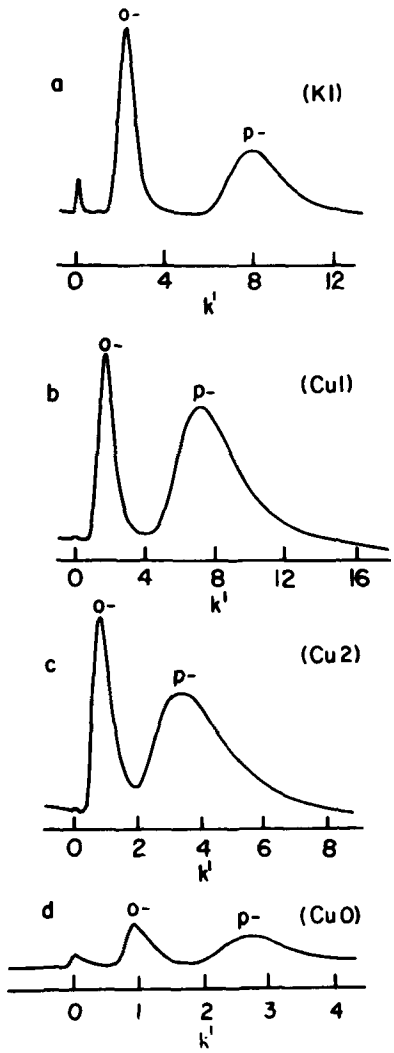


Figure 5. Separation of o- and p-chloronitrobenzenes on column a) [K1], flow, 1 ml/min; b) [Cu1], flow, 2 ml/min; c) [Cu2], flow, 1.5 ml/min; and d) [Cu0], flow, 0.2 ml/min. Mobile phase, 1% isopropanol in hexane; detection, UV, 260 nm.

Table 4 summarizes the capacity ratios of the three nitrophenol isomers with different eluents. The retention of the three bromophenol isomers was also measured, but was found to be considerably weaker than that of the phenols substituted with the strongly electronegative nitro group. The order of retention of the nitrophenol isomers varied with both the solid and liquid phases.

Flow characteristics

The mechanical properties of the solid phase improved with potassium halide treatment. Thus, as demonstrated in Table 5, a lower pressure (P) was needed in columns prepared with KTMs than in column [Cu0] to reach the same flow rate (F) with isopropanol

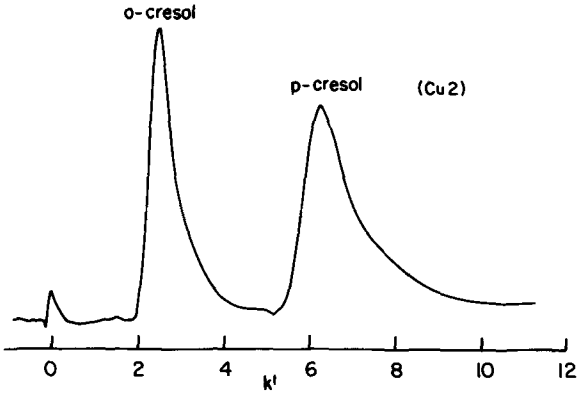


Figure 6. Separation of o- and p-cresols on column [Cu2], flow, 2 ml/min; mobile phase, 0.1% isopropanol in hexane; detection, UV, 260 nm.

containing solvents. Consequently, more polar eluents could be used with the KTMs than with the untreated Cu-montmorillonite without impairing the performance of the column. With all the solid phases except [Cu3], P/F increased appreciably with the polarity of the eluent. Among the KTMs, the largest increase was observed with [K1]. Changes in P/F were reversible as the polarity of the eluent was varied with all the KTMs, even after elution with pure isopropanol. In contrast, [Cu0] collapsed irreversibly after elution with only 1% isopropanol in hexane. The reversibility of P/F suggests that the changes in this ratio in the case of the KTMs are due to swelling of the clay. The tendency to swell was reduced by more prolonged potassium halide treatment (cf. [Cu1] and [Cu2] in Table 5).

More efficient separations and a higher mechanical stability were achieved with KTMs as solid phases than with systems not treated with potassium halides. How-

Table 4. Capacity ratios and acidity constants of o-, m- and p-nitrophenols on different clay columns.

Column	Eluent	Capacity ratio (k') for isomers: o-	m-	p-	Order of retention
[K1]	D	24.2	4.9	30.7	m < o < p
	E	19.8	0.5	1.8	m < p < o
[Cu1]	C	5.5	34.7	70.1	o < m < p
	D	4.1	2.2	3.3	m < p < o
	E	1.0	0.3	0.3	m = p < o
[Cu2]	D	0.8	0.5	1.4	m < o < p
	E	1.5	0.3	0.2	p < m < o
[Cu3]	E	1.5	1.2	1.2	m = p < o
[Cu0]	C	0.6			
Al-CLM[1]	F	>16	2.2	4.0	m < p < o
		acidity constant[2] (pK_a) 7.23	8.36	7.16	

Mobile phase: C) 1% isopropanol in hexane, D) 10% isopropanol in hexane, E) 50% isopropanol in hexane, F) 60% isopropanol in hexane.

[1] See footnote to Table 2.

[2] Rochester (1971).

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ever, prolonged heating often reduced the chromatographic efficiency (e.g., Tables 2 and 3). There may, thus, be a trade-off between chromatographic performance and mechanical stability or sensitivity to changes in the polarity of the mobile phase as the heating time lengthened (Table 5).

DISCUSSION

Effect of potassium halide treatment on the properties of the solid phase

Comparison between the KTMs and homoionic Cu-montmorillonite [Cu0] as stationary phases in HPLC demonstrated that the thermal reaction of montmorillonite with potassium halides improved both the retention capacity (Tables 2, 3, and 4) and the mechanical properties (Table 5) of the montmorillonitic solid phase. The KTMs displayed a reversible increase in the P/F ratio with the polarity of the eluent. [Cu0], on the other hand, did not swell upon glycolation despite its lower cation density (Table 1) and displayed a very high P/F ratio in the presence of isopropanol (Table 5), which increased irreversibly with the polarity of the eluent. The spray-dried aggregates of [Cu0] were apparently composed of large, non-swelling tactoids. The weak tendency of [Cu0] to swell may be a major cause of its poor chromatographic performance compared with that of [Cu1] and [Cu2] (Tables 2, 3, and 4) which, although exchanged with Cu after the potassium halide treatment, expanded when glycolated (Table 1). It appears that the presence of interlayer K ions facilitated resolution and swelling, probably because the ionic radius of K^+ is considerably larger than that of Cu^{2+}. Heller-Kallai (1975b) showed that montmorillonite saturated with the relatively small Mg^{2+} cation did not expand upon glycolation after heating in the absence of KBr in a manner similar to that employed in the present study. The same clay heated in the presence of KBr, while retaining almost all the Mg^{2+}, did expand. The strong tendency of a K^+ containing montmorillonite to rehydrate after heating was reported by Kawano and Tomita (1991). Denis et al. (1991) demonstrated that the presence of K^+ ions in a mixed Na,K montmorillonite led to larger basal spacings and faster water uptake at low moisture contents or high pressures. Since these conditions are analogous to those prevailing in our study, K^+ cations should have also facilitated the uptake of polar eluents such as isopropanol.

The strong tendency of K-containing montmorillonites to rehydrate may bring about partial dispersion and, hence, reduce the number of platelets per tactoid in the aqueous suspension from which the stationary phases were spray-dried. Smaller tactoids should result in more resilient spray-dried aggregates and, indeed, the KTMs displayed a much higher stability in polar eluents than the K poor [Cu0] (Table 5).

One important reason for the improved efficiency of the solid phase upon heating with a potassium halide is that the resulting deprotonation increases the cation density at the clay surface. Countercations are the most likely sites for interaction between benzenes substituted with electronegative or dipolar groups and the clay surface (e.g., Hayes and Mingelgrin, 1990).

Table 5. Pressure (P)-flow (F) relations of clay columns.

Column	Eluent:	P/F in hexane-isopropanol mixtures (PSI min/ml) A	C	D	E
[CuO]		450	>3000[1]	—	—
[K1]		600[2]	650	—	1600
[Cu1]		350	450	700	900
[Cu2]		—	320	350	550
[Cu3]		600	600	700	700

Mobile phase: A) hexane, C) 1% isopropanol, D) 10% isopropanol, E) 50% isopropanol.
[1] Irreversible collapse.
[2] 0.05% isopropanol.

Comparison of the performance of the KTMs

[K1], which was saturated with the monovalent K cation, often displayed a stronger retention capacity than the Cu-containing solid phases (Tables 2, 3, and 4), despite the divalence and the available *d* orbitals of Cu. The exceptional performance of [K1] may arise from the combined contribution of a number of factors. Thus, the larger ionic radius of K compared with that of Cu suggests a lower steric hindrance to the interaction of the K ion with the substituted benzenes. The effect of the ionic radius on surface interactions was previously discussed (e.g., Hayes and Mingelgrin, 1990). Related to the ionic radius of K^+ is the fact that an air-dried aqueous suspension of [K1] showed a basal spacing approximately 2.5 Å larger than corresponding samples of the other solid phases used for column packing (Table 1). The higher initial basal spacing and the greater tendency of [K1] to swell (as reflected, for example, by its swelling upon glycolation and flow properties) (Tables 1 and 5), render the interlayer spaces more accessible to the eluates. Finally, if as suggested above counter cations are the dominant active sites on the solid phase, [K1] has a density of active sites about twice as high as the corresponding Cu-containing KTMs, since K is monovalent while Cu is divalent. The larger number of active sites partly compensates for the stronger attraction between the divalent cations and the eluate.

The order of the P/F ratios of the KTMs as well as of the rates of increase in this ratio with the polarity of the eluent—[K1] > [Cu1] > [Cu2] (Table 5), suggests that, as expected, both extended thermal treatment with potassium halides and exchanging the KTM with Cu^{+2} reduced the swelling capacity. While more prolonged heating with potassium halide improved the mechanical properties of the columns, the effect of longer heat-

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ing on the retention characteristics of the columns was more complex. The KTMs were, by and large, more efficient than untreated clays; but when the reaction with the potassium halide proceeded for an excessively long time, a decline in performance was often observed, probably due to the reduced swelling capacity. The swelling of most solid phases upon glycolation (Table 1) suggests that, as the polarity of the eluent increases, an increase in the interlayer spacing is likely to occur. This swelling may eliminate the adverse effect of the longer potassium halide treatment. Accordingly, while retention on [Cu1] was generally higher than on [Cu2] with lower polarity eluents, the reverse, or at least a decrease in the difference, was observed with mobile phases of higher polarity. The bulkiness of the eluate molecule determined at which isopropanol to hexane ratio the retention order by the two columns was reversed (Tables 3 and 4).

Interpretation of the performance of column [Cu3] is further complicated by the presence of an additional Cu-containing phase in the interlayers. While increasing the number of potentially active sites, this reduces the swelling capacity (Table 5), resulting in increased steric hindrance to penetration of large molecules. However, sufficiently polar solvents can counter the effect of reduced swelling capacity. This is demonstrated by the relatively good performance of [Cu3] in the presence of the more polar eluents (Tables 2 and 4).

Solvent effect

In general, the k′ values on the KTM columns decreased as the polarity of the mobile phase increased, as previously observed with a cross-linked montmorillonite (Al-CLM) (Tsvetkov *et al.*, 1990). One important exception was the increase in k′ occasionally observed with column [Cu2] when the solvent was changed from pure hexane to a hexane-isopropanol mixture with a low isopropanol content (e.g., Table 3). The more polar component in the mobile phase may affect retention in two opposing ways: It may cause some swelling, which enhances the penetration of the adsorbates into the interlayer spaces; but, simultaneously, the isopropanol may compete with the eluates for the interaction sites on the solid phase. At sufficiently high isopropanol concentrations, swelling approaches an upper limit and competition becomes the dominant effect. The above-mentioned Al-CLM had a fixed basal spacing of 18.6 Å, which was sufficiently large to allow free access of the investigated eluates into the interlayers. Hence, the mobile phase affected retention mainly through competition and the capacity ratios were inversely related to the eluents' polarity (e.g., Table 2). Similarly, [K1] with its high initial basal spacing and tendency to expand, always displayed a decrease in retention as the polarity of the solvent increased. In contrast, column [Cu2], which was heated with KCl for 5 hr, displayed an increased retention, probably due to swelling, at low isopropanol concentrations. As polarity of the eluent was further raised, however, competition became more important and retention decreased. Column [Cu3], which underwent the most severe thermal treatment, displayed an increase in retention as the isopropanol fraction in the eluent increased at all isopropanol to hexane ratios tested (Table 2).

The ability to control the basal spacing at equilibrium by choosing solvents of various polarities may be used to great advantage since it enables the choice of a KTM-eluent system that will afford efficient size dependent separation for many monomeric mixtures of interest. The critical effect of the size of interlayer passages on the penetration of toluene and benzene in Wyoming montmorillonite saturated with an organic cation (basal spacing 13.8 Å) was demonstrated by Lee *et al.*, (1990). Variations in the cation density in the interlayer spaces (and thus the mean separation between the organic cations) affected the penetration strongly. The crucial importance of small changes in passage size in the separation of various substituted benzenes was also demonstrated for zeolites (Namba *et al.*, 1984; Richards and Rees, 1988) and for cross-linked montmorillonites (Tsvetkov *et al.*, 1990). The capacity to adjust the basal spacing by varying the polarity of the solvent, while useful, also entails an effect of the history of the column on its performance. Care in equilibrating the column with the desired eluent must thus be taken, more so than is required with non-swelling solid phases such as zeolites.

Comparison of the KTMs to a cross linked montmorillonite (Al-CLM) (Tables 2, 3, and 4), shows that the Al-CLM retained many eluates rather strongly. The strong retention resulted from the Al-CLM's large basal spacing, 18.6 Å (Tsvetkov *et al.*, 1990), which afforded easy accessibility of the interlayer surfaces, but at the same time made the capacity of that solid phase for size-selective uptake of adsorbate molecules lower than that of the KTMs with their narrow basal spacing and higher swelling capacity.

Role of cation density and the nature of the countercation

One important effect of thermal treatment with alkali halides is the increase in the cation density of the clay. The cation density of clay systems will affect the interaction with eluates in a complex manner. On the one hand, a higher cation population implies a higher density of strongly interacting sites. On the other hand, the higher the interlayer cation density, the narrower the passages in the interlayer spaces and the more restricted the mobility of the eluate molecule through them. The strong dependence of the penetration of substituted benzenes into interlayer spaces on the cation density was demonstrated by Lee *et al.*, (1990). Similarly, Mori and Suzuki (1991) demonstrated that

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the capacity of Al-pillared montmorillonite to catalyze the conversion of m-xylene was strongly dependent on the lateral distance between the pillars.

At a critical range of cation densities, an interaction between more than one site on the surface and different moieties on the eluate molecule becomes possible. The long axis of benzenes disubstituted in the p-position by halides, nitro, or other groups of a similar size is in the vicinity of 10 Å. The mean separation between monovalent cations in the interlayer space of low cation density smectites or between divalent cations in the interlayers of high cation density smectites is of the same magnitude. Hence, small changes in the cation density may transform the interlayer passages from a size suitable for simultaneous interaction of both p-substituents with interlayer cations to a size that enables only one cation-substituent interaction per eluate molecule at a time.

The nature and position of the countercations will strongly affect the interaction of the adsorbate with the stationary phase. For example, on heating montmorillonite, small interlayer cations may penetrate into the hexagonal holes or into the octahedral sheets. After resolvation they may or may not revert to the interlayers and, like the larger cations, be available for interactions with the eluates. Aside from electrostatic interactions common to all cations, transition metal cations such as Cu^{2+} also tend to interact with the π-electrons of aromatic rings (e.g., Doner and Mortland, 1969) to form π complexes, thus complicating the behavior of substituted benzenes on the Cu-containing solid phases.

Retention of o-, m-, and p-isomers of disubstituted benzenes

In systems in which the factor limiting retention is accessibility of the active surface sites, the o-isomer is retained less strongly than the two other, narrower isomers of disubstituted benzenes. Thus, the retention of o-bromophenol on an Al-CLM with a basal spacing of 15.3 Å was lower than that of the corresponding m- and p-isomers, while on an Al-CLM with a basal spacing of 18.6 Å, the o-isomer displayed the strongest retention (Tsvetkov *et al.*, 1990). Weaker retention of o-isomers of disubstituted benzenes was also observed on other solid phases with restricted passages such as zeolites (Namba *et al.*, 1984; Richards and Rees, 1988) or a solid phase of Werner type MX_2A_4 (Sybilska and Smolkova-Keulemansova, 1984). The relative order of retention of the isomers on solid phases in which the active sites are easily accessible or which expand in sufficiently polar solvents depends on the nature of the substituents (e.g., Tsvetkov *et al.*, 1990) and may change with the polarity of the solvent.

Accordingly, the o-isomers of the investigated disubstituted benzenes eluted through the KTMs faster than the other two isomers, with the exception of the nitrophenols eluted with the more polar mobile phases. A good resolution was obtained between the nitrotoluene isomers both on [K1] and on the Cu-KTMs (e.g., Figures 3 and 4). With cresol, too, the o-isomer was well resolved from the m- and p-isomers on all the KTMs (Table 3). The difference in retention was larger than can be explained by the differences in the acidity constants or the dipole moments between the cresol isomers. For nitrotoluene and cresol, the low retention of the o-isomer is in agreement with both the relative accessibility of the interlayers to the three isomers and the isomer's strength of interaction with the active sites at the surface (Tsvetkov *et al.*, 1990). The dominant role of steric hindrance to interlayer penetration in determining the order of retention of the isomers of disubstituted benzenes is, however, demonstrated by the fact that the o-isomer of chloronitrobenzene was also eluted first. This order of elution is contrary to that expected for the strength of interaction between the surface and the isomers of disubstituted benzenes (such as chloronitrobenzene), which have two electronegative sustituents (*ibid.*). Moreover, the retention of o-chloronitrobenzene was weaker than that of nitrobenzene, whereas the m- and especially p-chloronitrobenzenes were retained more strongly than nitrobenzene (Table 2).

Nitrophenol is a benzene substituted with one strongly electronegative (nitro) and one dissociable (phenolic hydroxide) substituent. The o-isomer may form a strong bidentate complex with the counter cations unless this is prevented by steric hindrance to penetration. Steric hindrance will decrease with increased swelling, i.e., with increased polarity of the eluent. The presence of an intramolecular H-bond between the phenolic H and an electronegative NO_2 group in the o-position (Kiselev *et al.*, 1980) also hinders bidentate interaction. The higher the valence of the countercation and the more polar the eluent, the greater the probability of breakage of that H-bond as well as of the dissociation of the phenolic hydroxyl. In agreement with both the steric considerations and the existence of the intramolecular H-bond, the p-isomer was retained more strongly than the o-isomer on all KTMs at low isopropanol concentrations, but this order was reversed with more polar eluents (Table 4). As expected, this reversal occurred at a lower isopropanol content with [Cu1] than with [Cu2]. The m-isomer was generally retained less strongly than the p-isomer, in agreement with the considerably higher acidity constant of the m-isomer (Table 4). This supports the suggestion that an interaction takes place between a Lewis acid site at the surface (e.g., the countercation) and the dissociated phenolic hydroxide (Tsvetkov *et al.*, 1990). However, the relative retention of the o-isomer did not conform to its acidity and differed in the various chromatographic systems. The complex behavior of the o-isomer probably resulted from the combined effect

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of the following factors: the ability of the isomer to form bidentate complexes (which enhances its retention relative to that of the other two isomers), its more restricted penetration into the interlayer spaces, and its capacity to form an intramolecular H-bond (which decrease the retention).

CONCLUSIONS

The conditions under which the KTMs were produced by thermal reactions with potassium halides were such that the added K cations remained largely exchangeable and could, therefore, be replaced with other cations (Table 1). Because polar, polarizable, anionic, and ionizable species often interact mainly with the surface cations, KTMs are potentially efficient heterogeneous catalysts and strong and versatile stationary phases in chromatography. The basal spacing of the KTMs can be controlled by the polarity of the eluent. Hence, with the proper choice of eluent, the KTMs afford a family of chromatographic systems that can be manipulated to achieve high resolution, shape- and size-dependent separations, and catalytic conversions of a wide range of substances.

The thermal treatment with potassium halides increases the cation density of the clay, while the bulky K^+ ions prevent collapse of the tactoids. Additional treatment, such as spray-drying or further heating improve the physical properties (e.g., sphericity and stability) of the solid phase. However, excessive heating, or too high a density of polyvalent cations may reduce the accessibility of the interlayer spaces to the eluates or, in extreme cases, cause an irreversible collapse of the tactoids. Eluents of high polarity may often counteract this effect by inducing swelling of the solid phase. KTMs with limited swelling capacity due, for example, to high surface cation density or polyvalent counter cations may be more suitable for use with polar eluents than other KTMs.

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