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Dedicated to Professor Lisa Heller-Kallai on the occasion of her 65th birthday

HPLC SEPARATIONS OF SOME SUBSTITUTED BENZENES ON THERMALLY TREATED CLAYS

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Abstract

HPLC columns were packed with quasi-spherical montmorillonite particles which were prepared by spray-drying and then thermally treated. Separations of phenylureas (linuron, neburon, diuron and monuron), phosphothioate phenyl esters (parathion, methyl parathion and paraoxon) and other smaller substituted benzenes were performed on the columns. The relative retention of the substituted phenyl pesticides demonstrated the important role polar substituents play in the eluate-surface interactions and the strong influence of steric factors on these interactions. The retention of the pesticides decreased sharply as the polarity of the mobile phase increased. The retention of the smaller substituted benzenes showed a similar trend, but for these smaller molecules this trend was partially counteracted by the increased accessibility of interlayer spaces due to swelling as the polarity of the liquid phase increased. The role of the exchangeable cation (Na^+, Co^{2+} and Cu^{2+}) in the adsorption was found to be complex. The cations determine both the strength of interaction, which increases with the valence of the cation, and the accessibility of the interlayer adsorption sites which decreased with the valence.

Keywords: adsorption, liquid chromatography, montmorillonite, organophosphate esters, phenylureas

Introduction

The development of high pressure liquid chromatography (HPLC) column packing based on clays provided a simple way to study clay-organic monomers interactions and to create efficient and inexpensive solid phases for filters and for analytical or preparative chromatographic columns.

In a previous publication [1], it was demonstrated that a properly executed thermal treatment of smectite-based solid phases, stabilizes them mechanically

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and enhances their interaction with eluates. As demonstrated below, the thermal treatment chosen (heating at 520°C) brought about binding at points of contact between contiguous clay plates, with little damage to the clay's surface properties.

HPLC is gaining acceptance as the preferred method for many chemical analyses, since it does not require vaporization at elevated temperatures, as does gas chromatography. A commonly used technique in HPLC of organic pollutants is reversed phase chromatography, where separation between eluates is brought about by the difference in their partition between a hydrophilic solvent and a hydrophobic stationary phase. One of the disadvantages of reversed phase partition chromatography for organic pollutant analysis and separation is the restricted solubility of many such pollutants in water, or in other highly polar solvents. Hydrophilic solid phases can be used for chromatographic separations of numerous low water solubility species from apolar solvents, and thus improve the analytical capacity for many organic pollutants. Such phases may also be efficient filtering materials for removing various undesirable components from gaseous and organic liquid systems.

Most substituted phenyl and related pollutants and many of their decomposition products are only slightly soluble in water but they do contain one or more polar moieties which are capable of strong interactions with the highly hydrophilic clays. Spray dried montmorillonite [SPM] was successfully used as a solid phase in HPLC [1]. It is characterized by a large accessible surface area and good flow properties for sufficiently apolar solvents. The use of organic solvents as the mobile phase in pollutant analysis simplifies the extraction and concentration steps of the analysis.

Clays and related materials are low cost, naturally occurring minerals possessing a high surface charge density and area. The HPLC procedure used in the present study offers a mean for screening clay-based materials for their suitability as solid phases in filtering and chromatography.

The affinity of clays, especially with exchangeable transition metals cations, to species containing unsaturated bonds is well known [2]. Formation of π complexes between arenes and Cu- or other transition metal-clays was postulated [3]. Stable interlamellar complexes of Co- and Cu-montmorillonite with organophosphorothioate pesticides were prepared by Choudary *et al.* [4] in an attempt to produce slow release formulations of the pesticides. The important role of the P=O group in the adsorption of organophosphate esters on Co-montmorillonite was discussed for example by Rodrigues *et al.* [5].

Tsvetkov *et al.* [6] have studied the adsorption of various aromatic pollutants including substituted phenyl pesticides on hydroxyaluminum cross-linked montmorillonites with basal spacings of 18.6 Å and 15.3 Å, ([CLM(w)] and

[CLM(n)], respectively). These authors discussed the importance of both interlamellar spacing and the nature of the adsorbate's functional groups in the adsorption process. In the present paper, the interaction of substituted phenyl pollutants and related substances with non-pillared montmorillonites, namely with clays in which the basal spacing is not fixed by interlamellar cross-linking, is studied.

Experimental

Preparation of clay columns

Spray-dried montmorillonite [SPM] columns (12×0.46 cm) were prepared as previously described [1]. Following spray drying, the solid phase was heated at 520°C for 24 h. Similar columns, ([SPCo-M] and [SPCu-M]), were prepared by spray drying homoionic Co and Cu-montmorillonites, respectively. The homoionic clays were made by exchanging a Wyoming montmorillonite, (Ward Natural Science Establishment, Rochester, N. Y.) through repeated suspension in the transition metal salt. Another column ([SPM-Cu], 25×0.46 cm) was prepared by spray drying the native montmorillonite and than washing it 3 times with a 0.1 *N* solution of copper chloride in a 80% ethanol-water mixture. Particles of apparent diameter of 5–7 μm were selected from the clay preparates by sedimentation in hexane-isopropanol mixtures and served as the solid phases.

Chemicals

Three organophosphate esters were studies: parathion [O,O-diethyl-O-4-nitrophenyl phosphorothionate], methyl parathion [O,O-dimethyl-O-4-nitrophenyl phosphorothionate] and paraoxon [O,O-diethyl-O-4-nitrophenyl phosphate]. The first two are widely used pesticides and the third is the first pesticide's active metabolite.

The investigated chlorosubstituted phenylureas (urons) were linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea], neburon [3-(3,4-dichlorophenyl)-1-buthyl-1-methylurea], diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] and monuron [3-(4-chlorophenyl)-1,1-dimethylurea]. Urons are selective herbicides for pre- and post-emergence control of various weeds.

Parathion, methyl parathion and paraoxon were obtained from Machteshim (Be'er-Sheva, Israel). The chlorosubstituted phenylureas were obtained from Agan Chemicals (Ashdod, Israel) and the other substituted benzenes from BDH Chemicals (Poole, England).

Instrumental and analytical procedures

Spray drying was performed by a laboratory spray dryer (Niro atomizer, Copenhagen, Denmark), using a peristaltic pump to feed the suspension. HPLC was run on a Tracor HPLC system equipped with a variable-wavelength UV detector model 970 A. XRD traces were recorded before and after thermal treatment. Thermal analyses (DTA, TG and DTG) were performed on a Stanton Redcroft TG-DTA analyzer model STA-781. The heating pattern during the thermal analyses emulated the thermal treatment of the solid phases [1].

Solvents of HPLC grade (E. Merck, Darmstadt) were used in all experiments. The columns used were: Silica (Si-100, Lichrosorb, 25×0.46 cm) and the above described spray-dried montmorillonite [SPM], spray-dried Co-montmorillonite [SPCo-M], spray-dried Cu-montmorillonite [SPCu-M] and spray-dried montmorillonite exchanged with Cu^{2+} [SPM-Cu].

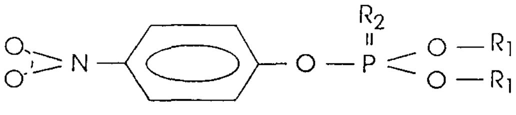
Results

Thermal treatment

Heating reduced the cation exchange capacity of the [SPM] by only 15%, from 0.81 to 0.69 meq/g [1]. The XRD patterns did not reveal any differences between the heated and unheated materials in the 1.4 to 34 Å interplanar spacing range, with the exception of the c-spacing which was reduced to approximately 9.5 Å in all systems from the initial air-dried value of 12.6, 12.4 and 15.6 Å for the Na, Cu and Co saturated systems respectively. The heating reduced the swelling capacity of all systems as determined by the XRD patterns following glycolation. The surface area of the heated [SPM] as determined by the EGME procedure was 28% lower than that of the preheated material [1]. The reduction in surface area of the Co and Cu containing materials was considerably larger (up to 75% in the case of [SPCo-M]). TEM observations of thin sections and SEM observations did not reveal significant differences between the heated and unheated [SPM] (ibid). The thermal analyses registered no significant weight loss or transformations which do not involve weight loss, except for a peak below 110°C assigned to loss of hydration water [7].

Organophosphate esters

The order of retention of the organophosphate esters (whose structures are presented in Fig. 1) on all solid phases tested was (Table 1): parathion < methyl parathion < paraoxon. Figures 2 and 3 display the separation of parathion, methyl parathion and paraoxon on the [SPM] and [SPCo-M] columns respec-



	R_1	R_2
Parathion	C_2H_5	S
Methyl parathion	CH_3	S
Paraoxon	C_2H_5	O

Fig. 1 Structure of parathion, methyl parathion and paraoxon

tively. Figure 3 demonstrates that a good resolution of parathion and methyl parathion was achieved under simple chromatographic conditions using [SPCo-M] as the solid phase. Separation of these pesticides on [SPM] could also be accomplished but only by programmed elution (Fig. 2). Paraoxon with its considerably more polar P=O group adsorbed much stronger on the clay surfaces than the P=S containing parathion and methyl parathion.

Table 1 Capacity ratios (k')[1] for parathion, methyl parathion, and paraoxon on spray dried Na-, Cu- and Co-montmorillonites ([SPM], [SPCu-M] and SPCo-M], respecively) and on wide and narrow spaced hydroxyaluminium cross-linked montmorillonites [CLM(w)] and [CLM (n)][2]. Mobile phase: (A) 1% isopropanol in hexane, (B) 10% isopropanol in hexane, (C) 50% isopropanol in hexane, (D) isopropanol and (E) 3% isopropanol in dichloromethane

	Column								
	[SPM]		[SPCu-M]	[SPCo-M]				[CLM(w)]	[CLM(n)]
	Eluent								
	A	E	A	A	B	C	D	D	D
Compound	k'								
Parathion	2.0	0.1	0.9	1.3	0.9	0.2	0.3	4.2	0.7
Methyl parathion	11.5	0.1	2.0	4.6	4.6	1.3	0.7	8.1	0.6
Paraoxon	>20.0	19.2	15.5	71.6	52.2	7.4	2.6	22.3	0.8

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[1] 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

[2] [6]

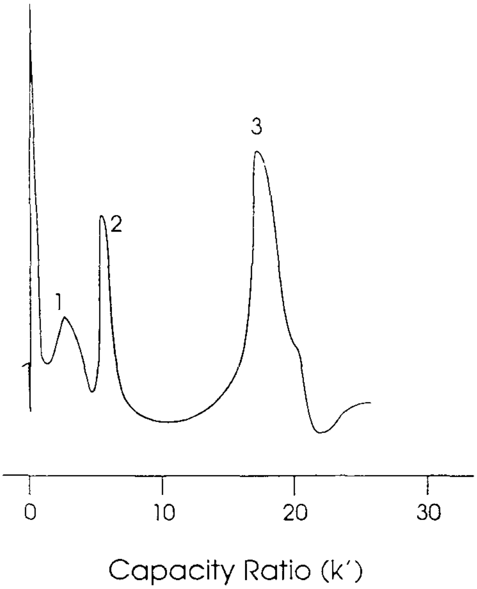

Fig. 2 Separation of (1) parathion, (2) methyl parathion and (3) paraoxon on [SPM]; programmed elution: Eluent changed from hexane to 25% isopropanol in hexane at constant rate (6.3% isopropanol/min), flow: 1.0 ml/min, detection: UV, 254 nm

Table 2 Capacity ratios (*k*', defined in Table 1) for some urons on [SPM], silica and a silica based cation exchanger (Silisorb S)[1] HPLC columns

			Eluent			
			10% isopropanol in dichlormethane		20% isopropanol in hexane	
			Column			
Compound	Solubility[2]/ ppm	Melt. point[2]/ °C	[SPM]	Silica	[SPM]	Silosorb S
			k'			
Linuron	75.0	93	0.1	0.0	1.2	0.7
Neburon	4.8	103	0.5	0.1	–	0.9
Diuron	42.0	158	1.5	1.2	5.3	3.2
Monuron	230.0	174	6.2	1..4	13.2	5.0

[1] [12]
[2] [27]

Chlorosubstituted phenylureas

Urons were already determined using both silica and reverse phase HPLC columns [8–11]. In the present study, the retention of linuron, neburon, diuron and monuron (whose structures are given in Fig. 4) was studied as a function of solvent polarity. Table 2 presents the capacity ratios (defined in footnote to Table 1) of the urons on silica-based columns including a silica based cation exchanger (exchange capacity 0.6 meq/g) [12] and on an [SPM] column run under the same chromatographic conditions. The order of elution of the urons on all columns and for all eluents was the same: linuron < neburon < diuron < monuron. The retention on both silica-based columns was weaker than on [SPM]. Figure 5 displays the separation of linuron, monuron and diuron by [SPM].

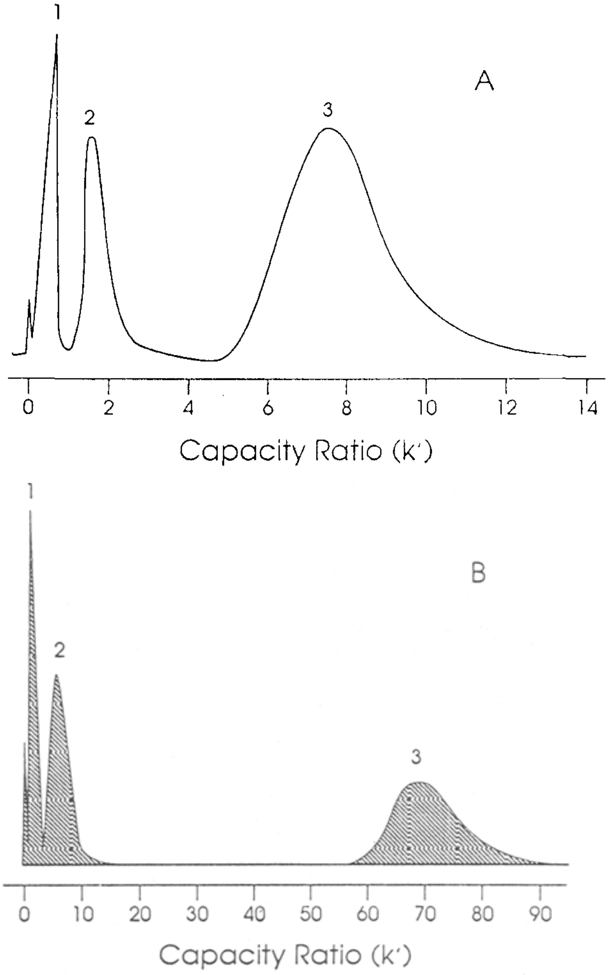

Fig. 3 Separation of (1) parathion, (2) methyl parathion and (3) paraoxon on [SPCo-M]. (a) mobile phase: 50% isopropanol in hexane, flow: 0.3 ml/min; and (b) mobile phase 1% isopropanol in hexane, flow: 2.0 ml/min. Detection UV, 250 nm

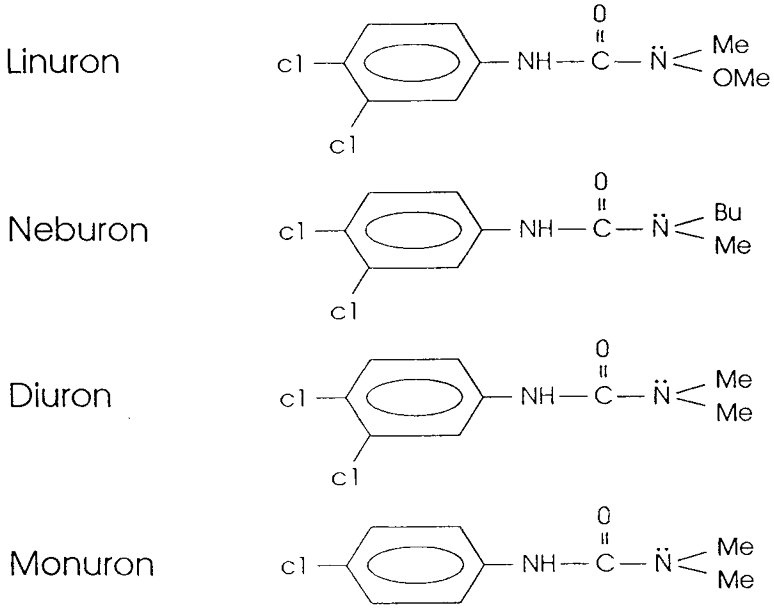

Fig. 4 Structure of linuron, diuron, neburon and monuron

Table 3 summarizes the influence of the polarity of the eluent on the retention of the urons on [SPM]. In all cases studied the retention of the urons decreased as the polarity of the eluent increased, but the order of retention of the urons was not affected by the solvent.

Table 3 Influence of eluent composition on the capacity ratios (*k*', defined in Table 1) of some urons on [SPM] HPLC column

	Eluent								
	Isopropanol in hexane/%				Isopropanol in dichlormethane/%				
	10	20	30	50	2	3	5	7	10
Compound	*k*'								
Linuron	1.2	1.2	0.6	0.05	0.4	0.3	0.2	0.2	0.1
Neburon	–	–	–	–	1.2	0.8	0.6	0.5	0.5
Diuron	5.3	5.3	1.5	1.3	17.4	8.4	4.0	3.7	1.5
Monuron	>28.7	13.2	4.6	3.1	>40.0	30.0	14.0	12.5	6.2

Other substituted benzenes

The retention of some substituted benzenes and phenols on various spray-dried clay columns is summarized in Table 4 and Fig. 6. While in the case of

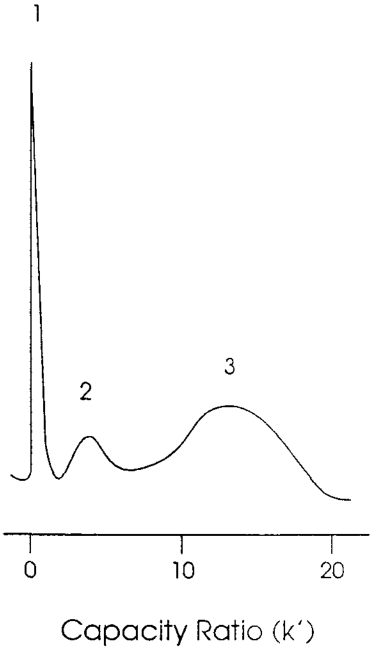

Fig. 5 Separation of (1) linuron, (2) diuron and (3) monuron on [SPM]; eluent: 5% isopropanol in dichloromethane, flow: 1.0 ml/min, detection: UV, 250 nm

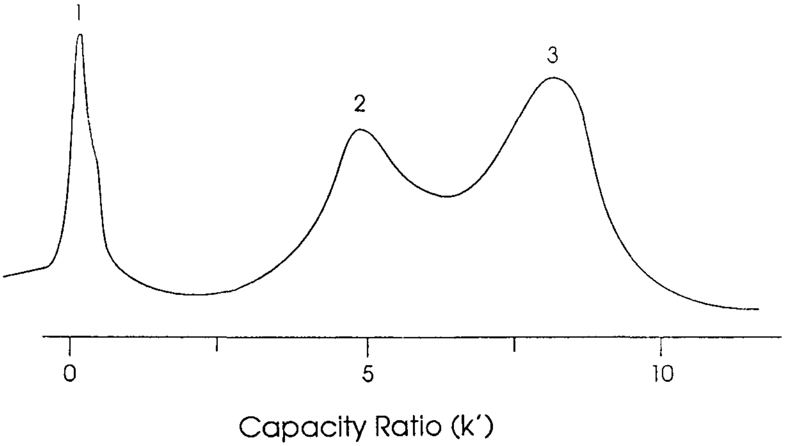

Fig. 6 Separation of (1) *o*-, (2) *m*- and (3) *p*-nitrophenol on [SPM-Cu]; eluent: 1.5% isopropanol in hexane, flow: 1.0 ml/min, detection: UV, 254 nm

the non-shrinkable, cross-linked [CLM-(w)] the retention of the various eluates decreased with the polarity of the solvent [6], retention on the non cross-linked, spray-dried clays did not display a monotonous dependence on the solvent's polarity. For example, the retention of the *o*- and *m*-isomers of nitrotoluene increased with solvent polarity on the Co and Cu containing stationary phases. The retention of the *p*-isomer decreased with the polarity of the solvent on all solid phases.

The order of retention of the isomers of the disubstituted benzenes was in most cases $o < m < p$. A notable exception was chloronitrobenzene whose *o*-isomer eluted, on [CLM(w)] the slowest (Table 4). An eluent dependent order of retention was observed in the past with some disubstituted benzenes where the relative retention of the *o*-isomer increased with the polarity of the mobile phase [13]. Another deviation from the more common order of retention was displayed by cresol, the *p*-isomer of which eluted from both [SP-Cu-M] and [SP-Co-M] faster than the *m*-isomer. An interpretation of these observations will be presented below.

Table 4 Capacity ratios (*k*', defined in Table 1) of some substituted benzenes on spray dried Cu- and Co-montmorillonites ([SPCu-M] and [SPCo-M], respectively) and on a hydroxyaluminum cross-linked montmorillonite [CLM(w)][1]. Mobile phase: (A) hexane, (B) 1% isopropanol in hexane, (C) 10% propanol in hexane

	Column						
	[SPCu-M]		[SPCo-M]		[CLM(w)]		
	Eluent						
	A	B	B	C	A	B	C
Compound	*k*'						
Nitrobenzene	1.2	1.3	–	–	–	–	–
o–cresol	1.1	–	0.5	–	–	2.9	0.8
m–cresol	1.4	–	0.9	–	–	5.3	1.3
p–cresol	1.0	–	0.8	–	–	5.9	1.3
o–chloronitrobenzene	1.4	0.8	–	2.3	–	2.7	2.6
m–chloronitrobenzene	2.7	2.0	–	8.0	–	0.9	0.9
p–chloronitrobenzene	3.5	2.5	–	13.2	–	0.5	0.4
o–nitrotoluene	–	1.3	4.8	8.2	6.4	–	0.9
m–nitrotoluene	2.7	3.6	8.2	12.7	10.4	–	1.0
p–nitrotoluene	6.2	6.1	35.6	28.0	13.1	–	1.1

[1] [6]

Discussion

Heat treatment, if executed properly, can considerably improve the efficiency of clay-based materials as stationary phases in chromatography. The peak corresponding to loss of structural water of montmorillonite in DTA appears at around 630°C [14]. At 520°C loss of structural water already takes place but at a very slow rate. Consequently, as indicated by a comparison between the properties of the heated and unheated materials, the mild thermal treatment performed affected the physical and chemical properties of the surface minimally, while strongly stabilizing (i.e., reducing the swelling of) the stationary phases. The stabilization arose apparently from a partial collapse of the tactoids. The observed decline in measured surface area also resulted most likely from the assumed collapse of the tactoids. Accordingly, the extent of reduction in surface area corresponded to the number of plates per tactoid, which is considerably larger in the Cu and Co-clays than in the Na-saturated [SPM]. Due to the very fast drying in the spray-drying process, the tactoids present in the original suspension become arranged in the resultant aggregates in a 'card-house' structure with no change in the number of plates per tactoid [1].

The collapse of the tactoids following thermal treatment was reversible to some extent, but the rate of recovery was slow. In all investigated systems, sufficiently long glycolation (of the Co- and Cu-systems) or exposure to air (of the Na-clay) resulted in some expansion as indicated by the XRD patterns.

The important role of the exchangeable cations (hydrated or otherwise) in the retention of the investigated eluates will be discussed below. Preheating resulted in partial dehydration of the surface and specifically, partial or full dehydration of the exchangeable cations. The polarity of the cations' hydration water increases as the hydration shell of the cation gets depleted [15]. Since cations interact with the investigated eluates as Lewis (or in extreme cases as Bronsted) acids, dehydration by the thermal treatment may enhance the strength of interaction of the eluates with the surface. Enhancement of the retention of dimethylanilines on spray-dried montmorillonite by the proposed thermal treatment was demonstrated [1]. Thus, while preheating enables the use of polar mobile phases [16], it does not significantly retard, and in some cases it even enhances the chromatographic efficiency of the clay.

The retention of an eluate molecule on the stationary phase is controlled both by the strength of interaction and by the accessibility of the interacting surface sites to the eluate. The existence of interlayer spaces in clay systems, the width of which is similar to the eluate's molecular dimensions, makes steric factors of utmost importance [6, 13]. Small differences in the structure of the molecule, such as between isomers and in the basal spacing, such as those existing in the presence of eluents of different polarities, may strongly affect the retention. It is possible, therefore, to achieve good resolution between similar molecules, geometrical isomers for example, by a proper choice of stationary phase or, in the case of expandable solid phases, also of the mobile phase. The retention of the investigated molecules on expandable clay-based stationary phases will be discussed below in terms of the balance between steric and mechanistic factors.

Organophosphate esters

Exchangeable cations are probably the dominant site of interaction between organophosphate esters and clays and hence the higher the cation's valence the stronger is the interaction expected to be [17, 18]. Yet, the present results indicate that among the homoionic, spray-dried clays, the highest retention of the organophosphate esters was on [SPM], the Na-saturated montmorillonite, rather than on the montmorillonites with the higher valence exchangeable cations, Cu^{2+} or Co^{2+}. One important reason for this apparently surprising result is that spray-drying leaves the Na-clay with a predominantly edge to face plate arrangement with a mean tactoid thickness of 1.4 plates [1]. Almost all the solid phase surfaces are thus accessible to the relatively large eluates. The Cu and Co-clays are composed of considerably thicker tactoids, with basal spacings in the air-dried state (before the thermal treatment) of 15.6 Å for the Co-montmorillonite and 12.4 Å for the Cu-clay. Tsvetkov *et al.* [6] demonstrated a drastic drop in the retention of organophosphate esters when the basal spacing of a cross-linked montmorillonite was reduced from 18.6 to 15.3 Å (Table 1). The considerable surface area in the interlayer spaces of the Cu- and Co-clays is, therefore, not freely accessible to the organophosphate esters.

Steric factors may also explain the higher retention of the organophosphate esters by the Co-clay as compared to the Cu-clay. While Co^{2+} is preferentially octahedrally or tetrahedrally coordinated, Cu^{2+} tends to form planar complexes [19]. The aforementioned lower basal spacing of the air dried Cu-clay is in agreement with the difference in preferred coordination. A higher resolution between the organophosphate esters was displayed by [SPCo-M] than by [SPCu-M]. The low retention of all organophosphate esters on [CLM(n)] (Table 1) which was only slightly narrower than the air-dried Co-clay, may suggest that the interlayer spaces of [SPCo-M], and even more so those of the Cu-clay, were not freely accessible to any of the organophosphate esters. The increase in penetrability into the interlayer spaces when the stationary phase was changed from the Cu- to the Co-clay is likely to be more pronounced for the less bulky methyl parathion (and paraoxon), while the more bulky parathion probably hardly penetrated the interlayer spaces even in the wider [SPCo-M].

The retention of methyl-parathion was considerably stronger than that of parathion on both the SP-clays and [CLM(w)]. Paraoxon was retained more strongly than the other two organophosphate esters. The fact that this order of retention was also observed on [CLM(w)] in which there should not be any constraint to the penetration of the eluates into the interlayer spaces may help to shed some light on the mechanism of interaction between the organophosphates and the solid phases. The order of retention supports the contention that the major molecular site of interaction with the surface is the phosphate moiety [17] and not the aromatic portion of the molecule. The P=O bond of paraoxon is more polar than the P=S bond of the other two eluates and hence should interact more strongly with the sorption sites (i.e. the counter-cations). The bulkier ethoxy groups of the parathion hinder the interaction of the phosphate moiety with the surface to a larger extent than the methoxy groups of its methyl analogue. Steric effects thus favour both the direct interaction of methyl parathion with the surface and its penetration into the interlayer spaces.

Urons

The order of retention of the urons on both the silica-based and [SPM] columns correlates with their melting point but not with their solubility in water (Table 2). The melting point depends on the energy of interaction between the molecules in the crystal. This energy has in common with the adsorption energy a dependence on both the molecule's polarity (or polarizability) and steric considerations. The more polar the molecules and the more exposed their polar moieties, the more dense is the crystal packing and the stronger is the interaction with a surface. Solubility has a completely different dependence on the molecular structure, since the small water molecules can reach polar moieties of the solute with considerably lower hindrance by the less polar parts of the solute molecule than do interacting sites in the rigid crystal or solid surface.

Urons interact with clay surfaces primarily through their urea moiety. Both the amide nitrogen and the carbonyl oxygen of the urea moiety may interact with the surface [20, 21]. Substitution at the amide nitrogen atom influenced very strongly the retention (Tables 2 and 3). If, as depicted in Fig. 4, a methyl group (diuron) is substituted by the more bulky butyl (neburon) or methoxy group (linuron), the strength of adsorption decreased. Replacing a methyl group by the more electronegative methoxy group may also draw electrons from the urea moiety, making it less susceptible to electron donating interactions with electrophilic surface sites such as counter-cations. These cations are the most likely interaction sites with the urons [20–22].

A comparison of the retention of diuron and monuron indicates that the absence of a chloro group in the meta-position to the urea increased the adsorption of the eluate molecule considerably. This may be due to an inductive effect on the adsorption process [23]. The inductive effect arises from the electronegative nature of the chloro substituent. Addition of the Cl atom to the aromatic ring draws electrons from the urea moiety and weakens its basic character, thus weakening the uron's retention.

The order of retention of the urons was the same in all the examined stationary-mobile phase combinations (Tables 2 and 3). This suggests that the mode of interaction is similar in all the tested chromatographic systems. As pointed out above, the urons are likely to sorb primarily through the urea moiety which interacts as a base with acidic surface sites (e.g counter-cations). The preceding discussion indicates that the order of retention is in agreement with this interaction mechanism.

An increase in polarity of the mobile phase decreased the retention of the urons (Table 3). Both addition of isopropanol to the less polar solvent and substituting dichloromethane for hexane as the major component in the mobile phase had this effect. The polarity of the mobile phase has two opposing effects on the retention of the eluates. Swelling of the expandable solid phases with increased polarity may enhance the accessibility of interlayer sorption sites and with it the retention. Competition on sorption sites between the solvent and the solute will, on the other hand, weaken the retention as the polarity of the solvent increases. An increase in polarity of the mobile phase did increase the capacity ratio of certain eluates on the expandable [SPCu-M] and [SPCo-M] stationary phases which have a large fraction of their surface in the interlayer spaces, (Table 4). [SPM], which is composed mainly of single plates connected in an edge to face arrangement [1], is less likely to display an increase in the retention with an increase in the mobile phase polarity. As demonstrated by Table 3, the competition between solvent and solute did dominate the effect of solvent polarity on the retention of urons by [SPM].

Other substituted benzenes

The relative retention of the three isomers of disubstituted benzenes is controlled by two types of considerations:

a. Direct effect on the eluate-surface interaction. If the access of the molecule to the sorption site is free, the mutual influence of one substituent on the interaction of the other with the surface and the substituents' commulative effect on the ring-surface interaction will determine the order of retention. For example, when both substituents are electronegative, the *o*-isomer is most likely to display the strongest retention because of its capacity to engage in bidentate interactions with a Lewis acid site at the surface. The order of adsorption of the chloronitrobenzene isomers on the non-shrinkable [CLM(w)] exemplifies such a situation (Table 4). If, on the other hand, one substituent is electronegative and the other apolar, the *o*-isomer is likely to elute first, due to the steric hindrance by the apolar substituent to the interaction between the surface and the electronegative substituent. This situation is exemplified by the order of retention of the cresols and nitrotoluenes on [CLM(w)] (Table 4).

b. Accessibility considerations. When a significant portion of the surface of the stationary phase is not freely accessible, the relative ease of penetration of the isomers may dictate their order of retention. The *o*-isomers are least likely to penetrate freely into the interlayer spaces of clays and related materials [6, 13]. This is probably the reason why *o*-chloronitrobenzene eluted faster than the *m*- and *p*-isomers on [SPCu-M] and [SPCo-M] (basal spacing 12.4 and 15.6 Å before the thermal treatment, respectively), opposite to the order of elution on [CLM(w)] which has a considerably higher basal spacing (18.6 Å) (Table 4).

In some cases, the swelling of the expandable stationary phases as the polarity of the mobile phase increases suffices to allow free penetration into the interlayer spaces of eluates displaying restricted penetration in the unswollen clay. Despite the competition between polar solvent molecules and the solute on sorption sites, increased polarity of the solvent may then increase the retention (e.g., *o*- and *m*-nitrotoluene on [SPCu-M] and [SPCo-M]; Table 4). With the more rigid [CLM-w)], swelling and shrinking of the stationary phase is less pronounced and should not affect the retention significantly. Accordingly, increase in the polarity of the mobile phase always reduced the capacity ratio of the eluates on [CLM(w)] (Table 4) and [6]. If the swelling is sufficiently large, an inversion in the order of retention of the isomers of disubstituted benzenes with two electrophilic substituents may take place as the polarity of the eluent increases. The *o*-isomer has the most hindered accessibility into the interlayer spaces and is likely to be eluted first from the unswollen clay. If as a result of the swelling its penetration becomes free, the relative retention of the isomers becomes a function of the strength of the intrinsic interaction between the eluate and the surface and the *o*-isomer should be eluted last [6]. Such an inversion in the order of retention of the isomers of nitrophenol was observed in the past on clay-based stationary phases [13].

If a substituted benzene possesses a dissociable acidic substituent (e.g. phenols), one mode of interaction with the stationary phase may be between the dissociated substituent and a Lewis acid site at the surface. While *m*-cresol is the strongest acid among the cresols, the *p*-isomer has the highest dipole moment [24, 25]. The fact that on both [SPCu-M] and [SPCo-M] the *m*-isomer is retained more strongly, while on the [CLM(w)] the *p*-isomer is retained stronger (Table 4), may suggest that the cresols tend to interact with the stationary phases which contain the transition metal cations mostly as phenolate ions, while with the Al containing stationary phase the interaction as undissociated phenol is more significant.

The separation of the nitrophenol isomers on [SPM-Cu] is presented in Fig. 6. The retention of other substituted benzenes on this stationary phase was also investigated [26]. This stationary phase was made by partially exchanging the Na in [SPM] by Cu. The resolution obtained (Fig. 6), indicates that by exchanging the counter-cation on [SPM], it is possible to produce stationary phases for HPLC with a wide array of cations in the exchange complex and consequently a broad spectrum of chromatographic properties.

Conclusions

Heat treated clay-based materials provide a basis for the design of resilient stationary phases for chromatographic systems optimized for specific uses. Transition metal counter-cations may participate in specific interactions between many eluates and the stationary phase. Both selective chromatographic separations and heterogeneous catalytic reactions may thus be achieved by loading the exchange complex of the stationary phase with the appropriate transition metal cations.

The sensitivity of the basal spacing of expandable clays to the nature of the exchangeable cation as well as to the polarity of the mobile phase, further enhances the capacity of the investigated family of clay-based stationary phases to effect good resolutions, including size controlled separations, of a wide range of eluate mixtures.

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Zusammenfassung — HPLC-Säulen wurden mit quasikugelförmigen Montmorillonit-Partikeln gefüllt, die durch Zerstäubungstrocknung und anschließende thermische Behandlung dargestellt wurden. An diesen Säulen wurde die Trennung von Phenylharnstoffen (Linuron, Neburon, Diuron und Monuron), von Phosphotioat-Phenylestern (Parathion, Methylparathion und Paraoxon) und anderen niedersubstituierten Benzolen durchgeführt. Die relative Retention der substituierten Phenylpestizide zeigte die wichtige Rolle polarer Substituenten bei den Eluat-Oberfläche-Wechselwirkungen und den starken Einfluß sterischer Faktoren auf diese Wechselwirkungen. Sobald die Polarität der mobilen Phase erhöht wird, fällt die Retention der Pestizide schroff ab. Die Retention der niedersubstituierten Benzole zeigt eine ähnliche Tendenz, jedoch wirkt für diese kleineren Moleküle dieser Tendenz eine wegen dem Anschwellen eintretende verstärkte Zugänglichkeit der Zwischenschichträume entgegen, sobald die Polarität der flüssigen Phase erhöht wird. Für die Rolle des austauschbaren Kationes (Na^+, Co^{2+} und Cu^{2+}) bei der Adsorption wurde ein komplexer Zusammenhang gefunden. Die Kationen bestimmen sowohl die Stärke der Wechselwirkung, die mit der Wertigkeit des Kations zunimmt, und auch die Zugänglichkeit von Zwischenschichten-Adsorptionsstellen, die mit der Wertigkeit abnimmt.