

Optimization of Adsorption of Hydrophobic Herbicides on Montmorillonite Preadsorbed by Monovalent Organic Cations: Interaction between Phenyl Rings

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This study aimed to optimize organo-clay formulations for reduction of leaching of the herbicides alachlor, metolachlor, and norflurazon, which include a phenyl ring in the structure. The adsorbed amounts of herbicides increased severalfold when montmorillonite was preadsorbed by an organic cation; benzyltrimethylammonium (BTMA) was more effective than benzyltriethylammonium (BTEA). Fourier transform infrared studies indicated interactions between alachlor molecules and adsorbed BTMA. The adsorption affinity of the herbicides increased with BTEA loading up to the cation exchange capacity (CEC) of montmorillonite but reached a maximum at a BTMA loading of 5/8 of the CEC. The enhanced adsorbed amounts of herbicides are mainly due to interactions between the phenyl rings of herbicide molecules and organic cations, which are favored with the smaller cation, BTMA. BTMA preadsorbed on the clay up to the CEC forms a fraction (14–18%) of charged dimers so that less phenyl rings are available for interacting with herbicide molecules. This effect is small for preloading by BTEA, so that the amounts adsorbed increase with the degree of preloading. Thus, optimization of clay-based herbicide formulations requires a selection of structurally compatible organic cations preadsorbed on the clay at optimal coverage.

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Introduction

The adsorption of organic cations on clays modifies the nature of clay mineral surface, transforming it from hydrophilic to hydrophobic. The modified clay mineral surface can adsorb organic molecules of low solubility in water (1–5). The herbicides alachlor and metolachlor have been studied with the purpose of producing organo-bentonite herbicide formulations, which would reduce their leaching, photodegradation, and volatilization (6, 7). In the latter studies, the idea was to achieve slow release of the hydrophobic herbicides by adsorbing them on a natural component of soil, e.g., the clay mineral montmorillonite, whose surface has been modified from hydrophilic to hydrophobic by preadsorbing on the clay suitable monovalent organic cations. Indeed, the organo-clay formulations of these herbicides yielded a significant reduction in their leaching as well as volatilization and photodegradation. The latter studies have introduced a new approach in the choice of organo-clay minerals.

It turned out that formulations of alachlor and metolachlor based on mont-hexadecyltrimethylammonium (HDTMA) were only marginally advantageous in reducing herbicide leaching, in accord with the relatively low affinity of sorption of the herbicides on this organo-bentonite. Satisfactory formulations were obtained when the monovalent organic cations chosen included a phenyl ring in their structure, which can match the phenyl ring in these herbicides (see Figure 1).

Comparing formulations based on three such organic cations, benzyltrimethylammonium (BTMA), benzyltriethylammonium (BTEA), and benzyltributylammonium (BTBA), showed more effective reduction in leaching by using a smaller organic cation according to the sequence BTMA > BTEA > BTBA.

An optimal formulation of alachlor was prepared by sorbing it on montmorillonite preadsorbed by BTMA at 0.5 mol/kg clay (denoted mont-BTMA 0.5), rather than up to the cation exchange capacity (CEC) of montmorillonite (0.8 mol/kg clay) (denoted mont-BTMA 0.8), where maximal transformation of the clay mineral from hydrophilic to hydrophobic might be expected. On the other hand, when employing BTEA, adsorption of alachlor (6) and metolachlor (8) on the organo-bentonite was maximal when montmorillonite was preadsorbed up to the CEC.

The current study aims to offer an explanation for the above pattern of adsorption. We present experimental and calculated results on the sorption of three hydrophobic herbicides, which include a phenyl ring, alachlor, metolachlor, and norflurazon (see Figure 1). It may be added that with these herbicides strong adsorption affinity paralleled slow release and reduced leaching (6–8 and unpublished results).

Since certain media may be rather saline (soils or recycled water), it was of interest to see the effect of salt on the adsorption of the hydrophobic herbicides by selected organo-clays. To test our mechanistic interpretation of the results, we added a small scale study on the adsorption of metolachlor on montmorillonite preadsorbed by phenyltrimethylammonium (PTMA), which is smaller than BTMA (Figure 1).

Experimental Section

Materials. The clay mineral used was Wyoming Na-montmorillonite Swy-1 obtained from the Source Clay Repository (Clay Minerals Society, Columbia, MO). Its CEC was 0.8 mmol/g clay (9). Analytical grades alachlor, purity 99.9%, and metolachlor, purity 99%, were purchased from Chem

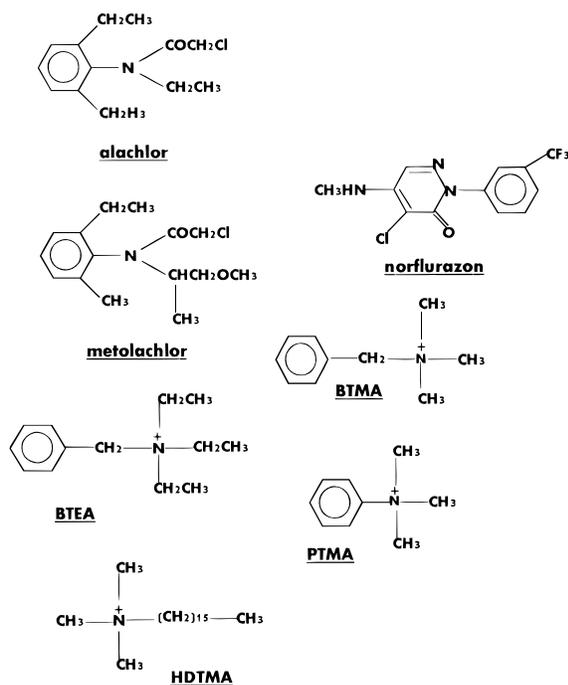


FIGURE 1. Molecular structures of the hydrophobic herbicides and organic cations studied.

Service Inc. (West Chester, PA). Analytical grade norflurazon, purity 99.9%, was kindly supplied by Novartis A.G. (Basel, Switzerland). Benzyltrimethylammonium (BTMA) (50 wt % in water solution) and phenyltrimethylammonium (PTMA) (98%) were obtained as chloride salts, and benzyltriethylammonium (BTEA) (99%) was obtained as bromide salt, from Sigma-Aldrich Chemical Co. (Milwaukee, WI). Hexadecyltrimethylammonium (HDTMA) (99%) was obtained as bromide salt from Sigma-Aldrich, and methylene blue (MB) was purchased from E. Merck (Darmstadt, Germany).

Methods. Preparation of the Organo-Clay Complexes.

The organo-clay complexes were prepared by dropwise addition of aliquots of 0.1 M aqueous solutions of HDTMA, BTMA, BTEA, PTMA, or MB to a 0.5% (w/w) aqueous suspension of the clay under continuous stirring for 24 h. After centrifugation (15 min, 30 000 g) the precipitate was freeze-dried for 24 h or more, as needed, ground to <50 μm , and kept in plastic tubes at room temperature.

Adsorption Isotherms. Norflurazon adsorption isotherms were carried out by adding 20 mL of aqueous solutions ranging from 13.17 to 65.85 μM under continuous stirring to 5 mL of 2.5% (w/w) clay/organo-clay suspension in 30 mL polycarbonate tubes. After shaking the tubes for 24 h at $20 \pm 1^\circ\text{C}$, the suspensions were ultracentrifuged at 10 000g for 1 h (Centrikon T-1170), and norflurazon concentration in the supernatant was determined by using a Merck-Hitachi HPLC equipped with fluorescence detector, as in ref 10.

The adsorption isotherms of alachlor and metolachlor were measured in the range of 0–700 μmol herbicide/g of clay-organic complex with clay-(BTMA, or BTEA, or PTMA) 0.5 or 0.8. Adsorption isotherms were measured by adding appropriate aliquots of an aqueous stock solution of 10^{-4} M alachlor or 10^{-3} M metolachlor diluted with distilled water in 25 mL and were added to 5 mL of 0.5% (w/w) clay-complex suspension in a 40 mL centrifuge tube. The final clay or clay-complex concentration was 0.83 g/L. The samples were kept under continuous horizontal agitation at $25 \pm 1^\circ\text{C}$ during 24 h. The supernatant was separated by centrifugation at 15 000g for 1 h. Extraction of the herbicides from the supernatant solutions was performed by adding sodium chloride (2.4 g) into glass tubes, containing 10 mL of supernatant and 10 mL

of ethyl acetate–isooctane (1:9). The tubes were sealed and mixed for 2 min using a vortex mixer (Model K-550-G) operating at the highest speed. The tubes were left at room temperature for 1 h until the ethyl acetate–isooctane phases were separated. Then the ethyl acetate–isooctane phase was collected into the 25 mL volumetric flasks, and the same procedure of extraction was repeated to ensure perfect extraction. Flasks were filled up to the mark by the ethyl acetate–isooctane (1:9). Crimp vials were filled with ethyl acetate–isooctane, sealed, and analyzed by GC as described in ref 6.

FTIR and UV–Visible Spectra. The interactions between alachlor and the clay mineral and its organo-derivatives were examined by Fourier transform infrared (FTIR) and UV–visible spectroscopy. The FTIR spectra were obtained using KBr pellets with a Nicolet Magna-IR 550. Spectra were recorded at room temperature in the range 4000–400 cm^{-1} . Difference spectra were obtained by subtracting the corresponding spectra of organo-clay or clay from the spectra of clay-organic–alachlor complexes. After sonication for 5 min the suspensions were diluted from 0.5% (w/w) of montmorillonite, to 0.025% (w/w). UV–visible spectra of the suspensions were measured using an HP8452 diode array spectrophotometer (Hewlett-Packard, Palo Alto, Ca) with quartz 1 cm cuvettes.

Model Calculations. a. Adsorption of Organic Cations.

The program used considers cation binding to the negatively charged surface sites of the clay mineral and the electrostatic Gouy–Chapman equations and solves iteratively for the solution concentrations of all cations in a closed system. Cation adsorption is obtained by considering specific binding and residence in the double layer region. If cation adsorption occurs at amounts below the CEC, then there is excess of cations in the double layer region, whereas, if charge reversal occurs as in the case of certain organic cations, then there is some exclusion of cations (11–13). The binding of organic monovalent cations is described in eqs 1–4 below.

Let X_i^+ denote a monovalent cation that binds to a singly charged negatively site, P^- , on the surface of the silicate

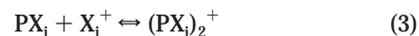


with a binding coefficient, K_i , given by

$$K_i = [PX_i]/([P^-][X_i(0)^+]) \quad (2)$$

in which $[X_i(0)^+]$ is the concentration of the cation at the surface.

Another type of complexation is considered in the case of organic cations



with a binding coefficient

$$\bar{K}_i = [(PX_i)_2^+]/([PX_i][X_i(0)^+]) \quad (4)$$

In eqs 2 and 4 the concentrations are given in units of mol L^{-1} or M, and the unit of K_i or \bar{K}_i is M^{-1} .

The calculations employed the same binding coefficients of BTMA and BTEA as in ref 14, $K = 5000 \text{ M}^{-1}$, whereas $\bar{K} = 20$ or 5 M^{-1} for BTMA or BTEA, respectively. The values of the other binding coefficients were as in refs 15 and 16. The focus in these calculations (Table 4) was on determining the fraction of charged complexes, which is given by $2 [P(X_i)_2^+]/[PX_i]$.

b. Sorption of Herbicides by Organo-Montmorillonite. The Scatchard equation, which is based on the assumption of the lack of interactions, i.e., lack of cooperativity between

TABLE 1. Binding Coefficients Describing Adsorption of Hydrophobic Herbicides with a Phenyl Ring, on Montmorillonite and Organo-Clay Complexes Prepared at Several Loads

system	organic cation	load (mol/kg)	k (M^{-1})	R^2
norflurazon	none		40	0.98
	BTMA	0.2	115	0.99
	BTMA	0.5	215	0.99
	BTMA	0.8	150	0.99
	BTEA	0.2	130	0.99
	BTEA	0.5	190	1.00
alachlor	none		50	0.99
	BTMA	0.5	1000	0.99
	BTMA	0.8	750	0.99
	BTEA	0.5	420	0.98
	BTEA	0.8	520	0.99
	HDTMA	0.8	200	1.00
metolachlor	none		45	0.99
	BTMA	0.5	680	0.96
	BTMA	0.8	480	0.97
	BTEA	0.5	340	0.97
	BTEA	0.8	400	0.95
	PTMA	0.5	2880	0.99
PTMA	0.8	1900	0.98	

TABLE 2. Effect of 0.067 M NaCl on the Sorption of Hydrophobic Herbicides by Clay-BTMA

herbicide and organo-clay	amount added (mmol/kg)	percent adsorbed	
		without salt	with salt
alachlor			
BTMA 0.5	700	33.2	32.9
BTMA 0.8	700	29.0	29.2
metolachlor			
BTMA 0.5	700	29.00	28.6
BTMA 0.8	700	23.1	22.9
norflurazon			
BTMA 0.5	8.95	43.9	38.8
BTMA 0.8	8.95	38.5	29.0

TABLE 3. FTIR Vibration Bands (cm^{-1}) of Alachlor and Alachlor Sorbed on Montmorillonite and Its Complexes^a

	$\nu_{C=O}$	ν_{C-N}	$\delta_{C\text{ aromatic-H}}$
free alachlor	1689	1370	793
clay	1671	1385	809
clay-BTMA 0.5	1679	1385	815
clay-BTMA 0.8	1679	1385	809
clay-BTEA 0.5	1679	1386	810
clay-BTEA 0.8	1679	1386	810

^a The infrared spectra of organo-clay complexes were subtracted from the corresponding spectra of alachlor-clay or alachlor-organo-clay.

adsorbed molecules, was used to describe the sorption of the herbicides by the clay or organo-clays. The Scatchard equation, which is equivalent to the Langmuir equation, includes two parameters, the binding coefficient, k , as in eq 2, and the number of surface sites, N , per particle, e.g., a clay platelet. As elaborated in ref 17 there is mathematical equivalence between (i) sorption on particles including N binding sites and (ii) a bimolecular association between the sorbing particles and the surface sites, by using the substitution $R_0 = NG_0$, in which R_0 is total molar concentration of surface sites and G_0 is the molar concentration of sorbing particles. The Scatchard equation can be brought to a form

$$\alpha = (L_0 - L)/L = R_0 k / (1 + kL) \quad (5)$$

TABLE 4. Fraction of Sorbed BTMA^a, BTEA^a, or PTMA^b as Charged Complexes (Dimers) in Montmorillonite Modified with BTMA, BTEA, or PTMA

organic cation	total concn (M)	clay concn (w/w)%	fraction of charged complex (%)
BTMA	10^{-2}	0.5	13.6
	$1.25 \cdot 10^{-2}$	0.5	15.5
	10^{-2}	1	18.2
BTEA	$2 \cdot 10^{-2}$	0.5	20.1
	$2.5 \cdot 10^{-3}$	0.5	2
	10^{-2}	0.5	5.8
	$1.25 \cdot 10^{-2}$	0.5	6.9
	$2 \cdot 10^{-2}$	0.5	7.3
PTMA	$2.5 \cdot 10^{-3}$	0.5	0.3
	$5 \cdot 10^{-4}$	0.1	11.4
	$3 \cdot 10^{-3}$	0.1	27.2

^a When the initial organic cation concentration was 10^{-2} M or higher, the amount adsorbed corresponded to the CEC, whereas for $2.5 \cdot 10^{-3}$ M the adsorption was almost quantitative and reached 5/8 of CEC. The fraction of sorbed molecules forming dimers was obtained as described in Experimental Section. ^b In this case the clay concentration (w/w) was 0.1%, and the initial concentration which yielded amounts of PTMA adsorbed corresponding to the CEC was $3 \cdot 10^{-3}$ M, whereas 5/8 CEC were reached at an initial PTMA concentration of $5 \cdot 10^{-4}$ M. For a clay concentration of 0.5% the calculated fraction of dimers was larger.

in which L_0 and L denote the molar concentration of total added herbicide molecules and those remaining free. In eq 5 α is the ratio between sorbed and free herbicide molecules. Equation 5 can be brought to a quadratic equation in

$$\alpha^2 + \alpha(1 + k(L_0 - R_0)) - kR_0 = 0 \quad (6)$$

The concentration of sorbed molecules is given by

$$L_0 - L = L_0 \alpha / (1 + \alpha) \quad (7)$$

In principle eq 5 can provide both parameters, R_0 and k . However, since a minimal number of parameters is preferred, we presented (Table 1) results based on the use of a single parameter, k . The parameter R_0 was fixed by a multiplication of the CEC of the clay mineral (mol/g clay) with the concentration of the clay (g/L). The applicability of the Scatchard equation (eq 5) was tested by its ability to adequately simulate the sorption results.

Results

The molecular structures of the hydrophobic herbicides alachlor, metolachlor, and norflurazon and the three monovalent organic cations BTEA, BTMA, and PTMA are shown in Figure 1. All these molecules include a phenyl ring. Figure 1 also shows the structure of HDTMA which has been widely employed in modifying clay surfaces from hydrophilic to hydrophobic (3, 4).

The adsorption isotherms of norflurazon on the clay mineral or a clay mineral preadsorbed by the monovalent organic cations are given in Figure 2. Table 1 gives a summary of the results in terms of the binding coefficient, k (M^{-1}), by using a Scatchard plot (eq 5). The results in Table 1 demonstrate that the Scatchard equation (eq 5), in which we fixed the number of sites by the CEC, yields good fits to the experimental values of adsorbed amounts. The root-mean-square errors (not shown) were within the experimental errors. We also tried to employ two parameters, e.g., modifying R_0 to correspond to larger or smaller values of the CEC, but the improvement achieved in the fits cannot constitute a definitive proof that the molar concentration of adsorption sites, R_0 , is larger or smaller than the product of the CEC and the clay concentration (g/L). The values of k in Table 1 provide a convenient scale for comparison rather

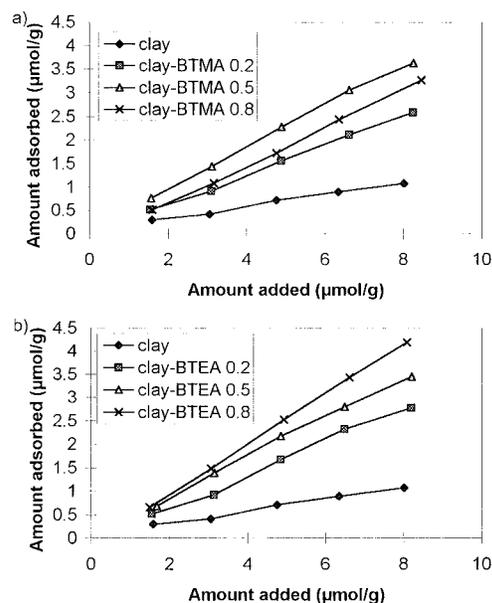


FIGURE 2. Adsorption isotherms of norflurazon on montmorillonite and on organo-montmorillonite: (a) mont-BTMA and (b) mont-BTEA.

than absolute values which can yield exact changes in free energy due to sorption.

Figure 2 demonstrates that the organo-clays enhance significantly the adsorbed amounts of norflurazon above their adsorption to the clay mineral itself. Table 1 expresses the enhanced adsorption of these hydrophobic herbicides by the optimal organo-clay (mont-BTMA 0.5), in terms of a 4–6-fold increase in k -values in the case of norflurazon. The enhancement is 15-fold in the case of metolachlor and 20-fold in the case of alachlor. The enhancement of metolachlor sorption on mont-PTMA is even larger, i.e., 60-fold. The herbicides alachlor and metolachlor have significantly higher binding affinities to the clay mineral preadsorbed by the smaller organic cation, BTMA, whereas norflurazon displays similar binding affinities to clay-BTMA and clay-BTEA. However, in the latter case k -values are relatively small, about 4-fold smaller than those describing the adsorption of alachlor by mont-BTMA 0.5.

A striking feature of the adsorption of all these herbicides by mont-BTMA is the maximum in adsorption affinity on mont-BTMA 0.5, rather than on the clay mineral preadsorbed by BTMA up to its CEC, i.e., clay-BTMA 0.8. This trend is also exhibited for mont-PTMA. In contrast, the adsorption affinity of these hydrophobic herbicides to clay-BTEA increases with the load of BTEA, being maximal for BTEA loading of 0.8 mol/kg (clay-BTEA 0.8). Possible explanations are given in the Discussion section.

Table 1 also provides information on the enhancement of adsorption by HDTMA. The adsorption affinities of alachlor and metolachlor are marginally enhanced by HDTMA. As reported earlier for other hydrophobic molecules (1, 18), the enhancement of adsorption affinity by HDTMA increases with its adsorbed amount, being maximal for mont-HDTMA 0.8 mol/kg (mont-HDTMA 0.8).

The effect of a moderately high salt concentration in the medium (0.067 mM NaCl) on the adsorbed amounts of the hydrophobic herbicides is illustrated in Table 2. The growth of salt sensitive plants is inhibited by about half of the above salt concentration (19–21). The sorbed amounts of alachlor and metolachlor on the organo-clay were not affected by the presence of the above salt concentration. This pattern is similar to that reported in ref 22 that the sorption of dissolved organic carbon by several soils was not a function of ionic strength between 0.001 and 0.1 M using NaCl. The amounts

of norflurazon sorbed by mont-BTMA 0.5 and mont-BTMA 0.8 were reduced in 0.067 M NaCl by 12% and 25%, respectively. The effect of added salt is not due to removal of BTMA, which amounts up to 6.7% release from mont-BTMA 0.8 for the lowest clay concentration used (14, unpublished results). Furthermore, such a release of BTMA from the load of 0.8 mol/kg clay should have resulted in increased sorption of the herbicide.

Infrared Spectra. The infrared spectra of sorbed alachlor show shifts of the absorption bands with respect to those of free alachlor (Table 3). The infrared spectra of organo-clay complexes were subtracted from the corresponding alachlor-mont and alachlor-organo-mont. The C=O and C aromatic-N stretching bands are shifted, respectively, for alachlor sorbed on Wyoming montmorillonite from 1689 to 1671 cm^{-1} and from 1370 to 1385 cm^{-1} , whereas for alachlor sorbed on mont-BTMA complexes, the corresponding peaks shift to 1679 and 1385 cm^{-1} . These shifts were ascribed in ref 23 to ion-dipole interaction between the C=O group and the exchangeable cation, i.e., alachlor would be adsorbed by a coordination bond, through a water bridge, between the C=O group and the exchangeable cation. For mont-BTMA 0.8 and mont-BTEA 0.8 the results (14) showed that all the exchangeable cations of the clay were replaced upon the addition of the organic cations. Thus, in our case, the same proposal should apply for BTMA and BTEA, which replace the exchangeable cations. It should be noted that the C=O band is shifted to lower frequencies, whereas the C-N band is shifted to a higher frequency. We see the same shift of the C(anilidic)-N as for alachlor-mont. Our deduction is that in addition to the main interaction with the organic ligands, the adsorbed alachlor still interacts with the clay mineral itself, even when it is preadsorbed by BTMA or BTEA up to the CEC.

The out-of-plane C aromatic-H deformation vibration of the herbicide molecules is shifted from 793 cm^{-1} for free alachlor to 809 cm^{-1} for alachlor sorbed on Wyoming montmorillonite and mont-BTMA 0.8 and to 815 cm^{-1} for alachlor adsorbed on mont-BTMA 0.5 mol/kg (Table 3). This shift indicates interaction of the aromatic ring of the herbicide with both the clay and organo-clays. This interaction appears stronger for the 0.5 mol/kg load of BTMA, showing a stronger influence on the C aromatic-H bonds. When the organic cation is BTEA, this absorption band is the same at the two loads (810 cm^{-1}) and close to that found for the herbicide adsorbed on the clay itself.

Discussion

The results of herbicide adsorption (Figure 2 and Table 1) demonstrate the adequacy of the Scatchard equation, which implies that no cooperativity exists in the adsorption of the herbicides on the organo-clays. The strengths of interactions between organo-clay complexes and the hydrophobic herbicides used in the current study depend on the following: (i) the degree of hydrophobicity of the complex, (ii) specific interactions between the phenyl ring of the herbicide molecule and the organic cation, and (iii) interactions between herbicide molecules and certain sites of the clay mineral.

The results in Figure 2 and Table 1 demonstrate that the interactions between the herbicides and the clay mineral are relatively weak in the presence of sodium ions, and consequently the amounts of herbicides adsorbed by the hydrophilic clay mineral alone are small. Except for the case of mont-BTMA (and mont-PTMA), the amounts of herbicides adsorbed by the organo-clays increase with the level of preadsorption by the organic cations up to the CEC.

The current results and those in refs 6 and 7 show that a clay mineral preadsorbed by a smaller organic cation, which includes a phenyl ring, is a better adsorbent for the hydrophobic herbicides used according to the sequence

BTMA > BTEA > BTBA. This trend might reflect that geometrically it is easier to establish stronger interactions between the phenyl rings of a herbicide and a small organic cation. We found that the adsorption of metolachlor (for which it was tested) satisfies the sequence PTMA > BTMA > BTEA > BTBA, in which PTMA (see Figure 1) is smaller than BTMA. The results in Table 1 also demonstrate significantly larger adsorbed amounts of metolachlor by mont-PTMA 0.5 than by mont-PTMA 0.8. Our preliminary results on the leaching of metolachlor from several organo-clay formulations (El-Nahhal (8) and unpublished) indicate that the optimal reduction of metolachlor leaching was achieved with the formulation mont-PTMA 0.5.

The argument regarding enhanced interactions between the phenyl ring of a herbicide molecule and that of a small organic cation can also imply enhanced pair interactions between the phenyl rings of the smaller organic cations preadsorbed by the clay mineral according to the above sequence. This order of pair interactions was indeed deduced by model calculations, which gave simulations and predictions for the amounts of BTMA and BTEA adsorbed by montmorillonite (14). Model calculations deduced the same binding coefficients ($K = 5000 \text{ M}^{-1}$) for formation of a neutral complex between either organic cation and a clay mineral site, whereas the binding coefficient for formation of a double complex, i.e., adsorption of another molecule on the neutral complex, is larger for BTMA than for BTEA, $\bar{K}_i = 20$ and 5 M^{-1} , respectively. It can be expected that the magnitude of intermolecular van der Waals interactions between the alkyl chains would increase with chain length, i.e., it would be larger for BTEA. Hence, the outcome of model calculations further emphasizes the preferred interactions between the phenyl rings of the smaller cations, BTMA and PTMA.

We will now employ our model to explain the larger adsorption affinity or larger sorbed amounts of the herbicides (Figure 2; Table 1) by mont-BTMA 0.5 than by mont-BTMA 0.8. The opposite trend is observed with BTEA and HDTMA. We have pointed out the larger tendency of BTMA than BTEA to form double complexes or dimers. Calculated values of the percents of adsorbed cations in dimers are illustrated in Table 4. Thus, the percents of cations in dimers are 2% and 14–18%, for mont-BTMA 0.5 and mont-BTMA 0.8, respectively. The corresponding fractions of dimers in mont-BTEA are 0.3 and 6–7%. The small increase in the fraction of dimers with clay content follows from eq 4, which gives that $[(PX)_2^+]$ is proportional to $[X_i(0)^+]$. For a given amount of total added organic cation (mol/kg clay) its concentration at the surface, $[X_i(0)^+]$, is somewhat larger at a larger clay concentration. We suggest that, in dimers of the organic cations, the phenyl rings are mostly inaccessible for interacting with the phenyl rings of herbicide molecules, which results in reduced adsorbed amounts of these herbicides by mont-BTMA 0.8 in comparison with mont-BTMA 0.5, despite the expected increase in overall hydrophobicity of the organo-clay with increasing coverage by the cations. The shift of the C aromatic–H bond is largest for mont-BTMA 0.5, in line with a stronger interaction between the phenyl rings of alachlor and BTMA. In addition, the positively charged dimers are not likely to attract the hydrophobic herbicides. In contrast, the reduction in the interactions between a phenyl ring of mont-BTEA 0.8 and that of a herbicide is a relatively minor effect, which is overcome by the enhanced hydrophobicity, similarly to the pattern seen with HDTMA. Further support for this suggestion is provided by an analysis of the adsorption of the smaller cation PTMA on montmorillonite (Y. El-Nahhal, S. Nir, and B. Rubín, unpublished). In this case the value of the binding coefficient for formation of a charged complex, \bar{K}_p , is about 100 M^{-1} ($50\text{--}200 \text{ M}^{-1}$), whereas the value of K_n , the binding coefficient for formation of neutral complexes, is 3000 M^{-1} ($\pm 1000 \text{ M}^{-1}$). Consequently, the results of

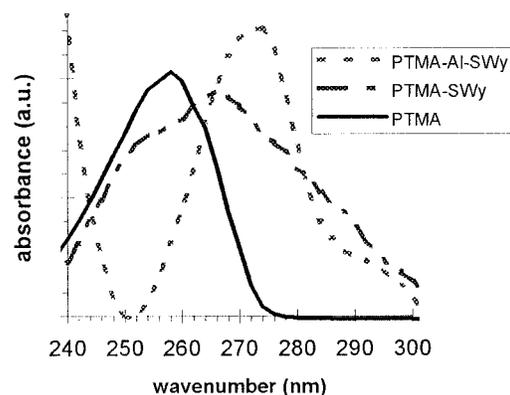


FIGURE 3. UV-visible absorption spectra of PTMA solution, and suspensions of montmorillonite with 0.5 mol of PTMA per kg clay and montmorillonite with alachlor and 0.5 mol of PTMA per kg clay

calculations (Table 4) give a relatively larger fraction of charged complexes for mont-PTMA 0.8.

The reduction in the adsorbed amounts of the herbicides by mont-BTMA 0.8 (or mont-PTMA 0.8) is not due to blocking of contacts between the herbicides and the clay mineral preloaded with BTMA. This effect might be more pronounced with the bulkier cation, BTEA. However, the amounts of herbicides adsorbed increased with the degree of preadsorption by BTEA. It is noteworthy, that our FTIR results suggest that the herbicides do interact directly with the clay mineral. In this context, Jaynes and Boyd (24) considered that the adsorbing surface is composed of siloxane oxygen, i.e., a large part of the siloxane surface in smectite has a hydrophobic nature. Despite the fact that the amounts of herbicides sorbed by the clay mineral alone are small, the direct interactions between the herbicide molecules and the clay mineral surface can play a role in photostabilization, where the clay mineral alone was shown to stabilize alachlor and metolachlor against photodegradation, albeit at a reduced efficiency in comparison with the organo-clays (7).

In a search for an organo-clay that may yield maximal adsorbed amounts of added hydrophobic herbicides, the choice of structural compatibility between the herbicide molecule and the organic cation, which is preadsorbed on the clay mineral, is of prime importance. In the current study, the sorbed fractions of the herbicides were maximized by choosing a small organic cation, such as BTMA (and PTMA), whose phenyl ring can interact with that of the herbicide. Support for the hypothesis that the phenyl ring of alachlor interacts with that of the preadsorbed organic cation was obtained by the adsorption results (Table 1) and by FTIR results (Table 3). Additional support was obtained by UV-visible spectroscopy (see Figure 3). When adsorbing alachlor to montmorillonite-PTMA 0.5 the $\pi\text{--}\pi^*$ absorption band of PTMA is shifted from 266 to 276 nm. Maximal adsorption of the herbicides was achieved by preloading the clay mineral by BTMA (or PTMA) at 5/8 of its CEC. This illustrates an example where incomplete charge neutralization of the clay mineral by an organic cation is advantageous in achieving maximal adsorption of herbicides.

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