ADSORPTION OF BENZYLTRIMETHYLAMMONIUM AND BENZYLTRIETHYLAMMONIUM ON MONTMORILLONITE: EXPERIMENTAL STUDIES AND MODEL CALCULATIONS

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Abstract—The adsorption of the monovalent organic cations benzyltrimethylammonium (BTMA) and benzyltriethylammonium (BTEA) to montmorillonite was studied as a function of their concentrations and ionic strength. At low ionic strength the adsorbed amounts of BTMA and BTEA reached values of the cation exchange capacity (CEC) of the clay. An increase in the ionic strength resulted in reduction in the adsorbed amounts of the organic cations, unlike the pattern observed previously with organic monovalent cationic dyes. The reduction in adsorbed amounts of BTMA and BTEA depended on the inorganic cations according to the sequence $Cs^+ > Na^+ > Li^+$, which follows the sequence of binding coefficients of these inorganic cations added. The type of the anion (that is, Cl^-, ClO_4^-, SO_4^{2-}) had no effect on the adsorbed amounts. An adsorption model which considers the electrostatic Gouy–Chapman equations, specific binding and closeness of the system could adequately simulate the adsorbed amounts of BTMA and BTEA and yield predictions for the effect of the ionic strength and concentration of electrolytes. The binding coefficient employed was $K = 5000\ M^{-1}$ for the formation of neutral complexes of BTMA and BTEA. This value is larger than those found for the inorganic cations but is several orders of magnitude below those found for the monovalent dyes. The binding coefficients for the formation of charged complexes of BTMA and BTEA were 20 and 5 M^{-1}, respectively. The basal spacing of the clay did not change significantly with the adsorbed amounts of both BTMA and BTEA up to the CEC.

Key Words—Basal Spacing, Benzylalkylammonium Adsorption, Cation Adsorption Model, Ionic Strength, Montmorillonite.

INTRODUCTION

The characteristics of the various types of clay–organic interactions have been widely reviewed (Mortland 1970; Theng 1974; Serratosa 1979; Lagaly 1987; Lagaly 1992). The adsorption of organic cations on clays changes the nature of the clay surface, transforming it from hydrophilic to hydrophobic. The modified clay surface can adsorb organic molecules of low solubility in water (Lee et al. 1989; Zhang et al. 1993).

The increased threat of the environmental pollution by pesticides and other organic pollutants promoted investigations on the use of organo-clays as sorbents for organic molecules (Gerstl and Mingelgrin 1979; Wolfe et al. 1985; Mortland et al. 1986; Boyd, Lee and Mortland 1988; Boyd, Shaobai et al. 1988; Jaynes and Boyd 1991; Hermosin and Cornejo 1993; Sanchez-Camazano and Sanchez-Martin 1994; Smith and Jaffe 1994; Cornejo and Hermosin 1995). Organoclays can stabilize pesticides and reduce their volatilization and photodecomposition (Margulies et al. 1992, 1993, 1994). Benzyltrimethylammonium and BTEA are quaternary amine monovalent cations that can be effective in modifying the surface of the clay for the enhanced adsorption of nonpolar organic molecules from water.

The objective of this work has been to elucidate the mechanism of adsorption of benzylalkylammonium cations on montmorillonite by combining the experimental adsorption results and model calculations with X-ray diffraction (XRD) studies.

The mechanisms of adsorption of monovalent organic cations (dyes) and divalent cations (diquat and paraquat) on montmorillonite have been recently discussed (Rytwo et al. 1995; Rytwo, Nir and Margulies 1996). The adsorption model employed combines specific binding and electrostatic equations in a closed system (Nir 1986; Nir et al. 1986, 1994). The adsorption of organic cations to negatively charged clay minerals is described by 2 binding coefficients (Margulies et al. 1988). The first one describes formation of a neutral complex between 1 organic cation and 1 clay mineral site; the second refers to the binding of an organic cation to the neutral complex. The binding coefficients for the formation of the clay–organic complexes were found to be several orders of magnitude larger than those previously reported for inorganic cations. It was shown that the ionic strength did not affect dye adsorption when the amounts of monovalent dyes were less than those required to saturate the exchangeable sites of montmorillonite (Margulies et al. 1988; Rytwo et al. 1995). When the dye concentration was higher than that required to saturate the CEC, the
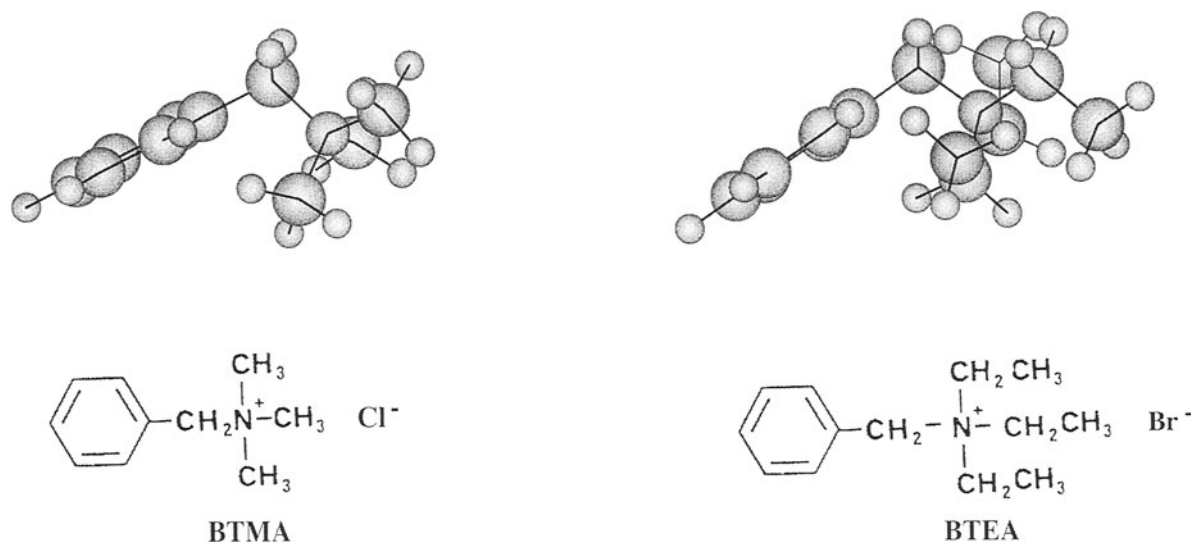
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Figure 1.   Structural formulae and the models of the molecules of BTMA and BTEA.

amount of the dye adsorbed could be enhanced by increasing the ionic strength, because of charge reversal. Alternatively, an increased ionic strength led to decreased adsorption of divalent organic cations, especially in solutions containing Cs^+ (Rytwo, Nir and Margulies). In the latter study, the quantification of the effect of ionic strength on the adsorption of the divalent organic cations paraquat and diquat to montmorillonite was essential in the determination of the binding coefficients describing the adsorption of these cations. In accordance, we considered the effect of ionic strength on the adsorption of BTMA and BTEA to montmorillonite. We have considered the competition of several monovalent cations (Cs^+, Na^+ and Li^+) with BTMA and BTEA and also investigated the effects of several anions on this adsorption.

MATERIALS AND METHODS

The clay mineral used was Wyoming Na-montmorillonite SWy-1 obtained from the Source Clays Repository (Clay Minerals Society, Columbia, Missouri). Benzyltrimethylammonium (50 wt% in water solution) was obtained as chloride salt and BTEA (99%) was obtained as bromide salt from Aldrich Chemical Company (Milwaukee, Wisconsin). Analytical grade salts were used in experiments. LiCl was purchased from J.T. Baker, Inc. (Phillipsburg, New Jersey). NaCl was obtained from Frutarom Laboratory Chemicals (Haifa, Israel); $NaClO_4$ was purchased from Fluka Chemie AG (Buchs, Switzerland); Na_2SO_4 was obtained from Analar BDH Chemicals (Poole, England); and CsCl was purchased from Merck (Darmstadt, Germany). All materials were used without further treatment or purification. The structural formulae and the models of molecules of BTMA and BTEA are shown in Figure 1.

Adsorption Isotherms

The adsorption isotherms were measured in the range of 0–4.1 mmol/g clay. To measure adsorption isotherms of BTMA and BTEA, appropriate aliquots of an aqueous 0.01 M solution of BTMA and BTEA were diluted by distilled water to 40 mL and were added dropwise under continuous stirring to 20 mL of 0.5% (w/w) clay mineral suspension in 100-mL polyethylene bottles. In experiments with different concentrations of electrolytes, the 40 mL volume was reached by using one of the following electrolytes: 0.1 M NaCl, 0.5 M LiCl, 0.5 M NaCl, 0.5 M $NaClO_4$, 0.5 M Na_2SO_4, 0.5 M CsCl, 1 M NaCl. The bottles were sealed and kept at 25 ± 1 °C under continuous agitation during 1, 3 and 7 d to determine the equilibration time. Supernatants were separated by centrifugation at 100,000 g for 30 min. The concentrations of BTMA and BTEA were determined by measuring the absorption at 262 nm using an HP8452A diode array UV-Vis spectrophotometer (Hewlett-Packard Co., Palo Alto, California). Equilibrium was reached within 1 d. The concentrations in supernatants of exchangeable cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) replaced by the organic cations were determined by using an inductively coupled plasma atomic emission spectrometer (Spectra Co., Kleve, Germany). The analysis of standard solutions of inorganic cations prepared in distilled water and in the 0.01 M solutions of BTEA and BTMA showed that the presence of organic cations did not interfere with the analysis of inorganic cations.

X-Ray Diffraction

The basal spacing of the BTMA- and BTEA-Na-montmorillonite complexes was measured in the same range of concentrations as in adsorption measure-

ments. Ten mL of organo-clay suspension prepared as described for measurement of adsorption isotherms, using 24 h of equilibration at 25 ± 1 °C, were sonicated for 5 min in a Sonifier B-12 sonicator (Branson Sonic Power Co., Danbury, Connecticut). Two milliliters of sonicated samples were dropped onto glass microscope slides and were allowed to sediment for 3 d in closed petri dishes. Then the covers were partially opened and the samples were left to dry for 4 more d. The basal spacings were measured using Philips 1030 X-ray diffractometer (Philips Scientific and Analytical Equipment, Eindhoven, The Netherlands) with Co$K\alpha$ radiation.

The conformations of the BTEA and BTMA molecules were taken from the Cambridge data base for low molecular weight organic molecules. Molecular modeling and estimations of the molecular sizes have been done using the MacImdad program (1994).

Model Calculations

The model used in this study has been described in Nir (1986); Margulies et al. (1988); and Nir et al. (1994). It considers the simultaneous adsorption of any number of cations and can also account for aggregation in solution of organic cations (Rytwo et al. 1995). The programs consider cation binding and the electrostatic Gouy–Chapman equations, and solve iteratively for the solution concentrations of all cations in a closed system. Cation adsorption is obtained by considering specific binding to surface sites and residence in the double layer region.

The binding equations are given below. Let X_i^+ denote a monovalent cation that binds to a singly charged negative site, P^-, on the surface of the silicate:

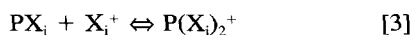$$P^- + X_i^+ \Leftrightarrow PX_i \qquad [1]$$

with a binding coefficient K_i, given by:

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

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

Another type of complexation is considered:

$$PX_i + X_i^+ \Leftrightarrow P(X_i)_2^+ \qquad [3]$$

with a binding coefficient:

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

In Equations [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}. We used the following relation:

$$X_i(0) = X_i Y_0^{Z_i} \qquad [5]$$

where X_i is the molar concentration of cation i in its monomeric form in the equilibrium solution, $Y_0 = \exp(-e\phi(0)/kT)$, Z_i is the valence of the given ion, e is the absolute magnitude of an electronic charge, $\phi(0)$

is the surface potential, k is Boltzmann's factor and T is the absolute temperature.

For a negatively charged surface, $Y_0 > 1$, and the concentration of the cation at the surface, $X_i(0)$, may be significantly larger than X_i. If charge reversal due to cation binding occurs, however, $\phi(0)$ is positive and $Y_0 < 1$. Here, the concentration of nonadsorbed cations in the double-layer region may be significantly smaller than their solution concentration.

The binding coefficients of the inorganic cations in the system were taken from our previous studies (Rytwo, Banin and Nir 1996; Nir et al. 1986). The intrinsic binding coefficients K_i and $\bar{K}_i$, which reflect the strength of the chemical binding in Equations [2] and [4], are considered to be parameters that can be determined from adsorption data. These parameters were determined as previously described in Margulies et al. (1988) and Rytwo et al. (1995). We first fixed the binding coefficient $\bar{K}_i$ from adsorption results near and slightly above the CEC. Then the parameter K_i was fixed. This procedure was followed by varying both parameters in order to maximize R^2 and minimize as possible the root mean square error.

RESULTS AND DISCUSSION

The isotherms of BTEA and BTMA adsorption are presented in Figures 2 and 3, respectively. Both isotherms are of the same shape. The CEC of the Na-montmorillonite calculated as the largest sum of the displaced exchangeable cations was 0.82 mmol/g, which is consistent with the values obtained previously for this clay by replacement of the exchangeable cations by methylene blue and crystal violet (Rytwo et al. 1991). The adsorbed amounts of BTMA and BTEA reached the value of the CEC.

The characteristics of BTEA and BTMA adsorption are illustrated by the values of the ratio of the amounts of BTEA and BTMA adsorbed to the sum of exchangeable cations displaced (Tables 1 and 2) as was suggested by Zhang and coworkers in their study of the adsorption of quaternary amine cations on montmorillonite (Zhang et al. 1993). This ratio would be equal to unity if the sorption of BTEA and BTMA were due to ionic exchange only. When BTEA or BTMA was added in the amounts of 2.2, 3.3 and 4.4 mmol/g, all ratios were slightly above unity. When 4.4 mmol BTEA or 3.3 BTMA was added per g clay, full displacement of the exchangeable cations occurred. In this range the mechanism of BTEA and BTMA adsorption appears to be primarily cation exchange. The amounts of BTMA and BTEA that are needed to replace inorganic cations to reach the CEC of the clay are 4 and 5 times higher than the CEC, respectively (Figure 2 and 3). Tables 1 and 2 show that cation exchange is a relatively fast process; the total amount of exchangeable cations displaced after 1 h by the addition of either organic cations is 90–94% of the CEC,
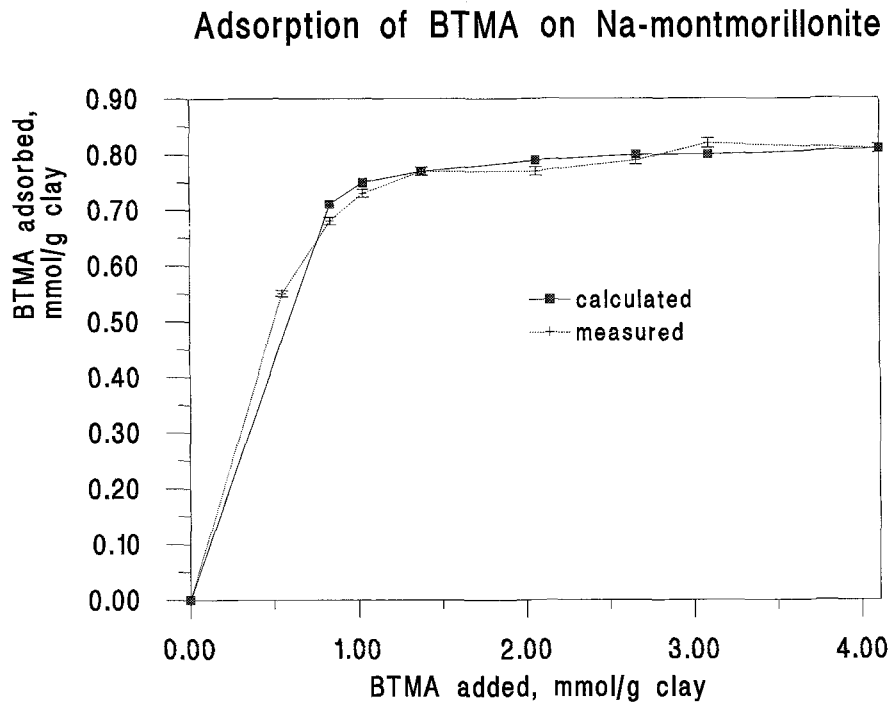
Adsorption of BTMA on Na-montmorillonite

Figure 2.   Adsorption of BTMA on Na-montmorillonite. The estimated standard deviation was about 0.01 mmol/g.
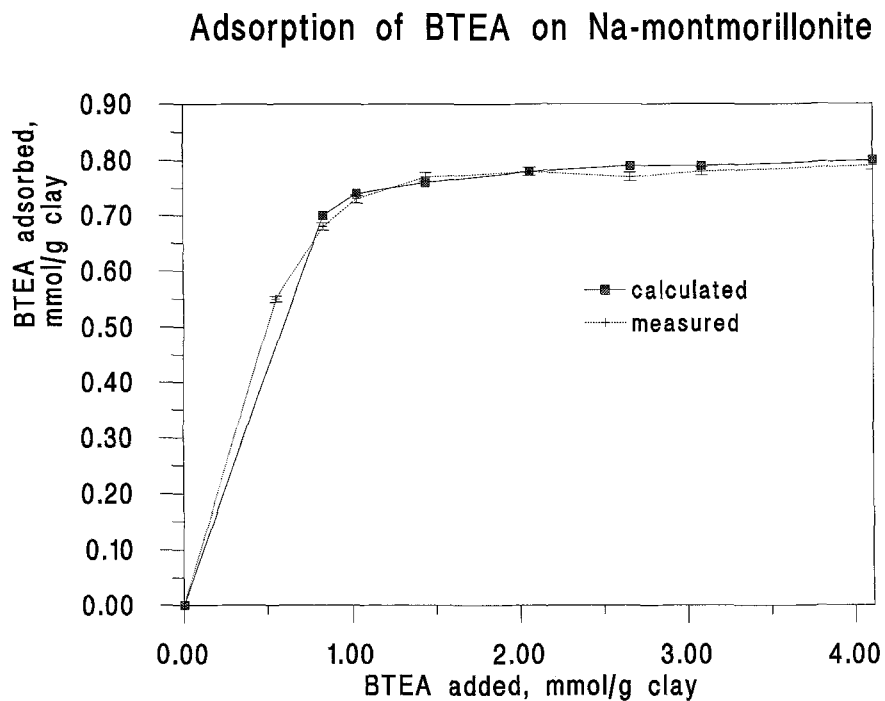
Adsorption of BTEA on Na-montmorillonite

Figure 3.   Adsorption of BTEA on Na-montmorillonite. The estimated standard deviation was about 0.01 mmol/g.

Table 1. Amount of BTMA adsorbed and exchangeable cations released from Na-montmorillonite.

Time	BTMA[†] adsorbed mmol/g	Ca²⁺ meq/g	Mg²⁺ meq/g	K⁺ meq/g	Na⁺ meq/g	SEC[‡]	Ratio
BTMA added: 2.2 mmol/g							
1 h	0.72	0.28	0.15	0.02	0.24	0.69	1.04
1 d	0.76	0.30	0.15	0.02	0.24	0.71	1.07
3 d	0.77	0.31	0.15	0.02	0.23	0.71	1.08
7 d	0.75	0.31	0.14	0.01	0.24	0.70	1.07
BTMA added: 3.3 mmol/g							
1 h	0.77	0.37	0.15	0.01	0.21	0.74	1.04
1 d	0.83	0.41	0.16	0.01	0.20	0.78	1.06
3 d	0.83	0.42	0.17	0.01	0.21	0.81	1.02
7 d	0.82	0.42	0.16	0.02	0.20	0.80	1.03

† The results are averages of 3 replicas. The standard deviation for the adsorption of BTMA was 0.01 mmol/g; the standard deviations for the cations released were respectively (mmol/g): for Ca²⁺, −0.017; for Mg²⁺, −0.002; for Na⁺, −0.016; for K⁺, −0.0003.

‡ SEC indicates the sum of exchangeable cations released in meq/g clay.

Table 2. Amount of BTEA adsorbed and exchangeable cations released from the Na-montmorillonite.

Time	BTEA[†] adsorbed mmol/g	Ca²⁺ meq/g	Mg²⁺ meq/g	K⁺ meq/g	Na⁺ meq/g	SEC[‡]	Ratio
BTEA added: 2.2 mmol/g							
1 h	0.66	0.23	0.14	0.02	0.23	0.62	1.06
1 d	0.75	0.29	0.15	0.02	0.24	0.70	1.07
3 d	0.74	0.29	0.16	0.02	0.24	0.71	1.04
7 d	0.75	0.29	0.16	0.01	0.24	0.70	1.07
BTEA added: 4.4 mmol/g							
1 h	0.80	0.34	0.17	0.02	0.24	0.77	1.04
1 d	0.85	0.40	0.16	0.02	0.24	0.82	1.04
3 d	0.85	0.40	0.17	0.01	0.24	0.82	1.04
7 d	0.84	0.39	0.17	0.02	0.24	0.82	1.02

† The results are averages of 3 replicas. The standard deviation for the adsorption of BTEA was 0.01 mmol/g; the standard deviations for the cations released were respectively (mmol/g): for Ca²⁺, −0.016; for Mg²⁺, −0.004; for Na⁺, −0.015; for K⁺, −0.0003.

‡ SEC indicates the sum of exchangeable cations released in meq/g clay.

which was obtained after 1 d of equilibration. Exchangeable Na^+, K^+ and Mg^{2+} are replaced within 1 h, whereas complete Ca^{2+} displacement takes more time, reflecting perhaps a restriction in accessibility of all sites occupied by Ca^{2+} to the organic cations.

The variations of basal spacings with the increase in the adsorbed amounts of benzylalkylammonium cations are shown in Table 3. In the absence of organic cations the basal spacing is 1.47 nm, which amounts to a plate thickness of 0.9 nm plus that of 2 water molecules. Basal spacings of BTMA- and BTEA-montmorillonite complexes increase insignificantly for the concentrations of organic cations below the CEC. The thickness of the BTMA molecule is 0.46 nm (Figure 1), which corresponds to the interlayer space. At BTMA concentrations below the CEC, the size of BTEA molecules is consistent with the basal spacing measured. The estimated thickness of the BTEA molecule is 0.52 nm (Figure 1). Thus the thickness of BTEA molecules fits the interlayer space at concentrations of up to the CEC in accord with the measured basal spacing. Possible alignment of the molecules on the clay surface is shown for BTEA in Figure 4.

Boyd and Jaynes (1992) suggested to divide organoclays to organophilic and adsorptive. Organophilic clays are formed when large hydrophobic quaternary ammonium cations (such as hexadecyltrimethyl ammonium bromide, HDTMA) saturate the clays. Exchange of HDTMA with the inorganic cations in the clay is essentially stochiometric. The alkyl hydrocarbon groups of these organic cations which have C-10 chains or more form an organic partition phase. Adsorption of organic molecules from water solutions on this phase is analogous to the partitioning of the organic compound between water and an organic sol-

vent. Adsorptive organo-clays are formed when small quaternary ammonium cations, such as tetramethylammonium or trimethylphenylammonium, are used to saturate the clay. Smith et al. (1990) suggested the sorption mechanism for the uptake of tetrachloromethane from water solution by BTMA- and BTEA-montmorillonite. To prepare adsorptive organo-clays, one needs to add the saturating organic cations at amounts of 3- to 5-fold larger than the CEC. Small organic cations exist as discrete entities on the siloxane surfaces of clays. According to this classification and taking into consideration particularities of the BTEA and BTMA adsorption, we can attribute the BTEA- and BTMA-saturated clays to the adsorptive organo-clays.

The increase of ionic strength of electrolyte solutions—LiCl, NaCl, NaClO₄, Na₂SO₄ and CsCl—resulted in reduced adsorbed amounts of the organic cations (Tables 4 and 5). The reduction in the adsorbed amounts of BTMA and BTEA was dependent on the inorganic cations according to the sequence: $Cs^+ > Na^+ > Li^+$ corresponding to the magnitudes of their

Table 3. Basal spacing of BTMA- and BTEA-Na-montmorillonite complexes at different loadings of BTMA and BTEA.

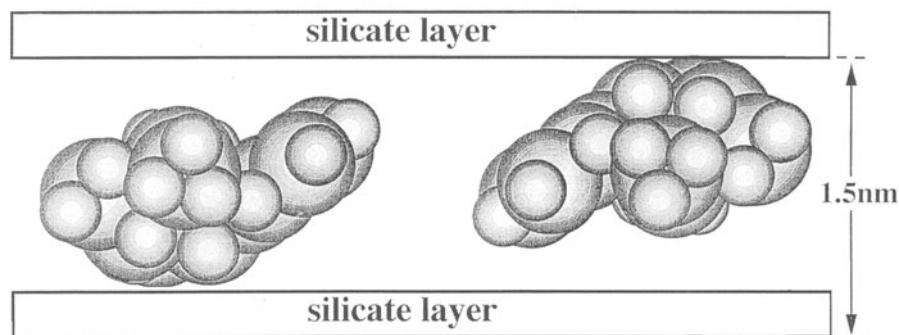| BTMA adsorbed, mmol/g	Basal spacing BTMA-montmor, nm	BTEA adsorbed mmol/g	Basal spacing BTEA-montmor, nm
0	1.47	0	1.47
0.55	1.47	0.55	1.48
0.70	1.48	0.69	1.49
0.72	1.49	0.72	1.49
0.75	1.49	0.76	1.49
0.77	1.50	0.85	1.53

BTEA-Na-montmorillonite

Figure 4.　Alignment of BTEA on Na-montmorillonite at concentrations up to the CEC.

binding coefficients (Nir et al. 1986). The maximal reduction in the amounts adsorbed was found when 3.3 mmol/g BTMA was added: 16% with 0.333 M LiCl, 30% with 0.667 M NaCl and 69% with 0.333 M CsCl.

The type of anion did not affect the adsorption of organic cations. For example, the adsorbed amounts of BTMA or BTEA in the presence of the 0.333 M sodium chloride or perchlorate are very close for both cations. The adsorbed amounts in the presence of

0.667 M sodium chloride are similar to the results in the presence of 0.333 M of the sodium sulphate.

These results are different from the previous data for the adsorption of thioflavin on montmorillonite in the presence of 3.5 M Cs (Margulies et al. 1988). Adsorption of the thioflavin on the clay below the CEC in the presence of 3.5 M Cs was similar to its adsorption in an aqueous suspension of the clay. According to the results obtained by Rytwo and coworkers (Rytwo et al. 1995), the adsorption of the monovalent or-

Table 4.　Effect of inorganic cations (Na^+, Cs^+, Li^+) and concentration of electrolytes on adsorption of BTMA on Na-montmorillonite.

Salt added		BTMA added mmol/g	BTMA adsorbed/mmol/g	
			experimental	calculated
0		0.55	0.55	0.51
0		1.1	0.72	0.72
0		3.3	0.83	0.81
NaCl,	0.667 M	0.55	0.54	0.50
		1.1	0.72	0.70
		3.3	0.77	0.81
NaCl,	0.333 M	0.55	0.52	0.44
		1.1	0.64	0.65
		3.3	0.63	0.81
NaCl,	0.667 M	0.55	0.50	0.40
		1.1	0.61	0.61
		3.3	0.58	0.80
Na_2SO_4,	0.333 M	0.55	0.52	0.40
		1.1	0.61	0.61
		3.3	0.61	0.80
CsCl,	0.333 M	0.55	0.14	0.05
		3.3	0.26	0.26
NaClO$_4$,	0.333 M	0.55	0.50	0.44
		1.1	0.63	0.65
		3.3	0.60	0.81
LiCl,	0.333 M	0.55	0.52	0.45
		1.1	0.69	0.66
		3.3	0.70	0.81

Table 5.　Effect of inorganic cations (Na^+, Cs^+, Li^+) and concentration of electrolytes on adsorption of BTEA on Na-montmorillonite.

Salt added		BTEA added mmol/g	BTEA adsorbed mmol/g	
			experimental	calculated
0		0.55	0.55	0.51
0		1.1	0.72	0.71
0		4.4	0.79	0.79
NaCl,	0.667 M	0.55	0.53	0.50
		1.1	0.73	0.69
		4.4	0.74	0.79
NaCl,	0.333 M	0.55	0.53	0.44
		1.1	0.60	0.64
		4.4	0.68	0.79
NaCl,	0.667 M	0.55	0.53	0.40
		1.1	0.56	0.60
		4.4	0.61	0.78
Na_2SO_4,	0.333 M	0.55	0.53	0.40
		1.1	0.55	0.60
		4.4	0.63	0.78
CsCl,	0.333 M	0.55	0.26	0.05
		1.1	0.31	0.09
		4.4	0.44	0.29
NaClO$_4$,	0.333 M	0.55	0.51	0.44
		1.1	0.61	0.64
		4.4	0.72	0.79
LiCl,	0.333 M	0.55	0.52	0.45
		1.1	0.68	0.65
		4.4	0.76	0.77

Table 6. Binding coefficients of organic and inorganic monovalent cations.

Cation	$K\dagger$ (M^{-1})	$\bar{K}\ddagger$ (M^{-1})	Source
BTMA	5000	20	This work
BTEA	5000	5	This work
Acriflavin	1.0×10^9	6.0×10^5	Rytwo et al. 1995
Crystal violet	1.0×10^6	8.0×10^9	Rytwo et al. 1995
Methylene blue	3.0×10^8	1.0×10^6	Rytwo et al. 1995
Li	0.6	—	Nir et al. 1986
Na	1.0	—	Nir et al. 1986
K	2.0	—	Nir et al. 1986
Cs	200	—	Nir et al. 1986
Ca	4.0	—	Rytwo, Banin and Nir 1996
Mg	2.0	—	Rytwo, Banin and Nir 1996

† K denotes the binding coefficients for the formation of neutral complexes.

‡ $\bar{K}$ corresponds to charged complexes.

ganic cations (acriflavin and crystal violet) to montmorillonite in amounts exceeding the CEC increased upon increasing the ionic strength. The explanation (see Equation 5) was that an increase in the ionic strength reduces the magnitude of the positive surface potential and thus enhances the adsorption of these monovalent organic cations. Adsorption of divalent organic cations diquat and paraquat decreased as the ionic strength increased (Rytwo, Nir and Margulies 1996). This phenomenon was explained by the possibility of formation of charged complexes between the divalent cation and 1 clay surface site. In the presence of large concentration of CsCl, Cs^+ competes with divalent cations for binding to the negative sites. In the case of the adsorption of benzylalkylammonium monovalent cations, an increase of concentration of electrolytes leads to the decrease of BTEA and BTMA adsorption. This difference in the behavior of benzylalkylammonium cations from that of the dyes could be explained by the difference in binding coefficients due to lower affinities of BTEA and BTMA for binding to the clay surface than those for the dyes. The binding coefficients of benzylalkylammonium cations compared to the binding coefficients of dyes and to binding coefficients of inorganic cations are shown in Table 6. The binding coefficients for formation of neutral complexes of BTEA and BTMA are higher than those of inorganic cations but significantly lower than those obtained for dyes. The binding coefficients of positive complexes of dyes are significantly higher than those of BTEA and BTMA. The affinities of such dyes as methylene blue or crystal violet for binding to the clay surface are much higher than the affinities of benzylalkylammonium cations. As was shown previously (Margulies et al. 1988; Rytwo et al. 1995), the adsorption of dyes on montmorillonite is essentially

stochiometric up to the CEC, in contrast to the adsorption of benzylalkylammonium cations.

Inspection of Figures 2 and 3 indicates that overall the adsorption model can adequately account for the adsorbed amounts of BTMA and BTEA. By employing the previously determined (Nir et al. 1986) binding coefficients of Li^+ and Na^+, the model could generate predictions for the effect of electrolyte concentrations (Tables 4 and 5). However, at high Na^+ and Li^+ concentrations, the model overestimated the amounts of organic cations adsorbed when 3.3 mmol/g of BTMA and 4.4 mmol/g of BTEA were added. These overestimations could be explained by the fact that the calculations were provided without considering the activity coefficients of the cations. The model underestimated the adsorbed amounts of both BTMA and BTEA in the presence of 0.333 M CsCl. One possibility is that the value of 200 M^{-1} for the binding coefficient of Cs^+ might be too high, or its relatively loose hydration shell promotes removal of water from the interlayer space, which promotes the adsorption of the organic cations.

CONCLUSIONS

1) The basal spacing of Na-montmorillonite did not change significantly with adsorbed amounts of BTMA or BTEA up to the CEC.

2) The increase of concentration of electrolyte solutions—LiCl, NaCl, $NaClO_4$, Na_2SO_4, CsCl—resulted in reduced adsorbed amounts of the organic cations. The reduction in the adsorbed amounts of BTMA and BTEA was dependent on the inorganic cations according to the sequence: $Cs^+ > Na^+ > Li^+$, corresponding to the magnitudes of their binding coefficients. The type of anion did not affect adsorption of organic cations.

3) The adsorption model that combined electrostatic equations with specific binding and considered neutral and positively charged complexes between clay surface sites and organic cations could yield good simulations of the adsorption isotherms and could yield quantitative predictions for the effect of concentration of electrolyte and type of inorganic cation added on the adsorption of BTMA and BTEA. The binding coefficients of these monovalent organic cations are several orders of magnitude larger than those of inorganic cations, but significantly smaller than those of several monovalent organic cations, such as the dyes (methylene blue, crystal violet, acriflavin, thioflavin) studied before.

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