MODEL FOR COMPETITIVE ADSORPTION OF ORGANIC CATIONS ON CLAYS

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Abstract—The adsorption on montmorillonite of two monovalent organic cations, methylene blue (MB) and thioflavin T (TFT), was studied in four different situations: (1) separate adsorption of MB or TFT; (2) competitive adsorption of TFT and Cs; (3) competitive adsorption of the two organic cations from their equimolar solutions; and (4) adsorption of TFT on a clay whose cation-exchange capacity (CEC) had been previously saturated with MB. MB and TFT adsorbed to as much as 120% and 140% of the CEC, respectively. Cs did not appear to compete with TFT for the adsorption sites of the clay. TFT molecules adsorbed more strongly than those of MB and displaced them from the clay surface. A model was developed to evaluate the strength of the clay-organic cation interactions. The specific binding of the cations to the negatively charged surface, determined by solving the electrostatic equations, appears to account for adsorption exceeding the CEC and formation of positively charged complexes, which are due to non-coulombic interactions between the organic ligands.

The charge reversal predicted by the model beyond the CEC of the clay was confirmed by microelectrophoretic experiments. Particles in a sample of montmorillonite loaded with 50 meq TFT/100 g clay moved to the positive electrode, whereas in samples containing the two dyes, MB and TFT, coadsorbed at a total concentration of 100–120 meq/100 g clay, the particles moved to the negative electrode. Binding coefficients describing the formation of neutral and charged complexes of TFT and the clay were larger than those for MB and the clay, thereby explaining the preferential adsorption of TFT observed experimentally. The binding coefficients for the formation of neutral complexes of either MB and TFT and the clay were more than six orders of magnitude larger than those previously reported for inorganic monovalent cations.

Key Words—Adsorption, Clay-organic, Methylene blue, Montmorillonite, Organic cation, Thioflavin T.

INTRODUCTION

The adsorption of organic molecules on clay surfaces has been extensively studied (e.g., Mortland, 1970; Theng, 1974). Several studies have focused on the adsorption of cationic organic dyes to negatively charged smectites (Chu and Johnson, 1979; De et al., 1974; Ghosal and Mukherjee, 1972; Grauer et al., 1984; Pham Thi Hang and Brindley, 1970; Narine and Guy, 1981; Venugopal and Nair, 1974). Margulies et al. (1985, 1987) suggested a method of photostabilization of pesticides which is based on coadsorbing on a clay surface the photolabile pesticide and an adequate organic cation that acts as energy acceptor. In such a system the organic cation must be strongly attached to the surface of the clay in order to prevent contamination of soil and water. Although it is well documented that organic cations adsorb to the clay surface significantly more strongly than inorganic cations, and that adsorption can proceed beyond the cation-exchange capacity (CEC) of the clay (De et al., 1974; Narine and Guy, 1981), no theoretical model has been suggested to evaluate the strengths of these interactions. Non-coulombic forces obviously play an important role in the adsorption of these usually large molecules. The present report describes such a model that quantifies the clay-organic cation interactions.

The coupling of specific binding of cations to negatively charged surfaces using electrostatic equations has been successfully employed in several studies of soil systems (Barrow et al., 1980; Bowden et al., 1977; Davis et al., 1978; Nir et al., 1986) and membranes (Eisenberg et al., 1979; Kurland et al., 1979; Nir et al., 1978; Nir, 1984). If cations bind to a negatively charged surface according to the mass action equations (*vide infra*, Eqs. (1–4)) the concentration of the cations at the binding sites is different from their bulk concentration (see Eq. (5)). Neglecting this distinction results in apparent binding coefficients whose values can vary by several orders of magnitude with changes in ionic strength and with different combinations of cations. For organic cations, where charge reversal can occur, this effect will be magnified. In Nir (1986) and Nir et al. (1986) the electrostatic equations were solved explicitly and yielded the surface potential. The amounts of cations adsorbed were shown to depend on specific binding as well as on the degree of excess or exclusion in the double layer regions around the surfaces. The model accounted explicitly for changes in solution concentrations of the cations due to adsorption. In the current work, the model has been extended to allow for formation of charged complexes by the monovalent organic cations due to the non-coulombic (and prob-

ably hydrophobic) interactions between the organic cations.

The extended model is applied to the adsorption of two monovalent cationic organic dyes to the surface of montmorillonite, namely methylene blue (MB) (Pham Thi Hang and Brindley, 1970; Narine and Guy, 1981) and thioflavin T (TFT), which has been found to be effective in photostabilizing an insecticidal nitromethylene heterocycle on the surface of montmorillonite (Margulies et al., 1987). The relative strengths of interactions between these organic cations and the clay are also compared with those of sodium and cesium. The relative strengths of the non-coulombic interactions between organic cations on the surface of the clay are also evaluated.

EXPERIMENTAL

Materials

The clay used was Na-montmorillonite SWy-1 obtained from the Source Clays Repository of The Clay Minerals Society. The CEC of this clay was reported to be 76.4 meq/100 g clay (van Olphen and Fripiat, 1979). Methylene blue and thioflavin T were obtained as the chloride salts from Aldrich Chemical Company, and cesium chloride from Merck. These chemicals were used without further purification.

Adsorption isotherms

To measure the adsorption isotherms of MB and TFT, aliquots of an aqueous solution containing 5×10^{-3} M of the dye were added dropwise, with continuous stirring, to 50 mg of clay suspended in distilled water. The total volume of suspension, after addition of the dye, was 30 ml for TFT and 25 ml for MB. After 24 hr at room temperature, the suspensions were centrifuged in an ultracentrifuge at 60,000 g. The concentration of the dye in the supernatant was determined by UV-VIS spectrophotometry: TFT has its longest wavelength absorption at $\lambda_{max} = 410$ nm ($\epsilon = 25,200$), whereas MB absorbs strongly at $\lambda_{max} = 663$ nm ($\epsilon = 52,000$) with almost no absorption at 410 nm. Absorption spectra were measured in a Uvikon 810 spectrophotometer.

The same procedure was followed to determine the coadsorption isotherm of MB and TFT, using a solution containing the two dyes at 5×10^{-3} M each. The absorption spectrum of the solution was a superposition of the separate absorptions of MB and TFT, indicating the absence of intermolecular interactions between the two dyes. The final volume of the suspension was 25 ml. Centrifugation and measurements were also carried out after equilibration times of 1 hr, 24 hr, and 3 wk after addition of the dye solution.

The adsorption isotherm of TFT on montmorillonite, on which MB had been previously adsorbed at a load of 90 meq/100 g clay, was carried out as follows:

9 ml of a 5×10^{-3} M aqueous solution of MB was added to 10 ml of 0.5% w/w clay suspension. After 24 hr, aliquots of 5×10^{-3} M TFT and distilled water were added to a total volume of 40 ml, and the whole system was allowed to equilibrate for (1) 24 hr and (2) 3 wk. The suspension was then centrifuged, and the supernatant was analyzed as described above.

To estimate the effect of possible adsorption of the dye on the internal surface of the glassware used, dye solutions (without clay) were kept in 50-ml flasks, as in the determination of adsorption isotherms, and the absorption was monitored after different periods of time. The maximum changes in absorption, in 10-mm cuvettes, were of about 0.01 absorbance units, which corresponds to about 0.01 meq dye/100 g clay. Therefore, this effect could be neglected.

All experimental data presented in this work are means of at least two replicates. Most differences between replicates were less than 5%.

Microelectrophoresis

A microelectrophoretic cell was prepared by allowing a ring of epoxy glue to dry on a microscope slide. The ring had an internal diameter of 10 mm and a height of 1.5 mm. Two metal wires (1 mm diameter, 15 mm long) were glued within the ring parallel to each other and to the diameter of the ring, and at 1 mm separation. The wires were connected to the positive and negative terminals of a DC power supply. A sonicated suspension of the clay-dye complex in water (0.5 ml, 0.01% w/w) was placed inside the epoxy ring, covering completely the two wire-electrodes. The direction of migration of the colored clay particles between the two electrodes was observed under a microscope at $50\times$ magnification. The voltages applied were 1–5 V.
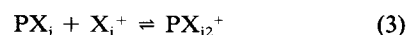
THEORETICAL MODEL

The following model is an extension of that described by Nir (1984, 1986) in the sense that the monovalent organic cations can form charged complexes, in addition to neutral ones. In the following equations X_i denotes a monovalent cation that binds to singly charged negative sites, P^-, on the surface of the clay (or membrane, etc.). The reaction is:
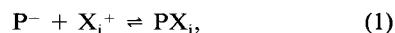
$$P^- + X_i^+ \rightleftharpoons PX_i, \tag{1}$$

that is,

$$K_i = [PX_i]/([P^-][X_i^+]). \tag{2}$$

Another type of association, or complex, may be considered for organic cations, as follows:

$$PX_i + X_i^+ \rightleftharpoons PX_{i2}^+ \tag{3}$$

and

$$\bar{K}_i = [PX_{i2}^+]/([PX_i][X_i^+]). \tag{4}$$
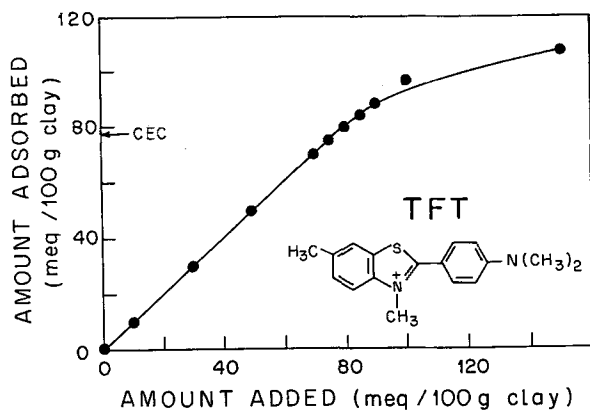
In Eqs. (2) and (4) the concentrations are given in

Figure 1. Adsorption isotherm of thioflavin T (TFT) on montmorillonite. ● = experimental results; —— = theoretical curve, calculated using binding coefficients $K = 10^9$ and $\bar{K} = 1.5 \times 10^6$ M^{-1} from Eqs. (1–4).
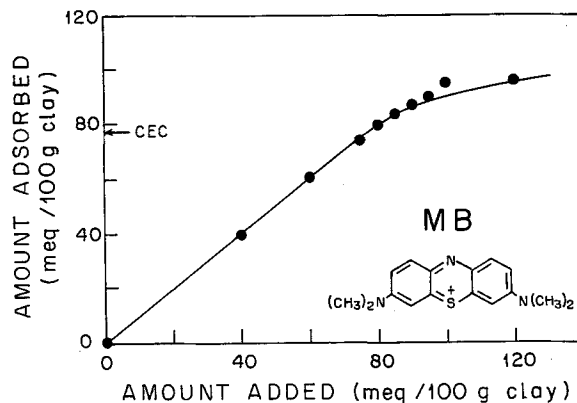

Figure 2. Adsorption isotherm of methylene blue (MB) on montmorillonite. ● = experimental results; —— = theoretical curve, calculated using binding coefficients $K = 10^8$ and $\bar{K} = 5 \times 10^5$ M^{-1} from Eqs. (1–4).

units of mole/liter, or M, and the unit of K_i and $\bar{K}_i$ is M^{-1}. The concentration of the cation, X_i, at the surface, is

$$X_i(0) = S_i Y_0^{Z_i}, \tag{5}$$

where $Y_0 = \exp(-e\psi(0)/kT)$, e is the absolute magnitude of an electronic charge, Z_i is the valence of an ion, being positive for a cation and negative for an anion, $\psi(0)$ is the surface potential, k is Boltzmann's factor, T is the absolute temperature, and S_i is the molar concentration of cation i in the solution, far away from the surface.

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

The intrinsic binding coefficients, K_i and $\bar{K}_i$, which reflect the strength of the chemical binding in Eqs. (2) and (4) are considered as parameters which can be determined from adsorption data and then be used to predict additional results.

For a given cation i only its total concentration, C_i, is known *a priori*, except in experiments applying dialysis. The total amount of cation i consists of an amount adsorbed, an amount in solution, and an amount in the double layer regions. If Q_1 is the excess concentration of monovalent cations in the double layer region above the bulk concentration, and if

$$S^{(1)} = \sum_{mono} S_i, \tag{6}$$

the total concentration C_i is given by:

$$C_i = S_i + [PX_i] + 2[PX_{i2}^+] + Q_1 S_i/S^{(1)}. \tag{7}$$

A similar expression using Q_2 and $S^{(2)}$ arises for divalent cations. The quantities Q_1 and Q_2 are given

analytically (Nir *et al.*, 1978). As shown in the Appendix the surface charge density σ, is related to σ_0, the surface charge density in the absence of cation binding according to:

$$\sigma/\sigma_0 = \{1 - Y_0^2[\Sigma K_i \bar{K}_i (S_i^+)^2 + \Sigma K_{j1} S_j^{2+}]\}$$
$$\div [1 + Y_0 \Sigma K_i S_i^+ + Y_0^2 \Sigma K_i \bar{K}_i (S_i^+)^2$$
$$+ Y_0^2 \Sigma K_j S_j^{2+}]. \tag{8}$$

The index j in Eq. (8) refers to divalent cations.

Divalent cations can form a neutral complex by an association with two surface sites, or they can yield charged complexes, with the respective binding coefficients K_{j2} and K_{j1}, where

$$K_j = K_{j1} + K_{j2}. \tag{9}$$

In the absence of charged complexes for the divalent cations, Eq. (8) indicates that charge reversal occurs if

$$Y_0^2 I = Y_0^2 \Sigma K_i \bar{K}_i (S_i^+)^2 > 1. \tag{10}$$

Because $Y_0 < 1$ if charge reversal occurs, Eq. (10) limits Y_0 as follows:

$$1 > Y_0 > 1/(I)^{1/2}. \tag{11}$$

The summation in Eq. (10) is limited to organic cations. The computational procedure is essentially as described by Nir (1986). The known quantities are C_i, C_j, and total concentration of surface sites, PT. For given values of K_i, $\bar{K}_i$, K_{j1}, and K_{j2} the program solves iteratively for S_i, S_j and Y_0. Hence, the program calculates the surface potential and the concentrations of the complexes PX_i and PX_{i2}^+.

RESULTS

The adsorption isotherms of TFT and MB on montmorillonite are presented in Figures 1 and 2, respectively. These data indicate that for amounts of added dye less than the CEC of the clay, practically all the added dye was taken up by the clay. No dye was de-
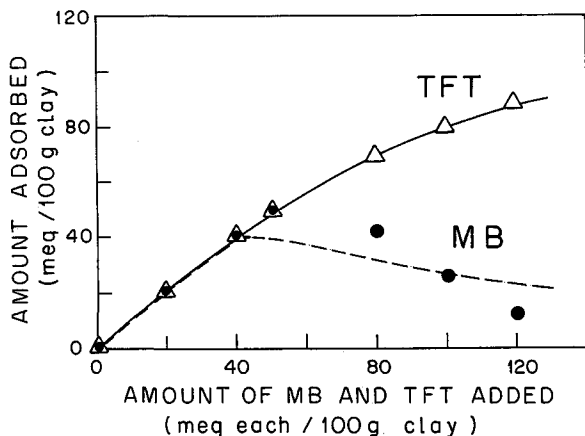
Figure 3. Adsorption isotherms of methylene blue (MB) and thioflavin T (TFT) on montmorillonite, from an equimolar aqueous solution of the two dyes. ● and △ = experimental results for MB and TFT, respectively; − − − and —— = theoretical curves, calculated for MB and TFT, respectively, using the same binding coefficients as in Figures 1 and 2.
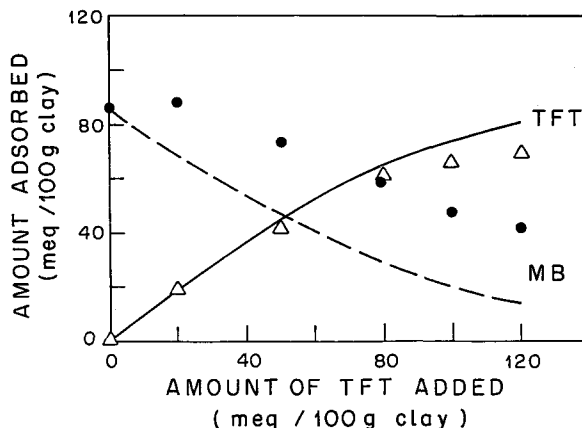

Figure 4. Adsorption isotherm of thioflavin T (TFT) and methylene blue (MB) on montmorillonite previously adsorbed with MB at a load of 90 meq/100 g clay. ● and △ experimental results for MB and TFT, respectively; − − − and —— = theoretical curves, calculated for MB and TFT, respectively, using the same binding coefficients as in Figures 1 and 2.

tected in the equilibrium solution, indicating concentrations of $<4 \times 10^{-7}$ M for TFT and $<2 \times 10^{-7}$ M for MB (after correcting for the adsorption to the glass; see Experimental). At values >CEC, adsorption reached about 110 meq/100 g clay for TFT and 95 meq/100 g clay for MB.

The adsorption of TFT at added concentrations of 50 and 120 meq dye/100 g clay was also measured by using dispersions of clay in a 3.5 M CsCl solution. The rationale was that Nir *et al.* (1986) showed Cs to be strongly bound to montmorillonite. Despite the large Cs/TFT concentration ratios, the amounts of TFT adsorbed were the same (within experimental error) as if the clay had been dispersed in distilled water. Thus, Cs cannot compete with this organic cation for the adsorption sites of the clay, and the results presented were not affected by the different exchangeable inorganic cations present in the clay.

Theoretical adsorption isotherms were calculated using the formulae presented above. According to our model, the adsorption of the organic cations can be described by two binding coefficients, K_i and $\bar{K}_i$ (see Eqs. (1–4)), which describe the formation of neutral and charged complexes, respectively. These coefficients were assumed to be independent of the extent to which the clay surface was covered by the organic dye and independent of the ionic strength. The calculated isotherms, obtained by using $K_1 = 10^9$ M^{-1}, $\bar{K}_1 = 1.5 \times 10^6$ M^{-1} for TFT, and $K_2 = 10^8$ M^{-1}, $\bar{K}_2 = 5 \times 10^5$ M^{-1} for MB, are also presented in Figures 1 and 2, respectively.

The different values obtained for the binding coefficients of TFT and MB on montmorillonite point to different strengths of intermolecular interactions at the surface of the clay. The competition between MB and TFT for the adsorption sites of the clay was studied

by adding the two dyes simultaneously (in an equimolar solution) to a clay suspension, and incubating the mixture for different periods of time. The values obtained for the amounts of adsorbed cations after 24 hr were higher by about 10% than those measured only 1 hr after addition of the dyes. Very small additional changes in adsorption (<4%), however, were measured after 3 wk, indicating that the system had reached equilibrium. The results obtained after 3 wk of incubation are shown in Figure 3. From this illustration, complete adsorption evidently took place in the region where the total amount of dye added was less than the CEC of the clay. Above that point, TFT adsorbed preferentially and MB preferentially remained in the solution. The theoretical curves, calculated using the same binding coefficients determined previously for each dye separately, are also presented in Figure 3. The trends in the experimental results are correctly predicted by the calculations; however, at high loads of dyes (i.e., >CEC), the calculated values do not closely match the experimental values for the adsorption of MB.

Figure 4 shows an adsorption isotherm of TFT on montmorillonite which had been previously contacted for 24 hr with MB at a load of 90 meq/100 g clay. The data were obtained after incubation of the whole system for 3 wk. Contrary to the results obtained in the previous experiment in which the two dyes were added simultaneously, significant differences in adsorption were noted for 24 hr and 3 wk of incubation. The amounts of TFT and MB adsorbed increased and decreased, respectively, by about 10%. Typical results are illustrated in Figure 5.

The displacement of MB molecules by added TFT can be deduced by the data shown in Figure 4, as expected by the stronger interaction of TFT with the

clay surface. The amounts of TFT adsorbed and MB released, however, were smaller than those measured in the previous experiment in which both cations were added simultaneously to the clay suspension. Calculations carried out using our model, with the same binding coefficients as employed for the single dye systems gave fair predictions for the amount of TFT adsorbed, but underestimated the amount of MB adsorbed on the clay.

Adsorption of the organic cations at concentrations higher than the CEC of a clay should result in charge reversal of the clay. To verify this, a microelectrophoresis experiment was conducted. Particles in a sample of montmorillonite loaded with 50 meq TFT/100 g clay moved to the positive electrode, whereas in samples containing the two dyes MB and TFT coadsorbed at a total concentration of 100–120 meq/100 g clay, the particles moved to the negative electrode; these data suggest that charge inversion took place if adsorption of the organic cations was in excess of the CEC.

DISCUSSION

The present model for the adsorption of the monovalent organic cations MB and TFT on montmorillonite combines the electrostatic equations with equations of cation binding to the clay surface. The model assumes the formation of a neutral complex as well as a charged complex. The formation of charged complexes results in adsorption in excess of the CEC of the clay, at which point charge reversal occurs. This behavior contrasts with the adsorption of inorganic monovalent cations such as Li, Na, K, and Cs. The binding strengths of the organic cations with the clay exceed by far those of the inorganic cations. For example, the binding coefficient K_1 is 0.6, 1, 2, and 200 M^{-1} for Li, Na, K, and Cs, respectively (Nir *et al.,* 1986), whereas for the organic cations MB and TFT the values are 10^8 and 10^9 M^{-1}, respectively. This difference in magnitude explains why the adsorption of TFT on the clay in the presence of 3.5 M Cs was similar to its adsorption in an aqueous suspension of the clay. One source of this difference in the strength of the interaction was the exclusion of water molecules from the binding sites of the organic cation on the clay. Such water exclusion was previously observed, using Fourier-transform infrared spectroscopy, for the adsorption of the cationic dye methyl green on montmorillonite (Margulies and Rozen, 1986). In contrast, inorganic monovalent cations interacting with clays (or membranes), still retain a part of their hydration shells (Shainberg and Kemper, 1966; McBride *et al.,* 1975a, 1975b; Kurland *et al.,* 1979), which amounts to a weakening of the interactions between cations and the clay sites.

The results in Figures 1 and 2 suggest that the present model can simulate and predict the amounts of organic
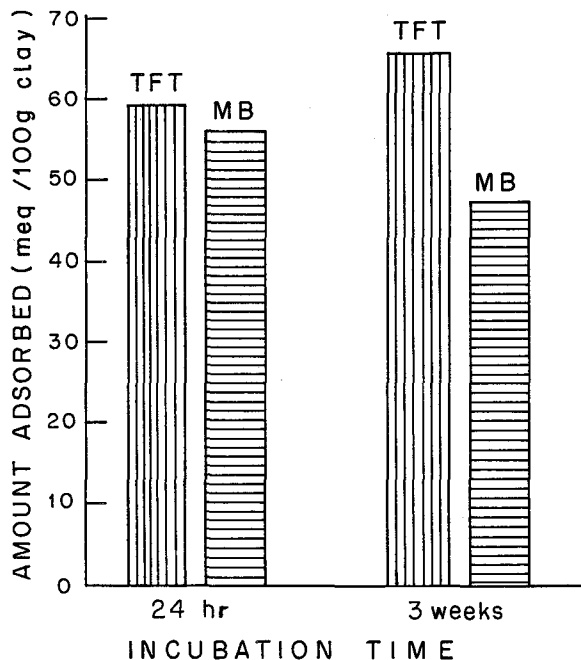

Figure 5. Amounts of methylene blue (MB) and thioflavin T (TFT) adsorbed on montmorillonite after different periods of incubation, following addition of TFT (100 meq/100 g clay) on montmorillonite previously adsorbed with MB (90 meq/100 g clay).

cations adsorbed. In particular, the binding coefficients determined from adsorption data for the separate cations yield reasonable predictions of their competitive adsorption. The saturation phenomena observed if the adsorption exceeded the CEC by about 20–40% can be explained in the framework of the model as due to charge reversal, which reduced the solution concentration of cations near the surface. In this context the model predicts that the amounts of adsorbed dyes will increase with the ionic strength whenever charge reversal occurs, in contrast with the behavior in the region where the surface potential is still negative. This effect is explained by Eq. (5) and is important at adsorbed amounts significantly in excess of the CEC. The low resolution of our experimental method at such high levels of dye concentration levels precluded testing this point.

The results in Figure 4 show that if MB had been allowed to be adsorbed by itself for 24 hr, the addition of TFT resulted in MB being released from the surface. Under these conditions, however, the amount of MB that remained adsorbed was significantly larger than if the competing dyes had been added simultaneously. If the same binding coefficients used in the calculations generating the curves in Figures 1–3 were used, the calculated values of adsorbed MB underestimated the experimental values. Binding coefficients which gave a better fit were not determined because four parameters would have had to be varied.

The underestimate in the amount of MB adsorbed was more serious if the system was incubated for just 24 hr instead of for 3 wk. Thus, the equilibration time was possibly much longer than 3 wk, due to the slow dissociation of the preadsorbed MB.

The combination of detailed electrostatic equations with specific binding and the distinction between the total concentration of cations and their solution concentrations enables us to explain and predict the adsorption of cations, including organic cations, on montmorillonite. The model in its present form, however, does not consider explicitly details of the intermolecular interactions. The strength of intermolecular interactions is implicitly expressed by means of the binding coefficients. Changes in binding coefficients needed for explaining experimental results can be an indication for changes in modes of interaction between cations and surface sites, as was previously found for membranes (Nir, 1984). Detailed accounting of such changes requires a combination of additional refined experimental and theoretical procedures.

APPENDIX

The computational procedure and notations used in this work are the same as those used by Nir (1984, 1986). The modified calculation includes additional terms arising from the positively charged complexes PX_{i2}^+ in Eqs. (3) and (4).

The Gouy-Chapman equation gives a relation between the surface charge density, σ, the surface potential, and the concentrations of ions in solution, according to

$$\sigma = \{\Sigma S_i (Y_0^{Z_i} - 1)\}^{1/2}/g, \tag{A1}$$

where $g = 272\{80 \times 298/(\epsilon T)\}^{1/2}$ in which ϵ is the bulk dielectric constant and T is the absolute temperature. The surface charge density is given in units of e/A^2, where e is the magnitude of the charge of an electron. The quantities S_i and Y_0 are defined in Eq. (5). Eq. (A1) can be written as

$$\sigma^2 = (AY_0^2 + BY_0 + C + D/Y_0)/g^2, \tag{A2}$$

in which

$$A = \Sigma S_j^{2+},$$
$$B = \Sigma S_i^+,$$
$$C = -(3A + 2B),$$

and

$$D = 2A + B.$$

Taking the square of Eq. (8) and dividing it into Eq. (A2), yields a polynomial equation for Y_0:

$$\sum_{n=0}^{7} b_n Y_0^n = 0, \tag{A3}$$

in which

$$b_7 = A\bar{E}^2,$$
$$b_6 = B\bar{E}^2 + 2A\bar{E}G,$$
$$b_5 = AG^2 + 2A\bar{E} + 2B\bar{E}G + C\bar{E}^2 - F\bar{H}^2,$$
$$b_4 = 2AG + 2B\bar{E} + BG^2 + D\bar{E}^2 + 2C\bar{E}G,$$
$$b_3 = A + 2BG + 2C\bar{E} + CG^2 + 2DG\bar{E} + 2\bar{H}F,$$
$$b_2 = B + 2CG + DG^2 + 2D\bar{E},$$
$$b_1 = C + 2DG - F,$$

and

$$b_0 = D;$$

and

$$E = \Sigma S_j^{2+} K_j \text{ (see Eq. (9))},$$
$$\bar{E} = E + I \text{ (see Eq. 10))},$$
$$F = \sigma_0^2 g^2,$$
$$G = \Sigma K_i S_i,$$
$$H = \Sigma S_j^{2+} K_{j1},$$

and

$$\bar{H} = H + I.$$

The solution of Eq. (A3) should yield $Y_0 > 1$ if $1 > \bar{E}$ and $1 > Y_0 > 1/(\bar{E})^{1/2}$ if $\bar{E} > 1$.

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NOTE ADDED IN PROOF: An experiment parallel to that shown in Figure 4, but in which TFT was adsorbed first at a load of 90 meq/100 g clay and different amounts of MB were added after 24 hr, showed that TFT and MB were adsorbed at higher and lower levels, respectively, than if they were added simultaneously.