

ADSORPTION OF MONOVALENT ORGANIC CATIONS ON SEPIOLITE: EXPERIMENTAL RESULTS AND MODEL CALCULATIONS

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Abstract—Adsorption of neutral organic molecules and the monovalent organic cations methylene blue (MB) and crystal violet (CV) to sepiolite was determined experimentally and investigated by an adsorption model. The largest amounts of MB and CV adsorbed were about 4-fold of the cation exchange capacity (CEC) of sepiolite. Consequently, it was proposed that most of the above described adsorption was to neutral sites of the clay. The adsorption model considered combines the Gouy-Chapman solution and specific binding in a closed system. The model was extended by allowing cation adsorption to neutral sites of the clay, in addition to adsorption to negatively charged sites and adsorption to neutral complexes formed from 1 cation adsorbed to a negative surface site. The amount of available neutral sites was determined from the adsorption of the neutral molecule Triton-X 100 (TX100). The model could adequately simulate the adsorption of the neutral molecules TX100 and crown ether 15-crown-5 (15C5) as well as the organic cations. Due to aggregation of MB molecules in solution, their adsorption was somewhat less than that of CV at the larger added concentrations. A consideration of the molecular dimensions of TX100, MB and CV suggested that their adsorption was mostly to external sites of the clay and that their entry to the sepiolite channels was largely excluded. This interpretation is supported by infrared spectroscopy (IR) measurements, which show large perturbations of the peak corresponding to vibrations of external Si-OH groups of the clay and confirm complete occupancy of external sites by MB and CV.

Key Words—Adsorption Model, Crystal Violet, Methylene Blue, Sepiolite.

INTRODUCTION

The clay mineral sepiolite is currently widely used as raw material due to its powerful sorbent properties (Alvarez 1984). Sepiolite has an open structure exhibiting a microfibrillar morphology with a high specific surface area (around $340 \text{ m}^2 \text{ g}^{-1}$) and a large micropore volume (around $0.44 \text{ cm}^3 \text{ g}^{-1}$) due to the existence of intracrystalline cavities (“tunnels”). These characteristics of sepiolite are related to its powerful sorbent properties and its ability to adsorb organic species of different nature: neutral molecules and organic cations.

Sepiolite with $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH},\text{F})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$ as unit cell formula (Brauner and Preisinger 1956; Santaren et al. 1990), is structurally formed by an alternation of blocks and tunnels that grow up in the fiber direction (*c*-axis) (Figure 1). Each structural block is constructed by 2 tetrahedral silica sheets enclosing a central magnesia sheet in a similar way that occurs in other 2:1 silicates, such as talc, although in sepiolite there are discontinuities of the silica sheets that give rise to those structural tunnels. Such an arrangement determines that some silanol groups (Si-OH) are present at the border of each block located at the “external surface” of the silicate (Alrichs et al 1975). These Si-

OH groups are usually accessible to organic species, acting as *neutral* adsorption sites (designated N). The N sites' content for the Vallecas-Vicalvaro (Spain) sepiolites can be estimated in the order of 0.60 mmol/g as was determined from grafting reaction of organochlorosilanes on the silanol groups covering the sepiolite surface (Ruiz-Hitzky 1974; Ruiz-Hitzky and Fripiat 1976). Certain isomorphous substitutions in the tetrahedral sheet, such as Al^{3+} for Si^{4+} , are responsible for the exchangeable cations that are needed to compensate for the electrical charge, and constitute the *charged* adsorption sites (P sites). The cation exchange capacity (CEC) for the considered sepiolites is in the range of 0.10 to $0.15 \text{ mol}_c \text{ kg}^{-1}$.

In this work the main aim has been to develop and test an adsorption model that quantitatively accounts for the adsorption of organic species on both types of sepiolite sites. We present here results for the adsorption to sepiolite of 2 monovalent organic cations, MB and CV, and 2 neutral molecules, 15C5 and TX100 (Figure 2).

METHODS AND MATERIALS

Materials

The dyes used were supplied by Carlo Erba (MB) and FLUKA (CV). The non-ionic surfactant TX100 and the 15C5 were supplied by Aldrich. We used Yun-

† Deceased.

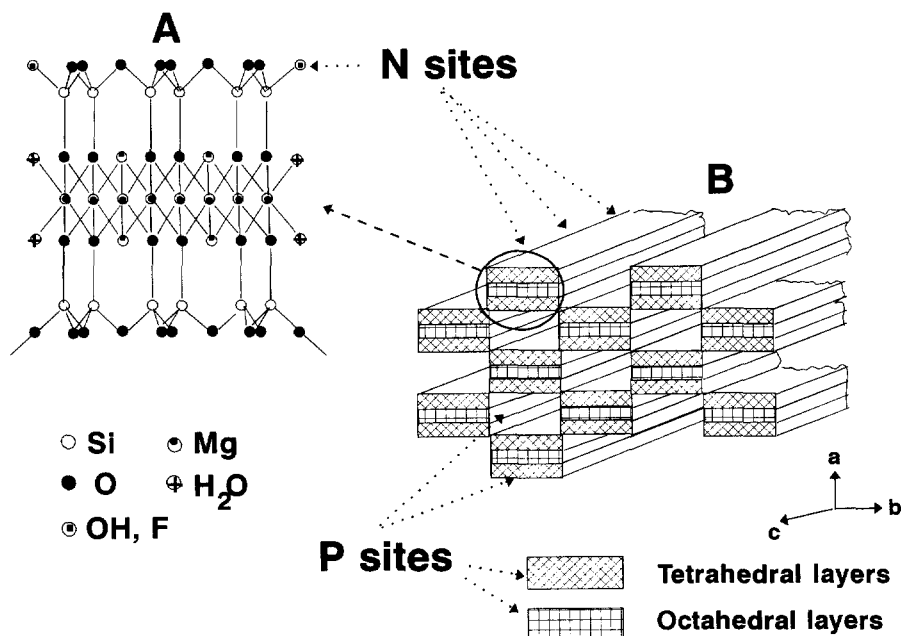


Figure 1. Structural model of sepiolite with indication of where the neutral (N) and charged (P) adsorption sites are located.

clillos sepiolite (<200 mesh) provided by TOLSA S.A., Madrid, Spain, with a 99% pure mineral content. The chemical composition of the clay is fully described in Ruiz-Hitzky and Casal (1985). The surface area (N_2 , Brunauer-Emmett-Teller [BET]) is $340 \text{ m}^2 \text{ g}^{-1}$ and the CEC is near $0.15 \text{ mol}_c \text{ kg}^{-1}$. The clay was essentially a Mg homoionic. Analyses showed that Na contributed to the CEC $0.03 \text{ mol}_c \text{ kg}^{-1}$, the rest being contributed by Mg.

Experimental Techniques

Aliquots of $5 \times 10^{-3} \text{ M}$ aqueous solutions of each compound were added to the adequate amount of sepiolite to reach a final suspension of 0.2% (w/w) of sepiolite. These suspensions were maintained at 25°C under continuous magnetic stirring for 3 d. The pH of the sepiolite suspension without the dye was 8, and after the dye addition it varied in the range of 7 ± 1 . The solid was separated by centrifugation for 20 min at 11,000 rpm and then air-dried. The amount of adsorbed oxyethylene species was measured by elemental analysis (CHN) in a Perkin-Elmer 2400 CHN apparatus. In order to establish the amount of adsorbed dyes, the concentrations of the dye solutions before and after the treatment with sepiolite were deduced from absorbance measurements at the maximum wavelength absorption (662 nm for MB and 588 nm for CV), using a Perkin-Elmer LAMBDA-16 U.V.-Vis spectrophotometer.

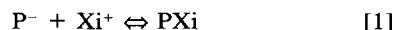
Solid samples were characterized by IR spectroscopy in a Fourier transform IR (FTIR) Nicolet 20SXC

spectrophotometer, using samples as self-supporting films (wafers).

Theoretical

MODEL EQUATIONS. The model employed is an extension of that described by Nir (1986), Margulies et al. (1988) and Rytwo et al. (1995), which accounts for the ability of charged organic monovalent cations to adsorb to neutral binding sites on the silicate layer. The rationale for such adsorption comes from analyzing results published by Alvarez et al. (1987), in which adsorption of the neutral molecule TX100 did not release exchangeable Mg to the solution. Consequently, we deduce that TX100 adsorbs to N sites.

For brevity's sake we present only the essential equations needed to comprehend the developments in the model. A detailed review of the model is given in Nir, Rytwo et al. (1994). Let Xi^+ denote a monovalent cation that binds to a singly charged negative site, P^- , on the surface of the silicate, creating the neutral complex PXi :



with a binding coefficient, K_i , which satisfies:

$$K_i = [PXi]/([P^-][Xi_{(0)}^+]) \quad [2]$$

in which $[Xi_{(0)}^+]$ is the concentration of the cation at the surface. The adsorption of another organic monovalent cation to the neutral complex creates a charged complex $P(Xi)_2^+$:

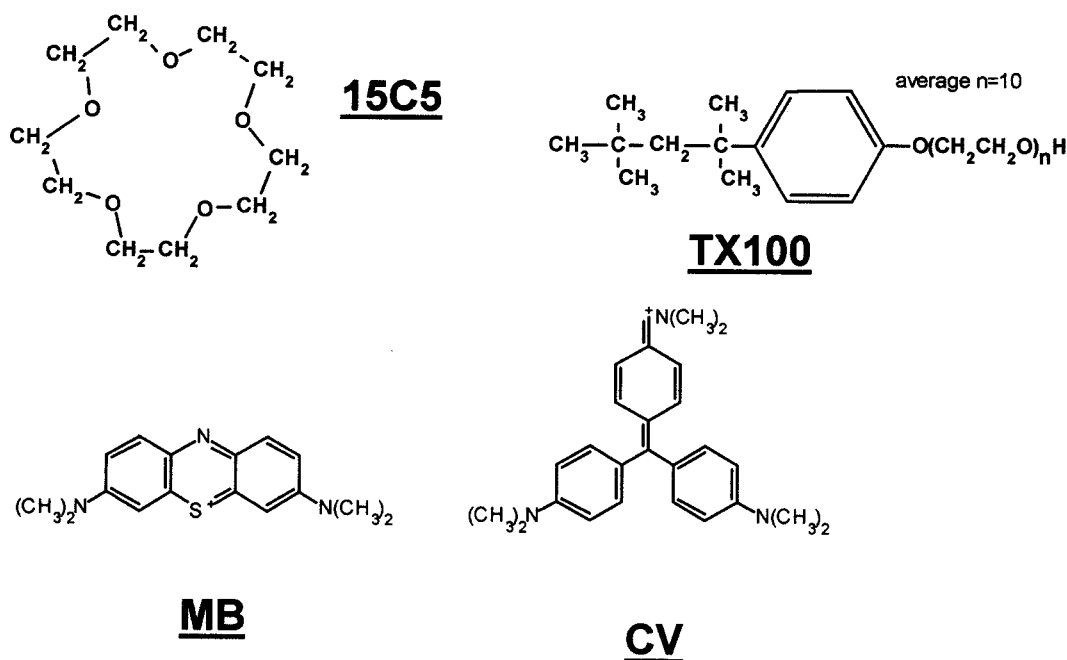
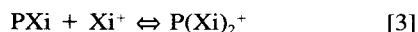


Figure 2. Molecular structure of MB, CV, 15C5 and TX100.



with a binding coefficient:

$$\bar{K}_i = \frac{[\text{P}(\text{Xi})_2^+]}{([\text{PXi}][\text{Xi}_{(0)}^+])} \quad [4]$$

Such reaction was essential to explain some well-known effects of the adsorption of organic monovalent cations to smectites, such as adsorption at amounts higher than the CEC of montmorillonite, or its charge reversal (Margulies et al. 1988).

When several organic monovalent cations interact with the clay we can have, in addition to Equations [3] and [4], the formation of mixed complexes, that is, the adsorption of the organic cation Xj^+ to the neutral complex PXi , to form the charged complex PXiXj^+ , and vice versa:



with the binding coefficients:

$$K_{ij} = \frac{[\text{PXij}^+]}{([\text{PXi}][\text{Xj}_{(0)}^+])} \quad [7]$$

$$K_{ji} = \frac{[\text{PXji}^+]}{([\text{PXj}][\text{Xi}_{(0)}^+])} \quad [8]$$

The mixed binding coefficients are not necessarily symmetrical, that is, $K_{ij} \neq K_{ji}$. Equations [5] through [8] are only required when competition for adsorption between 2 or more monovalent organic cations is considered.

In the calculations we employ the relation:

$$\text{Xi}_{(0)} = \text{Xi}Y_{(0)}^{Z_i} \quad [9]$$

where $\text{Xi}_{(0)}$ is the molar concentration of cation i in its monomeric form close to the mineral layer, Xi is the molar concentration in the equilibrium solution (at infinite distance from the clay), $Y_0 = \exp(-e\psi_{(0)}/kT)$, Z_i is the valence of the given ion, e is the absolute magnitude of an electronic charge, $\psi_{(0)}$ 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, $\text{Xi}_{(0)}$, may be significantly larger than Xi . When charge reversal occurs, $\psi_{(0)}$ is positive and $Y_0 < 1$, reducing significantly the concentration of non-adsorbed cations in the double layer region, below their equilibrium solution concentration. The excess concentration of cation i in the double layer region above the equilibrium concentration ($D_p(i)$), can be calculated by assuming that all cations of the same valency behave similarly in the double layer region. Thus, a proportion factor Q_z can be defined for each valency z , and $D_p(i)$ is given by:

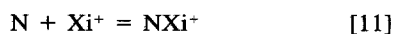
$$D_p(i) = Q_z \frac{\text{Xi}}{\text{Xi}(z)} \quad [10]$$

The quantities Q_z can be obtained analytically, when the system includes only mono- and divalent cations, and 1 type of anion (Nir et al. 1978). A numerical integration provides Q_z in the general case (Rytwo 1994).

The intrinsic binding coefficients, K_i and \bar{K}_i , which reflect the strength of the chemical binding in Equations [2] and [4], were determined for MB and CV in

the case of montmorillonite (Rytwo et al. 1995) from adsorption data.

The extension of the model for sepiolite required to consider the reaction:



with a binding coefficient, Kn:

$$Kn = [NXi^+]/([N][Xi_{(0)}^+]) \quad [12]$$

Some organic cations (MB) can form dimers, trimers and even higher order aggregates in solution (Spencer and Sutter 1979; Cenens and Schoonheydt 1988). Expressions for the general distribution of aggregates (Nir et al. 1983) yield that the total concentration of primary molecules in solution, Xi_t , is given by:

$$[Xi_t] = [Xi]/(1 - Kag [Xi])^2 \quad [13]$$

in which Kag is the corresponding coefficient (M^{-1}) for aggregation in solution. Aggregation of dye molecules reduces the concentration, Xi , of dye monomers. We have ignored the adsorption of dimers or higher-order aggregates, as the consideration of such effect would add more parameters and was not needed for the simulation of the adsorption results. It may be noted that dye aggregation in solution can only have an influence when its total added amounts are above the CEC of the clay, since below the CEC essentially all the dye is adsorbed (Rytwo et al. 1991, 1995; and current results on sepiolite).

For the simple case when no charged complexes are formed, the intrinsic surface charge density, σ_{ini} , is given by the charge per unneutralized surface site, that is, by the ratio of the CEC to the specific surface area (SSA) of the clay mineral. The total site concentration, PT, equals the sum of concentrations of all sites, free and complexed. The actual surface charge density, σ , depends on the amount of free sites on the clay,

$$\frac{\sigma}{\sigma_{ini}} = \frac{P^-}{PT} = \frac{P^-}{P^- + \Sigma PX^0} \quad [14]$$

where ΣPX^0 is the sum of concentrations of all neutral complexes. In cases where charged complexes due to binding to charged sites of the mineral may exist, the positively charged complexes decrease the negative value of σ . If ΣPX_2^+ is the sum of concentrations of all charged complexes between 2 monovalent organic cations and 1 charged clay site, then Equation [14] becomes:

$$\frac{\sigma}{\sigma_{ini}} = \frac{P^- - \Sigma PX_2^+}{P^- + \Sigma PX^0 + \Sigma PX_2^+} \quad [15]$$

In Equation [15] the possibility of charge reversal arises when $P^- < \Sigma PX_2^+$. For the case where charged complexes may also arise from binding to neutral sites, the actual surface density changes, but σ_{ini} remains unchanged. Thus, if ΣNX^+ is the sum of concentrations of all charged complexes formed by 1 monovalent or-

ganic cation and 1 neutral clay site, then Equation [15] becomes:

$$\frac{\sigma}{\sigma_{ini}} = \frac{P^- - \Sigma PX_2^+ - \Sigma NX^+}{P^- + \Sigma PX^0 + \Sigma PX_2^+} \quad [16]$$

The Gouy-Chapman equation yields:

$$\sigma^2 = \frac{\epsilon kT}{2\pi} \Sigma n_{\infty} (Y_0^{Z_i} - 1) = \frac{1}{G} \Sigma Xi (Y_0^{Z_i} - 1) \quad [17]$$

where ϵ is the dielectric coefficient of the medium, n_{∞} is the number of molecules of each ion in the equilibrium solution, and G depends on T , the Avogadro number, and the system of units (Nir 1984).

For the case of 1, 2, 3 and 4 valent cations, and mono- and divalent anions, the combination of Equations [16] and [17] gives a polynomial equation for Y_0 . The solution has been obtained by numerical procedures. In certain limiting cases of no binding, where all ions have the same valency, analytical solutions are also available.

The equations shown form a closed set. Thus, the mass balance of ion i may yield the values Xi , if Y_0 and P^- are known. Equation [16] may yield P^- , if the different Xi , NXi^+ and Y_0 are known. The combination of Equations [16] and [17] may give a value for Y_0 , if Xi , NXi^+ and P^- are known. By introducing the values of the binding coefficients, the equations can be solved iteratively by the following procedure:

- 1) An initial value for Y_0 and P^- is assumed.
- 2) The values of Xi are calculated by using Equations [1], [3], [9], [10], [11] and [13].
- 3) A new value of Y_0 is obtained by using Equations [16] and [17].
- 4) A new value is obtained for P^- , by subtracting from PT the amount of bound sites.
- 5) Another iteration starts from stage 2.

The iteration steps may be continued until the desired degree of convergence is reached. The determination of the binding coefficients that give the best fit of the calculated adsorbed amounts to the experimental values has been described in Nir et al. (1986); Hirsch et al. (1989); Rytwo et al. (1995); Rytwo, Nir and Banin (1996) and Rytwo, Nir and Margulies (1996). As will be elaborated, we have employed only 1 parameter, Kn, fixing the values of K and \bar{K} at the values determined for the adsorption of CV and MB to montmorillonite.

DETERMINATION OF THE CONCENTRATION OF NEUTRAL BINDING SITES, N . The experimental results provide the quantities L and B , that is, the concentrations of free and bound molecules, respectively. The simplest approach is to use the Scatchard equation whose derivation assumes independence of bound molecules. The Scatchard equation can be written as:

$$r/L = kn - rk \quad [18]$$

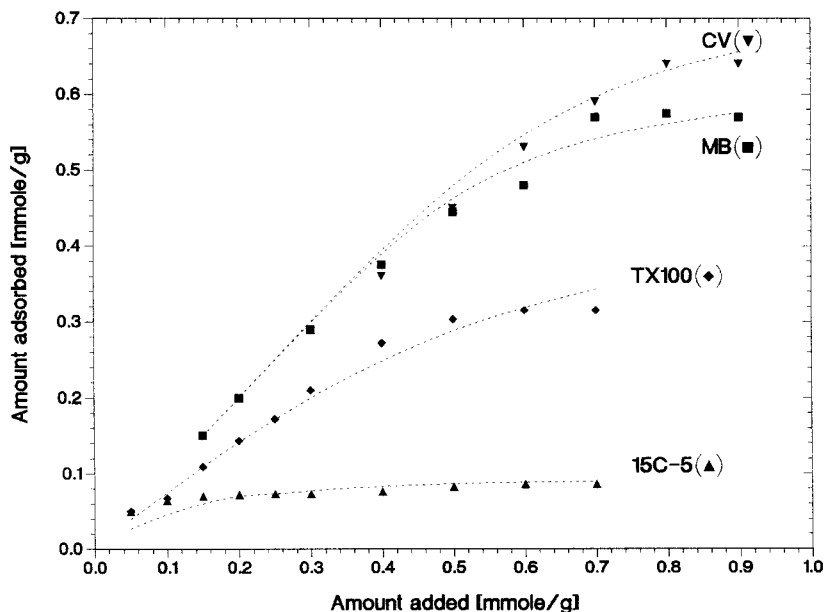


Figure 3. Adsorption isotherms of MB, CV, 15C5 and TX100 to sepiolite. Points represent measured results and lines represent calculated results.

in which r denotes the number of bound molecules per particle, and n denotes the number of binding sites per particle:

$$N = nG_0 \quad [19]$$

where G_0 is molar concentration of particles (Nir, Peled et al. 1994), and $k(M^{-1})$ is the binding constant. By using Equation [19] and noting that $r = B/G_0$, the rearrangement of Equation [18] gives:

$$B/L = kN - kB \quad [20]$$

or:

$$k = (B/L)/(N - B) \quad [21]$$

We have also employed the procedure in Nir, Peled and Lee (1994) for binding of neutral molecules to 2 types of binding sites.

Table 1. Binding coefficients for adsorption to sepiolite.

Molecule	Binding coefficient	Minimal value (M^{-1})	Optimal value (M^{-1})	Maximal value (M^{-1})
TX100	k	3000	3600	4000
15C5	k	5000	8000	10,000
CV†	\bar{K}	—	10^6	—
	\bar{K}_n	—	8×10^9	—
	K_n	—	3×10^6	—
MB†	\bar{K}	—	3×10^8	—
	\bar{K}_n	—	10^6	—
	K_n	—	3×10^6	—

† The parameters \bar{K} and \bar{K}_n were fixed at the values determined for montmorillonite (Rytwo et al. 1995).

RESULTS

We determined the adsorption to sepiolite of 2 neutral molecules, TX100 and 15C5, and 2 monovalent organic cations, CV and MB. The molecular structures are given in Figure 2. In order to minimize molecular aggregation in solution and at the same time reach large adsorbed amounts relative to the CEC of the clay, we reduced the concentration of the clay to 0.2% (2 g L^{-1}), which was still within the limits of sensitivity of the measurements. Indeed, the largest adsorbed amount of TX100 was $0.315 \text{ mol}_c \text{ kg}^{-1}$, that is, 25% more than the value in Alvarez et al. (1987) (Figure 3). The largest adsorbed amount of MB was $0.57 \text{ mol}_c \text{ kg}^{-1}$ clay, which was 25% more than in Aznar et al. (1992) (Figure 3). The largest adsorbed amount of CV was $0.64 \text{ mol}_c \text{ kg}^{-1}$, that is, 4.57-fold of the CEC of sepiolite (Figure 3).

The study of the adsorption of the neutral molecules to sepiolite was also intended to provide an estimate for the amount of neutral sites, N , which was required for calculating the adsorbed amounts of the organic cations MB and CV. In calculations according to Equation [21], we used the experimental values to obtain the values of the binding constants, k , by assuming a wide range of N values. We chose the value of N that gave the smallest variation of k -values. Next we determined the value of k that gave the best fit to all the experimental values.

The values of these parameters are given in Table 1. The analysis of TX100 adsorption gave $N = 3.4 \times \text{CEC}$, whereas the largest amount of TX100 adsorbed

was 2.25-fold of the CEC. The estimated number of binding sites for 15C5 was 0.71-fold of the CEC. In the case of TX100, we also tried to fit the data to 2 types of binding sites according to the procedure in Nir, Peled et al. (1994), but no improved fit was deduced, despite the addition of 2 parameters. The results in Figure 3 demonstrate that the simplest binding model, which assumes no cooperativity in the binding of the neutral molecules to sepiolite, can adequately explain the experimental data. The determination coefficient (R^2) for the measured and calculated adsorbed amounts of 15C5 was 0.934, with rmse of 0.11 in the range between 0–9 $\text{cmol}_c \text{ kg}^{-1}$. For TX100, $R^2 = 0.982$ and rmse = 0.18 in the range between 0–32 $\text{cmol}_c \text{ kg}^{-1}$.

For calculating the amounts of CV or MB adsorbed to sepiolite, the application of the model requires the employment of 3 parameters, K , \bar{K} and K_n (Equations [2], [4] and [14]). However, as explained below, we had to determine only the parameter K_n . Since the amount of neutral binding sites was estimated to be 3.4-fold larger than the CEC, and there was indication from previous results of Alvarez et al. (1987) that Mg was released for adsorption of cations at amounts up to the CEC, it seemed plausible that the charged sites would be the first to become bound by the organic cations. Furthermore, the results of Aznar et al. (1992) and those in Figure 3 demonstrate that for CV or MB in amounts up to 0.20 $\text{mol}_c \text{ kg}^{-1}$, all the dyes were adsorbed. This result would have been predicted by the calculations for any values of K_n for values of K , and \bar{K} in the range of the values deduced for the adsorption of monovalent organic cations to montmorillonite (Margulies et al. 1988; Rytwo et al. 1995), or even for 1000-fold smaller values of K and \bar{K} .

We fixed K and \bar{K} at the corresponding values determined from the adsorption of CV and MB to montmorillonite, and only determined the value of K_n . The values of the binding constants are given in Table 1. The results in Figure 3 demonstrate that by setting $K_n = 3 \times 10^6 \text{ M}^{-1}$, the calculations can adequately explain the adsorbed amounts of CV and MB. The larger amounts of CV adsorbed for total dye amounts above 0.60 $\text{mol}_c \text{ kg}^{-1}$ are due to the fact that MB molecules aggregate in solution in this range of concentrations (Bergmann and O'Konski 1963). We have accounted for MB aggregation in solution as in Rytwo et al. (1995). The determination coefficient (R^2) for the measured and calculated adsorbed amounts of MB is 0.989, with rmse of 0.25 in the range between 0–0.57 $\text{mol}_c \text{ kg}^{-1}$. For CV, $R^2 = 0.994$ and rmse = 0.27 in the range between 0–0.64 $\text{mol}_c \text{ kg}^{-1}$.

The IR spectra (Figure 4A) of sepiolite containing MB adsorbed at different concentrations indicate a decrease in intensity of the band at 3716 cm^{-1} (ν_{OH} vibrations of Si-OH groups) which is perturbed due to its association with the MB adsorbed species. Similar-

ly, Figure 4B indicates the participation of these N sites as centres for CV adsorption on sepiolite. The band at about 3680 cm^{-1} that corresponds to ν_{OH} vibrations of hydroxyl groups linked to Mg ions which are located in the interior of the sepiolite blocks (Figure 1) remains unperturbed despite dye adsorption.

DISCUSSION

The results in Figure 3 demonstrate that, for dye amounts of up to 0.3 $\text{mol}_c \text{ kg}^{-1}$, practically all the molecules of MB and CV adsorb to sepiolite, that is, up to 2.1-fold of the CEC. Table 2 gives a sample of the calculated values of the fractions of dye molecules in solution or in various complexes with the clay mineral sites. The almost complete adsorption (>99%) of dye molecules at total dye concentrations of 0.4 mM is a reflection of the large binding coefficients of the dye molecules to sepiolite sites. Employing the same binding coefficients as for montmorillonite, the calculations for CV give a complete charge reversal of the charged sites of sepiolite at a total dye concentration of 0.7 mM, which corresponds to approximately 2.5-fold of the CEC.

In the case of MB, the calculations give charge reversal of up to 86% of the charged sites, whereas in montmorillonite (Rytwo et al. 1995) the corresponding value is 50%. This difference is explained by the larger area per charged site in sepiolite (4.03 nm^2) in comparison with montmorillonite (1.56 nm^2), which results in relatively smaller values of surface potentials in sepiolite. Table 2 shows that up to a total concentration of 1 mM the adsorbed amounts of MB and CV are similar, whereas for 1.8 mM the amount of MB adsorbed is 13% less than that of CV. Since we have used the same value of the binding coefficient, K_n , in both cases the difference in adsorption between these cations is due to the aggregation of MB molecules in solution (Bergmann and O'Konski 1963; Rytwo et al. 1995; see Equation [13]).

As in the case of MB adsorption to montmorillonite (Rytwo et al. 1995), the model calculations ignored adsorption of MB aggregates to sepiolite. This does not imply that such adsorption cannot occur, but rather that the magnitudes of the binding coefficients for the adsorption of MB aggregates are significantly smaller than that of the monomer. Furthermore, if MB aggregates carry more than 1 charge, then according to Equation [9] for adsorption beyond the CEC, their exclusion from the surface is significantly larger than that of the monomers.

We have pointed out that for MB adsorption beyond the CEC, its adsorbed amounts (per kg of clay) can be increased upon lowering the solution concentration of MB. This is another reflection of the fact that MB aggregation in solution reduces its adsorption to the clay.

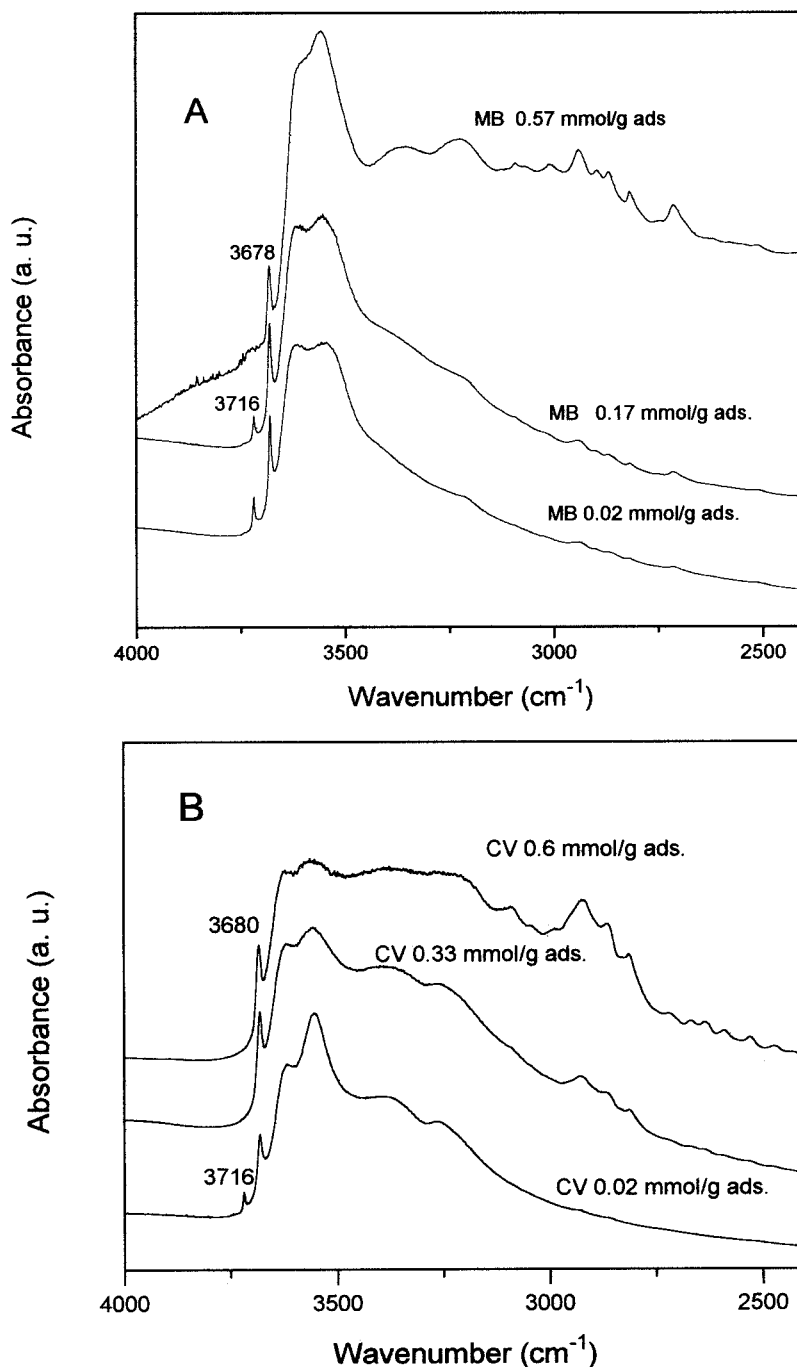


Figure 4. FTIR spectra of MB (A) and CV (B) adsorbed on sepiolite at different concentrations.

Table 2 also shows the calculated values of the surface potential. Beyond charge reversal ($\phi_0 > 0$) and at room temperature Equation [9] gives that the concentrations of all monovalent cations near the surface are reduced by $\exp(\psi_0/25)$. Our calculations, which account explicitly for the effect of cation exclusion from the double layer region, indicate that this exclusion

affects the adsorbed amounts negligibly, due to the large values of the binding coefficients and the small values of the ionic strengths. It should be pointed out that our calculations of the electrostatic equations treat the complex geometry of sepiolite as planar.

In Baruch et al. (1991), the calculated values of (ψ_0) were 12% smaller for a sphere of radius 3 nm than for

Table 2. Calculations of the fractions of dye molecules in the different species.

Dye	Total concentration (mM)	% in solution (as monomers)	% as neutral complex (PX) ⁰	% as charged complex (PX _n) ⁺ and in () conc. of complex (mM)	% as charged complex (NX) ⁺	Total amount complexed mmol/g	Surface potential ψ_0 (mV)
MB	0.4	0.059	66.8	5.43 (0.01)	27.7	0.20	49
	1	6.05	22.1	15.4 (0.08)	52.2	0.45	132
	1.8	11.4	9.92	13.4 (0.12)	37.8	0.55	147
CV	0.4	0.023	0.41	89.5 (0.18)	10.1	0.20	49
	1	3.96	0.022	59.7 (0.30)	36.3	0.48	137
	1.8	25.2	0.002	33.3 (0.30)	41.4	0.65	160

an infinite plane. Hence we can expect that the largest values of ψ_0 in Table 2 may be overestimated by 20 mV; this can amount to 2-fold at most in the value of Y_0 in Equation [9], which is effectively compensated by a 2-fold excess in the value of K_n in Table 1. It is of interest that K_n , the binding coefficient of the organic cations to the neutral sites of sepiolite, is at least 2 orders of magnitude larger than the values found for the neutral molecules. This difference might be largely due to a favored orientation of the organic cations relative to the surface of the clay mineral. Rytwo et al. (1995) concluded that MB molecules ($K = 3 \times 10^8 M^{-1}$) lie parallel to the montmorillonite plate, whereas CV molecules lie in a slightly inclined orientation ($K = 1 \times 10^6 M^{-1}$).

The results of this study raise the issue of whether the organic molecules studied can enter the interior of the sepiolite structure and adsorb to the channel sites whose cross section is 1.06 nm by 0.36 nm. In the case of the large molecule crown ether where the analysis gave that the number of binding sites is 30% less than the CEC, this result rules out penetration of the molecules into the interior. In the cases of TX100 and MB, where $N = 3.4 \times \text{CEC}$, geometrical considerations marginally allow the entry of these molecules into the channels. The dimensions of the planar molecule MB are 1.6 nm by 0.5 nm with a width of 0.3 nm. A problem arises of how to explain the large amount of adsorbed CV (larger than that of MB), since its shape is that of an equilateral triangle of side 1.6 nm and width 0.3 nm, which prohibits its entry into the sepiolite channels.

Considering the fact that adsorbed amounts of CV exceeded those of MB, we favor the view that none of these molecules enters the interior channels of sepiolite when high initial concentrations were used (formation of MB aggregates). Similarly, we view that only a small fraction of TX100 can enter the channels, although these molecules may adsorb at the ends of the channels through the oxyethylene molecular tail. The difference between the total amount of neutral sites found previously (Ruiz-Hitzky and Fripiat 1976), that is, $4 \times \text{CEC}$ and the TX100 value ($3.4 \times \text{CEC}$), may reflect the fraction of unaccessible neutral internal sites.

Close to saturation, most of the adsorption of CV and MB occurs to external neutral sites (silanol groups), which are fully covered as evidenced by FTIR spectra, that is, by the decrease in intensity of the band at 3716 cm^{-1} (ν_{OH} vibrations of Si-OH groups), up to its complete disappearance. The band at about 3680 cm^{-1} that corresponds to ν_{OH} vibrations of hydroxyl groups linked to Mg ions, located in the interior of the sepiolite blocks (Figure 1), remains unperturbed by the adsorption of MB or CV. Thus, the organic cations mostly adsorb to neutral sites in the outer surface, and to sites where large structural defects occur.

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