

## SORPTION OF SELECTED CATIONIC AND NEUTRAL ORGANIC MOLECULES ON Palygorskite and Sepiolite

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**Abstract**—Palygorskite and sepiolite show a high sorption capacity for organic molecules. Adsorption of 2 organic cations, methylene blue (MB) and crystal violet (CV), by palygorskite and sepiolite were examined. The maximum sorption of MB and CV far exceeded the cation exchange capacity (CEC) of these minerals. This shows that, besides the contribution of free negative sorption sites ( $P^-$ ), the sites satisfied with sorption of single cations ( $PX_i^0$ ) and neutral sorption sites (N) on clay surfaces may contribute to the sorption of organic cations. The number of neutral sites was determined by examining the sorption of 2 neutral organic molecules, triton-X 100 (TX100) and 15 crown ether 5 (15C5), and by application of the Langmuir isotherm.

To determine the contribution of different sites, an adsorption model that applies the Gouy-Chapman equation and takes into account the formation of different clay-organic complexes in a closed system was employed. Application of this model to sorption data provided the calculation of binding coefficients for neutral sites, as well as the surface potential of the minerals at different sorbate concentrations.

At sorption maxima, for both palygorskite and sepiolite, the contribution of neutral sites for sorption of organic cations was the highest, followed by the  $PX_i^0$  sites in case of CV sorption, while in sorption of MB the contribution of  $P^-$  sites was the second highest. The Fourier transform infrared (FTIR) patterns of clay-organic cation complexes compared with pure clays confirm that the sorption of organic cations is by silanol groups located at the edge of fibrous crystals, which account for neutral sorption sites.

**Key Words**—15 Crown Ether 5, Crystal Violet, Methylene Blue, Palygorskite, Sepiolite, Sorption Modeling, Triton-X 100.

### INTRODUCTION

Palygorskite and sepiolite are fibrous silicate clays, the so-called “special clays”, which are used in more than 100 different applications (Galan 1996). One of the principal applications of palygorskite–sepiolite clays involves uses that take advantage of their sorptive characteristics. In many applications, the sorptive characteristics of the clay surfaces are modified using organic cations (Gerstl and Mingelgrin 1979; Banerjee and Dureja 1995) or neutral surfactants (Gerstl and Yaron 1981). The sorption maxima of organic cations exceed the CEC of these minerals, showing that besides the contribution of CEC, sorption takes place on neutral sites and neutral complexes that are formed through sorption of an organic cation on a negative site.

Many studies have concluded that the silanol groups (Si-OH) of palygorskite and sepiolite, acting as neutral sites, can react directly with organic reagents to form compounds with true covalent bonds between the mineral substrate and the organic reactant (Ruiz-Hitzky and Fripiat 1976; Casal Piga and Ruiz-Hitzky 1977; Hermosin and Cornejo 1986). The sorption of organic cations on a negatively charged site that is already neutralized has been discussed by Nir (1986), Margulies et al. (1988) and Rytwo et al. (1995). Organic cation sorption on neutral sites and neutral complexes results in a charge reversal of the surfaces that in turn, alters the sorption characteristics and colloid behavior

of the clays. Using a micro electrophoresis device, Margulies et al. (1988) showed that the clay particles moved to the negative electrode, if adsorption of the organic cations was in excess of the CEC. Knowledge of the quantity of different complexes and inversely charged sites provides a better understanding of the colloid behavior that, in turn, leads to the more effective use of the clay in various applications.

This study is an attempt to quantify the contribution of different complexes in the sorption of 2 organic cations, MB and CV, by palygorskite and sepiolite. The contribution of the different complexes is assessed by using the Gouy-Chapman solution and modification of a sorption model described by Nir (1986) and Rytwo et al. (1995). The sorption characteristics of palygorskite and sepiolite for neutral organic molecules were also examined by the application of 2 neutral organic molecules, TX100 and 15C5.

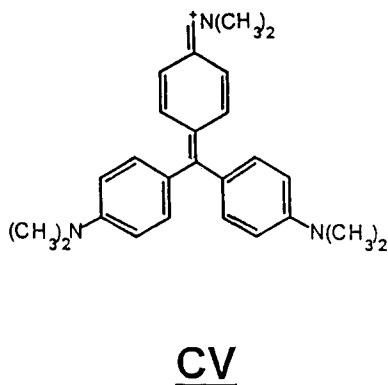
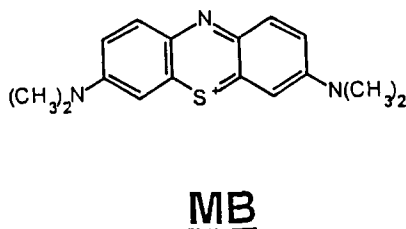
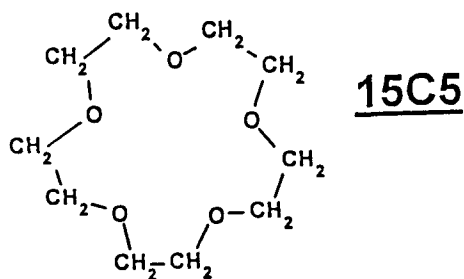
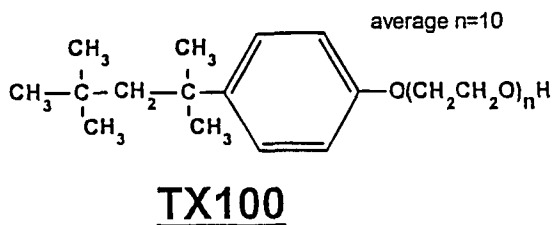
### MATERIALS AND METHODS

#### Materials

The minerals examined in this study were palygorskite from Florida (CMS source clay minerals PFI-1) and sepiolite from Eskishehir, Turkey. The clay samples were purified using the method described by Kunze and Dixon (1986) and homoionized with 1 M KCl. The excess salts were removed to an EC of 30  $\mu\text{S m}^{-1}$ , and the K-homoionized clays were then freeze-dried. The external specific surface area of the clay

Table 1. Surface area, CEC and chemical formula of palygorskite and sepiolite.

Mineral	SSA (m <sup>2</sup> g <sup>-1</sup> )	CEC (cmol <sub>c</sub> kg <sup>-1</sup> )	Chemical formula
Sepiolite	384 ± 7	11 ± 1	(Si <sub>11.86</sub> Al <sub>0.14</sub> )(Mg <sub>7.9</sub> Al <sub>0.07</sub> )O <sub>30</sub> (OH) <sub>4</sub> (OH <sub>2</sub> ) <sub>4</sub> ·8H <sub>2</sub> O
Palygorskite	222 ± 4	14 ± 1	(Si <sub>7.88</sub> Al <sub>0.12</sub> )(Mg <sub>2.2</sub> Al <sub>1.67</sub> Fe <sub>0.20</sub> )O <sub>20</sub> (OH) <sub>2</sub> (OH <sub>2</sub> ) <sub>4</sub> ·4H <sub>2</sub> O



minerals was determined using the N<sub>2</sub>-BET method with an Autosorb-1 (Quantachrome Corp., New York), and the CEC was measured using the BaCl<sub>2</sub> extraction method described by Hendershot et al. (1993). The chemical formula was established based on the total chemical composition of the clay samples (Table 1).

MB and CV as chloride salts, together with TX100 and 15C5, were obtained from Aldrich Chemical Company and used as sorbates without further treatment. The chemical structure of these sorbates is illustrated in Figure 1.

#### Adsorption Isotherms

A 1% clay/distilled water suspension was prepared and stirred gently overnight. The pH and electrical conductivity (EC) of suspensions were adjusted to 7 and 0.2 dS m<sup>-1</sup> before the sorption experiment using 0.05 M HCl or NaOH and 0.05 M KCl, respectively. Ten mL of the clay suspension was placed in a 50-mL polypropylene screw-cap centrifuge tube. Then 25 mL electrolyte contained sorbate, with the same pH and EC as the clay suspension, was added to the tube, while the suspension was being stirred. The sorbate applied provided a concentration range of 0.00 to 1.25 mmol g<sup>-1</sup> clay in the final suspension. All samples were duplicated. Blanks of sorbate adjusted to EC = 0.2 dS m<sup>-1</sup> and pH 7 were also run to correct the data.

The tubes were protected from light and placed in a rotary shaker for 3 d at room temperature (24 ± 1 °C) to ensure that a pseudo-equilibrium was reached (Hermosin et al. 1993). The pH of the suspensions was measured and reported as the pH of the equilibrium solution. The suspensions were then centrifuged at 20,000 g for 15 min. The supernatants were analyzed after filtering (Millipore, 0.2 μm). The non-adsorbed dye was spectroscopically quantified in the filtrate. After dilution, which is especially crucial in MB measurement (Hang and Brindley 1970), the absorbance was read at 662 nm for MB and 588 nm for CV solutions using a Beckman Model DU Spectrophotometer. The total carbon was measured using a Shimadzu total carbon analyzer Model TOC-5050A as an indicator of the TX100 and 15C5 concentration in the filtrates.

The amounts of sorbed organic cations and neutral compounds were calculated as the difference between the initial and equilibrium concentrations in the respective solutions. The adsorption isotherms for organic cations were obtained by plotting the amounts of sorption (mmol g<sup>-1</sup>) versus the total amount of sor-

Figure 1. Chemical structure of TX100, 15C5, MB and CV.

bate added to the system. These isotherms were described by using the intrinsic binding coefficients, as explained below. The adsorption isotherms of neutral organic molecules, TX100 and 15C5, were described using a Langmuir type of equation by which the concentration of neutral sorption sites was estimated. The validity of the models used to describe the sorption data was evaluated based on the values of the determination coefficient ( $R^2$ ) and mean square of residuals (MSR).

#### Diffuse Reflectance FTIR

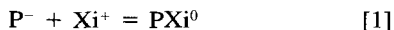
The clay surfaces were examined by diffuse reflectance Fourier transform infrared (DR-FTIR) spectrometry as suggested by Nguyen et al. (1990). Freeze-dried samples were examined by collecting 80 scans per second with a resolution of  $4 \text{ cm}^{-1}$ , using a Bio-Rad 3240 SPS microprocessor controlled spectrophotometer (Cambridge, Massachusetts). The spectra were compared against the reference spectrum of pure KBr and expressed in percent absorbance units. The spectrum of the homoionized clay was subtracted from that of the organo-clay complex after the sorption reaction to obtain the differential spectrum of the reaction product.

#### Adsorption Modeling

An extension of the model applied by Nir (1984, 1986), Nir et al. (1994) and Rytwo et al. (1995) was used to describe the sorption data. The main elements accounted for in this procedure were:

- 1) the cations tightly bound to the surface, which include cations sorbed to the neutral sorption sites in addition to the free and neutralized negative sites,
- 2) cations residing in the diffuse double layer,
- 3) polymerization of organic cations, and
- 4) solution of the Gouy-Chapman equation for a solid/liquid system containing monovalent cations and particles with planar surfaces. The concentrations of sorption sites in the solid/liquid system were included in the calculations with the units of mole  $\text{L}^{-1}$  ( $M$ ).

In the case of monovalent cations,  $\text{Xi}^+$ , that bind to uniquely charged negative sites,  $\text{P}^-$ , forming a neutral complex,  $\text{PXi}^0$ , on a clay surface, the reaction may be described as:



In this reaction, the magnitude of the intrinsic binding constant,  $\text{Ki}$ , is:

$$\text{Ki} = [\text{PXi}^0]/[\text{P}^-][\text{Xi}^+(0)] \quad [2]$$

where the concentrations are given in units of mol  $\text{L}^{-1}$  or molar ( $M$ ), and the unit of  $\text{Ki}$  is  $M^{-1}$ . The concentration of the cation,  $\text{Xi}^+$ , at the colloid surface is  $[\text{Xi}^+(0)]$ . If it is assumed that the clay surface is a plane with an evenly distributed negative charge, and if the counter-ions can be considered point charges in

a uniform liquid continuum, then the equilibrium distribution of exchange cations can be described quantitatively using the Boltzman equation (Van Olphen 1977) as:

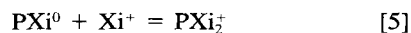
$$\text{Xi}^+(0) = \text{Xi}^+ \text{Y}(0)^{Zi} \quad [3]$$

in which  $\text{Xi}^+$  is the molar concentration of the cation in its monomeric form in the equilibrium solution,  $Zi$  is the valence of the given ion, and  $\text{Y}(0)$  is a parameter defined as:

$$\text{Y}(0) = \exp(-e\Psi(0)/kT) \quad [4]$$

where  $e$  is the absolute magnitude of an electronic charge,  $\Psi(0)$  is the surface potential,  $k$  is Boltzman's constant, and  $T$  is the absolute temperature. For a negatively charged surface,  $\text{Y}(0) > 1$ , and the concentration of the cation at the surface,  $\text{Xi}^+(0)$ , may be significantly larger than  $\text{Xi}^+$ . However, if charge reversal occurs,  $\Psi(0)$  is positive and  $\text{Y}(0) < 1$ .

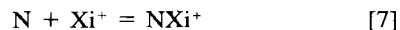
Another type of reaction is considered forming a charged complex ( $\text{PXi}_2^+$ ):



with a binding coefficient of:

$$\tilde{\text{Ki}} = [\text{PXi}_2^+]/[\text{PXi}^0][\text{Xi}^+(0)] \quad [6]$$

In the case of cation sorption by neutral sites, another reaction may also be considered forming a charged complex:



where the binding constant for this reaction can be defined as:

$$\text{Kn} = [\text{NXi}^+]/[\text{N}][\text{Xi}^+(0)] \quad [8]$$

In a closed system, for a given cation  $i$ , the total amount of the cation added to the system,  $Ci$ , consists of different proportions of ions adsorbed, residing in the solution and in the double layer regions. Analytical expressions for the latter were given by Nir et al. (1978). If  $Q_i$  is the excess amount of monovalent cations in the double layer region above their concentration in the solution, the total amount of cation in the system,  $Ci$ , is given by:

$$Ci = \text{Xi}^+ + \text{PXi}^0 + 2\text{PXi}_2^+ + \text{NXi}^+ + Q_i \quad [9]$$

Some organic cations (such as MB) can form dimers, trimers and even higher order of aggregates in solution (Spencer and Sutter 1979; Cenens and Shoonheydt 1988). Aggregation of molecules, which may be considered a proportion of added dye, reduces the concentration of monomer,  $\text{Xi}^+$ . The total concentration of primary molecules,  $\text{Xit}$ , in solution was given by Nir et al. (1983) as follows:

$$[\text{Xit}] = [\text{Xi}^+]/(1 - \text{Kag}[\text{Xi}^+])^2 \quad [10]$$

in which  $\text{Kag}$  is the corresponding binding coefficient

for aggregation in solution. The Kag may be determined from the adsorption spectrum of pure dye in solution. The adsorption of dye dimers or higher order aggregates may be ignored (Rytwo et al. 1991). Dye aggregation is significant when the dye addition exceeds the CEC of the clay, because below the CEC, almost all the dye is adsorbed.

If formation of  $PX_i^+$  is considered as complexation between a divalent cation and a single negative site, then according to Nir et al. (1994), in the absence of cation binding to the neutral sites, the surface charge density,  $\sigma$ , is related to  $\sigma_0$ , the surface charge density when no cation adsorbed to the surface, by:

$$\frac{\sigma}{\sigma_0} = \frac{P^- - \sum PX_i^+}{P^- + \sum PX_i^0 + \sum PX_i^+} \quad [11]$$

The  $\sigma_0$  is charge per unit surface area, which is defined as the ratio of the CEC to the specific surface area (SSA) of the clay. If CEC and SSA are expressed in units of  $\text{cmol}_c \text{kg}^{-1}$  and  $\text{m}^2 \text{g}^{-1}$ , respectively, the  $\sigma_0$  is calculated as  $0.96 \times \text{CEC/SSA}$  in units of Coulomb  $\text{m}^{-2}$  ( $\text{C m}^{-2}$ ). The  $\sigma_0$  corresponds to the total site concentration per unit area, PT, which is the sum of concentrations of all sites, both free and complexed. The actual surface charge density,  $\sigma$ , depends on the amount of free sites and the charged complex. The positively charged complex decreases the negative value of  $\sigma$ . The possibility of charge reversal arises when  $P^- < \sum PX_i^+$ . In cases where charged complexes due to binding to neutral sites of the mineral also exist, the actual surface charge density,  $\sigma$ , changes to more positive values, while  $\sigma_0$  remains unchanged (Equation 12):

$$\frac{\sigma}{\sigma_0} = \frac{P^- - \sum PX_i^+ - \sum NX_i^+}{P^- + \sum PX_i^0 + \sum PX_i^+} \quad [12]$$

The solution for the Gouy-Chapman equation by Delahay (1965) and Nir et al. (1978) for a planar surface gives a relation between the surface charge density,  $\sigma$ , the  $Y(0)$  parameter and the concentrations of ions in solution, as:

$$\sigma = \left[ \sum X_i^+ (Y_{(0)}^{z_i} - 1) \right]^{1/2} / g \quad [13]$$

where according to Nir (1986),  $g = 17 [80 \times 298 / (\epsilon T)]^{1/2}$  in which  $\epsilon$  is the bulk dielectric constant and  $T$  is the absolute temperature. The surface charge density is given in units of Coulomb per unit of surface area ( $\text{C m}^{-2}$ ).

By substitution of Equation [3] and considering the binding coefficients,  $X_i^+$  may be calculated from Equation [9] if the values of  $Y(0)$ ,  $P^-$  and  $N$  are known, and the  $X_i^+$  value may yield  $P^-$ ,  $N$  and  $Y(0)$  values in Equations [12] and [13]. This calculation may be done through an iterative procedure. The procedure consists of the following stages:

- 1) A guess is made for the values of  $Q_1$ ,  $Y(0)$ ,  $[P^-]$ , and  $[N]$ ,
- 2) the quantity of  $X_i^+$  is calculated using Equation [9],
- 3)  $Y(0)$  is calculated by knowing that  $Y(0) > 1$  if  $\sigma$  is negative, and  $Y(0) < 1$  if the summation of charged complexes exceeds the free sites,  $P^-$ ,
- 4) the concentrations of the complexed sites,  $PX_i^0$ ,  $PX_i^+$  and  $NX_i^+$ , are calculated,
- 5)  $P^-$  is calculated by subtraction of summation of  $PX_i^0$  and  $PX_i^+$  complexes from PT, total negative sites,
- 6)  $N$  is calculated by subtraction of  $NX_i^+$  from total  $N$  sites, and
- 7)  $Q_1$  is calculated with the analytical expressions in Nir et al. (1978). The solution concentration is then recalculated and another cycle of calculation of  $Y(0)$  begins.

Steps 2) to 7) are iterated and the criterion for convergence is the relative agreement of the values calculated in the previous cycle with those obtained in the current cycle. In case of MB sorption data, Equation [10] was also included to correct for the reduction of  $X_i^+$  due to aggregation of dye molecules. The intrinsic binding coefficients,  $K_i$ ,  $\bar{K}_i$  and  $K_n$ , may be chosen to provide the best estimation for the sorption data, as suggested by Rytwo et al. (1995), who established  $K_i$  and  $\bar{K}_i$  in the sorption of acriflavin (AF), MB and CV on montmorillonite. For the current work, values of  $K_i$  and  $\bar{K}_i$  are chosen as those determined for sorption of MB and CV on montmorillonite by Rytwo et al. (1995) to keep the calculation simple, and only  $K_n$  was estimated.

#### Estimation of Neutral Sorption Sites Concentration (N)

Assuming that neutral molecules are sorbed only by the neutral sorption sites, the sorption capacity of palygorskite and sepiolite for 2 neutral compounds, TX100 and 15C5, was examined. The sorption data were described by a Langmuir type isotherm and the sorption maximum was assumed to equal the number of neutral sorption sites. Using this equation, the molar concentration of sorbed neutral molecules,  $X$ , was described as:

$$X = \frac{KN[C]}{(1 + K[C])} \quad [14]$$

where  $[C]$  is the equilibrium molar concentration of free molecules in the solution,  $K$  is the Langmuir constant with a unit of  $M^{-1}$ , and  $N$  estimates the number of maximum sorption sites in units of  $M$ . The model was fitted to the sorption data based on  $R^2$  and MSR values using NLIN PROC of the SAS program (SAS Institute 1985).

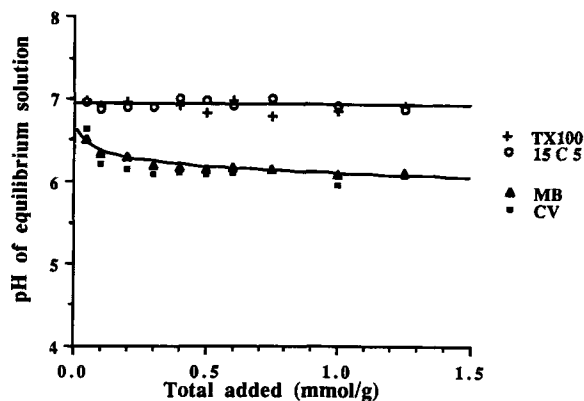


Figure 2. Sorption of neutral and cationic organic molecules by palygorskite and the pH of equilibrium solution.

## RESULTS AND DISCUSSION

### Sorption of TX100 and 15C5 by Palygorskite and Sepiolite

To estimate the quantity of the neutral sorption sites, the sorption of 2 neutral molecules, TX100 and 15C5, at different concentrations was examined. The justification for this experiment arises from the report given by Aznar et al. (1992) in which the sorption of surfactant TX100 by sepiolite did not replace the exchangeable  $Mg^{2+}$  from the clay surfaces. Furthermore, in our work, the sorption of TX100 and 15C5 did not decrease the pH, showing that the neutral molecules, TX100 and 15C5, did not interact with the cation exchange sites. Figure 2 shows the equilibrium pH of different suspensions. Sorption of organic cations, MB and CV, decreases the equilibrium pH more than 1 unit below the initial pH of the suspension, which was set up at 7. This is in accord with Wang et al. (1996) and Aznar et al. (1992), who reported that due to their high binding constants, organic cations such as MB in amounts above the CEC of clay minerals easily replace all inorganic exchangeable cations. The release of exchangeable  $H^+$  from the clay surfaces decreases the pH of the clay suspension, but in case of neutral molecules, sorption takes place on neutral sorption sites and no decrease in the initial pH of suspension was observed.

The molar concentration of sorbed molecules, when compared with the equilibrium concentration of free molecules, follows a Langmuir isotherm. Figure 3 il-

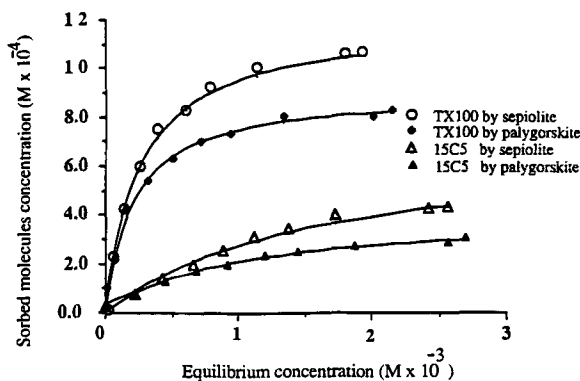


Figure 3. Sorption of neutral organic molecules, TX100 and 15C5, by palygorskite and sepiolite.

lustrates the sorption isotherms for TX100 and 15C5 by palygorskite and sepiolite, respectively. The  $N$ ,  $K$  and statistical values that estimate the sorption of neutral molecules by the 2 minerals are presented in Table 2. The sorption maximum of TX100 for palygorskite is  $9.3 \times 10^{-4} M$ , which exceeds the CEC of this mineral by more than a factor of 2. The application of this value as  $N$ , the total concentration of neutral sites, adequately described the sorption of organic cations on neutral sorption sites. The sorption maximum of palygorskite for 15C5 was  $4.1 \times 10^{-4} M$ , considerably lower than that of for sorption of TX100. The lower sorption of 15C5 may be due to its molecular size and the orientation of molecules on the clay surfaces.

Sorption of neutral molecules by sepiolite takes place in larger quantities than that of palygorskite, which may be a reflection of the larger surface area of sepiolite. The sorption maximum of TX100 by sepiolite was  $1.2 \times 10^{-3} M$ , which surpasses its CEC by about 4 times. Adsorption of 15C5 by sepiolite was lower than the adsorption of TX100, although it was still twice as much as the CEC of this mineral. The  $N$  value was also best estimated by the sorption maximum of sepiolite for TX100.

### Sorption of Organic Cations

Sorption of organic cations, MB and CV, by palygorskite and sepiolite was modeled to estimate the contribution of different sites involved in sorption processes. In this study, the intrinsic binding constants  $K_i$  and  $\bar{K}_i$  of both MB and CV in the formation of the neutral complex,  $PX_i^0$ , and the charged complex,

Table 2.  $N$ ,  $K$  and statistical values describing sorption isotherms of neutral molecules on palygorskite and sepiolite.

Clay mineral	Compound	$N$ (M)	$K$ ( $M^{-1}$ )	$R^2\%$	MSR
Palygorskite	TX100	$9.3 \times 10^{-4}$	4800	99.75	$9.2 \times 10^{-10}$
	15C5	$4.1 \times 10^{-4}$	1060	99.95	$2.1 \times 10^{-10}$
Sepiolite	TX100	$1.2 \times 10^{-3}$	3800	99.83	$1.5 \times 10^{-09}$
	15C5	$7.0 \times 10^{-4}$	4860	99.75	$9.2 \times 10^{-10}$

Table 3. The intrinsic binding constants and statistical values describing sorption of CV and MB on palygorskite and sepiolite.

Clay mineral	Compound	$K_i (M^{-1})$	$\bar{K}_i (M^{-1})$	$K_n (M^{-1})$	$R^2\%$	MSR
Palygorskite	CV	$1.0 \times 10^6$	$8 \times 10^9$	$6 \times 10^6$	99.18	$6.68 \times 10^{-5}$
	MB	$3.0 \times 10^8$	$1 \times 10^6$	$6 \times 10^6$	99.31	$1.78 \times 10^{-5}$
Sepiolite	CV	$1.0 \times 10^6$	$8 \times 10^9$	$6 \times 10^6$	99.50	$1.42 \times 10^{-4}$
	MB	$3.0 \times 10^8$	$1 \times 10^6$	$6 \times 10^6$	99.43	$3.44 \times 10^{-5}$

$PX_i^+$ , on montmorillonite previously reported by Rytwo et al. (1995) were applied. The logic behind this application was that the cation exchange reaction in different silicate clays may have a similar nature. Sorption of the cations at a lower level of addition, in which the formation of  $NXi^+$  is still negligible, was described satisfactorily using these coefficients. Therefore, only  $K_n$ , the binding constant of charged complex formation on neutral sites,  $NXi^+$ , was estimated in this work. A  $K_n$  of  $6 \times 10^6 M^{-1}$  provides the best estimate for the total CV sorption of sepiolite with a determination coefficient of 99.50% and MSR of  $1.42 \times 10^{-4}$  (Table 3). This value of  $K_n$  was also used to describe the sorption of the cations on neutral sites in other systems. The intrinsic binding constants applied in this study and statistical values evaluating the goodness of the estimations are presented in Table 3.

It is noteworthy that the quantities of cations residing in diffuse double layer that were calculated for different amounts of added sorbate were very low, at least 3 orders of magnitude smaller than the sorbed cations. Therefore, they were not presented as a constituent of total sorbed dye. This may reflect the relatively low concentration of ions in the experimental solution. Also, the high affinity of organic cations to form different clay-dye complexes is another factor that increases the proportion of sorbed cations over those residing in the diffuse double layer.

The contribution of the different complexes in sorption of CV by palygorskite is presented in Figure 4. The total sorption of CV by this mineral reached 0.5

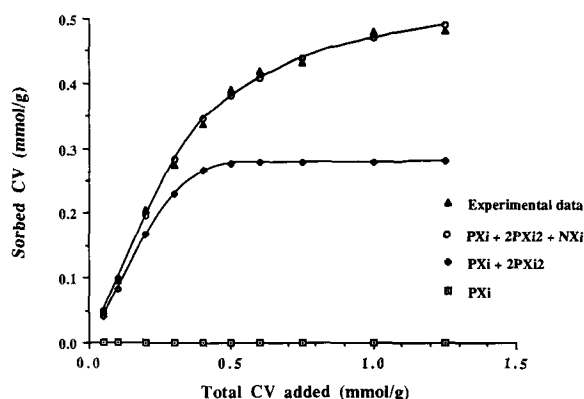


Figure 4. Contribution of different complexes,  $PXi^0$ ,  $PXi_2^+$  and  $NXi^+$ , to total CV sorbed by palygorskite.

mmol  $g^{-1}$ , which is 3.6 times as much as the CEC (Table 1) of this mineral. The quantity of CV adsorbed by montmorillonite, as reported by Rytwo et al. (1995), leveled off at close to 200% of the CEC. This suggests that in palygorskite, the neutral sites play a more significant role than montmorillonite in sorption of organic cations. The significance of neutral sorption sites increases with the level of cation addition.

It seems that at levels of addition below the CEC, the contribution of the  $NXi^+$  complex to total sorption is negligible. Due to the relatively high affinity of CV to form the  $PXi_2^+$  complex, the concentration of neutral complex  $PXi^0$  constitutes an insignificant portion of total clay-cation complexes. The amount of sorbed CV was somewhat higher than that of MB for both clay minerals. The higher affinity of this compound to form charged complexes,  $PXi_2^+$ , on negative sorption sites may be a factor explaining the higher sorption of this cation, but the main reason seems to be the tendency of MB to form aggregates in the solution, thereby reducing the monomer concentration (Cenes and Shoonheydt 1988; Rytwo et al. 1995). Rytwo et al. (1991) also reported that CV shows a better diffusion into the clay aggregates that leads to sorption of this cation, even after flocculation of clay particles that may occur due to sorption of cations. Inclusion of Equation [9], which accounts for aggregation of MB in the solution, in the iterative procedure, successfully described the lower sorption of MB for both clay minerals. The constant  $K_{ag}$ , which shows the tendency of MB molecules to form polymers, was chosen as  $5880 M^{-1}$ , which was the value suggested by Bergmann and O'Konski (1963) and also used by Rytwo et al. (1995).

The contribution of neutral sites in sorption of MB by palygorskite is also quite significant, while the neutral complex,  $PXi^0$ , forms a relatively large proportion of total sorbed cations (Figure 5). MB seems to form lower concentrations of charge reversal complexes,  $PXi_2^+$  and  $NXi^+$ , and therefore, in the case of sorption of MB, the surface potential is expected to be lower than that for the corresponding concentration of added CV. In several studies, MB and/or CV have been used to determine the CEC of silicate clay minerals (Rytwo et al. 1991; Wang et al. 1996). Considering the results of this work, it seems that MB sorption data would better estimate the CEC of silicate clay minerals than CV.

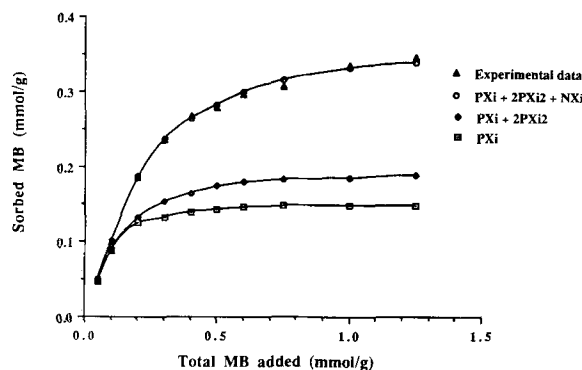


Figure 5. Contribution of different complexes,  $PXi^0$ ,  $PXi_2^+$  and  $NXi^+$ , to total MB sorbed by palygorskite.

Formation of different dye-sepiolite complexes is illustrated in Figures 6 and 7. The CV sorption of sepiolite levels off at close to  $0.6 \text{ mmol g}^{-1}$ , which is about 4.6 times as much as the CEC of this mineral. The contribution of neutral sorption sites at the maximum CV sorbed reaches more than 60% of total sorption. Due to the larger surface area and lower CEC of this mineral compared to palygorskite, the neutral sites play a more important role in sorption processes by sepiolite. Since the binding constant for neutral sites is less than for the charge reversal complex, as  $PXi_2^+$  (despite the higher sorption capacity of sepiolite for organic cations), the release of sorbed cations is expected to be easier in this mineral than palygorskite. This behavior makes sepiolite a more appropriate carrier for cationic organic molecules. In the case of MB sorption by sepiolite, the contribution of neutral sites reaches about 70% of the total sorption, which supports the above view.

#### Surface Potential of Dye-Clay Complexes

As suggested by Nir (1986), the surface potential of the clay minerals at room temperature and different levels of dye addition was estimated in mV using the

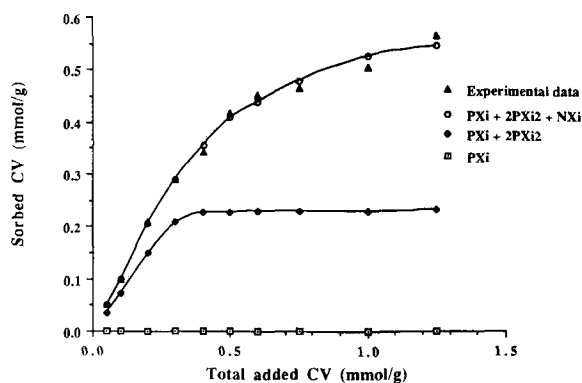


Figure 6. Contribution of different complexes,  $PXi^0$ ,  $PXi_2^+$  and  $NXi^+$ , to total CV sorbed by sepiolite.

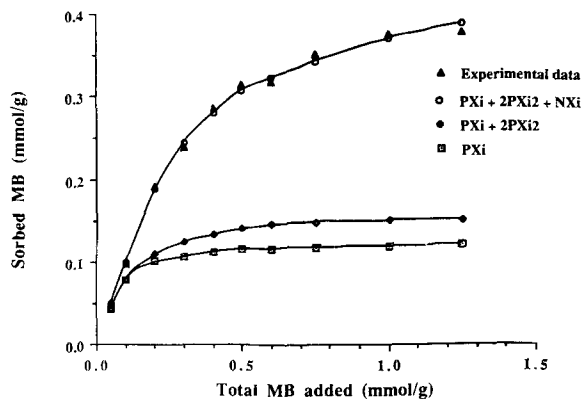


Figure 7. Contribution of different complexes,  $PXi^0$ ,  $PXi_2^+$  and  $NXi^+$ , to total MB sorbed by sepiolite.

experimental data, by a simplified form of Equation [4], as:

$$\Psi(0) = -25 \ln[Y(0)] \quad [15]$$

The calculated values of  $\Psi(0)$  for palygorskite and sepiolite at different levels of MB and CV addition are given in Table 4. Charge reversal occurs when the total dye of  $0.2 \text{ mmol g}^{-1}$  was added, which exceeds the CEC of palygorskite and sepiolite by about 40% and 60%, respectively. Sorption of CV seemingly induces larger positive values of surface potential, which is due to the larger quantities of sorbed CV that are exceeding the CEC of the minerals studied. As discussed earlier, the reason for this may be the larger binding coefficient of CV for the formation of charged complex,  $PXi_2^+$ , as well as the higher concentration of monomer in CV solution.

At very low levels of dye addition (for example,  $0.05 \text{ mmol g}^{-1}$ ), however, MB seems to be more efficient at reducing the surface potential of the minerals. The larger  $K_i$  value of MB than CV results in the formation of a higher quantity of neutral complex,

Table 4. Calculated values for surface potential of palygorskite and sepiolite at different levels of MB or CV addition.

Total addition (mmol sorbate/g clay)	Surface potential, $\Psi(0)$ (mV)			
	Pal-MB	Pal-CV	Sep-MB	Sep-CV
0.05	-129	-137	-91	-109
0.10	-105	-99	-67	-54
0.20	97	102	88	96
0.30	128	172	108	151
0.40	150	194	134	172
0.50	161	206	150	175
0.60	184	215	183	191
0.75	189	216	186	202
1.00	192	218	190	209
1.25	199	220	197	211

Key: Pal = palygorskite, Sep = sepiolite.

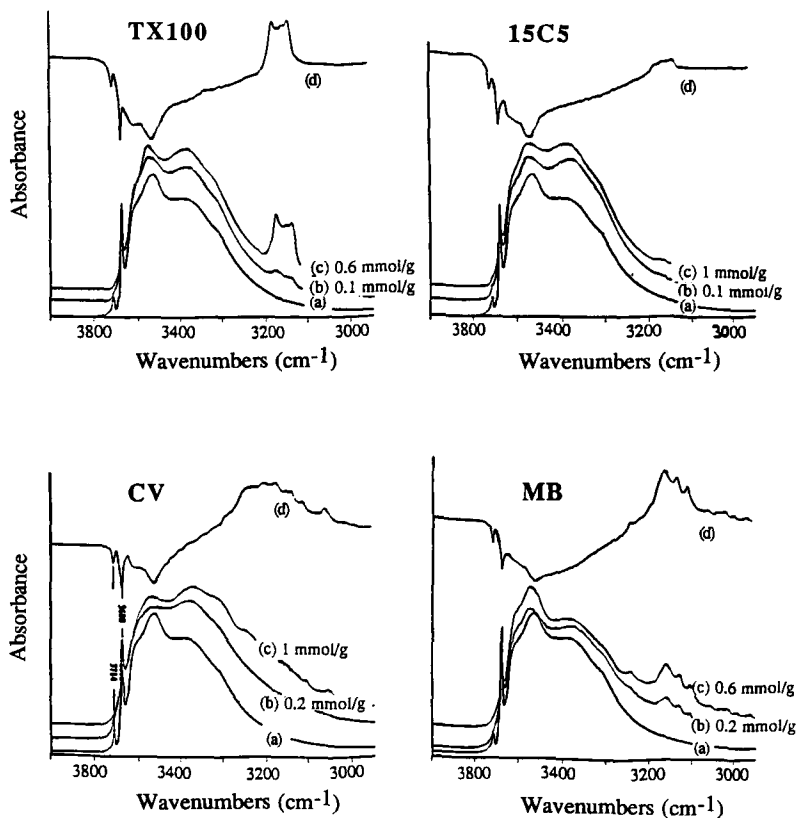


Figure 8. FTIR spectra of (a) sepiolite, (b) and (c) sepiolite with different levels of organic compound additions and (d) a differential spectrum of (c) minus (a).

PXi<sup>0</sup>, which is apparently the main sorption product at low levels of dye addition. This, in turn, results in a higher neutralization of surface negative charges by MB than CV at this level of dye addition.

The calculated surface potentials also showed larger values for palygorskite than for sepiolite in corresponding conditions. The difference between the 2 minerals may be explained by the larger surface area and lower CEC of sepiolite, which results in lower surface charge density and consequently lower surface potential. Palygorskite colloids showed a higher dispersability than sepiolite during the experiment. However, they consist of larger particles as revealed by surface area data and electron microscopy (Shariatmadari 1998). Higher surface potential values may induce more repulsion among the palygorskite colloids, causing the larger dispersability of this mineral.

#### FTIR Spectroscopy of the Organo-Clay Complexes

To understand the sorption mechanisms of neutral and cationic organic molecules, the clay-organic molecule complexes were examined by diffuse reflectance FTIR. The FTIR patterns of pure sepiolite were plotted against sepiolite-organic complexes. The FTIR patterns for sorption of neutral molecules TX100 and

15C5 are presented in Figure 8. The  $\nu_{\text{OH}}$  band at 3720  $\text{cm}^{-1}$ , representing the silanol group (Si-OH) in sepiolite (Ahlrichs et al. 1975), has disappeared due to the sorption of neutral molecules upon saturation of the mineral. Similar results were observed by Aznar et al. (1992) in sorption of MB on sepiolite gels. Since the silanol groups are located at the external edges of mineral fibers, they are easily accessible and interact almost totally with the sorbate molecules.

The differential spectra also show some perturbation of the  $\nu_{\text{OH}}$  3680  $\text{cm}^{-1}$  band that is related to the OH group attached to octahedral Mg. Since these bands are mainly located at the interior of crystal blocks, the relative perturbation may be due to physical hindrance by sorbate and involvement of these groups in sorption at sites of crystal defects.

The FTIR spectra of sorbed organic cations, MB and CV (Figure 8), show almost the same pattern as neutral molecules. This suggests that organic cations react with silanol groups by the same mechanism as neutral molecules. Since the neutral sites are located at the external surfaces of the fibrous clay particles, the external surface area is a major criterion controlling the number of neutral sorption sites and the contribution of these sites to total sorption.



The FTIR spectra of palygorskite (not shown) revealed a sharp band at  $3625\text{ cm}^{-1}$  assigned to  $\nu_{\text{OH}}$  in  $\text{Al}_2\text{-OH}$  of the octahedral structure (Serna et al., 1977). The presence of Si-OH groups in palygorskite was observed by a very weak shoulder at  $3704\text{ cm}^{-1}$  that was perturbed by sorption of organic molecules. The intensity of the  $3625\text{-cm}^{-1}$  band was also reduced possibly due to physical coverage of particles by sorbates. The low intensity of the Si-OH band in palygorskite indicates fewer edge surfaces or less imperfections than were observed for the sepiolite. The lower specific surface area of this mineral,  $220\text{ m}^2\text{ g}^{-1}$ , in contrast to  $380\text{ m}^2\text{ g}^{-1}$  for sepiolite, also suggests that palygorskite particles have fewer exposed edges.

### CONCLUSIONS

Palygorskite and sepiolite clay minerals are widely used in applications that take advantage of their sorptive characteristics. Sorption of 2 cationic and 2 neutral organic compounds on palygorskite and sepiolite was examined. The sorption maxima and the contribution of different sorption sites were compared for the 2 minerals. A sorption model that considers formation of different complexes described the sorption isotherms of the organic cations on palygorskite and sepiolite. Use of such a model in sorptive applications of the clays may improve understanding of colloid behavior and lead to more efficient use of these minerals.

For both palygorskite and sepiolite, the sorption of organic cations exceeds the CEC of minerals. The neutral sorption sites become more important as the sorption approaches its maxima. The sorption maxima of sepiolite, as well as the contribution of neutral sorption sites in the sorption of the organic cations on sepiolite, were larger than those of palygorskite. This shows that sepiolite may be a more appropriate carrier for organic cations than palygorskite. The calculated values of surface potential for palygorskite were somewhat larger than those for sepiolite which indicates a higher intrinsic surface charge density for this mineral. This may explain the larger dispersability of palygorskite over that of sepiolite in experimental suspensions.

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### REFERENCES

Ahrlrichs JL, Serna C, Serratos JM. 1975. Structural hydroxyls in sepiolite. *Clays Clay Miner* 23:119–124.  
 Aznar JA, Casal B, Ruiz-Hitzky E, Lopez-Arbeloa I, Lopez-Arbeloa F, Santaren J, Alvarez A. 1992. Adsorption of methylene blue on sepiolite gels: Spectroscopic and rheological studies. *Clay Miner* 27:101–108.  
 Banerjee K, Dureja P. 1995. Photo stabilization of quinalphos by crystal violet on the surface of kaolinite and palygorskite. *Pesticide Sci* 43:333–337.

Bergmann K, O'Konski CT. 1963. A spectroscopic study of methylene blue monomer, dimer, and complexes with montmorillonite. *J Phys Chem* 67:2169–2177.  
 Casal Piga B, Ruiz-Hitzky E. 1977. Reaction of epoxides on mineral surfaces. Organic derivatives of sepiolite. *Proc 3rd Eur Clay Conf; Oslo*, p 35–37.  
 Cenens J, Shoonheydt RA. 1988. Visible spectroscopy of methylene blue on hectorite, laponite B and barasym in aqueous suspension. *Clays Clay Miner* 36:214–224.  
 Delahay P. 1965. Double layer and electrode kinetics. New York: Interscience Publ. 321 p.  
 Galan E. 1996. Properties and applications of palygorskite-sepiolite clays. *Clay Miner* 31:443–453.  
 Gerstl Z, Mingelgrin U. 1979. A note on the adsorption of organic molecules on clays. *Clays Clay Miner* 27:285–290.  
 Gerstl Z, Yaron B. 1981. Attapulgitic pesticide interactions. *Residue Rev* 78:69–99.  
 Hang PT, Brindley GW. 1970. Methylene blue absorption by clay minerals. Determination of surface areas and CEC. *Clays Clay Miner* 18:203–212.  
 Hendershot WH, Lalonde H, Duquette M. 1993. Ion exchange and exchangeable cations. In: Carter MR, editor. Soil sampling and methods of analysis. Boca Raton, Florida. Lewis Publ. p 167–176.  
 Hermosin MC, Cornejo J. 1986. Methylation of sepiolite and palygorskite with diazomethane. *Clays Clay Miner* 34:591–596.  
 Hermosin MC, Martin P, Cornejo J. 1993. Adsorption mechanisms of monobutyltin in clay minerals. *Environ Sci Technol* 27:2606–2611.  
 Kunze GW, Dixon JB. 1986. Pretreatment for mineralogical analysis. In: Klute A, editor. Methods of soil analysis, Part 1: Physical and mineralogical methods, 2nd ed. Madison, WI: SSSA. p 91–100.  
 Margulies L, Rozen H, Nir S. 1988. Model for competitive adsorption of organic cations on clays. *Clays Clay Miner* 36:270–276.  
 Nguyen TT, Janik LJ, Raupach M. 1990. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy in soil studies. *Aust J Soil Research* 29:49–67.  
 Nir S. 1984. A model for cation adsorption in closed systems: Application to calcium binding to phospholipid vesicles. *J Colloid Interface Sci* 102:313–321.  
 Nir S. 1986. Specific and non specific cation adsorption to clays. Solution concentrations and surface potentials. *Soil Sci Soc Am J* 50:52–57.  
 Nir S, Bentz J, Wilschut J, Duzgunes N. 1983. Aggregation and fusion of phospholipid vesicles. *Prog Surf Sci* 13:1–124.  
 Nir S, Newton C, Papadhadjopoulos D. 1978. Binding of cations to phosphatidylserine vesicles. *Bioelectrochem Bioenerg* 5:116–133.  
 Nir S, Rytwo G, Yermiyahu U, Margulies L. 1994. A model for cation adsorption to clays and membranes. *Colloid Polym Sci* 272:619–632.  
 Ruiz-Hitzky E, Fripiat JJ. 1976. Organomineral derivatives obtained by reacting organochlorosilanes with the surface of silicates in organic solvents. *Clays Clay Miner* 25:25–30.  
 Rytwo G, Nir S, Margulies L. 1995. Interactions of monovalent organic cations with montmorillonite: adsorption studies and model calculations. *Soil Sci Soc Am J* 59:554–564.  
 Rytwo G, Serban C, Nir S, Margulies L. 1991. Use of methylene blue and crystal violet for determination of exchangeable cations in montmorillonite. *Clays Clay Miner* 39:551–555.  
 SAS Institute. 1985. SAS users guide: Statistics. Version 5 ed. Cary, NC: SAS Inst.

- Serna CJ, Van Scoyoc GE, Ahlrichs JL. 1977. Hydroxyl groups and water in palygorskite. *Am Mineral* 62:784–792.
- Shariatmadari H. 1998. Interactions of phosphates and selected organic molecules with palygorskite and sepiolite [Ph.D. thesis]. Dept. of Soil Science, Univ of Saskatchewan, Saskatoon, SK S7N 5A8 Canada. 195 p.
- Spencer W, Sutter JR. 1979. Kinetic study of the monomer-dimer equilibrium of methylene blue in aqueous solution. *J Phys Chem* 83:1573–1576.
- Van Olphen H. 1977. An introduction to clay colloid chemistry, 2nd ed. New York. J. Wiley. 318 p.
- Wang MK, Wang SL, Wang WM. 1996. Rapid estimation of cation exchange capacities of soils and clays with methylene blue exchange. *Soil Sci Soc Am J* 60:138–141.

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