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METHYLENE BLUE DIMERIZATION DOES NOT INTERFERE IN SURFACE-AREA MEASUREMENTS OF KAOLINITE AND SOILS

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Abstract—Methylene blue (MB) was adsorbed from aqueous solutions onto a kaolinite and four soil samples to determine the effects of MB dimerization on the measured surface area. Adsorption isotherms were prepared using four adsorbing solutions containing, respectively, 9, 46, 71, and 83% of MB molecules in the dimeric state. Langmuir-type isotherms were obtained in each case. The results indicate that equilibration occurs quickly. The aggregation state of MB molecules at the surface does not depend on the aggregation state in the initial adsorbing solutions, but on the final equilibrium concentration of MB. A comparison with the specific surface area measured by adsorption of ethylene glycol monoethyl ether indicates that MB adsorbs as a monomer, regardless of the aggregation number in solution. This result occurs owing to the strength of monomer-surface and monomer-monomer interactions. If monomer-surface interactions are favored, the MB dimer adsorbs in the monomeric form. If monomer-monomer interactions are favored, dimer adsorption may occur. The visible spectra of adsorbed molecules indicated that MB was present at the surface as a mixture of monomeric and dimeric species. These results suggest that dimers are formed in the contact region between two aggregating particles.

Key Words—Dye Adsorption, Ethylene Glycol Adsorption, Kaolinite Surface, Methylene Blue Dimerization, Specific Surface Area.

INTRODUCTION

The principle for estimating the specific surface area (S) of a powder material from adsorption experiments is simple. By adsorbing a chemical of known molecular cross section and determining the amount necessary for monolayer coverage, the surface area of the studied adsorbent is evaluated. However, the surface orientation and the packing density of an adsorbate can change from solid to solid owing to their intrinsic surface properties. Therefore, a precise evaluation of the effective molecular cross section of the adsorbed chemical species may be difficult, and the calculated surface area may be inaccurate.

The most suitable methods for evaluating the specific surface area of solids are those that do not change the surface and those that use the most appropriate adsorbate molecules. For example, if the area of a catalyst used for gas-phase reactions of small molecules is required, the suitable technique is gas adsorption of a small adsorbate. Either a polar or a non-polar adsorbate is used depending on the properties of the catalyzed molecules. If the sample is lake-sediment material, adsorption experiments from an aqueous solution are best. Adsorption of a polar liquid, such as ethylene glycol monoethyl ether (EGMEE) (Carter *et al.*, 1965), could also be useful for these sediments.

Adsorption of methylene blue (MB) from aqueous solution has frequently been used for the determination of S (Potgieter, 1991; Brina and De Battisti, 1987; Helmy *et al.*, 1999). This method is simple and versatile because MB has a strong affinity for most solid surfaces (Bergmann and O'Konski, 1963; Margulies *et al.*, 1988; Rytwo *et al.*, 1998). Methylene blue has a special affinity for negatively charged surfaces, and its concentration is easily quantified by spectrophotometry. Thus, an adsorption isotherm with a distinct plateau can be obtained and used for an accurate determination of monolayer mass. The MB method is convenient for surface-area measurements on sediments from water bodies and clay or soil samples where the properties of the clay-water or soil-water interface are important. Moreover, because MB is a heterocyclic cationic compound with molecular dimensions and chemistry similar to some herbicides, such as diquat and paraquat, the MB method is an appropriate technique to measure the surface area of soil materials where interactions with herbicides are of interest.

The applicability of the MB adsorption method for surface-area measurements is often disputed because chemisorption commonly occurs and the dye molecule may adsorb on specific sites rather than the total surface area (Van den Hul and Lyklema, 1968). Also, MB may form dimers or larger aggregates either in solution or in the adsorbed state (Spencer and Sutter, 1979; Bujdák and Komadel, 1997). The reaction $(MB)_2 \leftrightarrow 2MB$ with an equilibrium constant K_1 of 1.7×10^{-4} (Bergmann and O'Konski, 1963) indicates that dimer is present in relatively dilute solutions and that dimerization is favored by increasing MB concentration. Concerning the adsorbed state, Bergmann and O'Konski (1963) found that the visible spectrum of adsorbed MB is similar to that of dimeric or n-meric MB in solution. They concluded that MB aggregates

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Table 1. Composition (%) and cation-exchange capacity (CEC) of the studied solids.

Sample	Organic material	Clay	Silt	Sand	10^5 CEC (eq/g)
HAPL1	4.7	24	46	31	24
HAPL2	5.3	25	55	20	—
ARG1	3.7	33	51	16	26
ARG2	5.0	36	57	7.0	—
Kaolinite	—	—	—	—	7.9

— Not measured.

on the surface of montmorillonite even at very low surface coverage. Bujdák and Komadel (1997) determined that MB aggregation on montmorillonite strongly depends on the charge density of the clay and the equilibration time. Koopal (1978) also reported dimer adsorption of MB on silver iodide and Rytwo *et al.* (1998) postulated dimer formation on sepiolite. Because the dimer is a face-to-face association of two flat MB molecules (Bergmann and O'Konski, 1963), the dimer and the monomer occupy similar areas if they lay flat at the surface. Hence, the mass necessary to form a "monolayer" of dimers is about twice the mass necessary to form a monolayer of monomers. If dimerization at the surface is not considered, the estimated area will be twice the actual one.

It is sometimes assumed that dimer adsorption is avoided by working with dilute MB solutions, where dimers are absent (Brina and De Battisti, 1987). The assumption is that no change in the aggregation number occurs upon adsorption. Thus, if only monomers are present in solution, only monomers are adsorbed to the surface, and if only dimers are present, only dimers are adsorbed. However, there is no experimental evidence to support this assumption. In the presence of an interface, dimerization may be induced by special interactions with the surface or with previously adsorbed molecules. These interactions could lead to the formation of aggregates in the adsorbed state although they are absent in solution. The opposite phenomenon may also occur, *i.e.,* dimers from concentrated MB solutions may cover a surface in the form of only monomers.

No change in the aggregation number upon adsorption means that equilibration is kinetically inhibited by the surface. Although dimer formation and splitting are rapid processes in solution (Spencer and Sutter, 1979), the equilibration rate may be slowed by the surface. If this is the case, equilibration is not attained after a rapid adsorption of monomers and/or dimers, and the aggregation state of attached MB is dependent on the concentration of the adsorbing MB solution. The mass of MB required to saturate the surface will be higher for samples treated with concentrated solutions containing a larger fraction of dimers. In contrast, if equilibrium is quickly achieved, the aggregation state of attached MB will not depend on the monomer/dimer content of the initial solution but on the equilibrium concentration. Therefore, the mass of MB required to saturate the surface will be always the same regardless of the initial solution concentration.

The aim of this article is to evaluate whether dimerization of MB affects specific surface-area measurements of clay and soil samples. A possible condition for adsorption of MB in the monomeric form is discussed. A comparison of MB surface areas with the areas measured by EGMEE adsorption is given also.

MATERIALS AND METHODS

The studied solids were a kaolinite from Georgia, USA and four soil samples from the province of Córdoba, Argentina. The kaolinite X-ray diffraction pattern indicated that the sample is low-defect and nearly pure material. The soils were collected from the central region of the province of Córdoba, Argentina from Ap horizons at 0–18 cm. Two samples (ARG1 and ARG2) are typical Argiustolls and two samples (HAPL1 and HAPL2) were entic Haplustolls. The ARG1 and HAPL1 soils were cultivated, whereas the ARG2 and HAPL2 soils were uncultivated, having only their native vegetation. The samples were air-dried and sieved to separate the <2-mm size fraction. Prior to the studies, the soil samples and kaolinite were vacuum dried. No other special treatments were performed on the samples. Organic material (OM), silt, cation-exchange capacity (CEC), clay, and sand contents of the samples are shown in Table 1. The inorganic phase of these soils is dominated by illite with small quantities of smectite, quartz, feldspar, and chlorite (Velasco and De Pauli, 1993).

MB adsorption

Three MB solutions were used in the experiments with kaolinite, with concentrations of MB of 4.2×10^{-6}, 5.3×10^{-5}, and 2.3×10^{-4} M. The K_1 value of 1.7×10^{-4} indicates that the content of MB molecules in the dimeric state was 9, 46, and 71%, respectively. These solutions are hereafter referred to as 9, 46, and 71% adsorbing solutions. The solution used with the soil samples was more concentrated (6.8×10^{-4} M, 83% of molecules in dimeric state). The adsorption experiments were designed so that only one of the MB adsorbing solutions was added to a solid sample. Therefore, if no change in the aggregation number occurs during adsorption, the fraction of attached dimers is known and equal to that of the bulk solution.

The adsorbing solutions were prepared by dissolving MB and NaCl in a phosphate buffer solution (USA National Bureau of Standards, pH = 6.86). Because phosphate specifically adsorbs to oxide, clay, and soil surfaces, it helps to generate a surface with a relatively homogeneous negative charge that increases the affinity of MB for the surface and that decreases specific

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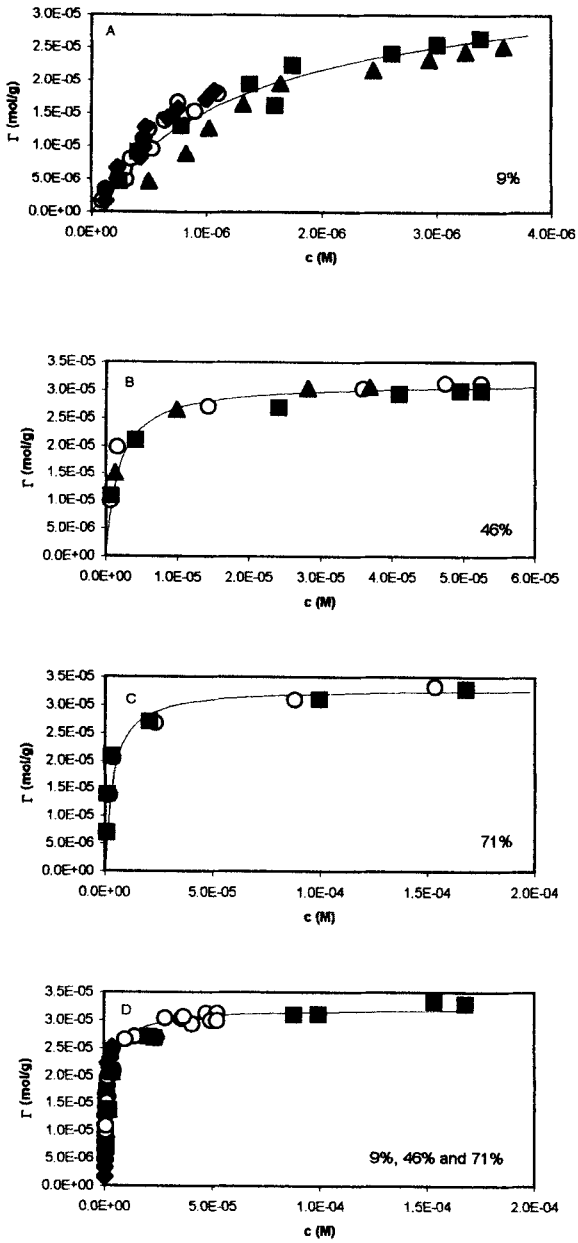


Figure 1. Adsorption isotherms of MB on kaolinite. The number in the right corner of each plot is the percentage of MB dimers present in the initial adsorbing solutions. Different symbols in the plots denote different experiments. Lines were calculated using the Langmuir equation, and parameters from Table 1. Figure 1D combines the data of Figure 1A to 1C.

sites present. The NaCl concentration used was 0.1 M. The high ionic strength improved the centrifugation of the suspensions and may have decreased the lateral repulsion between adsorbed MB molecules. Solid samples (0.1–0.2 g) were dispersed in a given adsorbing solution in a centrifuge tube. After adsorption occurred (~15 min), the dispersion was centrifuged, the supernatant transferred to a spectrophotometer cell for MB quantification, and a new aliquot of the adsorbing solution was added to the sample. This procedure was repeated until the concentration of MB in the supernatant was near that of the adsorbing solution. The mass of MB adsorbed in every step was calculated from the difference in concentrations of the adsorbing solution and the supernatant. The total mass adsorbed was calculated as the sum of the masses adsorbed in each step, and an adsorption isotherm was then calculated for each sample. The advantage of the method is that it allows the determination of an adsorption isotherm by treating the solid with only one of the MB adsorbing solutions. A disadvantage of the method is that the maximum equilibrium concentration that is attainable is that of the adsorbing solution. After the adsorption isotherm was obtained, the mass for monolayer coverage, Γ_m, and the adsorption constant, b, were calculated by using a nonlinear least-squares regression analysis (Schulthess and Dey, 1996) of the Langmuir equation, $\Gamma = \Gamma_m bc/(1 + bc)$, where Γ is the mass of MB adsorbed at the equilibrium concentration, c. The specific surface area was calculated from Γ_m assuming a cross section of 120 Å^2 for the MB molecule.

The Langmuir constant is not a true equilibrium constant. At the solid-water interface, adsorption reactions are actually exchange reactions where adsorbate molecules compete with other molecules for locations at the surface (Adamson, 1976). For the conditions here, MB may exchange with either solvent H_2O molecules or with sodium ions from the supporting electrolyte. In dilute MB solutions with a constant concentration of Na^+, the activity of water and Na^+ are constant. Then, b is related to the constant of the adsorption (exchange) reaction, K_L, by $b = K_L/a_x$ (Adamson, 1976), where a_x represents the activity of either water or Na^+.

The concentrations of MB in the supernatant solutions were measured spectrophotometrically by using a UV-1601 Shimadzu apparatus at 664 nm. Spectral curves between 400–800 nm were obtained for sample dispersions containing adsorbed MB. The conditions were selected so that $\Gamma > 0.9\Gamma_m$. The amount of MB in the bulk solution surrounding the particles was negligible with respect to the amount of attached MB.

EGMEE adsorption

The method used to measure S by adsorption of EGMEE was modified from Carter *et al.* (1965). The samples (7–10 g) were weighed in a glass beaker, 3 ml of EGMEE were then added, and the beaker was placed in a vacuum chamber containing $CaCl_2$ saturated with EGMEE. Vacuum was applied to the chamber until free liquid was no longer visible. Thereafter, cycles of 1-h vacuum followed by 1-h equilibration

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Table 2. Langmuir parameters for the adsorption isotherms of the studied samples and surface-area values as obtained from methylene blue and ethylene glycol monoethyl ether adsorption.

Sample	Adsorbing solution concentration (M)	MB			EGMEE
		Log(b)	$10^5\Gamma_m$ (mol/g)	S (m^2/g)	S (m^2/g)
Kaolinite	4.3×10^{-6}	5.80 ± 0.20[1]	3.7 ± 1.0[1]	26 ± 7[1]	19 ± 3[1]
	5.2×10^{-5}	5.75 ± 0.20	3.15 ± 0.20	23 ± 2	—
	2.3×10^{-4}	5.45 ± 0.20	3.30 ± 0.10	24 ± 1	—
HAPL1	6.8×10^{-4}	4.90 ± 0.20	15.0 ± 2	108 ± 12	102 ± 10
HAPL2	6.8×10^{-4}	4.60 ± 0.20	15.2 ± 2	110 ± 12	110 ± 10
ARG1	6.8×10^{-4}	5.00 ± 0.20	12.9 ± 2	93 ± 12	90 ± 10
ARG2	6.8×10^{-4}	4.30 ± 0.20	16.0 ± 2	116 ± 12	80 ± 10

[1] Error values are given as $\pm 2\sigma$.

and weighting steps were applied. The cycles were repeated until constant weight was reached. Under these conditions, a monolayer of EGMEE remains adsorbed. The mass for monolayer coverage was determined by weight differences and S was calculated assuming a cross-sectional area of 52.3 Å^2 for the EGMEE molecule (Carter *et al.*, 1965).

RESULTS AND DISCUSSION

Figure 1A, 1B, and 1C shows MB/kaolinite isotherms obtained using the 9, 46, and 71% adsorbing solutions, respectively. Figure 1D compares the previous curves. The concentration of MB in the 9% adsorbing solution seemed to be too low to achieve surface saturation because the isotherms in Figure 1A do not reach a distinct plateau. Isotherms with a distinct plateau were observed for the other adsorbing solutions. The relatively good agreement between experimental and theoretical data suggests that the system obeys the Langmuir equation under the studied conditions. Semilogarithmic plots (Γ *vs.* log$c$) and double-logarithmic plots (logΓ *vs.* log$c$) (not shown) showed that the shape of the curves is indeed Langmuirian, and not either Freundlich or Frumkin-Fowler-Guggenheim (FGG) (Lyklema, 1995). These results indicate that there is a relatively homogeneous distribution of surface sites and that lateral interactions between adsorbed molecules are very small or negligible. This is surprising because clay and soil surfaces are known to be heterogeneous and MB molecules are charged entities, which may result in lateral repulsion between the adsorbed molecules. Bergmann and O'Konski (1963) observed a non-Langmuirian behavior for MB adsorption on montmorillonite. They postulated the presence of two surface sites with different reactivity. One site was of high affinity for MB molecules and accounted for the interaction between positively charged MB and structural negative charges on the clay. The other site was of lower affinity and accounted for interaction between MB and edge surfaces or other non-negatively charged groups at the surface. The Langmuirian behavior of the MB/kaolinite system seems to be related to the conditions selected for the experiments, but there are no clear explanations for this. One possible explanation is that phosphate adsorption, which is known to largely occur on oxides and clays, populates the surface in a homogeneous way to create sites with similar affinity for MB. Together with this, the high ionic strength of the adsorbing solutions may have contributed to the Langmuirian behavior by screening lateral electrostatic repulsion between adsorbed molecules.

Figure 1D shows that the experimental points describe only one isotherm, regardless of the degree of dimerization of MB. This suggests that equilibration occurs rapidly and that the aggregation state of the adsorbed MB molecules does not depend on the aggregation number initially in the adsorbing solutions, but on the final equilibrium concentration. Table 2 shows the estimated values of Γ_m and b for three experimental conditions. The error in the value of Γ_m for the 9% adsorbing solution was high because the isotherms do not have data points near saturation values. The errors in Γ_m for the other two MB concentrations were considerably lower. For b, each estimated value has a relatively small standard deviation. The values of the parameters Γ_m and b were nearly the same for each condition studied, which emphasizes that the final state of adsorbed molecules is independent of the initial aggregation state of MB. The relatively high values of b indicate that MB has a strong affinity for the surface. The adsorption cannot be assumed to be purely electrostatic because competition with Na ions would impede any detectable MB adsorption. The chemical, intrinsic, or non-electrostatic component of the surface-MB interaction is more important than the electrostatic component. This explains why Γ_m and CEC are not correlated quantities.

The presented data do not indicate the aggregation number of MB at the surface. A comparison between the surface areas obtained by MB adsorption to another adsorption method may provide information about aggregation numbers. Table 2 compares the surface areas of the samples as measured by adsorbing MB and EGMEE. Except for sample ARG2, the agreement was generally good between the values estimated with both

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Table 3. Equilibrium reactions and values of constants (order of magnitude) involving MB molecules.

Type	Reaction	Equilibrium constant values[1]
Dimer splitting	$(MB)_2 \leftrightarrow 2MB$	$K_1 \approx 1 \times 10^{-4}$
Monomer adsorption	$MB + H_2O_{ad} \leftrightarrow MB_{ad} + H_2O$	$K_2 \approx K_L \approx 55.5b \approx 1 \times 10^7$
Dimer adsorption	$(MB)_2 + H_2O_{ad} \leftrightarrow (MB)_{2,ad} + H_2O$	$K_3 \approx K_2 \approx 1 \times 10^7$
Splitting adsorption	$(MB)_2 + 2\ H_2O_{ad} \leftrightarrow 2MB_{ad} + 2\ H_2O$	$K_4 = K_1K_2^2 \approx 1 \times 10^{10}$

[1]The equilibrium constant of the reaction $aA + bB \leftrightarrow cC + dD$ is defined as $K = (a_C)^c\ (a_D)^d/(a_A)^a\ (a_B)^b$. To estimate the values of the constants it was assumed that the activity of water was 55.5. The suffix "ad" denotes adsorbed.

adsorbates, perhaps because (1) the fractions of monomers, dimers, and n-mers in the adsorbed state were the same for MB and EGMEE or (2) both MB and EGMEE adsorb in monomeric form. Reason (1) is improbable. Monolayer coverage (2) is more likely to occur at surface saturation. Therefore, although a high proportion of MB molecules form dimers in the 46, 71, and 83% adsorbing solutions, these dimers seem to form monomers during adsorption.

Different reactions with their corresponding equilibrium constants are given in Table 3. In the adsorption reactions, water is assumed to compete with MB for adsorption. As indicated above, competition with sodium may also be postulated. Although the values of the equilibrium constants would change in the latter, their relative values would not vary and the following analysis and conclusions would not change. Because a dimer seems to adsorb flat to the surface, only one of its constituting monomers will be in direct contact with the surface. Therefore, the interaction forces between a dimer and the surface and between a monomer and the surface should be of the same order of magnitude. This implies that the equilibrium constant for adsorption of dimers (K_3) is similar to that for the adsorption of monomers (K_2), estimated from experimental *b* values. The equilibrium constant for adsorption of dimers from solution to give monomers at the surface (K_4) can be estimated if splitting of the dimer (K_1) is considered. A comparison of K_3 and K_4 values indicates that the sorption of MB is more favorable if splitting to a monomer occurs. The similarity of $K_4/K_3 \approx K_1K_2$, that can be obtained by combining reactions in Table 3, indicates that splitting plus adsorption is more favorable for a large K_2 (strong monomer-surface interaction) and a large K_1 (weak monomer-monomer interaction). Thus, dimers can only adsorb if K_2 is relatively small. This may occur for sample ARG2. This sample has the lowest value of K_2, which may lead to some dimer adsorption and an overestimation of S.

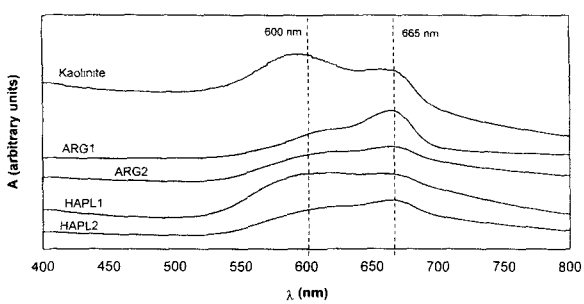


Figure 2. Visible spectra of MB adsorbed on the solid samples.

Figure 2 shows the spectra of MB adsorbed on each sample. Note the absorption band at ~665 nm and a band or shoulder at ~600 nm. The spectrum of MB adsorbed on sample ARG1 is very similar to that of monomeric MB in aqueous solutions (Boutton *et al.*, 1997) and to that of monomeric MB adsorbed on montmorillonite (Bergmann and O'Konski, 1963). The spectra of MB adsorbed on the other samples have a relative increase and broadening of the 600-nm band. (1) Bergmann and O'Konski (1963) and Jacobs and Schoonheydt (1999) attributed this behavior to the formation of dimers or higher aggregates at the surface, by analogy with the spectral changes that occur in solution when dimers are formed (Bergmann and O'Konski, 1963); (2) Garfinkel-Scweky and Yariv (1997) and Grauer *et al.* (1987), among others, attributed the spectral changes to π interactions between monomeric MB and the solid surface and they concluded that no aggregation at the surface occurs. Also, spectral changes after adsorption can be caused by the electrostatic field at the surface of the particle and by shifts relating to changes in polarity of the clay environment as suggested by Boutton *et al.* (1997). The state of MB molecules at the surface is beyond the scope of our study. The present data cannot differentiate between (1) or (2). The possibility of (2) is in agreement with surface-area measurements suggesting that MB saturates the surface forming a monolayer of monomers with a cross sectional area of ~120 Å^2. The possibility of (1) could also agree with surface-area measurements, if the flocculation of particles saturated with a monolayer of MB occurs. In this case, the formation of dimers by the reaction of monomers adsorbed to different particles is possible in contact regions between individual particles. The different adsorption processes should lead to different flocculation states of the particles. Light scattering or flocculation kinetics studies can help in understanding what occurs during adsorption.

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