

## INTERACTIONS OF SOME LARGE ORGANIC CATIONS WITH BENTONITE IN DILUTE AQUEOUS SYSTEMS

DEORAJ R. NARINE<sup>1</sup> AND ROBERT D. GUY

Trace Analysis Research Centre, Department of Chemistry, Dalhousie University  
Halifax, Nova Scotia B3H 4J1, Canada

**Abstract**—Adsorption studies indicate that paraquat, diquat, and thionine are bound on bentonite by amounts greater than the measured cation-exchange capacity (CEC) of the clay. Methylene blue, new methylene blue, and malachite green are bound by amounts equal to the CEC. The unipositive organocations form aggregates on the clay surface. Aggregation increases with ionic strength and increases the apparent adsorption capacity by 25%. The aggregates are removed by washing with distilled water. Desorption studies show that the dyes are irreversibly bound, whereas the dipositive organocations are reversibly bound. Ionic strength variation reduces adsorption by 15 and 36% in the monovalent and divalent organocation-clay systems, respectively. In the clay-divalent organocation systems adsorption is greater on Na-saturated clay than on K-saturated clay. Adsorption is unchanged over the pH range 4.5–8.5 and decreases steadily below pH 4.0. Changes in adsorption due to changes in temperature are small. The study indicates that ionic strength is the most important variable in clay-organocation interactions.

**Key Words**—Adsorption, Bentonite, Herbicide, Organocations, Smectite.

### INTRODUCTION

The interactions between charged organic molecules and clays play an important role in determining the environmental behavior of certain organocations, some of which exhibit herbicidal properties. The transport, persistence, and biological activity of an organocation in an aqueous system is determined by its concentration, which is regulated by the rate of chemical, photochemical, and microbial decomposition and by the extent of adsorption on organic and inorganic colloidal materials (Bailey and White, 1970). Many workers (e.g., Calderbank, 1968; Gillott *et al.*, 1970; Guy and Narine, 1980; Haque, 1975) have shown that clay has the ability to reduce drastically the effect of herbicides. For example, the herbicidal effects of paraquat and diquat, used in weed control, are greatly reduced in the presence of clay (Calderbank, 1968). Despite the large body of literature on clay-organocation adsorption in aqueous systems, many studies have had to be repeated in the present work for various reasons. For example, samples collected near the surface of water bodies typically contain suspended sedimentary loads of 1 to 100 mg/liter. Many adsorption studies in the literature were carried out with aqueous clay systems containing several grams of clay per liter. In practice, paraquat and diquat are applied as herbicides at the micromolar level (Akhavain and Linscott, 1968); however, in previous studies the equilibrium concentrations of these materials were reported at the millimolar level. The present study was carried out using the organocations shown in Figure 1 at the micromolar level and clay at the mg/

liter level, which represents better the situation found in natural aqueous environments.

The adsorption of monovalent organocations, especially methylene blue, on clays has been studied by a number of workers (Pham Thi Hang and Brindley, 1970; De *et al.*, 1973a, 1973b, 1974; Bergman and O'Konski, 1963). However, their conclusions are at variance with regard to the nature of the interactions. Bergman and O'Konski (1963) found that adsorption follows a Freundlich isotherm, whereas De *et al.* (1973a, 1973b, 1974) showed that the same system follows the Langmuir isotherm. Most of these studies were made using relatively simple conditions of ionic strength, pH, and temperature.

The present work defines the nature of the adsorption between the organocations, methylene blue (MB<sup>+</sup>), new methylene blue (NMB<sup>+</sup>), thionine (Th<sup>+</sup>), malachite green (MG<sup>+</sup>), paraquat (P<sup>2+</sup>), and diquat (D<sup>2+</sup>) and bentonite clay as a function of (1) ionic strength, size, and charge of the counterion, (2) pH, and (3) temperature. The ability of various inorganic ions to desorb the bound molecules and the tendency of the organocations to aggregate on the clay also are considered.

### EXPERIMENTAL

Materials and methods were described in detail elsewhere (Guy and Narine, 1980) and are described only briefly here.

#### Materials

Crude Wyoming bentonite (from Fisher Scientific Company) was converted to the potassium form by repeated equilibration with 1.0 M potassium nitrate solution. The clay concentration, after removal of larger particles by gravity settling, was determined by filtering

<sup>1</sup> Present address: School of Public and Environmental Affairs, Indiana University, Bloomington, Indiana 47405.

aliquots through a 0.20- $\mu\text{m}$  Nuclepore filter. Dialysis (4.8-nm pore diameter tubing) was used as a check. Filtration has the advantage over centrifugation because it is rapid (less than 5 min was required to filter an equilibrium solution) and the residue can be washed without peptization interference. A typical concentration was  $3.21 \pm 0.15$  mg clay/ml. The cation-exchange capacity (CEC) was determined by ammonium and calcium exchange (Chapman, 1965). Both methods gave a value of 62.0 meq/100 g clay.

The organocations were obtained as the hydrated salts, the moisture contents of which were determined by drying under vacuum using Anhydron as the drying agent. The divalent organocations were standardized by passing 25.00-ml aliquots of the stock solution through a Rexyn 100 cation-exchange resin in the hydrogen form. The protons released were titrated with standard base to a phenolphthalein endpoint.

### Methods

The distribution of the organocation between the solution and the clay particles was determined by two methods. The first was a series of bulk adsorption experiments in which 1 ml of clay suspension was added to 40 ml of an organocation solution in a 50-ml polyethylene centrifuge tube. The initial concentration of organocations varied from 0 to  $15.4 \times 10^{-5}$  moles organocation/liter, and the concentration of clay varied from 75.0 to 115  $\mu\text{g/ml}$ . The suspensions were stirred for 12 hr, and after the pH of the samples was measured, each suspension was filtered through a 0.20- $\mu\text{m}$  filter. The residue was washed with five 20-ml aliquots of water. The second method for organocation-clay adsorption studies utilized a dialysis bag. Known amounts of the organocation were added to glass jars (250-ml capacity) containing the clay suspension at a known ionic strength. A dialysis bag containing 10-ml of the ionic strength adjuster solution was added to each jar; the total volume per jar was 210-ml. The initial concentration in the jars varied from 0.0 to  $3.1 \times 10^{-5}$  moles/liter, and the clay concentration varied from 15.0 to 20.0  $\mu\text{g/ml}$ . The mixtures were agitated overnight on a mechanical shaker. Upon equilibration the dialysate was transferred to centrifuge tubes after thorough rinsing of the bag. The pH of each suspension was measured.

Desorption of the organocations was accomplished by transferring the filter membranes containing the washed clay-organocation residue obtained in the bulk adsorption experiments to centrifuge tubes containing 40-ml of the metal ion solution. Each mixture was stirred for 72 hr and then refiltered.

The aggregation experiments were performed in a similar manner as described for bulk adsorption, except that the filtrates and washings were collected separately. The amount of organocation in the washings was an indication of the degree of aggregation. Controls indicated that the organocations were not adsorbed on the

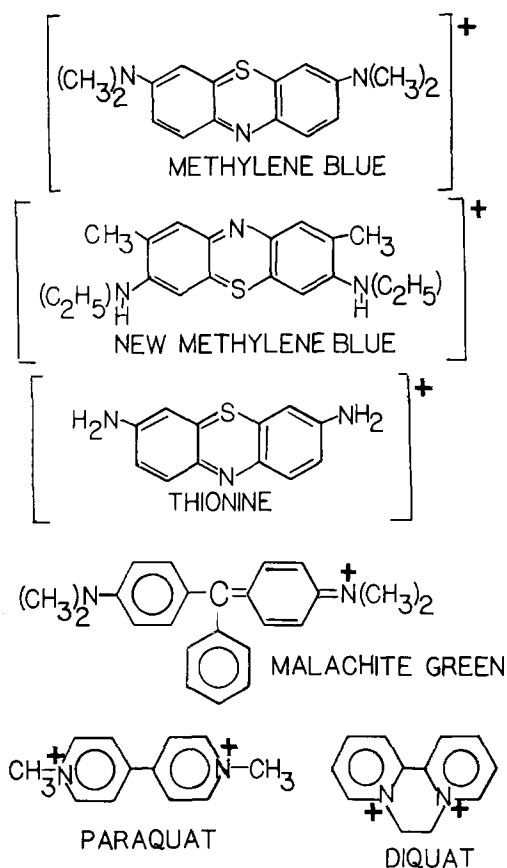


Figure 1. Structure of organocations used in this study.

centrifuge tubes, filters, dialysis bags, or associated glassware.

Table 1 shows the analytical conditions used in this study. For the monovalent organocations, visible spectrometry was employed to determine the amount of unbound dyes. For the divalent organocations, diquat and paraquat, ultraviolet and visible spectrometry were used. For paraquat, the visible method employed a modification of the procedure used by Calderbank (1968) and consisted of adding 1 ml of a 1% solution of sodium dithionite in 0.10 M NaOH solution to 10 ml of the analyte solution. The deep blue solution that developed on swirling was stable for a length of time that was more than adequate for scanning the spectrum from 450 to 370 nm. For those paraquat analyses that could not be done under basic conditions, ultraviolet spectroscopy was used. For diquat analyses the dithionite method offered no advantage over the ultraviolet method because the color of the diquat solution developed poorly and degraded rapidly. The amount of organocation adsorbed was determined by difference. Unless otherwise stated, the ionic strength was adjusted by using a salt solution containing the same inorganic cation as on the clay. For example, for Na-bentonite the ionic strength of the suspension was adjusted with

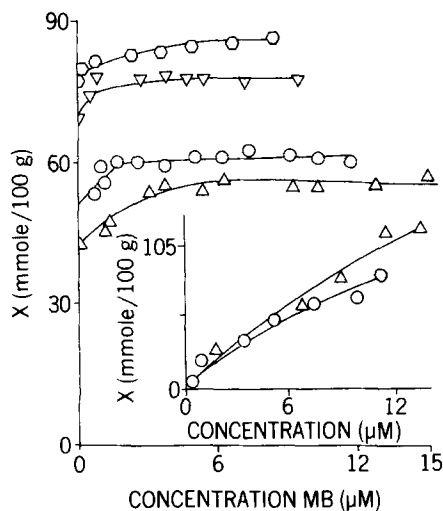


Figure 2. Adsorption isotherms for washed and unwashed (inset) clay/MB systems.  $\circ$  Na-clay/MB,  $I = 0.00$ ;  $\nabla$  Na-clay/MB,  $I = 0.50$ ;  $\triangle$  K-clay/MB,  $I = 0.00$ ;  $\circ$  K-clay/MB,  $I = 0.50$ . Inset:  $\circ$  Na-clay/MB,  $I = 0.00$ ;  $\triangle$  Na-clay/MB,  $I = 0.50$ ; Point size reflects experimental uncertainty.  $I$  is expressed in mole/liter, and  $X$  is the amount of dye adsorbed.

NaCl. The pH was adjusted with HCl or  $\text{NaHCO}_3$  solution.

## RESULTS AND DISCUSSION

Adsorption isotherms for clay/monovalent and clay/divalent organocations are shown in Figures 2 and 3, respectively. The inset of Figure 2 shows the adsorption isotherms for unwashed systems, i.e., those in which the residues on the filter membranes were not washed. The data in these figures indicate that for the washed systems the adsorption rapidly reached a maximum and remained invariant with increasing concentration of organocations. However, for the unwashed system, adsorption increased with increasing concentration, i.e., no adsorption maximum was observed. This behavior was observed in all clay/monovalent organocation systems tested but never in the clay/divalent organocation systems. The adsorption data for the

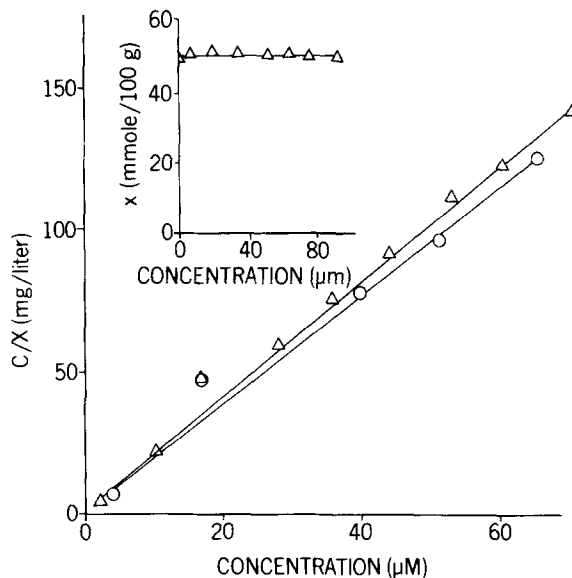


Figure 3. Adsorption isotherm (inset) for K-clay/ $\text{D}^{2+}$  and Langmuir isotherms for clay/divalent organocation systems;  $\triangle$  Na-clay/ $\text{P}^{2+}$ ,  $I = 0.00$ ;  $\circ$  Na-clay/ $\text{D}^{2+}$ ,  $I = 0.00$ ; Point size reflects experimental uncertainty.  $I$  is expressed in mole/liter,  $X$  is the amount of dye adsorbed, and  $C$  is the molar concentration of unbound organocation.

washed monovalent organocation systems (Narine, 1980) and the divalent systems, Figure 3, obeyed perfectly the Langmuir isotherm; in contrast, the unwashed systems, Figure 2 (inset) obeyed the Freundlich isotherm (Narine, 1980).

Many workers (e.g., Mukerjee and Ghosh, 1970a, 1970b; Ghosh and Mukerjee, 1970a, 1970b; Hertz *et al.*, 1968; Hertz, 1977) have observed that dye molecules, of which the monovalent organocations are a subgroup, tend to aggregate; that is, stack in aqueous solution, forming dimeric and polymeric species. They suggested that various factors contribute to this process among which are greater dispersive interactions and hydration effects on aggregation. In a clay/dye system it is possible that aggregation may be enhanced by the following factors: A dye molecule adsorbed on the clay will have

Table 1. Analytical characteristics of the organocations.

Cation	$\lambda_{\text{max}}$ (nm)	$10^{-4}\epsilon_{\text{max}}^1$	Linear range <sup>2</sup> ( $\mu\text{M}$ )	Lower limit <sup>3</sup> (1-cm cell)
Methylene blue	667	50.0	0.00–10.5	$0.50 \times 10^{-7}$ M
Malachite green	628	10.6	0.00–4.13	$2.00 \times 10^{-7}$ M
New methylene blue	644–646	6.83	0.00–5.10	$3.00 \times 10^{-7}$ M
Diquat	308–311	1.74	1.74–28.5	$1.00 \times 10^{-6}$ M
Paraquat	394	4.97	1.35–16.9	$0.60 \times 10^{-6}$ M
Paraquat	256	2.16	3.40–20.3	$1.00 \times 10^{-6}$ M
Thionine	603	5.55	0.00–7.15	$3.00 \times 10^{-7}$ M

<sup>1</sup> Extinction coefficient at wavelength of minimum adsorption.

<sup>2</sup> Range over which Beer's law is obeyed.

<sup>3</sup> Lower limit of detection for visible and ultraviolet analyses.

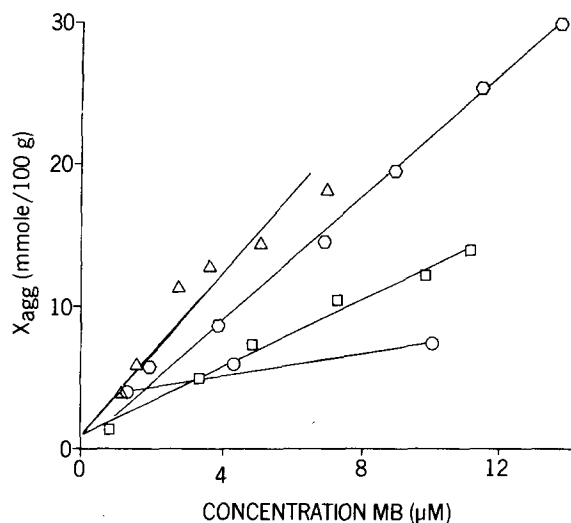


Figure 4. Aggregation in clay/MB systems as a function of MB concentration;  $\Delta$  K-clay/MB,  $I = 0.50$ ;  $\circ$  K-clay/MB,  $I = 0.00$ ;  $\square$  Na-clay/MB,  $I = 0.00$ ;  $\diamond$  Na-clay/MB,  $I = 0.50$ ; Point size reflects experimental uncertainty.  $I$  is expressed in mole/liter, and  $X_{agg}$  is the amount of aggregation on the clay.

its positive charge neutralized, hence, dye-dye repulsion due to similarity in charges should be reduced. There may be increased attractive dispersion forces between the dyes because the positive charge of the aggregating molecule can now interact to a greater extent with the  $\pi$ -electron system of the adsorbed molecule. The dye molecules at the clay surface may act as "nuclei" for stacking because of their greater localized concentration there; that is, the clay surface may act as a hydrophobic surface encouraging association between the large aromatic molecules. If the above arguments hold, aggregation in clay/dye systems should be observed at lower concentration levels than those used in the studies of the above authors. The data in Figure 4 show aggregation to be a function of equilibrium concentration. Table 2 shows that aggregation began as soon as the binding maximum was reached. Thus, the above arguments in favor of enhanced aggregation in clay/dye systems may be valid. In Figure 4 the differences in the slopes of the curves at the two ionic strength levels are due to the fact that different initial concentrations of methylene blue were used in each study.

For the washed dye/clay systems (Narine, 1980) it was observed that binding decreased by 15% as the ionic strength ( $I$ ) of the systems rose from 0 to 0.50 moles/liter. Aggregation and its consequences on binding as the ionic strength increased are shown in Figure 5. It is clearly seen that aggregation (curves 4, 5, 6), as measured by the amount of dye washed off the residue per 100 g of clay, increased with increasing ionic strength and that the apparent adsorption capacity (curves 1, 2, 3) of the clays increased by as much as 22%.

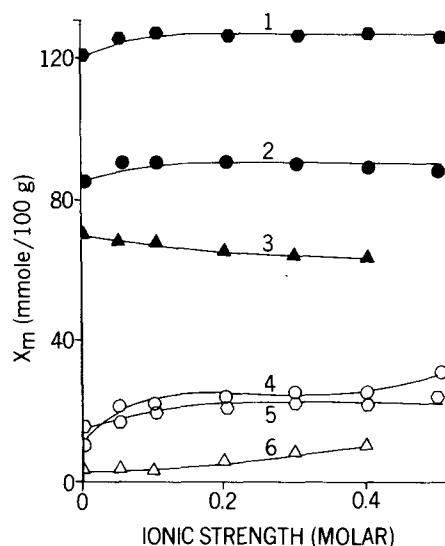


Figure 5. Effects of ionic strength and structure of organocations on aggregation and adsorption capacities in K-clay/dye system. Upper curves (1, 2, 3) measure adsorption capacity,  $\bullet$  K-clay/Th,  $\bullet$  K-clay/MB,  $\blacktriangle$  K-clay/MG; Lower curves (4, 5, 6) measure aggregation,  $\diamond$  K-clay/MB,  $\circ$  K-clay/NMB,  $\triangle$  K-clay/MG.  $X$  is the maximum adsorption and aggregation capacities.

The aggregation curves of Figure 5 show that the planar monovalent ions, methylene blue, new methylene blue, and thionine aggregated to a much greater extent than malachite green. This suggests that still another geometrical relationship, in addition to those outlined above, may influence aggregation. The structure of malachite green (Figure 1) may permit a twisting of the substituted aryl ring to a "propeller-like" configuration (Wheland, 1960) which would serve to minimize stress. This twisting may prevent the molecule from assuming a planar configuration, and hence cause reduced aggregation.

Of the organocations, methylene blue has found considerable usage in the determination of cation-exchange capacity (CEC) of clays (Pham Thi Hang and Brindley, 1970; De *et al.*, 1973a, 1973b, 1974; Bergman and O'Konski, 1963). The CECs obtained in the present study at zero ionic strength (Table 3) are different from those obtained by the above workers who studied similar Wyoming bentonite systems. Some of the discrep-

Table 2. Methylene blue (MB) adsorption on K-bentonite.

Ionic strength (moles/liter)	Equil. conc. of MB at adsorption maximum ( $\mu$ M)	Equil. MB conc. for aggregation initiation ( $\mu$ M)
0.00	46.0	44.0
0.01	43.6	44.1
0.10	41.0	42.0
0.50	37.5	38.5

Table 3. Maximum adsorption capacity ( $X_m$ )<sup>1</sup> at zero ionic strength.

Organocation	K-bentonite	Ca-bentonite	Na-bentonite
Methylene blue	64.0	60.0	84.0
New methylene blue	74.0	71.0	82.0
Thionine	107.0	110.0	112.0
Malachite green	66.0	66.0	67.0
Paraquat	96	—	100
Diquat	100	—	102

<sup>1</sup>  $X_m$  expressed as meq/100 g clay; relative error  $\leq 3.0\%$ .

ancies may result from different clay sizes,  $<2.0\text{-}\mu\text{m}$  for literature values and  $>2.0\text{-}\mu\text{m}$  for most of this work. However, the Na-bentonite samples used in the present study<sup>2</sup> consisted entirely of particles whose sizes were  $<2.0\text{-}\mu\text{m}$ , and the methylene blue CEC agrees with the value of Schramm and Kwak (1980). Hence, the discrepancies may be due to aggregation effects because the above workers (De *et al.*, 1973a, 1973b, 1974; Bergman and O'Konski, 1968) used centrifugation to separate the clay-dye complex from the decantate. Centrifugation can result in sedimentation of the stacked dye molecules and, because a washing step was not included at this point, the aggregated amounts will be included in the CEC estimates. The bulk method used to generate the data in Table 3 included a thorough washing of the residue.

For washed methylene blue/clay systems Guy *et al.* (1980) showed that the amount of inorganic cation released is equal to the amount of dye adsorbed. In the case of the K-saturated clay/diquat (K-clay/D<sup>2+</sup>) system they found that  $101.0 \pm 2.0$  meq of diquat was adsorbed on 100 g of clay, but that only  $63.0 \pm 2.0$  meq of K<sup>+</sup> was released. A similar result was obtained for paraquat. These results suggest that divalent organocations have the ability to remove other ions in addition to K<sup>+</sup>, such as those released by hydrolysis of the clay suspension and/or those held on the clay surface by hydration and electrostatic forces (Bailey and White, 1970). This argument is further strengthened by the fact that the CEC of Na-bentonite, measured under conditions where hydrolysis was negligible, was  $93.0 \pm 3.0$  meq K<sup>+</sup>/100 g clay. This value decreased to about 80.0 meq K<sup>+</sup>/100 g clay under aqueous conditions (Schramm and Kwak, 1980), suggesting that paraquat, diquat, and, perhaps, thionine can displace the adsorbed hydrated ions.

Considering the above data, it is apparent that, except for the pre-cleaned Na-bentonite, the adsorption capacity of the clay for the organocations is in the following order, Th<sup>+</sup> > D<sup>2+</sup>  $\geq$  P<sup>2+</sup> > NMB<sup>+</sup> > MG<sup>+</sup> > MB<sup>+</sup> at zero ionic strength. The effect of ionic strength

<sup>2</sup> Na-bentonite was prepared by the ultrafiltration/dialysis method of Schramm and Kwak (1980).

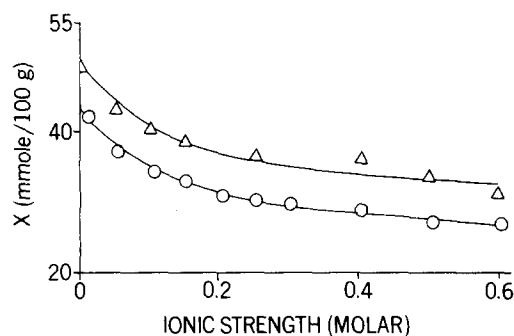


figure 6. Adsorption in K-clay/P<sup>2+</sup> systems at high and low concentrations of paraquat at all ionic strength levels used in this study.  $\Delta$  K-clay/P<sup>2+</sup>; initial concentration of paraquat, 69.1  $\mu\text{M}$ ;  $\circ$  K-clay/P<sup>2+</sup>; initial concentration of paraquat, 13.2  $\mu\text{M}$ . Point sizes reflect experimental uncertainty. X is the amount of bound organocation.

on the adsorption of the divalent ion for the clay systems (Table 4) indicates that sorption in these systems was more sensitive to ionic strength variation than was observed for the dye system. For example, in both divalent organocations/clay systems adsorption decreased by 36% as the ionic strength increased from 0 to 0.5 moles/liter. In addition, the amount of adsorption depends on the inorganic counterion on the clay. For systems using K-clay, adsorption was consistently lower than for those employing Na-clay. These data suggest that differences in the hydrated radius of K<sup>+</sup> and Na<sup>+</sup> may be responsible for the differences in adsorption. No aggregation effects were observed for diquat and paraquat/clay systems at any ionic strength.

Of all the organocations, only paraquat exhibited a mass action effect. The lower curve of Figure 6 depicts adsorption at a paraquat concentration that is five times lower than that used to generate the upper curve; in each case, however, the amount of paraquat was sufficient to saturate the clay.

It should be recalled that two methods, bulk (filtra-

Table 4. Adsorption<sup>1</sup> of diquat and paraquat on clay as a function of ionic strength and ionic radius.

Ionic strength (moles/liter)	$X_m$ K-bentonite/D <sup>2+</sup>	$X_m$ Na-bentonite/D <sup>2+</sup>	$X_m$ Na-bentonite/P <sup>2+</sup>	$X_m$ K-bentonite/P <sup>2+</sup>
0.01	50.0	51.0	42.0	42.0
0.05	42.4	45.5	39.0	37.0
0.10	38.0	44.0	38.0	34.0
0.15	—	—	37.0	33.0
0.20	35.0	38.0	35.0	31.0
0.25	—	—	34.0	31.0
0.30	34.0	35.0	34.0	30.0
0.40	31.0	35.0	31.0	29.0
0.50	31.0	34.0	32.0	27.0
0.60	—	—	32.0	27.0

<sup>1</sup> Adsorption ( $X_m$ ) expressed as mmole/100 g clay ( $\pm 3\%$ ).

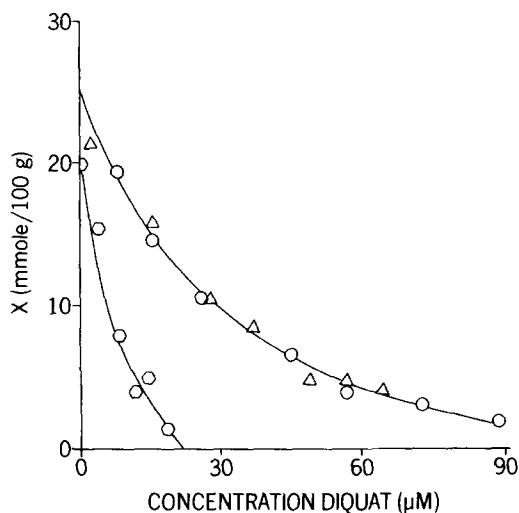


Figure 7. Effect of paraquat on the adsorption of diquat; y-axis measures the amount of diquat bound in mmole/100 g clay; x-axis measures the equilibrium concentration of diquat;  $\circ$  K-clay/D<sup>2+</sup>/P<sup>2+</sup>; K-clay conc., 114  $\mu\text{g/ml}$ ;  $\triangle$  Na-clay/D<sup>2+</sup>/P<sup>2+</sup>; Na-clay conc., 94  $\mu\text{g/ml}$ ;  $\diamond$  K-clay/D<sup>2+</sup>/P<sup>2+</sup>; K-clay conc., 20  $\mu\text{g/ml}$ . Point sizes reflect experimental uncertainty; data generated via dialysis. X is the amount of organocation adsorbed.

tion) adsorption and dialysis, were used to determine adsorption capacity. The lower curve in Figure 6 was generated by dialysis which resulted in lower paraquat concentrations. It is therefore important, at least in the case of paraquat, to specify the method used to generate the data.

The amount of organocation released from the clay after exposing the washed organocation-clay complex to 0.5 M solution of metal ions (Table 5) shows that methylene blue was held irreversibly on the clay, whereas diquat was displaced by as much as 25% of the amount adsorbed. Also, micromolar concentrations of paraquat released an inordinately large amount of diquat, suggesting that severe competition existed between these ions for the adsorption sites on clay. The results of an equimolar competition study (Figure 7) in-

Table 5. Desorption results<sup>1</sup> in presence of 0.5 M cations.

Cation	Ionic strength (moles/liter)	MB released (%)	D <sup>2+</sup> released (%)
K <sup>+</sup>	0.5	1.0	25.0
NH <sub>4</sub> <sup>+</sup>	0.5	1.0	22.0
Ba <sup>2+</sup>	0.5	1.0	20.0
Ca <sup>2+</sup>	0.5	1.0	15.0
Mg <sup>2+</sup>	0.5	1.0	6.0
Al <sup>3+</sup> (pH = 3.0)	0.33	—	25.0
Paraquat	$1.42 \times 10^{-6}$	—	4.5

<sup>1</sup> Studies done for K-clay only; desorption time = 72 hr; uncertainties in amount released  $\pm 3\%$ .

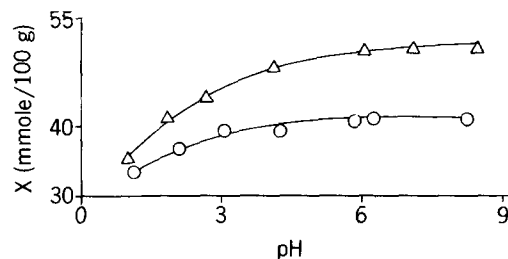


Figure 8. Effect of pH on adsorption of paraquat and diquat;  $\triangle$  K-clay/D<sup>2+</sup>; I = 0.01;  $\circ$  K-clay/P<sup>2+</sup>; I = 0.01; paraquat data generated by dialysis. I is expressed in mole/liter, and X is the amount of organocation adsorbed.

dicates that the competition was strongly dependent upon the initial concentration of clay and organocations. At higher clay levels, as is shown on the upper curve, more exchange sites were available to adsorb both diquat and paraquat. When the amount of organocations exceeded the CEC, the amount of diquat adsorbed decreased rapidly because of the competition.

Variation in adsorption as a function of pH is shown in Figure 8. Here it is seen that over the environmentally important pH range of 4.5 to 8.5, the adsorption changed slightly in the clay/D<sup>2+</sup> and clay/P<sup>2+</sup> systems. At pH > 4.0, adsorption decreased fairly rapidly, suggesting that hydrogen ions competed effectively for the adsorption sites on the clay. Similar changes were observed for the clay/dye systems. When the temperature was changed from 3° to 55°C, adsorption decreased from  $69.3 \pm 3.0$  to  $64.0 \pm 2.0$  meq MB/100 g clay, for a K-clay/MB system. Similar changes were observed for other dye/clay systems; however, in the clay/divalent organocation systems the change in sorption was smaller.

The results of this study indicate that adsorption interactions in clay/dye systems are different in many respects than adsorption interactions in clay/divalent organocation systems. The adsorptive force in clay/divalent cation systems is mainly an electrostatic ion-exchange force, whereas in the clay/dye systems, forces other than electrostatic are indicated. In the unwashed clay/dye systems the adsorption followed a Freundlich isotherm (Narine, 1980), which agrees with the work of Bergman and O'Konski (1963); whereas in the washed system, the data followed the Langmuir isotherm as De *et al.* (1970a, 1970b, 1974) indicated. These workers did not include a washing step in their procedure. These workers also showed that the adsorbed dye can be displaced from the clay surfaces. However, from the present work it can be seen that a thousandfold increase in salt content, relative to the organocation, released 1% of the adsorbed dye. A similar increase in salt content removed 25% of adsorbed diquat. Thus, ionic strength exerts the greatest influence on clay-organocation adsorption.

## CONCLUSIONS

From the above investigations, it can be concluded that (1) adsorption of organocations on clay is most sensitive to changes in ionic strength; (2) bentonite clay exhibits a greater affinity for paraquat than for diquat; (3) monovalent organocations bind more strongly on the clay than divalent organocations, (4) for divalent organocations, diquat is more easily displaced than paraquat; (5) for monovalent organocation/clay systems, adsorption is complicated by aggregation effects.

## ACKNOWLEDGMENTS

The authors thank L. Schramm and J. C. T. Kwak for preparing the Na-bentonite, and H. H. Murray, W. Reed and Ray Kaminsky for their advice and help in the preparation of this manuscript.

## REFERENCES

- Akhavein, A. A. and Linscott, D. L. (1968) The dipyrilidium herbicides, paraquat and diquat: *Residue Review* **23**, 97–135.
- Bailey, G. W. and White, J. L. (1970) Factors influencing the adsorption, desorption and movement of pesticides in soil: *Residue Review* **32**, 29–92.
- Bergman, K. and O'Konski, C. T. (1963) A spectroscopic study of methylene blue monomer and dimer and complex with montmorillonite: *J. Phys. Chem.* **67**, 2169–2175.
- Calderbank, A. (1968) The bipyridylum herbicides: *Adv. Pest Control* **8**, 127–190.
- Chapman, H. D. (1965) Cation exchange capacity: in *Methods of Soil Analysis*, C. A. Black, ed., American Society Agronomy, Madison, Wisconsin, 891–200.
- De, D. L., Das Kanungo, J. L., and Chakrabarti, S. L. (1973a) Studies of adsorption and desorption on methylene blue and crystal violet on and from feldspar: *J. Indian Soc. Soil Sci.* **21**, 251–253.
- De, D. L., Das Kanungo, J. L., and Chakrabarti, S. L. (1973b) Studies of adsorption and desorption of methylene blue on and from vermiculite and asbestos: *J. Indian Chem. Soc.* **1**, 507–510.
- De, D. L., Das Kanungo, J. L., and Chakrabarti, S. L. (1974) Adsorption of methylene blue, crystal violet and malachite green on bentonite, vermiculite, kaolinite, asbestos and feldspar: *Indian J. Chem.* **12**, 1187–1190.
- Ghosh, A. K. and Mukerjee, P. (1970a) Multiple association equilibria of self-association of methylene blue and other dyes: *J. Amer. Chem. Soc.* **92**, 6408–6412.
- Ghosh, A. K. and Mukerjee, P. (1970b) Ionic strength effects on activity coefficient of methylene blue and its self-association: *J. Amer. Chem. Soc.* **92**, 6413–6418.
- Gillott, M. A., Floyd, G. L., and Ward, D. V. (1970) The role of sediment as a modifying factor in pesticide-algae interaction: *Environ. Entomol.* **4**, 621–623.
- Guy, R. D. and Narine, D. R. (1980) A model system for the investigation of methods of herbicide speciation: in *Proceedings of Hydrocarbons and Halogenated Hydrocarbons in Aquatic Environment*, B. K. Afghan and D. Mackay, eds., Plenum Press, New York, 417–420.
- Guy, R. D., Narine, D. R., and DeSilva, S. (1980) Organocation Speciation I: *Can. J. Chem.* **58**, 547–554.
- Haque, R. (1975) Role of adsorption in studying the dynamics of pesticides in soil environments: in *Environmental Dynamics of Pesticide*, R. Haque and V. H. Freed, eds., Plenum Press, New York, 97–103.
- Hertz, A. H. (1977) Aggregation of sensitizing dyes in solution and their adsorption onto silver halides: *Adv. Colloid Interface Sci.* **8**, 237–250.
- Hertz, A. H., Danner, R. P., and Janusouis, G. A. (1968) Adsorption of dyes and their surface spectra: in *Adsorption from Aqueous Solution*, Advances Chem. Ser. 79, American Chemical Society, Washington, D.C., 173–210.
- Mukerjee, P. and Ghosh, A. K. (1970a) Thermodynamic aspects of self-association and hydrophobic bonding of methylene blue: *J. Amer. Chem. Soc.* **92**, 6419–6425.
- Mukerjee, P. and Ghosh, A. K. (1970b) The "iso-extraction" method and the study of self-association of methylene blue in aqueous solutions: *J. Amer. Chem. Soc.* **92**, 6403–6407.
- Narine, D. R. (1980) Characterization of organocation interactions with environmental materials in aqueous systems: Ph.D. Thesis, Dalhousie University, Halifax, Nova Scotia, 210 pp.
- Pham Thi Hang and Brindley, G. W. (1970) Methylene blue adsorption by clay minerals. Determination of surface areas and cation exchange capacities: *Clays & Clay Minerals* **18**, 203–212.
- Schramm, L. L. and Kwak, J. C. T. (1980) Application of ultrafiltration/dialysis to the preparation of clay suspensions: *Clays & Clay Minerals* **28**, 67–69.
- Wheland, G. W. (1960) *Advanced Organic Chemistry*: 3rd ed., Wiley, New York, 790–794.

(Received 19 November 1980; accepted 9 January 1981)

**Резюме**—Исследования по адсорбции показывают, что паракват, дикват, и тионин связаны в бентоните в количествах больших, чем измеренная катионообменная способность (КОС) глины. Голубой метилен, новый голубой метилен, и зелёный малахит связаны в количествах, соответствующих КОС. Униположительные органокатионы образуют агрегаты на поверхности глины. Агрегация увеличивается с увеличением ионной силы и приводит к увеличению видимой адсорбционной способности до 25%. Агрегаты удаляются при промывке дистиллированной водой. Исследования по десорбции показывают, что красители связаны необратимо, тогда как двухположительные органокатионы связаны обратимо. Изменение ионной силы уменьшает адсорбцию в одновалентных и двухвалентных системах органокатион-глина на 15 и 36% соответственно. В системах глина-двухвалентный органокатион адсорбция значительно больше на глине насыщенной натрием, чем на глине насыщенной калием. Адсорбция не изменяется в диапазоне pH 4,5–8,5, и уменьшается равномерно, если pH меньше 4,0. Изменения в адсорбции вследствие изменений температуры малы. Исследования показывают, что ионная сила является наиболее важным фактором в глино-органокатионных взаимодействиях. [Е.С.]

**Resümee**—Die Adsorptionsuntersuchungen deuten darauf hin, daß Paraquat, Diquat, und Thionin an Bentonite in größeren Mengen gebunden sind als die gemessene Kationenaustauschkapazität (CEC) der Tone erlaubt. Methylenblau, Neu-Methylenblau, und Malachitgrün sind in Mengen gebunden, die denen des CEC entsprechen. Die einwertigen organischen Kationen bilden auf der Tonoberfläche Aggregate. Die Aggregatbildung nimmt mit der Ionenstärke zu und vergrößert die scheinbare Adsorptionskapazität um 25%. Die Aggregate werden durch Waschen mit destilliertem Wasser entfernt. Desorptionsuntersuchungen zeigen, daß die Farben irreversibel gebunden sind, während die zweiwertigen organischen Kationen reversibel gebunden sind. Die Variation der Ionenstärke reduzierte die Adsorption um 15 bzw. um 36% in den einwertigen bzw. zweiwertigen organischen Kationen-Ton Systemen. In den Systemen Ton-aweiwertige organische Kationen ist die Adsorption an Na-gesättigten Ton größer als an K-gesättigten. Die Adsorption bleibt im pH-Bereich von 4,5 bis 8,5 unverändert und nimmt unter pH 4,0 regelmäßig ab. Änderungen in der Adsorption, die auf Temperaturänderungen zurückzuführen sind, sind klein. Die Untersuchung deutet darauf hin, daß die Ionenstärke die wichtigste Variable bei der Wechselwirkung Ton-organisches Kation ist. [U.W.]

**Résumé**—Des études d'adsorption indiquent que le paraquat, diquat, et la thionine sont liés à la bentonite en quantités plus grandes que la capacité d'échange de cations (CEC) mesurée de l'argile. Le bleu de méthylène, le nouveau bleu de méthylène, et le vert de malachite sont liés en quantités égales à la CEC. Les organocations unipositifs forment des agrégats sur la surface de l'argile. L'aggrégation croît proportionnellement à la force ionique et accroît la capacité d'adsorption apparente de 25%. Les agrégats sont retirés par un lavage à l'eau distillée. Des études de désorption montrent que les teintures sont liées irréversiblement, tandis que les organocations dispositifs le sont réversiblement. La variation de force ionique réduit l'adsorption de 15 et 36% dans les systèmes argile-organocations monovalents et divalents, respectivement. Dans les systèmes argile-organocations divalents, l'adsorption est plus grande sur l'argile saturée de Na que sur l'argile saturée de K. L'adsorption demeure inchangée sur l'étendue de pH 4,5–8,5 et décroît de manière constante sous un pH de 4,0. Les changements d'adsorption dûs à des changements de température soit petits. L'étude indique que la force ionique est la variable la plus importante dans les interactions argile-organocations. [D.J.]