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THE EFFECT OF ADSORBENT CHARGE ON THE COMPETITIVE ADSORPTION OF DIVALENT ORGANIC CATIONS BY LAYER-SILICATE MINERALS[1]

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ABSTRACT

Competitive adsorption isotherms for diquat (1,1′-ethylene-2,2′-dipyridilium dibromide) *vs* paraquat (1,1′-dimethyl-4,4′-dipyridilium dichloride) on three-layer clay minerals varying in surface charge density were determined. Both chemicals dissociate in water to form divalent organic cations. Paraquat was preferentially adsorbed on all montmorillonites and on the external surface of vermiculite whereas diquat was preferentially adsorbed on the internal surface of vermiculite and on the external surface of nonexpanded mica. At a surface charge density of about 8×10^4 esu/cm^2 adsorption of diquat and paraquat on external surfaces appeared to be equal. At lower surface charge densities, the widely spaced charge centers (7 Å) on paraquat could most effectively counter the adsorbent charge and this cation was preferentially adsorbed over diquat. With increase in surface charge density, adsorption sites are more closely spaced, and diquat was preferentially adsorbed due to the shorter separation of its charge centers (3.5 Å). The data indicate that structural charge on layer silicates is expressed as discrete adsorption sites rather than a smear of surface charge.

INTRODUCTION

Edwards, *et al.* (1965) reported that studies of negative adsorption by layer-silicate clay minerals gave more meaningful results when equations were developed assuming discrete electric charges on the clay mineral. This was a refinement of earlier work by Schofield (1947) in which, as a first approximation, clay charge was represented as a homogeneous smear of charge over the clay surface.

It occurred to us that the nature of clay surface charge could be demonstrated with studies of competitive adsorption using; (a) two divalent organic cations differing mainly in the distance between charge centers on (b) layer-silicate adsorbents of widely differing surface charge densities. If cations are adsorbed at specific sites on the clay surface, the character of the isotherm describing competitive adsorption should change, indicating selective or preferred adsorption of that cation whose charge separation best fits the distribution of charge sites on the clay surface. If the silicate charge is expressed or functions as a surface "smear," there should be relatively little change in the isotherms. Other factors which

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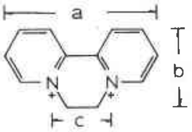
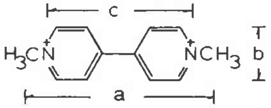
Adsorbate	Structure	Dimensions (A)			Cationic weight
		a	b	c	
Diquat		11-12	7-8	3-4	184.2
Paraquat		13-14	6-7	7-8	186.2

FIG. 1. Properties of adsorbates.

might affect the isotherms are steric hindrance among adsorbed cations and locations of charges in opposing faces of partially expanding layer-silicates, *i.e.*, vermiculites.

Adsorption of organic cations by layer-lattice clay minerals is well documented (Barrer and MacLeod, 1955; Greene-Kelly, 1956; Greenland, 1965; Grim, 1953; Hendricks, 1941; Kinter and Diamond, 1960; McAtee and Hackman, 1964; Reay and Barrer, 1957). These organic cations compete with inorganic cations for adsorption but are usually more tightly held. This is apparently due to the supplemental effect of van der Waals forces in the case of the large organic cation (Hendricks, 1941), an effect not operative in adsorption of the smaller inorganic cations. Hendricks (1941) showed that small organic cations were adsorbed up to the extent of the cation exchange capacity (CEC) of the clay. Very large cations, however, were adsorbed in lesser amounts, presumably because of steric hindrance.

Two materials that appeared to be ideally suited for a study of the type to be reported here are diquat (1,1′-ethylene-2,2′-dipyridilium dibromide) and paraquat (1,1′-dimethyl-4,4′-dipyridilium dichloride). These are soluble organic herbicides that ionize in water to form divalent organic cations. The cations differ structurally in the locations of the nitrogen atoms in the rings and in the flexibility of the molecules (Fig. 1). Assuming that the cationic charge is associated with the nitrogen atoms, it follows that charge location or distribution also differs between the two structures. The charges on the diquat are near the center of the molecule and are separated by about 3–4 Å. On the paraquat structure, charge separation is about 7–8 Å. Both cations are more or less planar, but the single carbon-carbon bond connecting the rings in paraquat permits rotation not possible in diquat. Extreme dimensions of the two cations are also significantly different with paraquat being somewhat longer (13–14 *vs* 11–12 Å) and narrower (6–7 *vs* 7–8 Å) than diquat.

Both diquat and paraquat are strongly adsorbed by cationic exchangers, including clay minerals and exchange resins (Weber, *et al.*, 1965). Maximum adsorption usually equals or approaches the CEC of the adsorbent, though this is a function of the adsorbent and the counterion initially present (S. B. Weed, unpublished data). On highly charged vermiculites, adsorption is less than the CEC determined by common techniques. Diquat adsorption exceeds paraquat adsorption on these vermiculites, probably due to the smaller size of the diquat ion, which results in less steric hindrance. The two adsorbed cations are mutually replaceable by each other, though the ease of replacement one with the other varies with the adsorbent.

The work discussed in this report is concerned with the competitive adsorption of diquat *vs* paraquat on a series of layer silicates differing in surface charge density.

MATERIALS AND METHODS

Analytical grade diquat and paraquat were obtained from the California Chemical Company.

Adsorbents selected for study included four montmorillonites, three vermiculites, and four micas (Table 1).

The montmorillonites were treated for removal of carbonates, after which they were dispersed and separated at the desired particle sizes. These were 20μ for the Utah Bentonite and 2μ for the other montmorillonites. Part of the Utah Bentonite was also separated at 2μ to provide a comparison with the coarser fraction. The cation exchange capacities of the two particle size fractions were similar.

The vermiculites were prepared by agitating the crude ore in distilled water to break up aggregates and pouring the mixture onto a 2-mm screen. This permitted selection of relatively clean flakes from the coarse fraction remaining on the screen. The flakes were then ball-milled in water to provide clay-size vermiculite.

The micas were hand-picked from large books and ball-milled under water. No attempt was made to obtain any particular ion saturation, and exchange sites were presumably occupied by K^+.

The montmorillonites and vermiculites were Na^+-saturated by re-

TABLE 1. LIST OF ADSORBENTS

Code	Clay	Size Fraction (μ)	CEC (meq/g)
S1	Utah Bentonite[a]	<20	1.03
	Utah Bentonite	<2	1.02
S2	Clay Spur Bentonite[b]	<2	0.83
S3	Belle Fourche Bentonite[b]	<2	0.89
S4	Volclay Bentonite[c]	.2–2	0.85
V1	Punky Vermiculite[d]	<5	0.81
V2	Poole Vermiculite[d]	<2	1.47
	Poole Vermiculite	2–5	1.43
V3	Young Vermiculite[d]	<2	1.39
B1	Biotite[e]	1–5	N.D.
B2	Biotite[f]	1–5	N.D.
M1	Muscovite[g]	1–5	N.D.
M7	Muscovite[h]	1–5	N.D.

[a] R. L. Smith, Utah State University, Logan, Utah.

[b] Wards Natural Science Establishment, Rochester, New York. S2 is reference clay mineral No. 26. S3 is reference clay mineral No. 27.

[c] The American Colloid Company, Chicago, Illinois.

[d] The Zonolite Company, Enoree, South Carolina.

[e] Dark brown biotite from western North Carolina.

[f] Dark green biotite from North Burgess, Ontario; obtained from Wards Natural Science Establishment, Rochester, New York.

[g] White muscovite from western North Carolina.

[h] Ruby muscovite from western North Carolina.

peated washings with *N* NaCl solution. Excess salt was removed by washing with water and finally by dialysis. All adsorbents were freeze-dried and aqueous suspensions containing 0.25 percent solid (one percent for the micas) were prepared for adsorption studies.

Adsorption was determined by equilibrating 25 mg of clay (100 mg mica) with varying relative concentrations of diquat and paraquat in a total volume of 25 ml. Total concentration was maintained constant for a given experiment, and was of the order 1×10^{-3} *N* in the equilibrium solution (2×10^{-4} *N* for the micas). The total amount of organic cation equilibrated with each clay sample was equal to about twice the adsorption capacity, *i.e.*, two symmetry. The Na^+-ion cannot compete favorably with diquat or paraquat for adsorption sites, and Na^+ was found to be completely displaced under the conditions imposed in this study. At equilibrium, which was attained rapidly, the supernatant solution contained one symmetry of Na^+ and about one symmetry of diquat plus paraquat. Sodium in solution was determined flame photometrically. The clay suspension was always added to the previously mixed diquat

+paraquat solution, and the solutions were agitated as the clay was added. The mixtures, held in glass-stoppered bottles, were agitated for 30 minutes, which was longer than the time needed to attain equilibrium. Studies were conducted at room temperature since relatively large temperature differences had no effect on the equilibrium (Weber *et al.*, 1965).

Diquat and paraquat remaining in the supernatant solution were determined spectrophotometrically by absorption at 307 and 257 mμ, respectively. It was necessary to correct the paraquat reading for absorption due to diquat in solution.

RESULTS AND DISCUSSION

Diquat and paraquat were adsorbed to the extent of the CEC on the montmorillonites but to somewhat less than this in the case of the vermiculites. X-ray diffraction studies of the clay saturated with either diquat or paraquat showed a basal spacing equal to the sum of the clay lattice plus one layer of the organic cation (Table 2). Since a single cation layer was adsorbed in the interlayer space, regardless of solution concentration, steric hindrance must account for the lower-than-CEC adsorption values on the more highly charged vermiculites. That is, there was insufficient space for the number of organic cations needed to completely counter the adsorbent charge without some overlapping of molecules, and this did not occur. The slightly smaller spacings shown by the paraquat-saturated clays as compared to the diquat-saturated materials are consistent with the difference in size of the two cations. Differences in spacings between S3 and V3 must be due to orientation or to keying of the cation to the clay surface since integral higher order reflections were observed in each case.

TABLE 2. BASAL SPACINGS OF REPRESENTATIVE ADSORBENTS SATURATED WITH PARAQUAT AND DIQUAT[a]

Clay	Na^+	Diquat	Paraquat
S2[b]	10.6 (K^+)	12.90	—
S3	12.28	12.90	12.81
V3	12.11	13.60	13.29

[a] Relative humidity = 30%.

[b] K-saturated and heated to 600°C before preparing specimens on ceramic blocks.

The adsorption isotherms are presented as the equivalent fraction of the CEC countered by diquat (q/q_0) at a given equivalent fraction of diquat in the equilibrium solution (c/c_0) (Figs. 2, 3, 4, and 5). The symbol q represents the me of diquat adsorbed, q_0 the sum of diquat plus paraquat adsorbed, c the equilibrium solution concentration of diquat, and c_0 the sum of diquat plus paraquat in solution.

The most striking aspect of the adsorption curves (Fig. 2) is that the competitive adsorption of diquat *vs* paraquat was dependent on the adsorbent. Paraquat was preferentially adsorbed by the four montmorillonites over the entire concentration range. Diquat, on the other hand, was preferentially adsorbed by the vermiculites, except at low relative solution concentrations of diquat. Under these conditions, the isotherms dipped below the diagonal, indicating preference for paraquat.

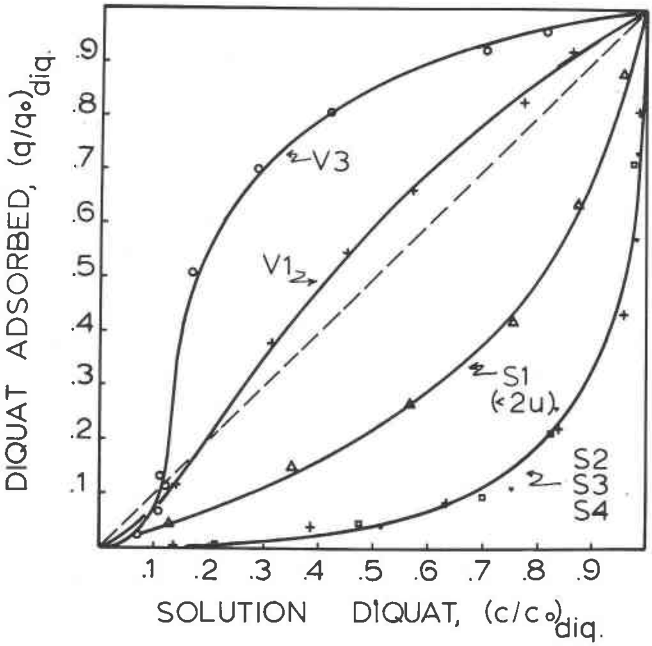


FIG. 2. Competitive adsorption of diquat vs. paraquat on various montmorillonites and vermiculites.

Preference for paraquat exhibited by the montmorillonites is explainable in terms of: (a) the comparative properties of the diquat and paraquat; (b) the relatively low surface charge densities of the montmorillonites (Table 3); (c) the unlimited expandability of the Na$^+$-montmorillonites; (d) lack of c-axis ordering in the montmorillonites.

Paraquat is a more flexible molecule than diquat, and more of the constituent atoms can approach an adsorbing surface. Hence, van der

Waals forces can make a greater contribution to the over-all adsorption energy than is likely in the case of diquat. The coulombic charges are the same for the two cations, and total number of atoms very nearly the same. Paraquat would therefore be expected to be preferentially adsorbed on an open, charged surface, whether or not the surface charge acted as discrete sites or a "smear." The highly dispersed Na^+-montmorillonites presented just such an open surface, and paraquat was preferred. The calculated surface charge density of the montmorillonites (Table 3) indicates that if charge acted as discrete sites, paraquat would still be preferentially adsorbed because of the more favorable separation of charge in this cation. This would permit the positive and negative charges to come more nearly into juxtaposition than would be likely with diquat.

TABLE 3. SURFACE CHARGE DENSITIES OF ADSORBENTS

Adsorbent	Surface charge density ($esu \times 10^4/cm^2$)	Estimated area per monovalent site ($Å^2$)
B1	8.98[a]	53
B2	9.22[a]	52
M1	10.68[a]	45
M7	10.01[a]	48
V3	6.6[b]	72
S1	3.9[b]	124
S2	3.4[b]	141
—	8.0	60

[a] Calculated from structural formulae plus cell dimensions determined by X-ray diffraction analysis.

[b] Estimated from CEC plus assumed total analyses.

Preferential adsorption of diquat by vermiculite (Fig. 2) can be explained by assuming discrete adsorption sites on these materials. Calculated surface charge density of V3 (Table 3) indicates a distribution of sites that could be countered about equally well by either diquat or paraquat on an exposed or external surface. This is based upon the assumption that these sites are homogeneously distributed over the adsorbing surface, though the actual distribution is, of course, not known. However, this assumption provides a model with which to compare site separation, adsorbate molecule size, and cation charge separation. Thus, charge density on V3 suggests that steric hindrance among adsorbate molecules and coincidence between positive and negative charges would result in more-or-less equal adsorption of diquat and paraquat on external surfaces. However, since charges in opposing faces must be countered, diquat is more ideally suited to accomplish this, both because of the more compact nature of the cation and because of the shorter distance of charge separation than in paraquat. When V3 was K-saturated and heated to minimize internal surface, paraquat was preferentially adsorbed (Fig. 3). However, preference for paraquat was not as pronounced as with the montmorillonites. This is in agreement with the difference in surface charge densities between these materials (Table 3).

Vermiculite V1 contained small amounts of kaolinite and talc, but the CEC still seems quite low for a vermiculite (Table 1). Electron micrographs showed very large thin flakes of vermiculite, which would give a relatively low proportion of internal to external surface. Vermiculites V2 and V3, in contrast to V1, consisted of particles that were relatively small in lateral dimensions, but quite thick, indicating many more platelets per particle. Both the lower surface charge density and the greater external surface of V1 would favor the observed displacement of its isotherm from that for V3 (Fig. 2).

The preferred adsorption of paraquat by vermiculite at low diquat concentrations indicates that diquat was excluded from the interlayer region under these conditions. The isotherm at this point represents com-

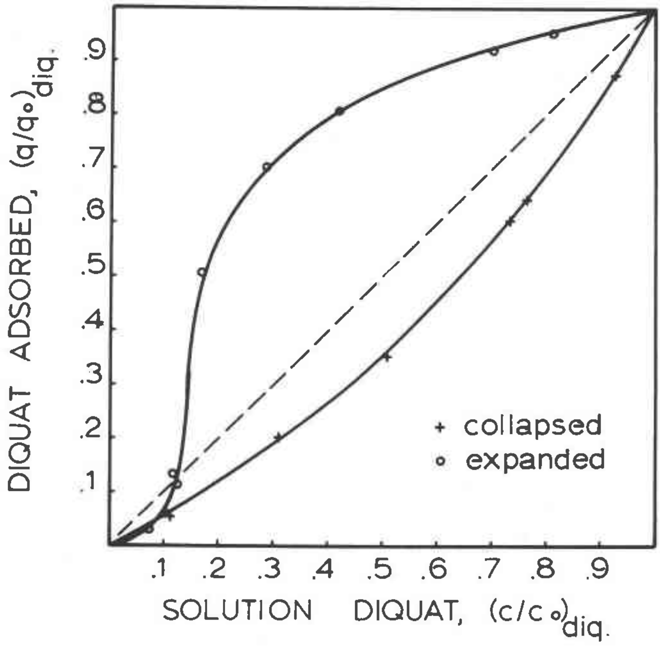


FIG. 3. Effect of lattice collapse on the competitive adsorption of diquat vs. paraquat on Young vermiculite (V3).

petitive adsorption on the external surface, and paraquat was preferred. This is supported by the coincidence in this region of the isotherms for V3 both expanded and collapsed (Fig. 3).

The Utah Bentonite S1 had a higher CEC (Table 1) and particles were in general much larger than was the case with the other montmorillonites. Both factors should favor displacement of the isotherm from those of the other montmorillonites (Fig. 2). The probably greater incidence of opposing faces and thus charge sites should result in a relative decrease in preference for paraquat.

The effect of particle-size on the isotherms is illustrated in Figure 4. The difference between the curves for the two Utah Bentonite fractions is slight. However, relatively little of the total clay-size fraction was present as particles having the typical montmorillonite morphology. In addition, the $<20\mu$ fraction included the $<2\mu$ fraction. Thus, it is concluded that the small displacement of the isotherm for the fine fraction is a reflection of the contribution of the more highly dispersed component, which was present in both fractions but made up a larger proportion of the small fraction.

The isotherms for the two size-fractions of vermiculite V2 (Fig. 4) are

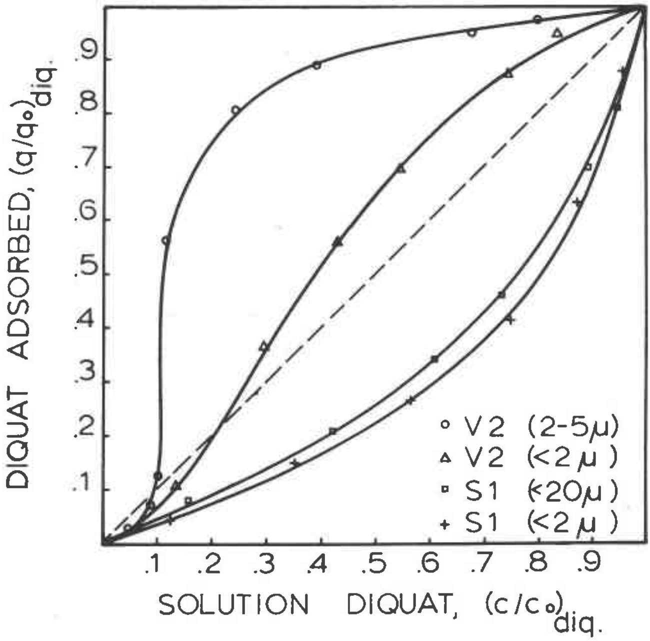


FIG. 4. Effect of adsorbent particle size on the competitive adsorption of diquat vs. paraquat on Poole vermiculite (V2) and Utah bentonite (S1).

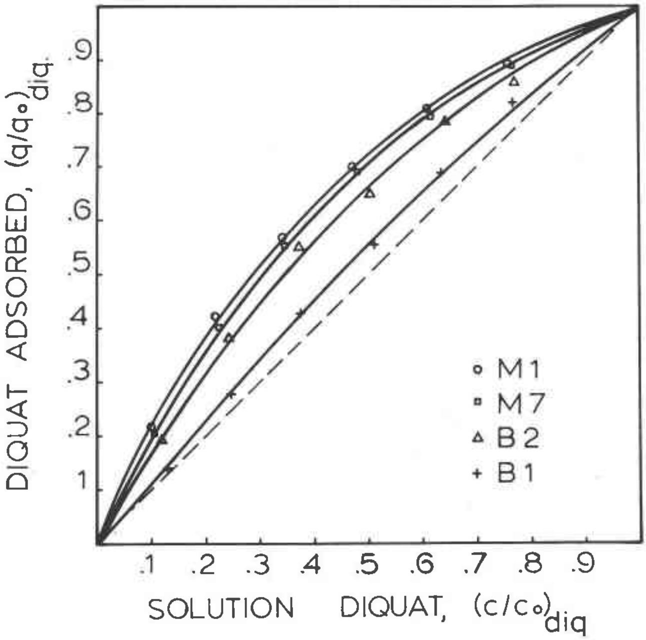


FIG. 5. Competitive adsorption of diquat vs. paraquat on ground micas (1–5μ fractions).

displaced relative to each other to a much greater extent than was the case for the Utah Bentonite. Both fractions had the same CEC (Table 1) and both came from the same large vermiculite flakes. Thus, the curve displacement reflects the thicker packets of platelets in the coarser fraction, which would be expected to show a relatively greater preference for diquat. Electron micrographs also indicated that particles in the coarse fraction were thicker than in the fine fraction.

The effect of surface charge density on isotherm position is illustrated in Figure 5, using four micas varying in structural charge from 8.98 to 10.68×10^4 esu/cm². Diquat was preferentially adsorbed by each mica, and the preference increased as surface charge density increased. These curves can be compared with that for the collapsed vermiculite V3 (Fig. 3), on which paraquat was preferred. The vermiculite had a considerably lower surface charge density, and the curve position lies in the direction anticipated. If the charge were expressed as a surface smear, it seems unlikely that isotherm position should change so markedly.

Using the equivalent fraction of diquat adsorbed at an equilibrium solution concentration of $(c/c_0)_D = 0.5$ as a means of comparison, it appears that at a surface charge density of about 8×10^4 esu/cm² there is no

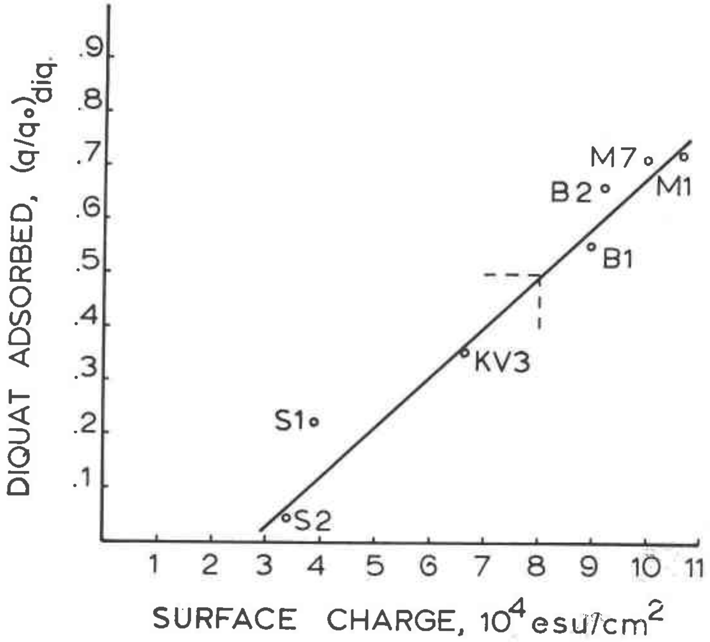


FIG. 6. Competitive adsorption of diquat vs. paraquat at $(c/c_0)_D = 0.5$ as related to surface charge density of adsorbent.

preferential adsorption of either diquat or paraquat on external surfaces (Fig. 6). In this plot data for unexpanded micas, collapsed vermiculite V3, and the montmorillonites were used. Surface charge densities of the montmorillonites were estimated from the CEC and from an ideal montmorillonite composition (Van Olphen, 1963). Charge densities of the micas were calculated from structural formulae and from cell dimensions obtained by X-ray diffraction analysis. The composition and cell dimensions of the collapsed V3 were assumed to be the same as for biotite micas B1 and B2, which were determined by analysis. Competitive adsorption on internal surfaces of montmorillonites S2, and S3, and S4 was probably the same as on external surfaces because of the low structural charge and rather complete state of dispersion. This was apparently not true for the Utah Bentonite (S1) and thus the point lies quite far from the line in Figure 6. An attempt was made to collapse the montmorillonites by K^+-saturation plus heat, but the diquat and paraquat always penetrated between the layers and replaced at least part of the K^+ (Table 2). This occurred even after heating S2 at 725°C for two hours.

Conclusions

The data indicate that two factors controlled the positions of the diquat *vs* paraquat competitive adsorption isotherms in the systems studied: (a) adsorbent surface charge density and (b) prevalence of opposing, *i.e.*, interlayer surfaces in an adsorbent particle. A relative increase in either or both of these factors resulted in a displacement of the isotherm in the direction of a relative preference for diquat (or less preference for paraquat). If adsorbent charge were expressed as a surface smear, one would anticipate little change in isotherm position as the above factors changed, except perhaps as steric hindrance might be a factor. However, if the charge acted as discrete surface adsorption sites, data of the type shown would be expected. The cation whose charge centers could most nearly approach the adsorption sites on the adsorbing surface would be preferred. On open or external surfaces, paraquat, with its greater distance of charge separation, provided a better match to sites on the lower-charged montmorillonites than did the diquat. On the more highly charged mica surfaces, the reverse was true, and vermiculite was intermediate. On internal surfaces, proximity of charge sites in opposing faces favored diquat adsorption because of the shorter distance between charge centers in this cation. A single layer of cations was adsorbed in any event (Table 2), and paraquat was thus at a disadvantage in the restricted interlayer space.

The data indicate that charge on layer silicates, at least as it pertains to adsorption of the divalent cations considered, is expressed as discrete adsorption sites rather than as a surface smear.

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