

## SURFACE CHARGE CHARACTERIZATION OF LAYER SILICATES BY COMPETITIVE ADSORPTION OF TWO ORGANIC DIVALENT CATIONS\*

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**Abstract**—Diquat<sup>2+</sup> (1,1'-ethylene-2,2'-dipyridinium ion) and paraquat<sup>2+</sup> (1,1'-dimethyl-4,4'-dipyridinium ion) were competitively adsorbed by Na-saturated kaolinites, smectites and expanded and collapsed vermiculites. The relative preference for one or the other cation varied with the surface charge densities of the adsorbents and the location of the adsorption site, i.e. internal or external. Minerals with high surface charge exhibited preference for diquat whereas minerals with low surface charge preferred paraquat. Expanded vermiculites preferentially adsorbed diquat on internal surfaces. Collapsed vermiculites generally showed a preference for paraquat. Smectites and kaolinites preferentially adsorbed paraquat.

Surface charge densities of the layer silicates vs. the relative preference for diquat revealed two linear relationships, one for internal adsorption and one for external adsorption. Internal adsorption was characterized by a strong preference for paraquat on low-charged smectites, a relative decreasing preference for paraquat with higher-charged smectites, and a strong preference for diquat on high-charged expanded vermiculites.

Preferential adsorption for paraquat by kaolinite was quite similar to adsorption of paraquat on the external sites of vermiculites. There was no apparent relationship between competitive adsorption and surface charge density of kaolinite.

### INTRODUCTION

DIQUAT<sup>2+</sup> (1,1'-ethylene-2,2'-dipyridinium ion) and paraquat<sup>2+</sup> (1,1'-dimethyl-4,4'-dipyridinium ion) are contact herbicides, usually supplied as the chloride or bromide salts. Both compounds are soluble in water and dissociate to give divalent organic cations, similar in composition, but differing in the locations of the nitrogens and thus the charges in the pyridine rings. Charge separation on the diquat ion is about 3.5 Å whereas it is about 7 Å on the paraquat ion. Weed and Weber (1968) suggested that this difference in charge separation could explain observed relationships between competitive adsorption of diquat vs. paraquat and surface charge densities ( $\sigma$ ) of layer silicate adsorbents.

Results of competitive adsorption of diquat vs. paraquat on external surfaces of micas and vermiculites have been interpreted in terms of the relative agreement between charge separation on the cations and charge separation on the minerals, due allowance being made for steric hindrance among adsorbed cations (Weed and Weber, 1968;

Philen, Weed and Weber, 1970). That is, they reflect the relative goodness-of-fit between positive and negative charges. When the two divalent, organic cations compete for adsorption on a mineral surface, that cation, both of whose charges can more nearly approach the adsorbent charge sites, is preferentially adsorbed. Philen, Weed and Weber (1970) used this relationship to devise a method for estimating  $\sigma$  of clay and silt-sized micas and vermiculites. They reported that the relative amounts of diquat and paraquat adsorbed from mixed solutions of the two cations varied linearly with the  $\sigma$  of the mineral adsorbent when adsorption was restricted to external surfaces. Diquat was preferred at high values of  $\sigma$ , whereas paraquat was preferred on lower-charged surfaces. Adsorption on internal surfaces appeared to accentuate the differences between diquat and paraquat adsorption, which meant that the utility of competitive adsorption for estimating  $\sigma$  demanded that the minerals be completely collapsed.

The same type of relationship between  $\sigma$  and competitive adsorption discussed above for external surfaces undoubtedly applies on internal surfaces. Here, however, the density of charges is effectively doubled, since there are two charged surfaces in association with the single layer of organic cations. Diquat and paraquat do not form double molecular

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layers in the interlayer space (Weed and Weber, 1968). A given adsorbed divalent cation might counter adsorbent charge on one or both of the surfaces. Again, the preferred cation would be the one whose positive charges could come into closest proximity to adsorption sites, whether in a single or opposing surfaces. On a highly charged external mica surface, if the adsorption sites are assumed to be distributed in the same pattern as the unit cells, with one site per unit cell surface, the  $\sigma$  is approximately  $10 \times 10^4$  esu/cm<sup>2</sup>. In the interlayer space, the density is effectively doubled, i.e.  $20 \times 10^4$  esu/cm<sup>2</sup>. This concentration of sites is too dense for complete countering by either diquat or paraquat (Weed and Weber, 1969). For an average surface charge density of  $8-9 \times 10^4$  esu/cm<sup>2</sup>, either diquat or paraquat can satisfactorily counter the charge on external surfaces, and there is no preferential adsorption (Philen, Weed and Weber, 1970). In the interlayer region, however, the more closely spaced charges on the diquat cation can presumably come into closer proximity to adsorbent sites in opposing surfaces with less steric hindrance among adsorbed cations. Actually, neither diquat nor paraquat is adsorbed to 100 per cent of the CEC on high-charged expanded micas and vermiculites (Weed and Weber, 1969). However, preference for diquat in the interlayer region of vermiculite is enhanced compared to adsorption on the external surface. With decreasing  $\sigma$ , this preference for diquat over paraquat decreases in accordance with space requirements and relative distances between positive and negative charge sites.

Smectites also vary widely in total charge and presumably in  $\sigma$ . Harward, Carstea and Sayegh (1969) studied a group of smectites exhibiting a range of cation exchange capacity (CEC) from 0.95 to 1.38 me/g. Schultz (1969) presented an extensive list of smectites varying in CEC from 0.87 to 1.74 me/g. In neither case were surface area data given, so that values for  $\sigma$  cannot be calculated. However, data obtained for smectites studied in our laboratory indicate that  $\sigma$  may differ by at least a factor of two for different clays.

If adsorption of diquat vs. paraquat could be limited to external surfaces of the smectites, it is probable that the relationship between  $\sigma$  and competitive adsorption reported for micas and collapsed vermiculites (Philen, Weed and Weber, 1970) would also apply to the smectites. However, earlier work on a small number of smectites (Weed and Weber, 1968) indicated that the usual procedure for collapsing a layer silicate, i.e. K-saturation plus heat (600°C in this case), did not prevent diquat and paraquat from entering the interlayer region. The utility of the previous work for characterizing

low-charged, expanding layer silicates is therefore limited.

The work to be reported herein was conducted to determine the nature of competitive adsorption of diquat vs. paraquat by expanded smectites and vermiculites as it relates to  $\sigma$ . Data are also reported for a group of kaolinite minerals.

#### MATERIALS AND METHODS

Kaolinite and smectite clay minerals were collected from various sources (Table 1). The smectites were treated for removal of carbonates (Jackson, 1956) and dispersed in water. The kaolinites were similarly dispersed, except that NaOH was added to give a suspension reaction of pH 8-9. Particles greater than  $2\mu$  were removed by sedimentation, the fine fraction was saturated with Na and excess electrolyte was removed by dialysis. The separated kaolinite suspensions were adjusted to pH 3.5 prior to Na-saturation. The suspensions were then freeze-dried and the clay stored dry. Vermiculites used were described by Philen, Weed and Weber (1970).

Cation exchange capacities of the kaolinites and smectites were determined by the method of Rich (1961) and by constructing adsorption isotherms using diquat or paraquat (Weed and Weber, 1968). In the latter technique, maximum adsorption was taken as a measure of CEC. Surface areas of Na-clays were determined by adsorption of ethylene glycol monoethyl ether (Carter, Heilman and Gonzalez, 1965).

Potassium contents of vermiculites were determined by decomposing the samples in HF plus H<sub>2</sub>SO<sub>4</sub> (Shapiro and Brannock, 1956) after which K was determined flame photometrically. Collapsed vermiculites were prepared by heating the K-saturated, freeze-dried mineral to 300°C for 1 hr.

Competitive adsorption isotherms were constructed as previously described using the Na-saturated clays (Philen, Weed and Weber, 1970). Approximately two symmetries of diquat plus paraquat were mixed with 50 mg of smectite or 100 mg of kaolinite. Relative amounts of the two cations were varied while the sum of the two was held constant. The mixtures were shaken for 30 min. Diquat and paraquat remaining in solution were determined spectrophotometrically by adsorption at 307 nm and 257 nm, respectively. Competitive adsorption isotherms for each mineral were constructed by plotting the equivalent fraction of diquat adsorbed against the equivalent fraction of diquat in the equilibrium solution. The Na ion, initially present as the adsorbed cation, was completely exchanged from the kaolinites, smectites, and collapsed vermiculites by the diquat and paraquat and is not included in the calculations.

Table 1. Sources of minerals used as adsorbents

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S1	Montmorillonite, Plymouth, Utah, obtained from R. L. Smith, Utah State University, Logan, Utah.
S2	Montmorillonite, commercial grade, from Industrial Distributors, Inc., New York.
S3	Montmorillonite, Technical Bentonite, from Murro Chemicals, Portsmouth, Pennsylvania.
S4	Montmorillonite, commercial grade Volclay Bentonite, American Colloid Company, Skokie, Illinois.
S5	Montmorillonite, commercial grade, Fisher Scientific Company, U.S.A.
S6	Montmorillonite, Black Hills Bentonite, commercial grade, from Industrial Minerals Company, Skokie, Illinois.
S7	Montmorillonite, Panther Creek Bentonite, commercial grade, American Colloid Company, Skokie, Illinois.
S8	Montmorillonite, Camargo Bentonite, obtained from Lester Reed, Oklahoma State University, Stillwater, Oklahoma.
S9	Montmorillonite, Wyoming Bentonite, mass sample, "high sodium", obtained from American Colloid Company, Skokie, Illinois.
S10	Montmorillonite, Wyoming Bentonite, mass sample, "normal sodium, high viscosity", obtained from American Colloid Company, Skokie, Illinois.
S11	Montmorillonite, Wyoming Bentonite, mass sample, "normal sodium, medium viscosity", obtained from American Colloid Company, Skokie, Illinois.
S12	Montmorillonite, Wyoming Bentonite, mass sample, "normal sodium, low viscosity", obtained from American Colloid Company, Skokie, Illinois.
S13	Montmorillonite, Wyoming Bentonite, mass sample, "high sodium, low viscosity", obtained from American Colloid Company, Skokie, Illinois.
S14	Montmorillonite, Wyoming Bentonite, Wyo-Gel, obtained from ArcherDaniels-Midland Company, Cleveland, Ohio.
S15	Regularly interstratified smectite and 10 Å mineral, Fort Sanderman, Pakistan, obtained from Ward's Scientific Establishment (labelled Beidellite).
S16	Hectorite, Hector, California, A.P.I. 34, obtained from Ward's Scientific Establishment.
S17	Montmorillonite, Burns, Mississippi, A.P.I. 21, obtained from Ward's Scientific Establishment.
S18	Montmorillonite, Amory Mississippi, A.P.I. 22, obtained from Ward's Scientific Establishment.
S19	Montmorillonite, Chambers, Arizona, A.P.I. 23, obtained from Ward's Scientific Establishment.
S20	Montmorillonite, Otay, California, A.P.I. 24, obtained from Ward's Scientific Establishment.
S21	Montmorillonite, Upton, Wyoming, A.P.I. 25, obtained from Ward's Scientific Establishment.
S22	Montmorillonite, Clay Spur, Wyoming, A.P.I. 26, obtained from Ward's Scientific Establishment.
S23	Montmorillonite, Belle Fourche, South Dakota, A.P.I. 27, obtained from Ward's Scientific Establishment.
S24	Montmorillonite, Bayard, New Mexico, A.P.I. 30A, obtained from Ward's Scientific Establishment.
S25	Montmorillonite, Cameron, Arizona, A.P.I. 31, obtained from Ward's Scientific Establishment.
S26	Nontronite, Garfield, Washington, A.P.I. 33A, obtained from Ward's Scientific Establishment.
K1	Halloysite, Iolta Bridge Mine, near Franklin, North Carolina, collected by O. D. Philen, Jr.
K2	Kaolinite, Bath, South Carolina, A.P.I. 5, obtained from Ward's Scientific Establishment.
K3	Kaolinite, Sandersville, Georgia, obtained from Theile Kaolin Company, Sandersville, Georgia.
K4	Halloysite, Wagon Wheel Gap, Colorado, A.P.I. 29, obtained from Ward's Scientific Establishment.
K5	Kaolinite, Monetto Clay Corporation, Aiken, South Carolina.
K6	Kaolinite, Raleigh, North Carolina, roadcut, collected by O. D. Philen, Jr.
K7	Kaolinite, Hephzibah, Georgia, obtained from Babcock & Wilcox, Hephzibah, Georgia.
K8	Kaolinite, Aiken County, South Carolina, obtained from United Sierra Division, Aiken, South Carolina.
K9	Kaolinite, Andersonville, Georgia, obtained from American Cyanamid Company, Andersonville, Georgia.
K10	Kaolinite, Kingsley Clay, United Clay Mines Corp. Sandersville, Georgia.
K11	Kaolinite, Burgess No. 10, Burgess Pigment Company, Sandersville, Georgia.
V1	Vermiculite, from western North Carolina, collected by S. B. Weed.
V2	Vermiculite, Poole Mine, obtained from Zonolite Company, Enoree, South Carolina.
V4	Vermiculite, Libby Montana.
V6	Vermiculite, Cooper Mine, obtained from Zonolite Company, Enoree, South Carolina.
V9	Vermiculite, Waldrop Mine, obtained from Zonolite Company, Enoree, South Carolina.

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Because of steric hindrance among adsorbed diquat and paraquat on high-charged surfaces, part of the adsorbed Na was not replaced from the expanded vermiculites (Weed and Weber, 1969). This was less than twenty per cent of the total Na. Again, this was not included in the calculations for these few minerals.

## RESULTS

Surface charge densities of the smectites and kaolinites, calculated from diquat adsorption and surface area values are given in Table 2. Values determined using diquat adsorption were generally higher than those obtained from CEC determined by Ca adsorption. This is attributable to hydrolysis

Table 2. Surface areas and charge characteristics of clay adsorbents

Adsorbent	Surface* area (m <sup>2</sup> /g)	CEC* (meq/100g)	Charge density (10 <sup>4</sup> esu/cm <sup>2</sup> )
S1	616(0.7)	112.4(1.3)	5.28
S2	693(0.3)	91.5(1.2)	3.82
S3	761(0.3)	93.3(0.3)	3.54
S4	799(0.1)	93.9(0.5)	3.40
S5	734(0.6)	93.9(0.1)	3.70
S6	729(0.3)	85.3(0.7)	3.38
S7	828(0.7)	92.7(0.0)	3.24
S8	710(1.6)	122.2(0.2)	4.98
S9	804(0.6)	98.1(1.1)	3.53
S10	810(0.3)	96.7(0.4)	3.45
S11	820(0.1)	90.8(1.2)	3.20
S12	798(0.4)	99.0(0.4)	3.59
S13	800(0.9)	93.6(0.9)	3.38
S14	760(1.0)	83.1(0.8)	3.16
S15	387(0.9)	61.9(2.0)	4.62
S16	819(0.3)	82.7(0.9)	2.92
S17	810(0.6)	99.4(0.3)	3.55
S18	711(0.8)	74.7(1.3)	3.04
S19	723(0.4)	117.3(0.9)	4.69
S20	675(0.4)	120.6(0.3)	5.17
S21	703(0.4)	90.5(0.1)	3.72
S22	686(0.1)	85.2(0.3)	3.59
S23	779(0.2)	91.6(0.8)	3.40
S24	696(0.6)	117.3(0.2)	4.94
S25	381(0.4)	71.1(0.1)	5.40
S26	465(1.5)	89.1(1.3)	5.54
K1	24(15)	3.1(0.6)	3.73
K2	17(3)	3.0(2.3)	5.10
K3	15(17)	3.0(1.3)	5.78
K4	20(10)	3.8(1.4)	5.49
K5	16(6)	3.9(1.3)	7.05
K6	11(6)	2.8(7.0)	7.36
K7	18(31)	2.6(6.0)	4.18
K8	23(26)	3.4(1.3)	4.27
K9	32(3)	4.9(3.0)	4.43
K10	20(6)	3.6(7.0)	5.20

\*Mean of three or four replicates. Relative standard deviation expressed as per cent in parentheses.

of Ca from the clay during the washing procedure to remove excess salt (Okazaki, Smith and Moodie, 1962, and unpublished data of the authors). When the CEC was determined in 1N CaCl<sub>2</sub>, i.e. both Ca and Cl were determined (Rich, 1962), the net charge was very nearly the same as the charge determined by diquat adsorption. Consequently, surface charge densities calculated from diquat adsorption were assumed to accurately characterize the clays.

Representative competitive adsorption isotherms of diquat versus paraquat for the kaolinites and smectites are shown in Fig. 1. Isotherms reported previously (Weed and Weber, 1968) for a mica, a collapsed vermiculite, and an expanded vermiculite are included for comparison. The axes represent

the equilibrium equivalent fraction of diquat adsorbed, and the equilibrium equivalent fraction of diquat in solution. The dashed line (diagonal) drawn from (0, 0) to (1, 1) represents no preferential adsorption. Isotherms lying to the left of (above) this diagonal indicate preferential adsorption of diquat; isotherms to the right (below) indicate preferential adsorption of paraquat. Intercepts of the isotherms with the other diagonal drawn from (1, 0) to (0, 1), were used to characterize competitive adsorption in each system (Philen, Weed and Weber, 1970). For convenience, this is labelled  $\chi$ .

The isotherms indicate that paraquat was preferentially adsorbed over diquat by all of the smectites and kaolinites. The degree of preference

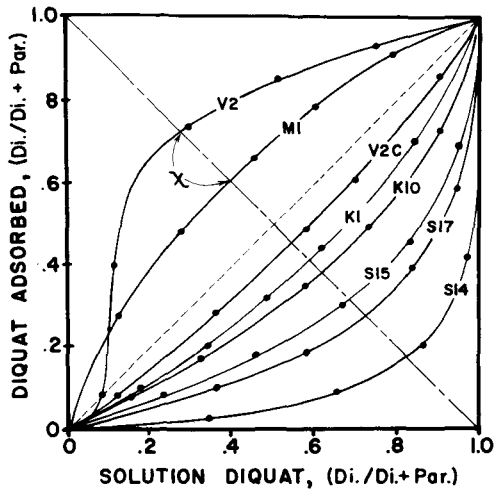


Fig. 1. Competitive adsorption isotherms of diquat vs. paraquat for selected kaolinites (K1, K10) and smectites (S14, S15, S17). Isotherms for a mica (M1), an expanded vermiculite (V2), and a collapsed vermiculite (V2C), taken from the work of Weed and Weber (1968) are included for comparison.  $\chi$  represents the equivalent fraction of diquat adsorbed at the intercept of the isotherm with the diagonal.

varied, being generally greater for the lower-charged clays. The smectites exhibited an especially strong preference for paraquat. At high solution concentrations of paraquat (low diquat concentration), diquat was essentially excluded from the adsorbed phase. This contrasts with the expanded vermiculite, which showed a strong preference for diquat, presumably on internal surfaces. On external adsorption sites, the vermiculite exhibited a preference for paraquat, whereas diquat was preferentially adsorbed by the mica. The kaolinites, as a group, showed a slight preference for paraquat over diquat. The isotherms for the kaolinites were quite similar to that obtained for the collapsed vermiculite.

Philen, Weed and Weber (1970) reported that for micas and collapsed vermiculites a linear relationship resulted when the values of the intercepts ( $\chi$ ) of the isotherms with the diagonal drawn from (1, 0) to (0, 1) were plotted vs.  $\sigma$ . The regression line for their data is included for comparison in Figs. 2 and 3 together with data for the smectites and kaolinites.

The smectites apparently are not from the same population as the micas and collapsed vermiculites, and the relationship between  $\chi$  and  $\sigma$  reported previously for the micas and vermiculites appears not to hold for the smectites.

The kaolinites also behaved quite differently

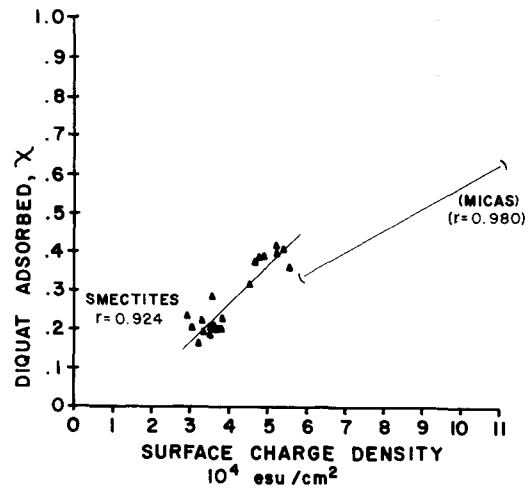


Fig. 2. Equivalent fraction of diquat adsorbed ( $\chi$ ) as related to surface charge densities of smectites. Regression line in parentheses refers to external adsorption by micas and collapsed vermiculites (Philen, Weed and Weber, 1970).

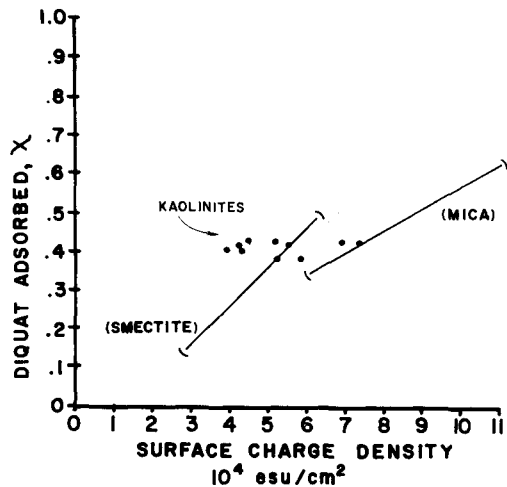


Fig. 3. Equivalent fraction of diquat adsorbed ( $\chi$ ) as related to surface charge densities of kaolinites. Regression lines in parentheses refer to adsorption by smectites (Fig. 2), and adsorption by micas and collapsed vermiculites (Philen, Weed and Weber, 1970).

than the other minerals. This may be partly attributable to excessive variability in determination of specific surface of these minerals. Because of the relatively small specific surface of kaolinite the error associated with its determination was quite large (Table 2).

The difference between preferential adsorption on external and internal surfaces of vermiculite is illustrated in Figs. 4 and 5. Potassium contents



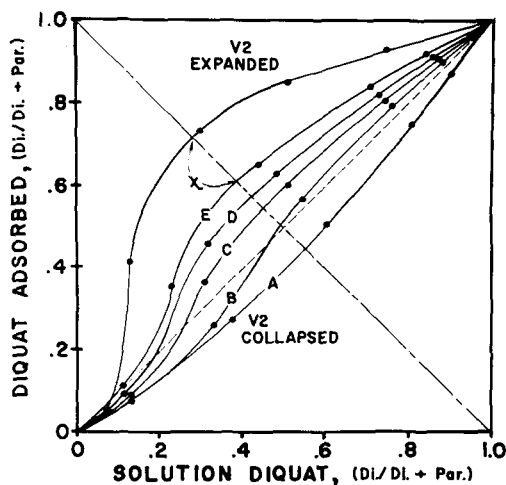


Fig. 4. Competitive adsorption isotherms of mixtures of expanded and collapsed vermiculite V2. Letters on curves refer to different amounts of expanded relative to collapsed vermiculite (see text).

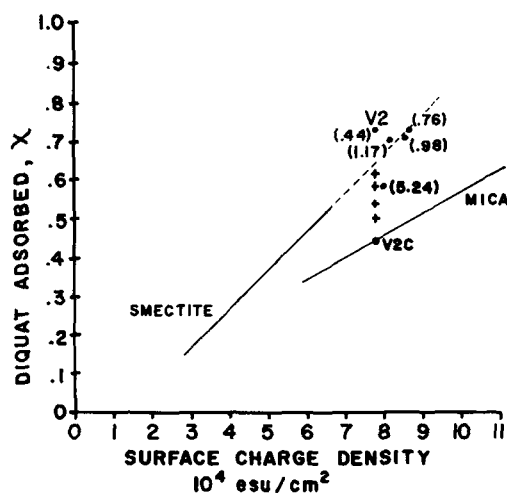


Fig. 5. Equivalent fraction of diquat adsorbed ( $\chi$ ) as related to surface charge densities of expanded vermiculites (●) and mixtures of expanded and collapsed vermiculite V2 (+; data from Fig. 4). Figures in parentheses refer to per cent K in vermiculite. Regression lines for adsorption by smectites and collapsed vermiculites included.

of the vermiculites are included in Fig. 5. These values were used to estimate the degree of expansion of the vermiculites, assuming that all K-ions were present in non-expanded interlayers and that each parent mica was ideal biotite, i.e. 7.5% K. The estimated degrees of expansion were 94, 90, 87, 84 and 30%, respectively, for 0.44, 0.76, 0.98, 1.17 and 5.24% K. The competitive adsorption data

indicate that results are markedly dependent on the degree of expansion of the vermiculite, i.e. on the relative amounts of internal and external surface. This effect is further illustrated by data obtained using mixtures of varying amounts of expanded and collapsed vermiculite V2 (curves A through D in Fig. 4). An attempt was made to maintain the total CEC of the mixtures constant, while changing the relative contributions of the expanded and collapsed clays. Potassium exchanged by diquat and paraquat from external surfaces of the collapsed form of the clay was found to be fixed in interlayers of the initially expanded form, thus reducing the amount of internal surface below that predicted. Hence, curve A (Fig. 4) is identical with that found for the completely collapsed clay though the initial mixture was prepared to contain approximately 25 per cent of the expanded form. The data, nevertheless, bear out that as the available interlayer adsorption surfaces decreased, preference for diquat also decreased. The lower extreme, i.e. adsorption on external surfaces only, corresponds to the micas and collapsed vermiculites. The upper extreme is probably not the limit of diquat preference for this material, inasmuch as the sample contained 0.44% native K. Removal of this K would increase internal surface and hence preferential adsorption of diquat. Expressing competitive adsorption as the intercepts of the diagonal with the isotherms ( $\chi$ ) yields the series of values designated by crosses in Fig. 5. The experimental value for competitive adsorption in any instance represents the sum effect of the two adsorption surfaces.

#### DISCUSSION

The smectites, as a group, were not as consistent as the micas and vermiculites in their competitive adsorption behavior. This may be attributable to real differences in the distributions of adsorption sites over the mineral surfaces, or to contaminants in the minerals, leading to inaccurate values for CEC and surface area. The samples were not treated for removal of free iron oxides or amorphous constituents prior to adsorption studies. Harward and Brindley (1966) reported increases in CEC of synthesized smectites following such treatments. Similarly, Harward, Carstea and Sayegh (1969) obtained CEC values 5–20 per cent greater than those reported herein for smectites common to both studies. They had included treatments for removal of free iron and amorphous silica and alumina, presumably present as diluents. The wide range in specific surface values found for the various smectites (Table 2) suggests that inert diluents may have been present in some of these samples, some interlayers may have been irreversibly collapsed,

or interlayer components may have blocked some exchange sites and surface area. X-ray diffraction data indicated some random interstratification of occasional collapsed (10 Å) layers with expanded (15 Å) layers in several of the smectites. Sample S25 exhibited considerable interstratification, an observation supported by the presence of 2.4% K in the Na-washed clay. Sample number S15 was labelled beidellite by the supplier. However, the X-ray data indicated a regular interstratification of collapsed (10 Å) and expanded (14–15 Å) spacings (rectorite?). The expanded portion behaved as a smectite.

Extrapolation of the smectite regression line to higher values of  $\chi$  might be expected to accommodate the completely expanded vermiculites, i.e. all K removed. The experimental data (Fig. 5) suggest that completely K-free vermiculites will exhibit a greater preference for diquat than the smectite line predicts, i.e. vermiculite points will lie above the regression line. On the other hand, this may simply be attributable to the scatter in the smectite data points. This scatter, in turn, may be due, not to experimental error, but to heterogeneity in the samples themselves.

The kaolinites exhibited a very narrow range in preference for paraquat (Fig. 3). The range in CEC was also narrow, though the range in apparent surface charge density was quite large (Table 2 and Fig. 3). These differences may not be real, but may reflect the uncertainties associated with surface area measurements. However, if the differences are real, the implications concerning charge expression by the kaolinites are quite interesting. If competitive adsorption on these minerals is truly independent of  $\sigma$ , and essentially constant, it suggests that the small amount of permanent charge possessed by the kaolinites behaves more as a surface smear of charge than as discrete adsorption sites, as exhibited by the triphormic minerals. Consequently, there should be little, if any, preferred adsorption of one cation over another of like charge and properties. The rather small preference for paraquat over diquat might be explained by the greater flexibility of the paraquat cation (Weed and Weber, 1968). This would permit closer approach of more constituent atoms to the clay surface, and thus a greater contribution of van der Waals forces in addition to the coulombic attraction.

The charged, three-layer silicates exhibit a unique correlation between competitive adsorption and surface charge density. If a mineral is either

completely collapsed or completely expanded this correlation provides a means of estimating surface charge density from a simple competitive adsorption isotherm. Since the sum of diquat plus paraquat adsorbed is a measure of total charge or CEC, one could also estimate surface area. This does not apply to the high-charged expanded vermiculites inasmuch as diquat plus paraquat adsorption on these minerals is less than the CEC (Weed and Weber, 1969).

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#### REFERENCES

- Carter, D. L., Heilman M. D. and Gonzalez, C. L. (1965) Ethylene glycol monoethyl ether for determining surface area of silicate minerals: *Soil Sci.* **100**, 356–360.
- Harward, M. E. and Brindley, G. W. (1966) Swelling properties of synthetic smectites in relation to lattice substitutions: *Clays and Clay Minerals* **13**, 209–222.
- Harward, M. E., Carstea, D. D. and Sayegh, A. H. (1969) Properties of vermiculites and smectites: expansion and collapse: *Clays and Clay Minerals* **16**, 437–447.
- Jackson, M. L. (1956) *Soil Chemical Analysis-Advanced course*. Published by the author, Soils Department, University of Wisconsin, Madison.
- Okazaki, R., Smith, H. W. and Moodie, C. D. (1962) Development of a cation-exchange capacity procedure with few inherent errors: *Soil Sci.* **93**, 343–349.
- Philen, O. D., Jr., Weed, S. B. and Weber, J. B. (1970) Estimation of surface charge density of mica and vermiculite by competitive adsorption of diquat<sup>2+</sup> versus paraquat<sup>2+</sup>: *Soil Sci. Soc. Am. Proc.* **34**, 527–531.
- Rich, C. I. (1961) Calcium determination for cation-exchange capacity measurement: *Soil Sci.* **92**, 226–231.
- Rich, C. I. (1962) Removal of excess salt in cation-exchange capacity determinations: *Soil Sci.* **93**, 87–94.
- Schultz, L. G. (1969) Lithium and potassium adsorption, dehydroxylation temperature, and structural water content of aluminous smectites: *Clays and Clay Minerals* **17**, 115–149.
- Shapiro, L. and Brannock, W. W. (1956) *Rapid Analysis of Silicate Rocks*. Geol. Surv. Bull. 1036-C.
- Weed, S. B. and Weber, J. B. (1968) The effect of adsorbent charge on the competitive adsorption of divalent organic cations by layer-silicate minerals: *Am. Mineralogist* **53**, 478–490.
- Weed, S. B. and Weber, J. B. (1969) The effect of cation-exchange capacity on the retention of diquat<sup>2+</sup> and paraquat<sup>2+</sup> by three-layer type clay minerals—I. Adsorption and release: *Soil Sci. Soc. Am. Proc.* **33**, 379–382.

**Résumé**—Le diquat<sup>2+</sup> (ion 1,1'-éthylène-2,2'-dipyridinium) et le paraquat<sup>2+</sup> (ion 1,1'-diméthyl-4,4'-dipyridinium) ont été adsorbés d'une manière compétitive par des kaolinites Na, des smectites et des vermiculites gonflées et fermées. La sélectivité relative pour l'un ou l'autre des deux cations varie avec

les densités de charge superficielle des adsorbants et la localisation interne ou externe du site d'adsorption. Les minéraux à forte charge de surface montrent une sélectivité pour le diquat alors que les minéraux à faible charge retiennent préférentiellement le paraquat. Les vermiculites gonflées adsorbent préférentiellement le diquat sur les surfaces internes. Les vermiculites fermées montrent en général une préférence pour le paraquat. Les smectites et les kaolinites adsorbent préférentiellement le paraquat.

La corrélation entre les densités de charge superficielle des phyllosilicates et la préférence relative pour le diquat révèle deux relations linéaires, une pour l'adsorption interne et une pour l'adsorption externe. L'adsorption interne a été caractérisée par une forte préférence pour le paraquat sur les smectites à faible charge, une préférence relative pour le paraquat qui diminue quand la charge des smectites augmente, et une forte préférence pour le diquat sur les vermiculites gonflées à forte charge.

L'adsorption préférentielle du paraquat sur la kaolinite est tout à fait semblable à l'adsorption du paraquat sur les sites externes des vermiculites. Il n'y a pas de relation apparente entre l'adsorption compétitive et la densité de charge superficielle de la kaolinite.

**Kurzreferat** — Diquat<sup>2+</sup>(1,1'-äthylan-2,2'-dipyridinium ion) und Paraquat<sup>2+</sup>(1,1'-dimethyl-4,4'-dipyridinium ion) wurden im Wettbewerb miteinander an Na-gesättigten Kaoliniten, Smectiten und aufgeblähten sowie zusammengeschrumpften Vermiculiten adsorbiert. Die relative Vorliebe für das eine oder das andere Kation änderte sich im Zusammenhang mit den Oberflächenladungsdichten der Adsorbenten und der Lage der Adsorptionsstelle, d.h. innerlich oder äusserlich. Minerale mit hoher Oberflächenladung zeigten Vorzug für Diquat während Minerale mit niedriger Oberflächenladung Paraquat vorzogen. Aufgeblähte Vermiculite adsorbierten vorzugsweise Diquat an den inneren Oberflächen, während die zusammengeschrumpften Vermiculite im allgemeinen dem Paraquat den Vorzug gaben. Smectite und Kaolinite adsorbierten mit Vorliebe Paraquat.

Eine Betrachtung der Oberflächenladungsdichten der Schichtsilikate in bezug auf die relative Vorliebe für Diquat zeigte zwei Linearbeziehungen, eine für interne Adsorption und eine für externe Adsorption. Interne Adsorption war gekennzeichnet durch eine starke Vorliebe für Paraquat auf niedriggeladenen Smectiten, eine relativ abnehmende Vorliebe für Paraquat bei höher geladenen Smectiten und eine deutliche Vorliebe für Diquat an hochgeladenen aufgeblähten Vermiculiten.

Vorzugsweise Adsorption für Paraquat durch Kaolinit war ganz ähnlich der Adsorption von Paraquat an den externen Stellen von Vermiculiten. Es ergab sich keine sichtbare Beziehung zwischen konkurrierender Adsorption und Oberflächenladungsdichte von Kaolinit.

**Резюме** — Сопоставлена адсорбция ионов дикуат<sup>2+</sup>(1,1'-этилен-2,2'-дипиридин) и паракуат<sup>2+</sup>(1,1'-диметил-4,4'-дипиридин) насыщенными натрием каолинитом, смектитом, а также вермикулитом в состоянии набухания и после удаления растворителя. Установлено, что преимущественная адсорбция одного или другого катиона варьирует в зависимости от плотности заряда на поверхности адсорбентов и внутреннего или наружного положения адсорбционных позиций. Минералы с высоким поверхностным зарядом преимущественно адсорбировали дикуат, а минералы с низким поверхностным зарядом — паракуат. Набухший вермикулит наиболее энергично адсорбировал дикуат на внутренней поверхности. После удаления растворителя вермикулит в общем более интенсивно поглощал паракуат. Смектиты и каолиниты избирательно извлекали из раствора паракуат.

Зависимость от плотности поверхностных зарядов слоистых силикатов преимущественной адсорбции дикуата выражается двумя линейными соотношениями: одно для внутренней адсорбции, другое — для внешней. Внутренняя адсорбция характеризуется сильным преобладанием поглощения паракуата у слабо заряженных смектитов; у сильно заряженных смектитов адсорбция паракуата относительно снижается; сильно заряженные набухшие вермикулиты обнаруживают сильное избирательное поглощение по отношению к дикуату. Преимущественная адсорбция паракуата каолинитом аналогична адсорбции паракуата на внешних позициях вермикулитов. У каолинитов не удалось установить определенного соотношения между избирательной адсорбцией и плотностью зарядов на поверхности.