

which also gives intensities observed on single crystal photographs. These correspond very well with the spacing and indexing for caryinite as given by Boström (1958). These are added to the last three columns of the table for comparison.

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## ADSORPTION OF DYES BY CLAY MINERALS

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## INTRODUCTION

Recent investigations on clay-organic complexes have led to the discovery of several commercial clay products (Grim, 1960). Adsorption study of organic compounds provides a rapid method of studying cation exchange, surface area and mineralogical composition of clay minerals (Faust, 1940; Grim, 1953; Hauser, 1955; MacEwan, 1948; Mackenzie, 1948; Bradley, 1945; Emodi, 1949; Bossazza, 1944; Ramachandran, Kacker and Patwardhan, 1961; Ramachandran, Garg and Kacker, 1961).

Much of the work on clay-organic complexes pertains to reactions between montmorillonite and halloysite and various organic compounds. Hendricks (1941) and Grim *et al.* (1947) found that small organic molecules replace the exchangeable cations on montmorillonite quantitatively, but with larger molecules the exchange is incomplete due to the "cover up effect."

In general the cation exchange capacity (CEC) values of clay minerals obtained by methylene blue adsorption are far less than those obtained by other standard methods (Worall, 1958; White and Cowan, 1960; Robertson and Ward, 1951). Much discrepancy is reported between surface areas calculated by methylene blue adsorption and B.E.T. methods (Kipling and Wilson, 1960).

In spite of a large amount of work there is still confusion about the exact mechanism involved in the adsorption of dyes by clay minerals. This note discusses the studies on adsorption of three basic organic dyes, *viz.*, malachite green (MG), methylene blue (MB) and methyl violet B

(MV) on three types of clay minerals viz., kaolinite, illite and montmorillonite and attempts to explain the cation exchange properties and orientation of molecules after adsorption.

#### MATERIALS

##### *Clay Minerals*

Particles of size less than one micron of the following samples were investigated:

<i>Group</i>	<i>Clay Mineral</i>	<i>Source</i>	<i>Cation Exchange Capacity</i> (m.e./100g)
Kaolinite	1. Kaolinite-I	Kerala, India	7.12
	2. Kaolinite-II	Amortex, India	6.00
Illite	1. Illite	Fithian, U.S.A.	27.00
Montmorillonite	1. Montmorillonite-I	B.D.H. Bentonite	80.61
	2. Montmorillonite-II	Nontronite, Rajasthan	77.21
	3. Montmorillonite-III	Wyoming, U.S.A.	93.00

##### *Organic Cations*

1. Malachite Green, E. Merck, Darmstadt
2. Methylene Blue, E. Merck, Darmstadt
3. Methyl Violet B, Riedel-de Hæn A.C.

#### ESTIMATION

Each of the clay minerals, kaolinite, illite and montmorillonite was first converted into  $H^+$  clay. Based on the method suggested by Worrall (1958) 0.2% aqueous solutions of MG, MB and MV were added in succession to a definite quantity of each of the clay minerals and were kept in contact with the clay minerals for 24 hours with occasional stirring. This was continued till there was a slight excess of unadsorbed dye. The unadsorbed dye was completely removed by filtration and thorough washing, and the dye content was estimated by means of a microptic colorimeter. The surface area was determined by B.E.T. method by using argon at  $-180^\circ C$ . The CEC of the clay minerals was determined by the standard ammonium acetate method (Piper, 1947).

#### DISCUSSION

Table I presents the CEC values for six clay minerals. For kaolinites and illites the CEC values based on MB and MV adsorption are almost the same as those obtained by the standard method. However, values

TABLE I. CATION EXCHANGE CAPACITIES OF CLAY MINERALS BY USING VARIOUS DYES\*

Clay Minerals	Ammonium Acetate	Malachite Green	Methylene Blue	Methyl Violet
Kaolinite-I	7.12	10.23	7.03	6.77
Kaolinite-II	6.00	6.65	5.94	6.29
Illite	27.00	15.01	26.00	19.48
Montmorillonite-I	80.61	26.77	64.07	62.15
Montmorillonite-II	77.21	22.60	58.34	48.22
Montmorillonite-III	93.00	30.21	59.70	58.40

\* Cation exchange capacities are expressed as m.e./100 gm.

obtained by MG adsorption are high for kaolinite and about 40% lower for illite. For montmorillonites the CEC values based on dye adsorption are considerably lower than the standard values by 30-35%, 60-80% and 60-80% for MG, MB and MV respectively.

Three typical clay minerals *viz.*, kaolinite-I, illite and montmorillonite-I were subjected to surface area studies before and after adsorption of the dyes, and the results are given in Table II. From surface area and standard CEC the area corresponding to each exchange site is calculated. The area corresponding to each dye molecule is obtained

TABLE II. ADSORPTION OF DYES ON CLAY MINERALS

	Kaolinite-I	Illite	Montmorillonite-I
Specific surface area (m <sup>2</sup> /g)	16.60	92.00	750.00 <sup>1</sup> (19.8) <sup>2</sup>
Specific surface area after adsorption of MG (m <sup>2</sup> /g)	13.15	—	10.65 <sup>2</sup>
Specific surface area after adsorption of MB (m <sup>2</sup> /g)	15.46	—	15.97 <sup>2</sup>
Area per exchange site (Å <sup>2</sup> )	38.71	56.57	154.50
Area associated with each MG molecule (Å <sup>2</sup> )	26.82	102.40	465.10
Area of contact of each MG molecule (Å <sup>2</sup> )	5.57	—	5.67
Area associated with each MB molecule (Å <sup>2</sup> )	39.17	58.75	194.30
Area of contact of each MB molecule (Å <sup>2</sup> )	2.69	—	0.99
Area associated with each MV molecule (Å <sup>2</sup> )	40.67	78.47	200.40

<sup>1</sup> Mean of theoretical and experimental values (Grim, 1953, Mooney *et al.*, 1952).

<sup>2</sup> Specific surface area as found by B.E.T. method.

from surface area and the number of dye molecules adsorbed. It can be seen that MB and MV molecules are adsorbed on kaolinite so that the area associated with each molecule is nearly the same as the area available per exchange site. Hence the CEC values based on MB and MV adsorption coincide with the CEC values determined by standard method. However, the area associated with each MG molecule is  $26.82 \text{ \AA}^2$  which, being much lower than the area per exchange site, results in higher CEC values. The area associated with each MB or MV molecule corresponds to the area of one edge of the major orientation of the dye molecule *i.e.*,  $39.5 \text{ \AA}^2$  (Kipling and Wilson, 1960). The area associated with each MG molecule corresponds to the area covered by an edge of the benzene ring *viz.*,  $25 \text{ \AA}^2$ .

The specific surface area of kaolinite after the dye molecules are adsorbed decreases from  $16.6 \text{ m}^2/\text{g}$  to  $15.46 \text{ m}^2/\text{g}$  for MB and from  $16.6 \text{ m}^2/\text{g}$  to  $13.15 \text{ m}^2/\text{g}$  for MG. Assuming that the difference in surface area before and after dye adsorption represents the area of dye in actual contact with the clay mineral, the values are found to be  $5.57 \text{ \AA}^2$  and  $2.69 \text{ \AA}^2$  for MG and MB respectively. This shows that although the molecule is associated with larger areas it probably has far less contact areas. The possibility that the molecule may be adsorbed on a corner of the aromatic ring should not be ruled out.

The area per exchange site for illite is  $56.57 \text{ \AA}^2$  while the area associated per molecule is  $102.40 \text{ \AA}^2$ ,  $58.75 \text{ \AA}^2$  and  $78.47 \text{ \AA}^2$  respectively for MG, MB and MV. The CEC values by MB and MV adsorptions are almost the same as the standard values. In illite the area associated with each MB molecule corresponds to a slightly lower value than the edgewise area  $75 \text{ \AA}^2$  for major orientation (Kipling and Wilson, 1960).

The surface area of montmorillonite by argon adsorption is only  $19.8 \text{ m}^2/\text{g}$ . This may be due to the inability of the argon molecules to penetrate between the layers in the vacuum dry state. A value of  $15.5 \text{ m}^2/\text{g}$  is quoted for the surface area of montmorillonite by Nelson and Hendricks (1943). The area of the dye in contact with the clay mineral is  $5.67 \text{ \AA}^2$  and  $0.99 \text{ \AA}^2$  for MG and MB molecules respectively. It seems that on the external surface of a clay mineral the dye molecule is always adsorbed on a small area of the aromatic ring. Thus the molecules have greater access to all the cation exchange sites on the external surfaces of kaolinite and illite in which the major source of CEC is due to broken bonds. For montmorillonite with the total surface area of  $750 \text{ m}^2/\text{g}$  the area associated with each adsorbed dye molecule is  $465.1 \text{ \AA}^2$ ,  $194.3 \text{ \AA}^2$  and  $200.4 \text{ \AA}^2$  respectively for MG, MB and MV. The MB molecule assumes an area of  $195 \text{ \AA}^2$  (White and Cowan, 1960) when it lies flat on the surface. This indicates that in montmorillonite the dyes are adsorbed flat, giving rise to "covering up effect" and a decrease in CEC. It is

likely that the dye molecules replace the inorganic cations in equivalent proportions on broken bonds of montmorillonite. But the broken bonds are responsible for a relatively small proportion (20%) of the total cation exchange capacity (Grim, 1953).

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