

METHYLENE BLUE ABSORPTION BY CLAY MINERALS. DETERMINATION OF SURFACE AREAS AND CATION EXCHANGE CAPACITIES (CLAY-ORGANIC STUDIES XVIII)

PHAM THI HANG and G. W. BRINDLEY

Department of Geochemistry and Mineralogy, and Materials Research Laboratory, The Pennsylvania State University, University Park, Pa. 16802

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Abstract—Under appropriate conditions, both surface areas and cation exchange capacities of clay minerals can be measured by absorption of methylene blue from aqueous solutions. The method has been applied to two kaolinites, one illite, and one montmorillonite, all initially saturated with Na⁺ ions. For Na-montmorillonite, the total area, internal plus external, is measured. For Ca-montmorillonite, entry of methylene blue molecules appears to be restricted by the much smaller expansion of the Ca-clay in water. X-ray diffraction data clarify the absorption behavior in Na- and Ca-montmorillonite, and in particular it is shown that two orientations of the methylene blue molecules are involved.

INTRODUCTION

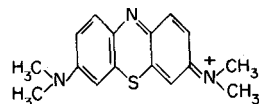
THE ABSORPTION of methylene blue dye by clay minerals is currently used for determining either their cation exchange capacities (Fairbairn and Robertson, 1957; Nevins and Weintritt, 1967) or their surface areas (Johnson, 1957; Worrall, 1958; Phelps and Harris, 1967). However, the usefulness of the method is often questioned (Hul, 1966; Faruqi, Okuda and Williamson, 1967; Bodenheimer and Heller, 1968), and confusions have arisen when it comes to understanding which of these properties is being primarily measured. In some cases, it appears that when the clay surface is more or less covered by methylene blue ions, a more or less complete exchange of the initial cations by the dye also takes place, which explains the difficulty of knowing which property primarily is measured.

The amount of methylene blue absorbed by or exchanged on to a clay from an aqueous solution is measured usually by determining with a colorimeter or spectrophotometer the amount remaining in solution. This measurement is complicated by the dimerization of methylene blue (Bergmann and O'Konski, 1963) when the concentration exceeds about 7×10^{-6} mole/l. corresponding to an optical density higher than about 0.6. The dimerization changes the spectral curve, so that unless concentration measurements are made under conditions of sufficient dilution, errors will arise from this cause. The change of color with concentration is related to the use of methylene blue as a field test for identifying clay minerals (Shukevich,

1954). The adsorption of methylene blue by glass surfaces is another possible source of error.

The present experiments were undertaken with a view to clarifying the nature of the results obtained by studying the absorption of methylene blue on a variety of clay minerals, kaolinite, illite, and montmorillonite, with parallel measurements of surface areas by the Brunauer, Emmett and Teller (B.E.T.) gas adsorption technique, and of cation exchange capacities by a conventional titration procedure. X-ray diffraction measurements have been made on Na- and Ca-montmorillonite after absorbing various amounts of methylene blue.

The formula of the methylene blue ion can be written:



The projected area of the molecule has been given as 135 \AA^2 (Kipling and Wilson, 1960; Hul, 1966), 132 \AA^2 (Johnson, 1957), and 130 \AA^2 (Kalousek and Blahnik, 1955; Los and Tompkins, 1956) and in the present work will be taken as 130 \AA^2 . The molecule can be regarded approximately as a rectangular volume of dimensions $17.0 \times 7.6 \times 3.25 \text{ \AA}$; similar dimensions are given by Johnson (1957).

EXPERIMENTAL

Clay minerals used. A delaminated kaolinite (grade Kaopaque) provided by the Georgia

Kaolin Company, and a finely divided Florida kaolinite were sodium saturated using 1N sodium chloride solution, following the procedure of Rich (1961), and were washed until chloride ion free as shown by the silver nitrate test, and then were given two further washings.

An illite belonging to the Oswego graywacke, Skytop, Pa., was purified and fractionated to $< 1 \mu$ according to the description given by Thompson and Brindley (1969, p. 859). The procedure left the illite in a sodium saturated form.

A Wyoming montmorillonite, "Mineral Colloid BP," supplied by the Georgia Kaolin Company, was sodium saturated and fractionated to $< 1 \mu$ particle size.

Surface area determinations. Krypton adsorption was used in a conventional B.E.T.-type apparatus (Ranc and Teichner, 1967; for a general description, see Young and Crowell, 1962, p. 190) for the kaolinites and for illite. For montmorillonite, the specific surface area was obtained by calculation from the lattice parameters and ideal composition.

Cation exchange capacity measurements. These were obtained by a titration technique based on the procedure described by Barnard, Broad and Flaschka (1956, 1957) using ethylene diamine tetra-acetic acid (EDTA) with hydroxy-naphthol as indicator, and by the method of Carlson and Johnson (1961), and Harward and Brindley (1964) using cyclohexanediaminetetra-acetic acid (CyDTA) with calcein and murexide as indicators.

The already sodium-saturated clays were converted to the calcium form using 1N calcium chloride solution as described by Rich (1961), and were washed until chloride ion free. Finally the clay was again exchanged to the sodium form and the Ca ions released were determined by the titration methods.

Methylene blue absorption measurements. The dye used was a "Methylene Blue, U.S.P. Crystals," No. M4490 from Aldrich Chemical Co., Inc., of molecular weight 373.9, which corresponds to the methylene blue hydrochloride, with $3\text{H}_2\text{O}$.

All containers used for methylene blue solutions were of polypropylene as suggested by Bergmann and O'Konski (1963).

For the most part, experiments were conducted in two ranges of concentrations: (a) low concentrations, $< 7 \times 10^{-6}$ m/l, when only monomers were present, (b) higher concentrations, 10^{-5} – 10^{-3} m/l, to give monomer-dimer equilibrium.

The experimental conditions for the various clays are shown in Table 1, and can be described with reference to the first entry for Florida kaolinite. From a suspension containing approximately 1 mg per ml, 5 ml of kaolinite suspension was

placed in a polypropylene beaker and 200 ml of water was added. MB solution of concentration approximately 1 mg/one ml was added to give amounts of MB ranging from 0.032 to 0.375 mg, i.e. from 1.69 to 19.7 meq MB/100 g clay. The concentration range of the MB prior to absorption was 0.42 – 4.9×10^{-6} moles/l. Here and elsewhere in the text, "100 g clay" refers to clay dried over-night at 110°C . The mixtures were stirred at intervals and left over-night to assure the absorption equilibrium (actually, 1 hr was considered sufficient by Bergmann and O'Konski, 1963). Later, the clay suspensions were centrifuged in a Sorvall SS-1 high speed angle centrifuge and the supernatant liquids, containing the remaining methylene blue, were diluted to proper concentration before making the measurements on a spectrophotometer. From the amount of methylene blue retained in solution, the quantity absorbed was determined.

Spectrophotometer measurements were made with a Beckman DU-spectrophotometer, with silica cells of length 1 cm. Optical densities were determined at the wave-length 6650 \AA which corresponds to the maximum absorption peak of methylene blue monomers (Rabinovitch and Epstein, 1941). The solutions involved were diluted to a concentration less than 7×10^{-6} m/l, giving optical densities in the range 0.100–0.600. A standard methylene blue solution of known concentration was used to find the molar extinction coefficient ϵ for monomeric methylene blue at 6650 \AA . Since

$$\epsilon = (\text{optical density}) / (\text{concentration} \times l),$$

where l is the path length of the cell, sample concentrations can be obtained directly from their optical densities when ϵ is known. Each reading for a sample was preceded by one for the standard solution to eliminate possible errors from absorption of methylene blue on the spectrophotometer cells. Small variations of ϵ around 8.20×10^4 were considered to arise from staining of the silica cell.

Determination of CEC's and surface areas from methylene blue absorption. In the course of the experiments it was observed that the flocculation behavior of the clay suspensions varied significantly as the amount of methylene blue absorbed by the clay was progressively increased. When sufficiently small increments of methylene blue absorption are taken, a value can be obtained visually within narrow limits corresponding to optimum flocculation of the clay. This is shown by the highest rate of sedimentation due to the size of the flocs forming. It is considered that the amount of methylene blue absorbed under these

Table 1. Experimental data for MB absorption experiments on clays

	Clay used		Water added (ml)	Methylene blue added		MB concentration prior to absorption (mole/l.)	MB absorbed, see Figs. 1-4
	Suspension (ml)	Clay (mg)		(mg)	(meq/100g) clay		
Florida kaolinite	5.0	5.1	200	0.032-0.375	1.69-19.7	0.42-4.9, $\times 10^{-6}$	Fig. 1, solid symbols Fig. 1, open symbols
	10.0	101.9	20	0.375-7.55	0.98-19.8	0.33-5.45, 10^{-4}	
Delaminated kaolinite	10.0	163.8	25	0.61-9.80	1.00-16.0	0.46-5.85, 10^{-4}	Fig. 2
	20.0	8.63	350	0.09-0.95	2.80-29.6	0.65-6.88, 10^{-6}	Fig. 3, solid symbols
	2.0	86.3	100	0.96-8.10	2.99-25.2	0.25-1.98, 10^{-4}	Fig. 3, open symbols (see text)
Na-montmorillonite	2.0	31.3	20	2.35-25.82	20.1-230.7	2.60-15.02, 10^{-4}	Fig. 4(a)
Ca-montmorillonite	20.0	5.76	20	0.43-2.59	20.0-120.0	0.56-3.06, 10^{-4}	Fig. 4(b)

conditions corresponds to a coverage of the clay surface with methylene blue molecules. This principle has been described by Kalb and Curry (1969) in a recent publication discussing flocculation and electrical conductivity of clays treated with surfactant solutions. If M_f meq of methylene blue are absorbed per 100 g clay when the surface is covered, and if A_m is the area per molecule in \AA^2 on the surface, then the surface area per g of clay is $M_f \times A_m \times 6.02 \times 10^{-2} \text{ m}^2/\text{g}$.

Maximum absorption of methylene blue, corresponding to complete exchange of the inorganic by the organic ions, occurs with larger amounts of methylene blue than are required for optimum flocculation.

The present experiments have been concerned particularly with determining the amounts of methylene blue absorbed (a) for optimum flocculation, and (b) for maximum exchange.

X-ray diffraction measurements. A Philips Norelco diffractometer was used with Ni-filtered $\text{CuK}\alpha$ radiation. The diffractometer was fitted with a special sample chamber which permitted control of pressure and humidity of the ambient atmosphere. Known amounts of Na- or Ca-montmorillonite suspensions were dried slowly on glass slides under open air conditions to give well-oriented samples. The slides were placed horizontally in methylene blue solutions of various concentrations and were held for periods of several days to about 2 weeks at 50–60°C to achieve equilibrium. The exchange reaction was retarded considerably by the use of oriented samples and the elevated temperature was used to accelerate the process. The good orientation of the clay was retained after methylene blue absorption and basal reflections up to 007 usually could be obtained when a single phase was present. Diffraction measurements were made with the still-wet slides after transference from the solutions to the diffractometer, and after progressive removal of water by evacuation.

RESULTS

Methylene blue absorption isotherms. Figures 1–4 show the amounts of methylene blue absorbed by the clay minerals plotted against the amounts of methylene blue in the initial solutions, where both quantities are expressed in meq of methylene blue per 100 g of clay used. The point of optimum flocculation is marked prominently by an arrow on each curve.

Surface area determinations. The specific surface areas of the clays are calculated from the amounts of methylene blue absorbed when flocculation is optimum by taking the area per absorbed molecule as 130 \AA^2 , which corresponds

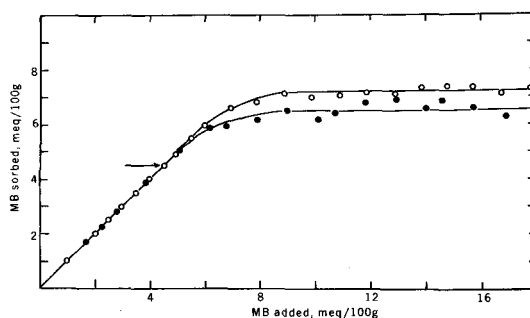


Fig. 1. Methylene blue absorption by a Florida kaolinite. Arrow indicates condition for optimum flocculation. Open and closed circles correspond to measurements with "high" and "low" (see text) organic concentrations.

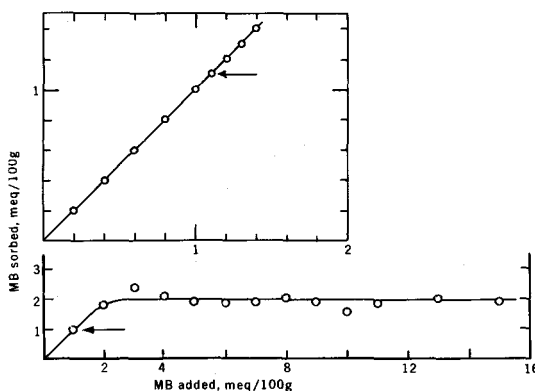


Fig. 2. Methylene blue absorption by a delaminated kaolinite. Upper diagram shows in detail the measurements for the initial part of the curve given in the lower diagram. Arrow indicates condition for optimum flocculation. Measurements correspond to "high" organic concentrations.

to the molecules lying flat on the clay mineral surfaces. The amounts of methylene blue absorbed and the resulting areas obtained are listed in Table 2; the experimental range for each value given corresponds to the estimated uncertainty in determining the optimum flocculation point. Areas about 4 percent larger will be obtained if the molecular area is taken as 135 \AA^2 .

The corresponding areas determined by the B.E.T. krypton-adsorption method also are given for kaolinite and illite. For Na-montmorillonite the calculated surface area is $750\text{--}800 \text{ m}^2/\text{g}$ where the range of values arises from the uncertain contribution from the edges of particles.

The agreement between the areas determined by methylene blue absorption and by gas adsorption or by calculation is everywhere very

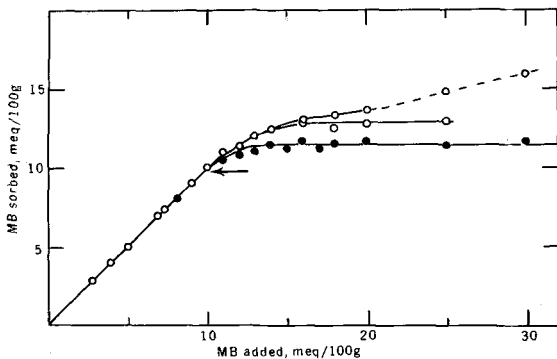


Fig. 3. Methylene blue absorption by Oswego illite. Arrow indicates condition for optimum flocculation. Open and closed circles correspond to measurements with "high" and "low" (see text) organic concentrations. Two sets of observations with "high" organic concentrations gave a divergence of the results as shown.

close. It is thought that the slightly higher values obtained by methylene blue absorption for delaminated kaolinite and illite may arise from a small amount of a swelling mineral in the clays which, under gas absorption methods, would collapse and contribute little to the total area.

It is noteworthy that the point of optimum flocculation occurs on each curve in the region where it begins to deviate from the initial 45° slope, i.e., where absorption is no longer 100 per cent. This corresponds to the end point determined by the spot test given by Nevins and Weintritt (1967), and by Phelps and Harris (1967).

Cation exchange capacities. These are determined from the plateaux of the curves in Figs. 1-4, which correspond to maximum exchange of the inorganic cations. The resulting C.E.C. values

are listed in Table 2 where they are compared with values obtained by the titration procedure. Close agreement is obtained between the values obtained in the two ways, more particularly when "strong" solutions of methylene blue are used in the exchange reaction. These results are shown by the open circles in the figures. It appears that when dilute solutions, wholly within the monomeric range of the methylene blue, are used (see solid

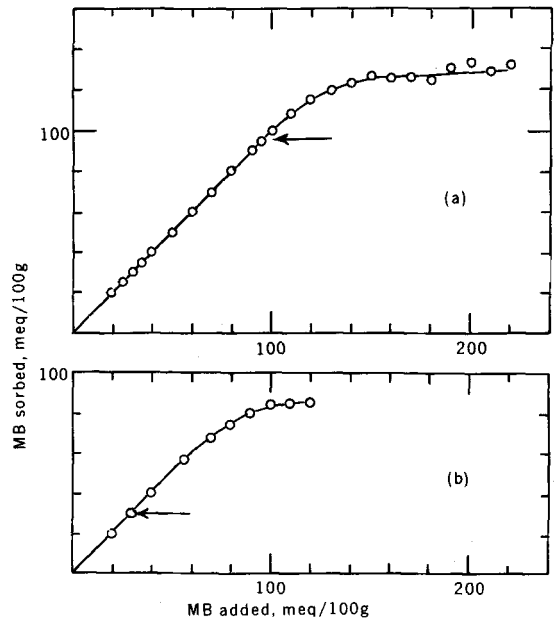


Fig. 4. Methylene blue absorption by (a) Na-montmorillonite, (b) Ca-montmorillonite. Arrows indicate conditions for optimum flocculation. Measurements correspond to "high" organic concentrations.

Table 2. Comparison of results by methylene blue absorption and by other methods

	Methylene blue absorbed at optimum flocculation (meq/100g clay)	Surface area, m ² /g of clay		Cation exchange capacity, meq/100g clay	
		BET meas.	MB absorption	Titration	MB absorption
Florida kaolinite	4.50 ± 0.25	33.0 ± 2	35.2 ± 2.0	7.3 ± 0.2	6.5 ± 0.4 (low conc.) 7.2 ± 0.3 (high conc.)
Delaminated kaolinite	1.10 ± 0.05	5.5 ± 0.6	8.6 ± 0.4	1.87 ± 0.03	1.95 ± 0.2 (high conc.)
Oswego illite	10.00 ± 0.25	68 ± 2	78 ± 2	13.9 ± 0.1	11.5 ± 0.4 (low conc.) 13.20 ± 0.25 (high conc.)
Na montmorillonite	95.0 ± 0.5	*	743 ± 4	124.9 ± 1	126 ± 2 (high conc.)

*Obtained by calculation to be 750-800 m²/g of clay.

circles in the figures) the exchange reaction does not go to completion. Also it is important to observe that the exchange capacity of the montmorillonite is obtained correctly only when the Na-form is used (Fig. 4(a)); the exchange reaction is far from complete when Ca-montmorillonite is used (Fig. 4(b)).

It is observed in Figs. 1 and 3 that although "high" concentrations of methylene blue are required to attain complete exchange of Na^+ ions, the point of optimum flocculation is not changed in going from "low" to "high" concentrations. Also in Fig. 3, two curves are shown with open symbols. The upper curve, with a dashed line, indicates an increasing absorption. Similar increases were obtained in other cases when the amount of methylene blue was increased beyond the range shown in the figures and these effects are probably due to physical absorption. The dashed curve is therefore only slightly "unusual" in that the rising absorption occurred, for some unknown reason, earlier than in other cases. Generally, the curves show clear plateaux corresponding to the exchange capacities of the clays.

It was observed that kaolinite and illite, when saturated with methylene blue, appeared blue, whereas montmorillonite when saturated presents a purple color and almost a metallic sheen. This is the basis of the field test using methylene blue to distinguish montmorillonite from kaolinite or illite.

X-ray diffraction data for methylene blue-montmorillonite complexes

The results are summarized in Table 3 where the observed spacings of Ca- and Na-montmorillonite after absorption of various amounts of methylene blue are tabulated under wet conditions with excess water, and under dry conditions produced by a vacuum of the order of 10^{-2} torr. Where the basal reflections correspond to a single phase, or where there are two phases well separated, the highest order of reflection measured is shown in parentheses and estimated accuracy of the basal spacing is indicated. Where two or more phases occur with overlapping reflections, the individual spacings were deduced from the shapes of the composite peaks and are somewhat less accurate.

Because Ca-montmorillonite gives better orientation of the clay on glass slides, X-ray measurements were made on this form of the clay for absorptions up to 90 meq/100 g clay, the limit obtained with Ca-clay (see Fig. 4(b)). For higher absorptions up to the exchange capacity of the mineral, Na-montmorillonite was used.

Under wet conditions, the basal spacing of the Ca-clay, normally $19.0 \pm 0.1 \text{ \AA}$, diminished to 15.9 \AA with a small absorption of methylene blue and to $15.7 \pm 0.1 \text{ \AA}$ as the absorption increased to the limit of about 90 meq/100 g clay. The basal spacing of the Na-clay in water remained very large or very irregular even after full exchange of the Na^+ by methylene blue cations; under aqueous

Table 3. X-ray data for methylene blue-montmorillonite complexes

MB absorbed meq/100g clay	Basal spacings, \AA , under wet conditions		Basal spacings, \AA , <i>in vacuo</i>	
Ca-montmorillonite				
0	19.05 ± 0.1			11.6 ± 0.04 (008)
20	18.96 $\pm 0.1(006)$	15.92 $\pm 0.06(005)$	12.6	11.7
40		15.74 $\pm 0.05(005)$	<u>14.8</u>	12.6
60		15.75 $\pm 0.05(005)$	15.6	<u>14.8</u> 12.6 minor
80		15.69 $\pm 0.1(005)$	<u>15.6</u>	14.8
90		15.8 ± 0.1 (005)	<u>15.6</u>	14.8
Na-montmorillonite				
90	no basal spacing observed		<u>15.6</u>	14.8
120	no basal spacing observed	<u>17.2</u>	15.6	

Underlined values are dominant spacings.

conditions no basal reflections were observable. This result is consistent with the full exchangeability of the Na^+ ions by methylene blue ions.

Under a vacuum of 10^{-2} torr, the basal spacings increased with the amount of methylene blue absorbed, and the various spacings listed in Table 3 were measured.

DISCUSSION

Effects of inorganic cations on the absorption. It is evident that methylene blue ions replace Na^+ ions from montmorillonite more easily than they do Ca^{2+} ions, probably because the montmorillonite remains expanded when methylene blue replaces Na, whereas it contracts when methylene blue replaces Ca even when no more than 20 per cent of the exchange capacity is satisfied by methylene blue. Full replacement of Na by methylene blue requires not only sufficient methylene blue in the system, but also a sufficient concentration, a concentration considerably greater than the monomeric range. That Ca ions are not fully replaced by methylene blue is probably the cause of failures in measuring surface areas (Hul, 1966) and exchange capacities (Faruki et al., 1967; Bodenheimer and Heller, 1968).

Effects of concentration of methylene blue

solutions. The data in Figs. 1 and 3 show that concentration as well as total amount of methylene blue seems to be important in bringing about the total exchange of Na ions, but appears to be less important for determining the point of optimum flocculation. However, the latter must be accepted cautiously until a wider range of experiments are carried out to test this point.

X-ray diffraction data. Possible interpretations of the X-ray spacing data given in Table 3 are shown in Fig. 5, where the methylene blue molecule is represented as a rectangular solid with approximate dimensions $17.0 \times 7.6 \times 3.25$ Å.

The behavior of Ca-montmorillonite will be considered first. Figure 5(a) illustrates the ideal silicon-oxygen network and shows two oxygen sheets separated under vacuum conditions by $11.6 - 9.4 = 2.2$ Å, with an interlayered $\text{Ca} \cdot 2\text{H}_2\text{O}$ group. The water molecules fit compactly between opposite pairs of oxygen ions and the arrangement is compatible with the observed regular spacing measured as far as 008. No claim is made for strictly $2\text{H}_2\text{O}$ per Ca ion (although this was found for a vermiculite-like mineral, Thompson *et al.*, 1967) and additional water molecules not coordinated with Ca ions could be present between the layers, as indicated by Glaeser and Mering (1968). The spacing 11.6 Å agrees very well with that

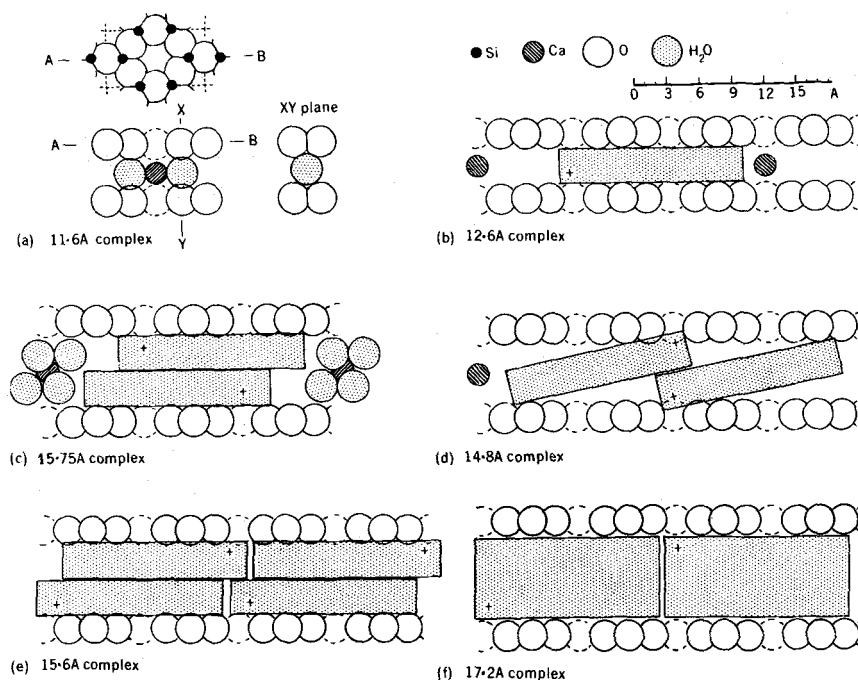


Fig. 5. Schematic representations of methylene blue-montmorillonite complexes under various conditions (see text).

found for Mg- and Ca-vermiculites and possibly is a result of the rather high exchange capacity of the present montmorillonite.

With small amounts of methylene blue absorbed, the 12.6 Å spacing found under vacuum conditions corresponds to the arrangement of Fig. 5(b) and agrees with data obtained with many flat-lying aromatic molecules (Greene-Kelly, 1955, 1956; Haxaire and Bloch, 1956; Van Olphen, 1968). The effective molecular thickness is $12.6 - 9.4 = 3.2$ Å which agrees with the small dimension of the methylene blue molecule.

With greater absorption of methylene blue, approximately 40–90 meq/100 g clay, a 15.75 Å spacing develops under wet conditions for Ca-montmorillonite and is represented by Fig. 5(c), which shows a double layer of flat lying methylene blue molecules and water molecules coordinated octahedrally around the Ca-ions. With about 40–60 meq/100 g clay of methylene blue absorbed, and under vacuum conditions, water is removed and the spacing is reduced to about 14.8 Å, which is insufficient for two sheets of flat lying molecules; Fig. 5(d) shows a possible arrangement. As the amount of methylene blue increases up to 90 meq/100 g clay, the 15.6 Å phase becomes increasingly prominent in the vacuum dried material. Evidently the arrangement of Fig. 5(d) is possible only with the smaller amounts of methylene blue.

When 90 meq/100 g clay of methylene blue are absorbed, which is near the condition for optimum flocculation (see Table 2), it appears that the methylene blue molecules cover most of the surfaces and this situation is shown in Fig. 5(e). The observed spacing under aqueous conditions and also in vacuo is then almost entirely that of the 15.6 Å phase; a small amount of the 14.8 Å is found under vacuum conditions.

With Na-montmorillonite and 90 meq/100 g clay of methylene blue absorbed, no basal spacing is observed; the spacing is too large to be recorded by the diffractometer, or, since this amount of methylene blue is close to the amount producing optimum flocculation, the silicate layers are arranged very irregularly with respect to one another. In either case, it is easily understandable that the surfaces remain accessible to methylene blue molecules so that further exchange of cations up to the limit of the exchange capacity of 125 meq/100 g clay may take place. With 120 meq/100 g clay of methylene blue absorbed, the montmorillonite under aqueous conditions still shows no measurable basal reflections, but in vacuo the dominant spacing is 17.1 Å which corresponds with a re-orientation of the molecules as shown in Fig. 5(f).

Questions relating to molecular packing

Since two molecular orientations are indicated by the diagrams of Fig. 5, it is important to consider the question of molecular packing particularly when the amounts of methylene blue absorbed correspond to the exchange capacities of the clays.

Table 2 shows that when optimum flocculation occurs considerable fractions of the exchange capacities are still satisfied by Na⁺ ions, yet the argument here given supposes that the surface is covered effectively by methylene blue ions. Under the aqueous conditions involved, the counter ions can be considered to form a double layer, but the methylene blue ions, because of their large size and van der Waals attractions, are likely to be held close to the silicate surfaces, with the unexchanged Na⁺ ions less strongly held and possibly somewhat dispersed with respect to the surface. It is difficult to see exactly what correction, if any, can be made to the estimated areas to take account of the Na⁺ ions. If they are unhydrated, their coverage of the surface is likely to be very small compared with that of the methylene blue ions, and this seems to be substantiated by the experimental results.

The packing of additional methylene blue ions needed to achieve full cation exchange will be possible only by a re-orientation of the molecules and the arrangement shown in Fig. 5(f) seems the most likely. The area per molecule is then $17.0 \times 3.25 = 55.2$ Å² when attached to a single surface, or twice this value when sandwiched between two surfaces as shown in Fig. 5(f). The following areas are required to accommodate the exchanged ions with an area of 55.2 Å²/molecule; in parentheses are given the available areas taken from Table 2: Florida kaolinite 23.8 m²/g (35.2 m²/g), delaminated kaolinite 6.46 m²/g (8.6 m²/g), Oswego illite 44.5 m²/g (78 m²/g), Na-montmorillonite 418 m²/g (743 m²/g). Thus there is no difficulty in accommodating the exchanged organic ions under the aqueous conditions of the experiment.

Under dry conditions *in vacuo*, no change in surface area is anticipated for kaolinite and illite, but for Na-montmorillonite the layers take up the spacing of 17.2 Å where each molecule between layers is touching two surfaces and the question arises whether the amount of methylene blue equal to the exchange capacity which is easily accommodated in the expanded aqueous state can also be accommodated in the dry state. To calculate the surface area required, allowance must be made for absorptions on external surfaces. If 10 per cent of the exchanged methylene blue is absorbed externally (55.2 Å²/molecule) and 90 per cent internally (110.4 Å²/molecule), then the required area is 794 m²/g; if the proportions are 20 per cent

and 80 per cent, the required area is 754 m²/g. These areas are consistent with the estimated area of the montmorillonite, so that most if not all of the exchanged methylene blue can be accommodated in the collapsed state of the mineral *in vacuo*.

CONCLUSIONS

The experiments show that methylene blue absorption can be used for the measurement of both surface areas and exchange capacities of clay minerals. The method has advantages over B.E.T. gas adsorption measurements in being readily applicable to a wide range of areas, and especially to minerals under aqueous conditions. The method is simple, rapid and economical. For cation exchange capacity measurements, the method is simple, easily applicable to a wide range of values, and less tedious than titration methods.

If the methylene blue molecule is treated as a rectangular solid with dimensions 17.0 × 7.6 × 3.25 Å, then optimum flocculation is obtained when the silicate surfaces are effectively covered by methylene blue ions lying on the 17.0 × 7.6 = 130 Å² face. Coverage of the surface in this way corresponds to considerably less than full exchange of the Na⁺ exchangeable cations. When the Na⁺ ions are fully exchanged, then the methylene blue molecules have the 17.0 × 3.25 = 55 Å² face in contact with the surface, with this orientation of the molecules, the available surface areas are sufficient to accommodate the exchanged methylene blue ions.

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Résumé—Dans les conditions appropriées, la superficie et la capacité d'échange de cations des minéraux argileux peuvent être mesurés par absorption du bleu de méthylène des solutions aqueuses. La méthode a été appliquée à deux kaolins, une illite, et une montmorillonite, tous ayant été préalablement saturés d'ions Na^+ . Pour la montmorillonite-Na, la superficie totale, interne et externe, a été mesurée. Dans le cas de montmorillonite-Ca, l'entrée des molécules du bleu de méthylène semble être restreinte par la dilatation bien plus petite de l'argile-Ca dans de l'eau. Les données de la diffraction des rayons X expliquent le phénomène d'absorption dans montmorillonite-Na et -Ca et on voit, en particulier, qu'il existe deux orientations des molécules du bleu de méthylène.

Kurzreferat—Unter geeigneten Bedingungen können sowohl Flächeninhalte als auch Kationenaustauschvermögen von Tonmineralen durch Absorption von Methylenblau aus wässrigen Lösungen gemessen werden. Die Methode wurde auf zwei Kaolinite, einen Illit und einen Montmorillonit, die alle ursprünglich mit Na^+ Ionen gesättigt waren, angewendet. Für Na-Montmorillonit wird die Gesamtfläche, innen sowie aussen, gemessen. Für Ca-Montmorillonit scheint der Eintritt der Methylenblaumoleküle durch die viel geringere Ausdehnung des Ca-Tons in Wasser begrenzt zu sein. Das Absorptionsverhalten in Na- und Ca-Montmorillonit wird durch Röntgenbeugungsdaten klargestellt, und insbesondere wird gezeigt, dass zwei Orientierungen der Methylenblaumoleküle beteiligt sind.

Резюме—Поглощение глинистыми минералами метилового голубого из водных растворов при благоприятных условиях может быть использовано для измерения как площади поверхности, так и катионо-обменной емкости. Предложенная методика была применена для исследования двух каолинитов, одного иллита и одного монтмориллонита; все образцы первоначально насыщались ионами Na^+ . Для Na-монтмориллонита определена общая (внутренняя и внешняя) поверхность. У Ca-монтмориллонита внедрение молекул метилового голубого, по-видимому, вызывает меньшее разбухание в воде. Рентгеновские данные позволили объяснить адсорбционные свойства Na- и Ca-монтмориллонитов и в частности указали на две ориентировки метилового голубого.