INTERSTRATIFICATION IN MONTMORILLONITE

by

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ABSTRACT

Direct analysis by Fourier transform methods revealed interstratification of three components for a homogeneous, potassium-treated and organic-solvated montmorillonite. An initial simple interpretation based on random mixing of two components was shown to be incorrect. Ethylene glycol solvation showed enhanced expansion in agreement with earlier investigations. Glycerol solvation produced a noteworthy contribution from a 14 Å component. An interpretation of the 14 Å component is suggested, based on an asymmetric distribution of layer charge. Regular interstratification, bending or curling of clay layers and anomalous dehydroxylation temperatures may be a consequence of asymmetric layer charge distribution in montmorillonites.

INTRODUCTION

Prior to about 1958, a common method for estimating the proportions of components in interstratified clays was that of utilizing peak migration curves similar to those given by Brown and MacEwan (1951). These curves illustrated apparent basal spacings as a function of the proportion of the components. Peak migration curves were constructed assuming strictly random interstratification and were generally applicable only to two-component mixtures or mixtures that could be reduced to two components.

A direct method for analyzing interstratified mixtures by Fourier transform techniques was formulated by MacEwan (1956). MacEwan, Ruiz Amil and Brown (1961) indicated the superiority of the transform technique over existing methods, since the identity and proportion of components (two or more) *and* the nature of the interstratification could be deduced from X-ray data.

Johns and Tettenhorst (1959) reported the results of an X-ray investigation on a group of pure dioctahedral montmorillonites. Separate portions of these clays were made homo-ionic with potassium and other cations. Solvation of the potassium montmorillonites with ethylene glycol and glycerol and subsequent X-ray examination followed. The proportion of collapsed (approximately 10 Å) material and re-expandable (presumably 18 Å) material was determined using peak migration curves as one of the methods. A con-

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clusion was that ethylene glycol invariably expanded more units than glycerol.

One of these montmorillonites (A.P.I. no. 20) was selected as being representative (no. 1 of the 1959 report) and was investigated further. Estimates of the proportion of nonexpandable layers for this potassium-treated montmorillonite based on X-ray data and peak migration curves was 45 per cent for glycerol solvation and 10 per cent for ethylene glycol solvation. All of the diffraction maxima observed were utilized to obtain a mean estimate of the proportion of nonexpandable units. Estimates of the proportion of nonexpandable units for several diffraction maxima clustered around the mean values with deviations not exceeding ±5 per cent. The previous good agreement, based on inclusion of all maxima, initially suggested that estimates were essentially correct, a conclusion now believed to be in error owing mainly to neglect of contributions from a third component having a 14 Å periodicity.

RESULTS

The focus of subsequent inquiry was the large diffraction maximum centered at about 14 Å on the diffractometer trace of the glycerol-solvated potassium-treated sample. Diffraction effects expected over the (2 sin θ/λ) range of 0.05—0.12 for a random mixture of 10 Å and 18 Å components were calculated using the relation

$$I = \Theta\,|F_l|^2\Phi \tag{1}$$

from MacEwan, Ruiz Amil and Brown (1961), where Θ is a geometrical factor whose form depends on experimental technique, $|F_l|^2$ is the layer-structure factor, and Φ is the Hendricks and Teller mixing function as given by Brown and MacEwan (1951).

Values of $\Theta|F_l|^2$ were calculated from an approximation of Bradley's form factor curve (Fig. 4, 1953) which has the form

$$\Theta|F_l|^2 = (3310)\exp(-29/d') - (1048/d') + 71 \tag{2}$$

between the (2 sin θ/λ) limits of 0.05–0.12, where d' is the apparent spacing in Å. This expression and the Hendricks-Teller function were programmed to obtain expected diffraction effects at all apparent spacings in 0.1 Å increments for proportions of expandable units ranging from 10–90 per cent in 10 per cent intervals. Peak migration curves were constructed from these data and are shown in Fig. 1.

Fig. 1 indicates that a strong peak centered at about 14 Å is not likely for *any* 10 : 18 random mixture, although a peak between 9–10 Å is clearly indicated. Since the X-ray diagram of the glycerol-solvated montmorillonite showed a 14 Å peak and lacked a 9–10 Å peak, it was concluded the interstratification was more complicated than originally conceived.

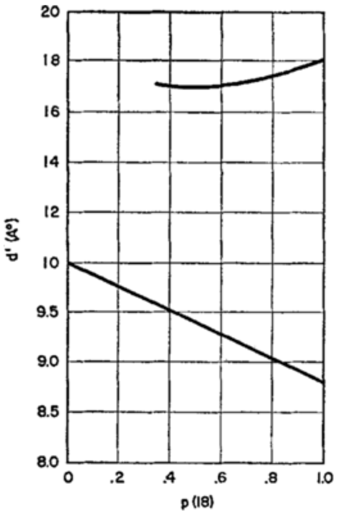

FIG. 1. Peak migration curves for a random mixture of 10 Å and 18 Å units, showing d_{001} vs. proportion of 18 Å component. The top curve is not extended below a p(18) of 0.35 as the peak is diffuse at small p(18) and it is difficult to define the position.

Subsequently, Fourier transform methods were used to deduce the nature of the interstratification. The equation employed in these calculations was formulated by MacEwan (1956) and can be written as

$$P(R) = \sum_R \frac{I}{\Theta |F_l|^2} \cos 2\pi \mu_R R \qquad (3)$$

where I is the integrated intensity, μ_R is the reciprocal spacing and its value and the values for Θ and $|F_l|^2$ are taken at the position of maximum intensity. Values for $\Theta|F_l|^2$ were estimated from Bradley's form factor curve. This cosine transform taken parallel to the projected c-axis direction of the clay layers defines the probability of the occurrence of a layer at a distance R from any arbitrary layer chosen as the origin. Five terms were available for the calculation of the transforms for potassium-saturated samples solvated with both glycerol and ethylene glycol (Table 1). The transforms are illustrated in Figs. 2 and 3 for glycerol and ethylene glycol respectively. Positions of maxima in the low two-theta range on the X-ray traces were corrected for rapidly declining geometrical factors (Johns, Grim, and Bradley, 1954).

Data in Table 2(a) were calculated from the glycerol transform shown in Fig. 2. Comparison of calculated heights based on random mixing gives adequate agreement with observed heights. Units are mixed in proportions of 28 : 59 : 13 for A(10 Å) : B(14 Å) : C(18 Å) respectively. The ethylene

TABLE 1.—INTERLAYER DISTANCES $2\pi\mu_R$ AND RELATIVE INTENSITIES $I/\Theta|F_l|^2$ FOR POTASSIUM-TREATED A.P.I. NO. 20 MONTMORILLONITE

Glycerol		Ethylene glycol	
$2\pi\mu_R$	$\dfrac{I}{\Theta\,\|F_l\|^2}$	$2\pi\mu_R$	$\dfrac{I}{\Theta\,\|F_l\|^2}$
26.28	27.90	21.30	13.10
76.43	25.00	40.70	7.69
104.35	12.93	63.38	3.23
127.66	2.50	82.00	5.33
180.90	2.11	105.26	6.54

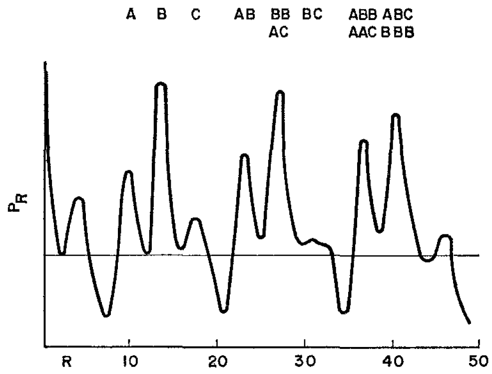

FIG. 2. Fourier transform of glycerol-solvated K–montmorillonite (A.P.I. no. 20).

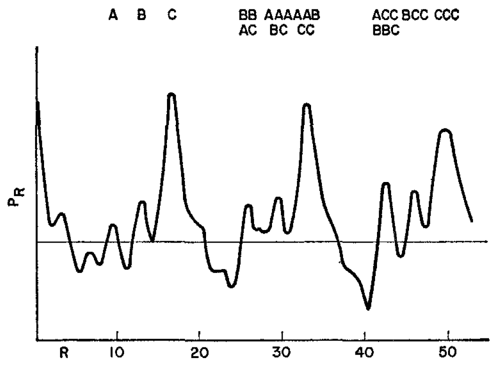

FIG. 3. Fourier transform of ethylene glycol-solvated K–montmorillonite (A.P.I. no. 20).

TABLE 2.—MEASURED AND CALCULATED HEIGHTS OF PEAKS (PROPORTIONS OF UNITS) FROM FOURIER TRANSFORMS OF POTASSIUM–MONTMORILLONITE. CALCULATED HEIGHTS BASED ON A COMPLETELY RANDOM DISTRIBUTION

(a) Glycerol			(b) Ethylene glycol		
Peak	Calc. rel. ht.	Obs. rel. ht.	Peak	Calc. rel. ht.	Obs. rel. ht.
A	0.28	0.28	A	0.08	0.08
B	0.59	0.59	B	0.19	0.19
C	0.13	0.13	C	0.73	0.73
AA	0.08	0	AA	0.01	0
AB	0.33	0.34	AB	0.03	0
AC+BB	0.42	0.56	AC+BB	0.15	0.19
BC	0.15	0.04	BC	0.28	0.23
CC	0.02	0			
AAA	0.02	0	AAA	0	0
AAB	0.14	0	CC+AAB	0.53	0.69
ABB+AAC	0.32	0.38	ABB+AAC	0.03	0
BBB+ABC	0.27	0.50			
BBC+ACC	0.16	0	BBC+ACC	0.24	0.29
BCC	0.03	0			
CCC	0	0	CCC	0.41	0.54

glycol transform gives proportions of A = 08, B = 19, C = 73 as shown in Table 2(b). Calculated relative heights based on random interstratification give adequate agreement with observed peak heights. Comparison of glycerol and glycol data indicate a greater expansion of these clay units with ethylene glycol. Some unexpanded (A) units with glycerol have become partially expanded (B) units with ethylene glycol; (B) units with glycerol are fully expanded (C) units with ethylene glycol. Enhanced expansion with ethylene glycol as compared to glycerol has been noted previously (Johns and Tettenhorst, 1959) and implications of this were cited. Presumably, glycerol is more sensitive to differences in composition, structure, layer charge, or other factors.

A check was made to determine whether additional organic molecules could be induced to penetrate clay layers to promote greater expansion and, thus, change the proportion of units listed in Table 2. Several clay flakes were immersed in glycerol and ethylene glycol for periods ranging up to two months at room temperature and 60°C. Organic liquids were replenished periodically as they deteriorated slowly at the elevated temperature. No change in X-ray pattern was noted.

DISCUSSIONS AND CONCLUSIONS

A noteworthy feature of the Fourier transforms is a strong contribution from a 14 Å component. The presence of a 14 Å component in montmorillonites saturated with large monovalent cations and solvated with glycerol has been noted (MacEwan, 1951), although no interpretation has been given.

The existence of a 14 Å component with ethylene glycol solvation is also indicated from these results, although it is not so pronounced as with glycerol.

A 14 Å component obtained, as described above, does not appear common to the montmorillonite end member of expandable clay minerals. This result suggests that A.P.I. no. 20 is not primarily the montmorillonite end member. One layer of organic molecules apparently separates adjacent clay units to give a 14 Å spacing. Restricted expansion with potassium in interlayer sites may be the result of an intermediate layer charge on adjacent clay units and/or the location of a layer charge in tetrahedral sites. An estimate of the layer charge was made using the lithium treatment of Greene-Kelly (1955). About 90 per cent of the clay collapsed irreversibly after lithium saturation, heating, and glycerol solvation. This result suggests that the layer charge of most units in the sample is low but does not necessarily imply that the locus of the charge is octahedral. On the contrary, data from potassium treatment suggest some tetrahedral charge and indicate the beidellite character of the sample. A structural formula presented for this clay by Kerr, Kulp and Hamilton (1951) is $(Al_{1\cdot53}Mg_{0\cdot31}Fe_{0\cdot19})(Al_{0\cdot15}Si_{3\cdot84})O_{10}(OH)_2$. Kerr, Kulp and Hamilton state that the chemical data indicate this clay to be a montmorillonite–beidellite intermediate, in agreement with results of this study.

The expandable character of clay minerals having a micaceous structure is intimately connected with layer charge among other factors. In general, nonexpansion is associated with a large layer charge and enhanced expansion is related to a low layer charge. A generally accepted interpretation of the three components noted in this study is that each is associated with some layer charge, octahedral and/or tetrahedral, this charge being equally divided between adjacent clay units. However, although a given amount of expansion depends upon some layer charge, the charge does not have to be distributed symmetrically with respect to the interlayer region. This hypothesis has general implications for montmorillonite structures and properties.

The present investigation is concerned primarily with variations in the interlayer region. These variations are related to differences in adjacent clay layers. An interpretation that emphasizes the interlayer region is outlined schematically in Fig. 4. The stippled portion of the diagrams represents the primary source of the layer charge for any given unit. The *amount* of layer charge is not implied by shading, although most A.P.I. no. 20 units have a low layer charge whether the location of the charge is tetrahedral or octahedral. Standard interpretations of micalike units and montmorillonite units are shown in Figs. 4a and 4b respectively.

The existence of a 10 Å component, as shown in Fig. 4a, does not necessarily imply substitution in the opposing tetrahedral sheets of a given clay layer in a randomly interstratified clay mineral such as A.P.I. no. 20. Other interpretations of charge distribution for two adjacent clay layers and suggested d_{001} spacings are outlined in Fig. 4. The feature of greatest import that emerges from these diagrams is an asymmetric distribution of layer

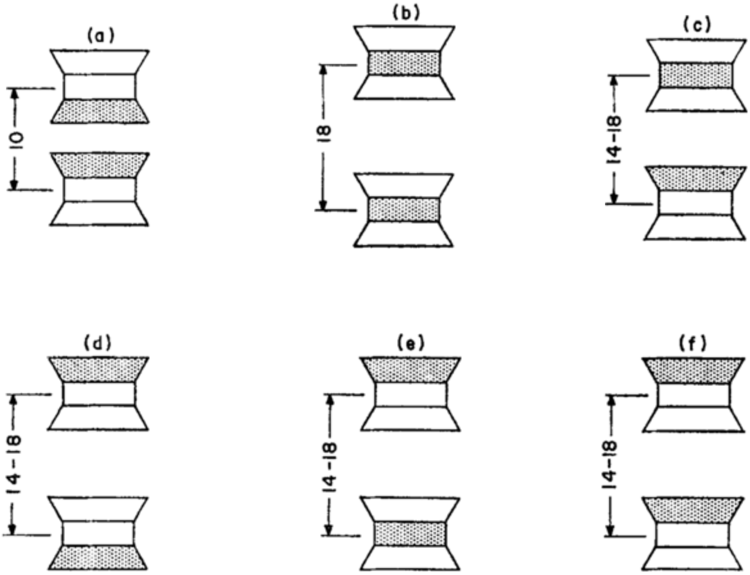

FIG. 4. Schematic representation of layer charge distribution for adjacent clay layers. Stippled areas represent primary source of layer charge. Magnitude of layer charge presumably is variable.

charge. The spacings suggested apparently depend on the magnitude of layer charge adjacent to a given interlayer region and the proximity of the layer charge to the interlayer ions.

Random interstratification of three components (interlayer spacings) indicates that any component can be contiguous with itself or any other. Attempts to construct a model that exhibits random mixing of three components with conventional (i.e. symmetrical layer charge distribution) mica units (high tetrahedral charge) and montmorillonite units (low octahedral charge *or* low tetrahedral charge) lead to an apparent difficulty. Spacings of 10 Å and 18 Å cannot be adjacent. An interpretation based on asymmetric layer charge obviates this difficulty and provides three interlayer regions with only two layer charge distributions. This interpretation appears to have an advantage of simplicity.

An alternative to account for random mixing of three components is the presence of units that exhibit more than two symmetrical layer charge distributions. A generalization of this alternative is that clay units may exhibit a continuum of layer charges. Although more conventional, this situation appears to be complex. However, some distribution of layer charge in A.P.I. no. 20 is indicated upon comparison of the transforms (Figs. 2 and 3), e.g. only some of the 10 Å units with glycerol have remained 10 Å units with ethylene glycol.

An asymmetric distribution of layer charge may be a reason for various regular interstratifications, e.g. those that involve alternation of micalike spacings with expanded spacings. One possible interpretation of regular 1 : 1 interstratification could be an ordered alternation of components (spacings) like those shown in Fig. 4a with those shown in Fig. 4d, e.g. the top unit in Fig. 4a followed by those in Fig. 4d and finally the lower unit in Fig. 4a, etc. The general idea of a polar charge distribution to explain regular interstratification in clays appears to have been noted first by Sudo, Hayashi, and Shimoda (1962).

Cowley and Goswami (1961) reported curved montmorillonite platelets as a result of an electron diffraction study. Although the tetrahedral sheet in micaceous minerals invariably contracts to fit an octahedral sheet by rotations of individual tetrahedra (Radoslovich and Norrish, 1962), an asymmetric layer charge is one means by which an unbalanced situation might be obtained in micaceous-type layers. A possible result of such an unbalancing could be bending or curling of the platelets.

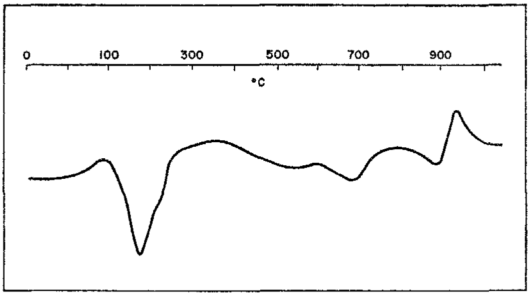

FIG. 5. Differential thermal curve for untreated, minus 1 μ fraction of A.P.I. no. 20. Heating rate was 12°C per minute. Pt–Pt10%Rh thermocouples with a nickel block and anhydrous aluminum oxide as the inert material were used.

A differential thermal trace of A.P.I. no. 20 montmorillonite is shown in Fig. 5. Kerr, Kulp, and Hamilton (1951) have discussed the thermal trace of this material and also noted the anomalous dehydroxylation peak at about 500°C and a somewhat low temperature (<900°C) for the high temperature endotherm. The abnormal character of the differential thermal curve may be partly a consequence of clay layers having an asymmetric layer charge distribution.

ACKNOWLEDGMENTS

We wish to thank Dr. R. B. McEuen of the Pure Oil Research Center, Crystal Lake, Illinois, for deriving equation (2) and Mr. Mahlon Smith for his generous assistance with the computer program. We are indebted to Dr. E. W. Radoslovich for calling our attention to the article by Sudo, Hayashi and Shimoda (1962). A portion of this work was supported by a grant from the National Science Foundation to one of us (R.T.).

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