

# SOME OBSERVATIONS ON MONTMORILLONITE-ORGANIC COMPLEXES

*By*

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## ABSTRACT

Fifteen pure montmorillonites selected on the basis of minor differences in x-ray diffraction and differential thermal analysis data were treated with ethylene glycol, piperidine, and dodecylamine. X-ray and differential thermal data of the resulting complexes lead to the following conclusions:

(1) The complexes of montmorillonites with a given organic compound show differences ascribable to differences in the character of the montmorillonites. Attempts to relate variations in organic complexes to exchangeable cations, chemical composition, and colloidal properties of the montmorillonites met with very limited success.

(2) All montmorillonites are mixed-layer sequences; i.e. adjacent layers differ from one another in composition, structure, or some other factor. It is suggested that mixed layering of this nature may also occur in other three-layer clay minerals.

## INTRODUCTION

It has been known for some time that montmorillonite is capable of adsorbing organic compounds between unit sheets. Organic compounds thus adsorbed fall into two groups: the polar compounds which displace the water normally held in interlayer positions, and the ionic compounds which irreversibly replace exchangeable inorganic cations.

Although the characteristics of montmorillonite-organic complexes have been studied for a large number of organic compounds, the possibility of variations in such complexes caused by variations in different montmorillonites has received very little attention. Allaway (1948) has recently shown that a group of montmorillonites treated with piperidine and subjected to differential thermal analysis give a series of curves differing considerably one from another. Allaway attempted to relate these differences to differences in the chemical composition of the montmorillonites. Whether or not such a relationship exists, it is clear that there are differences in the manner in which different montmorillonites hold piperidine and that these differences can be ascribed only to differences in the fundamental nature of montmorillonite. Allaway's results suggest that a comparative study of a group of montmorillonites treated with various organic substances might throw some light on the variations existing in montmorillonite.

The samples used in this study were selected from a large group of montmorillonites on the basis of preliminary x-ray and differential thermal analysis data. Fifteen samples were selected on the basis of purity and variations in the preliminary data which suggested some fundamental differences in their nature. Each sample was treated with an excess of ethylene glycol, which is a polar compound, and piperidine and dodecylamine, both of which are ionic compounds. In order to obtain the montmorillonite complexes, the ethylene glycol was added to dry montmorillonite whereas the ionic compounds were added to a montmorillonite suspension which was filtered, washed and dried. X-ray and differential thermal analysis data were obtained from the resulting complexes. X-ray data were also obtained from the complexes of the ionic compounds after treatment with an excess of ethylene glycol.

#### ACKNOWLEDGMENTS

This paper represents a portion of a Ph.D. thesis written at the University of Illinois under the supervision of Professor R. E. Grim, whose help throughout the course of the investigation is gratefully acknowledged. The investigation was carried out while the author held the National Lead Company fellowship in geology. He is grateful to the University of Illinois for making the award and to the National Lead Company for establishing the fellowship.

#### X-RAY DATA

Basal(001) spacings for all untreated montmorillonites and their organic complexes are given in Table 1. The spacings are constant for the ethylene glycol complexes, but they vary for the untreated samples and all other complexes. Furthermore, the higher orders of the basal reflections occur at "expected" positions, or with a regular periodicity, for only the ethylene glycol complexes. For the untreated montmorillonites and the other complexes, the c-axis periodicity varies from one unit sheet to the next.

The basal spacing of untreated montmorillonite is usually considered to be controlled by the nature of the exchangeable cations held between unit sheets (Hendricks and others, 1940). Those unit sheets having sodium as the dominant exchangeable cation adsorb one molecular layer of water at normal atmospheric humidity, resulting in a basal spacing of 12.4 Å. Those unit sheets holding calcium or magnesium adsorb two molecular layers of water, resulting in a basal spacing of 15.4 Å. On this basis, most of the samples used in this study consist of intimately interlayered unit sheets with one and two layers of adsorbed water, commonly with one or the other predominating. But samples 1 and 3 both have basal spacings under 12.4 Å, and therefore must contain some unit sheets with no associated water layers. This same phenomenon was observed by Roth

TABLE 1. — BASAL (001) SPACINGS OF UNTREATED MONTMORILLONITES AND THEIR ORGANIC COMPLEXES

Sample Number	Locality	Exchange-able cation	Untreated montmorillonite	Glycol complex	Piperidine complex	Dodecylamine complex	Glycol-treated piperidine complex	Glycol-treated dodecylamine complex
1	Wayne, Alberta, Canada	Na	11.3	17.0	13.8	16.4	17.3	38.4
2	Rosedale, Alberta	Na	12.5	17.0	13.6	17.7 (17.0)		34.0
3	Dorothy, Alberta	Na	11.5	17.0	13.8		17.0	17.7
4	Bickerdike, Alberta	Na	12.8	17.0	13.5	16.1		35.0
5	Montmorillon, France	Ca	15.2	17.0	13.6	17.6	15.5	34.0
6	Cheto, Arizona	Ca	14.7	17.0	14.0	18.6	16.8	37.7
7	Tatatila, Mexico	Ca	15.3	16.9	13.6	17.7		34.0
8	Belle Fourche, S. D.	Na	12.6	17.0	14.0	18.2		37.7
9	Belle Fourche, S. D.	Ca, Mg	15.0	16.9	13.8	17.7	16.7	33.2
10	Gonzales Co., Texas	Ca	14.7	17.0	13.6	18.0	16.5	36.8
11	Gonzales Co., Texas	Ca	14.4	17.0	13.8	15.8		34.7
12	Gonzales Co., Texas	Ca	14.4	17.0	13.7	15.8		17.2
13	Pembina Mt., Man., Canada	Ca	15.1	17.0	13.8	18.0	16.0	31.5
14	Ponza, Italy	Ca	14.5	17.0	13.6	17.0	16.5	
15	Marnia, Algeria	Na, Ca	13.6	17.0	13.8	20.1	16.1	35.0

(1951) in a comparative study of some Wyoming bentonites. He felt that the anomaly was best explained by assuming that those unit sheets with no adsorbed water had no associated exchangeable cations. This implies that these unit sheets differ from their neighbors in some respect. The general structural similarity of all unit sheets in all samples is indicated by the constant 17 Å spacing after treatment with ethylene glycol. The unit sheets with no associated water layers are therefore similar in general structure to their water-adsorbing neighbors. They probably differ in chemical composition, or possibly in the presence of some minor structural irregularity.

The variation in basal spacings of the piperidine and dodecylamine complexes cannot be ascribed to variations in water adsorbed between unit sheets. Since each sample was treated with an excess of each compound, fairly complete replacement of sodium and calcium by each organic compound would be expected. Examination of Table 1 shows no relationship between the basal spacing of the untreated montmorillonites and their organic complexes, so that residual inorganic exchangeable cations with associated water layers cannot explain the observed variations. Apparently each montmorillonite adsorbs each organic compound to a different extent. The differences in the amount of organic material adsorbed reflect differences in the fundamental nature of the montmorillonite. The nature of the differences must be fairly complex, inasmuch as there is no apparent relationship between the amount of piperidine and the amount of dodecylamine adsorbed by any sample.

The lack of regular periodicity along the *c*-axis observed for piperidine and dodecylamine has already been pointed out. This lack of regularity can be ascribed only to variations in the amount of adsorbed organic material from one unit sheet to the next. If the amount of organic material adsorbed by any unit sheet is dependent upon the nature of that unit sheet, then it follows that there are variations of some type within the montmorillonite lattice from one unit sheet to the next. The probable presence of some unit sheets of differing chemical composition or structure within the lattice of samples 1 and 3 has already been referred to. It now may be postulated that every montmorillonite is a mixed-layer sequence whose component unit sheets differ from one another in chemical composition or in the presence of some minor structural irregularity. The lack of correlation between the amount of piperidine and the amount of dodecylamine adsorbed by any sample suggests that there are at least several different types of unit sheets in any given sample.

The basal spacings of the piperidine and dodecylamine complexes after treatment with ethylene glycol indicate that glycol is adsorbed to a variable extent. Once again, each sample gives a mixed-layer type of reflection, lending further support to the mixed-layer hypothesis.

## DIFFERENTIAL THERMAL ANALYSIS DATA

Representative differential thermal curves of the montmorillonite samples before treatment and after treatment with ethylene glycol, piperidine, and dodecylamine are reproduced in Figures 1 to 4 inclusive. It will be noted that the curves for the untreated samples and for the dodecylamine complexes are essentially similar from one sample to the next, whereas those of the glycol complexes and the piperidine complexes vary from one sample to the next.

The curves of the untreated samples require little comment. The initial peak caused by loss of interlayer water is of the sodium type for those samples having a basal spacing of about 12.4 Å and is of the calcium type for those samples having a basal spacing of 15.4 Å. Sample 12 has an initial magnesium-type peak. The only other point worthy of note is the manner in which most samples behave as homogenous materials with respect to the various reactions which they undergo. Samples 11 and 15 show double dehydroxylation peaks at approximately 500° and 700°C; this is not surprising in view of the previous evidence that all samples are mixtures. The apparent homogeneity of the other samples can be explained only in terms of the essential similarity of the components in the mixture.

The most noteworthy feature of the curves of the glycol complexes is their complexity. Each consists of a variable group of partly superimposed endothermic peaks followed by an exothermic peak at 300° or 400°C. The remainder of the curve resembles that of the untreated samples. X-ray analyses of several samples heated to 400°C indicate the absence of interlayer glycol at this temperature.

The variations in the initial portion of each curve are caused by variations in the manner in which glycol is removed, which in turn is caused by some variation in the character of each sample. Accordingly, the variations in the curves were compared with variations in the x-ray and differential thermal data obtained from the untreated samples. Those samples having calcium as the dominant exchangeable cation give an exothermic peak at about 400°C, whereas those having sodium as the dominant exchangeable cation give an exothermic peak at about 300°C. The variations in the initial endothermic peaks could not be correlated with data from the untreated montmorillonites.

Several differential thermal curves of the glycol complexes were run in a nitrogen atmosphere, resulting in the elimination of the exothermic peak at 300° to 400°C. This peak thus represents an oxidation reaction which is controlled by the nature of the exchangeable cations.

In an effort to evaluate the meaning of the initial endothermic peaks, several samples were removed from the furnace after each endothermic reaction and subjected to x-ray analysis. The basal spacing shows a progressive decrease as illustrated by the spacings shown in Figure 2. Furthermore, the basal spacings observed after each reaction were of the

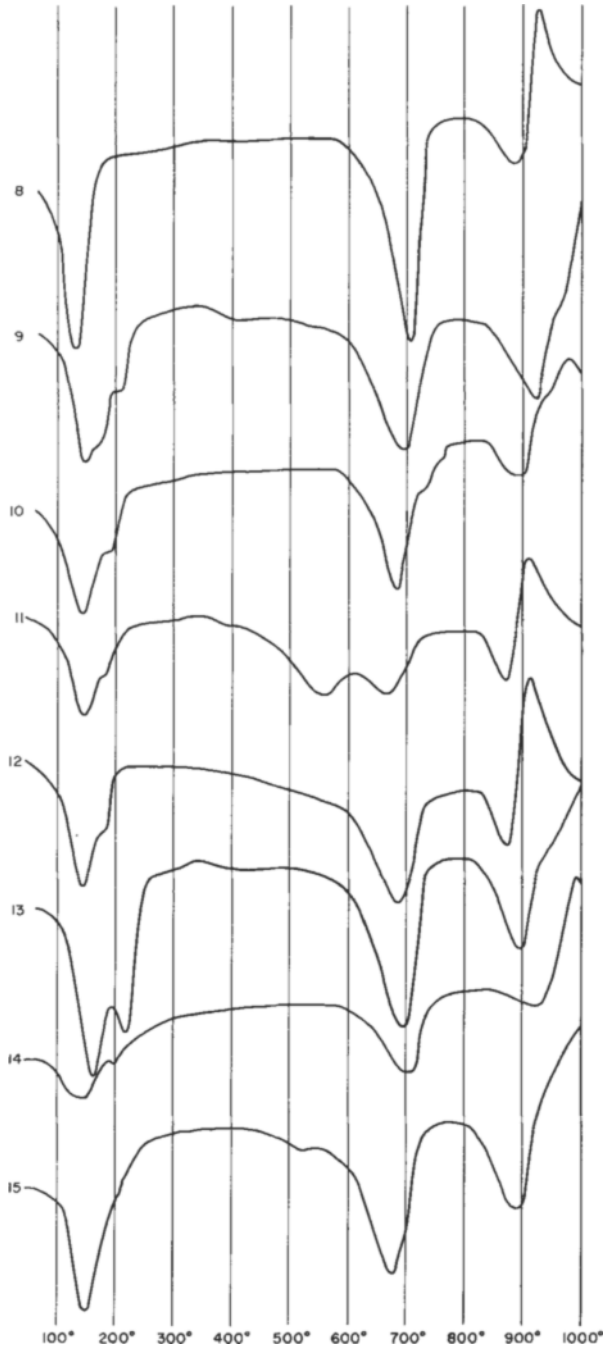


FIGURE 1. — Thermal curves of untreated montmorillonites.

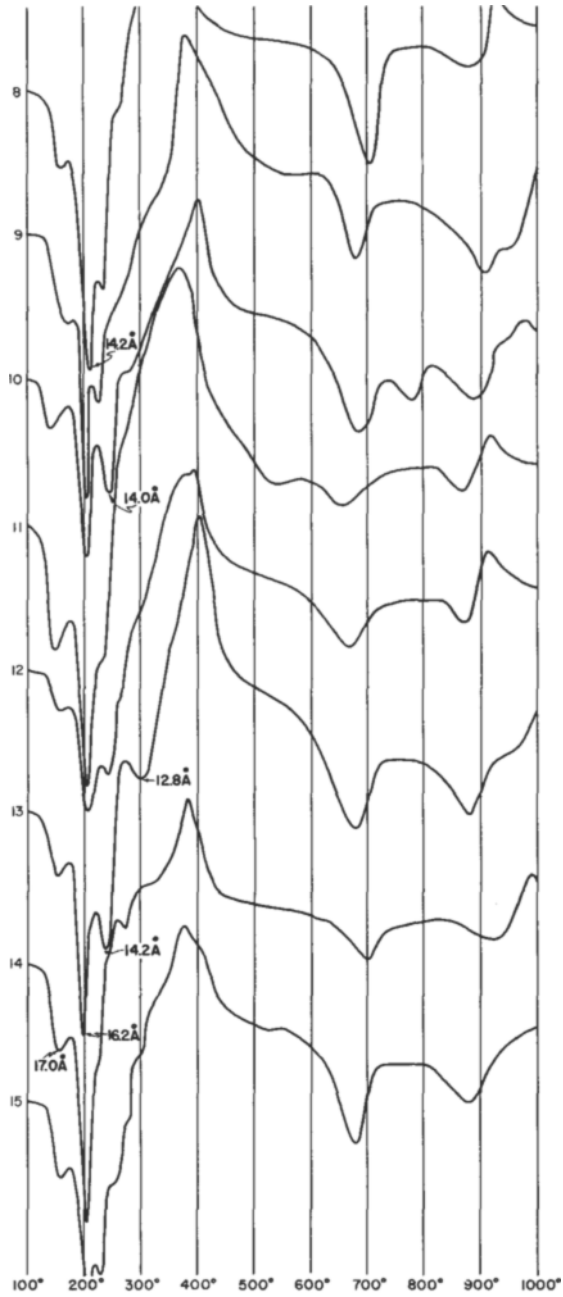


FIGURE 2.—Thermal curves of glycol complexes. Note 001 spacings at points indicated by arrows.

type normally given by a mixed-layer sequence. On the basis of the x-ray data, it was impossible to correlate a given reaction of a given sample with any reaction of any other sample. The only satisfactory theory which will cover the above observations is that each endothermic reaction represents the driving off of some portion of the glycol molecules between some unit sheets. This theory once again suggests that montmorillonite consists of several different types of unit sheets which are intimately interlayered. The presence of several fairly sharply defined endothermic reactions suggests that the variation between the different types of unit sheets is not continuous. It is of interest to note that the residual portion of the interlayer glycol molecules is apparently driven off from all unit sheets at the same temperature.

The differential thermal curves of the piperidine complexes shown in Figure 3 bear a general resemblance to those described by Allaway (1948). Each consists of a variable series of exothermic peaks superimposed on the normal differential thermal curve for the untreated sample. An attempt was made to apply Allaway's correlation between chemical composition and the temperature of the exothermic peaks for several samples for which chemical analyses were available, but none of the curves agreed with his conclusions. However, the curves can be explained quite adequately in terms of the previously enunciated mixed-layer hypothesis. Each exothermic reaction would thus represent the expulsion of interlayer organic matter from one group of similar unit sheets. However, the curves bear no apparent relationship to any other data; this suggests that the mixed layering may be more complicated than previously suggested.

The differential thermal curves of the dodecylamine complexes given in Figure 4 are, on the other hand, quite similar in form. They vary only in the intensity of the reactions. The nature and significance of these curves has already been discussed by Bradley and Grim (1948). They are included in this paper only to show the differences which may be encountered in differential thermal curves of organic complexes.

## SUMMARY AND CONCLUSIONS

Although all montmorillonites give similar x-ray patterns and differential thermal curves, and although they all adsorb two layers of ethylene glycol between unit sheets, they behave differently with respect to the manner in which the ethylene glycol is burned off and with respect to the amount of ionic compounds adsorbed in interlayer positions. Dodecylamine is burned off in essentially the same manner for all samples, but piperidine is burned off in a different manner for all samples.

The similarities and differences outlined above exist not only from one montmorillonite to the next, but also from one unit sheet to the next within the same montmorillonite. It is concluded that all montmorillonites are an intimate mixture of several different kinds of unit sheets interleaved one



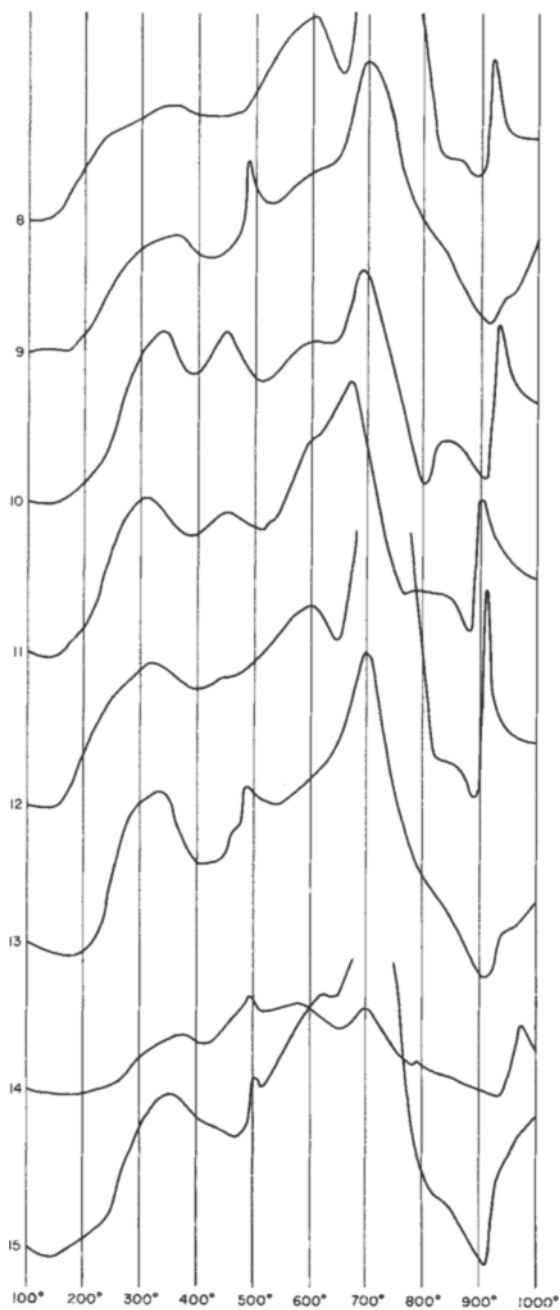


FIGURE 3. Thermal curves of piperidine complexes.

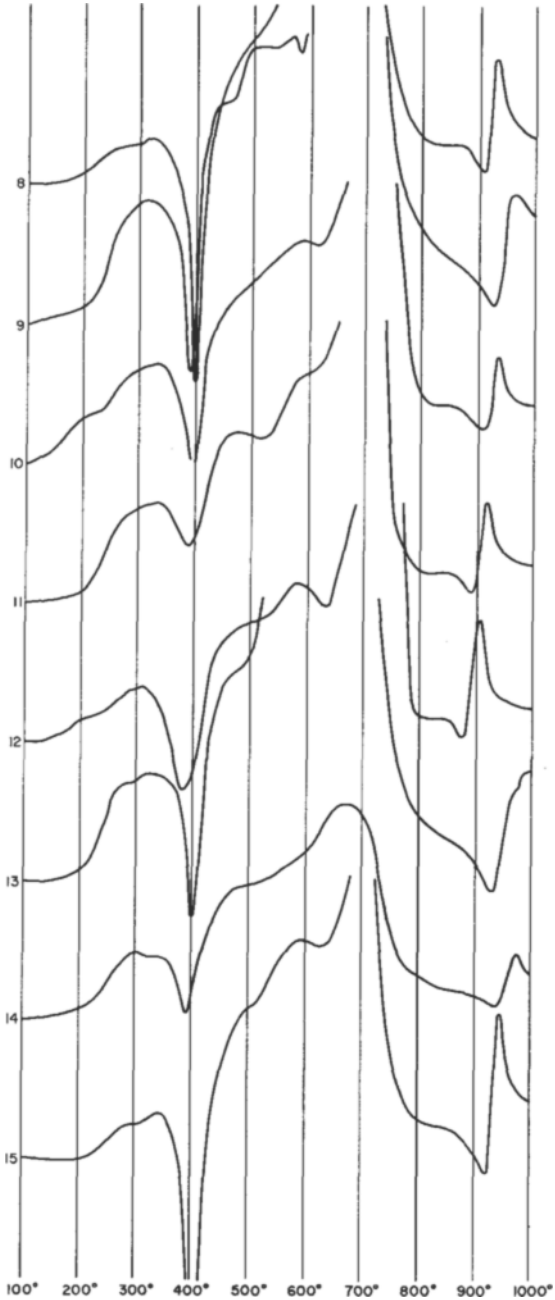


FIGURE 4.— Thermal curves of dodecylamine complexes.

with another. The unit sheets are sufficiently similar to react in the same way to some treatments.

If the above hypothesis is correct, no montmorillonite can be fully characterized by current analytical techniques. The differences observed in x-ray and differential thermal analysis of organic complexes have some promise in this respect. However, the lack of correlation between the various groups of data accumulated in this study indicates that the problem is complex and is not capable of easy solution.

In closing, it might be pointed out that there is no reason to suppose that mixed layering of the type postulated for montmorillonite does not exist in other apparently homogeneous three-layer clay minerals.

### REFERENCES

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### ADDENDA

Since this paper was presented, the author's attention has been drawn to a paper by Beavers and Larson\* in which the electrophoretic mobilities of several clays are described. Beavers and Larson report that Wyoming bentonite exhibits several discrete mobilities, suggesting the presence of several different components in the apparently homogenous clay. If one assumes that each particle is only a few unit cells thick, such a mixture would be indistinguishable from a mixed layer sequence. These observations lend further support to the hypothesis that all montmorillonites are intimate mixtures of several components.

### DISCUSSION

C. G. Dodd. — I gather that you had only a limited amount of analytical chemical data on your montmorillonite samples, and I would like to suggest that such data would permit an assignment of aluminum to tetrahedral and octahedral positions by a method such as that proposed by C. E. Marshall. The resulting assignments might result in some further correlation of the properties of your organic complexes. If chemical analyses corrected for the presence of nonclay impurities can be relied on

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\* Beavers, A. H., and Larson, B. L. (1953) *Electrophoresis of clays by the Schlieren moving boundary procedure*: Soil Sci. Soc. Am. Proc., v. 17, p. 22-25.

for calculations of aluminum substitution in tetrahedral coordination, these data might be expected to correlate with observed properties of complexes of molecules or ions adsorbed on the 001 planes of montmorillonoids, that is, directly in contact with the tetrahedral layers.

*P. J. S. Byrne.* — At the time the paper was presented, chemical analyses were available for only a few samples. Since then, a complete set of chemical analyses has been obtained. No correlation between chemical analyses and data on organic complexes could be found. If chemical differences do exist between adjacent layers, as I have suggested in this paper, then such a lack of correlation would be expected.

*Rustum Roy.* — It would seem that several precautions would have to be taken in order to make these data on the different montmorillonites comparable. Can the author tell us whether any attempt was made to:

1. Use comparable size fractions; since this may have a pronounced effect on the properties studied, especially if the purity were considered?

2. Obtain the clays in a comparable condition by either electro dialysis or saturation with the same ion. The bonding of both water and the various organic complexes is certainly influenced — and to different degrees — by the nature of the interlayer exchangeable cations.

3. Obtain equilibrium between each of the organic compounds and the clays. Since the three compounds have varying vapour pressures at the same temperature it is more than likely that the rate of solvation will be different for each. Perhaps some such method as refluxing (at reduced pressure if necessary) with the organic compound may help in obtaining equilibrium. Only under such conditions could the results be considered comparable.

*P. J. S. Byrne.* — None of the suggested precautions was taken for the following reasons:

1. Comparable size fractions of montmorillonite cannot be obtained by conventional sedimentation techniques, since the settling velocity of any particle is strongly affected by its shape and charge and the charge upon its neighbors. Furthermore, montmorillonite particles re-aggregate upon settling and drying. The possibility of variations in the organic complexes being caused by differences in particle size is vitiated by the observations on the differential thermal curves of the glycol complexes, which indicate a stepwise variation rather than a continuous one. Further evidence of stepwise variation is given in the addenda which was added to the paper after presentation.

2. No attempt was made to achieve saturation with the same ion, since information on the effect of exchangeable cations upon the organic complexes was desired. A study of Table 1 will show that the results obtained are dependent upon factors other than the exchangeable cation present. It is possible that the exchangeable cation does play some part, and this may be a partial explanation for the lack of correlation between the

various sets of data obtained. Further work of this nature upon homoionic systems is clearly desirable.

3. The only results which are considered to be comparable are those obtained from different montmorillonites treated with the same organic compound under the same conditions. A comparison seems to be quite legitimate in these circumstances. No attempt was made to reach equilibrium, since it was felt that differences between montmorillonites might show up more clearly under nonequilibrium conditions.