INTRACRYSTALLINE SWELLING OF MONTMORILLONITE IN SOME WATER-ORGANIC MIXTURES (CLAY-ORGANIC STUDIES. XVII)

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Abstract

Basal spacings of a Ca-montmorillonite equilibrated in aqueous solutions of methanol, ethanol, *n*-propanol, 1,2-ethanediol, 1,5-pentanediol, acetone, dioxane and morpholine, are measured at concentrations ranging from 0–100 mole percent organic component. With solutions of the monohydric and dihydric alcohols, the basal spacings increase with increasing mole fraction of the organic component up to a limit beyond which the spacing diminishes rapidly almost to that given by the pure organic material. The expansion limit occurs at the following mole fractions of organic material: methanol 47%, ethanol 35%, propanol 8%, ethanediol 7%, propanediol 8%. Acetone gives complete dispersion of Ca-montmorillonite in the range 0–10 mole percent, expansion to 26.5 Å in the range 20–60 mole percent, expansion to 22 Å in the range 80–90 mole percent. Dioxane and morpholine give constant spacings over the entire range from 1–100 mole percent. The significance of these results is discussed.

Introduction

The present study is concerned with the intracrystalline swelling of Ca-montmorillonite when immersed in various mixed liquid systems of water and simple organic compounds. The main objective was to explore the phenomena occurring when the composition of the liquid was changed progressively from pure water to pure organic. Compared with the many studies made on montmorillonites immersed in single liquids, initiated by Bradley (1945) and MacEwan (1948), very few have been made on mixed liquid systems. Why so little attention has been given to this kind of study is difficult to understand, but a partial explanation may be the difficulty or the impossibility of determining precisely the amounts of the two components absorbed by the clay from the mixed liquid phase. Heydemann and Brindley (1968) circumvented the problem by establishing equilibrium between mixed organic liquids and a montmorillonite via the vapor phase. Equilibrium was established very slowly and it may not always be the same as when the clay is immersed in the mixed liquids.

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Experiments similar to the present work have been made by Barshad (1952), by Ruiz Amil and MacEwan (1957), and by van Olphen and Deeds (1962). Barshad examined the basal spacings of a montmorillonite immersed in a few water-organic solutions and was concerned particularly with showing a possible relation between the dielectric constant of the medium and the equilibrium basal spacing. He considered that the decrease of the dielectric constant, such as that brought about by progressive addition of propanol to water, increases the Coulombic attraction between the exchangeable cations and the negative silicate surfaces and thereby diminishes the basal spacing. Ruiz Amil and MacEwan reported briefly on X-ray data for a Na-montmorillonite immersed in water-acetone mixtures. This system will be considered further in the present work. Van Olphen and Deeds studied water-pyridine and water-α-picoline interactions with Na-montmorillonite and demonstrated the formation of a sequence of water-organic complexes with spacings increasing with the percent of water.

Studies involving vapor phase interactions with montmorillonite such as the recent work of Dowdy and Mortland (1967, 1968) on ethanol-water interactions and ethylene glycol-water interactions have an important but indirect bearing on the present work. They have shown by detailed infrared analysis the importance of cation-dipole interactions between the exchange cations and polar organic molecules particularly for cations of high solvation energy. The phenomena observed with mixed liquid interactions may depend on competitive attractions of the exchange cations for water molecules and for polar organic molecules. Mackenzie (1948) measured the amounts of ethylene glycol and water in Ca-montmorillonite after various methods of sample preparation and compared them with the basal spacing of the mineral. His results can be compared only in a general way with the present work.

EXPERIMENTAL

Experiments have been carried out on a calcium saturated montmorillonite from Casper, Wyoming, supplied by the Georgia Kaolin Company, Elizabeth, N. J., with no X-ray detectable impurities and a cation exchange capacity of 115 meq/100 g for Ca-saturated material dried in vacuo at 150°C. The clay as supplied was a $<2\mu m$ size fraction mainly Na-saturated. The Ca-saturated material was prepared by two treatments with excess 1N calcium chloride solution, followed by washing with deionized water until chloride ion free. The organic liquids used were mainly reagent grade materials without further purification, namely: methanol, ethanol, n-propanol, 1,2-ethanediol (ethylene glycol), 1,5-pentanediol, acetone, 1,4-dioxane and morpholine.

Emphasis has been placed on obtaining accurate basal spacing measurements of the montmorillonite in equilibrium with mixed water-organic systems. The first experiments were made with the clay-liquid systems packed in sealed glass capillaries and mounted in a Debye-Scherrer X-ray powder camera. Subsequently a diffractometer technique was used

as follows: from a stock clay suspension containing about 30 mg clay/ml suspension, 2 ml portions were pipetted on to glass slides and allowed to dry slowly in air to form thin, well oriented aggregates. Water-organic solutions were prepared by weighing the components into glass containers with tightly fitting screw caps. The clay-covered slides were immersed in the liquids for one or several days. The amounts of water and organic material always greatly exceeded the 60 mg of clay on each slide so that the composition of the equilibrating solutions were always essentially those of the initial liquids.

X-ray data were obtained with a Norelco diffractometer fitted with a specially constructed sample chamber. A liquid-soaked clay slide could be transferred to the chamber together with several ml of the equilibrating liquid in a shallow tray and the chamber sealed within about 20–30 seconds. The clay-covered slide was observed through a window to check that no drying out of the sample occurred. With a few mixtures, notably water-acetone mixtures, a slow "drip-feed" arrangement was devised to keep the clay sample thoroughly wet during the X-ray examination.

RESULTS AND DISCUSSION

The results are summarized in Figures 1–4, where $d(001)$ in Å is plotted against mole percent of organic component in the mixed liquids. Solid symbols indicate spacings of well-ordered complexes; reflections were measured often as far as 009 and the mean deviation of the individual spacing values from the mean value was usually less than 0.05 Å. Open symbols indicate average spacings of less well ordered complexes. The deviations from regularity usually were such that "integral" orders
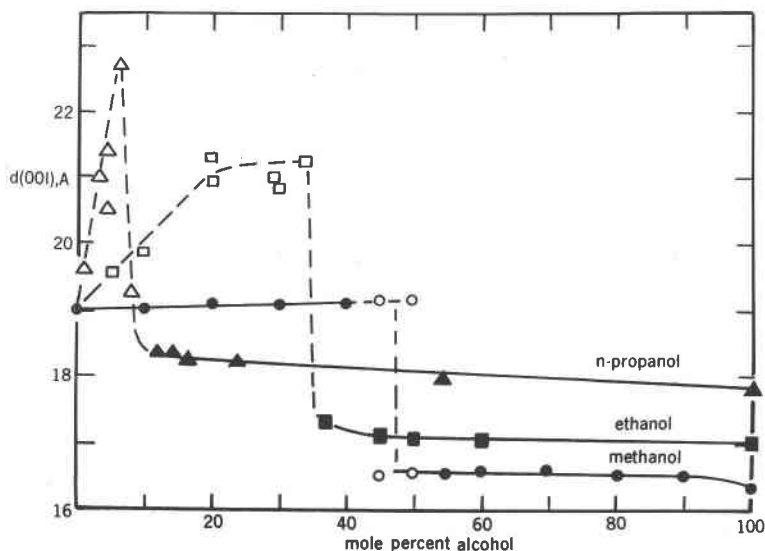

FIG. 1. Basal spacings of Ca-montmorillonite in equilibrium with water-alcohol mixtures. Solid symbols for well-ordered phases, open symbols for poorly ordered or mixed-layered phases.
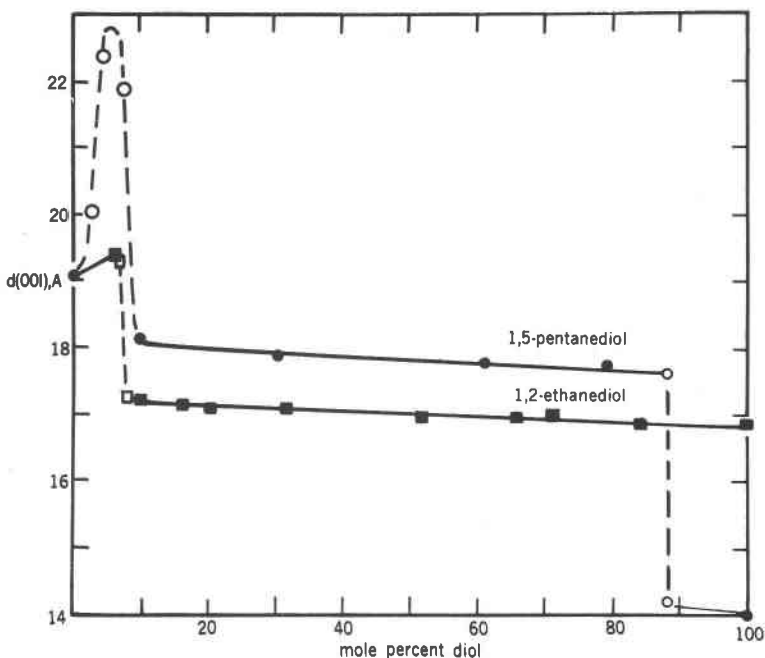
FIG. 2. Basal spacings of Ca-montmorillonite in equilibrium with aqueous solutions of 1,2-ethanediol and 1,5-pentanediol.

could be assigned to the diffraction peaks and average spacings determined to within 0.1 or 0.2 Å; in some cases no more than one or two diffraction peaks were obtainable and the resulting "spacings" can be regarded only as average values for highly disordered arrangements.

Ca-montmorillonite-alcohol-water systems. The results for aqueous solutions of methanol, ethanol and normal propanol are shown in Figure 1. As the mole fractions of alcohol increase, the equilibrium basal spacings of the clay, at first, increase. With methanol, the increase of spacing is very small and continues to about 45 mole percent methanol, and the spacings remain regular. With ethanol, the increase of spacing is considerably greater and continues to about 35 mole percent ethanol; the spacings become increasingly irregular. With propanol, the increase sets in very rapidly and the expanded spacings are highly irregular. As little as 1 mole percent of propanol causes a measurable increase and the maximum increase takes place at about 6 mole percent. With all three alcohols, the spacings diminish abruptly beyond the composition of maximum expansion.
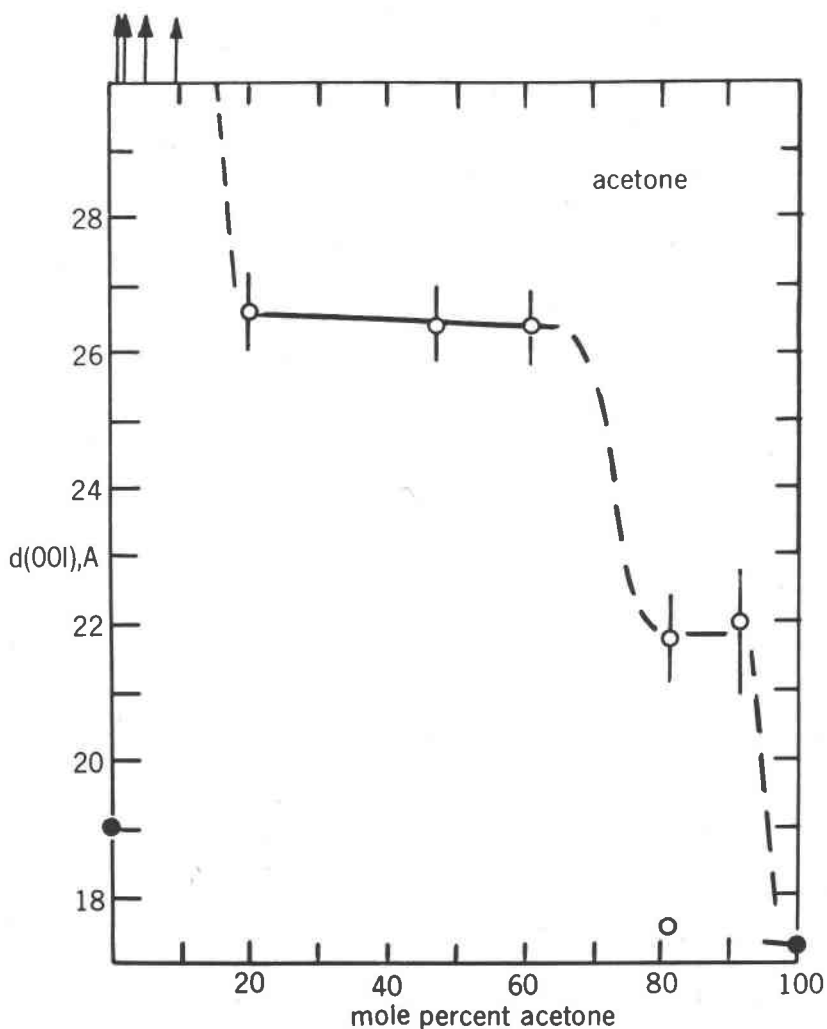
FIG. 3. Basal spacings of Ca-montmorillonite in equilibrium with water-acetone solutions. Arrows pointing upwards indicate spacings far outside the range of measurement.

The initial increase in basal spacing is determined by the balance of forces operating in the interlayer regions of the montmorillonite. This is a complex situation further aggravated by lack of knowledge of the precise composition of the absorbed liquid. The spacing of the Ca-montmorillonite in water, 19.01 ± 0.06 Å measured to 0.0.10, may arise from double hydration shells surrounding the Ca^{2+} ions located in the mid plane between the silicate layers, or possibly from a more dispersed arrangement
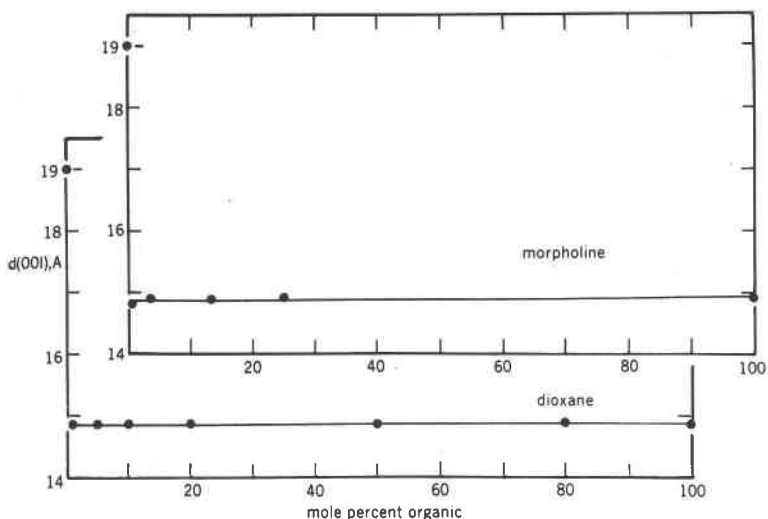
FIG. 4. Basal spacings of Ca-montmorillonite in equilibrium with aqueous solutions of dioxane, $O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2$, and morpholine, $NH\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2$.

of Ca^{2+} ions, each with a single hydration shell, corresponding to the development of an electrical double layer on the silicate surfaces. On the basis of the *first model*, the cohesive force would be primarily electrostatic between positive ions and negative surfaces. The increase in spacing with addition of alcohol is not compatible with the accompanying de-decrease of dielectric constant which would cause an increase in the Coulombic attractions. An explanation for the spacing increase must then be sought in an increased repulsion arising from the replacement of water molecules by the larger alcohol molecules which may lead to expansions in the sequence: methanol < ethanol < propanol. The small size of the methanol molecule is consistent with the very small increase in spacing and its continuance to a high mole fraction of methanol.

On the basis of the *second model*, the establishment of double layers, an explanation must be sought along the lines of double layer theory in which the cohesion is due primarily to van der Waals attractive forces in equilibrium with double layer repulsions. It is pertinent here to refer to the very detailed study by Mackor (1951b) of the stability of negative AgI sols in water-acetone mixtures in which he showed that with a few mole percent of acetone, of the order 2–7 percent, the stability of the dispersed sol is considerably increased contrary to the expectation that "a decrease of the dielectric constant seriously lowers the stability of a colloid." The detailed interpretation is based on the adsorption of a

monomolecular film of acetone on the AgI surfaces and its influence on the χ-potential (see Mackor, 1951a, p. 748). It seems very likely that similar considerations apply to the present data for the equilibrium separations of montmorillonite layers in water-alcohol mixtures, and even more directly to the water-acetone data given later. With long-chain alcohols and Ca-montmorillonite, Brindley and Ray (1964) showed that long basal spacings were developed consistent with OH-O bonds from the alcohols to the oxygen surfaces.

With continued addition of alcohol, instability eventually sets in and the equilibrium changes abruptly to spacings close to those for the clay immersed in the pure alcohol. It is possible that the collapse of the expanded state, which takes place at mole fractions of alcohol in the sequence: propanol < ethanol < methanol, may be partly attributable to an increase of Coulombic attractions arising from the diminished dielectric constants of the mixed liquids. The dielectric constants of the separate liquids are as follows: water, 80.4; methanol, 32.6; ethanol, 24.3; propanol, 20.1. The dielectric constants of the water-alcohol compositions at which the expanded spacings collapse are estimated as follows: water-methanol, 50-53; water-ethanol, 45–47; water-propanol, 62–67. It could be argued that the reduction in the dielectric constant from 80 to about 50–60 increases the Coulombic attractive energy sufficiently to bring the Ca^{2+} ions back into the mid plane positions. However, the significance of the numerical data is severely limited by the fact that they are based on the compositions of the liquids external to the clay, and there are no grounds for thinking that the internal composition will be the same as that of the external liquid.

Ca-montmorillonite-diol-water systems. Figure 2 shows results for 1, 2-ethanediol and 1,5-pentanediol-water systems. The main features are similar to those of Figure 1 and do not require detailed description. The important diagnostic spacing of the ethanediol complex persists from a value of 16.84 ± 0.02 Å, measured to 0.0.12 at 100 percent diol, to a value of 17.18 ± 0.04 Å, measured to 009 with 10 mole percent diol. Precise comparison with the results of Mackenzie (1948) is not possible, but he also reported the wide range of compositions giving a 17.1 Å spacing and noted that at high water contents when the samples "remained in a fluid state" a basal spacing of 19.5 Å appeared; this agrees with the value 19.4 Å at 6 mole percent ethanediol shown in Figure 2.

The dielectric constant of ethanediol, 37.7, is close to that of methanol, 32.6, so that from the standpoint of Coulombic attractions it might be expected that water-ethanediol mixtures would give results similar to those for water-methanol mixtures. This is clearly not the case. Possibly

the slow decrease of spacing with increasing diol content from 10–90 mole percent diol, see Figure 2, might be related to the decreasing dielectric constants.

Ca-montmorillonite-acetone-water system. The experimental results shown in Figure 3 agree generally with the previous data of Ruiz Amil and MacEwan (1957) who used a Na-montmorillonite. They are also in general accord with the results of Mackor (1951b) already mentioned. Up to about 10 mole percent acetone, the Ca-montmorillonite is dispersed so that basal spacings, if they exist at all, exceed 50 Å. From about 20–60 mole percent acetone, the clay is expanded to about 26.5 Å with very irregular diffraction maxima and in the range 80–90 mole percent, the spacing is about 22 Å and still highly irregular. Over this wide range of concentrations, it seems likely that equilibrium should be considered from the standpoint of double layer theory modified by adsorption of acetone on the silicate surfaces. With pure acetone, possibly containing small percentages of water arising from the use of air-dry clay, the spacing is regular at 17.30 ± 0.05 Å, measured to the 009 reflection.

By application of Fourier analysis to the disordered expanded systems, Ruiz Amil and MacEwan concluded that certain spacings recur close to the following series: 17.3, 22.0, 27.0 and 32.0 Å. The present results confirm a strong tendency towards the 22.0 and 26.5 Å complexes. The 32 Å component was not observed but may have been present in the highly dispersed state with 0–10 mole percent acetone. It is of interest to obobserve that van Olphen and Deeds (1962) found somewhat similar expanded phases with Na-montmorillonite in water-α-picoline mixtures, with spacings 21.9, 25.7, 27.9, 31.8, and 33.8 Å, and in water-pyridine mixtures, with spacings 23.3, and 29.3 Å.

The complete dispersion of Na-montmorillonite in water-acetone mixtures found by Ruiz Amil and MacEwan is less surprising than the dispersion of Ca-montmorillonite shown in the present work, since Na-montmorillonite is well known to show such dispersion in water whereas Ca-montmorillonite in water does not expand beyond about 19 Å. The dispersion of Ca-montmorillonite in water-acetone mixtures containing as little as 1 mole percent acetone has considerable potential interest for the dispersal of this form of montmorillonite.

Ca-montmorillonite-water-dioxane, and water-morpholine systems. The experimental results, see Figure 4, are considerably different from those given in Figures 1–3. The basal spacings are highly regular and almost unchanged from 100 mole percent dioxane or morpholine down to 1 mole percent of these compounds. The observed spacing is 14.85 ± 0.05 Å. The

dielectric constants of water-dioxane mixtures have been reported recently for compositions ranging from 17.3 to 82.1 mole percent dioxane (Büttner and Heydtmann, 1969). Graphical extrapolation of these data to the value 80.37 for pure water shows that with *small* additions of dioxane to water, the dielectric constant diminishes by about 3.0 units for each mole percent addition of dioxane. Consequently, there is no significant diminution in the dielectric constant of the liquid medium at the small concentrations of dioxane required to reduce the basal spacing of the Ca-montmorillonite from 19.01 Å to 14.85 Å. The constancy of the observed spacings and the ring structures of these molecules suggest that these compounds are strongly and preferentially absorbed by the clay; studies of the absorptions of these compounds are being undertaken.

Conclusions

Interesting variations are found in the intracrystalline swelling of a Ca-montmorillonite equilibrated in various water-organic solutions. For mono- and dihydric alcohols, an initial expansion of the basal spacing is found and, except for water-methanol mixtures, the expanded spacings are irregular to a degree which increases as the spacing increases. With water-acetone mixtures up to about 10 mole percent acetone, the expansion exceeds 50 Å and corresponds to a dispersion of the clay silicate layers. These increases in basal spacing cannot be reconciled with a decrease in dielectric constant of the liquid phase resulting from the addition of organic material to water, which would increase Coulombic forces of attraction. An explanation is to be sought along the lines of electrical double layer theory as developed by Mackor to explain the behavior of AgI sols in water-acetone mixtures.

At critical compositions of the water-organic mixtures, an abrupt decrease of spacing occurs to values near to the spacings of the clay-organic complexes. It is possible that a contributory factor to the collapse is the increased Coulombic attractions due to the diminished dielectric constant of the organic-water mixtures. Detailed considerations, however, are severely limited by the absence of knowledge of the amounts of water and organic material incorporated into the clay.

With the ring compounds, dioxane and morpholine, no expansion is obtained, and with as little as 1 mole percent of organic the spacing of the clay is practically the same as for 100 percent of organic. Strong preferential absorption of these compounds on the silicate layer surfaces is very likely.

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