

EFFECT OF 1,4-DIOXANE ON THE EXPANSION OF MONTMORILLONITE LAYERS IN MONTMORILLONITE/WATER SYSTEMS¹

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Abstract—Suspensions were produced by mixing Na-saturated, Upton montmorillonite with aqueous solutions containing different concentrations of 1,4-dioxane. Each suspension was deposited on a porous ceramic filter in an environmental chamber, and the solution was expressed from it by admitting gaseous helium to the chamber at a slightly elevated pressure. The chamber was fitted 1) with beryllium windows so that X-rays could be transmitted into and out of it and 2) with a drain so that the expressed solution could be conducted to the outside atmosphere. Once a filter cake had formed on the filter, the pressure of the gaseous helium was raised in successive increments and, after each increment, the c-axis layer spacing(s) was determined by X-ray diffraction. Increasing the concentration of 1,4-dioxane caused some of the fully expanded layers to collapse to the partially expanded state (c-axis spacing = 15 Å) and appeared to cause the remaining fully expanded layers to move farther apart, especially at the higher pressures. Alternative explanations were given for these apparently contradictory results.

Key Words—1,4-dioxane, Layer expansion, Montmorillonite, Swelling.

INTRODUCTION

Contamination of groundwater by organic molecules that escape from waste-disposal sites is a matter of great environmental concern. Such molecules are transported through the soil by convection and diffusion. Both of these processes can be affected by interaction of organic molecules with soil particles. For example, the organic molecules can be adsorbed by the soil particles, or they can induce a rearrangement of the particles. We decided, therefore, to study how simple organic molecules with different structures and functional groups interact with montmorillonite, a common clay mineral. Organic molecules selected for the study were: 1,4-dioxane, ethanol, phenol, urea, benzamide, ethylamine hydrochloride, acetic acid, and sodium acetate. In the earlier stages of this study (Chen *et al.*, 1987; Zhang *et al.*, 1990) it was found that 1,4-dioxane was the only neutral organic molecule that had a significant effect on the swelling and flocculation of the montmorillonite. Since we have a keen interest in swelling and flocculation, and since they can have a profound influence on the permeability of a soil (and, thereby, on diffusive and convective transport within it), the present study was undertaken. The specific objective of this study was to determine how 1,4-dioxane affects the interlayer distance in montmorillonite.

MATERIALS AND METHODS

The 1,4-dioxane that we used was of spectroscopic quality. It was mixed with deionized water to form

solutions with concentrations ranging up to 3.0 M. A supply of <2- μ m, Na-saturated, freeze-dried, Upton montmorillonite was prepared as described by Low (1980). About 300 mg of this montmorillonite was suspended for 24 hr in a 10⁻⁴ M solution of NaCl. Then the suspension was diluted with 3 ml of a solution containing sufficient 1,4-dioxane to establish the desired concentration of this compound in the resulting suspension. Following 24 hr of equilibration, the suspension was deposited on a ceramic filter enclosed within the environmental chamber described by Wu *et al.* (1989), and solution was expressed from it by gaseous He at successively higher pressures. The expressed solution was caught in a shallow reservoir where it remained in contact with the underside of the filter. This reservoir was connected to the outside atmosphere. Thus, the expressed solution was maintained at atmospheric pressure while it equilibrated with the filter cake on the opposite side of the filter. After the attainment of equilibrium at each pressure, the distance between the layers of montmorillonite in the filter cake was determined by X-ray diffraction. Before the first of these determinations, Silver Sheen mica (or kaolinite) was sprinkled on the surface of the filter cake to act as an internal standard. This method of introducing the internal standard was adopted because the particles of silica and kaolinite were relatively large and, had they been deposited from suspension with the montmorillonite, would likely have accumulated near the bottom of the filter cake beyond the depth to which the X-rays penetrated at low values of 2θ . The dimensions of the filter cake in directions perpendicular and parallel to the X-ray beam were 1.6 and 5.3 cm, respectively. The thickness decreased from ~0.2 cm to ~0.05 cm as the pressure increased from 0.5 to 7 atm. To compensate for this decrease, the environmental

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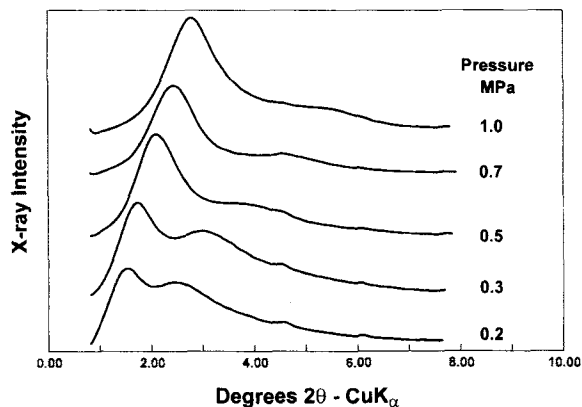


Figure 1. X-ray diffraction patterns of Na-saturated, Upton montmorillonite in the absence of 1,4-dioxane (Note: Each pattern is labeled with the pressure at which it was obtained).

chamber was moved upward until the internal standard was on the focusing circle of the diffractometer. Details of the above procedure have been described in earlier papers (Viani *et al.*, 1983; Wu *et al.*, 1989).

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the Na-montmorillonite equilibrated at different applied pressures with solutions containing different concentrations of 1,4-dioxane are shown in Figures 1–4. The relevant applied pressure is indicated to the right of each pattern. At equilibrium, the applied pressure equals the swelling pressure, Π , of the montmorillonite. Hence the terms “applied pressure” and “swelling pressure” are used interchangeably.

Figure 1 shows the X-ray diffraction patterns of the Na-montmorillonite in the absence of 1,4-dioxane.

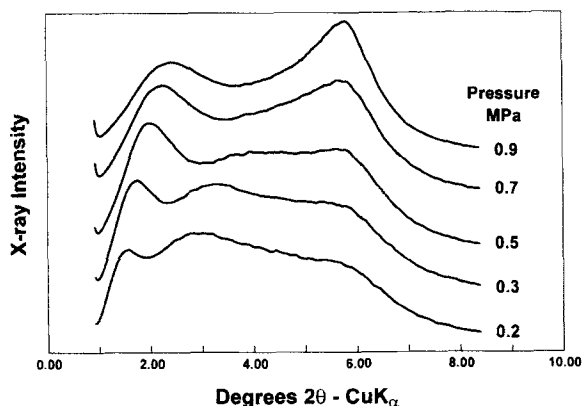


Figure 2. X-ray diffraction patterns of Na-saturated, Upton montmorillonite in a 0.5 M solution of 1,4-dioxane (Note: Each pattern is labeled with the pressure at which it was obtained).

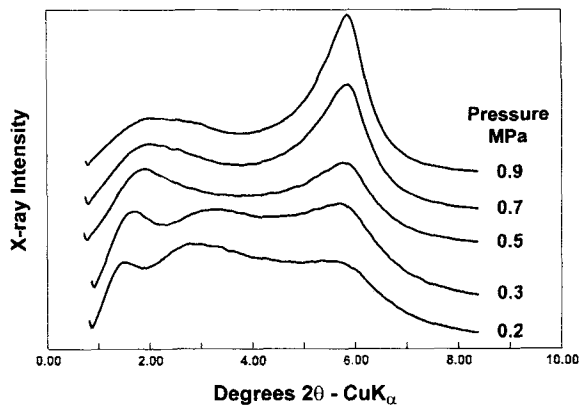


Figure 3. X-ray diffraction patterns of Na-saturated, Upton montmorillonite in a 1.0 M solution of 1,4-dioxane (Note: Each pattern is labeled with the pressure at which it was obtained).

These patterns are very similar to those obtained by Viani *et al.* (1983, 1985) and Wu *et al.* (1989) for different smectites and vermiculite. Only the first- and second-order peaks of the expanded layers are readily visible. These peaks shifted to higher values of 2θ with increasing pressure, and so we conclude that the c -axis spacing decreased as Π increased.

From the locations and relative intensities of the diffraction peaks in Figures 1–4, we see that 1,4-dioxane converted fully expanded layers ($2\theta < 3^\circ$, c -axis spacing $> 30 \text{ \AA}$) to partially expanded layers ($2\theta = 5.9^\circ$, c -axis spacing = 15 \AA) and that the degree of conversion increased with the concentration of 1,4-dioxane and with Π . Also we see that, regardless of the concentration of 1,4-dioxane, the diffraction peaks for the fully expanded layers shifted to higher values of 2θ (lower c -axis spacings) as the applied pressure increased but that the diffraction peaks for the partially expanded layers remained stationary at $2\theta = 5.9^\circ$.

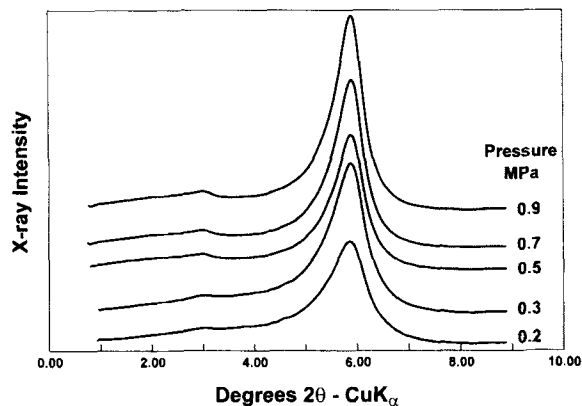


Figure 4. X-ray diffraction patterns of Na-saturated, Upton montmorillonite in a 3.0 M solution of 1,4-dioxane (Note: Each pattern is labeled with the pressure at which it was obtained).

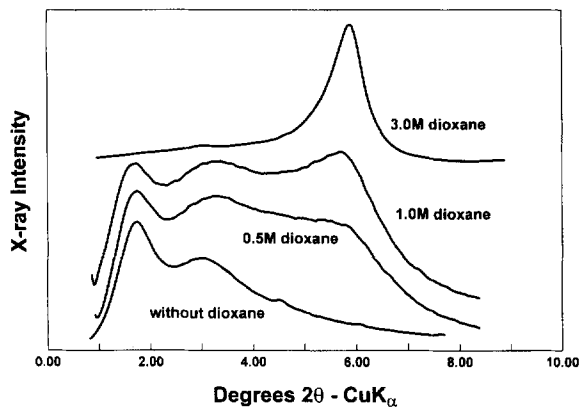


Figure 5. Effect of the concentration of 1,4-dioxane on the X-ray diffraction pattern of Na-saturated, Upton montmorillonite under an applied pressure of 0.3 MPa.

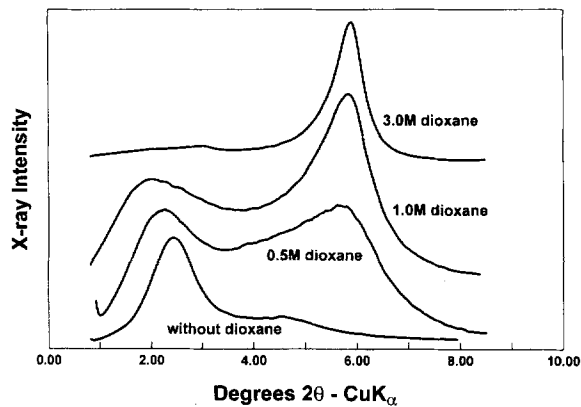


Figure 6. Effect of the concentration of 1,4-dioxane on the X-ray diffraction pattern of Na-saturated, Upton montmorillonite under an applied pressure of 0.7 MPa.

Figures 5 and 6 allow a comparison of the X-ray diffraction patterns of the Na-montmorillonite at two applied pressures, 0.3 and 0.7 MPa, and different concentrations of 1,4-dioxane. As the concentration of 1,4-dioxane increased from 0 to 3.0 M, the diffraction peaks for the fully expanded layers shifted to lower values of 2θ and became less intense relative to the stationary diffraction peak for the partially expanded layers. In fact, the diffraction peak for the fully expanded layers was no longer apparent when the concentration of 1,4-dioxane reached 3.0 M. It is evident, therefore, that the 1,4-dioxane had two simultaneous effects on the montmorillonite layers. It caused some of them to transfer abruptly from the fully expanded state to the partially expanded state but caused those remaining in the fully expanded state to assume lower values of 2θ and, therefore, to appear to expand further.

Previous investigations have demonstrated that the layers of montmorillonite can exist simultaneously in two states of expansion (Norrish, 1954; Viani *et al.*, 1983; Zhang and Low, 1989). One state, the partially expanded state, has a fixed interlayer distance of $<22 \text{ \AA}$. The exact value of this distance depends on such factors as the interlayer cation. The other state, the fully expanded state, has an interlayer distance that depends on m_w/m_c , the mass ratio of water to clay, or, alternatively, on II. If E , the energy of the clay/water system, is plotted against m_w/m_c , the partially expanded layers are found to be located in a narrow energy well and the fully expanded layers are found to be located beyond an energy barrier. Hence, the layers must surmount an energy barrier in going from one state of expansion to the other. The situation is illustrated in Figure 7, which was constructed from figures published for Na-montmorillonite by Zhang and Low (1989). The data in Figure 7a were obtained by X-ray diffraction, and the data in Figure 7b were obtained by differential calorimetry. Now, it is reasonable to as-

sume that the distribution of layers between the two states of expansion at equilibrium is governed by the Maxwell-Boltzmann distribution law, viz.:

$$n_1/n_2 = \exp[-(E_1 - E_2)/RT] \quad (1)$$

where n is the number of layers in a given state, E is the energy per mole of layers, R is the molar gas constant, T is the absolute temperature, and the subscripts 1 and 2 denote the partially and fully expanded states, respectively. We propose, therefore, that an increase in the concentration of 1,4-dioxane increased the depth of the energy well and, thereby, decreased the value of E for the partially expanded state. As a result, layers were transferred from the fully expanded state to the partially expanded state in keeping with Eq. 1. It is interesting to note that the value reported here for the c -axis spacing of the partially expanded layers in the aqueous solutions of 1,4-dioxane is 15 \AA . As illustrated by Figure 7a, this value is less than that for the partially expanded layers in pure water. However, it is the same as that reported by Bradley (1945) and MacEwan (1948), for montmorillonite layers in pure 1,4-dioxane. Hence, it is possible that, despite their high solubility in water, molecules of 1,4-dioxane segregate from the water molecules between the fully expanded layers and fill or nearly fill the space between the partially expanded layers. In other words, they may form a separate phase composed essentially of pure 1,4-dioxane between the partially expanded layers. It must be noted here that Zhang *et al.* (1990) obtained evidence indicating 1) that the accumulation of 1,4-dioxane between the partially expanded layers of Ca-montmorillonite in aqueous solutions of 1,4-dioxane was much greater than that between the fully expanded layers of Na-montmorillonite, and 2) that phenol existed as a separate phase between the partially expanded layers of Ca-montmorillonite in aqueous solutions of phenol.

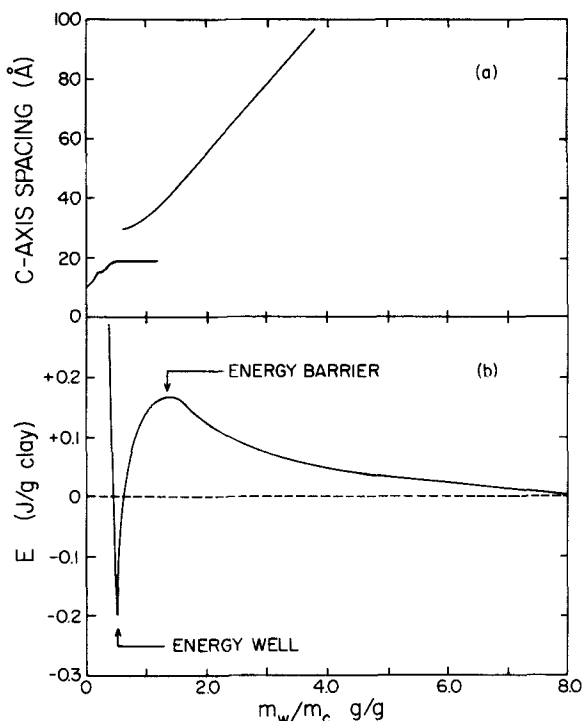


Figure 7. Relation between a) c-axis spacing and m_w/m_c and b) E and m_w/m_c for Na-saturated, Upton montmorillonite.

With reference to Figures 5 and 6, the effect of 1,4-dioxane on the value of 2θ for the fully expanded layers is surprising. Since 1,4-dioxane caused some of the fully expanded layers to collapse to the partially expanded state, a reasonable expectation would be that it would cause the remaining fully expanded layers to move closer together and, thereby, increase the corresponding value of 2θ . But the opposite occurred. These results have two plausible interpretations. One is that the transfer of layers from the fully expanded state to the partially expanded state decreased the number of reflecting elements (unit cells) in the former state and, consequently, caused 2θ to shift to lower values even though the actual c-axis spacing remained constant. This interpretation was brought to the authors' attention by a referee and is based on publications by MacEwan *et al.* (1961), Reynolds (1968), and Ross (1968). The other interpretation is that the decrease in 2θ was caused by an actual expansion of the layers. In this event, Figure 8 would depict the relation between the swelling pressure and interlayer distance, i.e., the c-axis spacing minus the thickness of an individual layer (9.3 Å). Figure 8 was constructed from our X-ray diffraction patterns with the help of Bragg's law.

To try to explain Figure 8, we took the following observations into account:

- (1) The forces between fully expanded and partially expanded layers are not the same, and so the two

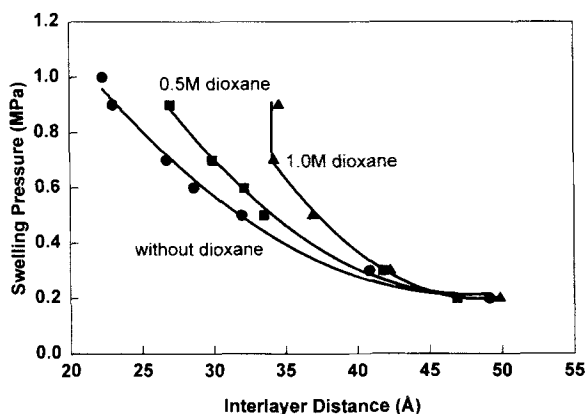


Figure 8. Effect of the concentration of 1,4-dioxane on the relation between swelling pressure and interlayer distance for Na-saturated, Upton montmorillonite.

kinds of layers need not respond the same way to a given solute, e.g., 1,4-dioxane (Low, 1993).

- (2) Reduction of the dielectric constant of the interlayer water by 1,4-dioxane is not responsible for its effect on the fully expanded layers (Zhang, 1992).
- (3) In the presence of water, 1,4-dioxane does not form bonds with the clay surface but accumulates at the clay/water interface because it lowers the interfacial tension (Zhang *et al.*, 1990).
- (4) Water between the layers of montmorillonite differs from bulk water in structure and properties (Low, 1979).
- (5) Molecules of water and 1,4-dioxane form hydrogen-bonded complexes (Goates and Sullivan, 1958; Schiöberg and Luck, 1979; Tanabe, 1984; Burneau, 1990; Kamogawa and Kitagawa, 1991).

Therefore, if the results in Figure 7 are valid, we propose that 1,4-dioxane interacts with the water molecules between the fully expanded layers to produce an open, coordinated structure and that the layers are forced apart because of the extra space required by this structure.

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