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X-RAY DIFFRACTION STUDY OF AQUEOUS MONTMORILLONITE EMULSIONS

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Abstract—An X-ray diffraction study of aqueous emulsions of a Na-montmorillonite shows that: (1) At low water content, the d-spacings of the montmorillonite increased stepwise with increasing water content; (2) At high water content, sharp (001) peaks due to regular stacking of montmorillonite layers were not detectable, but broad, halo patterns were observed in the low-angle scattering region; and (3) The addition of Ca^{2+} or H^+ to the aqueous emulsions caused Ca-montmorillonite or H-montmorillonite crystals to form. A zig-zag column model of montmorillonite layers fits the observed data for aqueous emulsions of Na-montmorillonite.

Key Words—Emulsion, Layer stacking, Low angle scattering, Montmorillonite, Water, X-ray diffraction.

INTRODUCTION

It is well known that montmorillonite forms intercalated compounds with various organic and inorganic compounds. This phenomenon is strongly related to the swelling behavior of montmorillonite by water molecules. The swelling of montmorillonite in salt solutions and at various water contents was studied by Norrish (1954), and the interfacial water structure in montmorillonite was described by Hawkins and Egelstaff (1980). These authors indicated that with increasing water content, the interlayer spacing of Na-montmorillonite increased stepwise from 10 Å to 20 Å, and jumps to 40 Å, followed by a linear increase in proportion to the total water content. The previous works, however, were concerned with the emulsion of low water content.

To understand the viscocity of an aqueous emulsion of montmorillonite and the mechanism of formation of intercalated compounds it is necessary to know the arrangement of montmorillonite layers in an aqueous emulsion of high water content. Accordingly, an X-ray powder diffraction study was made of aqueous emulsions containing montmorillonite with high water contents.

EXPERIMENTAL

Sample preparation

The sample used in this study was high purity montmorillonite fractionated from bentonite produced in Tohoku, Japan. This material is commercially available as KUNIPIA-F® from Kunimine Industries Co. Ltd. The cation-exchange capacity of the montmorillonite is 119 meq/100 g, and the exchangeable cations are Na^+ (87%), Ca^{2+} (10%), and K^+ (3%) (Kunimine Industries, 1978). This natural, Na-rich montmorillonite is referred to as Na-montmorillonite in this paper. A uniform mixture of the montmorillonite and water was made by gentle mixing in an alumina mortar. The samples were kept in sealed glass bottles for a week to obtain a thermal equilibrium before X-ray diffraction analysis. The composition of the emulsions are listed in Table 1. The content of the emulsion Ca′-8 is identical with that of emulsion Ca-8, but their preparation procedures are different. Namely, emulsion Ca-8 was prepared by mixing the aqueous emulsion of Na-montmorillonite and the aqueous solution of $CaCl_2$; and emulsion Ca′-8 was prepared by mixing the aqueous solution of $CaCl_2$ and Na-montmorillonite powder directly.

X-ray diffraction measurements

The X-ray diffraction (XRD) data were taken using a diffractometer designed for examination of liquids. As shown in Figure 1, the liquid sample container was placed horizontally, and the X-ray tube and the detector were moved upward and downward. The scattered X-rays from the free liquid surface were detected. In this arrangement the montmorillonite layers should have been oriented approximately parallel to the free surface, but not perfectly. In this geometry, the scattering vector, $\vec{Q}$, should have been approximately perpendicular to the lamella of montmorillonite. The measurements were made for two times on each sample to confirm that the structures were not changed during the measurements. The diffractometer was calibrated using a fluorophlogopite mica and thin film of tetradecanol. The d(001) of the fluorophlogopite mica was 9.98104 ± 0.00007 Å at 25.0°C (Hubbard, 1982); d(001) of tetradecanol was 39.90 Å. The d-values of these materials were checked by using Si powders.

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Table 1. Composition of emulsions.

Sample	Na-1	Na-2	Na-4	Na-8	Na-12	Ca-2	Ca-4	Ca-8	Ca'-8	H-1	H-8
Na-Mont. (g)	1	2	4	8	12	2	4	8	8	1	8
Water (g)	20	20	20	20	20	20	20	20	20	18.3	18.3
$CaCl_2 \cdot 2H_2O$ (g)	—	—	—	—	—	1.47	1.47	1.47	1.47	—	—
12 N HCl aq. (g)	—	—	—	—	—	—	—	—	—	1.7	1.7

Table 2. Conditions of X-ray powder diffraction.

	Anode	Tube voltage (kV)	Tube current (ma)	Slit width			Filter
				Entrance	Exit (1)	Exit (2)	
High angle	Cu	35	20	2°	0.15 mm	2°	Ni
Low angle[1]	Co	30	20	0.05 mm	0.15 mm	0.05 mm	Fe
Low angle[2]	Cu	35	20	0.5°	0.15 mm	0.5°	Ni

[1] Conditions for all other emulsions.
[2] Conditions for emulsions Na-1 and Na-2.

RESULTS

Aqueous emulsions of Na-montmorillonite

Aqueous emulsions of Na-montmorillonite are semi-transparent and dark brown. The intensities of diffracted X-rays from the emulsions and pure water are shown in Figures 2–4. The diffraction pattern of pure water is the same as that obtained by Narten (1972).

In the high-angle regions (Figure 2), (00*l*), (l = 1, 2, ...) peaks of montmorillonite were not observed; only the (02·), (20·), and (06·) peaks of montmorillonite and the halo pattern of liquid water were observed. In the low-angle region (Figures 3 and 4), broad halo patterns similar to the diffraction patterns of liquid or noncrystalline solids were observed. The peak positions of the halo pattern shifted to higher angles, and the peak intensities increased with increasing montmorillonite content.

The X-ray diffraction patterns of emulsion Na-12, a mixture of 12 g of Na-montmorillonite and 20 g of water, are shown in Figure 5. Pattern (1) is of the emulsion taken immediately after the preparation. Patterns (2), (3), and (4) are of the dried surface of the emulsion. Pattern (1) is similar to those shown in Figures 2–4. With the advance of drying, (00*l*) peaks of montmorillonite were observed, indicating that the layers of montmorillonite were stacking regularly. At high water contents, the (00*l*) peaks corresponding to 19.0 Å of the interlayer spacing were observed, followed by peaks at 15.4 Å with further drying.

Emulsion containing $CaCl_2$ or HCl

The addition of $CaCl_2$ or HCl to the aqueous emulsions of Na-montmorillonite decreased the viscosity and changed the color from semi-transparent dark brown to opaque white. The diffraction patterns of the montmorillonite emulsions containing $CaCl_2$ and containing HCl are shown in Figure 6 and Figure 7, re-

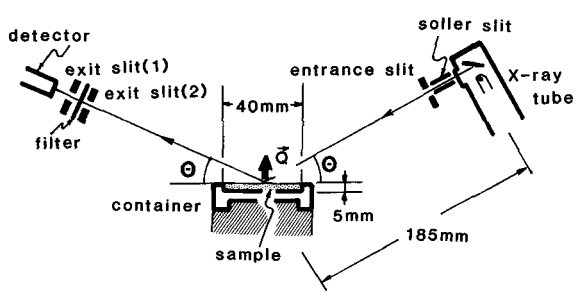


Figure 1. Geometry of the X-ray diffraction experiment.

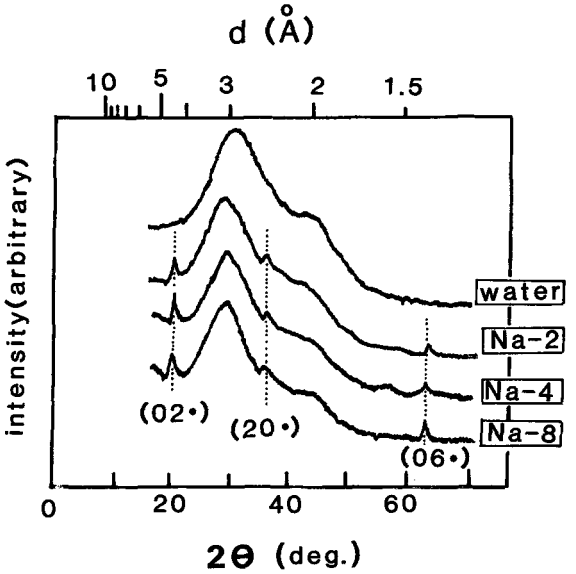


Figure 2. X-ray diffraction patterns of aqueous emulsions of Na-montmorillonite in high-angle region.

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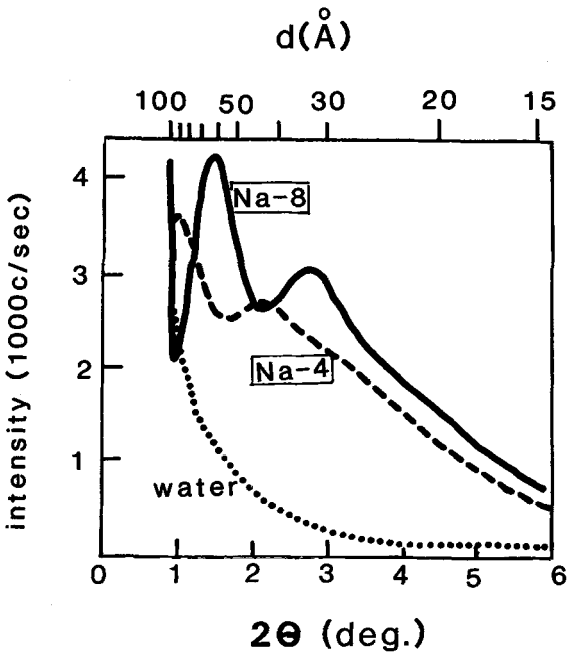


Figure 3. Diffraction patterns of aqueous emulsions of Na-montmorillonite in low-angle region.

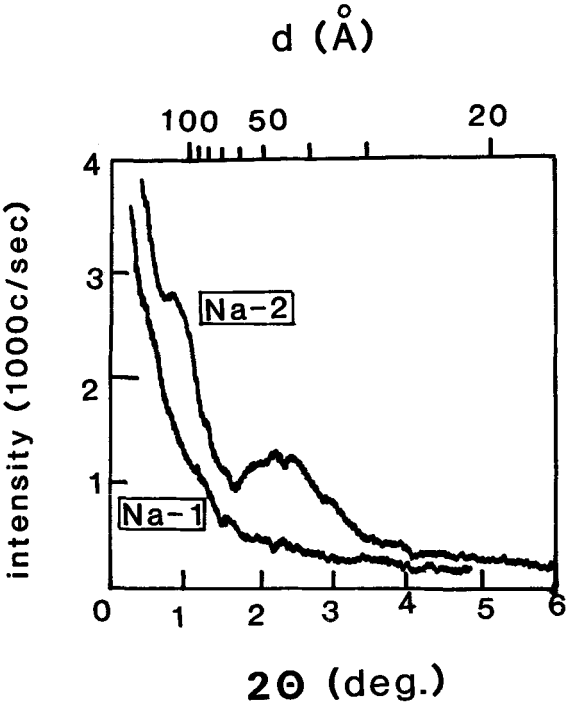


Figure 4. Diffraction patterns of aqueous emulsions of Na-montmorillonite in low-angle region.

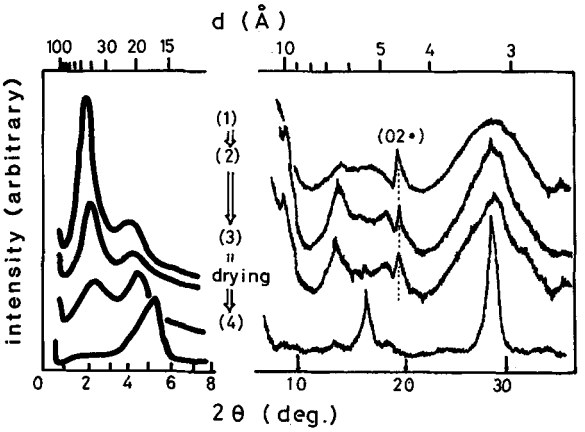


Figure 5. Change of the X-ray diffraction pattern of emulsion Na-12 by drying.

spectively. Here, not only the (0.2·), (20·), and (06·) peaks, but also the (00*l*) peaks corresponding to an interlayer spacing of 19.0 Å can be seen.

Effect of preparation procedure

The diffraction pattern of emulsions Ca-8 and Ca′-8 are shown in Figure 8. Emulsions Ca-8 and Ca′-8 were opaque white and dark gray, respectively, and the viscosity of emulsion Ca′-8 was lower than that of emulsion Ca-8.

The peak positions in the diffraction pattern of emulsion Ca′-8 were almost the same with those of emulsion Ca-8, but the relative intensities of the peaks and the pattern in the small angle region of emulsion Ca′-8 were different from those of emulsion Ca-8. Namely, the intensity of (00*l*) peaks of emulsion Ca′-8 were lower, and the intensities of (02·) and (20·) peaks and halo peak of water were higher than those of emulsion Ca-8.

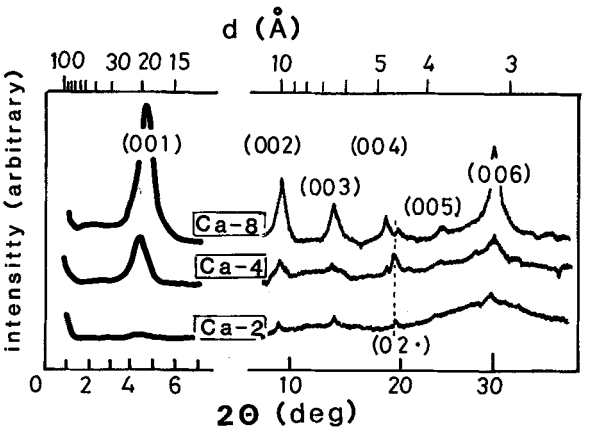


Figure 6. X-ray diffraction patterns of auqeous emulsions of montmorillonite containing $CaCl_2$.

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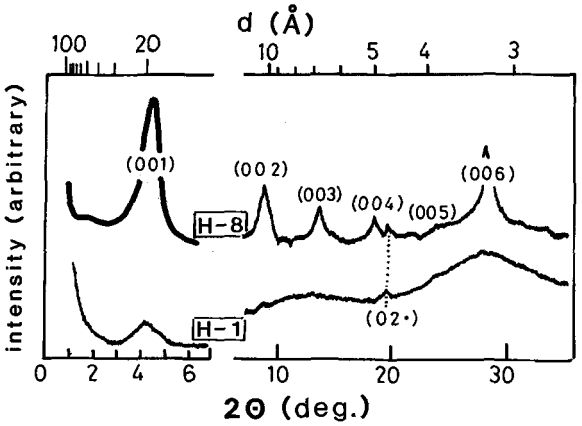


Figure 7. X-ray diffraction patterns of aqueous emulsions of montmorillonite containing HCl.

DISCUSSION

Structural model for aqueous emulsion of Na-montmorillonite

Figure 9 shows the relationship between the mean value of the interlayer spacing, d, in the aqueous emulsion of Na-montmorillonite and the water content, defined as the weight ratio of water to montmorillonite, C. The experimental results of Norrish (1954) are also shown. Where $C < 1.0$, the interlayer spacing increased stepwise with the water content; 9.5 → 12.4 → 15.4 → 19.0 Å (Norrish, 1954). In this region, two phases coexisted (Figure 5). Where $C > 1$, the interlayer spacing increased steadily from 41 Å to 160 Å with the water content.

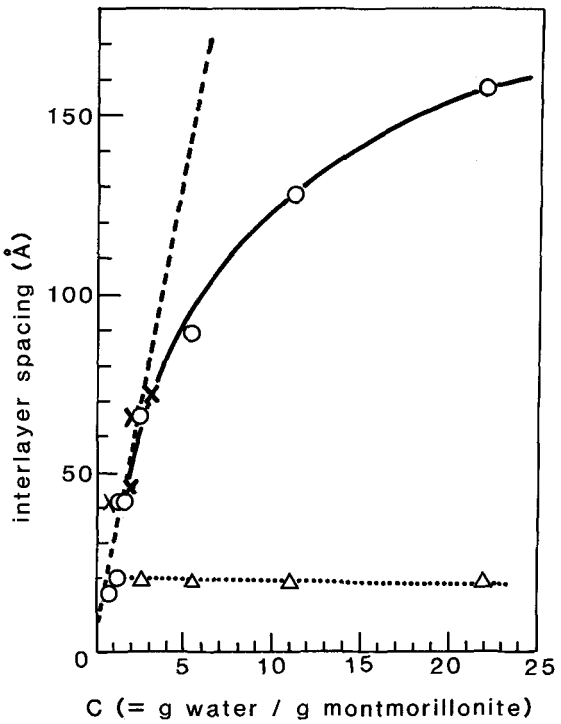


Figure 9. Relationship between the interlayer spacing, d, in the emulsions and the water contents, C: Experimental results of this work; ○ (Na-montmorillonite and water), △ (Na-montmorillonite, water and $CaCl_2$ or HCl), Experimental results by Norrish; X, and the calculated result by straight column model; – – –, and by zig-zag column model; ——.

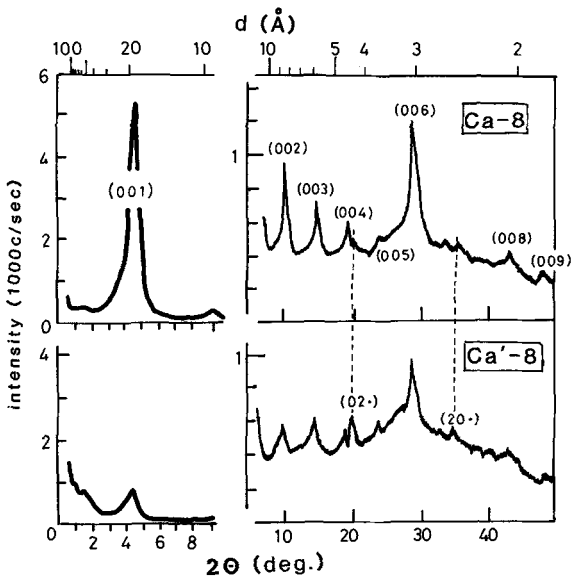


Figure 8. X-ray diffraction patterns of emulsions Ca-8 and Ca'-8.

Where $C > 1.0$, sharp (00*l*) peaks of montmorillonite were not detected, but broad halo patterns were observed in the low-angle region. From these results, the arrangement of montmorillonite layers in the emulsions appears to be irregular, i.e., these emulsions are not mixtures of montmorillonite crystals and water, but aqueous solutions of a $Na^+ \cdot$(montmorillonite layer)$^-$ compound.

For the analysis of the structure of the emulsion, the mean layer spacing, d, was calculated on the following assumptions: (1) the layers of the montmorillonite stack neatly as a straight column (straight column model; see Figure 10a). (2) The density of the interlayer water, ρ_w, is 1.0 g/cm^3. (3) The density of each layer of montmorillonite, ρ_c, is 2.6 g/cm^3. (4) The thickness of the layer, t, is 10.1 Å. The thickness and the density of each layer were calculated using the data of Sudo (1974), an idealized chemical composition of layer of montmorillonite, $Al_3Si_4O_{10}(OH)_2$ (Sudo, 1974), and the radius of a hydrogen-bonded oxygen atom which was calculated theoretically using the intermolecular potential of water by Rahman and Stillinger (1971). Using

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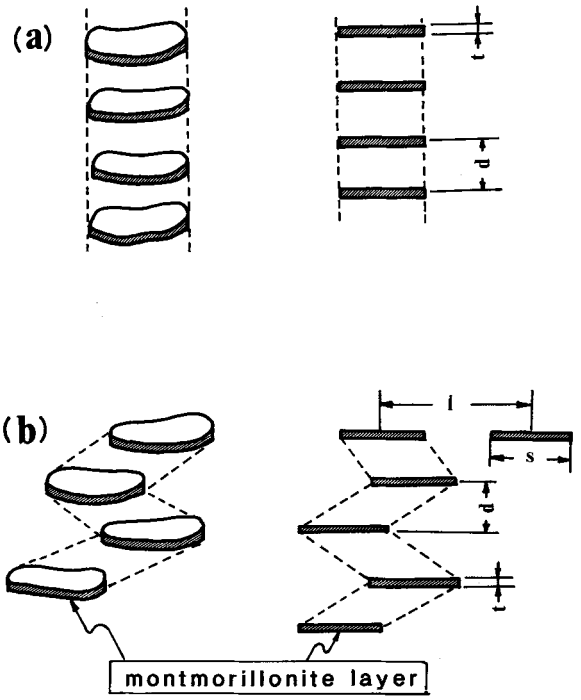


Figure 10. Schematic diagram of straight column model, (a), and zig-zag column model, (b), for the arrangement of layers in aqueous emulsions.

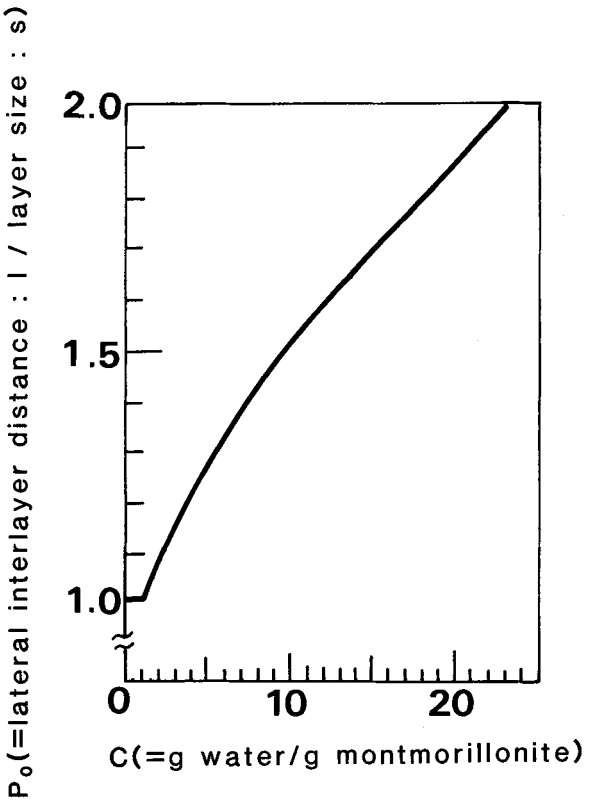


Figure 11. Calculated value of $P_0 = l/s$ vs. C; l and s are defined in Figure 10b.

these assumptions, the relationship between the mean value of interlayer spacing, d, and the water content in the emulsion, C, can be written:

$$C = (d - t)\cdot\rho_w/t\cdot\rho_c) = (d - 10.1)/26.3. \quad (1)$$

The calculated result according to Eq. (1) is shown by the broken line in Figure 9. These results are similar to those obtained by Norrish (1954). In the region of low water content, $C < 2$, the agreement of the calculated values with the experimental data is satisfactory, but the deviation becomes very large with increasing C. Two other models may be considered to explain the relationship between d and C. One is a heterogeneous model, where the layers of montmorillonite stack as shown in Figure 10a, but the emulsion is not uniform but consists of domains with water in-between. Another is a zig-zag column model, where the emulsion is uniform and the layers swell not only longitudinally but also laterally (Figure 10b). For the zig-zag column model, the relationship between d and C can be written as;

$$C = (d - t)\cdot\rho_w/t\cdot\rho_c\cdot P_0 = (d - 10.1)/26.3\cdot P_0, \quad (2)$$

where

$$P_0 = (l/s)^{-2}, \quad (3)$$

and where l is the distance between the layers in the direction parallel to the layers and s is the mean layer size. Values of (l/s) were calculated using the experimental results and Eqs. (2) and (3) (Figure 11). The calculated values of d using the data of Figure 11 and Eqs. (2) and (3) are shown by solid line in Figure 9. The schematic arrangement of layers according to the zig-zag column model and experimental results is shown in Figure 12, in which the layer size, s, is assumed to be 1.0 μm.

It cannot be decided which model is correct, the heterogeneous model or the zig-zag column model, but, the zig-zag column model is preferred because of: (1) The aqueous emulsion of Na-montmorillonite is semi-transparent. If the emulsion consists of domains, the domain is expected to be submicrometer or micrometer size, and the emulsion must be opaque. (2) The viscosity of the emulsion is very high, meaning that the water molecules in the emulsion are bound with layers, but few free water molecules exist between the domains. (3) When the system is in thermal equilibrium and the interlayer distance changes steadily in the region of high water content, the phase rule is not satisfied by the heterogeneous model. Namely, the number of degrees of freedom in this system, F, is three—temperature, pressure, and water content of the emul-

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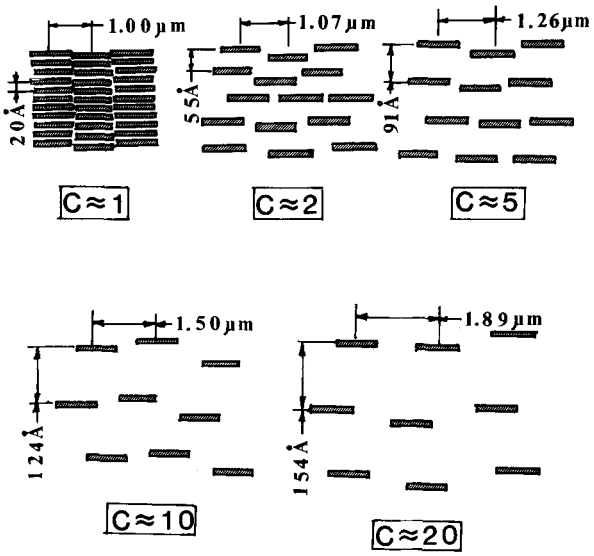


Figure 12. A tentative sketch of the arrangement of montmorillonite layers in aqueous emulsions based on the zig-zag column model.

sion; the number of the elements, C, is three—water molecules, Na^+ ions, and the layer; and the number of the phases, P, is three according to the heterogeneous model—water vapor, straight column domain, and the water between the domains. Here, $F = 3 \neq C - P + 2 = 2$. Therefore, the heterogeneous model is not valid. If the zig-zag column model is considered, the number of the phases, P, is two—water vapor and emulsion—and the phase rule is satisfied. Accordingly, the aqueous emulsion of Na-montmorillonite must be uniform, and the zig-zag column model is preferred. A more precise study, however, will be required to clarify this phenomenon.

Mixture of montmorillonite and $CaCl_2$ or HCl aqueous solution

The relationship between the interlayer spacing, d, in the aqueous emulsion containing $CaCl_2$ or HCl and the water content, C, is shown in Figure 9. In a 1.0 N $CaCl_2$ aqueous solution, montmorillonite does not swell as much as in the water system. From these results, the Na-montmorillonite must dissociate in water into Na^+ and a (montmorillonite layer)$^-$. When $CaCl_2$ or HCl is dissolved in the emulsion, however, the (montmorillonite layer)$^-$ ions bind with Ca^{2+} or H^+ ions and Ca-montmorillonite or H-montmorillonite crystals with interlayer spacing of 19.0 Å are created in the water.

The difference of the diffraction pattern due to different sample preparations may be due to different degrees of aggregation of montmorillonite crystals.

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Резюме—Исследование водных эмульсий Na-монтмориллонита методом рентгеновской порошковой дифракции показывает, что: (1) при низком содержании воды расстояние *d* монтмориллонита увеличивалось скочкообразно с увеличением содержания воды; (2) при большом содержании воды острые линии (001), соответствующие регулярной упаковке монтмориллонитовых слоев не присутствовали, но широкие гало-структуры были видимы в районе рассеяния на малых углах; и (3) результатом добавки Ca^{2+} или H^+ к водным эмульсиям было формирование кристаллов Ca-монтмориллонита или H-монтмориллонита. Модель зигзагообразных колонн монтмориллонитовых слоев соответствует наблюдаемым данным для водных змульсий Na-монтмориллонита. [E.G.]

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Resümee—Röntgendiffraktometer-Untersuchungen wässriger Emulsionen von Na-Montmorillonit zeigten, daß (1) bei niedrigem Wassergehalt die d-Werte des Montmorillonites stufenweise mit zunehmendem Wassergehalt zunahmen; (2) bei hohem Wassergehalt scharfe (001) Peaks, die auf eine regelmäßige Stapelung der Montmorillonit-Lagen zurückzuführen sind, nicht zu finden waren, während breite Reflexe im Kleinwinkelstreubereich beobachtet wurden; (3) die Zugabe von Ca^{2+} oder H^+ zu den wässrigen Emulsionen zur Bildung von Ca-Montmorillonit oder H-Montmorillonit führte. Ein Zickzack-Säulenmodell der Montmorillonitlagen entspricht den beobachteten Ergebnissen für wässrige Emulsionen von Na-Montmorillonit. [U.W.]

Résumé—Une étude à la diffraction des rayons-X d'émulsions aqueuses d'une montmorillonite-Na montre que (1) A basse teneur en eau, les espacements-d de la montmorillonite ont augmenté par étapes proportionnellement à une augmentation de la teneur en eau; (2) A haute teneur en eau, des pics (001) aigus dûs à l'empilement régulier de couches de montmorillonite n'étaient pas détectables, mais de larges clichés en forme d'auréoles ont été observés dans la region d'éparpillement de bas angles; et (3) L'addition de Ca^{2+} ou d'H^+ aux émulsions aqueuses à cause la formation de cristaux de montmorillonite-Ca ou de montmorillonite-H. Un modèle de couches de montmorillonite en colonne à zig-zags s'accorde avec les données observées pour les emulsions aqueuses de montmorillonite-Na. [D.J.]

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