INTRACRYSTALLINE SWELLING OF MONTMORILLONITES IN WATER-DIMETHYLSULFOXIDE SYSTEMS

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Abstract—The basal spacings of montmorillonites with Li, Na, K, Cs, Mg, Ca, Sr, Ba, and Pb interlayer cations were measured after immersion in dimethylsulfoxide (DMSO) and in water-DMSO mixtures. In DMSO alone, the spacings were in the range 18.3–19.3 Å and fell on or near a single curve when plotted against ionic field strength, q/r^2, where q = valence and r = ionic radius. These spacings correspond to double layers of DMSO molecules between the silicate layers. Water had practically no effect on the spacings when the mole fraction of DMSO exceeded about 35–45%. Osmotic swelling of Li-, Na-, and K-montmorillonite occurred up to mole percentages of DMSO 45%, 30%, and 10%, respectively. K- and Cs-montmorillonite formed single-layer complexes in appropriate water-DMSO mixtures with spacings of 14.3 Å prior to development of double-layer complexes when the mole fraction of DMSO exceeded 35% and 15%, respectively.

Key Words—Dimethylsulfoxide, Interlayer, Montmorillonite, Swelling, Water.

INTRODUCTION

The present work extends an earlier study of the behavior of montmorillonite in water-organic mixtures (Brindley *et al.*, 1969). The water-dimethylsulfoxide (DMSO) system is of interest because both molecules are highly polar, and in the previous study unusual behavior was observed with Ca-montmorillonite in water-acetone mixtures. Acetone, $O=C(CH_3)_2$, and DMSO ($O=S(CH_3)_2$) have similar molecular forms.

The structure of the DMSO molecule was determined by Thomas *et al.* (1966) by a detailed structure analysis of crystalline material at 5°C. The molecule is markedly pyramidal with the S atom 0.706 Å away from the nearly equilateral triangle formed by the atoms O, C_1, C_2, with OC_1 = 2.656 Å, OC_2 = 2.697 Å, and C_1C_2 = 2.685 Å (notation of Thomas *et al.*, 1966). The dipole moment of DMSO, 3.96 D (Dreizler and Dendl, 1964), arises mainly from the covalent S=O bond; the value is considerably greater than the dipole moment of water, 1.87 D.

Camazano and Garcia (1966) and Garcia *et al.* (1967) found that the basal spacings of DMSO-montmorillonite complexes decreased almost linearly with an increase of layer charge and increased linearly with the radius of the exchangeable cations, but on separate lines for R^+- and R^{2+}-montmorillonites. Camazano and Garcia (1968) studied DMSO-vermiculite complexes. Olejnik *et al.* (1974) and Berkheiser and Mortland (1975) concluded that the swelling of montmorillonites in various polar organic liquids could not be correlated in any simple way with bulk properties of the liquids, such as dielectric constant and surface tension, nor with their dipole moments. Berkheiser and Mortland (1975) considered that the degree of dehydration of the montmorillonite prior to solvation in the organic liquids

had little effect on the basal spacings of the complexes, but possibly had an effect on the positions of the interlayer cations.

The present experiments consider the swelling of montmorillonites in water-DMSO mixtures and, in particular, whether unusual swelling can occur similar to that found in water-acetone mixtures. Since water and DMSO are both strongly polar molecules, it was of interest to determine whether or not long-range osmotic swelling was possible in mixtures of the two liquids. It was also of interest to consider if the size or the electrical field of the interlayer cations is the more important factor determining the swelling of montmorillonite in DMSO.

EXPERIMENTAL

Materials

A Wyoming montmorillonite, previously saturated with Na and sedimented to give a particle size of <2 μm was saturated with Li^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+} by several treatments with 0.1 N chloride solutions followed by washing until free of Cl^- ($AgNO_3$ test). Particular attention was given to Cs^+ saturation, as will be described below. A chemical analysis of the Na-montmorillonite (A. Tsunashima, analyst) gave the following formula for material dried at 110°C:

$$Na_{0.34}(H_2O)_{0.31}(Al_{1.55}Fe_{0.19}Mg_{0.26})(Si_{3.92}Al_{0.08})O_{10}(OH)_2.$$
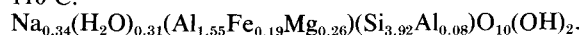
Solvation procedure

Thin, oriented samples of the montmorillonite were prepared on glass slides using materials dispersed in deionized water. They were dried in air near 35°–40°C and at relative humidities near 30%.

Water-DMSO solutions, prepared with desired mole

Table 1. Basal spacings of DMSO-montmorillonite complexes.

Cation	r (Å)	Present data		Other data		
		d(001)	ℓ_{max}	(1)	(2)	(3)
Li$^+$	0.76	18.91 ± 0.05	9	18.47	19.0	—
Na$^+$	1.02	19.25 ± 0.10	6	18.79	18.9	18.8
K$^+$	1.38	19.27 ± 0.07	9	18.98	—	—
Rb$^+$	1.52	—	—	19.11	—	—
Cs$^+$	1.67	19.11 ± 0.08	9	19.28	18.8	—
Mg^{2+}	0.72	18.35 ± 0.07	9	18.32	18.3	—
Ca^{2+}	1.00	18.78 ± 0.03	10	18.79	18.6	18.8
Sr^{2+}	1.18	18.97 ± 0.04	10	18.98	—	—
Ba^{2+}	1.35	19.24 ± 0.10	9	19.19	—	—
Pb^{2+}	1.19	18.83 ± 0.08	9	—	—	—

r (Å) Ionic radii given by Shannon (1976).
(1) Garcia *et al.* (1967).
(2) Olejnik *et al.* (1974).
(3) Berkheiser and Mortland (1975).

ratios, were contained in closed tubes in which the clay-coated slides stood vertically. The liquids overlapped part of the clay coating, and the remaining clay, to be examined by X-ray powder diffraction, was wet by imbibition. The slides with some excess liquid were transferred to the diffractometer enclosure after periods of about 1, 2, 4, . . . days. Usually no further change was observed after 1 day, but in a few cases longer periods were necessary to obtain maximum swelling of the clay. The open tube containing the water-DMSO solution also was placed in the diffractometer enclosure.

X-ray powder diffraction examination (XRD)

Data were obtained with Ni-filtered CuKα radiation, with a recording rate of 1°2θ/min and a chart speed of 2°2θ/inch. Recordings were made to the highest observable 00ℓ diffractions, usually ℓ = 9 or 10.

RESULTS AND DISCUSSION

DMSO complexes

The basal spacings of complexes formed with various cation montmorillonites are listed in Table 1, together

Table 2. Basal spacings of DMSO-montmorillonite complexes in order of q/r².

Cation	q/r²	d(001) (Å)
Cs$^+$	0.359	19.11 ± 0.08
K$^+$	0.525	19.27 ± 0.07
Na$^+$	0.961	19.25 ± 0.10
Ba^{2+}	1.097	19.24 ± 0.10
Pb^{2+}	1.412	18.83 ± 0.08
Sr^{2+}	1.436	18.97 ± 0.04
Li$^+$	1.731	18.91 ± 0.05
Ca^{2+}	2.000	18.78 ± 0.03
Mg^{2+}	3.858	18.35 ± 0.07

q = valency; r = ionic radius (Shannon, 1976).

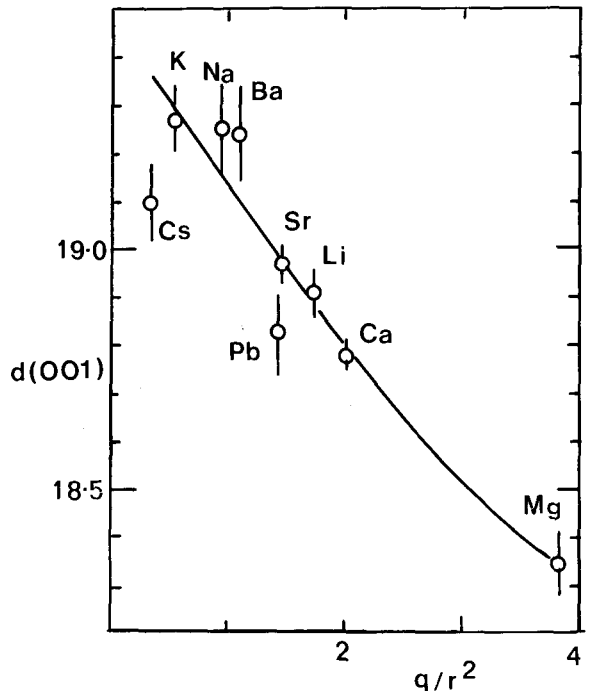
Figure 1. Basal spacings of DMSO-montmorillonite complexes plotted against q/r², where q = valency and r = ionic radius. Bar length indicates mean deviation of spacings for different 00ℓ diffractions from the average spacing.

with previously published data. For the R^{2+}-montmorillonites, the results obtained here and by other investigators are in very close agreement, but for the R$^+$-montmorillonites, the results in some cases vary considerably.

A relationship was sought to correlate the spacings for both series of montmorillonites. Table 2 and Figure 1 show that, within the limits of experimental error, most results fit a common curve when d(001) is plotted against q/r² (q = valency; r = radius of the exchangeable cations). The spacings for Cs- and Pb-montmorillonite are clearly off the curve. This result for Pb-montmorillonite may be a consequence of the electron configuration of the Pb^{2+} ion, which is not of the rare gas type. No obvious explanation can be given for the rather low value for Cs-montmorillonite; Garcia *et al.* (1967) obtained a somewhat larger spacing, 19.28 Å, which more nearly fits the curve in Figure 1.

The swelling of Na-, K-, Cs-, and Ba-montmorillonites in DMSO was noticeably slower than that of the other montmorillonites. These slow-swelling montmorillonites (i.e., in DMSO) contain interlayer cations having weak electrical fields. Na-, K-, and Ba-montmorillonite expanded to a 14.3-Å spacing prior to full expansion to 19.25 Å. These two levels of expansion correspond to single-layer and double-layer complexes with each layer about 4.8 Å thick. Cs-montmorillonite did not show a single-layer 14.3-Å spacing when ex-
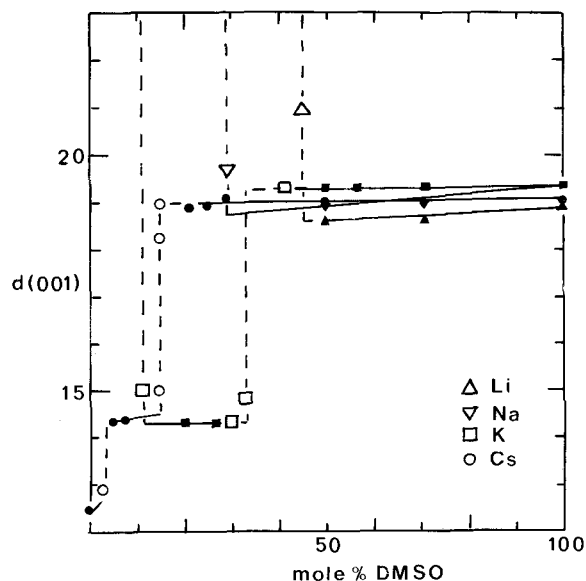
Figure 2.   Basal spacings of water-DMSO-R$^+$-montmorillonite complexes with excess liquid present vs. mole percent DMSO. Solid and open symbols indicate accuracy of measurements (see text).

Figure 3.   Basal spacings of water-DMSO-R^{2+}-montmorillonite. See legend to Figure 2.

posed to DMSO, but expansion to 19.1 Å appeared to be slow and possibly was incomplete.

Various methods of preparing Cs-DMSO-montmorillonite were used. In particular, after initial dispersion of the Na-montmorillonite in water, CsCl solution was added to give a resulting solution about 0.02 N; the clay remained dispersed. After partial settling of the clay by centrifugation, part of the solution was removed, and more CsCl solution was added. By repeating this process five or more times, a dispersed Cs-montmorillonite was obtained. After washing the clay and evaporating excess water, a gel was obtained which showed no basal spacings. DMSO was added to the gel, but a crystalline complex was not obtained until most of the liquid was evaporated. Despite these precautions to avoid flocculation during Cs saturation, the maximum spacing obtained with DMSO was 19.10 Å (Figure 1).

Swelling in water-DMSO mixtures

The results for R$^+$- and R^{2+}-montmorillonites are presented in Figures 2 and 3, respectively. Solid symbols indicate spacings obtained from integral or nearly integral 00ℓ diffractions, with ℓ extending to 9, 10, and occasionally 7. These values are considered to be accurate to ±0.05 Å. Open symbols indicate values less accurately known because of fewer diffractions and/or non-integral effects.

When the mole fraction of DMSO exceeded about 40%, the observed spacings were almost identical with those in 100% DMSO. The results fully confirm the statement of Berkheiser and Mortland (1975) who were
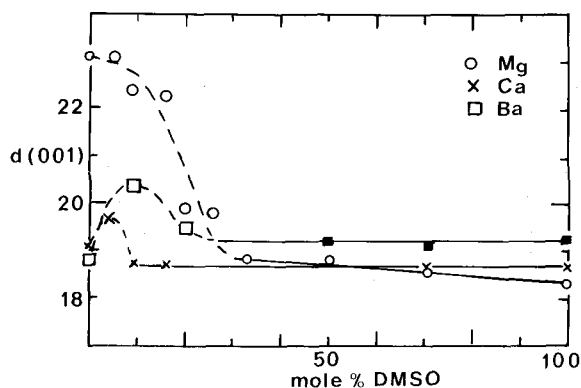
concerned only with the possible effects of small amounts of residual water. For R^{2+}-montmorillonites (Figure 3), small additions of DMSO to water tended to increase the basal spacings, but the results are not comparable with those previously found for Ca-montmorillonite in water-acetone mixtures.

The results for R$^+$-montmorillonites (Figure 2) are more diverse. Li-, Na-, and K-montmorillonite in water exhibited osmotic swelling, i.e., expansion beyond the crystalline state, where no basal reflections are obtained. This large scale swelling occurred also in water-DMSO mixtures up to about 45, 30, and 10 mole percent DMSO, respectively. Whereas Li- and Na-montmorillonite collapsed to spacings near 18.6 and 18.9 Å, respectively, when the limit of osmotic swelling was reached, K-montmorillonite collapsed to a 14.3-Å spacing from 10–30 mole percent DMSO, and then expanded to 19.1 Å when the proportion of DMSO exceeded about 35 mole percent. Cs-montmorillonite expanded in water to about 12.45 Å (a single water layer complex), but with small additions of DMSO (5–15 mole percent), a 14.3-Å spacing (single layer DMSO complex) was obtained. Beyond 20 mole percent DMSO, a 19.0–19.1-Å spacing (double layer DMSO complex) was formed. Thus, Cs- and K-montmorillonite were similar in giving complexes indicative of single layers of DMSO, though H$_2$O also may have been present. By contrast, Li- and Na-montmorillonite remained fully dispersed in the water-DMSO mixtures until the proportion of DMSO reached the level where the spacing was governed by double layers of DMSO.

CONCLUSIONS

The basal spacings of complexes formed by DMSO with R$^+$- and R^{2+}-montmorillonites are in the range 18.3–19.3 Å and, with two exceptions (Cs$^+$ and Pb^{2+}), fall on or near a common curve when plotted against q/r^2 (q = valence; r = radius of the R$^+$, R^{2+} ions). The spacings correspond to two layers of DMSO mol-

ecules modified slightly by the intensities of fields of the interlayer cations. In water-DMSO mixtures with more than about 40 mole percent DMSO, the observed spacings were almost identical with those developed in 100% DMSO. The results suggest that the DMSO molecules played a dominant role, with only secondary effects produced by the cations. The presence of DMSO did not suppress osmotic swelling of Li-, Na-, and K-montmorillonite until the mole proportion exceeded 45, 30, and 10%, respectively. Li- and Na-montmorillonite then collapsed to double-layer complexes, and K-montmorillonite to a single-layer complex. With an increase of DMSO, Cs-montmorillonite also formed a single-layer complex. Both K- and Cs-montmorillonite formed double-layer complexes at higher proportions of DMSO.

ACKNOWLEDGMENTS

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Резюме—Основные промежутки монтмориллонитов с межслойными катионами Li, Na, K, Cs, Mg, Ca, Sr, Ba, и Pb были измерены после погружения их в смесях диметилсульфоокиси (ДМСО) и вода-ДМСО. Для соединений, погруженных только в ДМСО, основные промежутки находятся в интервале от 18,3 до 19,3 Å и располагаются на или в поблизости одной кривой, если их начертить как функцию силы ионного поля q/r^2, где q = валентность и r = ионный радиус. Эти промежутки соответствуют двойным слоям молекул ДМСО, расположенным между кремниевыми слоями. Практически, вода не имеет никакого влияния на эти промежутки, когда молярная доля ДМСО выше 35–45%. Осмотическое набухание Li-, Na-, и K-монтмориллонитов появлялось, когда молярние проценти ДМСО не превосходили соответственно 45%, 30%, и 10%. K- и Cs-монтмориллониты фопмировали в соответствующи вода-ДМСО смесях одно-слойные комплексы с промежутками 14,3 Å перед постройкой двух-слойных комплексов, в случае, если молярные доли ДМСО превышали соответственно 35% и 15%. [Е.С.]

Resümee—Nach Behandlung mit Dimethylsulfoxid (DMSO) und mit Wasser-DMSO-Mischungen wurden die Basisabstände von Montmorilloniten mit Li, Na, K, Cs, Mg, Ca, Sr, Ba, und Pb als Zwischenschichtkationen gemessen. Im Fall von DMSO allein sind die Basisabstände im Bereich von 18,3 bis 19,3 Å und liegen auf oder nahe einer einzigen Kurve, wenn man sie gegen die Ionenfeldstärke, q/r^2, aufträgt, wobei q die Valenz und r der Ionenradius ist. Die Abstände entsprechen Doppellagen von DMSO-Molekülen zwischen den Silikatlagen. Wasser hat praktisch keinen Einfluß auf die Abstände, wenn die Molfraktion von DMSO 35–45% übersteigt. Ein osmotisches Quellen von Li-, Na-, und K-Montmorillonit trat bis zu DMSO-Molprozenten von 45%, 30% bzw. 10% auf. K- bzw. Cs-Montmorillonit bildete in entsprechenden Wasser-DMSO-Mischungen Einzellagenkomplexe mit Basisabständen von 14,3 Å bevor sich Doppellagenkomplexe bilden, wenn die Molfraktion von DMSO 35% bzw. 15% übersteigt. [U.W.]

Résumé—Les espacements de base de montmorillonites ayant des cations intercouche Li, Na, K, Cs, Mg, Ca, Sr, Ba, et Pb ont été mesurés après immersion dans la sulfide diméthyl (DMSO) et dans des mélanges eau-DMSO. Dans la DMSO seule, les espacements s'étagent de 18,3–19,3 Å, et tombent sur ou près d'une seule courbe lorsqu'ils sont relevés sur un graphe avec la force de champ ionique, q/r^2, ou q = valence, et r = rayon ionique. Ces espacements correspondent à des couches doubles de molecules DMSO entre les couches silicates. L'eau n'avait pratiquement aucun effet sur les espacements lorsque la fraction molaire de DMSO excédait à peu près 35–45%. Il y avait un gonflement osmotique de montmorillonite-Li, -Na, et -K jusqu'a des pourcentages molaires de DMSO de 45%, 30%, et 10%, respectivement. Les montmorillonites-K et -Cs ont formé des complexes à couche simple dans les mélanges eau-DMSO appropriés avec des espacements de 14,3 Å avant le developpement de complexes doubles lorsque la fraction molaire de DMSO excédait 35% et 15%, respectivement. [D.J.]