

SWELLING OF MONTMORILLONITE IN POLAR ORGANIC LIQUIDS

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Abstract—The crystalline and osmotic swelling of Na-, Cs-, Mg- and Ca-montmorillonite has been measured in dimethyl sulphoxide and in formamide, *N*-methyl formamide, dimethyl formamide, *N*-methyl acetamide and dimethyl acetamide. These liquids have similar dipole moments but their relative permittivities vary appreciably from values less than water to values greater than water.

Na-montmorillonite exhibits osmotic swelling (diffuse double layer development $-d(001) \gg 19 \text{ \AA}$) in formamide and *N*-methyl formamide and Cs gives osmotic swelling behavior in formamide. Cs-montmorillonite in the crystalline swelling region give spacings greater than those found for water with all liquids. Mg- and Ca-montmorillonite did not give spacings greater than 19 Å in any of the liquids studied.

The swelling behavior of montmorillonite is affected by relative permittivity but for liquids with a similar relative permittivity methyl substitution in the molecule may prevent the development of diffuse double layers on the particle surfaces.

INTRODUCTION

The swelling of montmorillonites in water has received considerable attention (e.g. Norrish and Quirk, 1954; Norrish, 1954; Warkentin and Schofield, 1962; Norrish and Raussel-Colom, 1963; Posner and Quirk, 1964a,b; Quirk, 1968) with the result that the swelling behavior of montmorillonites in relation to factors such as exchangeable cation, hydrostatic pressure and electrolyte concentration, is relatively well described. There still exists, however, some uncertainty in the detailed interpretation of the swelling behavior (Quirk, 1968) particularly in relation to the exchangeable cation and its polarizing power in affecting the properties of water in the neighborhood of the cation and the surface.

The literature reveals that montmorillonites show limited expansion [$d(001) < 19 \text{ \AA}$] with a wide variety of polar organic compounds; swelling in relation to the properties of organic compounds has previously been examined by Barshad (1952) and Greene-Kelly (1955a,b) and, although some very polar organic liquids have been used, for instance nitrobenzene (Yariv, Russell and Farmer, 1966), basal spacings greater than 15.2 Å have not been reported except for glycerol and ethylene glycol. Most of the earlier work deals with the bonding and mechanism of adsorption of organic compounds in montmorillonite or simply the spacing of the interlayer complexes.

The present work extends the information on swelling behavior of homoionic montmorillonites to an homologous series of substituted amides and dimethyl sulphoxide (Table 1). The swelling in relation to the exchangeable cation and liquid properties, particularly relative permittivity, is examined and contrasted with the known behavior of montmorillonite in water.

EXPERIMENTAL

Montmorillonite, $< 2 \mu\text{m}$ esd and homoionic with respect to Na, Cs, Mg and Ca cations was the same as used previously (Olejnik, Posner and Quirk, 1971).

The amides were purified according to Alexander *et al.* (1967) by drying over molecular sieves type 5A with intermittent shaking, for several days, followed by distillation at reduced pressure under a dry nitrogen atmosphere. A second drying and distillation was necessary with some amides to remove the water more completely; the DMSO was similarly purified. Infrared spectra showed that all the water had been removed from the liquids, or if not was present only in trace amounts.

Montmorillonite swells rapidly in these liquids and the outgassing and measurement of the interlayer spacings was identical to that given previously (pretreatment at 150°C and 4×10^{-4} mm of Hg for 16 hr to remove water, Olejnik *et al.*, 1971); the Na- and Cs-montmorillonite swollen in NMF however were only out-gassed in vacuum over P₂O₅. Ni filtered Cu K α

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radiation was used to record the diffraction pattern of Na- and Cs-montmorillonite in DMF and Na- and Ca-montmorillonite in DMA; Co K α radiation was used for the others. Thin ceramic tiles (about 1/16 in.) were used and these were wet with liquid prior to forming the thin layer of swollen montmorillonite. Unless special care is taken to completely pre-saturate the tile with liquid, small variations in hydrostatic suction exerted by the tile may cause appreciable variations in basal spacing of samples showing large swellings.

RESULTS AND DISCUSSION

Table 1 lists the interlayer spacings of montmorillonite in the polar liquids and shows that the swelling depends on the size and charge of the exchangeable cation and the liquid. It shows that Cs-montmorillonite can swell to very large spacings with formamide and for the other liquids investigated, the spacings are greater than any previously reported for Cs-montmorillonite; in water Cs-montmorillonite swells to only 13.2 Å (Edwards *et al.*, 1965). In formamide Na- and Cs-montmorillonite swell to greater than about 90 Å, the limit of the diffractometer; diffraction peaks first appear at approx. 50 Å when the interlamellar formamide is gradually removed by evacuation. Na-montmorillonite shows a peak at approx. 40 Å; this is probably the second order of the 75 Å peak.

Except for Cs-montmorillonite, integral higher orders of $d(001)$ were observed for montmorillonites with basal spacings of approx. 18–23 Å in the various liquids used. Cs-montmorillonite usually shows broad or diffuse diffraction peaks corresponding to basal spacings of approx. 17–18 Å which have relatively high, low angle backgrounds that drop away sharply to lower spacings. This is indicative of interstratification and although the predominant interlayer spacing is 17–18 Å there must also be substantial numbers of lamellae at basal spacings above this value. Similar effects have been reported by Norrish (1954) for potassium-montmorillonite.

The swelling of montmorillonite has been designated as crystalline or limited swelling for which $d(001)$ is less than 19 Å and extensive or osmotic swelling due to the development of diffuse double layers within the interlayer regions leading to $d(001)$ values which may be considerably greater than 19 Å. The equilibrium spacing for a given system results from a balance between attractive forces due to ion surface forces and repulsive forces. The repulsive forces result from solvation of the exchangeable ions (ion-dipole interaction) which, if large, may lead to the development of diffuse double layers.

Norrish (1954), by considering that the relationship of an ion to the clay surface is analogous to a point charge and that the hydration energy of an ion gives the repulsive energy, has arrived at a swelling index given by $U\epsilon/v^2$ in which U is the solvation energy, ϵ is the relative permittivity of the interlayer liquid and v is the valency of the ion. Thus, for a given valency, the larger the value of U and ϵ the greater the tendency of the clay system to swell.

The results for limited crystalline swelling show some unexpected features in relation to the application of the swelling index. It may be seen from Table 1 that the Δ -values (MacEwan, 1948) in all organic liquids examined are greater than the minimum molecular dimensions and for Cs are close to a value expected for two molecular layers and contrast with the one layer complex found for water. This result is obtained even though the solvation energy for the Cs ion in the various liquids is approximately equal to that in water (Table 1) and it cannot be readily explained by reference to the relative permittivity of the liquid since the values for the liquids range from about half that of water to more than double. It is therefore concluded that specific features of the ion-dipole interaction in the interlayer space, probably affecting the relative permittivity, is the basis for there being no clear relationship with relative permittivity.

With DMF, NMA and DMA, Na- and Cs-montmorillonite give only limited crystalline swelling with the respective spacings being greater for the Na-clay than the Cs-clay in accordance with the higher solvation free energy of the sodium ions. The spacings for all three liquids are similar for each homoionic montmorillonite even though it might have been expected that NMA with a relative permittivity of 179 would have given extensive crystalline swelling for Na-montmorillonite since formamide ($\epsilon = 109$) and NMA ($\epsilon = 171$) give extensive swelling. The correspondence of the spacings (20–21 Å) for Na-montmorillonite and (16–17 Å) for Cs-montmorillonite in DMF, NMA and DMA is also unexpected since DMF and DMA have relative permittivities of 37.

The decreased swelling in the series formamide, NMF and NMA, with respect to relative permittivity is associated with increasing methyl substitution with consequent increase in basicity of the carbonyl group and stronger ion-dipole association. The dipole moment of a molecule in the liquid differs from that measured in the vapor phase (Millen and Watts, 1967) due to the induction of an additional moment by the dipole field of its neighbors. Thus, in the interlayer environment of the cation and the amide, the effective dipole moment of the amide may be greater than that determined in the vapor phase (Table 1). This would

Table 1. Interlayer spacings, $d(001)$ Å, of montmorillonite in polar organic liquids and some physical properties of these liquids and Gibbs energy of solvation

	Dipole moment (Debye)	Relative permittivity	Gibbs energy of solvation [†] (kcal. mol ⁻¹)				Interlayer spacing (Å)			
			Na ⁺	Cs ⁺	Li ⁺	Na ⁺	Cs ⁺	Mg ²⁺	Ca ²⁺	
Dimethylsulphoxide (DMSO)	4.3*	48.9* _{20°C}	88	71	19.0	18.9	18.8	18.3	18.6	
Formamide	3.71†	108.7† _{25°C}	97	69		>90	>90	~17.4 ^b	19.9 ^b	
N-methylformamide (NMF)	3.83† _{110°C(vap.)}	171† _{25°C}	**	**		>75	17.7 ^{vb}	17.3	17.5	
Dimethylformamide (DMF)	3.82† _{110°C(vap.)}	37.2 _{25°C}	80	71		19.8	~17.3-17.6 ^b	19.2	19.1	
N-methylacetamide (NMA)	3.73† _{110°C(vap.)}	178.9† _{30°C}	—	—		21.0	~15.5-16.1	20.1	19.8	
Dimethylacetamide (DMA)	3.81† _{110°C(vap.)}	37.8 _{25°C}	87	72		21.1	16.6-17.2 ^b	21.2	20.8	
Water	1.87	78.5 _{25°C}	98	68		>90	13.2	19.3††	19.3††	

* Schlaifer and Schaffernicht (1960).

† Meighan and Cole (1964).

‡ Bass *et al.* (1964).

§ Leader and Gormley (1951).

|| Dorsey (1940).

• Müllen (1967).

** A. J. Parker (private communication) has indicated that the Gibbs energy of solvation for NMF are very similar to formamide.

†† Gibbs energy of solvation for Mg²⁺ and Ca²⁺ in water are 456 and 381 kcal. mole⁻¹ respectively.^b—broad.^{vb}—very broad.

effectively increase the magnitude of the dipole association between the amide and the surface, and the amide and the cation, and would result in reduced swelling; the organic molecule would act as a bridge between the cation and the surface.

In *N*-ethylacetamide, with ethyl substituted for a methyl group, the increase in basicity of the carbonyl oxygen and enhancement of the dipole moment is even greater than in NMA with the result that there is even less crystalline swelling of Na-montmorillonite (Tahoun, 1965) than in NMA.

Multivalent cations cause greater dielectric saturation of the medium than monovalent cations (Millen and Watts, 1967); as a result of the lower relative permittivity the attractive potential is increased which is the cause of the reduced swelling (Norrish, 1954; Quirk, 1968). This therefore prevents extensive crystalline swelling despite the fact that the value of the swelling index for Mg-montmorillonite (8.9×10^3) is greater than Na-montmorillonite (7.6×10^3) when the value of ϵ is taken as 78. As described above, NMF and NMA in Na-montmorillonite must also have a relative permittivity appreciably lower than indicated in Table 1.

The extensive crystalline swelling which occurs with Na- and Cs-montmorillonite in formamide for which the value of the swelling indices would be respectively 1.06×10^4 and 7.5×10^3 indicates that the relative permittivity of formamide in the interlayer region must be appreciably greater than NMF and NMA. Millen and Watts (1967) have discussed the relative permittivity of the solvation layers of an ion as a function of distance from the ion and suggest that the region of dielectric saturation is less for a monovalent ion than a divalent ion and as indicated above, Norrish (1954) has attributed differences in the swelling of montmorillonite in water to this cause. An alternative statement is that the relative permittivity in the interlayer spaces for Na-montmorillonite approaches more closely that of the bulk liquid water than Ca- or Mg-montmorillonite. As virtually identical swelling behavior is observed for Na- and Cs-montmorillonite in formamide it can be concluded that the relative permittivity in the interlayer spaces of Na- and Cs-montmorillonite is appreciable and perhaps approaches a value of 108.

The results reported here reveal the considerable complexity of the ion solvent dipole interaction in the interlayer spaces of homoionic montmorillonites.

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Résumé—Le gonflement cristallin et osmotique de montmorillonites Na, Cs, Mg, et Ca, a été mesuré dans le diméthylsulfoxyde, la formamide, la N méthylformamide, la diméthylformamide, la N méthylacétamide et la diméthylacétamide. Ces liquides ont des moments dipolaires voisins, mais leur permittivité relative varie d'une façon appréciable de valeurs inférieures à des valeurs supérieures à celle de l'eau.

La montmorillonite Na montre un gonflement osmotique (développement d'une double couche diffuse — $d(001) \gg 19 \text{ \AA}$) dans la formamide et la N méthylformamide, et l'argile Cs a un comportement de gonflement osmotique dans la formamide. La montmorillonite Cs donne, avec tous les liquides, dans la région de gonflement cristallin, des espacements plus grands que ceux qui sont trouvés avec l'eau. Les montmorillonites Mg et Ca ne donnent pas d'espacements supérieurs à 19 \AA dans aucun des liquides étudiés.

Le comportement gonflant de la montmorillonite est affecté par la permittivité relative, mais pour les liquides qui ont une permittivité relative semblable, la méthyl substitution dans la molécule peut empêcher le développement de doubles couches diffuses à la surface des particules.

Kurzreferat—Die kristalline und osmotische Quellung von Na-, Cs-, Mg- und Ca-Montmorillonit wurde in Dimethylsulphoxid und in Formamid, *N*-Methylformamid, Dimethylformamid, *N*-Methylacetamid und Dimethylacetamid gemessen. Diese Flüssigkeiten haben ähnliche Dipolmomente, aber ihre Dielektrizitätskonstanten variieren erheblich zwischen Werten, die geringer und solchen, die größer sind als die des Wassers.

Na-Montmorillonit zeigt osmotische Quellung (Entwicklung einer diffusen Doppelschicht — $d(001) \gg 19 \text{ \AA}$) in Formamid und *N*-Methylformamid und Cs ergibt osmotisches Quellungsverhalten in Formamid. Cs-Montmorillonit weist im Bereich der kristallinen Quellung mit allen Flüssigkeiten Schichtabstände auf, die größer als die mit Wasser gefundenen sind. Mg- und Ca-Montmorillonit ergaben mit allen untersuchten Flüssigkeiten keine Schichtabstände über 19 \AA .

Das Quellungsverhalten von Montmorillonit wurde durch die Dielektrizitätskonstante beeinflusst, jedoch kann für Flüssigkeiten mit ähnlicher Dielektrizitätskonstante Methylsubstitution im Molekül die Ausbildung einer diffusen Doppelschicht an den Teilchenoberflächen verhindern.

Резюме— Измеряют кристаллическое и осмотическое разбухание Na-, Cs- Mg- и Ca-монтмориллонитов в диметилсульфоксиде и в формамиде, в *N*-метилформамиде, в диметилформамиде, в *N*-метилацетамиде и в диметилацетамиде. Эти жидкости имеют одинаковые дипольные моменты, но их сравнительные диэлектрические проницаемости значительно различаются от числовых значений ниже воды до числовых значений выше воды.

Na-монтмориллонит выявляет осмотическое разбухание в формамиде и *N*-метилформамиде (развивается диффундирование двойных слоев — $d(001) \gg 19 \text{ \AA}$), а Cs выявляет поведение осмотического разбухания в формамиде. В области кристаллического разбухания Cs-монтмориллонит образует большие расстояния между атомами во всех этих жидкостях, чем в воде. Mg- и Ca-монтмориллониты не дали расстояний более, чем 19 \AA в экспериментальных жидкостях.

На поведение разбухания монтмориллонита влияет диэлектрическая проницаемость, но в жидкостях с тождественной диэлектрической проницаемостью замена метила в молекуле может предотвратить развитие диффундированных двойных слоев на поверхностях частиц.