

SWELLING OF FORMAMIDE-MONTMORILLONITE COMPLEXES IN POLAR LIQUIDS

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Abstract—A new osmotic-swelling system for montmorillonite with formamide (FA) is described. Water and a variety of polar organic liquids were used to swell FA-montmorillonite complexes. The post-swelling behavior of the complex is interpreted in terms of the bi-functionality of FA as an electron donor/acceptor and the magnitude of the donor number (DN) of the polar liquid relative to that of FA. The FA-montmorillonite complex shows limited swelling of $d(001) < 2.3$ nm for polar liquids with DNs larger than that of FA. In contrast, the FA-montmorillonite complex shows osmotic swelling when the DN of the polar liquid is smaller than that of FA.

Key Words—Donor Number, Formamide, Montmorillonite, Osmotic Swelling, Polar Liquids, Swelling.

INTRODUCTION

Montmorillonite is widely used in industry due to its unique osmotic-swelling properties in water. Uses include molding materials in foundries, viscosity-controlled reagents for drilling fluids in civil engineering, and barrier materials to prevent water migration from and into paddy fields (Konta, 1995). Although montmorillonite may swell with water infinitely, it exhibits only limited swelling in electrolyte solutions such as sea water. This reduced swelling in electrolyte solutions restricts the application of montmorillonite. Recently, Kondo (1996) found that a montmorillonite complex with propylene carbonate (PC) provides swelling behavior in brine solutions as well as in fresh water. Onikata *et al.* (1996) reported that the PC-montmorillonite complex is useful for environmental geotechnic applications; the PC complex shows satisfactory impermeability for sea water.

Onikata *et al.* (1999) proposed a possible mechanism for the osmotic swelling of PC-montmorillonite in electrolyte solutions as follows: When the swelling of montmorillonite shifts from the limited to the osmotic-swelling range, the basal spacing expands from ~ 2 to 4 nm. At high spacings, the interactions between silicate layers and the cations are much weakened, and a repulsive (osmotic) force between the electric double layers on the surface of the silicate layers is balanced by attractive van der Waals forces and electrostatic forces between the silicate layers bound by the interlayer cations. The driving force controlling the intercalation of solvent molecules into the interlayer of montmorillonite is primarily due to the solvation of the interlayer cations. The interactions become stronger when the cations with larger polarizing abilities are combined with solvents with a greater electron-donor ability.

The electron-donor ability of a solvent was discussed by Gutmann (1976) in terms of the donor number, DN, which is a measure of the basicity of a solvent. DN is defined as the negative enthalpy of reaction of a base with the Lewis acid antimony pentachloride, $SbCl_5$. Donor numbers provide an interesting comparison of the relative donor abilities of various solvents. Gutmann extended the concept to include an acceptor number (AN) that measures the electrophilic behavior of a solvent. H_2O molecules with a DN of 18.0 coordinate with interlayer cations to form the primary hydration shell. PC molecules have a lower DN (DN = 15.1) and coordinate with the cations through their hydration shell. In the hydration shell, H_2O is bi-functional and may act as an electron acceptor as a donor. H_2O molecules strongly bound by the cations act as acceptors to other H_2O and PC molecules.

The $d(001)$ -value of the PC complex can be as large as 1.9 nm, which is nearly in the critical range for osmotic swelling. In aqueous electrolyte solutions, H_2O molecules, which are stronger donors than PC, will be further attracted to the cations to form a larger hydration shell inside the PC coordination shell. If the $d(001)$ -value increases over a critical value by the adsorption of H_2O , montmorillonite shows osmotic swelling. However, if the electrolyte solution concentration is too high, the Debye length of the electrolyte solution will be very short and the silicate layers will be supported only by the PC molecules coordinating to the cations through water, *e.g.*, crystalline swelling. Onikata *et al.* (1999) showed that the concentration range of the electrolyte solutions in which osmotic swelling of montmorillonite is possible is extended to as high as 0.75 M NaCl with the association of PC. This value is much higher than the NaCl concentration in common sea water. This explains the swelling behavior of the PC-bentonite complex in brine solutions

Table 1. Physical properties of polar liquids used in this study, and the basal spacings of Na-rich montmorillonite and FA-montmorillonite complexes in polar liquids.

Polar liquids	Dipole moment (D) ¹	Relative permittivity ¹	Donor number ¹	Acceptor number ¹	<i>d</i> (001) in polar liquid (nm)	
					Na-rich mont ²	FA-mont ³
Triethylamine	0.66	2.4	61	—	1.40	1.67
Pyridine	2.37	12.4	33.1	14.2	2.06	2.39
N,N-Diethylacetamide	3.69	30.4	32.3	—	2.16	2.33
Ethanol	1.66	24.4	32	37.9	1.73	1.88
Methanol	2.87	32.6	30	41.5	1.73	1.84
N,N-Dimethylformamide	3.86	36.7	26.6	16.0	2.06	1.92
Ethylene glycol	2.28	40.8	20	42.8	1.77	1.73
Formamide	3.37	109.5	24	39.8	Osmotic	Osmotic
Tetrahydrofuran	1.75	7.4	20	8.0	1.50	Osmotic
Water	1.8 ⁴	78.5 ⁴	18 ⁴	54.8 ⁴	Osmotic	Osmotic
Acetone	2.69	20.6	17	12.5	1.88	Osmotic
Propylene carbonate	4.98	64.9	15.1	18.3	2.01	Osmotic
Sulfolane	4.81	43.3	14.8	19.2	1.52	Osmotic
Acetonitrile	3.44	35.9	14.1	18.9	2.01	Osmotic

¹ Barthel and Gores (1994).

² The ratio of montmorillonite/polar liquid = 1/2 by weight.

³ The ratio of montmorillonite/FA/polar liquid = 1/3/3 by weight.

⁴ Mayer *et al.* (1975).

as well as in fresh water as found by Onikata *et al.* (1996).

In this study, a new osmotic-swelling system with formamide (FA) was developed. The post-swelling behavior of a FA-montmorillonite complex was studied here with a variety of polar liquids. The post-swelling phenomena can be understood in terms of the bi-functionality of FA and the magnitudes of donor numbers of the polar liquids used.

EXPERIMENTAL

The natural Na-rich montmorillonite, "BEN-GEL A" from Hojun Yoko Co. Ltd. was used. This material is the <2- μ m fraction from a Wyoming bentonite. The cation exchange capacity (CEC) was determined to be 94 meq/100 g. Homoionic Na-rich montmorillonite was prepared by suspending 50 g of the Na-rich montmorillonite in 500 mL of 1 M NaCl solution for 18 h, centrifuging, and discarding the supernatant solution. This process was repeated six times and the excess solution was removed by washing with 80% ethanol/water until free of chloride ions, based on using AgNO₃. The Na-rich montmorillonite thus prepared was dried at 80°C for 24 h in air, ground with an agate mortar, and sieved through a 30- μ m mesh. Formamide (FA, reagent grade) was obtained from Kanto Chemical Co. Inc. and was used as received.

The FA-montmorillonite complex was prepared by mixing 1.0 g of Na-rich montmorillonite with 1.0, 2.0, and 3.0 g of FA using an agate mortar at room temperature. The complexes with the other polar liquids were prepared similarly. Various polar liquids were mixed at room temperature for 1 min so that the final composition of each mixture was 1/3/3 (montmorillonite/FA/polar liquid) by weight. Powder X-ray diffrac-

tion (XRD) patterns were recorded using a Rigaku diffractometer (Model Geiger RAD-IIA) with Ni filtered CuK α radiation. The wet samples were protected from drying by covering with Mylar or polyethylene film.

RESULTS

Na-rich montmorillonite was swelled in FA with a ratio of 1/1 (FA/clay) by weight. The product showed very weak and broad XRD peaks at 3.7 and 2 nm. With an increase in the ratio of FA/clay to 2–3, no distinct peaks were observed. The *d*(001)-values of montmorillonite complexes with different polar liquids (Table 1) were prepared in ratios of 1/2 (clay/polar liquid). These values are in good agreement with the values reported elsewhere: primary n-alcohol, MacEwan (1960); ethylene glycol, Bradley (1945), MacEwan (1944), Reynolds (1965); pyridine, Serratos (1966); amide, Tahoun and Mortland (1966); acetone, Glaeser (1948), Bissada *et al.* (1967); and acetonitrile, MacEwan (1948).

In Table 1, polar liquids are arranged in decreasing order of DN given by Gutmann (1976). The *d*(001)-values observed for FA-montmorillonite complexes swelled with these polar liquids are also given in the table. Note that with the exception of ethylene glycol, the polar liquids with DNs smaller than that of FA (DN = 24) show osmotic swelling. The other polar liquids showed limited swelling with values very similar to those observed for the swelling of Na-rich montmorillonite without FA.

DISCUSSION

The driving force for the intercalation of solvent molecules in the interlayers of montmorillonite is mainly due to cation-dipole interactions. For a given

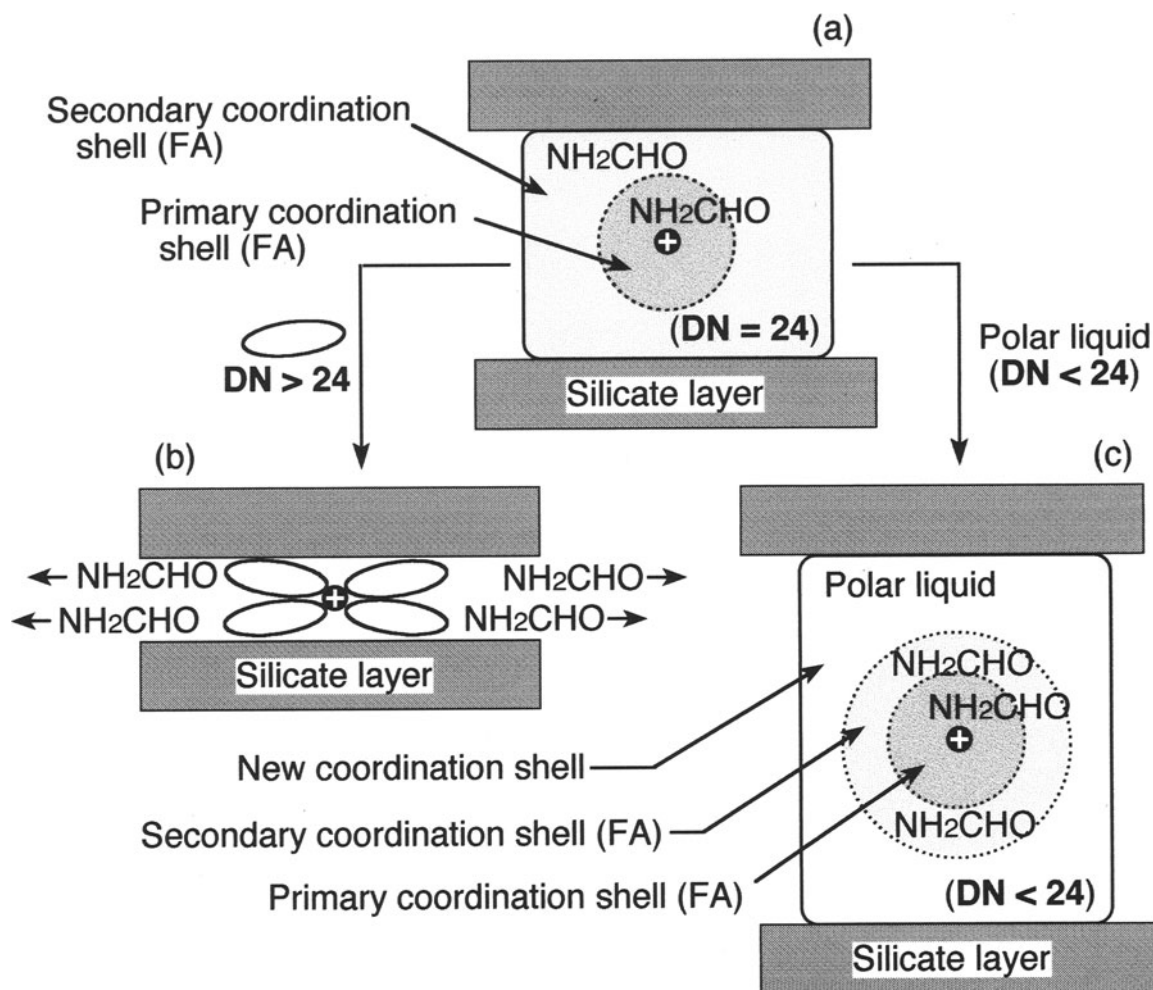


Figure 1. Schematic structural model of the post-swelling behavior of FA-montmorillonite complex: (a) FA-montmorillonite complex with FA (DN = 24) molecules in a strongly bound primary coordination shell and in a loosely bound secondary coordination shell between the silicate layers (osmotic swelling); (b) limited swelling (crystalline swelling) with polar liquids of DN > 24, FA molecules being expelled from the interlayer; (c) osmotic swelling with polar liquids of DN < 24.

solvent, the strength of the interaction is related to the polarizing power of the interlayer cation, Z/r , where Z = charge of interlayer cation and r = radius of cation (Yamanaka *et al.*, 1974, 1975). However, the strength of the attractive force is not always related to the magnitude of the dipole moment of the solvent. As shown by Onikata *et al.* (1999), interlayer H₂O molecules coordinated to a given cation with a dipole moment of 1.8 D could not be replaced with PC, which has a much larger dipole moment of 4.98 D. H₂O molecules were replaced with propyl alcohol, which has a dipole moment comparable to that of water. These results suggest that the coordination strength of solvent molecules to the interlayer cations may be better explained by the magnitude of the electron donor ability (*i.e.*, donor number, DN) of the solvent. The DNs of propyl alcohol, water, and PC are 18, 18, and 15.1, respec-

tively; PC has a very large dipole moment and is a weak electron donor.

To understand the swelling behavior of montmorillonite in polar liquids, Olejnik *et al.* (1974) used the swelling index $U\epsilon/v^2$, which was proposed originally by Norrish (1954), where U is the solvation energy, ϵ is the relative permittivity of the polar solvent, and v is the valence of the cation. According to Olejnik *et al.*, for a given valence and increasing values of U and ϵ , there is a greater tendency of the clay to swell. Although this index may explain the osmotic swelling of water, formamide, and N-methyl formamide with $\epsilon = 78.5, 109.5,$ and 171 , respectively, it does not explain the limited swelling of methyl-substituted molecules such as N-methyl acetamide, which have a very large relative permittivity ($\epsilon = 178.9$) similar to water, formamide, and N-methyl formamide. This suggests that

polar liquids have bi-functionality and are both electron donors and acceptors in osmotic swelling. The methyl-substituted molecules may suffer steric hindrance in the formation of donor-acceptor networks by hydrogen bonds. Note that there is no simple correlation between the dipole moment, donor number, and relative permittivity.

Onikata *et al.* (1999) described the post-swelling of a PC-montmorillonite complex in water and electrolyte solutions. The swelling behavior was interpreted based on the bi-functionality of water as an electron donor-acceptor and H₂O has a larger DN than PC. The results in Table 1 suggest that the post-swelling behavior of FA-montmorillonite with polar solvents can be explained similarly. Formamide is a bi-functional molecule with an electron donor group, -NH₂ at one end and an electron acceptor group, -CHO, at the other. FA has a donor number of 24, which is in the middle of range of values in Table 1. If a FA-montmorillonite complex is treated using polar liquids with larger donor numbers, the polar liquids can penetrate into the coordination shell of FA to directly coordinate to the interlayer cations and thus, the FA is expelled from the interlayer (Figure 1). In contrast, if the FA-montmorillonite complex swells with polar liquids with a smaller donor number than FA, the FA molecules remain coordinated to the cations. The bi-functional FA molecules act as acceptors for polar liquids, expanding the interlayer to an osmotic swelling range.

Ethylene glycol is the only exception in Table 1. Ethylene glycol has a smaller donor number than FA, although it is very close to that of FA. Note that ethylene glycol is also bi-functional, and may form a special interlayer network with hydrogen bonds. Montmorillonite preferentially reacts with ethylene glycol to form a complex with a characteristic basal spacing of 1.7 nm, and this complex is widely used for identification of smectites from other phyllosilicate minerals (MacEwan and Wilson, 1980). With only this exception, the relative donor number order of polar liquids to formamide appears to explain systematically the post-swelling behavior of montmorillonite.

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