COMPLEX FORMATION OF CATION-EXCHANGED MONTMORILLONITES WITH PROPYLENE CARBONATE: OSMOTIC SWELLING IN AQUEOUS ELECTROLYTE SOLUTIONS

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Abstract—Montmorillonites saturated with Li^+, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, or Ni^{2+} ions can form complexes with propylene carbonate (PC) by intercalation; the $d(001)$ of montmorillonite expands to 19 Å. In the infrared absorption spectra of these complexes, the $C=O$ stretching band of the intercalated PC molecules shifts to lower frequencies, and the amount of the shift increased with the increase of the polarizing power of the interlayer cations. Water molecules were strongly bound to the cations. The PC molecules interacted with the cations by way of H_2O molecules. With the removal of H_2O, the PC molecules directly coordinate to the cations and the PC molecules show a much larger red-shift in the $C=O$ frequency. The PC-montmorillonite complexes exhibited osmotic swelling, even in aqueous electrolyte solutions. This finding is interpreted in terms of the formation of thick electric double-layers consisting of PC and H_2O between the 2:1 layers.

Key Words—Infra-Red Spectroscopy, Intercalation Complex, Montmorillonite, Osmotic Swelling, Propylene Carbonate.

INTRODUCTION

Smectites are unusual among naturally occurring materials because they swell in water and may form intercalation complexes with various organic compounds by adsorption and cation exchange. Owing to these unusual characteristics, montmorillonite in particular, is widely used in industry, for example, in foundries as molding materials, in civil engineering as viscosity- and plasticity-control reagents, and in agriculture as a carrier of insecticides (Konta, 1995). Reviews on montmorillonite-organic complexes were given by Mortland (1970), Theng (1974), and MacEwan and Wilson (1980). The interlayer cations of montmorillonite play an important role in the formation of organic complexes; cation-dipole interactions influence the stability of the complexes, and H_2O molecules associated with these cations also affect the orientation of interlayer organic molecules (Yamanaka *et al.*, 1974, 1975). Although Na- and Li-rich montmorillonites swell with H_2O infinitely, they show limited swelling in electrolyte solutions such as sea water. Norrish and Quirk (1954) reported that Na-rich montmorillonite showed limited expansion only to 19 Å in NaCl solutions with concentrations of >0.3 M, suggesting simple crystalline swelling. In more dilute solutions, the swelling increased with decreasing concentration owing to osmotic swelling. Recently, Kondo (1996) found that propylene carbonate (PC) forms complexes with montmorillonite and activates osmotic swelling of montmorillonite, even in aqueous electrolyte solutions such as sea water. Onikata *et al.* (1996) reported an environmental geotechnical application of

PC bentonite complexes as an impermeable soil material in areas of coastal brines. In this study, the interactions between cation-exchanged montmorillonites and PC were investigated to better understand the mechanism of osmotic swelling.

EXPERIMENTAL

The natural Na-rich montmorillonite, "BEN-GEL A" from Hojun Yoko Co. Ltd. (Tokyo, Japan) was used. This material is the <2-μm fraction from Wyoming bentonite. The cation exchange capacity (CEC) of 94 meq/100 g was determined. Montmorillonite saturated with different cations was prepared by suspending 50 g of the Na-rich montmorillonite in 500 mL of 1 M chloride solutions of Li, Na, K, Ca, Mg, Ba, or Ni, and a 1 M ammonium acetate solution for 18 h. The supernatant solutions were discarded after centrifugation. This process was repeated six times and the excess ions were removed by washing with an 80% ethanol solution until free from chloride and NH_4 ions as determined against $AgNO_3$ and Nessler's reagents, respectively. The cation-exchanged montmorillonites thus prepared were dried at 80°C for 24 h in air and ground in an agate mortar, followed by sieving through a 30-μm mesh. Propylene carbonate (PC) with a purity of 98% was obtained from Showa Denko K. K. (Tokyo, Japan).

The complexes were prepared by mixing the cation-exchanged montmorillonites with different amounts of PC using an agate mortar at room temperature for 5 min. The mixing ratios examined were in the range of 15–45% by weight for cation-exchanged montmorillonites, corresponding to a mixing of 1.5–4.4 moles of
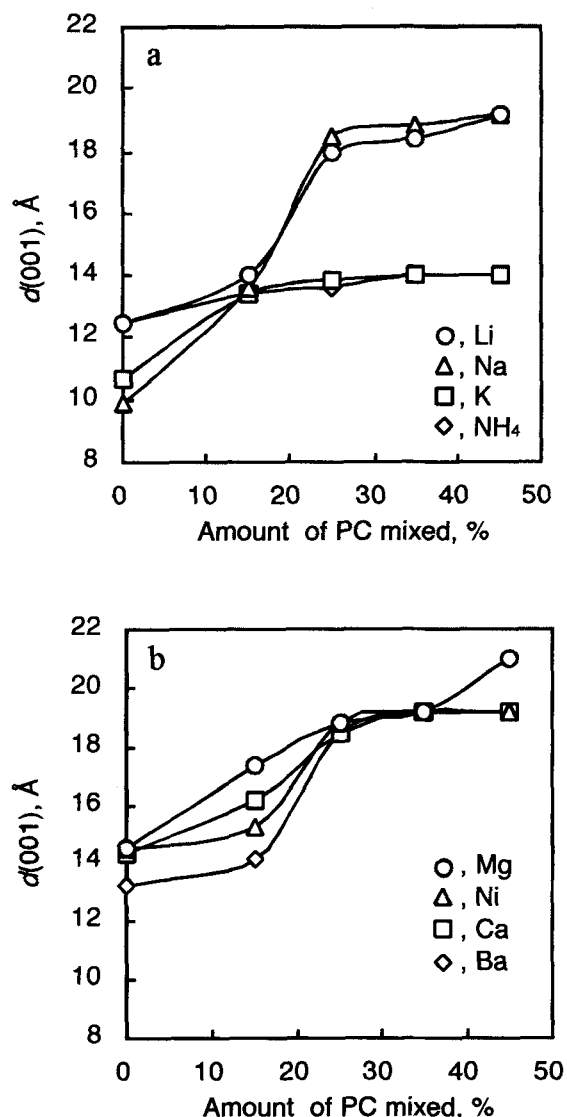
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Figure 1. The $d(001)$ of PC-montmorillonite complexes as a function of the quantity of PC mixed with the montmorillonites. Cation-exchanged montmorillonites are shown with (a) monovalent and (b) divalent ions.

PC/kg of clay. Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku diffractometer (Model Geigerflex RAD-IIA) with Fe filtered CoKα radiation at 25 kV and 15 mA. For wet samples, the samples were covered by Mylar or polyethylene film, and a Mac Science diffractometer (Model M18X-HF) with graphite monochromated CuKα radiation was used at a power of 40 kV and 100 mA.

Fourier transform infrared (FTIR) absorption spectra were measured on thin films of cation-exchanged montmorillonites deposited on the surface of Si(100) wafers (0.4 mm in thickness) from aqueous dispersions using a Perkin Elmer Paragon 1000 spectrometer. The complexes were formed by adding PC on the films

and drying at different heating conditions at a temperature of 70–105°C for 1 h. The films of highly dehydrated PC-montmorillonite complexes were prepared as follows: H_2O molecules between the 2:1 layers were first replaced with n-propyl alcohol (PA) by dispersing montmorillonite in PA, and then thin films of montmorillonite were deposited on Si(100) wafers from the dispersion. After the films were air-dried, the complexes were formed by adding PC on the PA-rich films and drying at 105°C for 1 h.

Thermogravimetric analyses (TGA) of PC-montmorillonite complexes were performed using a Shimazu TAS 100 in air with a heating rate of 10°C/min. Swelling power of the clay samples was determined by measuring the expanded apparent volume of 2.0 g of PC-complexes in 100 mL of a 0.5 M NaCl aqueous solution in accordance with the standard method of Japan Pharmacopoeia's Swelling Power Test of Bentonite.

RESULTS

XRD

The observed $d(001)$-values for various PC-montmorillonite complexes are summarized in Figure 1 as a function of the amount of PC mixed in wt. %. The $d(001)$-value increased with increasing amount of PC to 25%. The montmorillonite saturated with monovalent cations of low polarizing power, such as NH_4^+ and K^+, formed a complex with a $d(001)$-value of 14 Å, suggesting formation of a monolayer of PC between the layers. Montmorillonites saturated with monovalent cations of greater polarizing power, such as Na^+ and Li^+, formed two types of complexes with $d(001)$-values of 14 and 19 Å for small and large amounts of PC mixed, respectively. The $d(001)$-values correspond to a mono-layer and bi-layer of PC molecules between the layers, respectively. The samples that were cation exchanged with divalent cations also formed complexes with different spacings, depending on the type of the interlayer cations and the amount of PC mixed as shown in Figure 1; the complexes formed with a large amount of PC had a $d(001)$ of 19 Å indicating a bi-layer of PC molecules in the interlayer.

TGA

Complexes were prepared by mixing cation-exchanged montmorillonites with an amount of PC three times greater by weight, and heating for 20, 40, and 60 min at 105°C. During this treatment, some of the PC slowly evaporated. TGA was performed on the samples after this heat treatment. The results are shown for the Mg-rich montmorillonite complex in Figure 2. Weight loss to 280°C is attributed to the loss of PC and H_2O. The weight loss near 650°C is due to the loss of the structural hydroxyl groups from the 2:1 layers. Weakly and strongly bound PC is lost in the
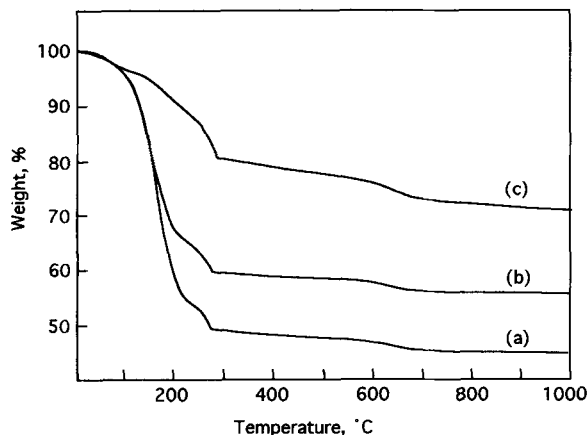
Figure 2. TGA curves of PC-Mg-montmorillonite complexes measured after thermal treatment at 105°C for (a) 20, (b) 40, and (c) 60 min.

Figure 4. FTIR spectrum of PC-Mg-montmorillonite complexes dried on Si(100) wafer at 70°C.

temperature ranges of 100–200°C and 200–280°C, respectively; the weakly bound PC molecules were primarily removed on heating at 105°C. Weight loss observed to 280°C on samples heated at 105°C for 60 min is shown in Figure 3 as a function of the polarizing power of the interlayer cations. Polarizing power (Z/R) is defined as a ratio of the charge of the cation (Z) to its ionic radius (R), and is directly related to the strength of the electric field of the cation. Clearly, the greater the polarizing power of the cations, the greater the number of PC molecules that remain in the complex. Also, the PC molecules are more strongly bound

by the montmorillonite samples with the cations having greater polarizing power.

FTIR

A typical FTIR spectrum of one PC-montmorillonite complex is shown in Figure 4. Note the characteristic C=O stretching band of PC. Liquid PC has the C=O stretching band at 1792 cm^{-1}. A red-shift is observed for the C=O stretching band upon the adsorption of PC in the interlayer of montmorillonite. Figure 5 shows the C=O frequencies observed as a function
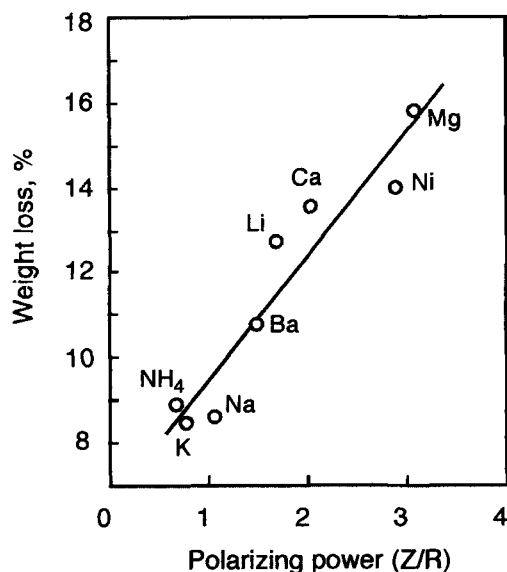

Figure 3. Weight loss observed on heating PC-montmorillonite complexes to 280°C as a function of the polarizing power of the interlayer cations. The samples were pre-heated at 105°C for 60 min before the measurements. See text for the definition of polarizing power.
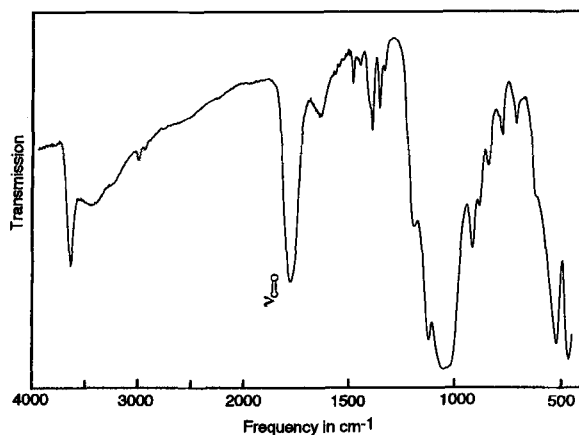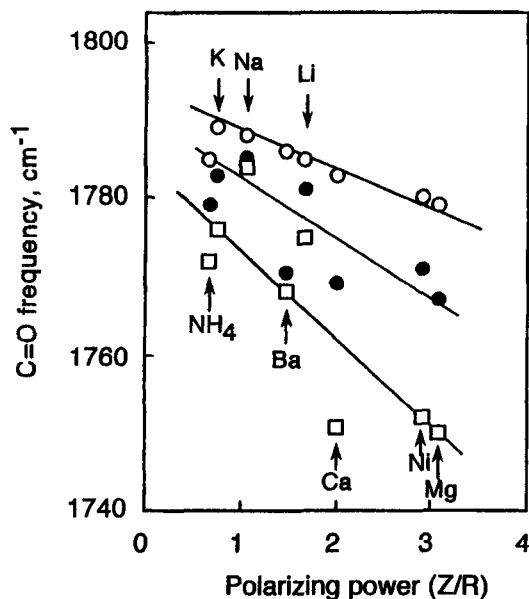

Figure 5. The C=O frequency of PC-montmorillonite complexes measured after different heat treatments as a function of the polarizing power of the interlayer cations: ○, heated at 70°C for 60 min; ●, heated at 105°C for 60 min; □, dehydrated with *n*-propyl alcohol prior to the formation of the PC complex, and heated at 105°C for 60 min.
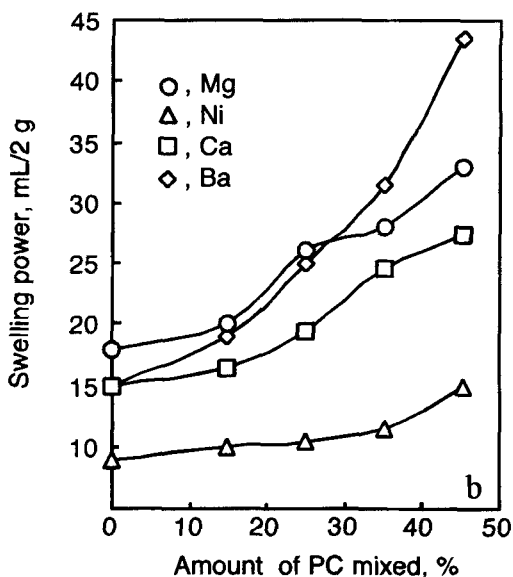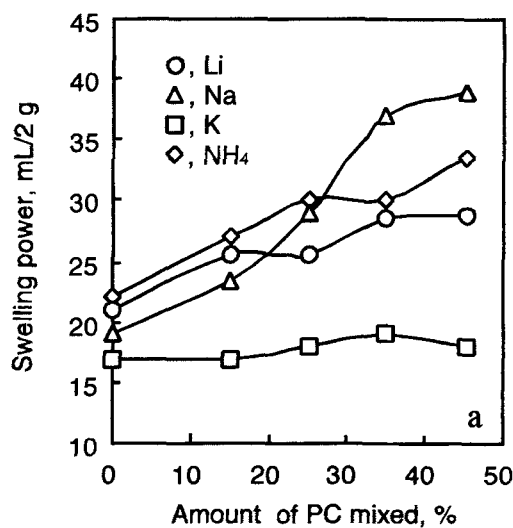
Figure 6. The swelling power (mL/2 g of clay) in a 0.5 M NaCl aqueous solution for PC-montmorillonite complexes as a function of the amount of PC mixed with montmorillonites that were cation exchanged with (a) monovalent and (b) divalent ions.

Figure 7. The $d(001)$-values of Na-rich montmorillonite in different concentrations of NaCl aqueous solutions with (●) and without (○) PC. The $d(001)$-values for the system without PC are from Norrish and Quirk (1954).

toward 1750 cm^{-1}; the shift reverted to 1780 cm^{-1} upon re-adsorption of H_2O from air.

Swelling with aqueous electrolyte solutions

Figure 6 shows that swelling power increases with the amount of PC in the montmorillonite. The swelling power of the montmorillonite complex with 45 wt. % PC follows the order: Ba > Na > NH_4 > Mg > Li > Ca ≫ K > Ni. This order is not related to the polarizing power of the cations. A portion of the interlayer cations coordinated with H_2O and PC may have been exchanged with Na ions from the solution used in the swelling-power test. Note that montmorillonite with both monovalent and divalent interlayer cations and with considerable polarizing power shows large swelling power in the electrolyte solution.

The Na-rich montmorillonite containing 45 wt. % PC was mixed with NaCl solutions twice as large as the clay by weight, and the lattice expansion of the clay was determined by XRD. The concentration of the NaCl in solution ([NaCl]) was varied from 0.1 to 2 M. The results are compared with data from by Norrish and Quirk (1954) on Na-rich montmorillonite in NaCl solutions without PC (Figure 7). With the presence of PC, the $d(001)$-value increased from 19 to 22–23 Å in [NaCl] = 1–2 M. The spacing increased to 45 Å at [NaCl] = 0.75 M. In dilute solutions, the d-value increased with decreasing NaCl concentration. For montmorillonite without PC, Norrish and Quirk reported a similar increase in swelling from 19 to 40 Å at [NaCl] = 0.3 M, and then the spacing increased linearly with respect to $1/\sqrt{[NaCl]}$. Note that with the presence of PC, montmorillonite can show osmotic swelling even at concentrations as high as [NaCl] = 0.75 M.

of the polarizing power (Z/R) of the interlayer cation. The magnitude of the red shift increased with an increase in the polarizing power of the interlayer cation. This shift was also influenced by the drying conditions of the complexes. The complexes dried by heating at 105°C showed a larger shift than the complexes dried at 70°C. The highly dehydrated complexes prepared using montmorillonite dehydrated with PA showed a much larger shift. The highly dehydrated Mg-rich montmorillonite complex showed the largest red-shift
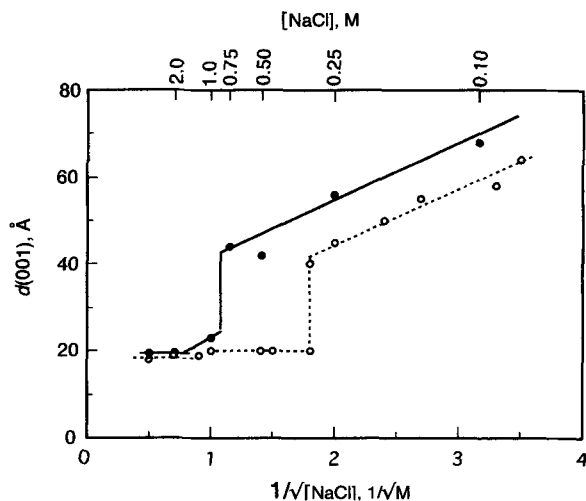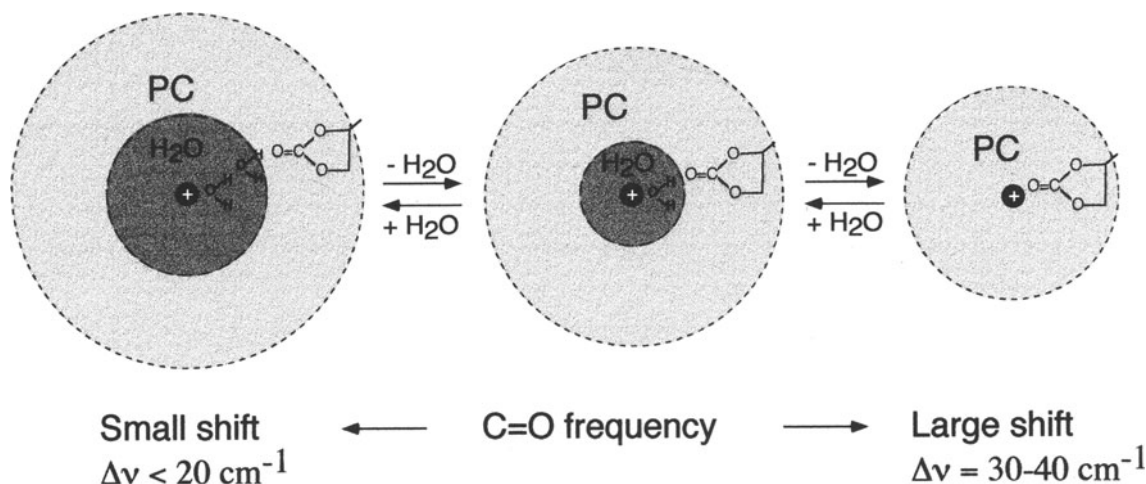
Figure 8. Schematic structural model of the arrangement of H_2O and PC molecules around the interlayer cations. The PC molecules coordinate to the interlayer cations through the hydration shell. The shift of the C=O frequency increases as the thickness of the hydration shell decreases upon dehydration.

DISCUSSION

The IR spectra of montmorillonite complexes with various carbonyl compounds have been extensively studied by many investigators: acetone, Glaeser (1948); ketone, Tensmeyer *et al.* (1960); acetone, acetylacetone, and 2.5 hexanedione, Parfitt and Mortland (1968); carbaryl, Fusi *et al.* (1986); fluarifop-butyl and fluazifop, Fusi *et al.* (1988); dimepiperate, Pusino *et al.* (1993); and rimsulfuron, Calamai *et al.* (1997). According to these studies, carbonyl compounds coordinate to the interlayer cations via H_2O molecules and the shift of the C=O stretching band is $\sim 20{-}30$ cm^{-1}. However, the band shows a much greater red-shift of $40{-}50$ cm^{-1} if the C=O group coordinates to the interlayer cations directly. The relatively small shifts of the C=O frequency observed for the PC-montmorillonite complexes with different interlayer cations suggest that the PC molecules are bound to the interlayer cations through H_2O molecules. The H_2O molecules are so strongly bound to the interlayer cations in the complexes that heating at 105°C cannot remove the H_2O molecules. Dowdy and Mortland (1967) showed that ethanol was capable of displacing H_2O that was strongly bound to interlayer cations. In this study, PA was used to obtain highly dehydrated montmorillonite. The C=O absorption band of the PC-montmorillonite complexes obtained from the PA-rich sample showed a much larger red-shift than the samples obtained from hydrated montmorillonite complexes (see Figure 5). A proposed model for the arrangement of H_2O and PC molecules around the interlayer cations are shown schematically in Figure 8 for different degrees of dehydration. For the complexes with H_2O, PC molecules coordinate to the interlayer cations of montmorillonite through H_2O molecules which are bound strongly to the cations. Thus, the shift of the C=O frequency is a

function of the polarizing power of the cation, as well as the thickness of the hydration shell.

The bonding forces between the 2:1 layers of montmorillonite are primarily electrostatic through the interlayer cations. The attractive forces are balanced by repulsive forces resulting from the solvation of the interlayer cations. The $d(001)$ expands depending on the size, orientation, and the number of the solvent molecules. This is referred to as *crystalline swelling*. Norrish and Quirk (1954) used electrolyte solutions to control the swelling of montmorillonite with water. They found that Na-rich montmorillonite swelled to $d(001)$-values of 19 Å in aqueous NaCl solutions with concentrations of >0.3 M but increased sharply to 40 Å for montmorillonite in 0.3 M NaCl (Figure 7). In more dilute solutions, the spacing increased with decreasing concentration of the electrolyte. At high spacings (*e.g.*, ~ 40 Å), the interactions between the 2:1 layers by way of the cations are much weakened, and a repulsive (osmotic) force between the electric double layers on the surface of the 2:1 layers is balanced with attractive van der Waals forces. Since the thickness of the electric double layers, or the Debye length, increases with decreasing concentration of the electrolyte solution (Israelachvili, 1991), the $d(001)$ increases with decreasing concentration. A similar sharp increase in the spacing from 20 to 45 Å was observed in this study for the swelling of PC-montmorillonite complexes in NaCl solutions. The $d(001)$-value of 20 Å is probably a critical value where the electrostatic attractive force between the 2:1 layers by way of the cations is sufficiently weak that the crystalline swelling is transformed into an osmotic swelling with spacings of >40 Å. Olejnik *et al.* (1974) studied the osmotic swelling of montmorillonite in polar organic liquids with large permittivities, such as formamide and

N-methylformamide. They also noted that there was a critical d(001)-value near 19 Å for osmotic swelling.

The driving force for the intercalation of solvent molecules into the interlayer of montmorillonite is primarily the solvation of the interlayer cations. The interactions become stronger when cations with larger polarizing power are combined with a solvent which has a large electron donor ability, or a large donor number (DN) (Gutmann, 1976). Water molecules with a DN of 18.0 strongly coordinate to the interlayer cations, forming a primary hydration shell. PC molecules are weaker electron donors (DN = 15.1) and therefore tend to coordinate to the cations through a hydration shell. n-Propyl alcohol has a DN of 18.0, which is comparable to that of H_2O and thus, n-propyl alcohol can replace the H_2O molecules around the cations. Water molecules are bifunctional, and can act as electron donors and electron acceptors. The H_2O molecules that are strongly bound to the cations can act as electron acceptors to H_2O as well as PC molecules. The d(001) of the PC complex is as large as 19 Å, and is already near the critical value for osmotic swelling. In an aqueous electrolyte solution, H_2O molecules will be further coordinated around the cations, thereby forming a larger hydration shell within the PC coordination shell (Figure 8). If the spacing increases above a critical value by the adsorption of H_2O, montmorillonite will show osmotic swelling. However, if the concentration of the electrolyte solution is too high, the Debye length of the electrolyte solution is very short; the 2:1 layers will be supported only by the PC molecules coordinating to the cations via H_2O, $e.g.$, crystalline swelling.

Note that the range of osmotic swelling in an electrolyte solution may be as high as 0.75 M with the association of PC, which is much higher than the concentration of normal sea water. This result explains the swelling behavior of PC-bentonite complexes in brine solutions as well as fresh water as found by Onikata $et\ al.$ (1996).

REFERENCES

Calamai, L., Pantani, O., Pusino, A., Gessa, C., and Fusi, P. (1997) Interaction of rimsulfuron with smectites. *Clays and Clay Minerals,* **45,** 23–27.

Dowdy, R.H. and Mortland, M.M. (1967) Alcohol-water interactions on montmorillonite surfaces. I. Ethanol. *Clays and Clay Minerals,* **15,** 259–271.

Fusi, P., Ristori, G.G., and Franci, M. (1986) Interactions of carbaryl with homoionic montmorillonite. *Applied Clay Science,* **1,** 375–383.

Fusi, P., Franci, M., and Bosetto, M. (1988) Interaction of fluazifop-butyl and fluazifop with smectites. *Applied Clay Science,* **3,** 63–73.

Glaeser, R. (1948) On the mechanism of formation of montmorillonite-acetone complexes. *Clay Minerals Bulletin,* **1,** 88–90.

Gutmann, V. (1976) Empirical parameters for donor and acceptor properties of solvents, *Electrochimica Acta,* **21,** 661–670.

Israelachvili, J.N. (1991) *Intermolecular and Surface Forces, 2nd edition.* Academic Press, London, 450 pp.

Kondo, M. (1996) US Patent 5,573,583.

Konta, J. (1995) Clay and man: Clay raw materials in the service of man. *Applied Clay Science,* **10,** 275–335.

MacEwan, D.M.C. and Wilson, M.J. (1980) Interlayer and intercalation complexes of clay minerals. In *Crystal Structures of Clay Minerals and Their X-ray Identification,* G.W. Brindley and G. Brown, eds., Mineralogical Society, London, 197–248.

Mortland, M.M. (1970) Clay-organic complexes and interactions. In *Advances in Agronomy, Volume 22,* N.C. Brady, ed., Academic Press, New York, 75–117.

Norrish, K. and Quirk, J.P. (1954) Crystalline swelling of montmorillonite. Use of electrolytes to control swelling. *Nature,* **173,** 255–256.

Olejnik, S., Posner, A.M., and Quirk, J.P. (1974) Swelling of montmorillonite in polar organic liquids. *Clays and Clay Minerals,* **22,** 361–365.

Onikata, M., Kondo, M., and Kamon, M. (1996) Development and characterization of a multiswellable bentonite. In *Environmental Geotechnics,* M. Kamon ed., A.A. Balkema Publishers, Rotterdam, 587–590.

Parfitt, R.L. and Mortland, M.M. (1968) Ketone adsorption on montmorillonite. *Soil Science Society America Proceedings,* **32,** 355–363.

Pusino, A., Liu, W., and Gessa, C. (1993) Dimepiperate adsorption and hydrolysis on Al^{3+}-, Fe^{3+}-, Ca^{2+}-, and Na^+-montmorillonite. *Clays and Clay Minerals,* **41,** 335–340.

Tensmeyer, L.G., Hoffmann, R.W., and Brindley, G.W. (1960) Infrared studies of some complexes between ketones and calcium montmorillonite. Clay-organic studies. Part III. *Journal of Physical Chemistry,* **64,** 1655–1662.

Theng, B.K.G. (1974) *The Chemistry of Clay-Organic Reactions.* Adam Hilger, London, 343 pp.

Yamanaka, S., Kanamaru, F., and Koizumi, M. (1974) Role of interlayer cations in the formation of acrylonitrile-montmorillonite complexes. *Journal of Physical Chemistry,* **78,** 42–44.

Yamanaka, S., Kanamaru, F., and Koizumi, M. (1975) Studies on the orientation of acrylonitrile adsorbed on interlamellar surfaces of montmorillonites. *Journal of Physical Chemistry,* **79,** 1285–1288.