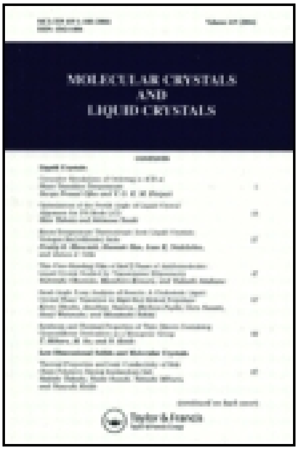

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Complex Formation of Homoionic Montmorillonites with Propylene Carbonate and Osmotic Swelling in Aqueous Electrolyte Solutions

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Homoionic montmorillonites saturated with several kinds of cations can form complexes with propylene carbonate (PC) by intercalation. The PC molecules interact with the interlayer cations by way of H_2O molecules between the silicate layers. The PC-montmorillonite complexes exhibit osmotic swelling even in aqueous electrolyte solutions. This is interpreted in terms of the formation of thick electric double-layers consisting of PC and H_2O between the silicate layers. Although the PC molecules are gradually hydrolyzed to propylene glycol between the layers, the hydrolyzed complex also shows a similar swelling power in aqueous electrolyte solutions.

Keywords: montmorillonite; propylene carbonate; osmotic swelling; aqueous electrolyte solution; hydrolysis; propylene glycol

INTRODUCTION

Montmorillonite can form complexes with various organic compounds by intercalation. The interlayer cations of montmorillonite play an important role in the formation of the organic complexes; the cation-dipole interactions influence stabilization of the complexes, and water molecules associated with the interlayer cations also influence the orientation of interlayer organic molecules[1-4]. Although Na- and Li-montmorillonites swell with water infinitely, they show limited swelling in electrolyte solutions such as seawater. Kondo found that propylene carbonate (PC) formed complex with montmorillonite and activated the osmotic swelling of montmorillonite, even in aqueous electrolyte solutions (5).

In this study, we have investigated the interactions between various homoionic montmorillonites and PC, and a possible mechanism of the osmotic swelling in electrolyte solutions is proposed.

EXPERIMENTAL

The PC-complexes were prepared by mixing homoionic montmorillonites saturated with Li^+, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, or Ni^{2+} ions with different amounts of PC using an agate mortar at room temperature. The mixing ratios examined were in the range of 15-45% PC by weight for homoionic montmorillonites. Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku diffractometer with Co$K\alpha$ radiation. Fourier transform infrared (FTIR) absorption spectra were measured using a Perkin Elmer Paragon 1000 spectrometer on the film samples deposited on the surface of Si (100) wafer (0.4 mm in thickness): homoionic montmorillonites were deposited on the Si wafer from the dispersions in water or propyl alcohol (PA); the complexes were formed by adding PC onto the films and drying at temperatures of 70 - 105 °C for 60 min.

The complexes containing 45 wt.% PC were aged in a sealed glass tube for 30 days at room temperature or at 70 °C to investigate the stability against hydrolysis. The hydrolyzed products of the PC-montmorillonite with water were analyzed by gas chromatography (Simadzu GC-14B). Swelling powers of PC-montmorillonite complexes were measured in accordance with the standard method of Japan Pharmacopeia's Swelling Power Test of Bentonite; the expanded apparent volumes of 2.0 g of PC-complexes were measured in 100 ml of NaCl solutions with concentrations in a range of 0.1 to 2.0 M.

RESULTS AND DISCUSSION

Complex formation

Homoionic montmorillonites saturated with monovalent and divalent cations with large polarizing powers (Z/R) formed PC-complexes with basal spacings larger than 19 Å corresponding to bi-layer of the interlayer PC molecules. Montmorillonites with small polarizing-power interlayer cations such as K- and NH_4 formed complexes with spacings of 14 Å with monolayer PC molecules.

Figure 1 shows the C=O frequencies observed by FTIR on the complexes as a function of the polarizing power of the interlayer cations. The C=O frequency showed a red-shift upon the complex formation, and the magnitude of the shift increased with the increase of the polarizing power of the interlayer cations. Highly dehydrated samples were prepared by the treatment of montmorillonite with PA prior to the formation of PC-complexes, which showed the largest red-shifts as shown in Figure 1. Evidently, the PC molecules coordinate to the interlayer cations by the C=O groups through water molecules, that are strongly bound by the interlayer cations. A schematic arrangement of water and PC molecules around the interlayer cations is shown in Figure 2 for different degrees of dehydration. 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 [6] .

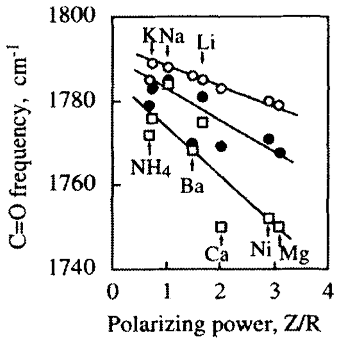

FIGURE 1 The C=O frequency of the complexes measured after different heat treatments as a function of the polarizing power of the interlayer cations: ○ heated at 70 °C for 60 min; ●, heated at 105 °C for 60 min; □, dehydrated with propyl alcohol prior to the formation of the complex, and heated at 105 °C for 60 min.

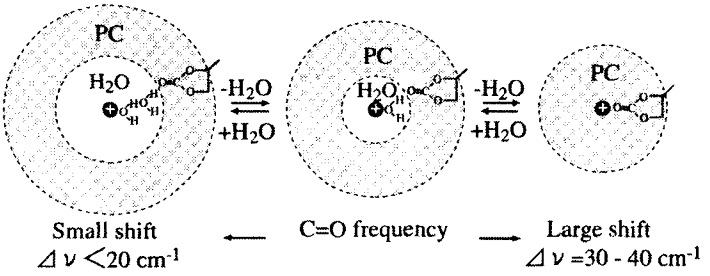

FIGURE 2 Schematic structural model of the arrangements of water and PC molecules around the interlayer cations.

Swelling properties in electrolyte solutions

The Na-montmorillonite containing 45 wt.% PC was mixed with NaCl solutions twice as large as the complexes by weight. The PC-complexes swelled in the solutions immediately, and the basal spacings were measured after standing for 0.5 h for equilibrium. Figure 3 shows the basal spacings of the PC-complexes swelled in NaCl solutions of different concentrations. The basal spacings were compared with those reported by Norrish and Quirk on Na-montmorillonite in NaCl solutions [7]. Na-montmorillonite showed osmotic swelling in NaCl solutions with concentrations [NaCl] < 0.3 M, where the basal spacings are > 40 Å. In the presence of PC, the osmotic swelling range is expanded to [NaCl] < 0.75, where the basal spacing jumped to 45 Å from 19 Å.

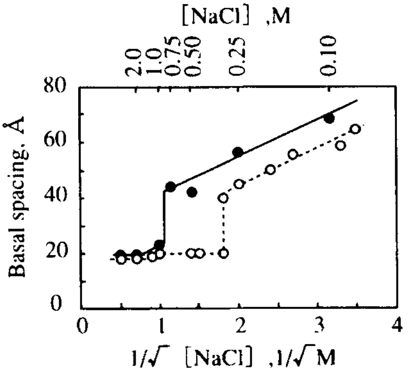

FIGURE 3 The basal spacings of Na montmorillonite with (●) and without (○) the presence of PC in NaCl solutions with different concentrations.

The osmotic swelling behavior of the PC-complexes in electrolyte solutions can be explained as follows: when the swelling behavior of montmorillonite moves from the limited to the osmotic swelling range, the basal spacing expands from 20 to 40 Å. At large spacings, the interactions between silicate layers and the cations are much weakened. The driving force for the intercalation of solvent molecules into the interlayer space of montmorillonite is primarily due to the solvation of the interlayer cations. The interactions become stronger when the cations with larger polarizing powers are combined with solvents with greater electron-donor ability. Gutmann related the electron-donor ability of a solvent as the donor number, DN [8]. It is defined as the negative enthalpy of reaction of a base with the Lewis acid antimony pentachloride, $SbCl_5$. Water molecules with the DN of 18.0 coordinate with interlayer cations to form the primary hydration shell. PC molecules have a lower DN (DN= 15.3) and coordinate the cations through the hydration shell. PA molecules have a DN of 18.0, which is comparable to that of water and can replace the water molecules around the cations.

In the hydration shell, bifunctional water molecules can act as electron donors and electron acceptors. Water molecules strongly bound to the cations act as acceptors to water and PC molecules. The basal spacing of the complex can be as large as 19 Å, which is nearly in the critical range for osmotic swelling. In aqueous electrolyte solutions, water molecules, which are stronger donors than PC, would be further adsorbed to the cations to form a larger hydration shell inside the PC coordination shell. If the basal spacing would increase over a critical value of about 20 Å by the adsorption of water, montmorillonite would show osmotic swelling. We have reported a very similar swelling behavior of formamide-montmorillonite complexes in polar liquids, which can be systematically explained in terms of DNs [9].

Hydrolytic stability of complexes

PC is hydrolyzed to propylene glycol (PG) in acidic as well as in alkaline aqueous solutions [10]. It is well known that the water molecules bound by the interlayer cations of montmorillonite act as weak acids or proton-donors, and enhance the decomposition and hydrolysis of organic compounds between the silicate layers [11]. PC molecules between the silicate layers also suffer the hydrolysis to PG. Figure 4 shows the amount of PG formed by the hydrolysis in the PC-montmorillonite complexes after aging at 70 °C for 30 days. The amount of PG formed apparently increased with the increase of the polarizing power of the interlayer cations of the complexes. However, the amount of interlayer water bound by the complex also increased with the polarizing power as shown in Figure 4. The amount of PG formed is directly proportional to the amount of interlayer water available for hydrolysis. Aging the complexes at room temperature hardly hydrolyzed PC.

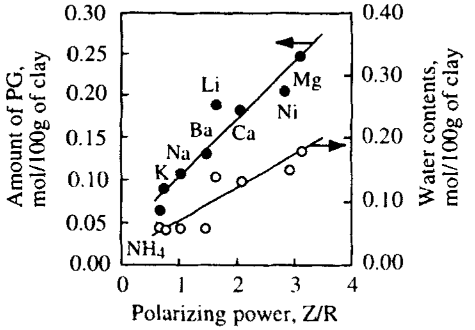

FIGURE 4 The relationship between the amount of PG formed after aging the PC-montmorillonite complexes at 70 °C for 30 days and water content as a function of the polarizing power of the interlayer cations.

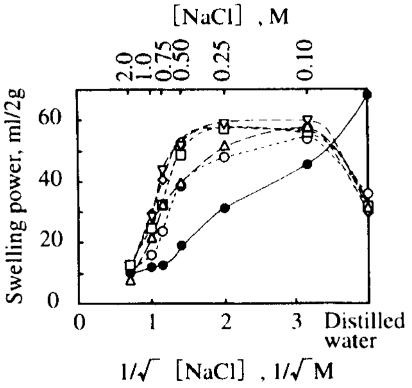

FIGURE 5 Swelling powers of PC/PG-montmorillonite complexes in NaCl solutions with different concentrations in comparison of the swelling behavior of Na-montmorillonite. ●; Na-montmorillonite, △; PC, ○; PG, and PC/PG (molar ratio) = ▽, 3/1; ◇, 1/1; □, 1/3.

Although we observed little hydrolysis of PC-montmorillonite complexes at room temperature, the effect of the hydrolysis on the swelling properties must be studied for industrial applications of the complexes after a long term storing. Figure 5 shows swelling power of the Na-montmorillonite complexes containing PC/PG mixtures in different ratios in NaCl solutions with different concentrations. It is interesting to note that PG-montmorillonite complex showed a swelling power similar to PC-complex, and all of the PC/PG complexes showed a rapid increase in the swelling power at [NaCl] ≦ 1.0 M. It is very likely that the PC-complex can keep its swelling power even after hydrolysis by a long term storing. The complexes are expected to be useful industrial material as a rheology-controlling agent for various electrolyte solutions.

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