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Intercalation of a Triethylenetetraminated Cyclodextrin by Na-, Ca-, Zn-, and Cu-Montmorillonites

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The uptake of mono[6-[(8-amino-3,6-diazaoctyl)amino]-6-deoxy]-β-cyclodextrin (CDtrien) by Na-, Ca-, Zn-, and Cu-montmorillonites has been examined at 25 °C. All of the minerals form only one intercalated phase in which the CDtrien molecules are arranged as a bilayer with their cavity axes perpendicular to the silicate layers. The modes of intercalation for Na- and Ca-montmorillonites are explained differently by an ion exchange of the interlayer Na^+ ions with the divalent cationic forms of CDtrien and by the formation of CDtrien$(H_2O)_2$-Ca complexes, respectively. The intercalation by Zn- and Cu-montmorillonites proceeds by complexation at low uptakes and by the combined modes of ion exchange and complexation at higher loadings.

Inclusion phenomena have aroused increasing interest in the field of organic and inorganic chemistry, but little attention has been paid to the complexation of two or more kinds of host components. Recently, we have prepared several intercalates of layered montmorillonites and zirconium phosphate with α-, β-, and γ-cyclodextrins and their derivatives containing methoxyl or 2-aminoethylamino (en) substituents.[1–5] Some models have been proposed for the arrangement of intercalated cyclodextrin molecules in the interlayer space of the layered crystals. It was also suggested that a family of cyclodextrin intercalates may be useful as artificial enzymes, solid supports in gas or liquid chromatography and as micro-encapsulating agents of unstable substances. In order to develop these functional possibilities, further studies would be required for similar intercalates with cyclodextrin derivatives having longer chain or polyfunctional substituents. Cyclodextrins functionalized with polyamines interact with such metal ions as Cu^{2+} or Zn^{2+} in aqueous solution and the resultant cyclodextrin–metal complexes act as a metal enzyme model endowed with specific metal-substrate binding interaction.[6] If similar complexes are formed in the interlayer space of Cu- or Zn-monlmorillonite, any intercalation effect may be added to their catalytic properties.

We have, thus, attempted to prepare the intercalates of montmorillonite with mono[6-[(8-amino-3,6-diazaoctyl)amino]-6-deoxy]-β-cyclodextrin (CDtrien). This paper reports on the intercatation behavior of CDtrien for Na-, Ca-, Zn-, and Cu-montmorillonites.

Experimental

The Na-, Ca-, Zn-, and Cu-montmorillonite samples used were the same as those used in the preceding studies.[2–5] CDtrien was prepared by a manner similar to that reported for mono[6-(2-aminoethylamino)-6-deoxy]-β-cyclodextrin (CDen).[1,5] β-CD was tosylated with 0.5 equivalent of *p*-toluenesulfonyl chloride in dry pyridine at 5 °C for 2 days. The resulting mono[6-*O*-(*p*-toluenesulfonyl)]-β-CD (CDts) was dissolved in water and recrystallized. The CDts was reacted with triethylenetetramine (trien) at 70 °C for 5 h under nitrogen atmosphere. The crude product was purified by chromatography, using a carboxymethylcellulose column with 0.1 mol dm^{-3} ammonium hydrogencarbonate as an eluent, followed by repeated evaporation of the elute in the presence of a small amount of ammonia, and CDtrien was obtained in a 17% yield based on CDts. The montmorillonite sample was soaked in an aqueous solution containing various amounts of CDtrien at 25 °C for 10 days, centrifuged, fully washed with water, and air-dried at 40 °C.

Results

The uplakes of CDtrien for Na-, Ca-, Zn-, and Cu-montmorillonites are plotted against the amount of CDtrien added in Fig. 1, along with the amount of metal ion released into solution in the intercalation process. Figure 2 shows the variation of the CDtrien concentration and pH of the equilibrated solution in the uptake process.

The interlayer spacings of the dried forms of the resulting complexes were determined from the 001

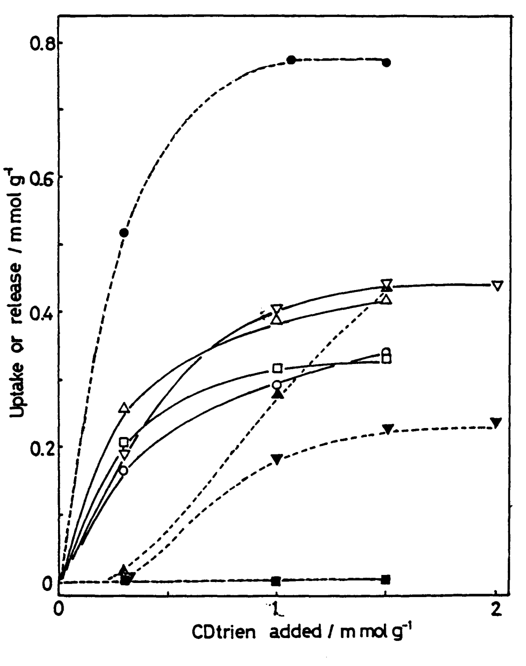

Fig. 1. CDtrien taken up by (○) Na-, (□) Ca-, (△) Zn-, and (▽) Cu-montmorillontes and release of (●) Na^+, (■) Ca^{2+}, (▲) Zn^{2+}, and (▼) Cu^{2+} ions as a function of CDtrien added.

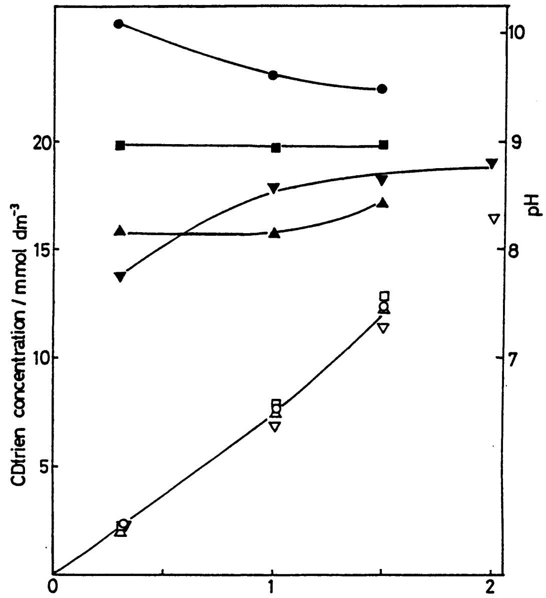

Fig. 2. Plots of the CDtrien concentration (open) and pH (closed) of equilibrated solution against CDtrien added. Key as in Fig. 1.

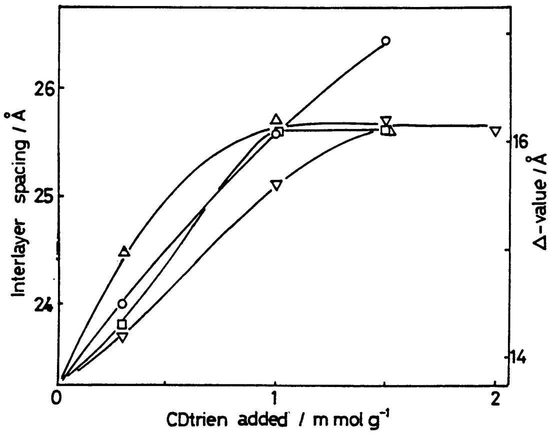

Fig. 3. Interlayer spacing or Δ value (see text) as a function of CDtrien added for the CDtrien intercalates of Na-, Ca-, Zn-, and Cu-montmorillonites. Key as in Fig. 1.

reflections in the X-ray diffraction patterns. The results are shown in Fig. 3, where the Δ values on the right ordinate indicate the thickness of the intercalated layer obtained by subtracting the thickness of the silicate layers, 9.5 Å, from the observed spacings. At a level of 0.3 mmol CDtrien added per gram of each clay, a phase with a Δ value of 14.2—14.7 Å appeared and coexisted with a small amount of its parent host phase. At a level of 1.5 mmol g^{-1}, the solid was totally converted to a single phase with a Δ value of 16.9 Å for the Na-complex and 16.1 Å for the others, and the uplake level of CDtrien became almost constant.

Table 1 summarizes the interlayer spacing and composition of intercalates of Na-, Ca-, Zn-, and Cu-montmorillonites with CDtrien at its full loadings. Our previous study[2)] revealed that the content of releasable metal ions in Na-riched montmorillonite was comparable to that of interlayer cations compensating the negative charge of the silicate layers, while the Cu-exchanged mineral possesses two types of copper ions, one held as interlayer ions and one adsorbed as any neutralized species on the external surface of crystals. It was also conceivably possible that the cupric ions in the latter mineral are assigned to $[CuOH]^+$ ions as well as Cu^{2+}. This assignment, however, was inconsistent with the data for the amount of cupric ion desorbed in the intercalation of CDen by the Cu-exchanged mineral. Ca- and Zn-montmorillonites also contained releasable metal ions in some amount exceeding that of interlayer cations.[5)] The excess amount of these divalent metal ions also probably exists as any neutralized species with low solubilities. The initial amounts of the interlayer cationic and the neutralized forms of metal ions in montmorillonites are thus evaluated and listed in Table 1 as v_{1i}° and v_{1e}°, respectively. In Tables 1 and 2, the sub- and superscripts are 1=releasable metal ion, 2=CDtrien, i=interlayer, e=external, °=initial, d=desorbed, and r=remaining.

Discussion

CDtrien Uptake Mechanism. As can be seen in Fig. 1, the uptake of CDtrien for Na-montmorillonite is

Table 1. Characterization of Intercalates of Na-, Ca-, Zn-, and Cu-Monmorillonites with CDtrien at Its Full Loadings

Interlayer metal ion	Interlayer spacing/ Å	Δ Value/Å	Amount of CDtrien/ mmol g^{-1} clay[a)] v_2	Amount of releasable metal ion/mmol g^{-1} clay[a)] Initial total v_1°	Initial int[b)] v_{1i}°	Initial ext[b)] v_{1e}°	Desorbed v_1^{d}	Remaining v_1^{r}
Na	26.4	16.9	0.34	0.91	0.91	0	0.77	0.14
Ca	25.6	16.1	0.33	0.74	0.54	0.20	0.02	0.72
Zn	25.6	16.1	0.42	0.66	0.54	0.12	0.44	0.22
Cu	25.6	16.1	0.44	0.63	0.54	0.09	0.24	0.38

a) Anhydrous form of clay. b) $v_{1i}^{\circ}$is the amount of exchangeable cation held as interlayer counter ions for the negatively charged silicate layers and v_{1e}° is that of adsorbed as any neutralized species on the external surface of crystals.

accompanied by the release of Na^+ ions of about twice the CDtrien uptake or more in molar amount on the entire range of CDtrien added. On the other hand, the Ca^{2+} release for Ca-montmorillonite is kept at a level as low as 0.02 mmol g^{-1}. The release of Zn^{2+} or Cu^{2+} ions from Zn- and Cu-analogues at low addition levels of CDtrien remains at an extremely low value, but increases remarkably with any further addition of CDtrien. The pK_{a_i} (i=1—4) values for trien are 3.32, 6.67, 9.20, and 9.92,[7] which are likely to be close to those for CDtrien. The uptake reaction for Na-montmorillonite takes place in the pH range of 9.5—10.1, while that for the others occurs below 9. In these two pH ranges the molecules of CDtrien would exist predominantly as $CD\text{-}NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2\text{-}NH_2$(CDtrien) and $CD\text{-}NH(CH_2)_2NH(CH_2)_2H(CH_2)_2\text{-}NH_3^+$ (CDtrienH$^+$) and as CDtrienH$^+$ and $CD\text{-}NH_2^+(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_3^+$ (CDtrien2H$^+$), respectively. The CDtrien uptake data are, thus, explained as follows: Na-montmorillonite takes up CDtrien by a two-step reaction. In the first step one mole of CDtrien is taken up as monovalent cation CDtrienH$^+$ by ion exchange with one mole of Na^+ ions. This ion exchange would be followed by the protonation of the CDtrienH$^+$ into CDtrien2H$^+$ in the interlayer medium, with an accompanying release of Na^+ and OH^- ions. On the other hand, Ca-montmorillonite intercalates neutral CDtrien molecules to form complexes with intercayer Ca^{2+} ions over the entire range of CDtrien added. Zn- and Cu-analogues also form similar complexes allow addition levels. The intercalation of CDtrien by Zn- and Cu-montmorillonites with an accompanying release of interlayer metal ion could be interpreted in terms of the combined modes of complexation and an ion exchange of Zn^{2+} or Cu^{2+}/CDtrien2H$^+$.

According to previous studies,[2,5] the neutral species on the external surface of Cu-monlmorillonite are feasibly desorbed in a CDen solution of low concentration, while those for Ca- and Zn-montmorillonites remain undissolved, even at high concentration. The dissolution of the neutral copper(II) species are probably caused by the high stability of a CDen-Cu^{2+} complex in solution. The stability constant of $10^{10.7}$ $mol^{-1}\,dm^3$ for a 1 : 1 CDen-Cu^{2+} complex in solution is comparable to $10^{10.72}$ for a 1 : 1 en-Cu^{2+} complex.[8] Therefore, the stability constants of 1 : 1 CDtrien-Cu^{2+} and 1 : 1 CDtrien-Zn^{2+} complexes would be as high as close to $10^{20.4}$ for trien-Cu^{2+} and $10^{12.1}$ for trien-Zn^{2+},[9] respectively. This leads us to predict that the extremely high stability of CDtrien-Cu^{2+} and CDtrien-Zn^{2+} complexes would cause not only a dissolution of the copper(II) and zinc species adsorbed on the external surface of montmorillonite crystals, but also the succeeding desorption of interlayer Cu^{2+} and Zn^{2+} ions by an ion exchange with ionized CDtrien. The amount of interlayer metal ion desorbed in the intercalation process, $v_{\mathrm{li}}{}^{\mathrm{d}}$, can be estimated by $v_{\mathrm{li}}{}^{\mathrm{d}}=v_{\mathrm{l}}{}^{\mathrm{d}}-v_{\mathrm{le}}{}^{\circ}$ for the case of $v_{\mathrm{l}}{}^{\mathrm{d}}>v_{\mathrm{le}}{}^{\circ}$. Results are listed in Table 2. The $v_{\mathrm{li}}{}^{\mathrm{d}}$ data give an expected value for the amount of the ionized form of CDtrien taken up by ion exchange. The v_2 value of 0.34 mmol g^{-1} for the sodium complex is close to an expected value of 0.385 mmol g^{-1} for the ion exchange of two moles of interlayer Na^+ ion with one mole of divalent cation CDtrien2H$^+$. Furthermore, the observed value of 0.42 mmol g^{-1} of CDtrien intercalated by Zn-montmorillonite is more than the 0.32 mmol expected for the interlayer ion exchange of Zn^{2+}/CDtrien2H$^+$ and much less than 0.64 CDtrien mmol g^{-1} expected for that of Zn^{2+}/CDtrienH$^+$. This fact indicates that CDtrien acts as a divaent cation CDtrien2H$^+$ for ion exchanges with interlayer Zn^{2+} ions in montmorillonite crystals. A similar mechanism would also be applicable to Cu-montmorillonite. These considerations enabe us to evaluate the amounts of both neutral and ionized forms of intercalated CDtrien (Table 2).

Arrangement of Intercalated CDtrien. The interlayer thickness (Δ value) of the CDtrien-montmorillonite complex is independent of the interlayer metal ions, except for the sodium complex: the Δ value of the sodium complex is also only slightly larger than that of the others. The Δ value of 16.1 Å for the calcium, zinc, and copper(II) complexes is in good agreement with twice the 8.0 Å for the van der Waals thickness of torus-shaped parent molecule. This suggests that the CDtrien molecules would be arranged as a bilayer with their cavity axes perpendicular to the silicate layers and with trien groups alternatively pointing up- and downward. The lateral packing of the CDtrien mole-

Table 2. Parameters for the Full Uptakes of CDtrien by Na-, Ca-, Zn-, and Cu-Montmorillonites

Inter-layer metal ion	Amount of inter-layer metal ion released/mmol g^{-1} $v_{\mathrm{li}}{}^{\mathrm{d}}$	Amount of CDtrien/mmol g^{-1}[a)] Total	Neutral form	Divalent cationic form	ξ/Å[b)]	Mode of intercalation[c)]
Na	0.77	0.34	0 (0)	0.34(100)	5.1	E
Ca	0	0.33	0.33(100)	0 (0)	5.3	C
Zn	0.32	0.42	0.10(23.8)	0.32(76.2)	2.9	E+C
Cu	0.15	0.44	0.29(65.9)	0.15(34.1)	2.5	E+C

a) Contents in mol% are given in parentheses. b) See text. c) E, ion exchange; C, complexation.

cules in the interlayer may be drawn by the following estimation. If we assume that CDtrien molecules, each 15.4 Å in diameter, are hexagonally packed at a distance of $15.4+\xi$ in Å (center to center), the effective area per molecule is given by $(\sqrt{3}/2)\,(15.4+\xi)^2$ in $Å^2$. As the surface area of one face of the unit cell of montmorillonite is estimated as being 46 $Å^2$,[10] the CDtrien content, v_2, is represented by $v_2=2\times46/\{(\sqrt{3}/2)(15.4+\xi)^2w_0\}$, where w_0 is the unit-cell weight of the host montmorillonite. The ξ values evaluated using the v_2 data are listed in Table 2. Referring to the structural characteristics of well-known complexes of Ca, Zn, and Cu(II),[11] the interlayer Ca^{2+}, Zn^{2+}, and Cu^{2+} ions in the CDtrien intercalates are likely to form coordination groups $[Ca(trien)(H_2O)_2]^{2+}$, $[Zn(trien)]^{2+}$, and $[Cu(trien)]^{2+}$ which are octahedral, tetrahedral and square planar in the atomic configuration, respectively, as illustrated in Fig. 4(a). Thus, models are proposed for the packing of CDtrien moecules in the interlayer space of montmorillonite, as exemplified for the copper complex in Fig. 4(b). The order of the CDtrien content in the resulting complexes is $\mathrm{Ca}\sim\mathrm{Na}<\mathrm{Zn}\sim\mathrm{Cu}$. This may be tentatively explained as follows. The relation of $\mathrm{Ca}<\mathrm{Cu}$ is probably due to the octahedral coordination group $[Ca(trien)(H_2O)_2]^{2+}$ in the calcium complex being more voluminous than the planar $[Cu(trien)]^{2+}$ in the copper one. The v_2 value for the sodium complex is as small as that for the calcium one, suggesting that, in the sodium complex, the trien groups in divalent cationic forms woud largely attract water molecules which would results in the loose packing of CDtrien molecules. Although three quarters of the CDtrien molecules in the zinc complex exist in the same form as in the sodium complex, the CDtrien content in the former is close to that in the copper complex. A possible explanation of this may be that the uptake of CDtrien by Zn-monlmorillonite occurs initially by complexation, followed by the release of Zn^{2+} ion induced by the ionization of the trien group in the interlayer space.

Previously, we reported the CDen intercalates of Cu- and Zn-montmorillonites in which the CDen molecules form a bilayer with a thicknesses of 23.9 or 25.2 Å. The bilayered structure was attributed to a dimerization of pairs of 1 : 1 $CDen(H_2O)_2$-Cu^{2+} or CDen-$(H_2O)_2$-Zn^{2+} complexes with a tail-to-tail arrangement in the interlayer space. The present observations, on the other hand, indicated that the molecules of CDtrien are also placed as a bilayer, but that the bilayered molecules are in contact with each other in

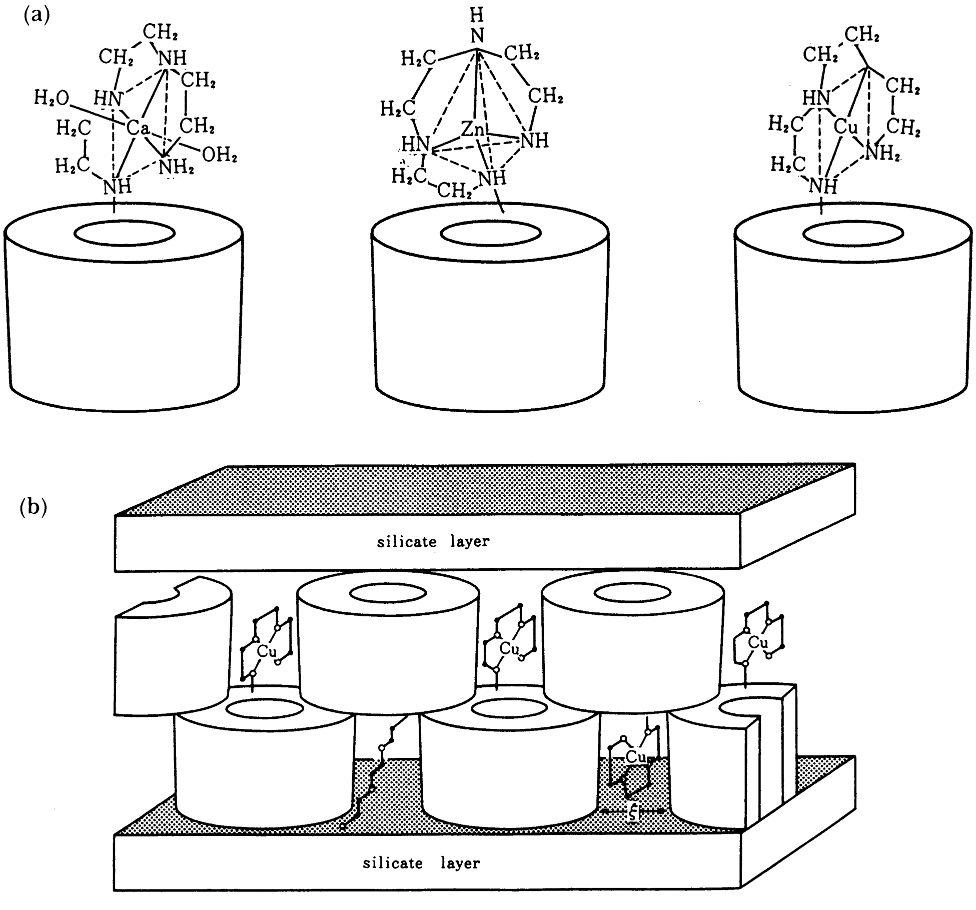

Fig. 4. Models proposed for (a) the atomic configuration of $CDtrien(H_2O)_2$-Ca^{2+}, CDtrien-Zn^{2+}, and CDtrien-Cu^{2+} complexes in montmorillonite and (b) the packing of CDtrien molecules in the interlayer space of Cu-montmorillonite. ●, C; O, N.

the van der Waals distance. The distinct difference between the thicknesses of the cyclodextrin layers may be explained by referring to Fig. 4: Cu^{2+} or Zn^{2+} ions make a complex with the tail of CDtrien or CDen, as shown in Fig. 4(a). In the present case, the tails and the bodies of CDtrien-Cu^{2+} or CDtrien-Zn^{2+} complexes are arranged in an interfingered manner, as shown in Fig. 4(b), while they are faced and dimeraized in the previous case of CDen. The dimerization in the CDen intercalates is essentially due to a hydrogen bond by which one of the two water molecules associated with one CDen molecule is linked to one of the seven primary hydroxyl groups in the other CDen molecule faced.

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