

Tsuyoshi Kijima, Michiko Kobayashi and Yoshihisa Matsui\*  
National Institute for Research in Inorganic Materials,  
Niiharigun, Ibaraki, 305 Japan  
\*Department of Agricultural Chemistry, Shimane University,  
Nishikawazu, Matsue, 690 Japan

**ABSTRACT.** The uptake reaction of Cu(II)-montmorillonite with mono-(6- $\beta$ -aminoethylamino-6-deoxy)- $\beta$ -cyclodextrin (CDen) has been examined at 25 °C. The CDen molecules in their neutral or cationic forms are taken up by forming complexes with the interlayer Cu(II) ions ( $\text{Cu}_{\text{int}}$ ) and by displacing protons at the clay surface. At low uptakes of CDen, 1:1 complexes of CDen with  $\text{Cu}_{\text{int}}$  are intercalated as a monolayer of 13.7 Å in thickness, with their opening faces parallel to the interlayer surface. At higher contents, the CDen- $\text{Cu}_{\text{int}}$  complexes are more voluminously packed to form two intercalated phases with larger spacings until a bilayer of 23.9 Å in thickness is formed. The uptake by the mode of ion exchange proceeds increasingly at the intermediate uptake stage. At higher levels, however, this additional uptake is decreased rapidly due to the increase in the pH of solution, resulting in a maximum in the curve of CDen uptake against CDen added.

## 1. INTRODUCTION

The clay mineral montmorillonite is made up of negatively charged layers with a typical composition of  $(\text{Al}, \text{Fe}, \text{Mg})_{2-3}(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2$  and interlayer cations compensating the positive charge deficiency of the silicate layers [1]. Due to the high expansibility of the layers, the clay mineral intercalates with a variety of organic compounds. Cyclodextrins are cyclic oligosaccharides of D-glucopyranose. They possess a cylindrical cavity capable of including various molecules, together with catalytically active hydroxyl groups. Therefore, the cyclic dextrins and their derivatives are useful as micro-encapsulating agents for stabilizing volatile or toxic substances and as a model of enzymes such as chymotrypsin and penicillinase [2].

Various classes of compounds, including montmorillonite and cyclodextrin, are known to serve as host compounds having several types of inclusion spaces, such as three-dimensional cages, single or parallel channels and layers [3]. In spite of the variety of host compounds, little attention has been paid to the possible complexation of two or more host components of different kinds: all inclusion

compounds so far reported use a single component as the host structure [2]. However, there is a possibility that the layered clay mineral complexes with any cyclodextrin molecule to form a combined host compound.

A preliminary experiment showed that no complex is formed between Cu(II)-montmorillonite and  $\beta$ -cyclodextrin. Attempts were thus made to form complexes of layered montmorillonite with cyclodextrin derivatives. This paper reports the complexation behavior of Cu(II)-montmorillonite towards mono-(6- $\beta$ -amino ethylamino -6-deoxy)- $\beta$ -cyclodextrin (CDen). The CDen is a derivative of  $\beta$ -cyclodextrin, in which the 1,2-diamino-ethane group is attached to a primary alcohol group on the narrow side of the truncated cone-shaped cyclodextrin molecule. The structural properties of the product formed at the final uptake stage were already discussed in the previous paper [4].

## 2. EXPERIMENTAL

CDen was prepared by the same manner as described in ref. 5. The montmorillonite with a chemical composition ( $\text{Ca}_{0.09}\text{Na}_{0.16}\text{K}_{0.03}$ ) ( $\text{Al}_{1.48}\text{Fe}_{0.13}\text{Mg}_{0.40}$ ) [ $\text{Si}_{3.99}\text{Al}_{0.01}$ ]  $\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$  (from Tsukinuno mine, Yamagata, Japan) was placed in a 1.0 M  $\text{CuCl}_2$  solution at 25°C for 10 days to exchange the interlayer cations with Cu(II) ions. The product was fully washed with hot water, centrifuged and lyophilized. The Cu(II) exchanged mineral was soaked in an aqueous solution containing varying amounts of CDen at 25°C for 10 days, centrifuged, and air-dried at 40°C. The pH of the supernatants was measured by a Toa autotitrator. The amount of cupric ion released to the solution as well as that in the starting solid was determined by atomic absorption analysis. X-ray diffraction pattern was taken with a Nippon-Denshi diffractometer at a rate of  $1/2^\circ \text{ min}^{-1}$  using  $\text{Fe-K}_\alpha$  rays. Thermogravimetry (TG) was made with a heating rate of  $10^\circ \text{C min}^{-1}$ . The uptake amount of CDen was determined as difference between the observed weight losses for the resulting and the starting solids in TG.

## 3. RESULTS AND DISCUSSION

The CDen uptakes are plotted against the amount of CDen added in Figure 1. The basal spacings of the wetted and the dried forms of the resulting CDen-Cu(II)-montmorillonite complexes were determined from the (001) reflections in their X-ray diffraction patterns. The results are summarized in Figure 2, where  $\Delta$  values on the right ordinate were obtained by subtracting 9.5 Å (the assumed thickness of the aluminosilicate layer)[1] from the observed basal spacings. At a level of less than 0.8 mmol CDen added per gram of clay, a phase with a  $\Delta$  value of 13.7 Å and two other phases with larger interlayer spacings formed successively, all of which coexisted with the parent host phase. At higher levels, the solid was totally converted to a single phase with a  $\Delta$  value of 23.9 Å and the CDen uptake curve showed a maximum, immediately followed by a plateau with a value of 0.58 mmol  $\text{g}^{-1}$ . Among the four phases

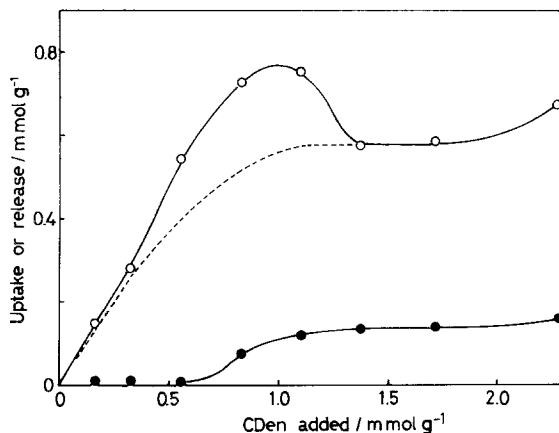


Figure 1. CDen taken up (O) by Cu-montmorillonite and cupric ions released (●) as a function of CDen added.

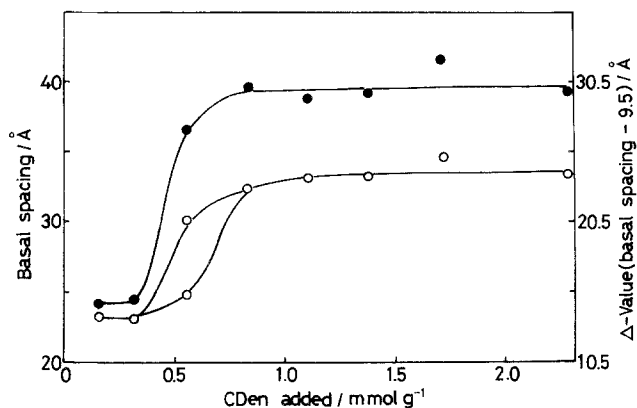


Figure 2. Basal spacing or  $\Delta$ -value (see text) variation of the dried (O) and the wetted (●) forms of CDen-Cu-montmorillonite as a function of CDen added.

characterized by their interlayer spacings, the 13.7 and 23.9 Å phases will be denoted as complexes I and II, respectively.

The latter half uptake of CDen was accompanied by the release of cupric ion, with a maximum value of 0.144 mmol g<sup>-1</sup> (Figure 1). This value was in good agreement with the difference of 0.145 mmol g<sup>-1</sup> between an observed value of 0.691 mmol g<sup>-1</sup> for the cupric content in the Cu(II)-montmorillonite sample used and 0.546 mmol g<sup>-1</sup>, estimated from the composition of its aluminosilicate layer. This suggests that the parent host phase possesses two types of Cu(II) with different feasibilities of elution, one (0.547 mmol g<sup>-1</sup> in amount) being strongly held as interlayer counter ions for the negatively charged silicate layers and

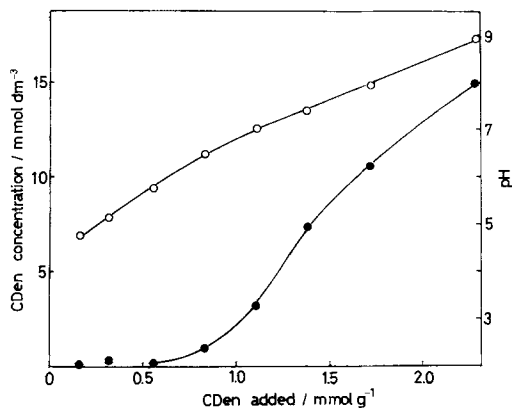


Figure 3. Plots of the CDen concentration (●) and pH (○) of equilibrated solution against CDen added.

one ( $0.144 \text{ mmol g}^{-1}$ ) being adsorbed excessively as any neutralized species on the external crystal surface. These two types of Cu(II) ions will be denoted as  $\text{Cu}_{\text{int}}$  and  $\text{Cu}_{\text{ex}}$ , respectively.

Figure 3 plots the CDen concentration and pH of equilibrated solution against the amount of CDen added. It is interesting to note that the release of Cu(II) commences to rise at the same addition level of CDen as the CDen concentration in equilibrated solution does. According to Matsui et al. [5], CDen forms highly stable complexes with Cu(II) in an aqueous solution. This supports such a suggestion that an increase in the CDen concentration in solution would induce the liberation of cupric ion from the solid phase and the subsequent formation of CDen-Cu(II) complexes in solution until the  $\text{Cu}_{\text{ex}}$  ions with high feasibility of elution are completely released. At a level of  $1.0 \text{ mmol g}^{-1}$ , the CDen uptake has a maximum (Figure 1) and the pH of the equilibrated solution is 6.7 (Figure 3). This value ( $=\text{pH}_C$ ) is fairly close to the average  $\text{pK}_a$  ( $=7.4$ ) of the  $\text{pK}_{a1}$  and  $\text{pK}_{a2}$  values for the NH and  $\text{NH}_2$  groups of CDen which are 5.6 and 9.2, respectively [5]. The molecules of CDen exist predominantly as  $\text{CD-NH}(\text{CH}_2)_2\text{NH}_3^+$  near  $\text{pH}=\text{pK}_a$  and as neutral species at higher pH.

The above data and considerations suggest that the observed uptake of CDen is equal to the sum of the uptake due to the complexation of CDen with  $\text{Cu}_{\text{int}}$  and that due to a second adsorption. The former contribution would be represented roughly by a broken line in Figure 1. The second adsorption could be ascribed either to the formation of CDen -  $\text{Cu}_{\text{ex}}$  complexes at the crystal surface or to the ion exchange of positively charged CDen with the protons produced by the dissociation of the SiOH or AlOH species that exist at the crystal surface. The former possibility, however, appears to be improbable because at a level of 0.5 to  $1.0 \text{ mmol}$  CDen added the content of the CDen adsorbed by the second mode shows a tendency to increase in the reverse of that of  $\text{Cu}_{\text{ex}}$  ion. The latter mechanism, on the other hand, accounts for the peak characteristic of the second adsorption curve. A lowering of the proton concentration in solution would favour the dissociation of the surface SiOH

TABLE I. Characterization of Cu-mont and two CDen-Cu-mont complexes (= complexes I and II) obtained at addition levels of 0.321 and 1.38 mmol CDen per gram of clay (mont = montmorillonite).

	interlayer <sup>a</sup> [Cu <sub>int</sub> ]	Content/mmol g <sup>-1</sup> clay			CDen		Water obs	Ratio [CDen] <sub>obs</sub> [Cu <sub>int</sub> ]		Δ-value/Å		Type of complex
		Cu <sup>2+</sup> ions		total	obs	calc		obs	obs	calc		
		surface excess <sup>a</sup> [Cu <sub>ex</sub> ]									obs	
Cu-mont	0.547	0.144	0.691	—	—	4.4	—	4.6				
Complex I	0.547	0.134	0.681	0.28	0.298	5.5	0.51	13.7	13.5	monolayer		
Complex II	0.547	0.0	0.547	0.58	0.596	6.7	1.06	23.9	22.0 <sup>b</sup> 25.8 <sup>c</sup>	bilayer		

<sup>a</sup>See text. <sup>b</sup>tail-to-tail dimer <sup>c</sup>head-to-head dimer

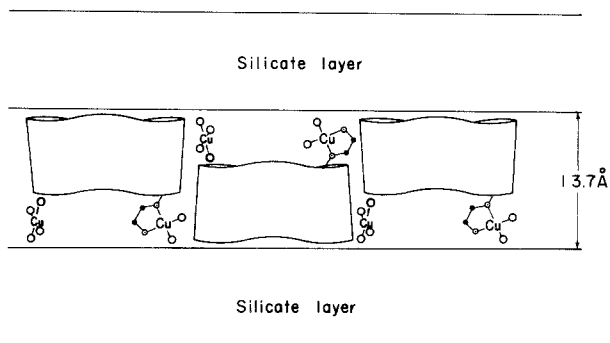


Figure 4. A model proposed for the packing of CDen molecules in the interlayer space of complex I. ●, CH<sub>2</sub> group; ⊙, NH<sub>2</sub> or NH group; ○, water molecule.

and AOH groups. Hence, the pH of solution increases as a result of an increase in the amount of CDen added, the adsorption by cation exchange would be accelerated. This tendency, however, would be counteracted by the tendency of the CDen in solution to become neutral at pH > pK<sub>a</sub>, resulting in a maximum in the total uptake curve. The difference between pH<sub>c</sub> and pK<sub>a</sub> might be related to the properties of solution, e.g., ionic strength.

Table I summarizes the uptake parameters, i.e., the CDen and cupric contents and basal spacings for complexes I and II. The ESR spectrum of complex II showed that the Cu<sub>int</sub> ion forms a coordination group [Cu(II) (en)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> (en; aminoethylamino group) with its square plane perpendicular to the silicate layer [4]. A similar observation was made on complex I. The ESR parameters for complex I are g<sub>⊥</sub> = 2.078, g<sub>∥</sub> = 2.263, A<sub>⊥</sub> ≈ 0 and A<sub>∥</sub> = 182 G. The data for complex II listed in table I were also reported previously [4]. These data, in combination with the ESR result, suggested that pairs of 1:1 complex of Cu(II) with CDen are dimerized with tail-to-tail or less likely head-to-head arrangement in the interlayer space of complex II. A similar consideration for complex I enables us to propose that CDen molecules with a coordination group [Cu(II) (en) (H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> are intercalated as a monolayer with their

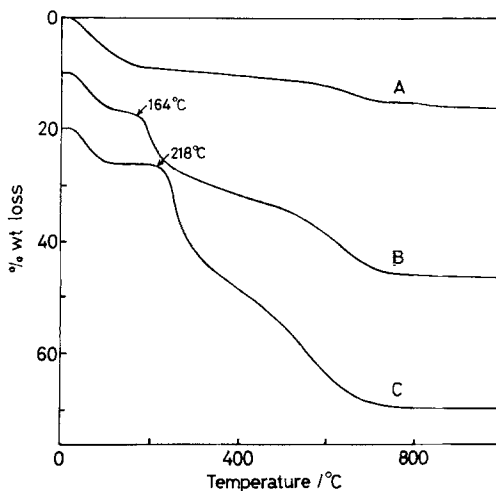


Figure 5. TG curves for (A) Cu-mont, (B) complex I, and (C) complex II with a heating rate of  $10^{\circ}\text{Cmin}^{-1}$ . Abbreviations as in TABLE I.

opening faces parallel to the silicate layers of montmorillonite, as illustrated in Figure 4. By using the same bond parameters as described previously [4], the vander Waals thickness of the monolayered CDen-Cu(II) complex was calculated to be  $13.5 \text{ \AA}$ , which is in good agreement with the observed value. On the assumption that the CDen-Cu(II) complexes are hexagonally close-packed in the monolayer, the CDen content can be evaluated as  $0.298 \text{ mmol g}^{-1}$  of clay. This value is fairly close to  $0.28 \text{ mmol g}^{-1}$ , observed for the sample consisting of complex I and a small amount of the parent host phase. The molar ratio of CDen to  $\text{Cu}_{\text{int}}$  in the same sample is 0.51, indicating that each half of the  $\text{Cu}_{\text{int}}$  ions form coordination groups  $[\text{Cu(II)}(\text{en})(\text{H}_2\text{O})_2]^{2+}$  or  $[\text{Cu(II)}(\text{H}_2\text{O})_4]^{2+}$  in the interlayer space. The molecular packing model for complex I suggested above is also consistent with the fact that the effective area of CDen molecule ( $205 \text{ \AA}^2$ ) is comparable to that of  $\text{Cu}_{\text{int}}$  ion or  $224 \text{ \AA}^2$ , estimated using  $0.205$  for the number of  $\text{Cu}_{\text{int}}$  ion per unit cell and  $46 \text{ \AA}^2$  for the surface area of one face of the unit cell.

Figure 5 shows the TG curves for complexes I and II, together with that for the Cu(II)-montmorillonite sample used. For these three samples, the weight loss observed at temperatures below  $150^{\circ}\text{C}$  is due to the desorption of water. The weight losses at higher temperatures for both complexes can be correlated with the desorption of CDen and the condensation of the hydroxyl groups of the parent host phase. It is interesting to note that the degradation temperature at  $218^{\circ}\text{C}$  for complex II is much higher than the  $164^{\circ}\text{C}$  for complex I. This suggests that the CDen molecules with dimeric arrangement are more strongly held in the interlayer space than those in monolayered form.

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