

Complexes of Na-, Ca-, and Zn-Montmorillonites with an Aminated Cyclodextrin

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Abstract. The uptake of mono-(6- β -aminoethylamino-6-deoxy)- β -cyclodextrin (CDen) by Na-, Ca- and Zn-montmorillonites has been examined at 25 °C. Each of the first two minerals forms only one intercalated phase in which the CDen molecules are intercalated as a monolayer, while the third yields a mixture of two intercalated phases whose interlayer spaces are occupied by mono- and bilayers of the guest molecules. Intercalation proceeds by ion exchange with the interlayer cations for the Na-complex and by forming metal-aminoethylamino chelate complexes for the others.

Key words: Montmorillonite, aminated cyclodextrin, intercalation.

1. Introduction

Recently we prepared a complex of layered Cu(II) montmorillonite with mono-(6- β -aminoethylamino-6-deoxy)- β -cyclodextrin (CDen) [1]. It was also found that the CDen molecules in their neutral or cationic forms are taken up by the formation of complexes with the interlayer Cu(II) ions and by displacing protons at the clay surface [2]. These findings aroused our interest in a comparative study on montmorillonites with other interlayer cations.

An attempt was thus made to examine the intercalation properties of CDen toward Na-, Ca-, and Zn-montmorillonites.

2. Experimental

The Na-montmorillonite sample was supplied by Kunimine Industry Co. Ltd. The Ca and Zn exchanged minerals were prepared as described previously [3]. The compositions and characteristics of these clay minerals are given in Table I. CDen was prepared in the same manner as described previously [1, 2].

Each mineral sample was soaked in an aqueous solution containing 1.0 and 2.0 mmol of CDen per gram of clay at 25 °C for 10 days, centrifuged and air-dried at 40 °C. The X-ray diffraction patterns were taken with a Nippon-Denshi diffractometer at a rate of 1/2° min⁻¹ using FeK α radiation. Silicon was used as an external standard.

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Table I. Compositions and interlayer spacings of Na-, Ca- and Zn-montmorillonites

Sample ^a		Interlayer spacing (Å)
Na-mont	$\text{Na}_{0.34}\text{K}_{0.008}\text{Ca}_{0.03}(\text{Al}_{1.60}\text{Fe}_{0.10}\text{Mg}_{0.32})[\text{Si}_{3.83}\text{Al}_{0.17}]\text{O}_{10}(\text{OH})_2 \cdot 6 \text{H}_2\text{O}$	12.6
Ca-mont	$\text{Ca}_{0.278}(\text{Al}_{1.60}\text{Fe}_{0.10}\text{Mg}_{0.32})[\text{Si}_{3.83}\text{Al}_{0.17}]\text{O}_{10}(\text{OH})_2 \cdot 10 \text{H}_2\text{O}$	14.9
Zn-mont	$\text{Na}_{0.005}\text{Zn}_{0.250}(\text{Al}_{1.60}\text{Fe}_{0.10}\text{Mg}_{0.32})[\text{Si}_{3.83}\text{Al}_{0.17}]\text{O}_{10}(\text{OH})_2 \cdot 11 \text{H}_2\text{O}$	12.3

^a mont = montmorillonite

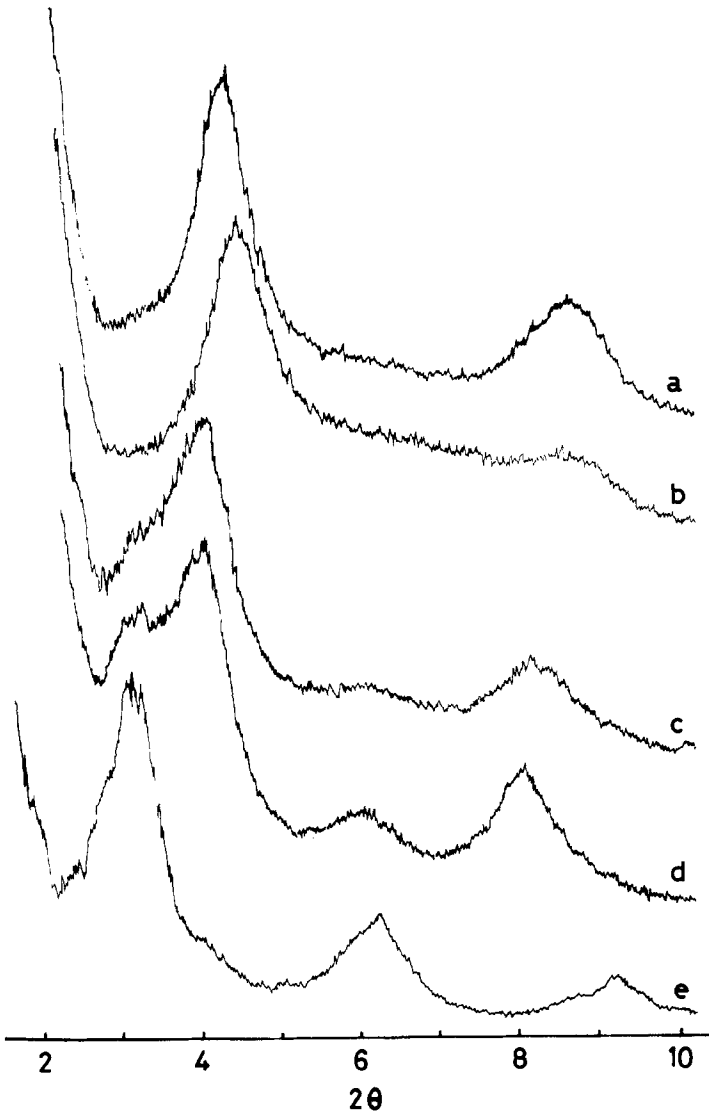


Fig. 1. X-ray diffraction patterns of Na-(a), Ca-(b), Zn-(c,d) and Cu-(e) montmorillonite complexes with CDen (FeK α radiation). CDen addition levels (mmol g⁻¹): 1.0 (a-c), 2.0 (d), 1.4 (e). The data for the Cu-complex are from [1].

Thermogravimetry was performed at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The amount of CDen taken up was determined as the difference between the weight losses for the resulting and the starting solids in TG. The amounts of interlayer cations released to solution were determined by atomic absorption analysis.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the resulting solids, along with that of the CDen-Cu(II)-montmorillonite complex which has an interlayer spacing of $33.4\text{ }\text{\AA}$ [1]. Table II summarizes the intercalation parameters for the complexes obtained. Here the Δ value indicates the thickness of the intercalated layer determined by subtracting $9.5\text{ }\text{\AA}$ for the thickness of the silicate layer [1] from the observed spacing. On the assumption that the CDen molecules are placed with their cavity axes perpendicular to the inorganic sheets and hexagonally close-packed to form mono- and bilayers in the interlayer space, the CDen content can be evaluated as 0.30 and 0.60 mmol per g of clay, respectively [2]. These packing models, in combination with an assumption for the location of interlayer cations, also enable us to calculate the Δ value for each complex.

Table II. Characterization of montmorillonite-CDen complexes with various interlayer cations. The data for the Cu(II)-complex are from [2].

Inter-layer cation	Inter-layer spacing (\AA)	Δ value (\AA)		Amount of CDen/ m mol g^{-1} clay ^c		Amount of water/ m mol g^{-1} clay ^c	Amount of interlayer cation/m mol g^{-1} clay ^c		Type of arrangement
		obs.	cal.	obs.	cal.		obs.	desorbed	
Na	25.6	16.1	15.8	0.35	0.30	6.0	0.70	0.22	I
Ca	24.0	14.5	13.5	0.32	0.30	7.7	0.007	0.736	II
Zn	26.9	17.4	13.5	0.69 ^b	0.30	11	0.046	0.645	II
	34.7	25.2	22.0 ^a		0.60				III
Cu	23.2	13.7	13.5	0.28	0.30	5.5	0.01	0.681	II
	33.4	23.9	22.0 ^a	0.58	0.60	6.7	0.144	0.547	III

^a tail-to-tail dimer model

^b mixture

^c anhydrous form of clay

From the above data, some characteristics are noticed for the intercalation behavior of CDen towards montmorillonites. Each of the Na- and Ca-montmorillonites forms only one intercalated phase with an interlayer spacing of 25.6 or 24.0 \AA , while Zn-montmorillonite yields a mixture of two intercalated phases whose interlayer spacings are 26.9 and 34.7 \AA . It is also inferred that the 34.7 \AA phase for Zn-montmorillonite is a bilayered complex with structure III in Figure 2 and that the other three phases can be ascribed to monolayered phases with structures I and II. Except for the Na-complex, the amounts of cation desorbed during intercalation are much less than those of CDen taken up. This suggests that CDen molecules are taken up by ion exchange with the interlayer cation in the Na-complex and by forming metal chelate complexes in the others. It is well known that the stability constants for metal-ethylenediamine complexes increase in the order of $\text{Na} < \text{Ca} < \text{Zn} < \text{Cu}$ [4]. Thus, CDen is likely to form a bilayered intercalate only with montmorillonites

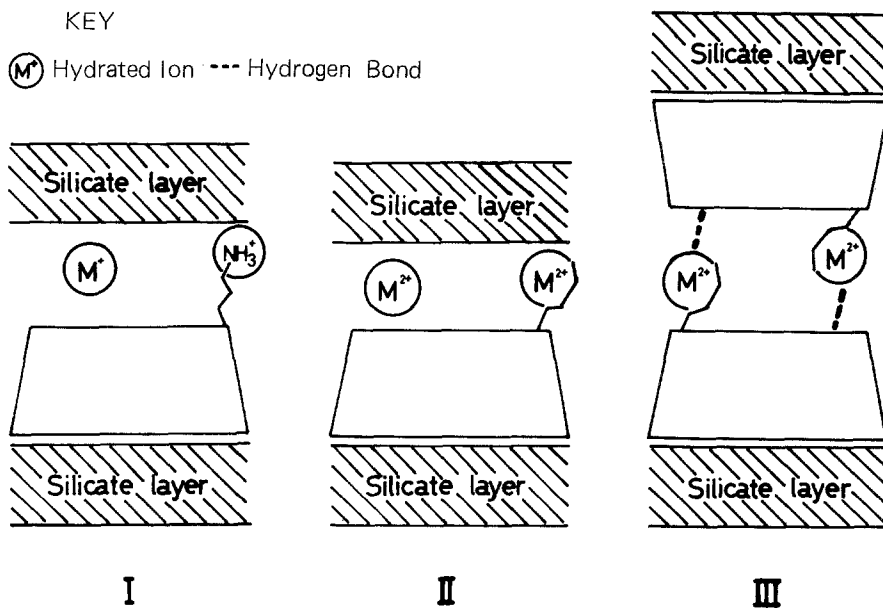


Fig. 2. Models proposed for CDen-montmorillonite formed by ion exchange of the terminal -NH_3^+ group with the interlayer monovalent cation (I) and by coordination of the aminoethylamino group to the interlayer divalent cation (II and III); M = Na, Ca, Zn, and Cu(II).

bearing interlayer cations with a high stability constant for the aminoethylamino group. In the previous report on the bilayered CDen-Cu-montmorillonite complex, we presumed that pairs of 1:1 complexes of Cu(II) with CDen are dimerized with either a tail-to-tail or, less likely, a head-to-head arrangement in the interlayer space [1, 2]. The present observation that Ca-montmorillonite forms only a monolayered complex supports the former arrangement because, if CDen molecules were dimerized head-to-head with hydrogen bonds between their secondary hydroxyl groups in the interlayer space of Cu(II)-or Zn-montmorillonite, such an arrangement would also be observable for the Ca exchanged form which takes up CDen by the same mechanism as the other two divalent forms.

References

1. T. Kijima, J. Tanaka, M. Goto, and Y. Matsui: *Nature* **310**, 45 (1984).
2. T. Kijima, M. Kobayashi, and Y. Matsui: *J. Incl. Phenom.* **2**, 807 (1984).
3. T. Kijima: *J. Incl. Phenom.* **4**, 333 (1986)
4. O. Yamauchi and M. Chiguma: *Inorganic Biochemistry* (ed. O. Yamane, H. Tanaka, and N. Kidani), Nankodo, Tokyo (1980) chap. 3.