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Complexation of Na-, Ca-, and Cu-montmorillonites with Some Parent and Methylated Cyclodextrins

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Abstract. The uptake of α-, β-, γ-, hexakis-2,6-di-O-methyl-α- (DM-α-), heptakis-2,6-di-O-methyl-β- (DM-β-) and heptakis-2,3,6-tri-O-methyl-β- (TM-β-) cyclodextrins (CD's) by Na-, Ca-, and Cu-montmorillonites has been studied at 25°C. Each of α-, DM-α-, DM-β-, and TM-β-CD's forms a complex with all of these montmorillonites in which the guest molecules are arranged as a monolayer with their open faces parallel to the silicate sheet of montmorillonite. On the other hand, γ-CD is intercalated only by the Na form and β-CD cannot be taken up by any of the clays used. The interlayer spacing of the α-CD complex varies from 18.0 to 21.5 Å with replacement of the interlayer cation, but those of the methylated α- and β-CD complexes remain unchanged, being *ca.* 21 and 18 Å, respectively. The different behaviour of the parent and methylated CD's is explained in terms of the structural and physicochemical characteristics of the individual CD's and interlayer cations.

Key words: Cyclodextrin, montmorillonite, complexation, complex, intercalation.

1. Introduction

Recently we have prepared a complex of layered Cu(II)-montmorillonite with mono-(6-β-aminoethylamino-6-deoxy)-β-cyclodextrin (β-CDen) [1,2]. This complex is unique because it consists of two components with the ability to act as host matrices, one layered and one single channel-like. The previous study also showed that in contrast to β-CDen, β-cyclodextrin (β-CD) forms no complex with Cu(II)-montmorillonite [2]. However, one cannot exclude the possibility that polar but unchargeable cyclodextrins other than β-CD are taken up by montmorillonite. The complexes thus obtained may be useful as solid supports in gas or liquid chromatography and as micro-encapsulating agents of medicines.

An attempt was thus made to examine the complexation properties of α-, β-, γ-, hexakis-2,6-di-O-methyl-α- (DM-α-), heptakis-2,6-di-O-methyl-β- (DM-β-), and heptakis-2,3,6-tri-O-methyl-β- (TM-β-) cyclodextrins toward Na-, Ca-, and Cu-montmorillonites.

Table I. Compositions and some characteristics of the montmorillonite samples

Sample[a]	Composition	W[b]	Interlayer spacing (Å)	A_i[c]/Å^2
Na-mont	$Na_{0.34}K_{0.008}Ca_{0.03}(Al_{1.60}Fe_{0.10}Mg_{0.32})[Si_{3.83}Al_{0.17}]O_{10}(OH)_2 \cdot 6H_2O$	744	12.6	56.4
Ca-mont	$Ca_{0.278}(Al_{1.60}Fe_{0.10}Mg_{0.32})[Si_{3.83}Al_{0.17}]O_{10}(OH)_2 \cdot 10H_2O$	748	14.9	113
Cu-mont	$Cu_{0.237}(Al_{1.60}Fe_{0.10}Mg_{0.32})[Si_{3.83}Al_{0.17}]O_{10}(OH)_2 \cdot 5H_2O$	756	12.4	113

[a] mont = montmorillonite. [b] Unit cell weight of the anhydrous form. [c] Effective area per interlayer cation.

2. Experimental

Na-montmorillonite with a chemical composition $Na_{0.34}K_{0.008}Ca_{0.03}(Al_{1.60}Fe_{0.10}Mg_{0.32})[Si_{3.83}Al_{0.17}]O_{10}(OH)_2 \cdot 6H_2O$ was supplied from Kunimine Industry Co. Ltd. The Ca and Cu(II) exchanged minerals were prepared by placing the Na form in 1 M $Ca(NO_3)_2$ and 1 M $Cu(NO_3)_2$ solutions at 25 °C for 7 days, respectively. The products were fully washed with water, centrifuged, and lypophilized. The compositions and characteristics of these clay mineral samples are given in Table I. Alpha-, β-, γ-, DM-α-, DM-β-, and TM-β-CD's were reagent grade and used without further purification.

Each mineral sample (0.1 g) was soaked in 8 cm^3 of an aqueous CD solution of 12.5, 25 and 100 mmol dm^{-3} at 25 °C for 10 days, centrifuged and air-dried at 40 °C. X-ray diffraction and TG measurements were made as previously described [2]. Surface tension was measured by the Wilhelmy method using a Kyowa hydrobalancing meter.

3. Results and Discussion

The X-ray diffraction profiles of the clay minerals used were not affected by treating with β-CD solution. Figure 1 shows the X-ray diffraction patterns of the other resulting solids. These findings indicate that α-, DM-α-, DM-β-, and TM-β-CD's form complexes with Na-, Ca-, and Cu-montmorillonites, whereas γ-CD is intercalated only by the Na form and β-CD cannot be taken up by any of them. Among the former four CD's, the methylated ones show a tendency to be significantly taken up at much lower levels of CD added than the other. A similar observation was made on the intercalation of sugars by montmorillonite [3]. For all the CD's used it was also found that the intercalated CD can be removed by washing the solids with water.

The thickness of the intercalated layer, Δ, for each complex was determined by subtracting 9.5 Å (the assumed thickness of the aluminosilicate layer) [4] from the observed interlayer spacing. The results are summarized in Table II, together with the data of CD content obtained by TG analysis. It is of much interest that the Δ value for the α-CD complex varies from 8.5 to 12.0 Å with replacement of the interlayer cation, whereas those for the methylated α- and β-CD complexes remain fixed, being *ca.* 12 and 8 Å, respectively.

Surface activity may be available as a measure of the tendency of CD molecules to be intercalated by montmorillonite. Uekama reported that DM-β- and TM-β-CD's are highly surface-active, in contrast to β-CD [5]. Our measurements on the CD's used in this study showed that the order of surface activity is TM-β-CD (48) $\gg$ DM-β-CD (57) $>$ DM-α-CD (61) $\gg$ γ-CD (68) $>$ α-CD (72) $>$ β-CD (74), where the surface tension (in mN/m) of each CD solution at 12.5 mmol dm^{-3} (25 °C) is given in parentheses. The observed order of surface activity is in good agreement with that of the intercalation tendency of the CD's towards montmorillonite (TM-β-CD $>$ DM-β-CD $\sim$ DM-α-CD $>$ α-CD $>$ γ-CD $\gg$ β-CD) as noted from Figure 1. This fact suggests that it would be energetically favourable for the methylated CD molecules to penetrate between the silicate layers of montmorillonite and displace the interlayer water, due to their high surface activity.

In the CD complexes, the interlayer cations M^{n+} ($n = 1$ for M = Na, $n = 2$ for M = Ca, Cu) are likely to exist as ions having the square planar form $M^{n+}(H_2O)_4$ about 3 Å in thickness, h_i. Therefore, the observed Δ for the complexes, being less than twice the thickness of CD (h) and also less than the molecular diameter (D), range from h

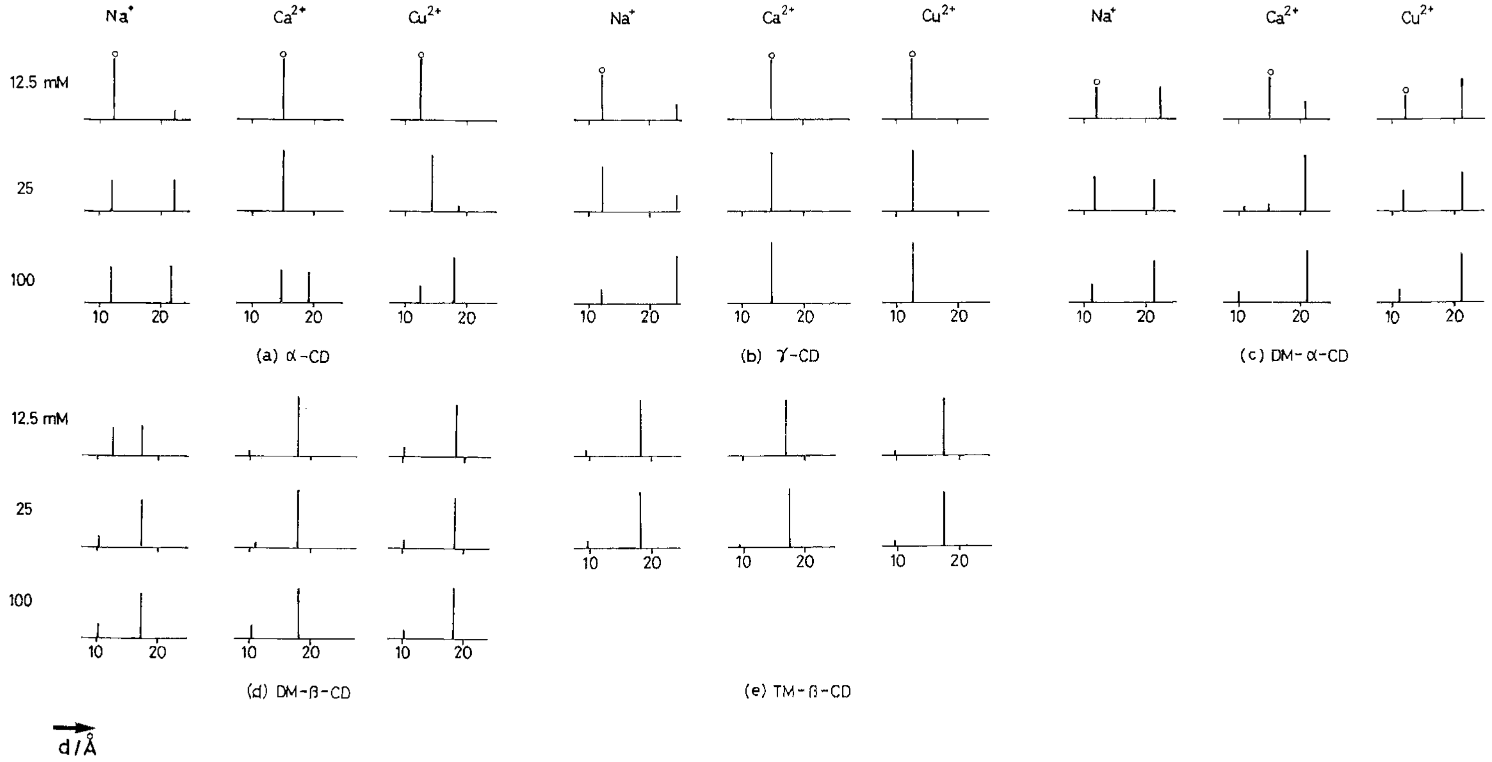

Fig. 1. X-ray diffraction patterns of the complexes of Na-, Ca- and Cu-montmorillonites with α-, γ-, DM-α-, DM-β-, and TM-β-CD's obtained at varing initial concentrations of CD; ○, (001) reflection of parent host.

Table. II. Characterization of montmorillonite-cyclodextrin complexes with various interlayer cations

Interlayer cation	Cyclodextrin compound	D(Å)	h(Å)	A_m(Å^2)	Interlayer spacing (Å)	Δ value (Å)		$\delta = A_m/A_i$	CD content (m mol g^{-1})		Type of arrangement of intercalant[a]	Probable conformation of methylated groups
						obs.	cal.		obs.	cal.		
Na	α-CD	13.2	8.0	151	21.5	12.0	14.0	2.7	0.41	0.43	I	—
Ca					19.2	9.7	11.0	1.3	0.31		II	
Cu					18.0	8.5	11.0	1.3	0.27		II	
Na	γ-CD	17.5	8.0	265	24.2	14.7	14.0	4.7	0.94	0.23	I	—
Na	DM-α-CD	13.2	8.0–12.0	151	21.4	11.9	12.0	2.7	1.7	0.43	III	extended
Ca					21.3	11.8		1.3	0.96			
Cu					21.2	11.7		1.3	0.43			
Na	DM-β-CD	15.4	8.0–12.0	205	17.1	7.6	8.0	3.6	0.90	0.30	III	folded
Ca					17.9	8.4		1.8	1.6			
Cu					18.3	8.8		1.8	0.34			
Na	TM-β-CD	15.4	8.0–12.0	205	18.1	8.6	8.0	3.6	0.32	0.30	III	folded
Ca					17.4	7.9		1.8	0.13			
Cu					17.4	7.9		1.8	0.16			

[a] See Figure 2.

to $h + 2h_i$. The effective area of the CD molecule, A_m, and that of the interlayer cation, A_i, can be evaluated by $A_m = 2\sqrt{3}(D/2)^2$ [2] and by dividing 46 Å^2 [6] for the surface area of the one face of the unit cell, A_o, by the number of cations per unit cell, respectively. These two quantities enable us to calculate the molar ratio of interlayer cation to CD molecule in the complexes, $\delta = A_m/A_i$. The A_i, A_m, and δ values thus obtained are cited in Tables I and II. On the basis of the above data and considerations, we can assume that α- and γ-CD molecules are intercalated as a monolayer with their open faces parallel to the silicate sheets of montmorillonite and are in contact with aquo Na^+ ions on both faces of the CD ring (type I in Figure 2) or with aquo Ca^{2+} or Cu^{2+} ions on one face of it (type II). The difference between the Δ values calculated on this assumption and the observed ones indicates that the thickness of the aquo cation for the α-CD complexes is apparently decreased in the order of Na > Ca > Cu. This suggests that the interlayer cation with the higher polarising power would form an aquo complex in which all or part of the four coordinating water molecules are located more deeply in the cavity of CD molecule. On the other hand, the Δ values of 12 and 8 Å observed for the methylated α- and β-CD complexes correspond to those for the CD molecules with their methylated side-chains in the fully extended and folded conformations, respectively. The surface activity data also suggest that the methylated CD molecules might be much less compatible with the aquo cations in the interlayer space than the unsubstituted ones. Thus, the intercalation behaviour of the methylated CD molecules could be explained by assuming that their macrocyclic rings are oriented in a manner similar to that of the unsubstituted molecules and that the interlayer aquo cations are not located between the silicate sheet and the CD layer but are embedded within the intercalant layer (type III in Figure 2). From Figure 1 it is also evident that α- and γ-CD's tend to be taken up only by Na-montmorillonite or by it at a lower concentration than by the Ca and Cu forms, but the reverse tendency is found for the methylated CD's. In contrast to Ca- and Cu-montmorillonites, the Na form is completely dispersed in aqueous suspension [7]. These facts lead to the suggestion that the intercalation of the methylated CD molecules proceeds by a mode in which the principal driving force is the attractive energy of the intercalant layers on the interlayer surface of clay, while that of the unsubstituted ones would be promoted by the osmotic effect produced in the second stage of interlayer swelling [8].

Based on the above models, the maximum content of CD in each complex, w, was evaluated by $w = A_o/A_m \cdot W$ where W is the unit cell weight of the montmorillonite samples used (Table I). The results are listed in Table II. The observed values of w for the DM-α- and DM-β-CD complexes with Cu-montmorillonite and those for all of the α- and TM-β-CD

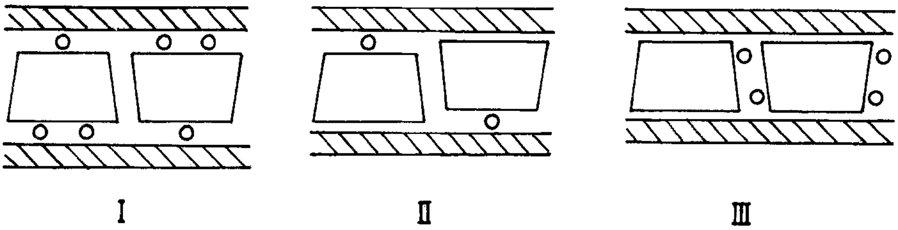

Fig. 2. Schematic representation of three types of probable arrangement of CD molecules and interlayer cations (O) in the interlayer space of montmorillonite; I, CD layer + cation layer × 2; II, CD layer + cation layer × 1; III, (CD + cation) layer.

complexes are nearly equal to or less than their calculated values. The large difference between the observed and calculated values of w for the other complexes would be because an excess of CD remains in each solid resulting from the drying of its gelatinous form without rinsing.

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