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Double Inclusion of Methylated Cyclodextrin and Sodium Benzenesulfonate by Na-, Ca-, and Cu-Montmorillonites

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Synopsis. The uptake of methylated α- and β-cyclodextrins by Na-, Ca-, and Cu-montmorillonites at 25 °C in the presence of sodium benzenesulfonate has been studied. X-Ray diffraction data revealed that the cyclodextrin molecules that embrace benzenesulfonate anion are intercalated as monolayer in the interlayer space of the clay minerals.

Inclusion phenomena have attracted increasing attention in inorganic chemistry. In the recent papers concerning molecular inclusion, we have reported the complexation of layered montmorillonites and α-zirconium phosphate with several cyclodextrins containing a cylindrical cavity capable of including a variety of substances.[1—4] Further inclusion property of the complexes towards any other guest molecules would be intrigued. For the complex of α-zirconium phosphate with an aminated cyclodextrin, we showed that it is similar to zeolites because the water within the cavity of cyclodextrin molecule is released and readsorbed reversibly.[3] No examination, however, has been made for other complexes hitherto obtained.

The montmorillonite intercalates not only positively charged cyclodextrins but also polar but unchargeable ones such as parent and methylated cyclodextrins.[4] This paper reports that molecules of hexakis(2,6-di-*O*-methyl)-α-(denoteded DM-α- for short) and heptakis(2,6-di-*O*-methyl)-β-(DM-β-)-cyclodextrins (CD) accompanied by sodium benzenesulfonate (NaBS) are intercalated by Na-, Ca-, and Cu-montmorillonites.

Experimental

The Na-, Ca-, and Cu-montbmorillonite samples were the same as those used in the preceding work.[4] DM-α- and DM-β-cyclodextrins and sodium benzenesulfonate were of reagent grade and used without further purification.

Each mineral sample (0.1 g) was immersed in 8 cm^3 of a 1 : 1 (vol.) mixture of 50 mmol dm^{-3} aqueous cyclodextrin and 1 mol dm^{-3} sodium benzenesulfonate solutions at 25 °C for 5 d. Since methylated cyclodextrin taken up by montmorillonite is easily washed away with water,[4] the reaction mixture was centrifuged and rinsed with the starting cyclodextrin solution and then air-dried at 40 °C to give the complex sample. The similar procedure was applied to the system without sodium benzenesulfonate.[4] X-Ray diffraction measurements were made as similarly as in the previous work.[4]

Results and Discussion

Figure 1 compares the X-Ray diffraction patterns of CD-NaBS-montmorillonite with those of CD-montmorillonite. The results suggest that Na-, Ca-, and Cu-montmorillonites form one complex with DM-α-cyclodextrin and a mixture of two complexes with DM-β-cyclodextrin. The X-Ray diffraction profiles of the clay minerals were not changed by treating with sodium benzenesulfonate solution, indicating that the montmorillonite cannot take up benzenesulfonate anion solely.

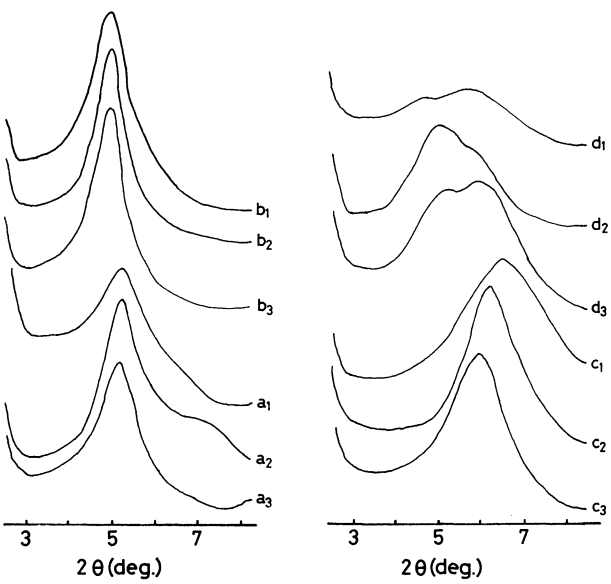

Fig. 1. X-Ray diffraction patterns of (a$_i$) DM-α-CD-mont, (b$_i$) DM-α-CD-NaBS-mont, (c$_i$) DM-β-CD-mont, and (d$_i$) DM-β-CD-NaBS-mont complexes for Fe*K*α rays (i=1—3, mont=montmorillonite). Interlayer cations, Na (i=1), Ca (i=2), Cu (i=3).

The conditions for preparing the complex samples suggest that they contain excess amounts of cyclodextrin and sodium benzenesulfonate. It is, therefore, difficult to determine the equilibrium contents of each compound in the resulting complexes. The complexes were characterized only by their interlayer spacings and change of thickness of intercalated layer (Δ value); the obtained values are summarized in Table 1. The Δ value was determined by subtracting 9.5 Å for the thickness of the silicate layer[5] from the observed interlayer spacing. The increase of interlayer thickness in the range of 1—5 Å caused by the presence of sodium benzenesulfonate will be attributed to the double inclusion of methylated cyclodextrin and sodium benzenesulfonate by montmorillonite.

The interlayer thickness data in Table 1 also show that the difference of interlayer thickness between CD-NaBS-montmorillonite and CD-montmorillonite complexes with DM-β-cyclodextrin varies from 2.9 to 5.2 Å with the interlayer cation, while the interlayer thickness of complexes with DM-α-cyclodextrin is hardly affected by the variation of interlayer cation. According to the crystal structure analysis of the α-CD-NaBS complex,[6] the benzenesulfonate anion is arranged in the channel which is formed by the stack

Table 1. Characterization of Cyclodextrin–Montmorillonite4) and Cyclodextrin–Sodium Benzenesulfonate–Montmorillonite Complexes with Various Interlayer Cations

Interlayer cation	Cyclodextrin	CD–montmorillonite complex		CD–NaBS–montmorillonite complex[a]	
		Interlayer spacing/Å	Δ value/Å	Interlayer spacing/Å	Δ value/Å
Na	DM-α-CD	21.4	11.9	22.1	12.6
Ca		21.3	11.8	22.2	12.7
Cu		21.2	11.7	22.4	12.9
Na	DM-β-CD	17.1	7.6	23.3 (19.2)	13.8 (9.7)
Ca		17.9	8.4	22.0 (19.4)	12.5 (9.9)
Cu		18.3	8.8	21.2 (18.6)	11.7 (9.1)

a) Values for the low spacing phases are given in parentheses.

of α-cyclodextrin rings. The benzene ring is located in the cavity, while the sulfonato group is outside the cavity and hydrogen-bonded to the primary hydroxyl groups of the adjacent α-cyclodextrin molecule. The preceding study[4] revealed the following characteristics on the inclusion behavior of methylated cyclodextrins in montmorillonite; (1) the cyclodextrin molecules with cavity axes perpendicular to the silicate layer are intercalated as monolayer with their methylated side chains in fully extended (DM-α-cyclodextrin) and folded (DM-β-cyclodextrin) conformations which give the molecular thickness of 12 and 8 Å, respectively, and (2) the hydrated cations are bound in the intermolecular space within the cyclodextrin layer with hydrophobic methoxyl groups of cyclodextrin molecule. Referring to the structure data in Ref. 5, we assume the length of benzenesulfonate anion to be 9 Å. If we combine the above data and observations with the assumption that the methylated cyclodextrin molecules accompanied by sodium benzenesulfonate are intercalated with the same conformations as in the methylated CD-montmorillonite system, the benzenesulfonate anion would be included completely in the molecular cylinder of fully stretched DM-α-cyclodextrin or partly in the molecular cage of DM-β-cyclodextrin capped by the primary methoxyl groups, as illustrated in Fig. 2. It is also conceivable that the interlayer hydrated cations of DM-α-CD-NaBS-montmorillonite complexes are located in the intermolecular space within the cyclodextrin layer, due to repulsion against the hydrophobic methoxyl groups. As for the high spacing complexes of DM-β-CD, the cations are between the silicate layer and the sulfonato group protruding from the O(2), O(3), side of the cavity, due to the hydrophilic attraction of the sulfonato group. The interlayer thickness of the latter complexes decreases in the order of Na>Ca>Cu. This could be explained by assuming that the interlayer cation with higher polarizing power forms an aqua complex in which all or a part of four coordinating water molecules are located more closely to the sulfonato group, as observed in the case of inclusion of α-cyclodextrin by Na-, Ca-, and Cu-montmorillonites.[4] Furthermore, the interlayer thickness of the low spacing complex of DM-β-CD remains unchanged at 9—10 Å with different interlayer cations. It is likely that the low spacing complex is an intermediate phase whose interlayer space is occupied predominantly by the methylated CD molecules and only partly by those including benzenesulfonate anion.

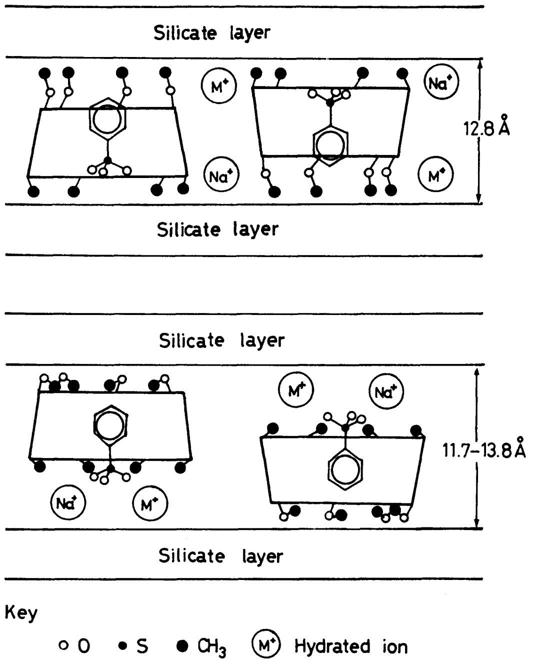

Fig. 2. Models proposed for their probable arrangement of CD molecules, benzenesulfonate anions and interlayer cations in the interlayer space of montmorillonite; (upper) DM-α-CD, (bottom) DM-β-CD (high spacing complex).

We conclude that the methylated cyclodextrin molecules including sodium benzenesulfonate are intercalated as monolayer by Na-, Ca-, and Cu-montmorillonites. The double inclusion method developed in this study may be applied to the micro-encapsulation of various substances such as drugs and dyes for laser.

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