Intercalation of a Trimethylammoniomethylated Calix[4]arene by Cu(II)-Montmorillonite

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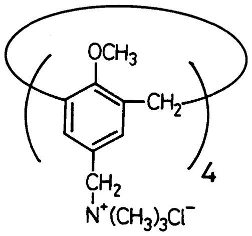
The uptake of 5,11,17,23-tetrakis(trimethylammoniomethyl)-25,26,27,28-tetramethoxycalix[4]arene tetrachloride by Cu(II)-montmorillonite was examined at 25 °C. The mineral forms an intercalated phase in which the calixarene molecules are arranged as a 9.5 Å thick monolayer, with a cone-type conformation, with their cavity axes perpendicular to the silicate layers. Thermogravimetric and copper(II) release data suggest that the guest molecules are taken up in their tetra- and tri-valent forms during the initial and final uptake stages, respectively.

Much attention has been devoted to new families of microporous materials which can be obtained by the pillaring of inorganic layered compounds with polynuclear complex ions or bulky organic molecules.1) We have attempted to develop a novel class of organic and inorganic double-host materials,2–5) with the expectation that they would act as including agents with high selectivity. So far, cyclodextrins have been employed as the organic host component to be intercalated in layered parent hosts, such as montmorillonites and zirconium phosphates. Calixarenes are cyclic oligomers made from phenol and formaldehyde and have been expected to serve as a new class of host molecules whose functions are different from those of cyclodextrins.6–7) Hence, the combination of montmorillonites or zirconium phosphates and calixarenes in place of cyclodextrins may afford double-host materials with new characteristic functions.

This paper describes the first attempt to examine the intercalation of cationic calix[4]arene (**1**) by Cu(II)-montmorillonite.



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Experimental

The Cu(II)-montmorillonite used as a starting mineral was the same as that used in preceding studies.4,5) The synthesis of the chloride salt of **1** was described elsewhere.8) The Cu(II)-clay was soaked in an aqueous solution containing 0.25, 0.5, and 1.0 mmol of **1** per gram of clay at 25 °C for 10 d, centrifuged, fully washed with water, and freeze-dried. Thermogravimetry (t.g.) was carried out for the resulting solids at a heating rate of 10 °C min^{-1}. The amount of copper(II) ions released to solution was determined by atomic absorption analysis. X-Ray diffraction measurements were made using Cu $K\alpha$ radiation; 1-tetradecanol having a long d-spacing (39.90 Å) was used as an external standard.

Results

Figure 1 shows X-ray diffraction patterns of the

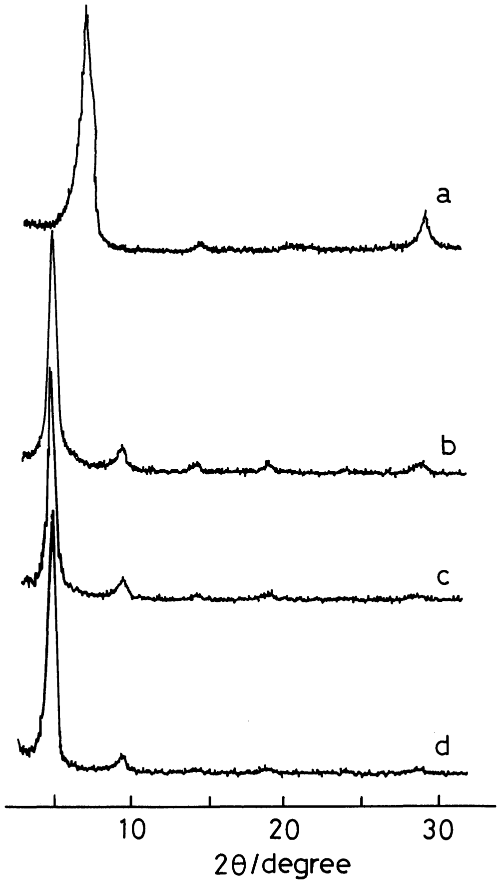

Fig. 1. X-Ray diffraction patterns of Cu(II)-montmorillonite (a) and its intercalates with calix[4]arene **1** (Cu $K\alpha$ radiation). Calixarene addition levels (mmol g^{-1}): 0.25 (b), 0.5 (c), and 1.0 (d).

Table 1. Characterization of Intercalates of Cu-Montmorillonite with a Trimethylammoniomethylated Calixarene at Various Loadings

Amount of calixarene added	Interlayer spacing	Δ	Amount of calixarene	Amount of releasable Cu^{2+} ion/mmol g^{-1} clay[a]					Cu^{2+} ion/ Callixarene ratio
mmol g^{-1} clay[a]		Å	mmol g^{-1} clay[a]	Initial			Desorbed	Remaining	
				Total	Int	Ext			
0.25	18.9	9.4	0.13	0.63	0.54	0.09	0.26	0.37	2.8
0.5	19.1	9.6	0.26	0.63	0.54	0.09	0.35	0.28	1.1
1.0	19.0	9.5	0.25	0.63	0.54	0.09	0.37	0.26	1.0

a) Anhydrous form of clay.

resulting solids. As a result of the addition of **1**, the diffraction peaks attributable to the host phase disappeared, while a new diffraction peak corresponding to $d \approx 19.0$ Å appeared, along with its higher-order counterparts. This indicates that the mineral phase is coverted into an intercalated phase with an interlayer spacing of ca. 19.0 Å. The thickness of the intercalated layer (Δ) was obtained by subtracting 9.5 Å,[2,4] the thickness of the silicate layer, from the observed *d*-spacings. Table 1 summarizes the structural data thus obtained.

The calixarene contents in the intercalated solids were evaluated with the combined use of t.g. and Cu^{2+} release data as follows.

T.g. curves for the intercalated solids are shown in Fig. 2, along with that for the host phase. The first weight loss at below 100 °C is due to the desorption of water. This was followed by a loss of intercalant species, commencing at 200 °C, with an accompanying weight loss due to condensation of the hydroxyl groups in the host phase. The intercalant species correspond to the calixarene molecules taken up as a mono- (m=1), di- (m=2), tri- (m=3) or tetra- (m=4) valent cation with the composition $CLXtma^{4+}$ $(4\text{-}m)Cl^-$ or their mixture, where CLXtma refers to the macrocyclic cation moiety of **1**. The most probable combination for the mixture would be m=1 and 2, m=2 and 3 or m=3 and 4. Thus, if the average valence of intercalant species is taken as n, the t.g. data give a straight line for the relationship between the calixarene content, in moles per gram of clay, and n, as shown in Fig. 3. The solid symbols indicate the special case of n=m in which the intercalant species have a unique valence.

The total amount of Cu^{2+} ions desorbed from the solids is cited in Table 1, along with the initial amounts of metal

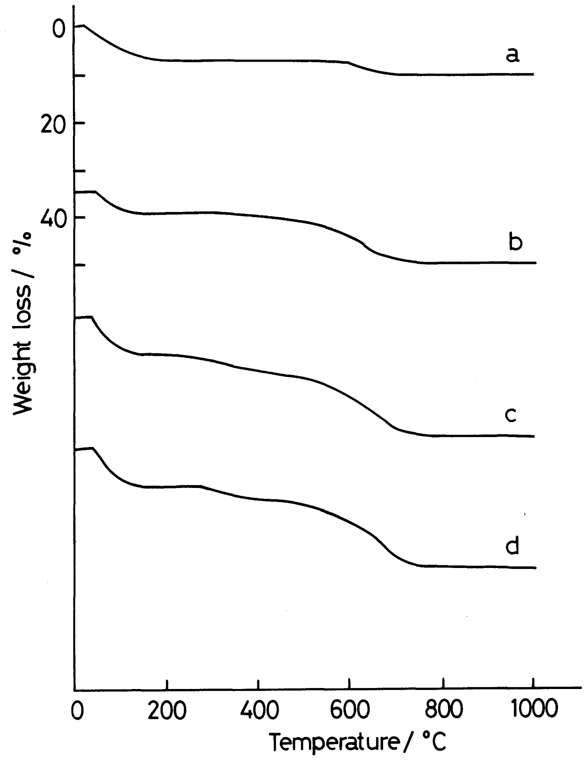

Fig. 2. T.g. curves for Cu(II)-montmorillonite (a) and its intercalates with calix[4]arene **1**. Calixarene addition levels (mmol g^{-1}): 0.25 (b), 0.5 (c), and 1.0 (d).

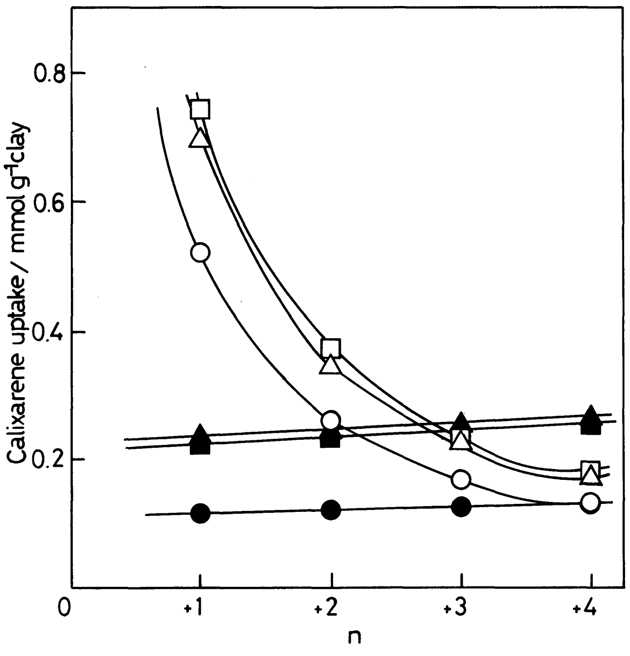

Fig. 3. Calixarene uptake by Cu(II)-montmorillonite as a function of the average valence (n) of the intercalant molecule. The calixarene uptakes were evaluated from the t.g. (—●—, —▲—, —■—), and the Cu^{2+} ion release (—○—, —△—, —□—) data. Calixarene addition levels (mmol g^{-1}): 0.25 (—●—, —○—), 0.5 (—▲—, —△—), and 1.0 (—■—, —□—).

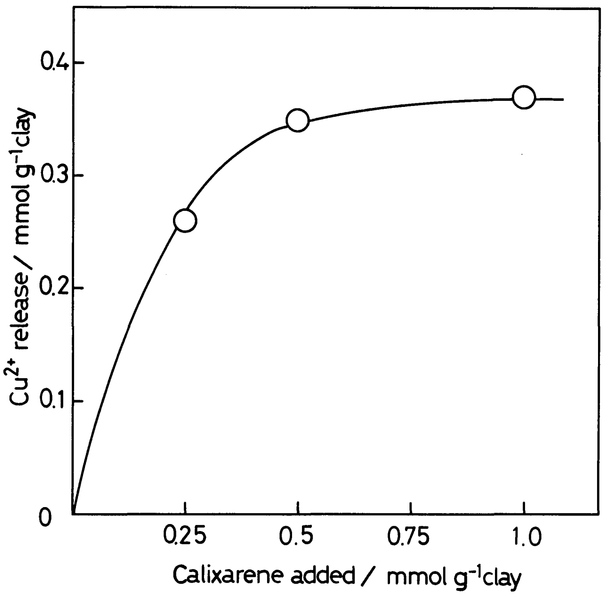

Fig. 4. Plots of the release of interlayer Cu^{2+} ion against the added calixarene.

ions held as interlayer cations, and as any neutralized species on the external surface of the crystals. As previously described,[5] the neutral species on the external surface of the mineral are feasibly desorbed in preference to interlayer Cu^{2+} ions. The amount of interlayer Cu^{2+} ions desorbed by ion exchange with calixarene molecules can be obtained by subtracting the amount of neutral species from the total amount of desorbed metal ions. The release of interlayer Cu^{2+} ions, thus obtained, is plotted as a function of the amount of calixarene added in Fig. 4. The calixarene content as a function of n expected from the Cu^{2+} release data is given by the curves in Fig. 3, including the case of $n=m$ (indicated by open symbols).

In Fig. 3, each curve and straight line for the samples formed at the low and the high uptake stages intercept at $n=4$ and 3, respectively, yielding the valence and the amount of intercalant. The calixarene content data, thus obtained, are listed in Table 1, along with those of Cu^{2+} ion remaining in the solid.

Discussion

The calix[4]arenes can exist generally as four discrete types of conformational isomers, referred to as the "cone", "partial cone", "1,2 alternate", and "1,3 alternate" conformers.[6] Recently, Nagasaki et al.[8] have found that in an aqueous system the calix[4]arene used in the present work adopts a 1,3 alternate conformation which has never been observed as a major species in organic solvents. However, the Δ value of 9.5 Å observed for the calix[4]arene intercalate is much smaller than the molecular thickness of the 1,3 alternate conformer, but is in good agreement with 9.5 Å for the cone conformer (estimated according to its CPK molecular model). This indicates that the calixarene molecules are arranged as a monolayer with their cone conformation and with their cavity axes perpendicular to the silicate layers in montmorillonite. A similar monolayered structure was observed on neutral or permethylated cyclodextrin intercalates of montmorillonite.[4] The molecular cross section of the calix[4]arene with its cone coformation can be taken as 205 Å^2 at maximum. The unit cell weight of Cu-montmorillonite is 756 and the surface area of one face of the unit cell is estimated to be 46 Å^2. Assuming that the calixarene molecules are closely packed in the monolayer, the maximum content of calixarene can be evaluated as being (46/205)/756 or 0.30 mmol g^{-1} of clay, which is consistent with the observations (Table 1).

It is most likely that molecules of the calix[4]arene used exist preferentially as a tetravalent cation in an aqueous solution. The above-mentioned data, however, suggest that the calixarene molecules at low uptakes would be intercalated in the same tetravalent cationic form as that in an aqueous solution, while those at the high uptake stage would be incorporated in the trivalent cationic form. The positively charged trimethylammonium groups in the intercalated calixarene molecule are located at the bottom of the truncated cone, as large as 7.5 and 16 Å in the top and the bottom diameters and 9.5 Å in thickness. As cited in Table 1, the molar ratios of Cu^{2+} to calixarene in the intercalates formed at the low and the high uptake stages are approximately 3 : 1 and 1 : 1, respectively. The interlayer Cu^{2+} ions are most likely to be not located between the silicate layer and the calixarene layer, but to be embedded within the intercalant layer, as suggested by the arrangement of Cu^{2+} ions in the Cu(II)-montmorillonite–methylated cyclodextrin complexes.[4] It is also reasonable to assume that the effective area per unit charge for the negatively charged silicate layers in the monmorillonite used is equal to that per interlayer monovalent cation in it or 56.4 Å^2.[4] Thus, the probable arrangement of calixarene molecules

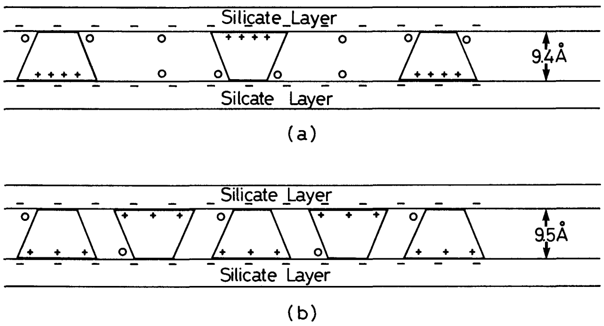

Fig. 5. Schematic representation of the probable arrangement of calixarene molecules and interlayer Cu^{2+} ions (○) in the interlayer space of montmorillonite for the intercalates formed at the low (a) and the high (b) uptake stages. The charge distribution is also illustrated by symbols + (positive) and − (negative).

and Cu^{2+} ions in the intercalated solids formed at the low- and the high-uptake stages, as well as the charge distribution in the solids, could be explained in terms of the models schematically shown in Fig. 5. It is noted that the negative charge of the silicate layer on the top (methoxy) side of intercalated calixarene molecules is compensated for by interlayer Cu^{2+} cations. Model b indicates that if the calixarene molecules are intercalated in the tetravalent cationic form at the high-uptake stage, it would result in a further decrease in the Cu^{2+} content, leading to destabilization of the solid. This is consistent with the above deducation that the calixarene molecules would be intercalated in the trivalent cationic form at the high-uptake stage.

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