

Host-Guest Interaction in α -Cyclodextrin Inclusion Complexes

Takuma Kaneko, Hirokazu Takahashi, Kenryo Ohminami, Takehisa Konishi,
Masaki Ueda, Shin-ichi Nagamatsu and Takashi Fujikawa

Graduate School of Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Abstract. We measured XAFS spectra of aqueous Br^- and I^- ion- α -cyclodextrin solutions in which α -cyclodextrin forms inclusion complexes, and compared the experimental data with results of molecular dynamics calculations. In the Br^- system, little difference in XANES spectra was observed upon formation of inclusion complex. In the I^- system, slight difference in line shape was observed. This suggests that there are changes in the electronic and local geometric structure around an I^- ion when it is included in the cavity of an α -cyclodextrin molecule. Molecular dynamics calculation showed that Br^- ion is included in α -cyclodextrin together with its first hydration shell. In contrast, I^- ion is dehydrated upon inclusion.

Keywords: inclusion compound, cyclodextrin, XAFS, multiple-scattering theory, molecular dynamics
PACS: 61.10.Ht, 82.20.Wt, 82.30.Nr

INTRODUCTION

Cyclodextrin(CD) is composed of several glucoses which are circularly linked and called α -, β - and γ -CD, respectively, and CDs composed of 6, 7 and 8 glucoses. A CD molecule has a cavity in which various molecules or ions can be included, and its inside is hydrophobic while its outside is hydrophilic. In many cases, the main interaction between CD and guest molecules is Van der Waals force.

X-ray Absorption Fine Structure (XAFS) is a technique which probes electronic and geometrical structure. In particular, X-ray Absorption Near Edge Structure (XANES), which refers to the region up to 50 eV above the absorption edge, has been used to obtain information about local electronic and geometric structure around X-ray absorbing atoms.

Molecular Dynamics (MD) calculation is a computer simulation method which solves the equations of motion of atoms using approximate interatomic interaction potential. Three dimensional structural information which XAFS does not easily provide, can be obtained by MD calculation.

Although I_3^- ion is well known as a guest specie in α -CD inclusion complexes, we used Br^- and I^- in this study because such a monoatomic ion guest is more feasible for EXAFS analysis. First, since scattering by a heavy atom affects EXAFS spectra strongly, atoms that belong to an α -CD molecule which binds a monoatomic ion would be observed better than in the case of I_3^- . In this case, association constant between α -CD and the anion is not very high and this must be taken into account in analysis of the spectra. Various values of the associa-

tion constant obtained have been reported by electrometric [1], conductimetric [2] and other techniques.

EXPERIMENTAL

Aqueous solutions of 0.05 M KBr, 0.05M KBr + 0.05 M α -CD, 0.15 M KI and 0.15 M KI + 0.12 M α -CD were prepared from KBr (Wako, >99.0%), KI (Wako, >99.5%) and α -CD (Wako, >97.0%) for XAFS measurement. Quartz cells (optical path 10 mm) were used for the Br^- system. For I samples, plastic cells with optical path length of 0.2 mm which has Mylar window was used.

XAFS measurements were carried out in transmission mode with a laboratory XAFS spectrometer EXAC820 (Technos Co.,Ltd.) which was equipped with a LaB_6 cathode and a Mo rotating-anode. Measurements were done using a Ge(111) curved crystal monochromator. All the measurements were done at room temperature.

CALCULATIONS

We performed MD simulations using the velocity Verlet method. The potential used in the simulation consists of Lennard-Jones (LJ) potentials and Coulomb potentials which are a subset of AMBER [3] potentials. Instead of a bonding potential between the atoms, constraints calculated by relaxation method [4] (RATTLE [5]) were introduced in order to reduce the number of potential parameters.

The potential parameters are given in Table 1. Parameters of atoms were estimated using values from rare gases [6] and the literature [7, 8]. The values we used for

TABLE 1. Potential parameters for the MD simulation.

element	charge	$\sigma(\text{\AA})$	ϵ	bonding element(s)
H	0.33	0.55	8.90	O
	0.00	0.55	8.90	C
O	-0.66	1.16	26.0	HH
	-0.33	1.16	26.0	CH
	0.00	1.16	26.0	CC
C	0.00	1.10	19.1	
K	1.00	3.83	119	none(ion)
Br	-1.00	4.13	167	none(ion)
I	-1.00	4.57	225	none(ion)

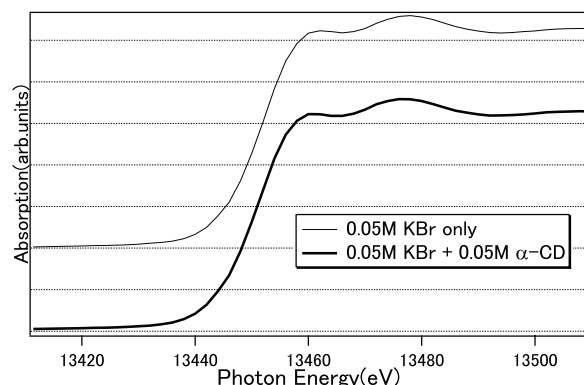


FIGURE 1. Br K XANES spectra of KBr and KBr- α -CD system.

the charge of covalently bonded atoms were set to zero, while for bound oxygen and hydrogen, charge transfer between them was assumed.

RESULTS AND DISCUSSION

Figure 1 shows Br K-edge XANES spectra of the samples with and without α -CD. There are no large difference between them. Association rate of a bromide ion and α -CD in this condition is estimated to about 13% [9]. Difference in the time shapes of the two spectra should be visible if the spectrum changes before and after inclusion. Therefore it is that the coordination environment around the bromide ion does not change noticeably when it is included. Bromide ion in aqueous solution is in a hydration state with water molecules. Our result suggests that Br^- is included into α -CD while keeping its general hydrated structure. Figure 2 shows the result of simulation of bromide ion and atoms around it. It is seen that Br^- is included in α -CD together with some water molecules.

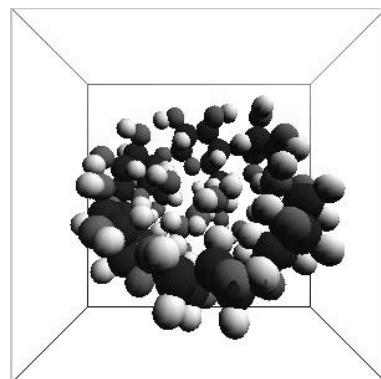


FIGURE 2. Snapshot of MD simulation for the KBr- α -CD system.

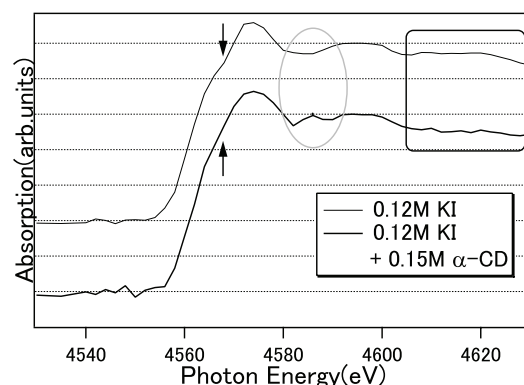


FIGURE 3. I L_3 XANES spectra of the KI and KI- α -CD system.

Figure 3 shows I L_3 -edge XANES spectra. In the I^- system, it is seen that the spectra change according to whether α -CD exists or not. The association rate of an iodide ion and α -CD is estimated to be about 35% [10]. This change in the spectra is due to a change of the local structure around the iodine atom. Because of the larger radius of an iodide ion than that of a bromide ion, it is considered that hydrating waters are dehydrated as it is included into α -CD. The result of MD calculations

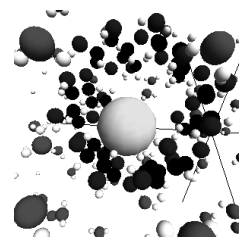


FIGURE 4. Snapshot of MD simulation for the KI- α -CD system.

for the iodide ion- α -CD system is shown in Figure 4. I^- is included without hydrating waters unlike Br^- . It indicates that the energy of association with α -CD of an iodide ion is larger than that of its hydration.

CONCLUSION

We measured XANES spectra of halide ion- α -CD inclusion complexes and potassium halide aqueous solutions for comparison. In the bromine system, a difference between the spectra before and after inclusion into α -CD was not seen. MD simulation showed that the similarity between the two spectra in the Br^- system results from the inclusion of a bromide ion keeping the hydration structure. A change between them in I^- system results from the inclusion of an iodide ion into α -CD after dehydration.

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