Iodine *L*-edge XAFS study of linear polyiodide chains in amylose and α-cyclodextrin

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We performed iodine L edge XAFS measurements on blue-black amylose-iodine complex to obtain information about the electronic and geometrical structures of polyiodide chain included in amylose helix. Measurements were also carried out on crystalline α-cyclodextrin-iodine complex (α-cyclodextrin)$_2$·Cd$_{0.5}$·I$_5$·27H$_2$O, in which the polyiodide chain is known to consist of I$_5^-$ unit. It was found that the XANES spectra of these complexes have similar line shapes except for some minor differences, indicating that there are close similarities in the nature of polyiodide chains in these complexes. Besides their similarity, difference in the intensity of the peak at the L$_1$ absorption edge was observed. Its implication for the electronic and geometrical structures is also discussed.

Keywords: iodine inclusion compound; amylose-iodine complex; XANES.

1. Introduction

There are many inclusion-type compounds containing iodine, which show interesting physical and chemical properties. Among them, blue-black starch-iodine complex formation with its striking color change is a well-known example. In their pioneering works, Rundle *et al.* have shown that linear iodine chains are formed in the amylose helix in starch-iodine complex by optical and X-ray investigations(Rundle & Baldwin, 1943, Rundle & French, 1943). Although there have been number of studies since then, details of the structure of the included iodine chains and the mechanism of the complex formation still remain unclear. One of the models for starch-iodine complex, which has been widely accepted, is that iodine is present as linear chains of I$_3^-$ anions(Reddy *et al.*, 1964, Robin, 1964). More recently, Teitelbaum *et al.* concluded that the major component of iodine in the amylose helix is in the form of I$_5^-$ from resonance Raman and iodine Mössbauer spectroscopies(Teitelbaum *et al.*, 1978, Teitelbaum *et al.*, 1980). As for the interaction in the complex, it is not resolved whether main contribution comes from dispersion force, or it originates from induced dipole in iodine molecules(Stein & Rundle, 1948), or there are charge transfer from amylose oxygen to iodine chains(Murakami, 1954).

α-Cyclodextrin(α-CD, C$_{36}$H$_{60}$O$_{30}$) also forms inclusion complexes with iodine. In particular, when iodide anions are present, it crystallizes in channel-type structure containing linear polyiodide chains(Noltemeyer & Saenger, 1976, Noltemeyer & Saenger, 1980). These complexes have similar properties to those of the amylose-iodin complex and can be considered as models for the amylose-iodine complex(Noltemeyer & Saenger, 1980).

XAFS spectroscopy has an advantage to be able to directly probe the local electronic and geometrical structures around specific atom species. To obtain further insight about the complex formation, we performed iodine L edge XAFS measurements on the amylose-iodine complex. We also performed measurement on one of the crystalline α-CD-iodine complex (α-CD)$_2$·Cd$_{0.5}$·I$_5$·27H$_2$O, which contains polyiodide chains formed of nearly linear I$_5^-$ anions(Noltemeyer & Saenger, 1980). Since the detailed crystal structure of (α-CD)$_2$·Cd$_{0.5}$·I$_5$·27H$_2$O is known from X-ray diffraction(Noltemeyer & Saenger, 1980), it serves as a well-defined reference in studying amylose-iodine spectra.

2. Experimental

X-ray absorption measurements of iodine L absorption edge region were done on amylose-iodine complex and (α-CD)$_2$·Cd$_{0.5}$·I$_5$·27H$_2$O. We also measured the spectra of solid I$_2$, in which the constituent is I$_2$ molecule, and KI, which is an ionic crystal, for comparison. Samples of amylose-iodine complex were prepared by putting amylose(from nacalai tesque, inc., M.W. ~ 16000) into aqueous solution containing 0.07 mol/l of I$_2$ and KI. Resulting blue-black complex was filtered and washed with deionized water until no I$^-$ could be detected using AgNO$_3$ solution. Obtained complex was mixed with graphite, powdered and pressed into tablets for measurements. Crystalline (α-CD)$_2$·Cd$_{0.5}$·I$_5$·27H$_2$O were obtained by crystallization from aqueous solution of α-CD containing CdI$_2$ and iodine using the same method described in the paper by Noltemeyer & Saenger, 1980. Resulting crystals were ground to powder and pressed into tablets with graphite. Tablets of solid I$_2$ and KI were prepared also after mixing with graphite.

XAFS measurements were performed in transmission mode using a laboratory XAFS measurement system EXAC820(Technos Co. Ltd.) which is equipped with a Mo rotating-anode X-ray source. Measurements were done using a Ge(111) curved crystal monochromator. Photon energies were carefully calibrated using La L characteristic emission lines from cathode material(LaB$_6$) which is evaporated on the anode of the X-ray source. Therefore, although absolute value has some ambiguities, relative energies are accurate within ± 0.1 eV. All the measurements were done at room temperature.

3. Results and Discussion

Figure 1 shows measured iodine L$_3$ XANES spectra of amylose-iodine complex and (α-CD)$_2$·Cd$_{0.5}$·I$_5$·27H$_2$O, with spectra of solid I$_2$ and KI for comparison. Iodine L$_2$ XANES spectra have identical line shapes(not shown). It is seen from the figure that the spectra of amylose-iodine complex and (α-CD)$_2$·Cd$_{0.5}$·I$_5$·27H$_2$O, have very similar line shapes, indicating similarities in electronic and geometrical structures. Also seen from the figure is that the absorption edge energies do not significantly vary in these four spectra.
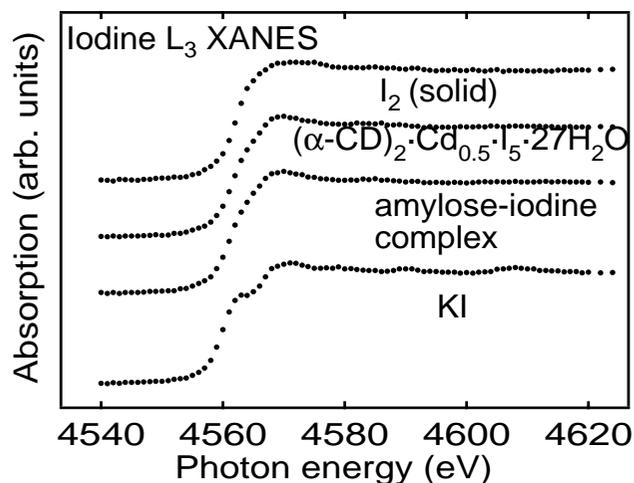
Figure 1
Iodine L_3 XANES spectra of solid I_2, $(\alpha\text{-CD})_2\cdot Cd_{0.5}\cdot I_5\cdot 27H_2O$, amylose-iodine complex, and KI. Spectra are normalized at high energy side of the absorption edge.

Results of iodine L_1 edge XANES measurements are shown in Fig. 2. They have quite different line shapes from those of L_3 edge, and again the spectra of amylose-iodine complex and $(\alpha\text{-CD})_2\cdot Cd_{0.5}\cdot I_5\cdot 27H_2O$ resemble each other with a peak at $h\nu \simeq$ 5187 eV and a broad structure at $h\nu \simeq 5192 \sim 5211$ eV. Together with the similarities in L_3 spectra, this strongly suggests that iodine atoms are in very similar environment in these complexes.
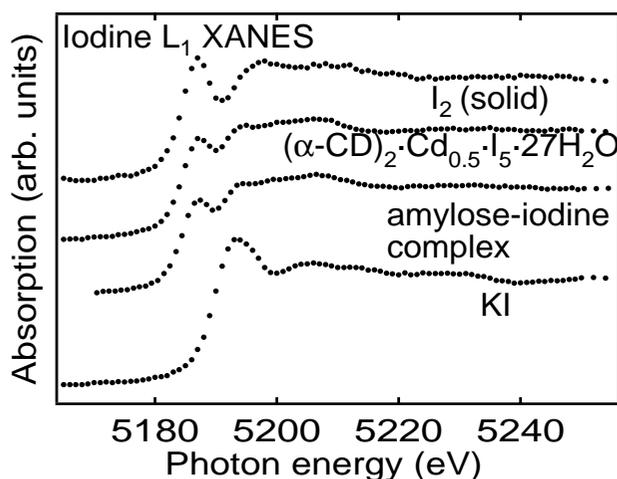
Figure 2
Iodine L_1 XANES spectra of solid I_2, $(\alpha\text{-CD})_2\cdot Cd_{0.5}\cdot I_5\cdot 27H_2O$, amylose-iodine complex, and KI. Spectra are normalized at high energy side of the absorption edge.

The $h\nu \simeq$ 5187 eV peak also appears in solid I_2, while it is absent in the spectrum of KI(apparent shift of the absorption edge in KI L_1 spectrum is not likely to be attributed to shift of the continuum threshold energy because there is no such significant shift of the edge energy in the L_3 spectrum). From the fact that it only appears in L_1 spectra and that it is absent in KI, it can be assigned to $2s \rightarrow 5p$ transition. In the case of I_2 molecule, this

corresponds to the transition from the $2s$ core level to the antibonding $5p\sigma^*$ states. Figure 3 shows an enlarged view of the spectra around this peak. It can be seen from the figure that position of the peak in amylose and α-CD complexes is almost unchanged from that of solid I_2. On the other hand, area of the peak is considerably smaller in these complexes than in solid I_2. This is consistent with the idea that the average formal valency of iodine is -1/5 in $(\alpha\text{-CD})_2\cdot Cd_{0.5}\cdot I_5\cdot 27H_2O$(there are 2 unoccupied MOs derived from the $5p$ orbitals in case of linear I_5^- with 1/5 more electrons per iodine atom), if the area of the peak reflects the vacancy in the iodine $5p$ states.
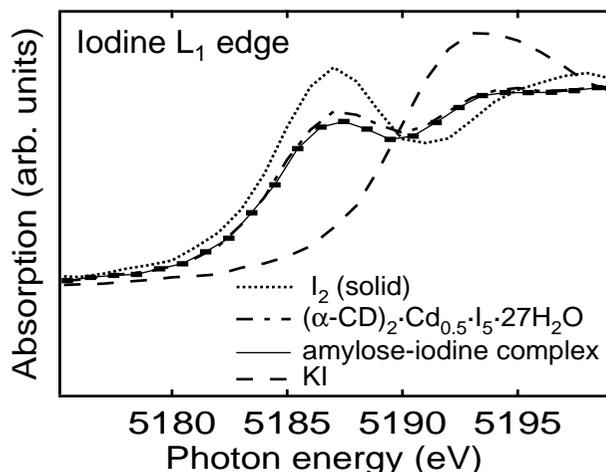
Figure 3
Enlarged view of the iodine L_1 absorption edge of solid I_2, $(\alpha\text{-CD})_2\cdot Cd_{0.5}\cdot I_5\cdot 27H_2O$, amylose-iodine complex, and KI. Statistical error bars are shown on the spectrum of amylose-iodine complex.

Further, the peak area is slightly smaller in amylose-iodine complex compared to the α-CD complex. If we tentatively use the area of this peak as a measure of the occupancy of the iodine $5p$ levels, this means that the average valency of the iodine in amylose-iodine complex is slightly lower than in the α-CD complex. In $(\alpha\text{-CD})_2\cdot Cd_{0.5}\cdot I_5\cdot 27H_2O$, charge transfer from α-CD oxygen to iodine is not likely to occur since oxygen atoms are known to locate rather far away from iodine chains(Noltemeyer & Saenger, 1980). Therefore, if above interpretation of the peak area holds, there are two possibilities. One is that in amylose-iodine complex, $I_2:I_3^-$ ratio is different(more I_3^-) from the value in $(\alpha\text{-CD})_2\cdot Cd_{0.5}\cdot I_5\cdot 27H_2O$ in which the ratio is formally 1:1. The other possibility is that there is charge transfer from amylose oxygen to the unoccupied iodine $5p$ states, which implies that conformation of amylose is somehow different from that of α-CD in $(\alpha\text{-CD})_2\cdot Cd_{0.5}\cdot I_5\cdot 27H_2O$. This will be important in understanding the complex formation, and still further studies are needed.

4. Conclusion

We have measured iodine $L_{1,2,3}$ edge XANES spectra of amylose-iodine complex and $(\alpha\text{-CD})_2\cdot Cd_{0.5}\cdot I_5\cdot 27H_2O$. Iodine L_2 and L_3 XANES spectra of these complexes were found to be very similar. L_1 XANES spectra were also very similar. These facts strongly indicate that the polyiodide chains in amylose-iodine complex have similar structure to the polyiodide chains in $(\alpha\text{-CD})_2\cdot Cd_{0.5}\cdot I_5\cdot 27H_2O$, which consists of I_5^- anions. Near iodine L_1 edge, a peak which can be assigned to iodine $2s \rightarrow 5p$ transition

was observed at about the same energy as in the spectrum of solid I_2. The area of this peak was slightly smaller in amylose-iodine complex than in $(\alpha\text{-CD})_2 \cdot Cd_{0.5} \cdot I_5 \cdot 27H_2O$, implying that there are some differences in electronic or geometrical structure between these complexes.

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