Analysis of the Hydration of the Transition Metals in Supercritical Water

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Introduction
Solvation of ions in supercritical water attracts much attention of a lot of chemists. Since EXAFS can approach the coordination structure around ion species, this method has been applied to ions in supercritical water from the earlier stage of researches on supercritical water[1]. In this paper we have measured the EXAFS spectra of cobalt (Co) K-edge at different temperatures and pressures of cobalt(II) bromide (CoBr2) aqueous solution[2]. Kajimoto et al. have measured the pressure and temperature dependence of the d-d absorption spectrum of Co2+ in sub- and supercritical water[3]. Under the ambient condition, CoBr2 is dissolved in water as [Co(H2O)6]2+, and shows very weak absorption around 510 nm. However with increasing temperature, the absorption band shape shows a drastic change from 300 ºC to 400 ºC at 40 MPa, which was interpreted as the consequence of the coordination structure changes from the octahedral to the tetrahedral. Our results suggest that the coordination number of water around cobalt ion reduces in accordance with the change of the absorption spectrum.

Experimental
In measuring the EXAFS spectrum, CoBr2 aqueous solution was flowed at 0.2 cm3 min-1 through a high-temperature and high-pressure EXAFS cell by a HPLC pump and the system pressure was regulated by a back pressure regulator. The EXAFS cell was equipped with two optical windows made of synthesized diamond (Sumitomo Denko TypeIa or Type Ib; diameter: 3.5 mm thickness: 0.5 mm). The optical path length was 2 mm, and the bore of the window was 2 mm diameter. The temperature of the EXAFS cell was monitored by a thermocouple inside the cell, and controlled by a sheathed heater (1kW) and a thermoregulator. The EXAFS spectra of Co K-edge were taken in a transmission mode at BL-9A and 12C.

Results and Discussion
Figure 1 shows the Fourier transformed data of k3χ(k) for CoBr2 aqueous solutions at different temperatures and pressures. The plot clearly indicates that the number of the nearest neighbor atoms decreases with increasing temperature, and another peak around 2.2 Å gradually increases to 350 ºC. The peaks which appear at the shorter distances than ~1 Å are due to an artifact arising from the Fourier transform of k3χ(k) that mostly contains a residual contribution from the background function. The solid lines in Fig. 1 represent the results of the fitting. The data at RT and 250 ºC were fit by a contribution of a single species (oxygen atom). On the other hand, at 350 ºC including another atomic species (bromide) resulted in better result. The coordination numbers obtained from the fit are listed in Table 1. Under the ambient condition, Co2+ is in a octahedral form [Co(H2O)6]2+. With increasing the temperature, the coordination number of oxygen decreases and bromide anion becomes to contribute to the spectrum, although the coordination numbers at the higher temperature have larger errors due to the poor S/N. Our results support that the coordination structure of Co(II) in aqueous solution changes from the octahedral structure to the tetrahedral structure including bromide anion as counter species. The structure in supercritical region is under investigation.

Table 1. Coordination numbers from EXAFS analysis of CoBr2 aqueous solutions at different temperatures and pressures.

<table>
<thead>
<tr>
<th>T / ºC</th>
<th>P / MPa</th>
<th>d / g cm-3</th>
<th>Conc. / mM H2O Br</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>0.1</td>
<td>1.00</td>
<td>100</td>
<td>6.0</td>
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<td>250</td>
<td>20</td>
<td>0.82</td>
<td>100</td>
<td>4.5</td>
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<tr>
<td>350</td>
<td>20</td>
<td>0.60</td>
<td>50</td>
<td>2.7</td>
</tr>
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References
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