Pressure-induced Hydration Number Change of the Eu$^{3+}$ ion in Aqueous EuCl$_3$ Solutions

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Abstract. We have carried out Raman spectroscopic measurements on aqueous EuCl$_3$ $\cdot$ 20H$_2$O solution as a function of pressure at room temperature. Pressure dependence of the frequency shift of the totally symmetric stretching vibration of the aquo-europium earth ion ($\nu_2$) is examined in conjunction with the hydration number change. We found that the population of Eu$^{3+}$ ion holding eight water molecules in their inner most hydration spheres increases with applied pressure, which means that the lower aquo-complexes become dominant species at high pressures.

1. Introduction

It is now fairly established that the hydration number change takes place in the aqueous solutions [1-3]; in view of the frequency change of the Ln-H$_2$O stretching Raman band ($\nu_2$) across the rare earth series (Ln = rare earth ion) [2], it was concluded that two kinds of aquo-rare earth ions, [Ln(H$_2$O)$_9$]$^{3+}$ and [Ln(H$_2$O)$_8$]$^{3+}$, are in equilibrium in the solutions of middle region of the rare earth series (Gd-Ho or Er). Moreover, the inner-sphere hydration number change takes place from nine for the light rare earth members to eight for the heavy ones.

In this study, Raman spectroscopic measurements were carried out for the aqueous EuCl$_3$ $\cdot$ 20H$_2$O solution where the hydration number change occurs as a function of pressure in the liquid state with a special interest in which hydration number (eight or nine coordination) of the Ln$^{3+}$ ion becomes dominant if we apply the pressure to the system.

2. Methods

The sample of EuCl$_3$ $\cdot$ 20H$_2$O solution were prepared just by dissolving the anhydrous EuCl$_3$ in doubly distilled water by weight. The detailed procedure for the sample preparation was basically the same as described in the previous paper [2, 3]. Each sample solution was filtered through a millipore filter (pore size 10 $\mu$m) to eliminate small particles in the solution.

Raman spectral changes were measured by microspectroscopy together with a diamond anvil cell (DAC) at room temperature. The sample and a few ruby chips were held in a DAC using a stainless steel gasket. To determine the pressure, we used the pressure dependence on the spectral shift of the $R_1$
fluorescence line of the ruby chip [4]. Raman spectra were collected by a JASCO NR-1800 spectrometer equipped with a CCD detector. The 514.5 nm line of argon ion laser excitation (∼300 mW) was selected to use.

3. Results and Discussion

Figure 1 shows the results on Raman spectral changes of the EuCl₃・20H₂O solution as a function of pressure. The spectrum at 0.1 MPa shows a large asymmetry with two bands which we can ascribe the lower frequency band at around ∼385 cm⁻¹ to the 9-coordinated aquo-rare earth ions, [Ln(H₂O)₉]³⁺ and the higher band at 410 cm⁻¹ to the 8-coordinated ones, [Ln(H₂O)₈]³⁺ [2]. Thus the chemical equilibrium reaction expressed in the following way exists in the solution. The observed spectra were

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[\text{Ln(H}_2\text{O)}_9]^{3+} \rightleftharpoons [\text{Ln(H}_2\text{O)}_8]^{3+} + \text{H}_2\text{O}
\]

able to be fitted well by two components, and Figure 2 shows the changes in their curve-fitted spectra of the two species (8- and 9-coordinations) in the solution at various pressures.

Figure 3 shows the pressure dependences of the frequencies for the respective species. Interestingly, the frequencies remain constant or decrease slightly up to 750 MPa, but increase drastically upon further applied pressure which means that the interaction between europium ions and water molecules gets stronger at higher pressures above 750 MPa. We suppose that the components having a lower partial molar volume should become more stable as the applied pressure increases.

We estimated the intensity fractions of the 9-coordinated species, [Ln(H₂O)₉]³⁺ and 8-coordinated species, [Ln(H₂O)₈]³⁺ from the relative integrated Raman intensities. The pressure dependences of the respective intensity fractions are shown in Figure 4. We found that the intensity of 8-coordinated band drastically increase with increasing pressure, which means that the lower aqua-complexes become
dominant species at high pressures. More specifically at a normal pressure the 9-coordinated species are major ones but at about 750 MPa the two intensity fractions becomes almost identical and upon further compression the 8 – coordinated species are in turn dominant ones. This is in accordance with the results of the pressure dependences of the frequencies stated above. We notice that the two intensity fractions keep constant values above 1.2 GPa, which means that at higher pressures the lower aquo-complexes of 8-coordination are stable.

In this respect, it should be referred that anomalous concentration dependence of the inner-sphere hydration number change of aqua-lanthanide ions is reported in aqueous LnCl$_3$ and Ln(ClO$_4$)$_3$ solutions [5-7]; 9-coordinated species increase in population despite a decrease in water content in the solutions. It was suggested that the outer-sphere complex formation along with the chemical equilibrium reaction between 8-coordinated species and 9-coordinated ones is the main reason for the anomalous behavior [7]. Therefore, important conclusion from the present results is that pressure does not work same direction as the salt-concentration effect for the formation of aqua-complexes. It is intriguing whether the similar behavior for the variation of $\nu_w$ frequency with pressure would be observed in the solutions of other rare earth series, because the equilibrium reaction between 8- and 9-coordinations is displaced to one side in e.g. SmCl$_3$ (8-coordination) and TbCl$_3$ (9-coordination) solutions. Thus, ionic radius of the rare earth ion is the important factor determining the coordination behavior of water molecules to rare earth ions in the aqueous LnCl$_3$ solutions. We are now investigating this subject, and this will be published elsewhere.

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