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To cite this article: K Nakajima et al 2010 J. Phys.: Conf. Ser. 215 012072

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Effect of Pressure on the Coordination Structure of Acetate-Rare Earth Complex in Water

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Abstract. Pressure-induced coordination structural changes of the acetate-rare earth complex in water (LnCl₃·20H₂O·CH₃COOLi) have been investigated using Raman spectroscopy. From the analysis of Raman CC stretching band of acetate ion, the integrated Raman intensity of polymeric chain structure decreases with increasing pressure throughout the rare-earth series. The monodentate ligand appears at around 0.6 GPa in the middle-heavy rare earth region. We have determined the difference in the partial molar volume (PMV) (ΔV) among three coordination structures. The rank ordering of the PMV of three coordination structures is as follows: monodentate ligand < bidentate ligand < polymeric chain structure. The absolute values of ΔV_{Polymeric→ Bidentate} and ΔV_{Bidentate→ Monodentate} become larger with decreasing ionic radius of Ln³⁺ ion, and these are probably due to the size effect of Ln³⁺ ion.

1. Introduction

There have been some studies on the coordination structure of the Ln³⁺ ion in solution [1-3]. It is well known that the decrease in the ionic radius of lanthanide (Ln³⁺) ion owing to lanthanide contraction induces coordination structure changes of rare earth electrolytes (LnX; X=anion) in water [4,5], alcohol [6,7], and protic solvent [8,9]. Although it has been investigated that the coordination structure of rare earth electrolytes (LnX; X=anion) solutions at room and low-temperatures, but the pressure effect on the coordination structure of LnX solutions has been never so far. It is interesting to investigate the coordination structure of LnX solutions at high pressure from the viewpoint of solution chemistry.

Another interesting topic concerning the Ln³⁺ ions is the use for probes of Ca²⁺-binding site (mainly Asp and Glu residues) in protein such as calmodulin [10]. The study of the coordination behavior of the carboxyl (COO⁻) ion with Ln³⁺ ion is important for understanding the substitution effect of Ln³⁺ ions on the Ca²⁺-binding protein [11] because the ionic radius of Ln³⁺ ion is close to that of Ca²⁺ ion. Generally, increasing pressure shifts the equilibrium state to the one with a smaller partial molar volume (PMV)[12]. The carboxylate (COO⁻) - M⁺ (cation) complex dissociates with increasing pressure, and the volume change accompanying with the dissociation of carboxylate (COO⁻) - M⁺ (cation) complex shows the large negative value due to the electrostriction. Increasing pressure shifts
to the elimination of the metal (M⁺) ion from the binding site in the polypeptide and protein having the M⁺ ion [13, 14]. Here, we can expect that the combined use of the Ln³⁺ ion and pressure may control the elimination of the metal ion from the binding site in proteins.

Recently, we have investigated the coordination structure of an acetate-rare earth complex in water (LnCl₃·2H₂O·CH₃COOLi) at 298 [15] and 77 K [16] to investigate the coordination relationship between the Ln³⁺ ion and acetate ion in water. Some reasons that we employed LnCl₃·2H₂O·CH₃COOLi solutions as the reagents are as follows. (1) As the solubility of rare earth acetates in water is not too high (at most Ln(CH₃COO)₃·200–250H₂O), the Raman Ln³⁺—OH₂ stretching (ν₇) band which is a measure of the coordination number change of a Ln³⁺ ion is not observed in the aqueous Ln(CH₃COO)₃ solutions. (2) The information of the coordination number change of Ln³⁺ ions in the glassy rare earth chloride solutions (LnCl₃·2H₂O; in this system, Cl⁻ ion does not coordinate to Ln³⁺ ion.) is available in the literatures[4,5]. (3) Metal (Ln³⁺ ion) to ligand (CH₃COO⁻ ion) ratio of 1:1 might be better than 1:3 to simply identify the coordination behavior of the acetate ion with a Ln³⁺ ion, because the acetate ion in aqueous Ln(CH₃COO)₃ solutions might make more complex coordination structures.

In this study, we have investigated that pressure-induced coordination structural change of the acetate-rare earth complex in the LnCl₃·2H₂O·CH₃COOLi by Raman spectroscopy. We determined the difference in the PMV (∆V) between the coordination structures in the LnCl₃·2H₂O·CH₃COOLi solution.

2. Methods

Anhydrous rare earth chlorides (LnCl₃; Ln³⁺ = La³⁺ – Lu³⁺) were obtained from Soekawa Chemical Co. Lithium acetate (CH₃COOLi) was obtained from Wako Junyaku Co. Ltd. All sample solution (LnCl₃·2H₂O·CH₃COOLi) was prepared by dissolving the required amounts of LnCl₃ and CH₃COOLi in water.

Raman spectra were measured by a JASCO NR-1800 Raman spectrophotometer equipped with a single monochromator and a CCD detector. The exposure time of each run and spectral resolution were 300 s and 12.0 cm⁻¹, respectively. The 514.5 nm line from Lexel Ar⁺ ion laser was used as an exciting source with a power of 350 mW. For the high pressure experiments, we used a diamond anvil cell (DAC). The sample solutions were placed together with a small amount of powdered ruby chip in a SUS301 gasket mounted on the DAC. The ruby chip was used for a pressure calibrant [17,18]. All the measurements were made at a room temperature (298 K). The obtained spectra were fitted with the Gaussian–Lorentzian mixing functions using the GRAMS/386 software (Galactic Ind. Co. Ltd.) to analyze the CC stretching band.

3. Results and Discussion

Figure 1 shows the typical Raman spectra of the CC stretching band of LnCl₃·2H₂O·CH₃COOLi (typically shown here for Ln³⁺ =Pr³⁺, Eu³⁺, and Lu³⁺) at various pressure. The CC stretching band (ν(CC) of acetate ion has a strong Raman intensity, and is sensitive to the coordination structure of the acetate ion in the LnCl₃·2H₂O·CH₃COOH [16]. According to our previous studies [15, 16], the two peaks at 946 and 958 cm⁻¹ of ν(CC of the acetate ion are assigned to a bidentate ligand and a polymeric chain structure, respectively. In the present results, the peaks at around 946 and 957 cm⁻¹ were determined by the second derivative analysis of original spectra at normal pressure throughout the series. These peaks are good agreement with the previous assignments of the acetate ion.

The Raman intensity of the bidentate ligand increases with increasing pressure throughout the series, and that of the polymeric chain structure decreases. In the middle—heavy rare earth region (after Tb³⁺ ion), the peak at 938 cm⁻¹ appears at above 0.6 GPa. Wang et al.[19] reported that the monodentate
ligand in the aqueous (CH₃COO)₂Mg solution was observed at around 940 cm⁻¹, and this peak is close to the peak at 938 cm⁻¹ in the LnCl₃·2H₂O·CH₃COOLi. Thus, the peak at 938 cm⁻¹ is assigned to the

![Figure 1](image1)

**Figure 1.** Raman CC stretching spectra of the LnCl₃·2H₂O·CH₃COOLi (shown here Ln³⁺=Pr³⁺, Eu³⁺, and Lu³⁺) at several pressures.

monodentate ligand.

A remarkable point in Fig. 1 is that the free acetate ion, which is the complete dissociation state, is not observed at high pressure throughout the series. This result means that the combined use of the Ln³⁺ ion and pressure can control the elimination of the Ln⁻ ion from the Ln⁻-acetate complex.

To discuss more about experimental results, we determined the difference in the partial molar volume (PMV) of the coordination structures of LnCl₃·2H₂O·CH₃COOLi using the pressure dependence of the relative Raman intensities between the coordination structures. Assuming that the ratio of the Raman cross sections between the coordination structures is independent of a pressure [20], the volume differences (ΔV_polymeric→bidentate and ΔV_bidentate→monodentate) are given by

\[
ΔV^{a→b} = -RT \left( \frac{\partial \ln(I_2/I_1)}{\partial p} \right)
\]

where \( R \), \( T \), and \( p \) indicate the gas constant, temperature, and pressure, respectively. \( I_1 \) and \( I_2 \) shows the integrated Raman intensity of each coordination structure. Figure 2 shows the plots for ln \( K \), which is equal to the (a) \( \ln(I_{\text{bidentate}}/I_{\text{polymeric}}) \) or (b) \( \ln(I_{\text{monodentate}}/I_{\text{bidentate}}) \), versus pressure at 298 K. The values of \( ΔV \) obtained by the slopes of the linear line in Fig. 2 are summarized in Figure 3. \( ΔV_{\text{polymeric→bidentate}} \) and \( ΔV_{\text{bidentate→monodentate}} \) show negative values throughout the series. This means that a pressure causes the dissociation of the acetate–Ln³⁺ complex in the LnCl₃·2H₂O·CH₃COOLi solution. The rank ordering of the PMVs among three coordination structures is as follows: monodentate ligand < bidentate ligand < polymeric chain structure. As seen in Fig.3, the absolute values of these \( ΔV \) become
larger with increasing ionic radius of Ln$^{3+}$ ion, and these values show a good linear correlation with the ionic radius of Ln$^{3+}$ ion. Clearly, the changes in the $\Delta V$Polymeric$\rightarrow$Bidentate and $\Delta V$Bidentate$\rightarrow$Monodentate with decreasing ionic radius of Ln$^{3+}$ ion have large contribution from the size effect of Ln$^{3+}$ ion resulting from the lanthanide contraction.

Here we discuss the pressure-induced CC stretching frequency ($\nu_{CC}$) shifts of three coordination structures. When the intermolecular electrostatic interaction between the Ln$^{3+}$ and acetate ions becomes stronger, the force constant of the CC bond of the acetate ion weakens and the $\nu_{CC}$ frequency shifts to a higher frequency [15]. On the whole, $\nu_{CC}$ frequencies of three coordination structures shift to a higher frequency with increasing pressure. This shows that the intermolecular electrostatic interaction between the Ln$^{3+}$–acetate complexes becomes stronger with increasing pressure. Figure 4 shows the pressure dependence of the CC stretching frequency shifts ($\partial \nu_{CC}/\partial p$) of three coordination structures in the LnCl$_2$·20H$_2$O·CH$_3$COOLi solution as a function of ionic radius of Ln$^{3+}$ ion. The value of ($\partial \nu_{CC}/\partial p$) of the polymeric chain structure decreases with decreasing ionic radius of Ln$^{3+}$ ion, though those values of bidentate and monodentate ligands increase. This result shows that the intermolecular electrostatic interaction of the Ln$^{3+}$ – bidentate/monodentate ligands under high pressure becomes stronger with decreasing ionic radius of Ln$^{3+}$ ion. On the other hand, that of Ln$^{3+}$–polymeric chain structure accompanying with pressurization becomes weaker.

Next we discuss the pressure-induced coordination structural change of the Ln$^{3+}$ ion in the LnCl$_2$·20H$_2$O·CH$_3$COOLi solution. In view of the Raman Ln$^{3+}$–OH$_2$ stretching ($\nu_w$) frequency (~350 cm$^{-1}$) change [21] in the concentrated aqueous rare earth solution across the series together with the X-ray diffraction data [22], it was concluded that the coordination numbers for the light and heavy rare earth regions are nine and eight, respectively. On the basis of these results, recently we showed that the coordination structure of the Ln$^{3+}$ ion composed by the acetate ions and water molecules in the LnCl$_2$·20H$_2$O·CH$_3$COOLi solution changes with decreasing ionic radius of Ln$^{3+}$ ion using the Raman $\nu_w$ and $\nu_{CC}$ bands [15, 16]. It was found that the change in the coordination structure of Ln$^{3+}$ ion across the rare earth series is mainly due to the change from the polymeric chain structure to the bidentate ligand of acetate ion rather than the elimination of one water molecule. In other word, the increase of bidentate ligand population is a main cause for the coordination structural change of the Ln$^{3+}$ ion in the LnCl$_2$·20H$_2$O·CH$_3$COOLi solution. The present result showed that the population of the bidentate ligand largely increases with increasing pressure throughout the series, and the PMV of bidentate ligand is smaller than that of polymeric structure. On the basis of previous and present results, we can suggest that the coordination structure of Ln$^{3+}$ ion in the LnCl$_2$·20H$_2$O·CH$_3$COOLi solution also changes with increasing pressure. Moreover, a monodentate ligand appeared in the middle–heavy rare earth region at above 0.6 GPa (above Tb$^{3+}$ ion). The monodentate ligand has the smallest PMV in
three coordination structures. Therefore, the cause for the pressure-induced coordination structural change of Ln$^{3+}$ ion in the light—middle region might be different with that in the middle—heavy rare earth region. However, it is difficult to say more about this. More experimental study such as the pressure dependence of the Raman Ln$^{3+}$—OH$_2$ stretch ($\nu_w$) spectra in this system will be needed for the understanding of the coordination structural change of Ln$^{3+}$ ion.

In summary, we have investigated the pressure effect on the coordination structure of acetate-rare earth complex in water using Raman spectroscopy. Our results showed that the rank ordering of the PMV of three coordination structures is the following; monodentate ligand < bidentate ligand < polymeric chain structure. The absolute values of $\Delta V$ become larger with decreasing ionic radius of Ln$^{3+}$ ion probably due to the size effect of Ln$^{3+}$ ion. The increases of population of the bidentate and monodentate ligands with increasing pressure might induce coordination structural change of Ln$^{3+}$ ion in the acetate-rare earth complex in water. Moreover, the combined use of the Ln$^{3+}$ ion and pressure could control the elimination of the metal ion from the binding site in proteins.

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