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

K Nakajima1, A Shimizu1, T Takekiyo*, Y Yoshimura2, and T Koizumi2

1 Department of Environmental Engineering for Symbiosis, Soka University, 1-326 Tangi-cho, Hachioji, Tokyo, 192-8577, Japan
2 Department of Applied Chemistry, National Defense Academy, 1-10-20 Hashirimizu, Yokosuka, Kanagawa, 239-8686, Japan

*E-mail: take214@nda.ac.jp

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 ΔVpolymeric→bidentate and ΔVbidentate→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·CH₃COOH) at 298 [15] and 77 K [16] to investigate the coordination relationship between the Ln³⁺ 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 (νw) 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 (ΔV) 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 solutions (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 (νCC) 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 νCC 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 (CH$_3$COO)$_2$Mg solution was observed at around 940 cm$^{-1}$, and this peak is close to the peak at 938 cm$^{-1}$ in the LnCl$_3$$\cdot$2H$_2$O$\cdot$CH$_3$COOLi. Thus, the peak at 938 cm$^{-1}$ is assigned to the 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 Ln$^{3+}$ ion and pressure can control the elimination of the Ln$^{3+}$ ion from the Ln$^{3+}$-acetate complex.

To discuss more about experimental results, we determined the difference in the partial molar volume (PMV) of the coordination structure s of LnCl$_3$$\cdot$2H$_2$O$\cdot$CH$_3$COOLi using the pressure dependence of the relative Raman intensities between the coordination structures. Assuming that the ratio of the Raman cross sections between the coordination structures is independent of a pressure dependence of the relative Raman intensities between the coordination structures. Figure 2 shows the plots for ln(IBidentate/IPolymeric) of the LnCl$_3$$\cdot$2H$_2$O$\cdot$CH$_3$COOLi. The straight lines represent the results of the least-squares analysis.

\[
\text{\Delta V}^{\text{Polymeric} \rightarrow \text{Bidentate}} = -RT \left( \frac{\partial \ln(I_s/I_b)}{\partial p} \right)_{I_b}
\]

where $R$, $T$, and $p$ indicate the gas constant, temperature, and pressure, respectively. $I_b$ and $I_s$ 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 $\Delta V$ obtained by the slopes of the linear line in Fig. 2 are summarized in Figure 3. $\Delta V^{\text{Polymeric} \rightarrow \text{Bidentate}}$ and $\Delta V^{\text{Bidentate} \rightarrow \text{Monodentate}}$ show negative values throughout the series. This means that a pressure causes the dissociation of the acetate$-$Ln$^{3+}$ complex in the LnCl$_3$$\cdot$2H$_2$O$\cdot$CH$_3$COOLi 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 $\Delta V$ become

![Figure 1. Raman CC stretching spectra of the LnCl$_3$$\cdot$2H$_2$O$\cdot$CH$_3$COOLi (shown here Ln$^{3+}$=Pr$^{3+}$, Eu$^{3+}$, and Lu$^{3+}$) at several pressures.](image1)

![Figure 2. Pressure dependences of (a) ln($I_{\text{Bidentate}}$/$I_{\text{Polymeric}}$) and (b) ln($I_{\text{Monodentate}}$/$I_{\text{Bidentate}}$) of the LnCl$_3$$\cdot$2H$_2$O$\cdot$CH$_3$COOLi. The straight lines represent the results of the least-squares analysis.](image2)
larger with increasing ionic radius of Ln$^{3+}$ ion, and these values show a good linear correlation with the ionic radius of Ln$^{3+}$ ion. Clearly, the changes in the $\Delta V^{\text{Polymeric-Bidentate}}$ and $\Delta V^{\text{Bidentate-Monodentate}}$ 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 ($\left(\frac{\partial \nu_{CC}}{\partial p}\right)_T$) of three coordination structures in the LnCl$_3$·20H$_2$O·CH$_3$COOLi solution as a function of ionic radius of Ln$^{3+}$ ion. The value of ($\frac{\partial \nu_{CC}}{\partial p}$)$_T$ 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$_3$·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$_3$·20H$_2$O·CH$_3$COOLi solution changes with decreasing ionic radius of Ln$^{3+}$ ion using the Raman $\nu_w$ and vCC 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$_3$·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$_3$·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

![Figure 3](image-url3.jpg)

**Figure 3.** Volume difference among the bidentate, monodentate ligands, and polymeric chain of LnCl$_3$·20H$_2$O·CH$_3$COOLi as a function of ionic radius of Ln$^{3+}$ ion. The straight lines represent the results of the least-squares analysis. The standard errors of $\Delta V$ value are estimated by the errors of the linear slope in Fig. 2.

![Figure 4](image-url4.jpg)

**Figure 4.** Pressure dependence of the $\nu_{CC}$ frequency for each coordination structure as a function of ionic radius of Ln$^{3+}$ ion. The closed and open circles, and open triangle represent the polymeric chain, bidentate ligand, and monodentate ligand, respectively. The standard errors are estimated by the errors of the linear slope of the pressure vs $\nu_{CC}$ frequency.
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$_2$ stretching ($\nu_w$) 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.

References
[1] Alexander A 1995 Chem. Rev. 95 273
[2] Supkowski R M and Horrocks Jr W D 2002 Inorg. Chim. Acta 340 44
[3] Yoshimura Y, Hirayama K, and Makiguchi H 2007 J. Raman Spectrosc. 38 819
[4] Kanno H and Hiraishi J 1982 J. Phys. Chem. 86 1488
[5] Kanno H and Hiraishi J 1984 J. Phys. Chem. 88 2787
[6] Kanno H, Namekata S, and Akama Y. 1998 J. Alloys Compd. 36 275
[7] Yoshimura Y, Namekata S, and Kanno H 2001 J. Solution Chem. 30 213
[8] Ishiguro S, Kato K, Nakasone S, Takahashi R, and Ozutumi K. 1991 J. Chem. Soc., Faraday Trans. 87 3379.
[9] Takekiyo T, Yoshimura Y, Ikeji Y, Hatano N, and Koizumi T 2008 J. Phys. Chem. B 112 13355
[10] Song Y Y, Xu Y Z, Weng S FG, Wang L B, Li X F, Zhang T F, and Wu J G 1999 Biospectroscopy 5 371
[11] Welch J T, Kearny W R, and Franklin S J 2003 Proc. Natl. Acad. Sci. USA 100 3725
[12] Haman S D In Modern Aspects of Electrochemistry, Conway B E, Bockris J O’M Eds; Plenum, London, 1974 Vol. 9 Chap. 2
[13] Dzwolak W, Kato M, Shimizu A, and Taniguchi Y 1999 Biochim. Biophys Acta 1433 45
[14] Takekiyo T, Yoshimura Y, Okuno A, Shimizu A, Kato M, and Taniguchi Y 2008 J. of Phys. Conf. Ser. 121 042003
[15] Takekiyo T and Yoshimura Y 2007 J. Phys. Chem. A 111 6039
[16] Yoshimura Y, Takekiyo T, and Shimizu A 2007 Cryobiol. Cryotech 53 167 (in Japanese)
[17] Mao H K, Bell P M, Shaner J W, and Steinberg D J 1978 J. Appl. Phys. 49 3276
[18] Mao H K, Xu J, and Bell P M 1986 J. Geophys. Res. 91 4673
[19] Wang L Y, Zhang Y H, and Zhao L 2005 J. Phys. Chem. A 109 609
[20] Takekiyo T and Yoshimura Y 2006 J. Phys. Chem. A 110 10829
[21] Kanno H and Hiraishi J 1980 Chem. Phys. Lett. 75 553
[22] Habenschuss A and Spedding F H 1979 J. Chem. Phys. 70 2797