Pressure Effect on the Coordination of Cl\(^{-}\) ions to Ln\(^{3+}\) ions in Anhydrous Methanol LnCl\(_3\) Solutions

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Abstract

We have carried out Raman spectroscopic measurements on the anhydrous LnCl\(_3\) \(\cdot\) 20MeOH solutions (Ln\(^{3+}\)=Pr\(^{3+}\) and Ho\(^{3+}\)) as a function of pressure at room temperature. Pressure dependence of the frequency of the Ln-Cl Raman band (\(\nu_{\text{Ln-Cl}}\)) is examined in conjunction with the formation of chloro-complexes. We have found that the \(\nu_{\text{Ln-Cl}}\) wavenumber decreases with increasing pressure, which means that the higher chloro-complexes become dominant species at high pressures.

1. Introduction

In previous studies on anhydrous LnCl\(_3\) (Ln\(^{3+}\)=rare earth ion) salt solutions, we reported the coordination behavior of Cl\(^{-}\) ions to Ln\(^{3+}\) ions in anhydrous alcohols [1-4]. Typically, the coordination number change (from 8- to 7-coordinated species) occurs in the middle of the rare earth series (Gd\(~\rightarrow\)Ho or Er) in the solutions [2]. The higher chloro-complexes become dominant in the case of heavy rare earth ions in anhydrous methanol LnCl\(_3\) solutions in the glassy state [2, 3]. Moreover, the salt concentration dependence of the frequency for the Ln-Cl stretching Raman band (\(\nu_{\text{Ln-Cl}}\)) of the anhydrous LnCl\(_3\) \(\cdot\) 20MeOH \(\cdot\) XLiCl solutions (Ln\(^{3+}\)=Gd\(^{3+}\) and Ho\(^{3+}\), \(X=0\sim4\)) increases with increasing concentration (\(X\)), which apparently means that the lower chloro-complexes become dominant with an increase in the salt concentration [4]. This is anomalous in the sense of an apparent reversal of the law of mass action. We suppose that the similar behavior for the variation of \(\nu_{\text{Ln-Cl}}\) frequency against the applied pressure may be observed, because salt concentration and pressure often give a same effect on the system [5].

In this study, Raman spectroscopic measurements were carried out for the anhydrous LnCl\(_3\) \(\cdot\) 20MeOH solutions (Ln\(^{3+}\)=Pr\(^{3+}\) and Ho\(^{3+}\)) as a function of pressure in the liquid state with a special interest whether the pressure effect on the \(\nu_{\text{Ln-Cl}}\) frequency is the same as the concentration effect on the formation of chloro-complexes.

2. Experimental details

Anhydrous LnCl\(_3\) \(\cdot\) 20MeOH solutions (Ln\(^{3+}\)=Pr\(^{3+}\), Ho\(^{3+}\)) were prepared just by dissolving the required amounts of anhydrous rare earth chlorides (Mitsuwa, \(>99.9\%\)) in methanol (Wako pure chemicals, \(>99.9\%\)) by weight. The detailed procedure for the sample preparation was basically the same as described in the previous papers [2-4]. Each sample solution was filtered through a millipore filter (pore size 10 \(\mu\) m) to eliminate small particles in the solutions.

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 [6]. 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

Firstly, Figures 1 shows the Raman spectral changes of the PrCl₃ • 20MeOH solution at room temperature as a function of pressure. The band at around ∼235 cm⁻¹ is ascribed to the stretching vibration of chloride ions coordinated to Pr³⁺ ions (ν Ln-Cl band). As reported previously, the ionic environments are not composed solely of alcohol molecules and they include chloride anions [2]. In this study, we have found that the ν Ln-Cl wavenumber decreases with increasing pressure. Basically, the formation of a higher halogeno complex generally results in the decrease of the ν Ln-Cl stretching frequency [7, 8]. Thus, the results mean that the higher chloro-complexes become dominant species at high pressures.

Next, we present what changes are observed in the formation of rare earth complex for the HoCl₃ • 20MeOH solution chosen as a typical example for the middle/heavy rare earth solutions where the coordination number changes (Figure 2). The ν Ln-Cl wavenumber of the HoCl₃ • 20MeOH solution also decreases with increasing pressure. The peak frequencies for the measured solutions plotted against the pressure are complied in Figure 3. We found that the solution solidified at around 1.1 GPa (shown as a red closed triangle in Figure 3). As a comparison, Figure 4 shows the results for anhydrous LnCl₃ • 20MeOH • XLiCl solutions at a normal pressure (Ln³⁺ = Pr³⁺ and Ho³⁺, X=0 ∼4). As can be seen in Figure 3, the frequency of the ν Ln-Cl band for the LnCl₃ • 20MeOH solution decreases with an increase in the pressure, which is normal behavior in the sense that higher chloro-complexes are favored at higher pressures. Therefore, in viewing of the obtained results, the pressure dependence is not curious. Notably, this is just opposite of what the concentration effect on the formation of chloro-complexes in the HoCl₃ • 20MeOH • XLiCl solution shows: the ν Ho-Cl shifts to a higher frequency side with increasing concentration X as shown in Figure 4.
In addition, by comparing the effect of pressure with that of salts, we can see that the former is larger but the $\nu_{\text{Ln-Cl}}$ stretching frequency becomes almost constant in the higher pressure region. This result implies that the concentration of the ligand ions (Cl$^-$) per one Ln$^{3+}$ ion might be saturated at higher pressures, ($p>400\text{-}500\text{ MPa}$) though the explanation is speculative at the moment.

We explain the present results by applying the same mechanism used previously reports [3, 4] as follows. That is, assuming that the average inner-sphere complexes for light rare earth ions in methanolic LnCl$_3$ solutions are [LnCl$_x$(MeOH)$_y$]$^{z+}$ ($x+y=8$; $x=1$, $z=2$ or $x=2$, $z=1$), the two kinds of equilibria, $i.e.$, the equilibrium reactions between the two coordination numbers (8- and 7-coordinated species) and between higher and lower chloro-complexes, simply shift to the higher chloro-complexes sides with applied pressure, resulting in the decrease of the $\nu_{\text{Ln-Cl}}$ frequency.

8-coordinated

$$[\text{LnCl}_x(\text{MeOH})_y]^+ + \text{Cl}^- \quad \rightarrow \quad [\text{LnCl}_{x+1}(\text{MeOH})_{y+1}]^{(z-1)+} + \text{MeOH}$$

7-coordinated

$$[\text{LnCl}_x(\text{MeOH})_{y+1}]^{z+} + \text{Cl}^- + \text{MeOH} \quad \rightarrow \quad [\text{LnCl}_{x+1}(\text{MeOH})_{y+2}]^{(z-1)+} + 2\text{MeOH}$$

On the other hand, in the case of salt concentration effect on the $\nu_{\text{Ho-Cl}}$ frequency (Figure 4), the reaction shifts to the lower total coordination number side with increasing salt (LiCl) concentration $X$. In this condition, there may be a sharing of solvent alcohol molecules between cations: as the salt concentration $X$ increases, some methanol molecules outside of the inner-sphere solvation (coordination) shells become a kind of dangling state due to a lack of alcohol molecules and this induces a breakdown of the outer second hydration spheres. Some of these
dangling alcohol molecules enter into the innermost coordination spheres. In this relation, it may be interesting to refer that this peculiar concentration dependence of the coordination of Cl\(^-\) ions to Ln\(^{3+}\) ions in the anhydrous methanol LnCl\(_3\) solutions is only observable for the middle rare earth solutions (Gd~Ho) in which a coordination number change occurs. That is, the \(\nu_{\text{Ln-Cl}}\) frequencies of the light and heavy rare earth salt solutions show normal behavior. Accordingly, the phenomenon is related to the coordination number change of the Ln\(^{3+}\) ions in the transition region.

In conclusions, we have investigated the pressure dependence of the frequency for the Ln-Cl stretching Raman band \( (\nu_{\text{Ln-Cl}}) \) of the anhydrous light (PrCl\(_3\)) and middle/heavy (HoCl\(_3\)) rare earth chloride solutions in the liquid state at room temperature. The present results exhibit important aspects of the complexation of the alcohol rare earth chloride solutions: pressure does not give a same effect on the system as salt concentration.

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