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Raman study of alcoholic solutions of anhydrous rare earth chlorides

H. Kanno[a,*], S. Namekata[a], Y. Akama[b]

[a]Department of Chemistry, National Defence Academy, Yokosuka 239, Japan
[b]Department of Chemistry, Meisei University, Hino, Tokyo 191, Japan

Abstract

Raman Ln–Cl stretching spectra (Ln=rare earth ion) were measured for alcoholic solutions (alcohol=methanol, ethanol and n-propanol) of anhydrous rare earth chlorides. From the extended s-shaped variation of the frequency for the Ln–Cl stretching Raman band across the series, it is concluded that the inner-coordination number of rare earth ions decreases by one in the latter region of the rare earth series.

Keywords: Alcoholic solutions; Anhydrous rare earth chlorides; Coordination; Number change; Raman spectra

1. Introduction

After a long dispute [1–6], it is now widely accepted that the inner-sphere hydration number of rare earth ions in aqueous rare earth salt (chloride, perchlorate, etc.) solutions changes from nine for light rare earth members to eight for heavy ones in the middle of the series. The main cause for this hydration number change is the decrease of the ionic radius of rare earth ions from La^{3+} to Lu^{3+} which gives rise to a large difference between the ionic radius and the size of the hydration sphere and causes a decrease of the hydration number by one to fit the size of the hydration sphere to the ionic radius of the rare earth ion [3,6,7]. The important point is that the hydration number change is the major cause for various irregularities observed for aqueous rare earth electrolyte solutions [8,9].

In recent years, a similar solvation (coordination) number change for rare earth ions has been observed in several nonaqueous solution systems of rare earth electrolytes [10–13]. In view of these observations, it would be interesting to determine whether or not the coordination number of rare earth ions in alcohol solution shows a change across the series because there are many varieties of alcohols and their solutions are similar in some respects to aqueous solutions. Since the size of alcohol molecules is different from that of water molecules, the coordination number change, if it occurs in alcohol solutions, will give a deeper insight into the mechanism.

In this work, we chose $LnCl_3$ (Ln=rare earth ion) as the electrolyte and measured the Ln–Cl stretching Raman spectra of alcoholic $LnCl_3$ solutions [alcohol=methanol (MeOH), ethanol (EtOH) and n-propanol (PrOH)] to observe the coordination behavior of rare earth ions across the series.

2. Experimental details

All anhydrous rare earth chlorides (purity >99.9%) were obtained from Mituwa and were used as received. Alcohols (alcohol=methanol, ethanol and n-propanol, purity >99.8%) were purchased from Wako. All sample solutions were prepared in a glove box by dissolving the anhydrous rare earth chloride in absolute alcohol by weight. Special care was taken to prevent chemical decomposition upon dissolution of the anhydrous rare earth chloride in the alcohol: the anhydrous rare earth chloride was moistened with alcohol vapor overnight before liquid alcohol was slowly added to the weighed $LnCl_3$. Several sample solutions were also prepared by adding a small amount of water or LiCl to observe the effect of water or excess chloride ions on the Raman spectra of the solutions. All solutions were filtered with a millipore filter of pore size 10 μm to eliminate small particles in order to obtain a better Raman spectrum. The salt concentration of the solution was expressed by R (=moles of alcohol/moles of rare earth chloride). An R value of 20 was employed in this work to obtain a strong Raman band.

Raman spectra were recorded with a JASCO NR-1800 Raman spectrometer using ~100 mW of the 514.5 nm line of a LEXEL argon ion laser as excitation source. The

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*Corresponding author. Fax: +81 468 44 5901.

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frequency calibration was performed by use of the ν_4 band (at 218 cm^{-1}) for carbon tetrachloride.

3. Results and discussion

Fig. 1 shows typical Raman spectra of alcoholic $GdCl_3$ solutions (alcohol=methanol, ethanol and n-propanol). For all alcohol solutions we clearly observe a Ln(Gd)–Cl stretching Raman band (a ν_1 band) in the frequency region from 218 to 270 cm^{-1}, indicating that inner-sphere chloro–rare earth complexes are formed in these solutions. A very weak Ln–O stretching Raman band is also observable in the spectrum for the methanolic $GdCl_3$ solution at ~350 cm^{-1}, but it is too weak to be given a precise frequency assignment. Therefore, we concentrate only on the frequency variation of the ν_1 band across the series. The main object of this study is to determine whether or not a coordination number change of rare earth ions takes place in alcoholic $LnCl_3$ solutions, therefore several points must be clarified before the ν_1 data are used for determining the series behavior of the ν_1 frequencies.

In order to confirm that a small amount of water does not seriously affect the frequency of the ν_1 band, a few Raman measurements were carried out on $PrCl_3 \cdot 20MeOH$ solution by adding 1 and 3 mol% H_2O and the results obtained were as follows: neat $PrCl_3 \cdot 20MeOH$ solution, $\nu_1 = 232 \pm 2\ cm^{-1}$; $PrCl_3 \cdot 20MeOH$ solution with 1 mol% H_2O, $\nu_1 = 231 \pm 2\ cm^{-1}$; and $PrCl_3 \cdot 20MeOH$ solution with 3 mol% H_2O, $\nu_1 = 230 \pm 2\ cm^{-1}$. Therefore, it is evident that a small amount of water in the methanolic $LnCl_3$ solutions has only a small effect on the frequency of the ν_1 band and that this frequency shift is small enough to be neglected in monitoring the ν_1 series behavior.

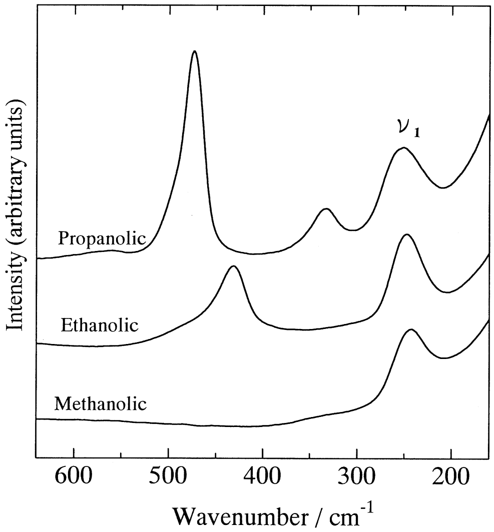

Fig. 1. Typical Raman spectra of alcoholic $GdCl_3$ solutions (alcohol=methanol, ethanol and n-propanol), $R=20$. Bottom spectrum, methanolic $GdCl_3$ solution; middle spectrum, ethanolic $GdCl_3$ solution, the Raman band at 433 cm^{-1} is due to ethanol; top spectrum, n-propanolic $GdCl_3$ solution, the Raman bands at 326 and 465 cm^{-1} are due to n-propanol.

Another point which must be checked is the salt concentration dependence of the ν_1 frequency because all the rare earth chloride solutions could not be prepared exactly at $R=20$ due to the slight decomposition of $LnCl_3$ in the process of its dissolution in alcohol. We carried out a few Raman measurements on the methanolic $PrCl_3$ solutions by changing the R value from 20 to 30. A very small downward frequency shift is observed on going from the $PrCl_3 \cdot 20MeOH$ solution ($\nu_1 = 232 \pm 2\ cm^{-1}$) to the $PrCl_3 \cdot 30MeOH$ solution ($\nu_1 = 231 \pm 2\ cm^{-1}$), demonstrating that the average chemical form of the chloro–Pr^{3+} complexes does not change very much on dilution from $R=20$ to 30. Therefore, it is evident that a small concentration change does not alter the average chemical form of the Ln^{3+} complexes at this high salt concentration.

A comment must be made about the ν_1 frequency shift on addition of LiCl to $PrCl_3 \cdot 20MeOH$ solution: $\nu_1 = 232 \pm 2\ cm^{-1}$ for $PrCl_3 \cdot 20MeOH$ solution, and $\nu_1 = 230 \pm 2\ cm^{-1}$ for $PrCl_3 \cdot LiCl \cdot 20MeOH$ solution. The small, but detectable, frequency decrease should be ascribed to the increased formation of higher chloro-complexes such as $[PrCl_2(MeOH)_n]^-$ and $[PrCl_3(MeOH)_m]$. In aqueous ZnX_2 solutions (X=Cl, Br and I) [14], it is well established that the frequency of the M–X stretching Raman band decreases on going from di-, tri- to tetra-halogeno complex ions: e.g., $ZnBr_2$, $\nu_1 = 208$; $ZnBr_3^-$, $\nu_1 = 183$; and $ZnBr_4^{2-}$, $\nu_1 = 172\ cm^{-1}$. Therefore, the small frequency shift indicates that the shift of the chemical equilibria among Ln species is small in the case of the addition of LiCl to $LnCl_3 \cdot 20MeOH$ solution. With these preparatory results, we observed the ν_1 bands of methanolic, ethanolic and n-propanolic $LnCl_3$ solutions of $R=20$.

Fig. 2 shows the ν_1 results for methanolic $LnCl_3$ solutions. A remarkable point is that the ν_1 frequency

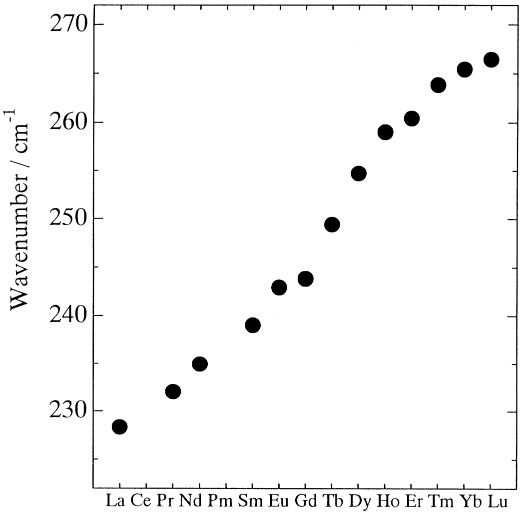

Fig. 2. Frequency variation of the ν_1 band for methanolic $LnCl_3$ solution across the rare earth series.

increases rather linearly from La to Gd, and then increases rapidly from Gd to Ho by about 15 cm^{-1} to begin another linear variation from Ho to Lu. This overall extended s-shaped variation is the same as frequently observed for various thermodynamic and transport properties for aqueous rare earth electrolyte solutions [8,9,15,16] where a coordination (hydration) number change is observed in the middle of the series. From the smooth decrease in the ionic radius for rare earth ions across the series, it is expected that the frequency ν_1 should vary monotonously with ionic radius (atomic number) if there is no coordination number change. Accordingly, the extended s-shaped variation of the ν_1 frequency strongly suggests that the coordination number of rare earth ions should change in the series. Although Raman spectroscopy does not give a definite picture of the coordination number around rare earth ions, a plausible value may be estimated from available experimental data. There have been a few X-ray diffraction studies of methanolic $LaCl_3$ and $NdCl_3$ solutions [17,18]. Wertz and coworkers [17,18] reported the existence of $[LaCl_3(MeOH)_5]$ and $[NdCl_2(MeOH)_6]^+$ as the average inner-sphere complexes in 1.95 M $LaCl_3$ and $NdCl_3$ solutions, respectively. From these results, it can be concluded that the coordination number is eight for light rare earth ions in methanolic $LnCl_3$ solutions. Thus the coordination number change along the series should be from eight to seven. It is needless to say that this speculative conclusion must be tested by a more direct spectroscopic method such as X-ray diffraction in the future.

Fig. 3 shows the summarized ν_1 data for ethanolic $LnCl_3$ solutions. The initial linear region apparently appears to end at about Nd (or Pm), but closer examination reveals that it continues up to about Gd and then there is the middle region where two coordination numbers coexist with a gradual shift of the equilibrium reaction to the lower coordination number side to reach the latter region (Tm–Lu) where all rare earth ions have the lower coordination number. A notable feature of the ν_1 data for the ethanolic solutions is that the value of ν_1 in the end region of the series is a little higher than that for the corresponding methanolic solution. As noted before, the frequency of the M–X (M=metal ion, X=halide ion) stretching Raman band decreases on going from mono-, di-, tri- to tetrahalogeno metal complex ions [14]. Therefore, the higher ν_1 value for the ethanolic solutions indicates that the lower halogeno–lanthanide ions are more abundant than in the methanolic solution.

Fig. 4 shows the ν_1 data for the n-propanolic $LnCl_3$ solutions of $R=20$. In the propanolic $LnCl_3$ solutions, we again observe a clear-cut s-shaped series variation of the ν_1 value. The value increases linearly up to Tb and then increases rapidly by ~15 cm^{-1} to Er, reaching a linear end region (Er–Lu). Therefore, it is evident that the coordination number change occurs in the Tb–Er region in n-propanolic $LnCl_3$ solutions. With these three data sets, it is now firmly established that the coordination number of rare earth ions in alcoholic $LnCl_3$ solution changes in the latter region of the series.

When we compare the ν_1 frequencies among the alcoholic $LnCl_3$ solutions, we immediately notice the following two characteristic features: (1) the ν_1 value for the n-propanolic $LnCl_3$ solution is lower in the first half region and higher in the latter half region than that for the methanolic $LnCl_3$ solution; and (2) the ν_1 value for the ethanolic $LnCl_3$ solution is higher by about 2 cm^{-1} than that for the methanolic $LnCl_3$ solution after Sm to Lu, but is lower than that for the n-propanolic $LnCl_3$ solution in

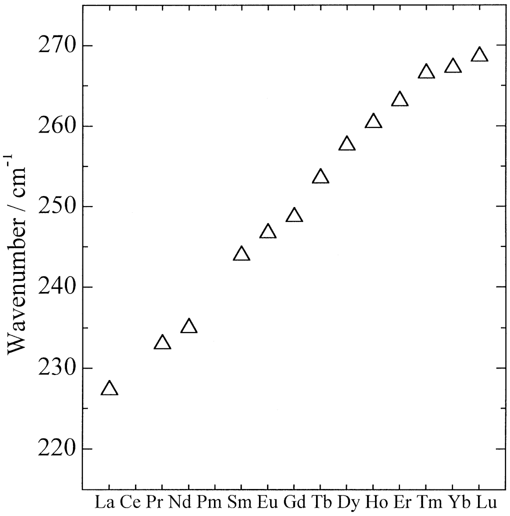

Fig. 3. Frequency variation of the ν_1 band for ethanolic $LnCl_3$ solution across the rare earth series.

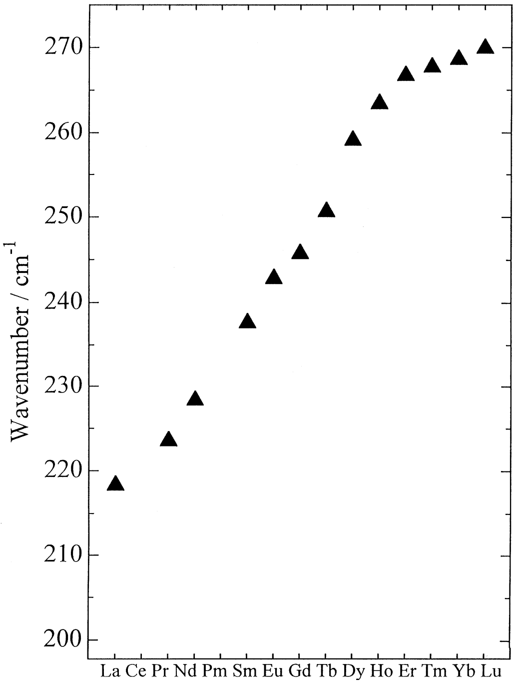

Fig. 4. Frequency variation of the ν_1 band for n-propanolic $LnCl_3$ solution across the rare earth series.

the latter region from Dy to Lu. There has been a relatively large number of reported overall stability constants for the formation of rare earth chloro-complexes in anhydrous methanol, ethanol and n-propanol [19–22]. Due to the diverse experimental conditions (various supporting electrolytes, concentrations and spectroscopic methods), reported stability constants show some scatter, but the trend shows that the stability constant for chloro-complexes in propanol is larger than those in ethanol and methanol, in accordance with the order of the dielectric constants: methanol, 32.6; ethanol, 24.3; and n-propanol, 20.1 at 25°C. Therefore, the lower ν_1 value for the n-propanol solution in the first half region can be ascribed to the formation of higher chloro-complexes such as $[LnCl_3(PrOH)_p]$ and $[LnCl_2(PrOH)_{p+1}]^+$ (p may be 5 or 4). As a higher chloro-complex gives a lower ν_1 value, the observed higher ν_1 value in the latter half region for the n-propanol $LnCl_3$ solution indicates that the main chloro-complexes should be lower than those in ethanolic $LnCl_3$ solutions. The largest frequency difference between the n-propanolic $LaCl_3$ and $LuCl_3$ solutions ($\Delta\nu_1 = 50.8\ cm^{-1}$) among the three alcoholic $LnCl_3$ solutions ($\Delta\nu_1 = 38.1$ and $41.3\ cm^{-1}$ for methanol and ethanol solutions, respectively) can be ascribed to two factors (in addition to the gradual increase due to the decrease in the ionic radius of the rare earth ion): (1) the gradual shift of the chemical equilibrium reactions to lower chloro-complex ions, e.g. $[LnCl_3(PrOH)_p \rightarrow [LnCl_2(PrOH)_{p+1}]^+$; and (2) the change in coordination number in the Tb–Er region.

The next problem is to determine the chemical entity exiting from the inner-coordination sphere of the rare earth ion in the coordination number change region, a chloride ion or an alcohol molecule. A plausible estimation may be obtained from the fact that, for all the alcoholic $LnCl_3$ solutions studied here, the coordination number change occurs in the narrower region (Gd–Ho or Er) than the region (Nd–Dy) in aqueous $LnCl_3$ solution [3]. A chloride ion ($r = 181$ pm) is larger than the oxygen atom ($r = 140$ pm) of an alcohol molecule so that shrinkage of the coordination sphere by exclusion of one member (chloride ion or oxygen atom) is larger for a chloride ion than for an oxygen atom. Therefore, it is highly probable that an alcohol molecule is the entity excluded from the inner-coordination sphere in the transition region (Gd–Ho or Er).

The fact that the coordination number change occurs in the latter region (Gd–Ho or Er) of the rare earth series is also indicative of the notion that an alcohol molecule is the entity exiting from the inner-coordination sphere.

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