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The effects of the coexisting anions on the complex formation of rare earth ions with thiocyanate ions in aqueous solution

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Abstract

Complex formation of rare earth ions with thiocyanate ions was investigated in the presence of coexisting anions (Cl^- or $ClO_4{}^-$ ions). From the frequency variations of the CS and CN stretching Raman bands, it is shown that both the coordination number change in the middle of the series and the complex formation of rare earth ions with thiocyanate ions are affected by the coexisting anions. Some discussion was made on the anomalous behavior of the coordination number change with the salt concentration.

Keywords: Rare earth ion; Thiocyanate complex; Raman spectrum; Coexisting anion; Coordination number

1. Introduction

It is now fairly well established that anomalous salt concentration dependence of the hydration number change of rare earth ions in the middle of the series is caused by the outer-sphere complex formation [1–4]. From the enormous data reported by Spedding and coworkers [5–8], the anomalous salt concentration dependence is shown to be a general phenomenon in aqueous rare earth chloride and perchlorate solutions at all concentrations. Therefore, it would be interesting and important to see how the outer-sphere complex formation affects the inner-sphere complex formation in aqueous rare earth electrolyte solution.

In this paper, we report how the complex formation of rare earth ions with thiocyanate ions is affected by the coexisting anions such as chloride and perchlorate ions. We have measured the Raman spectra of the CS and CN stretching vibrations in the $LnA_3{\cdot}NaSCN{\cdot}30H_2O$ solutions (Ln: rare earth ion, A = Cl or ClO_4) across the series. From the frequency variations of the CS and CN stretching Raman bands across the series, we evaluated the effects of the coexisting anions on the coordination number change in the middle and the thiocyanate complex formation in the solution.

2. Experimental details

Aqueous solutions of rare earth chloride and perchlorate solutions were prepared by dissolving rare earth oxide in corresponding acid and subsequent heating on a hotplate. The sample solutions were made by mixing the resultant rare earth salt solution with aqueous NaNCS solution. The final solution composition was set to be $LnA_3{\cdot}NaSCN{\cdot}30H_2O$ (A = Cl or ClO_4).

Raman spectra were measured with a JASCO NR-1800 Raman spectrometer equipped with a microscope and a CCD detector. The spectra were excited with about 100 mW of 514.5 nm radiation from a Lexcel argon ion laser. When Raman spectra of glassy samples were measured, we used a special apparatus to maintain the sample at liquid nitrogen temperature. Vitrification of a sample solution on a glass plate was achieved by immersing the solution in liquid nitrogen. Overall cooling rate was estimated to be over 10^3 K/min.

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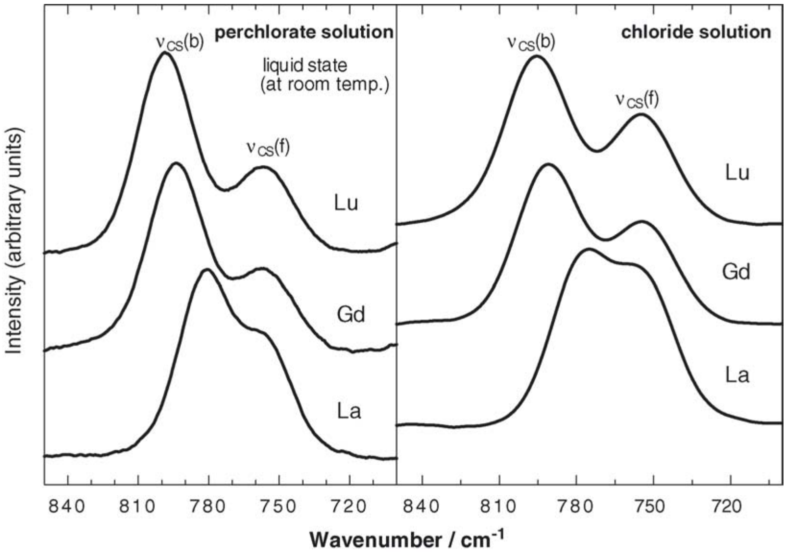

Fig. 1. Raman spectra of the CS stretching vibrations for the $LnCl_3 \cdot NaSCN \cdot 30H_2O$ and $Ln(ClO_4)_3 \cdot NaSCN \cdot 30H_2O$ solutions at room temperature.

3. Results and discussion

First we show the typical Raman spectra of the CS stretching Raman bands for the $LnCl_3 \cdot NaSCN \cdot 30H_2O$ and $Ln(ClO_4)_3 \cdot NaSCN \cdot 30H_2O$ solutions at room temperature (Ln = La, Gd and Lu) in Fig. 1. Every Raman spectrum consists of two Raman bands. The low frequency Raman band $\{\nu_{CS}(f)\}$ is ascribed to the CS stretching vibrations of “free” SCN^- ions (“free” means that SCN^- ions are not bound to rare earth ions). The assignment is substantiated by the fact that the frequency of the ν_{CS}(f) band remains unchanged throughout the series. The higher frequency Raman band $\{\nu_{CS}(b)\}$ is therefore assigned to the CS stretching vibrations of the SCN^- ions bound to rare earth ions. There are two possibilities in the binding of an SCN^- ion to a rare earth ion: S-end binding and N-end one. The frequency range of the ν_{CS}(b) band (775 cm^{-1} for the La-solution to 795 cm^{-1} for the Lu-solution) suggests the N-end binding in these solutions. Literature data also support the assignment: hard cation prefers N-end binding to S-end binding [9–11].

When the ν_{CS}(b) frequency is plotted against the reciprocal of ionic radius of rare earth ion (Fig. 2), we see the rapid ν_{CS}(b) frequency increase in the Nd–Gd region, which is surely ascribable to the result of the coordination number change (probably from 9 to 8). The extended s-shaped variation is often observed in the series behavior of various complex formation constants for rare earth ions [12]. The frequency change by ~10 cm^{-1} in the coordination number change is almost the half of the value for the hydration number change of aqua-rare earth ions [13]. It is a common phenomenon that the coordination number change is associated with the rapid change in various properties (complex formation constant, thermodynamic properties, etc). A remarkable point is that the ν_{CS}(b) band of the perchlorate solution is always a few wavenumber higher than that of the chloride solution. As seen in the ν_{CS} spectra shown in Fig. 1, the intensity ratio of the ν_{CS}(b) Raman band to the ν_{CS}(f) band for the $Ln(ClO_4)_3 \cdot NaSCN \cdot 30H_2O$ solution is much higher than that for the $LnCl_3 \cdot NaSCN \cdot 30H_2O$ solution. This is attributed to the larger formation constant of isothiocyanato-rare earth complex ion in the perchlorate solution. An important result from this comparison is that complex formation of thiocyanate ions with rare earth ions is greatly influenced by the coexisting anions. Perchlorate ion is a well-known structure breaker so that the interaction between SCN^- ions and sur-

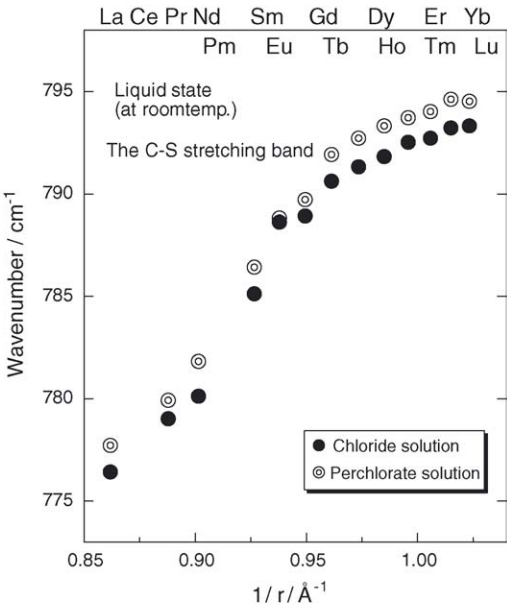

Fig. 2. Frequency variations of the CS stretching bands for the $LnCl_3 \cdot NaSCN \cdot 30H_2O$ and $Ln(ClO_4)_3 \cdot NaSCN \cdot 30H_2O$ solutions at room temperature.

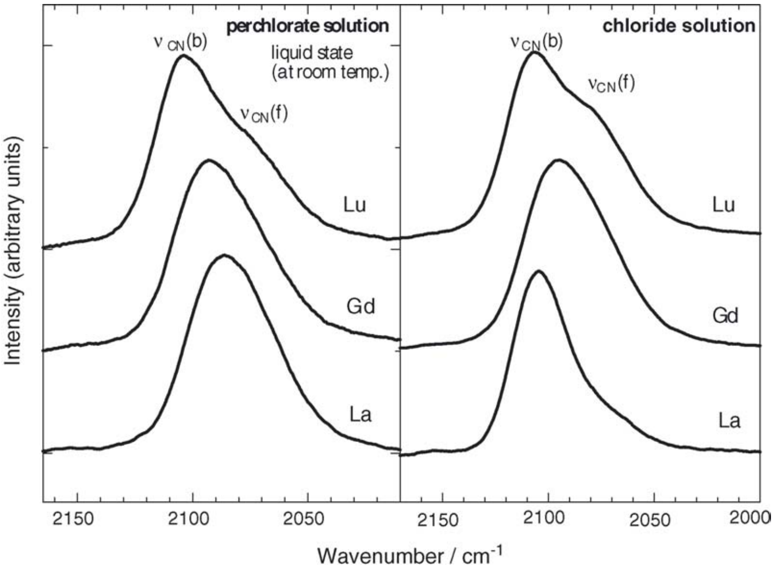

Fig. 3. Raman spectra of the CN stretching vibrations for the $LnCl_3 \cdot NaSCN \cdot 30H_2O$ and $Ln(ClO_4)_3 \cdot NaSCN \cdot 30H_2O$ solutions at room temperature.

rounding water molecules is expected to become weaker to lead the stronger complex formation.

In the previous Raman study on aqueous $Ln(SCN)_3 \cdot 20H_2O$ solutions [11], it is shown that the average number of the SCN^- ions coordinated to Ln^{3+} ions is ∼2.7, demonstrating that SCN^- ions are mostly bound to Ln^{3+} ions at room temperature. When we compare the ν_{CS}(b) frequencies with those for the $Ln(SCN)_3 \cdot 20H_2O$ solutions, we immediately notice that the ν_{CS}(b) frequency of the $LnCl_3 \cdot NaSCN \cdot 30H_2O$ solution is always lower by a few wavenumbers than that for the $Ln(SCN)_3 \cdot 20H_2O$ solution.

Next, we show the Raman spectra of the CN stretching frequency region for the $LnCl_3 \cdot NaSCN \cdot 30H_2O$ and $Ln(ClO_4)_3 \cdot NaSCN \cdot 30H_2O$ solutions at room temperature (Fig. 3).

It is clear that the spectrum consists of two Raman bands: the higher frequency band {ν_{CN}(b) band} is ascribed to the CN stretching vibrations of the NCS^- ions coordinated to rare earth ions, while the lower frequency one {ν_{CN}(f) band} is due to "free" NCS^- ions. As compared with the CS stretching spectrum, the splitting of the CN stretching bands {ν_{CN}(b) and ν_{CN}(f) bands} is small so that the curve fitting method is applied to the frequency evaluation of the two bands. It is evident that the ν_{CN}(b) band increases in frequency with decrease in ionic radius of rare earth ion while the ν_{CN}(f) band remains unchanged in frequency across the series (Fig. 4). The rapid ν_{CN}(b) frequency decrease in the Nd–Gd region is caused by the coordination number change. The frequency change of the ν_{CN}(b) band shows an extended z-shaped behavior across the series. It seems that the coordination number change results in the small decrease in the interaction between a rare earth ion and its coordinated NCS^- ion, probably due to the steric effect caused by the jammed ligands (water molecules and a NCS^- ion) in the first coordination sphere. From the previous Raman study [11], the coordination number change in the middle of the series is shown to take place by ejecting one water molecule from the inner-coordination sphere. Yoshimura et al. [11] also showed that although the ratio $S(\nu_{CS}(b))/S(\nu_{CS}(f))$ increases with decreasing ionic radius, the average number of the SCN^- ions bound to a rare earth ion is nearly constant throughout the series in the $Ln(SCN)_3$ solutions at room temperature. This fact is very suggestive because the Raman ν_{CS}(b) intensity increases with decreasing ionic radius even when the number of the SCN^- ions bound to a rare earth ion remains unchanged across the series.

Ishiguro and coworker [14,15] have a number of studies on the complex formation of rare earth ions in mixed organic solvents and showed that the steric effects play a decisive role in the coordination number of rare earth ions. Similar conclusion was obtained by Bünzli et al. [16,17] in their FT-IR studies of rare earth salts in various organic solvent systems. It must be stressed here that the coordination number change in the intermediate region of the rare earth series is a common phenomenon in most aqueous and organic solvent systems [17,18]. The location where the coordination number change takes place shifts from one system to another, depending on the size of a solvent molecule, solute concentration and temperature. Despite extensive outer-sphere complex formation in a rare earth electrolyte in organic solvent systems, there has been no experimental evidence for anomalous dependence of salt concentration on coordination number change as observed in aqueous solution systems. However, considering the fact that the anomalous behavior has been observed only in thermodynamic and transport properties even in aqueous rare earth electrolyte solutions, there might be a possibility that similar anomalous behavior of the solute concentration dependence on thermodynamic and/or transport properties will be found in non-aqueous solutions of rare earth electrolytes.

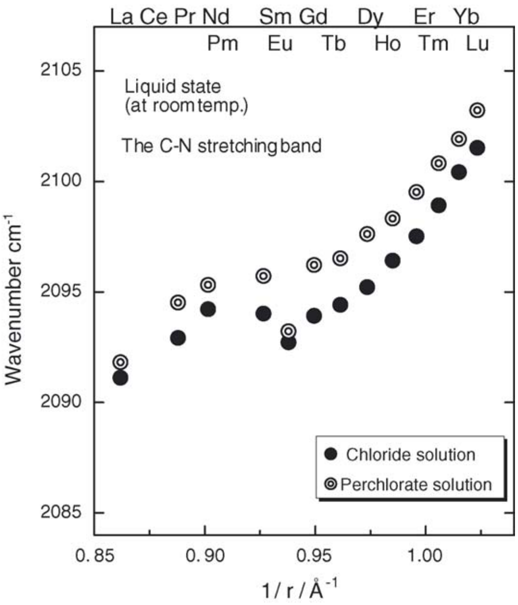

Fig. 4. Frequency variations of the CN stretching bands for the $LnCl_3 \cdot NaSCN \cdot 30H_2O$ and $Ln(ClO_4)_3 \cdot NaSCN \cdot 30H_2O$ solutions at room temperature.

Now, we move on to discuss the Raman results of the glassy $LnCl_3 \cdot NaSCN \cdot 30H_2O$ solutions to see the temperature effects on the complex formation of rare earth ions with thiocyanate ions. As glass transition temperature is the lowest temperature limit of liquid state, glassy state usually represents the liquid state at the lowest temperature. Fig. 5 shows the typical Raman spectra of the glassy $LnCl_3 \cdot NaSCN \cdot 30H_2O$ solutions.

Comparison of the CS stretching spectra for the $LnCl_3 \cdot NaSCN \cdot 30H_2O$ solution in both liquid and glassy states clearly indicates that the magnitude of the mole fraction of the SCN^- ions coordinated to Ln^{3+} ions increases on going from the liquid state at room temperature to the glassy state at nitrogen temperature. This means that thiocyanate complex formation is enhanced with lowering temperature. Figs. 6 and 7 show the frequency variations of the CS and CN stretching Raman bands for the $LnCl_3 \cdot NaSCN \cdot 30H_2O$ solutions in the glassy state, respectively, together with those for the solutions at room temperature.

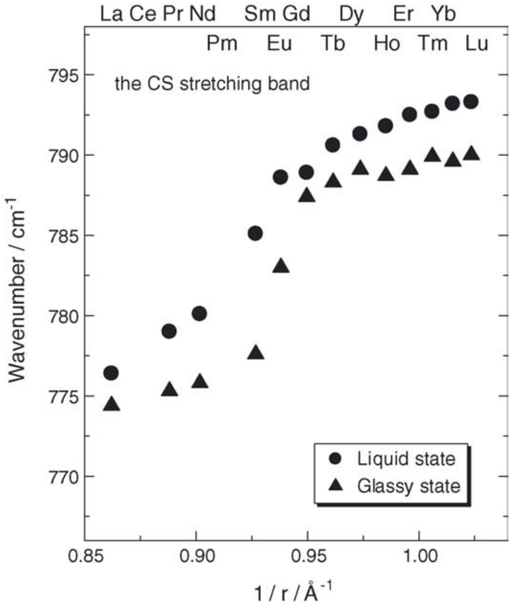

Fig. 6. Variations of the CS stretching Raman band frequencies for the $LnCl_3 \cdot NaSCN \cdot 30H_2O$ solutions in both liquid and glassy states.

The frequency of the ν_{CS}(b) band goes down from the liquid state at room temperature to the glassy state at liquid nitrogen temperature. From the frequency increase of the ν_{CN}(b) band on vitrification, we know that the interaction between a rare earth ion and its coordinated SCN^- ion apparently becomes stronger on going from liquid state to glassy state. Thus, the frequency decrease of the ν_{CS}(b) band may be caused by the increase in interaction between an

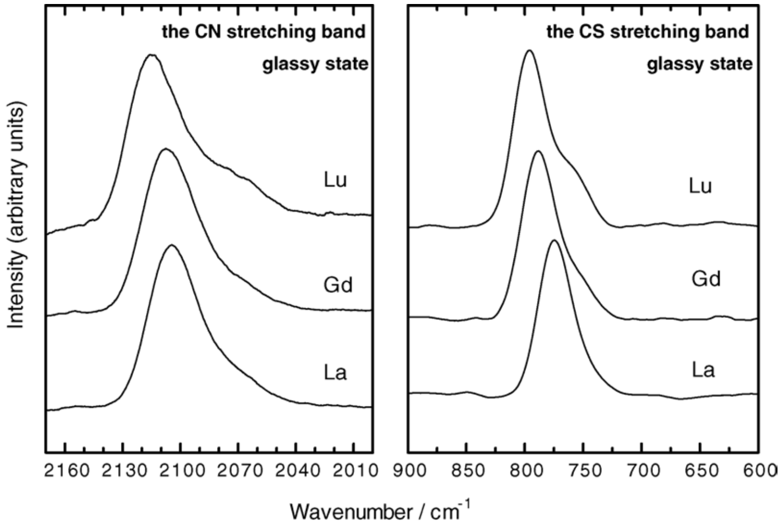

Fig. 5. Raman spectra of the CS and CN stretching bands for the $LnCl_3 \cdot NaSCN \cdot 30H_2O$ solutions in the glassy state.

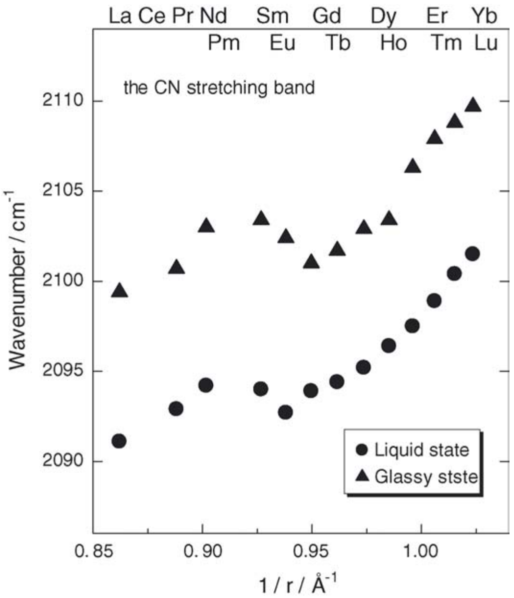

Fig. 7. Variations of the CN stretching Raman band frequencies for the $LnCl_3 \cdot NaSCN \cdot 30H_2O$ solutions in both liquid and glassy states.

SCN^- ion and its surrounding water molecules. These frequency changes are very interesting because little frequency change was observed in the ν_4 band of nitrato-rare earth complex ions in the $Ln(NO_3)_3$ solution on vitrification [19]. This difference must be attributed to the difference of the coordination manners between SCN^- ion and NO_3^- ion: SCN^- ion binds to a rare earth ion in a unidentate way while NO_3^- ion coordinates to a rare earth ion in a bidentate way. The latter binding is rigid but the former binding may be amenable to the changes in the first and second coordination spheres. The frequency increase of the ν_{CN}(b) band indicates the increase of the interaction between a rare earth ion and its coordinated SCN^- ion. The frequency increase of the ν_{CN}(b) band on vitrification is about 10 cm^{-1}, and it is almost the same increase as that observed on going from La^{3+} to Lu^{3+}.

In the theoretical treatment by Marcantonatos et al. [1], it is shown that the outer-sphere complex formation can be a cause for the anomalous salt concentration dependence for the hydration number change. As an extension of the theory by them, Kanno [4] has shown that the observed formation constant (K_{ob}) obtained by the conventional experimental methods is expressed by

$$K_{ob} = BK_9 + (1 - B)K_8 \tag{1}$$

$$B = \frac{1}{1 + K_h} \tag{2}$$

where $K_8 = [LnYH_7]/\{[LnH_8]\ [Y]\}$, $K_9 = [LnYH_8]/\{[LnH_9]\ [Y]\}$, $K_h = [LnH_8]/[LnH_9]$ and Y^- is a unidentate ligand which will make an inner-sphere complex with a rare earth ion. Here, $LnYH_7 = [LnY(H_2O)_7]^{2+}$, $LnYH_8 = [LnY(H_2O)_8]^{2+}$, $LnH_8 = [Ln\ (H_2O)_8]^{3+}$ and $LnH_9 = [Ln\ (H_2O)_9]^{3+}$. It must be pointed out that the outer-sphere complex formation will affect the formation of an inner-sphere complex formation through the following relation:

$$\frac{K_8(\text{out})}{K_9(\text{out})} = \frac{K_A}{K_H} \tag{3}$$

where $K_8(\text{out}) = [LnH_8\text{–}X]/\{[LnH_8]\ [X]\}$, $K_9(\text{out}) = [LnH_9\text{–}X]/\{[LnH_9]\ [X]\}$, $K_A = \{[LnH_8\text{–}X]\ [H_2O]\}/[LnH_9\text{–}X]$ and $K_H = \{[LnH_8]\ [H_2O]\}/[LnH_9]$. Here, $LnH_8\text{–}X = \{[Ln(H_2O)_8]X\}^{2+}$ and $LnH_9\text{–}X = \{[Ln(H_2O)_9]X\}^{2+}$ represent the outer-sphere rare earth complexes of eight and nine coordination numbers, respectively, and X^- is Cl^- or ClO_4^-. Therefore, although the formation constants for the outer-sphere complex reactions are not explicitly included in Eq. (1), they are implicitly contained in Eq. (3) through which the outer-sphere complex formation affects the inner-sphere complex formation. From the Raman results obtained in this work, it is difficult to give an adequate mechanism for the anomalous salt concentration dependence of various transport and thermodynamic properties. However, the fact that the coexisting anions affect greatly the complex formation of rare earth ions with thiocyanate ions can be taken as a favorable evidence for the explanation by Marcantonatos et al. [1]. They reasoned that anomalous salt concentration dependence, which is generally observed in many transport and thermodynamic properties, can be realized with the condition $K_8(\text{out})/K_9(\text{out}) < 1$. As Ln^{3+} ions are classified as a hard acid, and water, Cl^- and ClO_4^- are all grouped into hard bases, it is considered that $[Ln(H_2O)_9]^{3+}$ ions should be softer than $[Ln(H_2O)_8]^{3+}$ ions. Therefore, the former aqua-rare earth ion should give a higher formation constant for an outer-sphere complex formation with Cl^- or ClO_4^- ion. Despite the anomalous concentration dependence of the coordination number change, which is a general phenomenon, in aqueous rare earth chloride and perchlorate solutions, the observed K_{ob} shows apparently no anomalous behavior across the series. Together with the theoretical consideration outlined in Eqs. (1)–(3) and if the higher formation constant for the outer-sphere complex is expected for the rare earth solvates of the higher coordination number, it is inferred that similar anomalous behavior as observed in aqueous chloride and perchlorate solutions may be observed in the rare earth electrolyte solutions in organic solvents as outer-sphere complex formation is reported to be extensive in these solutions.

Finally, from Figs. 6 and 7, Sm^{3+} ions in the glassy $SmCl_3 \cdot NaSCN \cdot 30H_2O$ solution belong to the nine-coordination group while they are intermediate region between the nine-coordination and the eight-coordination groups in the solution at room temperature. This indicates that the higher coordination is favored at low temperatures. This trend is in consistent with the previous Raman studies [13,20] in which the anomalous concentration dependence of the hydration number change was clearly observed.

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