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Anomalous Concentration Dependence of the Inner-Sphere Hydration Number Change in Aqueous EuCl_3 and GdCl_3 Solutions

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Raman spectra of the aquo-rare earth ions $[\text{Ln}(\text{H}_2\text{O})_n]^{3+}$ (Ln^{3+} denotes a rare earth ion, $n = 8$ and/or 9) in glassy rare earth chloride solutions were obtained as a function of salt concentration. The population of rare earth ions holding nine water molecules in their innermost hydration spheres increase with increasing salt concentration in EuCl_3 and GdCl_3 solutions. A qualitative discussion is given for this peculiar behavior.

Introduction

Recent X-ray diffraction¹ and Raman² studies together with accumulated transport and thermodynamic properties³⁻⁶ of aqueous rare earth electrolyte solutions have clearly shown that the inner-sphere hydration number of rare earth ions changes from nine for light rare earth members to eight for heavy ones. Furthermore, this coordination number change may be a major cause^{3,5,7} of the irregularities observed for $\log K$ (K is the stability constant) vs. Z (atomic number) or r (ionic radius) plots, which are called such things as "tetrad",⁸ "double-double",⁹ or "inclined W"¹⁰ effects.

According to the extensive work by Spedding et al.,^{4,11} the average hydration number gradually changes from nine to eight in the Nd^{3+} to Th^{3+} region at ordinary temperatures. On the other hand, a drastic change is observed in the T_g (glass transition temperature) vs. Z plot for rare earth perchlorate solutions.⁶

The significance of these observations is that solution properties are greatly dependent on the inner-sphere hydration number of ions in solution, indicative of the importance of the discreteness in solvent molecules to solution properties.

In this Letter, we report the anomalous behavior of the concentration dependence of the hydration number change between eight and nine in aqueous EuCl_3 and GdCl_3 solutions: the rare earth ions holding nine water molecules in their innermost coordination spheres increase in number with increasing salt concentration in solution.

Experimental Section

Aqueous rare earth chloride solutions were prepared by dissolving their oxides in excess HCl , subsequently drying under an infrared lamp, and diluting with distilled water.

Some EuCl_3 and GdCl_3 solutions were also made just by weighing out and mixing the required amounts of commercially available $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ crystals and distilled water thereby confirming that solutions made by different methods give the same results.

Details of the Raman measurements were essentially the same as previously reported.² As a glass is in a nonequilibrium quenched state, the final quenched state is dependent on a cooling rate from a liquid state to a glassy state and thermal histories of the glass.¹² Therefore, several measurements on the same sample solution quenched at different cooling rates were made to ascertain whether the quenched ratio of $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$ ions to $[\text{Ln}(\text{H}_2\text{O})_8]^{3+}$ ions (Ln^{3+} denotes a rare earth ion) in the glassy solution is sensitive to the cooling rate of the sample solutions. We found that changes in the cooling rate (400–900 K/min) gave rise to only a small structural changes in these glassy aqueous solutions.

Results and Discussion

Figure 1 displays the summarized ν_1 results (ν_1 is the totally symmetric stretching vibration of the aquo-rare earth ion $[\text{Ln}(\text{H}_2\text{O})_n]^{3+}$) as a function of the ionic radius of the rare earth ion to show the frequency change of the ν_1 bands across the series. All ν_1 results except for the GdCl_3 solution were obtained in glassy rare earth chloride solutions of $R = 24$ (R is the moles of water/moles of salt). In the GdCl_3 solution, the ν_1 results for the $R = 20$ solution were included in the diagram. The important advantage of carrying out Raman measurements on aqueous solutions in the glassy state is that accurate frequency assignment of the weak ν_1 band is only possible in the Raman spectrum for the solution in the glassy state.^{2,13} A glassy state is of course a nonequilibrium state, reflecting a liquid state at a certain temperature at or higher than the glass transition temperature (T_g). Thus it is certain that a value obtained for a glassy state is the one for the liquid state at a temperature very near to T_g . From the results shown in Figure 1 together with X-ray diffraction studies of Habenschuss and Spedding,¹ we know that there are two kinds of aquo-rare earth ions, namely $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$ and $[\text{Ln}(\text{H}_2\text{O})_8]^{3+}$ ions, in the glassy EuCl_3 ($R = 24$) and GdCl_3 ($R = 20$) solutions.

The Raman results for the concentration dependence of the hydration number change between eight and nine

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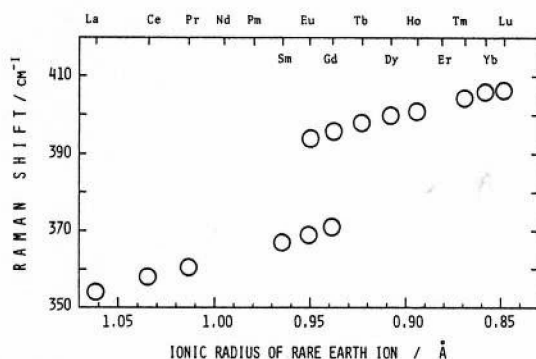


Figure 1. Frequencies of the ν_1 bands for the $[\text{Ln}(\text{H}_2\text{O})_n]^{3+}$ ions ($n = 8, 9$) in glassy rare earth chloride solutions.

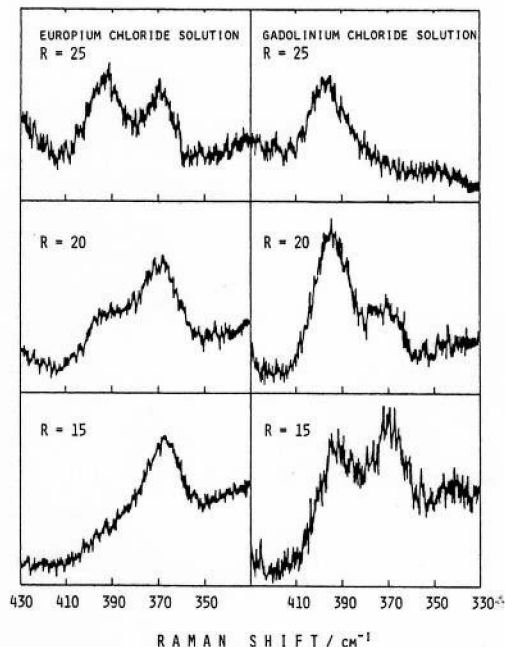
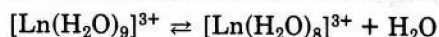


Figure 2. Variation of the ν_1 band with salt concentration in glassy EuCl_3 and GdCl_3 solutions.

in the glassy EuCl_3 and GdCl_3 solutions are shown in Figure 2. Examination of Figure 2 shows that in the case of the EuCl_3 solution the Raman peak at $\sim 369 \text{ cm}^{-1}$, which corresponds to $[\text{Eu}(\text{H}_2\text{O})_9]^{3+}$ ions, increases in intensity with an increase in salt concentration while the peak at $\sim 394 \text{ cm}^{-1}$, corresponding to $[\text{Eu}(\text{H}_2\text{O})_8]^{3+}$ ions, decreases and almost disappears when $R = 15$. This indicates that most europium ions are in the form of $[\text{Eu}(\text{H}_2\text{O})_9]^{3+}$ in the glassy EuCl_3 solution of $R = 15$. Similarly although most gadolinium ions exist in the form of $[\text{Gd}(\text{H}_2\text{O})_8]^{3+}$ in the glassy GdCl_3 solution of $R = 25$, the $[\text{Gd}(\text{H}_2\text{O})_9]^{3+}$ species appears in the $R = 20$ solution and becomes more dominant than the $[\text{Gd}(\text{H}_2\text{O})_8]^{3+}$ species in the glassy $R = 15$ solution. An anomalous point of these observations is that the rare earth ions having the larger inner-sphere hydration number (i.e., 9) increase in number with a decrease in water content in the solutions. A straightforward conclusion from the experimental results is that, when sufficient water molecules are not available to form a complete second hydration sphere around a Eu^{3+} or Gd^{3+} ion, the coordination number of nine becomes more stable than eight at low temperatures. This anomalous behavior is an apparent reversal of what the law of mass action tells us when we consider the reaction expressed in a conventional way, i.e.



Unfortunately we cannot at present give a clear-cut ex-

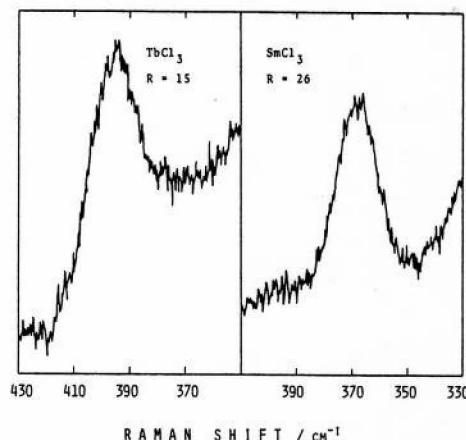


Figure 3. Raman spectra of glassy aqueous SmCl_3 ($R = 26$) and TbCl_3 ($R = 15$) solutions in the frequency region of the ν_1 band.

planation for this peculiar concentration dependence.

In the recent X-ray diffraction study,¹ the average water coordination number of Eu^{3+} ions in 3.23 M aqueous EuCl_3 solution ($R \approx 17$) at room temperature was determined to be about 8.3, which means that about 70% of the Eu^{3+} ions are eight coordinated. On the other hand, we estimate from Figure 2 that about 90% of the Eu^{3+} ions are nine coordinated in the $R \approx 17$ solution in the glassy state. The trend that lowering temperature favors a higher coordination number is in parallel with the equilibrium reactions between tetrahedral and octahedral coordinations for various divalent 3d-metal ions in various environments.^{14,15} As an extension of this parallel observation, it may be worthwhile to further examine the analogy between the hydration number change in rare earth aquo ions and the tetrahedral-octahedral coordination number change in various 3d metal ions as there have been many documented experimental data for the latter case¹⁴⁻¹⁹ and the mechanism is already fairly well clarified.¹⁵ We are currently examining the possibility that the hydration number change in rare earth ions may be interpreted by the analogy.

Some comment must be made here about the concentration dependence of the SmCl_3 and TbCl_3 solutions. As shown in Figure 3, almost all samarium ions are nine coordinated even in the glassy $R = 26$ solution and almost all terbium ions are eight coordinated even in the glassy $R = 15$ solution. Knowing that the average water coordination number is 8.8 for Sm^{3+} ions in the 3.23 M SmCl_3 solution ($R \approx 17$) at room temperature,¹ we conclude that the equilibrium reaction between eight and nine coordinations is displaced to one side in SmCl_3 and TbCl_3 solutions at low temperatures, at least, in the glass-forming composition region ($R = 14-26$). Thus, the data shown in Figures 1-3 clearly lead us to conclude that ionic radius is the primary factor determining the actual coordination of rare earth ions in aqueous chloride solutions.

In the $R = 15$ solution, there are 15 water molecules for each rare earth ion and three chloride ions. Therefore, if we allocate 8-9 water molecules to the innermost hydration

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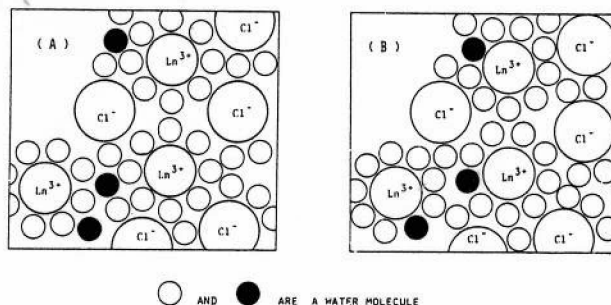


Figure 4. Schematic two-dimensional presentation of a concentrated aqueous rare earth chloride solution: (A) all rare earth ions are eight coordinated; (B) all rare earth ions are nine coordinated. Some of the type 3 water molecules (closed small circles) in the A solution enter into the primary hydration spheres in the B solution so that they become more stable. Comparison of the two solutions shows that the molar volume of the B solution is smaller than that for the A solution, which means that more effective approaches between cations and anions are possible in the B solution.

shell of a rare earth ion, there remain only 6–7 water molecules to share between each hydrated rare earth ion and three chloride ions. The scarcity of solvent water molecules imposes extensive sharing of water molecules between cations and anions. With this fact in mind, a tentative, qualitative explanation for the anomalous concentration dependence of the hydration number change may be given as follows.

In these concentrated chloride solutions, there is no more intrinsic tetrahedral water structure and instead there are three typical water configurations: the first one is the configuration where a water molecule coordinates to both rare earth and chloride ions (a type 1 water); the second is one where a water molecule coordinates to either a rare earth ion or a chloride ion (a type 2 water); and the third is one where a water molecule coordinates to neither a cation nor an anion (a type 3 water molecule, it may be

weakly hydrogen bonded to other water molecules). Among water molecules trapped in these three configurations, the water molecules in the first environment (type 1) are considered to be the most stable at low temperatures. Next in stability are those in the second configuration and the most unstable ones are those in the third configuration.

From X-ray diffraction studies,^{1,20} it is now firmly established that even in these concentrated chloride solutions ($R = 15$ –25) the innermost coordination around a rare earth ion is made up exclusively of water molecules. As the salt concentration increases, some water molecules outside of the inner-sphere hydration shells become a kind of dangling state due to a lack of water molecules and the resulting breakdown of the second hydration spheres. Therefore, maximization of the type 1 water molecules or minimization of the type 3 water molecules, which means that some of these dangling water molecules (type 3 water molecules) enter into the innermost hydration spheres, is the most stable state for the solutions at low temperatures, resulting in the increase of nine-coordinated rare earth ions. This situation may be well exemplified schematically in Figure 4 in which type 3 water molecules in the A solution are shown to enter into the innermost hydration spheres in the B solution to become more stable.

At the moment the explanation is rather speculative and it is evident that closer examinations are needed before we get a full quantitative account of the behavior. More extensive work is in progress and will be reported shortly.

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