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Ultrasonic Relaxation Measurements on Erbium Chloride in Water and Aqueous Methanol*

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Based upon Freed's spectroscopic observations in water and aqueous ethanol and early ultrasonic results we developed an ultrasonic technique to measure lanthanide coordination number changes [1–5]. Confirmation of lanthanide coordination number changes as a function of solvent composition is found in the FT-IR spectral work of Bünzli [6–8].

In aqueous methanol solutions of Er(III), a coordination number change occurs for the bulky ligands NO_3^- [3], ClO_4^- [9], Br^- [10] and I^- [10], but is absent for the smaller Cl^- [5]. Hence, we proposed steric crowding in the inner sphere as the cause of the coordination number change [10]. Studies on $ErCl_3$ in DMSO [11] and DMF [12] indicate that the coordination number change can also be caused by bulky solvent groups in the inner sphere. Changing to either Nd(III) or Gd(III) in aqueous methanol results in the coordination number change for the chlorides [13]. The use of this ultrasonic technique to determine coordination number changes is not unique to the lanthanides. The existence of an octahedral–tetrahedral change has been confirmed for $ZnCl_2$ in aqueous methanol, DMSO and DMF [14] and we demonstrated that La(III) and Y(III) are chemically similar to the lanthanide chlorides, whereas Sc(III) is not [15].

In 0.096 M $ErCl_3$ solutions the data show the absence of coordination number changes [5], but the 0.200 M solutions have significant scattering at low water mole fractions (X_w) [11], which is where lanthanide coordination number changes occur. In glassy lanthanide solutions a coordination number change occurs at high salt concentrations, with the surprising observation that the higher coordination number species is favored as the ratio of water to salt decreases [16]. Thus, we believe that a coordination number change may occur at higher concentrations in the $ErCl_3$ system [17, 18].

Results and Discussion

The equipment and ultrasonic techniques have been previously described [5, 15]. In water, the sound absorption was approximately 25×10^{-17} nepers cm^{-1} s^2, and frequency independent from 10 to 170 MHz, indicating the absence of inner sphere complexes between Er(III) and Cl^-, consistent with the measurements on 0.038 M Er(III) in the presence of 4.89 M Cl^- [18]. Upon the addition of methanol to the 0.600 M $ErCl_3$ solutions, the sound absorption increased and varied with frequency, indicating chemical relaxations are present. The ultrasonic absorption data were calculated using our standard double relaxation curve fitting programs with the high frequency relaxation identified with outer sphere and the low frequency with inner sphere complexation.

Figure 1 is a graph of μ_{max} as a function of X_w. The first question is what is the expected variation of μ_{max} with solvent? No equilibrium study has been carried out on a lanthanide chloride system as a function of solvent, however, we have recently evaluated the $Eu(NO_3)_3$ system in aqueous methanol [19]. In water both $EuNO_3^{2+}$ and $Eu(NO_3)_2^+$ are present, and upon the addition of methanol the tris complex forms. As X_w decreases, a smooth increase in each successive stability constant at ionic strength of 3.00 occurs [19]. Hence, at constant salt concentration, a smooth increase in μ_{max} with decreasing X_w should be observed, as occurs for 0.096 M $ErCl_3$ [5]. When a coordination number change is coupled to complexation, μ_{max} increases as water is added to the methanol, reaching a maximum at less than 50 volume percent water, dependent upon the anion, and then μ_{max} decreases. For 0.200 M $ErCl_3$, experimental scatter at low X_w prevented a confirmation of

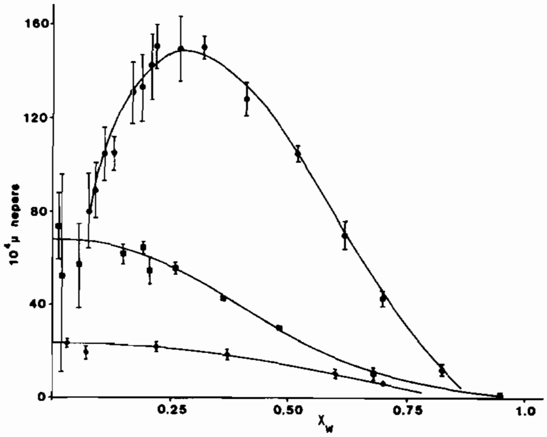

Fig. 1. The excess absorption maxima as a function of solvent composition for $ErCl_3$ at 25 °C: (◆) 0.096 M [5], (■) 0.20 M [11], (●) 0.600 M.

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the absence or presence of this coordination number change. The present data between X_w of 0.07 and 0.3 clearly demonstrate that μ_{max} increases upon the addition of water to the 0.600 M $ErCl_3$ salt solutions. Above a value of X_w of 0.3, the μ_{max} values decrease again, as expected for decreased ionic association.

Multiple possibilities exist to explain the maximum in the curve near X_w of 0.3. First, there could be a parallel abnormality in equilibrium constants within this solvent region, but, based upon the $Eu(NO_3)_3$ results, we believe this effect will not be observed.

Second, as water is added to the methanol, there is a strong preference for water over methanol in the Er(III) inner solvation shell and the increasing μ_{max} represents the difference in volume due to the replacement of the larger methanol by the smaller water molecules. If valid, then both μ_{max} and the X_w value where the maxima occur should be similar as the ligand changes. For Er(III) the amplitudes vary between 55 and 75×10^{-4} nepers as the ligands vary from Br^- to NO_3^- for 0.2 M salt solutions [3, 5, 9, 10]. However, the X_w value corresponding to the maximum in μ_{max} depends on the ligand, being below 0.05 for ClO_4^- and about 0.5 for NO_3^- [3, 9], a variation too great for a result which is a function of the cation alone. Evidence against this argument also comes from the NMR results of McCain [20] and Brucher *et al.* [21].

Third, the maximum may be due to viscosity changes as a function of X_w. McCain measured a maximum viscosity at $X_w = 0.53$ [20], but in the case of $LaCl_3$ in aqueous methanol the maximum in μ_{max} occurs below $X_w = 0.2$ [15]. Thus, viscosity is not the cause of the observed maximum in our data.

Fourth, an abnormality in the complexation enthalpies may invalidate the assumption that the enthalpy is small at low X_w values. Measurements of the enthalpies of solution for lanthanides in aqueous methanol reveal unusual variations in this solvent region [22], however, the enthalpy of solution contains unknown contributions from complex formation and from any coordination number change. Hence, the maximum in enthalpy may actually parallel our results. Furthermore, the complexation enthalpy data for $Eu(NO_3)_3$ in aqueous methanol show no discontinuities at low X_w [19].

Fifth, a second reaction may be coupled to complex formation, involving an equilibrium between two forms of inner sphere complex, differing in coordination number. We believe this explanation is correct. Meerbach has used NMR to measure an equilibrium between eight- and nine-coordinate DMF complexes with Nd(III) in the presence of ClO_4^- [23].

An extrapolation of the 0.600 M data below X_w = 0.07 implies that μ_{max} is lower than that for the 0.200 M solution, which means that the coordination number of the higher concentration species is different than that present at 0.200 M. Additional information about lanthanide chemistry is obtained from the variation of f_{III} with X_w. Temperature jump measurements on the complexation of Dy(III) with acetate reveal that f_{III} is greater when bis complexes are present [24]. An abnormally high relaxation frequency within a lanthanide salt system provides evidence for higher complexes. The normal behavior in lanthanide systems is for f_{III} to increase as X_w increases [3]. At $X_w = 0.07$ to 0.09, f_{III} is approximately 6.8 MHz; the addition of water decreases the relaxation frequency until about $X_w = 0.24$, after which f_{III} increases as expected, similarly to the 0.096 M $ErCl_3$ solutions in the absence of a coordination number change. Hence, we believe that below $X_w = 0.24$, there are higher complexes present and the coordination number change may be triggered by the formation of higher complexes, as occurs in $Er(ClO_4)_3$ [9] and $ZnCl_2$ [14]. The presence of a coordination number change at high concentrations implies that structural information from one concentration range may not be valid in another concentration range.

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