Differences in Er^{III} Complexation with Chloride and Nitrate Ions Determined by the Ultrasonic Relaxation Technique

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Summary A comparison of the ultrasonic relaxation results for erbium chloride complexation in aqueous methanol with those for erbium nitrate demonstrated that the mechanism differs for the two ligands, with a solvation number change occurring for the nitrate and not for the chloride salts.

Two problems of continuing interest in lanthanide chemistry involve the examination of the complexation mechanisms operating in aqueous and other media, and the determination of whether the lanthanide solvation number change is a function of cation alone. We have attempted to answer these questions by applying kinetic measurements to Freed's spectroscopic data in aqueous alcohols of rare earth chlorides and nitrates, from which he predicted different environments surrounding the same cations with different ligands.[1] Previous relaxation measurements indicated that the spectral observations and kinetic data for $Er(NO_3)_3$ could only be explained by invoking a solvation number change in the mixed solvents.[2] We have carried out similar measurments on $ErCl_3$ to determine if the same complexation mechanism operates in both systems.

The ultrasonic relaxation apparatus and techniques employed were similar to those described earlier.[2] All solutions contained 0·096M $ErCl_3$, as determined using a standard ion exchange technique.[3]

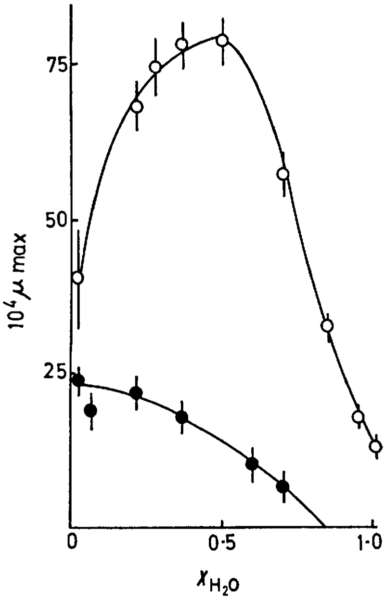

FIGURE. *The variation of μ_{max} with water content at* 25 °C *(μ_{max} is proportional to the square of the volume change of the reaction):* ○ $Er(NO_3)_3$ 0·22 M, ● $ErCl_3$ 0·096 M.

The excess absorbance observed in all of the aqueous alcohol solutions could be interpreted in terms of double relaxation behaviour. By analogy to other ultrasonic investigations, the low frequency relaxation was attributed to the formation of inner sphere complex.[4] In water no excess absorbance was found, indicating that the chloride complex in water is predominantly outer sphere, to which the ultrasonic measurements are insensitive. In methanol the relaxation frequency, f_R, of the chloride was 18 MHz, but upon the addition of water the value dropped to 10 MHz for the same salt concentration. On the addition of more water, a linear increase in f_R was observed as the mol fraction of water increased. This indicates a mechanistic difference from the nitrate case where f_R was essentially constant from water mol fraction 0·2 to 0·7.

However, an even more remarkable difference occurs between the ligands upon examining the relaxation amplitude data. The excess absorbance, μ_{max}, is given by equation (1) where A is the relaxation amplitude and v is

$$2\mu_{max} = A \cdot f_R \cdot v \qquad (1)$$

the sound velocity in the solution. Using the equations obtained by Tamm,[5] μ_{max} is proportional to the square of the molar volume change occurring during the chemical reaction.[5] The sound velocities were assumed to be identical for the salt solutions and for solvent of the same composition, with the velocity data interpolated from Nomoto's work.[6] The Figure shows a startling difference between erbium nitrate and chloride when μ_{max} is plotted as a function of water mol fraction. For the chloride the regular decrease in μ_{max} as water is added is consistent with a decrease in concentration of inner sphere ion pairs. With the nitrate μ_{max} passes through a maximum in the mol fraction range of 0·2 to 0·7, and this had led to the conclusion that the complexation step must involve a solvation number change.[2] This difference in μ_{max} behaviour is evidence that the complexation mechanism cannot be identical for the two ligands. Furthermore, one cannot invoke the existence of a co-ordination number change for the chloride salt. Thus, the solvation number change is a function of the solvated lanthanide–ligand complex, with a major dependence upon the ligand, supporting the deuterium oxide studies which also demonstrated ligand dependence in the overall complexation mechanism.[7] Through the use of the ultrasonic measurements it is thus possible to determine which lanthanide cations are involved in solvation number changes, and hence to look at individual steps in a sequence of chemical reactions.

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