ERBIUM CHLORIDE COMPLEXATION IN AQUEOUS DMF

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In water or mixed aqueous solvents, ErCl\(^{2+}\) complexation occurs via the following multi-step mechanism:

\[
\text{Er}^{3+}(S) + \text{Cl}^-(S) = \text{Er}^{3+}(S)\text{Cl}^- = \text{ErCl}^{2+}(S)
\]  

(1)

where S represents bound solvent, Er\(^{2+}\)(S)Cl\(^-\) is an outer-sphere complex and ErCl\(^{2+}\)(S) is an inner sphere complex. The ultrasonic adsorption, \(\alpha/f^2\), equals:

\[
\alpha/f^2 - B = A_{\text{os}}/(1+(f/f_{\text{os}})^2) + A_{\text{is}}/(1+(f/f_{\text{is}})^2)
\]

(2)

where \(A_{\text{os}}\) and \(A_{\text{is}}\) are the amplitudes of the outer and inner sphere complexes, \(f_{\text{os}}\) and \(f_{\text{is}}\) are the respective relaxation frequencies and \(B\) is the solvent background. The excess adsorption maximum \(\mu_{\text{max}}\) is equal to the product of one-half of the relaxation frequency, the relaxation amplitude and the solution sound velocity. At constant salt concentration, \(\mu_{\text{max}}\) is proportional to the square of the reaction volume change. If a coordination number change accompanies complexation, a plot of \(\mu_{\text{max}}\) as a function of water mole fraction, \(X_{\text{H}2\text{O}}\), has a maximum. In the absence of a coordination number change, \(\mu_{\text{max}}\) decreases with increased water content due to reduced complexation. For ErCl\(^{2+}\) formation in aqueous methanol (2) the coordination number change is absent, but is present in aqueous DMSO (3). This study in aqueous DMF was initiated to study the effect of solvent on coordination number in the Er(III) system.

RESULTS

The experimental \(\alpha/f^2\) data are shown in the Table. At low \(X_{\text{H}2\text{O}}\) a double relaxation is present, which becomes a single relax-
ation upon the addition of more water. The calculated $\mu_{\text{max}}$ values are plotted in Figure 1, based upon a single relaxation. Our experience has demonstrated that $\mu_{\text{max}}$ for inner sphere complexation is essentially unchanged whether a single or double relaxation calculation is used. A large increase in $\mu_{\text{max}}$ below $X_{\text{H}_2\text{O}}$ of 0.25 is consistent with a coordination number change. The sharp drop in $f$ occurring as water is initially added to the DMF solutions is indicative of a change from bis to mono-complexation (2).

A lower amplitude coordination number change appears at high water mole fraction, a feature not yet observed in any other lanthanide(III) system we have studied. In order to insure that this observation is not an artifact of the calculations, Figure 2 is a plot of $a/f^2$ at two frequencies as a function of $X_{\text{H}_2\text{O}}$. The data at 7.0 MHz are indicative of inner sphere complexation, whereas the 151.7 MHz data contains a small contribution from inner sphere complexes coupled to the outer-sphere results. At 7.0 MHz the data mimic the $\mu_{\text{max}}$ curve, confirming the results of Figure 1. At high frequency, this effect is absent and if the results were an artifact, even if caused by impurities, the effect would be present. At 151.7 MHz the small increase at low water compositions is a result of the increasingly high amplitudes of the low frequency relaxation.

$$10^4 \mu_{\text{max}} \text{ np}$$

Figure 1. $\mu_{\text{max}}$ for ErCl$^{2+}$ in aqueous DMF at 25C.