Absorption Spectra of Erbium TTA-TOPO Complexes Extracted from Aqueous Perchlorate Solutions

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It has been reported that the absorption spectra of neodymium, holmium and erbium complexes extracted into toluene containing 2-thenoyltrifluoroacetone (TTA) and tri-*n*-octyl phosphine oxide (TOPO) from an aqueous acetate solution had a strong band in the visible region with a maximum of 584, 452 and 520 mμ, respectively, and the formulae of these complexes were estimated to be Ln(TTA)$_3$2TOPO.[1]

In the present paper, we will describe the preliminary results of a spectrophotometric study of erbium TTA-TOPO complexes extracted into organic solvents with a series of various dielectric constants (ε) from aqueous solutions containing various amounts of perchlorate ions.

Figure 1 shows the absorption spectra for erbium complexes extracted into cyclohexane (ε: 2.02), isopropyl ether (ε: 3.88), chlorobenzene (ε: 5.62), dichloromethane (ε: 9.08) and 1,2-dichloroethane (ε: 10.36) from aqueous solutions containing a slight excess of perchlorate ion with respect to erbium ion. With increase in the dielectric constant of the organic solvents, a new sharp band appeared and grew regularly at 518 mμ. Moreover, even in the case of cyclohexane, a similar variation of the absorption band at 518 mμ was observed with increase in the concentration of perchlorate ion in an aqueous solution. The intensity at 518 mμ almost linearly increased with increase in $[\mathrm{ClO}^-_4/\mathrm{Er}^{3+}]_{\mathrm{org}}$, which represented the mole ratio of perchlorate and erbium ions extracted into various organic solvents, and became constant in the region above a 1 : 1 ratio of $[\mathrm{ClO}^-_4/\mathrm{Er}^{3+}]_{\mathrm{org}}$. When the intensity at 518 mμ was studied using 1,2-dichloroethane as a function of the mole ratio of TTA to erbium in the presence of excess TOPO, the break occurred at a mole ratio of TTA : Er = 2 : 1. On the other hand, in the case of mixtures containing excess TTA and various amounts of TOPO, the break was observed at a mole ratio of TOPO : Er = 5 : 1. Both intensities were almost constant with concentration of TTA and TOPO above these breaks. From these results and considering the coordination number of heavy lanthanide, it is felt that the complex in 1,2-dichloroethane prefers the formula $[\mathrm{Er(TTA)_2 5TOPO}]^+\mathrm{ClO}^-_4$ to $[\mathrm{Er(TTA)_2ClO_4 5TOPO}]$.

Since the absorption spectrum obtained using cyclohexane coincides with that of the Er(TTA)$_3$-2TOPO complex in a previous paper,[1] it is supposed that the following equilibria may exist as a function of dielectric constant of the organic solvents and concentration of perchlorate ion in an aqueous solution.

$$\mathrm{Er}^{3+} + 2\mathrm{HTTA}_{(0)} + 5\mathrm{TOPO}_{(0)} + \mathrm{ClO}_4^- \rightleftarrows [\mathrm{Er(TTA)_2 5TOPO}]^+\mathrm{ClO}_4^-{}_{(0)} + 2\mathrm{H}^+$$

An investigation using other lanthanide is in progress. Further discussion of the results and details of this study will be published later.

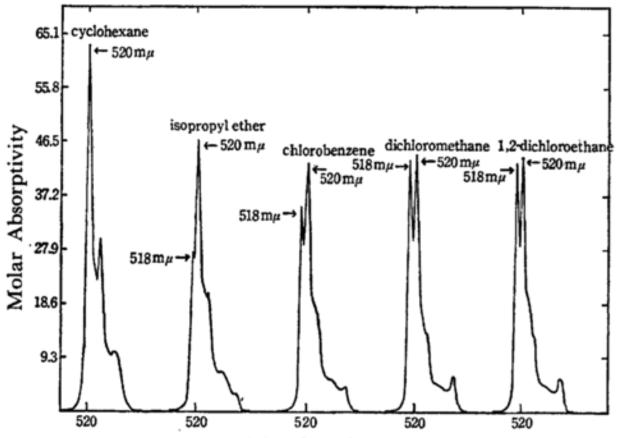

Fig. 1. Absorption spectra of erbium TTA-TOPO complexes in various organic solvents.

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[1] T. Taketatsu and C. V. Banks, *Anal. Chem.*, **38**, 1524 (1966).