The Synergic Solvent Extraction of Rare Earths. II. The Absorption Spectra of Neodymium-, Holmium-, and Erbium-TTA-TOPO Complexes with ClO_4^-, CNS^-, NO_3^-, and Cl^- Ions

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The synergic solvent extraction behavior of neodymium, holmium, and erbium in $Ln^{3+}/X^-/HTTA/TOPO$ systems ($X^- = ClO_4^-$, CNS^-, NO_3^-, and Cl^-) have been investigated. When the rare earths are completely extracted into an organic layer, the following equation is assumed:

$$Ln(TTA)_3(TOPO)_{2(o)} + 3TOPO_{(o)} + H^+_{(a)} + X^-_{(a)} \rightleftharpoons (Ln(TTA)_2(TOPO)_5)^+X^-_{(o)} + HTTA_{(o)}$$

for which the mixed equilibrium constant is defined by $k_3 = [(Ln(TTA)_2(TOPO)_5)^+X^-]_{(o)}[HTTA]_{(o)}/[Ln(TTA)_3(TOPO)_2]_{(o)}[TOPO]^3_{(o)}[H^+]_{(a)}[X^-]_{(a)}$. The log k_3 value for the holmium/ClO_4^-, /CNS^-, /NO_3^-, and /Cl^- systems are about 8.3, 6.5, 5.3, and 3.6 respectively. An obvious difference between $Ln^{3+}/SO_4^{2-}/HTTA/TOPO$ and $Ln^{3+}/ClO_4^-/HTTA/TOPO$ systems is observed in the order of the distribution ratio on the extraction of a series of rare earths with an increase in the atomic number.

In the previous paper,[1] when holmium and erbium were completely extracted from aqueous perchlorate solutions into various organic solutions containing 2-thenoyltrifluoroacetone (TTA) and tri-*n*-octyl phosphine oxide (TOPO), it was shown that the following equation held:

$$Ln(TTA)_3(TOPO)_{2(o)} + 3TOPO_{(o)} + H^+_{(a)} + ClO^-_{4(a)} \rightleftharpoons (Ln(TTA)_2(TOPO)_5)^+ClO^-_{4(o)} + HTTA_{(o)}$$

for which the mixed equilibrium constant was defined by $k_3 = [(Ln(TTA)_2(TOPO)_5)^+ClO_4^-]_{(o)}[HTTA]_{(o)}/[Ln(TTA)_3(TOPO)_2]_{(o)}[TOPO]^3_{(o)}[H^+]_{(a)}[ClO_4^-]_{(a)}$ and in which the k_3 linearly increased with an increase in the dielectric constant of the organic solvent used.

In the present paper, we will describe a spectrophotometric study of neodymium-, holmium-, and erbium-TTA-TOPO complexes extracted from aqueous solutions containing perchlorate, thiocyanate, nitrate, chloride, sulfate or acetate ions, also, we will discuss the formation of these metal TTA-TOPO complexes associated with various anions.

Experimental

The preparation of the reagents and all the experimental procedures were the same as in the previous paper.

Results and Discussion

(i) Absorption Spectra in $Nd^{3+}/HTTA/TOPO/ClO_4^-$ System. The absorption spectra of a cyclohexane solution containing neodymium-TTA-TOPO complexes extracted from an acetate solution and of a 1,2-dichloroethane solution containing the complexes extracted from the perchlorate solution by the extraction procedure are given in Fig. 1. The patterns of these spectra are defined as α- and β-types respectively. The pattern of the α-type is identical with that of the $Nd(TTA)_3(TOPO)_2$ complexes in the literature.[2,3)]

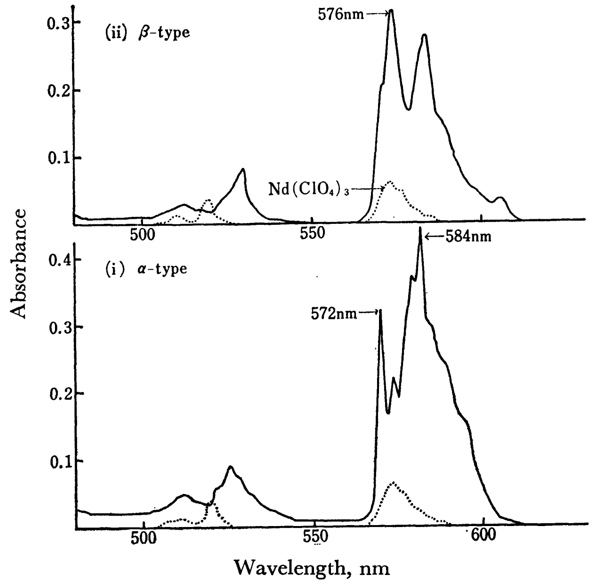

Fig. 1. Absorption spectra of organic solutions containing Nd-TTA-TOPO complexes.
(i) Aqueous layer: 0.00943M Nd^{3+}, 0.4M CH_3COO^-
Organic layer: 0.1M HTTA, 0.1M TOPO, cyclohexane
(ii) Aqueous layer: 0.00943M Nd^{3+}, 0.4M CH_3COO^-, 1.0M ClO_4^-
Organic layer: 0.1M HTTA, 0.1M TOPO, 1,2-dichloroethane

The absorption spectra of all the organic solutions containing the metal complexes extracted from the acetate solution gave an α-type spectrum. On the other hand, in the case of extraction from perchlorate solutions, the pattern of the spectra changed from the α- to the β-type with an increase in the dielectric constant of the organic solvent used, as was also observed in the cases of holmium and erbium.[1]

The variations in the absorption spectra of 1,2-dichloroethane solutions containing the neodymium-TTA-TOPO complex were studied as a function of the concentrations of perchlorate ions added to the acetate solution and of the hydrogen ions of the solutions containing a definite quantity of perchlorate ions.

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[1] T. Taketatsu and N. Toriumi, *J. Inorg. Nucl. Chem.*, **31**, 2235 (1969).

[2] T. V. Hearly and J. R. Ferraro, *ibid.*, **24**, 1449 (1962).

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

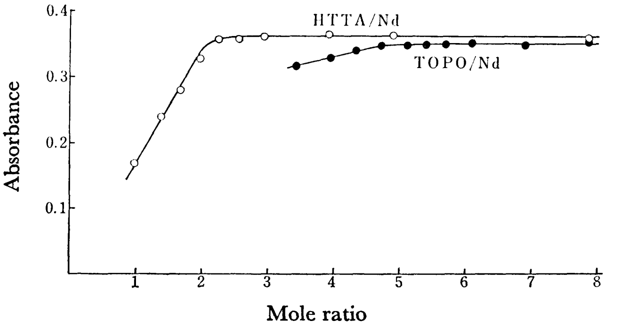

Fig. 2. Variation in absorbance with increasing of concentration of HTTA in the presence of excessive amount of TOPO and with that of TOPO in the presence of excessive amount of HTTA.
Aqueous layer: 0.0102M Nd^{3+}, 1.0M ClO_4^-, 0.5M CH_3COO^-.
Organic layer: varying HTTA, 0.1M TOPO or 0.1M HTTA, varying TOPO, 1,2-dichloroethane

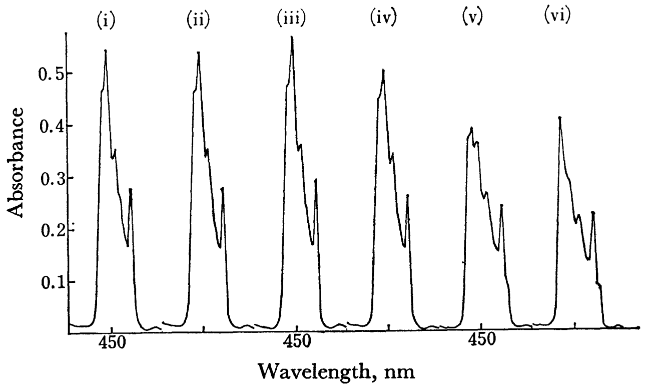

Fig. 3. Variation in absorption spectra with increasing of dielectric constant (ε) of organic solvents used in the Ho^{3+}/NO_3^-/HTTA/TOPO system.
Aqueous layer: 0.00541M Ho^{3+}, 1.20M NO_3^-.
Organic layer: (i) benzene (ε 2.28) (ii) trichloroethylene (ε 3.42) (iii) isopropyl ether (ε 3.88) (iv) chlorobenzene (ε 5.62) (v) dichloroethane (ε 9.08) (vi) 1,2-dichloroethane (ε 10.32), 0.2M HTTA, 0.2M TOPO.

The change in these absorption spectra from the α- to the β-type also progressed with an increase in the concentration of perchlorate or hydrogen ions.

The variations in the absorbance at 576 nm were studied as a function of the concentration of TTA *vs.* the neodymium added to the aqueous layer, using 1,2-dichloroethane solutions containing various amounts of TTA and a fixed, excessive amount of TOPO; we also studied them as a function of the concentration of TOPO *vs.* neodymium, using organic solutions containing a fixed, excessive amount of TTA and various amounts of TOPO. The results are given in Fig. 2. Breaks are observed at mole ratios of TTA: Nd=2:1 and TOPO: Nd=5:1 though the latter break is somewhat obscure.

It is supposed that the β-type complex has the chemical composition of $(Nd(TTA)_2(TOPO)_5)^+ClO_4^-$ for the

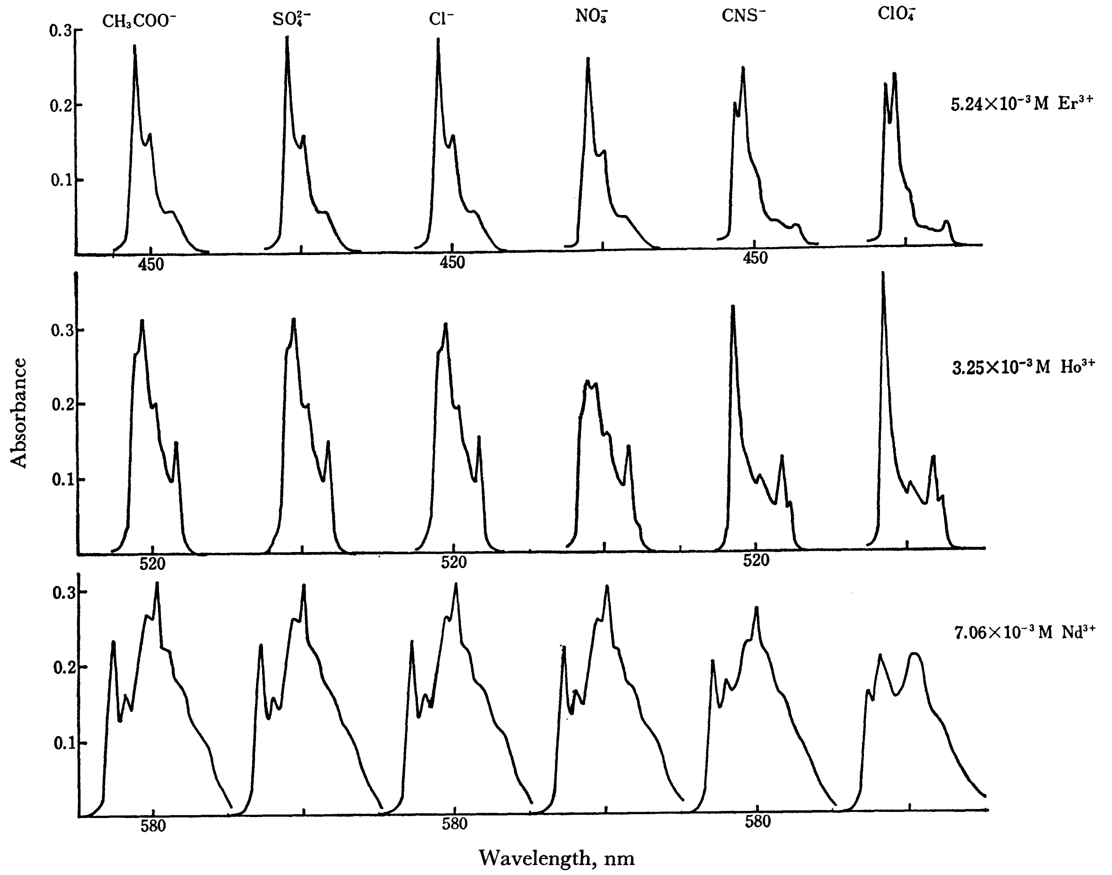

Fig. 4. Absorption spectra of 1,2-dichloroethane solutions in Er^{3+}, Ho^{3+}, and Nd^{3+}/CH_3COO^-/X^{n-}/HTTA/TOPO systems.
Aqueous layer: 0.1M SO_4^{2-}, Cl^-, NO_3^-, CNS^-, and ClO_4^-, 0.04M CH_3COO^-
Organic layer: 0.1M HTTA, 0.1M TOPO

electric conductivity of 1,2-dichloroethane solutions containing the neodymium complexes increases almost linearly with an increase in the absorbance at 576 nm, as was observed in the cases of holmium- and erbium-TTA-TOPO complexes.

Although the estimation of the k_3 value using the assumption described in the previous paper is not always accurate because the new band at 576 nm of the β-type spectrum appears in the middle of the bands at 572 and 584 nm of the α-type spectrum, it is assumed that the $\log k_3$ value for neodymium using 1,2-dichloroethane is approximately 6 and that it is lower than that ($\log k_3 \fallingdotseq 8$) of holmium and erbium.

(*ii*) *Absorption Spectra in $Ln^{3+}/HTTA/TOPO/X^-$ Systems.* The behavior of the absorption spectra of organic solutions containing rare earth-TTA-TOPO complexes extracted from an aqueous solution containing thiocyanate, nitrate, chloride, or sulfate ions in place of perchlorate ions was investigated. As an example, the absorption spectra of various organic solutions containing holmium extracted from acetate solutions containing a definite amount of nitrate ions are given in Fig. 3. It can be seen that the patterns of these spectra change from the α- to the β-type in accordance with an increase in the value of the dielectric constant, as was also observed in the case of the perchlorate ion. This phenomenon suggests that the nitrate ion associates with the TTA-TOPO complexes just as does the perchlorate ion.

The absorption spectra of 1,2-dichloroethane solutions containing neodymium, holmium, and erbium extracted from acetate solutions containing definite amounts of perchlorate, thiocyanate, nitrate, chloride, and sulfate ions are shown in Fig. 4. It can be seen that the extent of the change from the α- to the β-type is different according to the species of anions used and that the order of the effect is $ClO_4^- > CNS^- > NO_3^- > Cl^- > SO_4^{2-}$. It is considered that sulfate ions as well as acetate ions form scarcely any ion-associate complex because the α-type spectrum is not affected by the addition of a large amount of the ions.

From these results, it is assumed that the formula of the β-type complex can be represented as $(Ln(TTA)_2(TOPO)_5)^+X^-$: X^-=anions such as ClO_4^-, CNS^-, NO^-_3, and Cl^-. If the assumption for the $Ln^{3+}/HTTA/TOPO/ClO_4^-$ system described in the previous paper can be generalized for the $Ln^{3+}/HTTA/TOPO/X^-$ system, the following equation may be used:

$$Ln(TTA)_3(TOPO)_{2(0)} + 3TOPO_{(0)} + H^+_{(a)} + X^-_{(a)} \rightleftharpoons (Ln(TTA)_2(TOPO)_5)^+X^-_{(0)} + HTTA_{(0)}$$

for which:

$$k_3 = \frac{[(Ln(TTA)_2(TOPO)_5)^+X^-]_{(0)}[HTTA]_{(0)}}{[Ln(TTA)_3(TOPO)_2]_{(0)}[TOPO]^3_{(0)}[H^+]_{(a)}[X^-]_{(a)}}$$

Here, the k_3 value can be estimated spectrophotometrically from the degree of enhancement of a specific absorption band. The results for holmium-TTA-TOPO complexes using 1,2-dichloroethane solutions are given in Table 1. The average values of $\log k_3$ for ClO_4^-, CNS^-, NO_3^-, and Cl^- systems are about 8.3, 6.5, 5.3, and 3.6 respectively.

TABLE 1. MIXED EQUILIBRIUM CONSTANT k_3 FOR Ho^{3+}/X^-/HTTA/TOPO/1,2-DICHLOROETHANE SYSTEMS

X^-	Concentration of X^- (M)	$[H^+]_{(a)}$ (M)	Absorbance at 445 nm	x[a]	$\log k_3$
ClO_4^-	0.004	3.49×10^{-4}	0.387	1.58	8.33
ClO_4^-	0.006	3.16×10^{-4}	0.465	3.13	8.25
ClO_4^-	0.008	3.16×10^{-4}	0.502	4.82	8.18
SCN^-	0.2	3.89×10^{-4}	0.529	7.32	6.52
SCN^-	0.3	4.07×10^{-4}	0.542	9.40	6.44
SCN^-	0.5	3.98×10^{-4}	0.557	13.62	6.39
NO_3^-	0.2	6.76×10^{-4}	0.328	1.00	5.37
NO_3^-	0.3	6.76×10^{-4}	0.352	1.20	5.28
NO_3^-	0.4	6.76×10^{-4}	0.376	1.45	5.24
Cl^-	0.5	1.41×10^{-3}	0.124	0.137	3.74
Cl^-	1.0	1.59×10^{-3}	0.150	0.202	3.56
Cl^-	1.5	1.62×10^{-3}	0.160	0.232	3.44

0.2M HTTA and 0.2M TOPO in organic layer and 0.00541M Ho^{3+} in aqueous layer before shaking.

a) x represents the mole ratio of $(Ln(TTA)_2(TOPO)_5)^+X^-$ *vs.* $Ln(TTA)_3(TOPO)_2$

Calibration curves used:

absorbance at 445 nm	$(Ho(TTA)_2$-$(TOPO)_5)^+ClO_4^-$	$Ho(TTA)_3$-$(TOPO)_2$
0.590	0.00541 M	0.00 M
0.050	0.00	0.00541

In order to investigate the effect of the anion extracted into the organic layer on the equilibrium relation between α- and β-type complexes, the distribution ratio, D, of the X^- anion, $D = X^-_{(0)}/X^-_{(a)}$, where $X^-_{(0)}$ and $X^-_{(a)}$ are the total molar concentrations of the anion in a 1,2-dichloroethane soultion of 0.1M TOPO and an aqueous solution respectively, was measured using 0.05M sodium perchlorate, nitrate, and chloride solutions of about pH 3. The results obtained for ClO_4^-, NO_3^-, and Cl^- ions were 0.711, 0.082, and 0.011 respectively. In Fig. 5, it is shown that the plots of the $\log k_3$ values for $Ho^{+3}/HTTA/TOPO/ClO_4^-$, $/NO_3^-$, and $/Cl^-$ systems against the logarithm values of D for ClO_4^-, NO_3^- and Cl^- ions almost give a linearity.

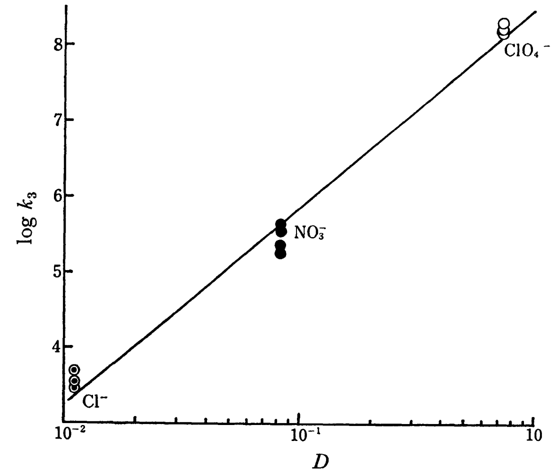

Fig. 5. Relationship between $\log k_3$ for Ho^{3+} and distribution ratio D of ClO_4^-, NO_3^-, and Cl^-.

for $\log k_3$: Aqueous layer: 0.00541M Ho^{3+}, varying ClO_4^-, NO_3^-, and Cl^-
Organic layer: 0.2M HTTA, 0.2M TOPO, 1,2-dichloroethane
for D: Aqueous layer: 0.05M ClO^-_4, NO^-_3, and Cl^-
Organic layer: 0.1M TOPO, 1,2-dichloroethane

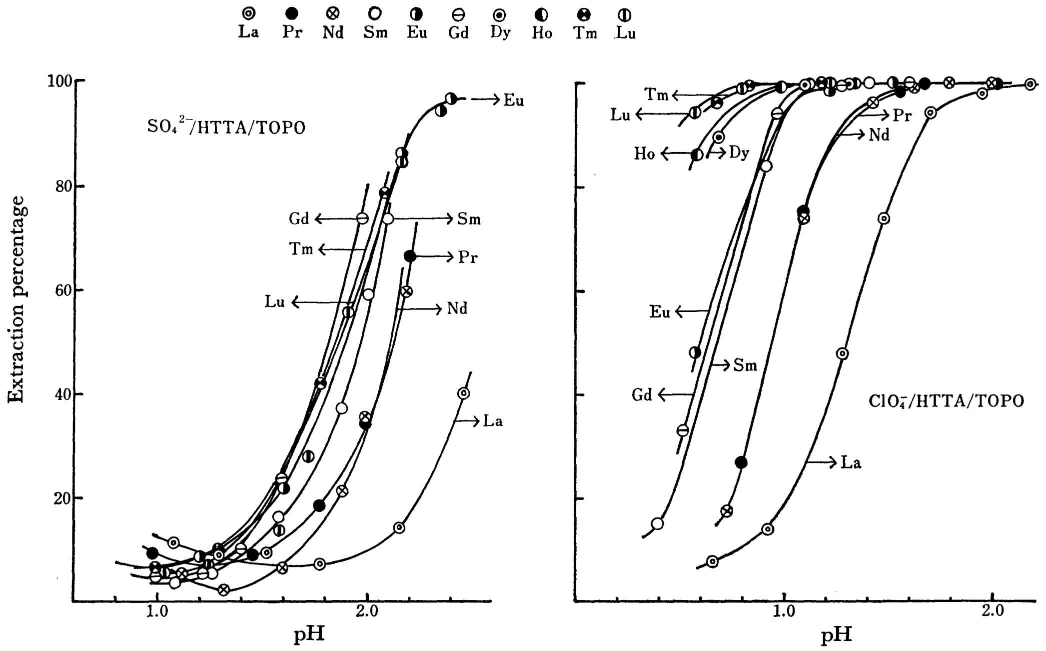

Fig. 6. Discrepancy of extracted amount of rare earths between ClO_4^-/HTTA/TOPO and SO_4^{2-}/HTTA/TOPO systems as a function of pH.
Aqueous layer: 0.1 M SO_4^{2-} or ClO_4^-, rare earth acetates
Organic layer: 0.1 M HTTA, 0.1 M TOPO, 1,2-dichloroethane

Conocchioli, Tocher, and Diamond[4] reported that perchloric acid was extracted into a carbon tetrachloride solution of TOPO by the formation of the ion-associate complex $H_3O^+ \cdot n\mathrm{TOPO} \cdot ClO_4^-$ ($n=1$ and 3). Therefore, it is assumed that the change from $\mathrm{Ln(TTA)_3(TOPO)_2}$ to $\mathrm{(Ln(TTA)_2(TOPO)_5)^+X^-}$ depends upon the molar concentration rather than on the kind of anion extracted with TOPO into the organic layer.

(iii) Extractability of Ln^{3+} in ClO_4^-/HTTA/TOPO and SO_4^{2-}/HTTA/TOPO Systems. An obvious discrepancy is observed in the order of extractability of a series of rare earths in relation to the formation of $\mathrm{Ln(TTA)_3(TOPO)_2}$ and $\mathrm{(Ln(TTA)_2(TOPO)_5)^+ClO_4^-}$ complexes. When the individual rare earth was extracted into a 1,2-dichloroethane solution containing TTA and TOPO from an aqueous acetate solution, the extractability of these elements was studied as a function of the pH value, which was adjusted with perchloric or sulfuric acid. The results are given in Fig. 6. For a perchloric acid system, the extractability of rare earths increases as the atomic number increases. On the other hand, for a sulfuric acid system, though the extractability of the lighter rare earth increases as the atomic number increases, that of heavier rare earths is the reverse with an increase in the atomic number.

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[4] T. J. Conocchioli, M. I. Tocher, and R. M. Diamond, *J. Phys. Chem.*, **69**, 1106 (1965).