LIQUID-LIQUID EXTRACTION OF YTTRIUM(III) FROM THIOCYANATE SOLUTIONS WITH SULPHOXIDES AND THEIR MIXTURES—COMPUTER-AIDED ANALYSIS

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The extraction of yttrium(III) from thiocyanate solutions by alkyl and aryl sulphoxides and tri-*n*-octyl phosphine oxide and their mixtures in benzene has been studied. Synergistic effects have been observed with a mixture of extractants which are ascribed to the formation of mixed ligand complexes. These extraction data have been analysed theoretically by taking into account aqueous-phase speciation and all plausible complexes extracted into the organic phase. The extraction behaviour of yttrium(III) has also been compared with that of some lanthanides. It was observed that yttrium(III) behaves like a lighter rare earth in thiocyanate solutions during extraction with dialkyl sulphoxides. Separation factors have also been evaluated. The influence of metal ion concentration and of the diluent on the extraction of yttrium(III) has also been investigated.

Introduction

Organic sulphoxides have for many years been considered attractive potential extractants in the solvent extraction of metals^{4-6, 8)}. Because of the advantages of a more abundant source, higher extraction ability and cheaper cost than tri-*n*-butyl phosphate, sulphoxides have stimulated the interest of investigators in many countries. They have been successfully employed for the extraction of actinides⁷⁾, lanthanides⁹⁾ and transition elements¹⁰⁾ with efficiency. Reddy *et al.* have studied the extraction of some lanthanides with sulphoxides and their mixtures¹¹⁾. They were not able to establish the reaction mechanisms with mixtures of sulphoxides due to the limitations of the slope analysis methods they adopted for analysis of the equilibrium data. However, no detailed studies relevant to the extraction of yttrium(III) from thiocyanate solutions with sulphoxides and their mixtures have been reported in the literature. Further, no one has compared the extraction behaviour of yttrium(III) with that of lanthanides using sulphoxides as extractants from thiocyanate media.

The extraction equilibria of Lu(III) from various aqueous solutions with sulphoxides in the presence of a chelating agent (HTTA) have been studied¹²⁾. In continuation of this work, the extraction of yttrium(III) from thiocyanate solutions has been studied, using di-*n*-pentyl sulphoxide (DPSO), di-*n*-octyl sulphoxide (DOSO), diphenyl sulphoxide (DPhSO) and their mixtures in benzene medium, with a view to elucidate the nature of the metal ion species extracted into the organic phase. For comparison, studies have also been carried out with tri-*n*-octyl phosphine oxide (TOPO). In addition, the extraction behaviour of some lanthanides has been examined

in order to obtain information about the relative extraction behaviour of yttrium in thiocyanate media. Separation factors of yttrium with respect to various lanthanides have also been calculated. Due to the limitations of the graphical methods traditionally used for the interpretation of solvent extraction data, for mixed solvents in particular, recourse was taken to theoretical analysis using a computer in the present study^{13, 14)}.

1. Experimental

1.1 Apparatus and reagents

A Hitachi 220 double-beam microprocessor-controlled spectrophotometer was used for measuring absorbances. An Elico digital pH meter was used for pH value measurements. All the programs were written in FORTRAN 77 and executed on a 32-bit minicomputer (HCL, Horizon III).

Stock solutions of rare earths were prepared from their oxides (Rare Earth Products, Cheshire, UK, 99.99%) by dissolving in concentrated hydrochloric acid and diluting to 100cm³ with distilled water. The solution was standardized by a known method¹³⁾. Initial metal ion concentration was maintained at 1×10^{-6} mol dm⁻³ except in the experiments on the effect of metal ion concentration. Sulphoxides were synthesized in our laboratory according to the procedure already described⁷⁾. TOPO was obtained from Aldrich Chemical Co. Ammonium thiocyanate concentration was maintained at 3 mol dm⁻³ except in the experiments on the effect of thiocyanate concentration. The pH was adjusted to 3.0 to ensure stability³⁾, using dilute perchloric acid.

Arsenazo I (Fluka, Switzerland) solution was prepared by dissolving 25 mg of this reagent in 250 cm³ of

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Fig. 1 Effect of ammonium thiocyanate concentration on the extraction of yttrium(III) by 0.3 mol dm⁻³ DOSO in benzene. Y(III) = 1 × 10⁻⁶ mol dm⁻³.

distilled water. Ammonium acetate buffer (pH = 7.5) was prepared by dissolving 19.25 gms in 250 cm³ of distilled water and adjusting the pH with HCL/NaOH. All the other chemicals were of analytical grade.

1.2 Extraction equilibrium procedure

Distribution coefficients were determined by shaking equal volumes of aqueous and organic phases for 15 minutes in a separating funnel at 303 ± 1°K. Preliminary experiments showed that the extraction equilibrium is attained within 5 minutes. After allowing the phases to settle, 5 cm³ aliquots of aqueous phase were pipetted into a 25 cm³ beaker and 1 cm³ of ammonium acetate buffer and 5 cm³ of arsenazo I solution were added. After adjusting the pH to 7.5, the solution was transferred into a 25 cm³ volumetric flask and made up to the mark. The absorbances of the solutions were measured at 575 nm and the metal concentrations were computed from the respective calibration graphs. The rare earth concentration in the organic phase was obtained by material balance. These concentration values were used to obtain the distribution coefficient, *D*.

2. Results and Discussion

2.1 Extraction with sulfoxides

The yttrium ion in the aqueous phase takes a variety of complex forms in the presence of thiocyanate ions, but under the present experimental conditions it is sufficient to consider only the first complex as shown by Eq. (1):

Then the total concentration of yttrium (III) in the aqueous phase (*Y_t*) is given by

$$Y_t = [Y^{3+}] + [Y(SCN)^{2+}] = [Y^{3+}] \{1 + \beta_1 [SCN^-]\} \quad (11)$$

The stability constant, $\beta_1 = 0.85$, was obtained from the literature¹⁵.

Fig. 2 Log-log plots for the variation of extraction of yttrium(III) with concentration of DPSO, DOSO, DPhSO and TOPO in benzene. Aqueous phase: 3.0 mol dm⁻³ NH₄SCN of pH~3, Y(III) = 1 × 10⁻⁶ mol dm⁻³

The mechanism of extraction of yttrium (III) from thiocyanate media by sulfoxides (*R*₂SO) can be written as in Eq. (3):

The values of *D* of yttrium (III) were obtained as a function of pH at constant thiocyanate and sulfoxide concentration and were found to be constant in the range of pH from 2.5 to 4.5. Thus it is clear that H⁺ ions do not participate in the extractable complex and hence the value of 'a' (shown in Eq. (3)) is zero. Thus the extraction equilibrium is shown in Eq. (4):

Then the *D* of yttrium (III) can be represented as

$$D = \frac{\sum [Y(SCN)_x \cdot z(R_2SO)]_{org}}{[Y^{3+}]\{1 + \beta_1[SCN^-]\}} \quad (14)$$

Results of the extraction of yttrium (III) by 0.3 mol dm⁻³ DOSO in benzene at various concentrations of ammonium thiocyanate are presented in **Fig. 1**. The distribution coefficient rapidly increases with increase in SCN⁻ concentration. The slope of the plot log {*D* (1 + β₁ [SCN⁻])} against log [SCN⁻] is 3, suggesting that the metal species extracted into the organic phase are associated with three thiocyanate ions.

The variation of *D* of yttrium (III) with the concentration of DPSO, DOSO, DPhSO and TOPO was

Table 1. Equilibrium constants for extraction of yttrium(III) with DPSO, DOSO, DPhSO and TOPO

Extractant	Complex	Equilibrium constant
DPSO	$Y(SCN)_3 \cdot 4DPSO$	$4.4 \times 10^1 [(mol\ dm^{-3})^{-7}]$
DOSO	$Y(SCN)_3 \cdot 4DOSO$	$3.7 \times 10^1 [(mol\ dm^{-3})^{-7}]$
DPhSO	$Y(SCN)_3 \cdot 4DPhSO$	$3.0 \times 10^{-3} [(mol\ dm^{-3})^{-7}]$
	$Y(SCN)_3 \cdot 5DPhSO$	$5.8 \times 10^{-4} [(mol\ dm^{-3})^{-8}]$
TOPO	$Y(SCN)_3 \cdot 3TOPO$	$2.7 \times 10^7 [(mol\ dm^{-3})^{-6}]$

Fig. 3 Effect of metal ion concentration on the extraction of yttrium(III) with $0.3\ mol\ dm^{-3}$ DOSO in benzene. $NH_4SCN = 3.0\ mol\ dm^{-3}$ of pH~3

studied, using $3.0\ mol\ dm^{-3}$ thiocyanate (pH~3) as the aqueous phase, and the results are shown in **Fig. 2**. From the values of the slopes obtained from these log-log plots it is clear that four molecules of DPSO, DOSO or DPhSO and 3 molecules of TOPO are associated with the extractable complex in the respective extractions. A slightly higher slope of 4.3 in the extraction of DPhSO may be due to the formation of an additional complex involving the association of five molecules of DPhSO. From these results, it may be concluded that the complexes formed in extraction with these extractants were $Y(SCN)_3 \cdot 4DPSO$, $Y(SCN)_3 \cdot 4DOSO$, $Y(SCN)_3 \cdot 4DPhSO$, $Y(SCN)_3 \cdot 5DPhSO$ and $Y(SCN)_3 \cdot 3TOPO$. The formation constants for these species are given in **Table 1**. Similar solvation numbers have been reported in the extraction of trivalent lanthanides from thiocyanate media with sulphoxides⁹) as well as with neutral organophosphorus²) extractants. The extraction efficiency of these extractants is in the order: TOPO > DPSO > DOSO > DPhSO.

The log-log plot of the equilibrium organic-phase yttrium(III) concentration against the equilibrium aqueous-phase yttrium(III) concentration (**Fig. 3**) is linear with a slope of unity, indicating that the extracted species are mononuclear. The extraction of yttrium(III) by $0.3\ mol\ dm^{-3}$ DOSO in various diluents is in the order: xylene ($D = 3.7$) > toluene > benzene > carbon tetrachloride > chloroform ($D = 0.02$). Very poor extrac-

Fig. 4 Extraction of yttrium(III) with mixtures of DPSO + DOSO in benzene. Aqueous phase: $3.0\ mol\ dm^{-3}$ of NH_4SCN of pH~3, $Y(III) = 1 \times 10^{-6}\ mol\ dm^{-3}$

tion was observed when chloroform was employed as diluent, which may be due to hydrogen bond formation between the acidic diluent and the weakly basic extractant.

2.2 Extraction of yttrium (III) with mixture of dialkyl sulphoxides

When yttrium (III) is extracted with a mixture of DPSO and DOSO from thiocyanate solutions, the ideal extraction equilibrium may be written as

The equilibrium constant, $K_{z,4-z}$, is given by

$$K_{z,4-z} = \frac{[Y(SCN)_3 \cdot zDPSO \cdot (4-z)DOSO]_{org}}{[Y^{3+}][SCN^-]^3[DPSO]_{org}^z[DOSO]_{org}^{4-z}} \quad (16)$$

where $z = 0, 1, 2, 3$ and 4 .

Then the distribution coefficient, D , can be represented as

$$D = \frac{\sum_{z=0}^4 K_{z,4-z} [SCN^-]^3 [DPSO]_{org}^z [DOSO]_{org}^{4-z}}{\{1 + \beta_1 [SCN^-]\}} \quad (17)$$

The effect of the mixtures of sulphoxides (DPSO + DOSO) on the extraction of yttrium (III) from $3.0\ mol\ dm^{-3}$ thio-cyanate solutions (pH~3) has been studied and the results are shown in **Fig. 4**, where D represents the distribution coefficient of yttrium (III) with the mixture of extractants and $\Sigma D = D_{DOSO} = D_{DPSO}$. About 5- to 8-fold synergistic enhancement has been observed with mixtures of dialkyl sulphoxides. These distribution data

Table 2. Equilibrium constants for extraction of yttrium(III) with mixtures of (DPSO + DOSO) and (DOSO + TOPO)

Complex	Equilibrium constant
$Y(SCN)_3 \cdot 3DPSO \cdot DOSO$	$8.9 \times 10^3 [(mol\ dm^{-3})^{-7}]$
$Y(SCN)_3 \cdot 2DPSO \cdot 2DOSO$	$2.3 \times 10^3 [(mol\ dm^{-3})^{-7}]$
$Y(SCN)_3 \cdot DPSO \cdot 3DOSO$	$1.1 \times 10^4 [(mol\ dm^{-3})^{-7}]$
$Y(SCN)_3 \cdot 3TOPO \cdot DOSO$	$9.8 \times 10^8 [(mol\ dm^{-3})^{-7}]$
$Y(SCN)_3 \cdot 2TOPO \cdot 2DOSO$	$3.6 \times 10^7 [(mol\ dm^{-3})^{-6}]$
$Y(SCN)_3 \cdot TOPO \cdot 3DOSO$	$4.7 \times 10^5 [(mol\ dm^{-3})^{-7}]$

Fig. 5 Extraction of yttrium(III) with mixtures of DOSO + TOPO in benzene. Aqueous phase: $3.0\ mol\ dm^{-3}\ NH_4SCN$ of pH~3, $Y(III) = 1.0 \times 10^{-6}\ mol\ dm^{-3}$

were analysed using Eq. (8), and the best fit between experimental and calculated distribution coefficients was obtained when formation of the mixed species was assumed. The equilibrium constants for these data were again obtained by nonlinear regression analysis and are shown in Table 2.

2.3 Extraction of yttrium (III) with mixture of TOPO and DOSO

The extraction of yttrium (III) from $3.0\ mol\ dm^{-3}$ thiocyanate solutions (pH~3) with a mixture of neutral organophosphorus extractant (TOPO) and DOSO has also been studied (Fig. 5). A fivefold enhancement in extraction has been observed. These distribution data have again been analysed by assuming a set of mixed species extracted into the organic phase. The results could be simulated by assuming the formation of the spe-

Fig. 6 Effect of ammonium thiocyanate concentration on the extraction of yttrium(III) and some lanthanides with $0.3\ mol\ dm^{-3}\ DOSO$ in benzene. $Ln(III) = 1 \times 10^{-6}\ mol\ dm^{-3}$

Table 3. Separation factors for some lanthanides with respect to yttrium at various thiocyanate concentrations

[SCN⁻] [mol dm⁻³]	La/Y	Nd/Y	Gd/Y	Dy/Y	Ho/Y	Er/Y	Lu/Y
1.0	0.4	1.2	1.3	1.7	2.0	2.7	3.3
2.0	0.5	1.4	1.7	2.0	2.4	3.1	4.0
3.0	0.6	1.4	1.7	2.2	2.5	3.2	4.0

cies $Y(SCN)_3 \cdot DOSO \cdot (TOPO)_3$, $Y(SCN)_3 \cdot (DOSO) \cdot (TOPO)_2$ and $Y(SCN)_3 \cdot (DOSO)_3 \cdot TOPO$. The formation constants for these species are given in Table 2. It is unlikely that there exists the same type of species as reported in the case of mixtures of dialkyl sulphoxides because of the considerable difference in magnitude of the equilibrium constant values of TOPO and DOSO. The relatively small synergistic enhancement in the extraction of yttrium (III) with mixtures of neutral extractants observed in the present study may be attributed to the formation of more stable mixed solvents.

2.4 Extraction of lanthanides with DOSO

To determine the relative extraction behaviour of yttrium (III) from thiocyanate solutions by $0.3\ mol\ dm^{-3}\ DOSO$ with respect to lanthanides, extraction studies have been carried out for La, Nd, Gd, Dy, Ho, Er and Lu at different thiocyanate concentrations. As can be seen from Fig. 6, yttrium (III) behaves like a lighter lanthanide in thiocyanate media with sulphoxides as reported in the literature for the rare earth-thiocyanate-Aliquat 336 system¹⁾. It can also be seen from Fig. 6 that

the extraction increases with increasing atomic number of lanthanides (La < Nd < Gd < Dy < Ho < Er < Lu). The separation factors for some lanthanides with respect to yttrium have also been calculated and are given in **Table 3**. This suggests the possibility of separating yttrium from heavier lanthanides by extraction with dialkyl sulphoxides from thiocyanate media.

Conclusion

The extraction equilibria of yttrium (III) with alkyl and aryl sulphoxides, TOPO and their mixtures in benzene was carried out. The extraction efficiency of these extractants was found to be in the order: TOPO > DPSO > DOSO > DPhSO. The extraction behaviour of yttrium(III) was also compared with that of some lanthanides. It was observed that yttrium extracts like a lighter rare earth from thio-cyanate solutions with dialkyl sulphoxides.

Nomenclature

a	= stoichiometric coefficient	[-]
D	= distribution coefficient	[-]
$K_{x,z}$	= extraction constant of the complex defined by Eq. (4)	$[(\text{mol}/\text{dm}^3)^{-x-z}]$
$K_{z,4-z}$	= extraction constant of the complex defined by Eq. (6)	$[(\text{mol}/\text{dm}^3)^{-7}]$
Y_t	= total concentration of yttrium (III) in aqueous phase	$[\text{mol}/\text{dm}^3]$

β_1 = first stability constant of yttrium thiocyanate complex $[(\text{mol}/\text{dm}^3)^{-1}]$

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