SOLVENT EXTRACTION OF SCANDIUM(III), YTTRIUM(III) AND SOME LANTHANOID(III) IONS WITH N-ALKYLCARBONYL SUBSTITUTED N-PHENYLHYDROXYLAMINES

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Abstract - The extraction behavior of scandium(III), yttrium(III) and certain lanthanoid(III) ions, namely praseodymium, europium and ytterbium, from aqueous solutions into carbon tetrachloride solutions containing various N-alkylcarbonyl-N-phenylhydroxylamines(R-PHAs) has been studied at 298 K and the ionic strength, 0.1(NaNO₃). The chelating extractants studied were N-octanoyl-N-phenylhydroxylamine (C8-PHA), N-(2-propylpentanoyl)-N-phenylhydroxylamine(PP-PHA) and N-(2-hexyldecanoyl)-N-phenylhydroxylamine(HD-PHA). The metal ions studied were all extracted with all the R-PHAs as self-adducts of the form $ML_3(HL)_2$, where L and HL represent the ligand anion and neutral ligand, respectively. The extraction constants and separation factors for the extraction systems were evaluated. HD-PHA and PP-PHA were excellent extractants for the separation of yttrium from heavy lanthanoids.

Keywords N-alkylcarbonyl-N-phenylhydroxylamines, solvent extraction, scandium, yttrium, lanthanoids

There is a sharp rise in demand of lanthanoids, yttrium and scandium, due to the quick growth of advanced industries, such as electronics and new ceramics. Because of the similarity in chemical properties of these elements, it is generally difficult to separate these individual elements. Solvent extraction is a simple and effective separation technique and widely employed in separation of metal ions. For an industrial-scale separation of lanthanoids and yttrium, di(2-ethylhexyl)phosphoric acid(D2EHPA) has mainly been employed as an extractant[1]. However, the development of more selective extractants is desired in order to establish effective separation process of the metal ions.

In a previous paper[2], we have reported that the extraction and separation of lanthanoids(III) by the use of some N-alkylcarbonyl-N-phenylhydroxylamines (R-PHAs). Among the R-PHAs employed, N-(2-hexyldecanoyl)-N-phenylhydroxylamine (HD-PHA) was a good choice for the intragroup separation of heavy lanthanoids, while N-octanoyl-N-phenylhydroxylamine(C8-PHA) was suitable for separation of light lanthanoids. The present study is thus extended to the extraction of scandium and yttrium with R-PHAs in relation to the separation of these metal ions from lanthanoids. The extraction equilibria of scandium(III), yttrium(III), praseodymium(III), europium(III) and ytterbium(III) from aqueous solutions into carbon tetrachloride with C8-PHA, HD-PHA and N-(2-propylpentanoyl)-N-phenylhydroxylamine(PP-PHA) have been studied.

EXPERIMENTAL

Apparatus The concentration of metal ions in the aqueous phase was measured with a Shimadzu GVM-1000P ICP atomic emission spectrometer. A Toa HM-15A pH meter was employed for measuring the pH values in the aqueous phase. A Yamato SA-31 shaker was used for mixing the two phases. A Kokusan H-200 centrifuge was also used for rapid and complete separation of the two phases.

Reagents R-PHAs were prepared as described previously[2,3] in a similar fashion to the method of Agrawal and Tandon[4]. Stock solutions of metal ions ($1.0 \times 10^{-2} \text{ mol dm}^{-3}$) were prepared by dissolving the metal nitrates (>99.99%, Raremetallic Inc.) in $10^{-3} \text{ mol dm}^{-3}$ nitric acid. All other chemicals were of analytical grade. Distilled-deionized water was used throughout the experiments.

Procedure A 30.0-cm^3 aliquot of aqueous solution containing a specified metal ion ($5.00 \times 10^{-5} \text{ mol dm}^{-3}$), sodium nitrate (0.1 mol dm^{-3}), sodium tartrate ($1.0 \times 10^{-2} \text{ mol dm}^{-3}$) and an appropriate buffer component ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$) was shaken with a 5.00-cm^3 aliquot of carbon tetrachloride in which the R-PHA concentration was in the range from 1.58×10^{-3} to $1.58 \times 10^{-2} \text{ mol dm}^{-3}$ for 1 h for equilibration at $298 \pm 1 \text{ K}$. If necessary, 1 mol dm^{-3} sodium hydroxide or nitric acid was also added for controlling the pH value of the aqueous phase. After centrifuging for 10 min at 1500 rpm, the pH as well as metal-ion concentration of the aqueous phase were determined. The metal concentration in the organic phase was calculated on the basis of the material balance.

RESULTS AND DISCUSSION

When a free metal ion is predominant in the aqueous phase, the extraction of trivalent metal ion (M^{3+}) with a R-PHA(HL) can be generally described according to

where the subscript, (o), refers to the species in the organic phase. The extraction constant, K_{ex} , is thus defined by

$$K_{ex} = [ML_n(HL)_m]_{(o)} [H^+]^n / [M^{3+}] [HL]_{(o)}^{(n+m)} \quad (2)$$

The distribution ratio, D_M , of a metal ion between the two phases can be written as

$$D_M = [ML_n(HL)_m]_{(o)} / [M^{3+}] \quad (3)$$

Fig. 1. Relationships between $\log D_M$ vs. pH for the extraction of metal ions with HD-PHA
 $[M^{3+}] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$. $[HL]_{(o)} = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$

However, since the present system involves tartrate, the formation of tartrate complexes must be taken into account for the expression of D_M .

$$D_M = [ML_n(HL)_m]_{(o)} / [M^{3+}] \alpha_M, \quad (4)$$

where α_M is the side reaction coefficient of a metal ion with tartrate in the aqueous phase. Therefore, Eq.(4) becomes

$$D_M = K_{ex} \alpha_M [HL]_{(o)}^{(n+m)} / [H^+]^n. \quad (5)$$

As described previously[2] since under the present experimental conditions the value of α_M can be regarded as being constant, we can define the conditional extraction constant, K'_{ex} , in combination of α_M with K_{ex} , so that, Eq.(5) reduces to a logarithmic form as Eq.(6):

$$\log D_M = \log K'_{ex} + (n + m) \log [HL]_{(o)} + npH. \quad (6)$$

Accordingly, the extracted species can be examined by a slope analysis of the equilibrium data. The relationships of $\log D_M$ vs. pH at constant R-PHA concentration and $(\log D_M - 3pH)$ vs. $\log [HL]_{(o)}$ at constant pH for the extraction with HD-PHA are shown in Figs.(1) and (2). From these figures, slopes of 3 with respect to pH and 5 with respect to $\log [HL]_{(o)}$ were obtained within the experimental error for all the metals studied. Similar results were obtained in the extraction with C8-PHA and PP-PHA. Thus, it is concluded that the metals studied are extracted with R-PHAs as a self-adducted form, $ML_3(HL)_2$. The evaluated conditional extraction constant (K'_{ex}) for the extraction systems studied are summarized in Table 1.

As shown in Table 1, the $\log K'_{ex}$ values of C8-PHA are larger than those obtained for PP-PHA or HD-PHA for all the extraction systems. This indicates that the extractability of C8-PHA is larger than that of PP-PHA or HD-PHA. The most likely reason for this observation is a steric hindrance of the substituent, because PP-PHA and HD-PHA have an additional alkyl substituent neighboring to the chelating group.

Separation factors (SF) for Y/Pr, Y/Eu, Yb/Y, Sc/Yb and Sc/Y pairs were compared in order to evaluate the extraction selectivity of R-PHAs. The separation factor is defined as the ratio of K'_{ex} values for a pair of metal ions,

$$(SF) = K'_{ex}(I) / K'_{ex}(II), \quad (7)$$

where the subscripts, (I) and (II), refer to different metal ions. The $\log (SF)$

Fig. 2. Plots of $(\log D_M - 3pH)$ vs. $\log [HL]_{(o)}$ for the extraction of metal ions with HD-PHA

TABLE 1. Conditional extraction constants, $\log K'_{ex}$

Extractant	Sc(III)	Y(III)	Pr(III)	Eu(III)	Yb(III)
C8-PHA	-5.86	-9.85	-12.19	-10.96	-9.34
PP-PHA	-4.45	-11.35	-14.44	-13.30	-9.85
HD-PHA	-5.50	-13.06	-15.40	-14.38	-11.50

TABLE 2. Logarithmic values of separation factor

Extractant	log (SF)				
	Y/Pr	Y/Eu	Yb/Y	Sc/Yb	Sc/Y
C8-PHA	2.34	1.11	0.51	3.48	3.99
PP-PHA	3.09	1.95	1.50	5.40	6.90
HD-PHA	2.34	1.32	1.56	6.00	7.56
D2EHPA*1	2.91	1.68	1.02		
Aliquant 336*2	0.62		-0.06		
TBP*2	0.65		-0.03		
Versatic 10*2	0.44		0.58		

*1: Ref. [5] *2: Ref. [6]

values obtained for R-PHAs are shown in Table 2 along with those for other extractants which are already known[5,6]

The log (SF) value for Sc/Yb pair of C8-PHA (3.48) is considerably smaller than that of PP-PHA (5.40) or HD-PHA (6.00). However, the separation of scandium from ytterbium, or lanthanoids, will be complete by the use of these extractants, since the log (SF) values are sufficiently large. Similarly, the separation between scandium and yttrium can be attained easily with these extractants.

Typical commercial extractants for industrial use, namely Aliquant 336, TBP and Versatic 10, have small separation factors for both Y/Pr and Yb/Y pairs as seen in Table 2. D2EHPA, on the contrary, has relatively large separation factors for both Y/Pr and Yb/Y pairs. Therefore, D2EHPA is mainly employed for an industrial-scale separation of yttrium from lanthanoids[1,6]. The log (SF) value for Yb/Y pair for C8-PHA is smaller than that for D2EHPA. On the other hand, those values for PP-PHA and HD-PHA are larger than that for D2EHPA. Thus, it can be concluded that PP-PHA and HD-PHA are very promising extractants for the separation of yttrium from heavy lanthanoids. Furthermore, the log (SF) values for Y/Pr pair for R-PHAs are almost comparable to that for D2EHPA. The result indicates that R-PHAs studied are useful extractants for the separation of yttrium from light lanthanoids.

As shown in Table 2, the comparison of log (SF) value for Yb/Y pair for C8-PHA to those for PP-PHA and HD-PHA shows that the introduction of an appropriate alkyl group at the α -position of the carbonyl group in a R-PHA can enhance the separation factor for Yb/Y pair significantly. A similar enhancement of selectivity was observed for the intragroup separation of heavy lanthanoids[2]. However, further studies are necessary for elucidation of the detailed mechanism of the enhancement of selectivities.

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