Solvent Extraction of Lanthanoids(III) with *N*-Alkylcarbonyl-Substituted *N*-Phenylhydroxylamines

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Several *N*-alkylcarbonyl-substituted *N*-phenylhydroxylamines (R-PHAs) were synthesized for use in lanthanoids(III) extraction. They were *N*-octanoyl-, *N*-(3,5,5-trimethylhexanoyl)-, *N*-(4-butylcyclohexanoyl)-, *N*-(4-butylbenzoyl)-, *N*-(2-propylpentanoyl)-, and *N*-(2-hexyldecanoyl)-*N*-phenylhydroxylamines. The distribution ratio of a lanthanoid(III) ion between the carbon tetrachloride and aqueous phases was examined as functions of the pH and R-PHA concentration at 298 K and the ionic strength, 0.1 (NaNO₃). Sodium tartrate (1×10^{-2} mol dm⁻³) was present in the aqueous phase. Lanthanoids(III) were extracted as a self-adducted chelate, ML₃(HL)₂, with all the R-PHAs used. The conditional extraction constants and the separation factors of lanthanoids(III) with R-PHAs were evaluated. Among the R-PHAs, *N*-(2-hexyldecanoyl)-*N*-phenylhydroxylamine was most promising for the separation of heavy lanthanoids(III). Appropriate branching at the α -position of the carbonyl group seemed to transmit the R-PHAs different chemical properties with respect to the straight chain R-PHAs.

Keywords *N*-Alkylcarbonyl-*N*-phenylhydroxylamines, lanthanoids(III), solvent extraction, separation factor

N-Benzoyl-*N*-phenylhydroxylamine (BPHA) and its analogues have been employed as gravimetric, spectrophotometric, and extracting reagents.¹ They are bidentate ligands; their complexation with metal ions occurs through the carbonyl and hydroxyl oxygens. They are therefore likely to react with "hard" metal ions, including lanthanoids(III). In fact, BPHA^{2,3} and its derivatives^{4,5} are capable of extracting lanthanoids(III) from aqueous media.

Attention is recently being paid to chelating reagents having long-chain alkyl groups, because of their successful use in hydrometallurgical separation.⁶ They have a high solubility in nonpolar solvents and a low solubility in water. The former is related to the loading capacity of the chelating reagents; the latter prevents their loss during multicyclic extractions. In this respect, we reported earlier that several alkylcarbonyl derivatives of *N*-phenylhydroxylamines (R-PHAs) are promising extractants for some divalent metal ions.⁷

Despite many reports in the literature concerning the elucidation of structural factors of chelating reagents which affect complexation with metal ions, very little attention has been devoted to factors regarding substituted alkyl groups which affect the selectivity of the chelating reagents. In this regard, 2-methyl-8-quinolinol is well known as a sterically hindered ligand.⁸ It is very useful for extracting metal ions from an aluminum(III) matrix, since the small aluminum(III) ion does not complex with 2-methyl-8-quinolinol. Its complex

formation is affected by the methyl group, which becomes more significant with the smaller ionic radii of metal ions. It has recently been reported that BPHA derivatives with the *o*-methyl substituent on either the phenyl or acyl ring do not generally extract metal ions including lanthanoids(III), probably because of a steric hindrance of the substituent.^{5,9}

As described previously⁷, since R-PHAs are fairly easily synthesized, they are interesting extractants. This is not only because they can provide the basic information required for hydrometallurgical separation, but that comparisons of their mutual properties might well shed light on useful structural factors affecting their selectivity for the extraction of metal ions. The present study was thus concerned with the extraction of lanthanoids(III) in order to evaluate structural factors concerning the alkylcarbonyl groups, which may introduce some differences in the selectivity of R-PHA. Of the six R-PHAs tested, *N*-(2-hexyldecanoyl)-*N*-phenylhydroxylamine (HD-PHA) was a good choice for the extraction of heavier lanthanoids(III). The separation factors of HD-PHA for heavy lanthanoids(III) are comparable to those of di-(2-ethylhexyl)phosphoric acid (D2EHPA), which is currently employed for the intragroup separation of lanthanoids(III).

Experimental

Reagents

All of the R-PHAs synthesized in the present study were obtained as white crystalline products. Their confirmation was carried out by melting-point measurements, elemental analyses, as well as measurements of their H-NMR, IR and MS. Lanthanoid(III) stock solutions (1×10^{-2} mol dm $^{-3}$) were prepared by dissolving their nitrate hexahydrates (99.99%, Raremetallic Inc.) in 1×10^{-3} mol dm $^{-3}$ nitric acid. Working solutions of respective lanthanoids(III) were made by appropriate dilution of the stock solutions with 1×10^{-3} mol dm $^{-3}$ nitric acid. A sodium tartrate solution (0.1 mol dm $^{-3}$) and a sodium nitrate solution (2 mol dm $^{-3}$) were prepared by dissolving the respective compounds in water. These solutions as well as buffer solutions were cleansed of any metal contaminants by complexation with 2-(5-bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulfopropylamino)phenol (Dojindo Lab.) and adsorption of its metal chelates on an ODS silica column (Develosil 15/30, Nomura Chem. Co.). All other reagents used were of analytical grade.

Apparatus

The chelating reagents (R-PHAs) extracted into the organic phase were determined with a Hitachi 320 double-beam spectrophotometer equipped with 1-cm quartz cells in a thermostated bath at 298 ± 1 K. The concentration of lanthanoids(III) in the aqueous phase was measured with a Shimadzu GVM-1000P inductively coupled plasma 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.

Procedure for distribution of R-PHA

A 25.0-cm^3 portion of the aqueous phase and a 5.00-cm^3 portion of carbon tetrachloride containing a specified R-PHA (1.00×10^{-4} mol dm $^{-3}$) were shaken in a 60-cm^3 glass vial for 1 h at 298 ± 1 K. For the distribution of HD-PHA, the aqueous phase was 1000 cm^3 . The pH of the aqueous phase was adjusted by the addition of a phosphate buffer (2×10^{-2} mol dm $^{-3}$) in conjunction with sodium hydroxide. The ionic strength in the aqueous phase was kept at 0.1 with sodium nitrate. The R-PHA concentration in the organic phase was determined by measuring the absorbance at 260 nm. The concentration in the aqueous phase was calculated on the basis of a material balance of the R-PHA.

Procedure for extraction of lanthanoids(III)

A 30.0-cm^3 aliquot of an aqueous solution containing a specified metal ion (5.00×10^{-5} mol dm $^{-3}$), sodium nitrate (0.1 mol dm $^{-3}$), sodium tartrate (1.0×10^{-2} mol

dm $^{-3}$), and an appropriate buffer component (1×10^{-3} 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 1.58×10^{-2} mol dm $^{-3}$, for 1 h for equilibration at 298 ± 1 K. If necessary, 1 mol dm $^{-3}$ sodium hydroxide or nitric acid was also employed for controlling the pH values of the aqueous phase. The buffer components used were sodium tetraborate, 2-(*N*-morpholino)ethanesulfonic acid, and tris-(hydroxymethyl)-aminomethane. The ionic strength was kept at 0.1 with sodium nitrate. Sodium tartrate was employed for preventing the hydrolysis of lanthanoids(III). After centrifuging for 10 min at 1500 rpm, the aqueous phase was submitted to a determination of the pH values as well as metal-ion concentrations. The metal concentration in the organic phase was calculated by using a material balance technique.

Results and Discussion

Preparation of chelating reagents

All R-PHAs were prepared in a similar fashion to that described by Agrawal and Tandon¹⁰, by the addition of appropriate acid chlorides to *N*-phenylhydroxylamine (PHA) in an ether solution in the presence of an aqueous suspension of sodium hydrogen-carbonate at a temperature below 273 K. The products, thus obtained, were purified by recrystallization from either an ether-hexane or an ethyl acetate-hexane solution. The acid chlorides were prepared by refluxing the corresponding carboxylic acid with thionyl chloride and distilling out the acid chlorides. The R-PHAs, thus prepared in the present study, were *N*-octanoyl-PHA (C8-PHA), *N*-(3,5,5-trimethylhexanoyl)-PHA (tC9-PHA), *N*-(4-butylcyclohexanoyl)-PHA (C4Hx-PHA), *N*-(4-butylbenzoyl)-PHA (C4Ph-PHA), *N*-(2-propylpentanoyl)-PHA (PP-PHA) and *N*-(2-hexyldecanoyl)-PHA (HD-PHA). Table I gives the melting-points and elemental compositions of these R-PHAs.

Distribution equilibrium of R-PHA

The distribution ratio, D_L , of a specified R-PHA (HL) between the aqueous and the organic phases can be given by

$$D_L = [\text{HL}]_o / ([\text{HL}] + [\text{L}^-]), \quad (1)$$

where the subscript (o) refers to the species in the organic phase. Equation (1) is rewritten in terms of the hydrogen ion concentration and two equilibrium constants, the acid dissociation constant, K_a , and the distribution constant, K_d , for R-PHA:

$$\log D_L = \log K_d - \log(1 + K_a[\text{H}^+]^{-1}), \quad (2)$$

$$K_a = [\text{H}^+][\text{L}^-] / [\text{HL}],$$

and

Table 1 Structures, melting-points and elemental compositions of R-PHAs, $R-C(=O)-N(OH)-C_6H_5$

Compound	Substituent (R-)	Melting-point/ °C	C, % Found(Calc.)	H, % Found(Calc.)	N, % Found(Calc.)
C8-PHA	$CH_3(CH_2)_6-$	64.5–65.5	69.66(69.54)	8.22(8.27)	6.77(6.76)
tC9-PHA	$(CH_3)_3CCH_2CHCH_2-$ CH_3	90.0–91.0	72.46(72.25)	9.26(9.30)	5.60(5.62)
C4Hx-PHA	$CH_3(CH_2)_3-$	124.0–125.0	74.16(74.18)	9.15(9.09)	5.00(5.09)
C4Ph-PHA	$CH_3(CH_2)_3-$	98.5–99.5	75.84(75.84)	7.10(7.06)	5.11(5.20)
PP-PHA	$CH_3(CH_2)_2-$ $CH-$	49.0–50.0	71.46(71.34)	9.00(9.16)	5.95(5.93)
HD-PHA	$CH_3(CH_2)_2-$ $CH-$ $CH_3(CH_2)_7-$ $CH-$ $CH_3(CH_2)_5-$	36.0–37.0	76.03(75.80)	10.73(10.98)	4.03(4.00)

Fig. 1 $\log D_L$ of R-PHA as a function of the pH. C8-PHA (●); tC9-PHA (■); C4Hx-PHA (▲); C4Ph-PHA (□); PP-PHA (△); HD-PHA (○).

$$K_d = [HL]_o / [HL]$$

Plots of the $\log D_L$ values for the respective R-PHAs against the pH in the aqueous phase are shown in Fig. 1. A curve-fitting method¹¹ has been applied in order to determine a set of K_a and K_d values for the respective R-PHAs. In Fig. 1, the experimental plot approaches two straight lines which are theoretical asymptotes for normalized best fit curves for the experimental plots. The equilibrium constants, thus obtained are listed in Table 2. However, we could not obtain the pK_a values for HD-PHA and C4Hx-PHA, because of the horizontal linear relationship of $\log D_L$ vs. pH (Fig. 1.). We therefore determined the K_a values

Table 2 $\log K_d$ and pK_a values of R-PHAs at $\mu=0.1$ (NaNO₃) and 298 K

R-PHA	$\log K_d$	pK_a
C4-PHA ^a	0.39	8.57
C5-PHA ^a	1.14	8.60
C6-PHA ^a	1.89	8.63
C8-PHA	2.88	8.76
C9-PHA ^a	3.42	8.75
C10-PHA ^a	3.79	8.53
tC9-PHA	2.00	9.90
C4Hx-PHA	2.30	8.42
C4Ph-PHA	2.59	9.25
PP-PHA	2.46	9.26
HD-PHA	4.00	9.74

a. Ref. 7.

for the two R-PHAs in aqueous dioxane according to a method described by Kiyokawa and Kawase.¹² The K_a values in water were obtained by extrapolating data for aqueous dioxane. The minus logarithmic values of K_a (pK_a) are shown in Table 2, which also include the pK_a values for R-PHAs with a linear alkyl chain.⁷

It can be seen in Table 2 that the pK_a values for R-PHA with a linear chain are in the range from 8.5 to 8.8, whereas those for R-PHA with a branched chain, except for C4Hx-PHA, are in the range 9.3 to 9.9. The basicity of branched-chain R-PHAs is greater than that of linear-chain R-PHAs. This is probably attributable to a steric effect of the alkyl groups in branched-chain R-PHAs. The carbonyl and hydroxyl groups in a branched-chain R-PHA approach each other by a steric repulsion between these groups and the neighboring two alkyl groups. Accordingly, intramolecular hydro-

gen bonding between the carbonyl oxygen and the hydroxyl hydrogen of a branched-chain R-PHA is stabilized. As a result, the release of hydrogen ions from the branched-chain R-PHAs comes to be difficult compared to that from a linear-chain R-PHA.

The K_d value increases with an increase in the carbon number in the substituent of both linear and branched-chain R-PHAs. This should be ascribed to an increase in the hydrophobicity. However, the K_d value for a linear-chain R-PHA is greater than that of a branched-chain R-PHA having the same number of carbon atoms in the substituent.

Extraction equilibrium of metal ion

Ytterbium(III) was extracted with HD-PHA in order to test the extraction periods necessary for equilibration. A 5.00-cm³ HD-PHA solution (1×10^{-2} mol dm⁻³) in carbon tetrachloride was shaken with a 30.0-cm³ portion of an aqueous solution containing Yb(III) (5×10^{-5} mol dm⁻³) at pH 7.50 for periods from 5 up to 80 min. The extraction yield (%) of Yb(III) (75%) was independent of the shaking periods. Thus, the two phases were shaken for 60 min in subsequent experiments.

The extraction of a trivalent lanthanoid (M^{3+}) with a R-PHA can be generally described according to

provided that a free metal ion is predominant in the aqueous phase. The extraction constant, K_{ex} , is thus defined by

$$K_{ex} = [ML_n(HL)_m_o][H^+]^n / [M^{3+}][HL_o]^{(n+m)}. \quad (4)$$

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

$$D_M = [ML_n(HL)_m_o] / [M^{3+}]. \quad (5)$$

However, since the present system involves tartrate, the formation of tartrate complexes, $M(tart)^{(3-2i)+}$, must be taken into account for the expression of D_M ,

$$D_M = [ML_n(HL)_m_o] / [M^{3+}] \alpha_M, \quad (6)$$

where α_M is the side reaction coefficient of a metal ion for complex formation with tartrate, $tart^{2-}$, in the aqueous phase. It is written with stability constants, β_i , of the tartrate complexes,

$$\alpha_M = 1 + \sum \beta_i [tart^{2-}]^i. \quad (7)$$

Therefore, Eq. (6) becomes

$$D_M = K_{ex} \alpha_M [HL_o]^{(n+m)} / [H^+]^n. \quad (8)$$

As the second acid dissociation constant, K_{a2} , of tartaric acid¹³, H_2tart , is $10^{-3.94}$, the dianion, $tart^{2-}$, should be

present exclusively when the pH range in the aqueous phase is well above 3.94. Under the present experimental conditions, the value of α_M can be regarded as being constant. We can therefore define the conditional extraction constant, K'_{ex} , in combination of α_M with K_{ex} , so that, Eq. (8) reduces to Eq. (9), and then to a logarithmic form, as Eq. (10):

$$D_M = K'_{ex} [HL_o]^{(n+m)} / [H^+]^n \quad (9)$$

and

$$\log D_M = \log K'_{ex} + (n+m) \log [HL_o] + npH. \quad (10)$$

Accordingly, the extracted species can be examined by a slope analysis of the equilibrium data. Plots of $\log D_M$ against the pH at a constant concentration of HD-PHA exhibited a slope of 3 for all of the lanthanoid(III) ions tested (Fig. 2). A slope of 5 was obtained for a plot of $\log D_M$ vs. $\log [HL_o]$ at a constant pH value for the extraction of all the metal ions with HD-PHA (Fig. 3). These results support the validity of the model described by Eq. (10). Similar results were obtained in the extraction with other R-PHAs. It is thus concluded that the lanthanoids(III) are extracted with R-PHAs as a self-adducted chelate, $ML_3(HL)_2$. The evaluated conditional extraction constants ($\log K'_{ex}$) are summarized in Table 3.

The $\log K'_{ex}$ values of HD-PHA in Table 3 are smaller than those of C8-PHA. However, in the extraction of heavy lanthanoid ions from Ho(III) to Lu(III), the differences in the $\log K'_{ex}$ values between two adjacent lanthanoids(III) are greater than those of C8-PHA. This suggests that HD-PHA is superior to C8-PHA

Fig. 2 Relationship between $\log D_M$ and the pH for the extraction of lanthanoid(III) with HD-PHA. $[M^{3+}] = 5.0 \times 10^{-5}$ mol dm⁻³, $[HL_o] = 1.0 \times 10^{-2}$ mol dm⁻³, $\mu = 0.1$ (NaNO₃), 298 K.

Table 3 Conditional extraction constant, $\log K'_{ex}$

	Pr	Nd	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
C8-PHA	-12.19	-12.10	-10.96	-10.87	-10.15	-9.73	-9.58	-9.49	-9.34	-9.25	-9.13
tC9-PHA	-12.70	-12.55	-11.50							-9.94	
C4Hx-PHA	-12.10	-12.85	-11.89							-10.54	
C4Ph-PHA	-11.26	-11.14	-10.33				-9.07			-8.74	
PP-PHA	-14.44	-14.20	-13.30							-11.20	
HD-PHA	-15.40	-15.31	-14.38	-14.29	-13.81	-13.27	-13.03	-12.73	-12.34	-11.74	-11.53

Fig. 3 Plot of $(\log D_M - 3pH)$ vs. $\log[HL]_0$ for the extraction of lanthanoids(III) with HD-PHA $[M^{3+}] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $\mu = 0.1$ (NaNO_3), 298 K.

Table 4 Logarithmic values of separation factor for Eu/Pr and Yb/Eu with various extractants

Extractant	Extracted species	$\log(SF)$	
		Eu/Pr	Yb/Eu
C8-PHA ^a	$ML_3(HL)_2$	1.23	1.71
tC9-PHA ^a	$ML_3(HL)_2$	1.20	1.56
C4Hx-PHA ^a	$ML_3(HL)_2$	0.21	1.35
C4Ph-PHA ^a	$ML_3(HL)_2$	0.93	1.59
PP-PHA ^a	$ML_3(HL)_2$	1.14	2.10
HD-PHA ^a	$ML_3(HL)_2$	1.02	2.64
BPHA ^b	$ML_3(HL)$	1.24	0.68
PBBHA ^c	$ML_3(HL)_2$	0.88	1.05
HQ ^b	$ML_3(HL)_3$	2.0	1.9
diBrHQ ^b	$ML_3(HL)$	0.94	2.01
Kelex 100 ^b	ML_3	1.58	2.10
PANP ^b	ML_3	1.13	1.87
D2EHPA ^d	$M(LHL)_3$	1.26	2.70

PBBHA, *N-p-t*-butylbenzoyl-*N*-phenylhydroxylamine; HQ, 8-quinolinol; diBrHQ, 5,7-dibromo-8-quinolinol; Kelex 100, 7-dodeceny-8-quinolinol; PANP, 2-(2-pyridylazo)-4-nonylphenol.

a. Present work.

b. Ref. 14.

c. Ref. 5.

d. Ref. 15.

regarding the separation of heavy lanthanoids.

For a further elucidation of the selectivity of R-PHAs, we compared separation factors (SF) for two pairs of lanthanoid ions. Two pairs, Eu/Pr and Yb/Eu, were chosen in order to determine the selectivity in both the lighter and heavier members of the lanthanoids(III). The separation factors are defined as the ratio of K'_{ex} values for a pair of lanthanoids(III),

$$(SF) = K'_{ex(I)} / K'_{ex(II)}, \quad (11)$$

where the subscripts, (I) and (II), refer to different metal ions. In Table 4 the $\log(SF)$ values for C8-PHA and HD-PHA are shown along with those for other extractants already reported by other workers.^{14,15}

The $\log(SF)$ value of C8-PHA for a pair of Eu/Pr (1.23) is very close to that of di-(2-ethylhexyl)-phosphoric acid (D2EHPA)(1.25) which is currently used for the separation of lanthanoids. For a pair of Yb/Eu, though the $\log(SF)$ of C8-PHA (1.71) is considerably smaller than that of D2EHPA (2.70)¹⁵, the

HD-PHA (2.64) is comparable to D2EHPA. From the experimental results thus far obtained, it can be concluded that HD-PHA is a very promising extractant for the separation of heavy lanthanoids(III) when tartrate is in the aqueous phase.

In Eq. (11) the separation factor is defined as the ratio of two conditional extraction constants including the term of α_M . Freiser *et al.*¹⁶ have pointed out that lanthanoid(III) ions are present exclusively in the form of a ditartrate complex when tartrate is in the aqueous phase. Hence, Eq. (7) is reduced to the following, where β_2 is the formation constant of the ditartrate complex:

$$\alpha_M = \beta_2 [\text{tart}^2]^{-2}. \quad (12)$$

Therefore, the intrinsic separation factor, *i.e.* the ratio of the extraction constants, can be expressed as follows in the logarithmic form:

$$\log(K_{\text{ex(I)}}/K_{\text{ex(II)}})=\log[(\text{SF})(\beta_{2(\text{II})}/\beta_{2(\text{I})})]. \quad (13)$$

The logarithmic values of β_2 for Pr(III), Eu(III) and Yb(III) are reported as 6.9, 7.4 and 7.3, respectively.^{13,16}

Therefore, the logarithmic value of the intrinsic separation factor was calculated to be 1.5 for Eu/Pr and 2.5 for Yb/Eu, respectively, in extraction with HD-PHA. From these results we can conclude that HD-PHA is inherently excellent for the separation of heavy lanthanoids(III). Appropriate branching at the α position of the carbonyl group will provide a good means for improving the selectivity of R-PHAs for the extraction of heavy lanthanoids(III).

However, if this improvement of the selectivity is caused by a steric hindrance of the branched chain, the extractability should decrease upon decreasing the ionic radii of the lanthanoids(III), or increasing atomic number. This is not in agreement with the present findings. The effect of a branched alkyl structure on the extraction of lanthanoids(III) seems to be different from that of the 2-methyl group in 8-quinolinol.⁸ The extraction mechanism with R-PHAs still remains obscure; further studies are thus in progress.

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