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Solvent Extraction of Lanthanoids(III) and Yttrium(III) with *N*-Alkylcarbonyl-*N*-(4-chlorophenyl)hydroxylamines

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We investigated the effect of halogen substitution of *N*-alkylcarbonyl-*N*-phenylhydroxylamines on the extraction of lanthanoids(III). A *p*-chloro substituent of a phenyl group increased the acidity of R-PHAs by 0.3—0.5 pK_a units, and a bromo substituent on the α carbon of the acyl group increased it by 1.5 pK_a units. In the former substitution, the separation factor for pairs of lanthanoids(III) and yttrium(III) remained unchanged, whereas in the latter the separation factor was considerably reduced. Hence, the chloro substitution at the phenyl group was a good choice for lowering pH values in the extraction of lanthanoids(III). The pH region was suitable for extracting lanthanoids(III) while preventing the formation of their hydroxo complexes.

We have previously proposed a series of *N*-alkylcarbonyl-*N*-phenylhydroxylamines (R-PHAs) with primary to tertiary alkyl chains for extraction of lanthanoids(III).[1,2] These R-PHAs are bidentate ligands in which complexation occurs through carbonyl and hydroxyl oxygens. Branching of alkyl chains in the acyl group gave marked influence on the selectivity in the extraction of lanthanoids(III). Among the R-PHAs tested, *N*-(2,2-dimethylvaleryl)-*N*-phenylhydroxylamine (DV-PHA) having a tertiary alkyl moiety was most promising, and separation factors for pairs of Yb/Eu and Y/Yb were two to three times greater than those of bis(2-ethylhexyl)hydrogenphosphate currently used for hydrometallurgical separations.[1]

However, the pH range depended upon branching and moved to higher ranges in the following order: primary<secondary<tertiary. In the extraction with DV-PHA, lighter members of lanthanoids(III) were extracted at higher pH regions than heavier members of lanthanoids(III). In the extraction of praseodium(III), a $\mathrm{pH}_{1/2}$ of DV-PHA was 9.5, while that of *N*-octanoyl-*N*-phenylhydroxylamine (C8-PHA) having a normal acyl group was 7.7.[1,2] Here, the $\mathrm{pH}_{1/2}$ value is a pH value at which the distribution ratio (D_M) of a metal ion is taken to be 1.00.

The extraction of metal ions at a high pH range is unfavorable in regard to the formation of their hydroxo complexes. Furthermore, hydrometallurgical extraction favors a neutral or a slightly acidic medium, because of convenience for back extraction.[3] In order to appreciate the most suitable design of R-PHAs, we must take into account the pH values required for extraction, in addition to selectivity. The pH values for extraction are closely related to the basicity of R-PHAs and thus to the donor strength of electrons from two oxygens of an R-PHA molecule to a metal ion. In view of the electron-withdrawing character of a halogen substituent, its introduction onto chelating reagents was often effective to lower the pH region in the extraction of metal ions. For instance, metal ions can be extracted with the halogen derivatives of 8-hydroxyquinoline[4,5] and thenoyltrifluoroacetone[6] from more acidic solution than with those of parent ligands. Thus, the introduction of a halogen atom onto the phenyl group or at a alkyl group seems likely to enhance the acidic strength of the hydroxyl group, thereby leading to extraction at a lower pH value than that of the parent R-PHAs.

Thus, we have explored the possibility of controlling the pH values for extraction of lanthanoids(III) and yttrium(III) without lowering the selectivity. For this purpose, we prepared three *N*-alkylcarbonyl-*N*-(4-chlorophenyl)hydroxylamines (R-PHACls). They are *N*-octanoyl-*N*-(4-chlorophenyl)-hydroxylamine (C8-PHACl), *N*-(2-propylvaleryl)-*N*-(4-chlorophenyl)hydroxylamine (PV-PHACl), and *N*-(2,2-dimethylvaleryl)-*N*-(4-chlorophenyl)hydroxylamine (DV-PHACl). For comparisons with R-PHACls, *N*-(2-bromovaleryl)-*N*-phenylhydroxylamine (αBr-PHA), which has a bromo substituent on the α carbon of the acyl group, was also tested.

Experimental

Reagents. According to the method of Tandon et al.,[7,8] R-PHACls were newly synthesized from the corresponding acid chlorides and 4-chlorophenylhydroxylamine. Also, αBr-PHA was prepared by a similar manner to that for R-PHACls. Their identification was made by elemental analysis and measurements of ^{1}H NMR, IR, and MS. All the solutions used were made according to the method stated previously.[1,2]

Apparatus. All the instruments used in the present study were the same as those explained previously.[1,2]

Procedure for Extraction of R-PHACls and αBr-PHA. An appropriate volume of an aqueous solution containing sodium nitrate (0.1 $\mathrm{mol\,dm^{-3}}$) and an appropriate buffer component (1×10^{-3} $\mathrm{mol\,dm^{-3}}$) were placed in a 60-$\mathrm{cm^3}$ glass vial. The buffer component consists of 2-(*N*-morpholino)ethanesulfonic acid, tris(hydroxylmethyl)amionomethane, and 3-cyclohexylaminopropanesulfonic acid. After addition of an appropriate amount of carbon tetrachloride containing a specified R-PHACl (or αBr-PHA) (1.00×10^{-4} $\mathrm{mol\,dm^{-3}}$) to the vial, the whole mixture was shaken for 15 min at 298±1 K. The volume ratio of the aqueous to organic phases varied with the value of $\log K_d$ determined. Then, the mixture was centrifuged for 10 min at 1500 rpm. The ionic strength in the aqueous phase was kept at 0.1 with sodium nitrate. The pH value in the aqueous phase was measured. The concentration of R-PHACl (or αBr-PHA) in the organic phase was determined by measuring the absorbance at 260 nm. The concentration of R-PHACl (or αBr-PHA) in the aqueous phase was calculated by the material balance.

Procedure for Extraction of Metal Ions. A 30-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 the buffer component (1.0×10^{-3} mol dm^{-3}) described above was placed into the 60-cm^3 glass vial. Then, a 5-cm^3 portion of carbon tetrachloride containing an appropriate amount of R-PHACl (or αBr-PHA) (typically, 1.00×10^{-2} mol dm^{-3}) was also added to the vial. The ionic strength in the aqueous phase was maintained at 0.1 with sodium nitrate. The whole mixture was shaken and then centrifuged as before. The pH value and the concentration of a metal ion in the aqueous phase were measured with a pH meter (Toa HM-15A) and an inductively plasma atomic emission spectrometer (Shimadzu GVM-1000P). The concentration of the metal ion in the organic phase was calculated by the material balance.

Results and Discussion

Distribution Equilibria of R-PHACls and αBr-PHA. The distribution ratio (D_L) of R-PHACls (and αBr-PHA) (HL) between the two phases can be given by Eq. 1, when the self-association of HL in the organic phase is negligible.

$$\log D_L = \log K_d - \log(1 + K_a[\mathrm{H}^+]^{-1}), \tag{1}$$

where K_a is the acid dissociation constant and K_d is the distribution constant of HL. Plots of $\log D_L$ vs. pH are shown in Fig. 1 in the extraction with R-PHACls and αBr-PHA. The equilibrium constants (K_a and K_d) were determined by applying the curve fitting method[9] to the data in Fig. 1 and are summarized in Table 1 along with those obtained previously on the parent compounds (R-PHAs).

Distribution Equilibria of Metal Ions. Sodium tartrate is involved in the aqueous phase to prevent hydrolysis of metal ions. Thus, the distribution ratio of a metal ion (M^{3+}) can be written in general as Eq. 2,

Table 1. Minus Logarithmic Acid Dissociation Constants (pK_a) and Logarithmic Partition Constants ($\log K_d$) of R-PHAs and R-PHACls

Extractant	pK_a	$\log K_d$
C8-PHA[a]	9.16[c]	2.88
C8-PHACl	9.06	3.45
PV-PHA[a]	9.26	2.46
PV-PHACl	9.21	3.08
DV-PHA[b]	10.05	1.96
DV-PHACl	10.00	2.80
αBr-PHA	5.15	2.36

a) Ref. 2. b) Ref. 1. c) Calculated from the data in Ref. 2.

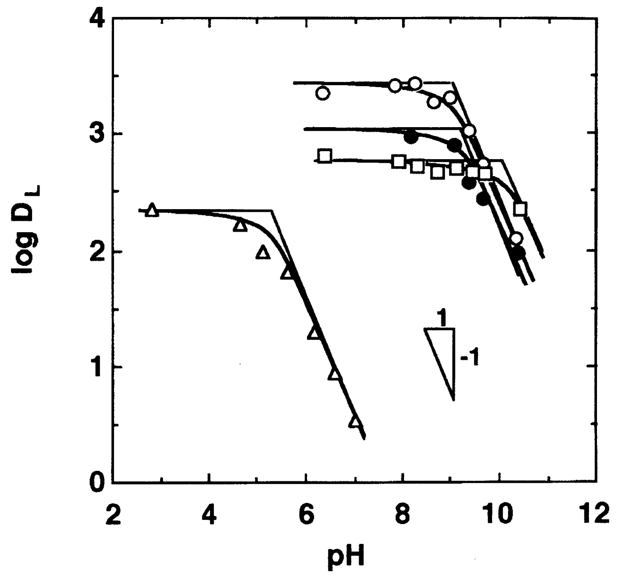

Fig. 1. $\log D_L$ against pH of R-PHACls. (○) C8-PHACl, (●) PV-PHACl, (□) DV-PHACl, (△) αBr-PHA.

$$D_M = [\mathrm{ML}_n(\mathrm{HL})_m]_o/([\mathrm{M}^{3+}]\alpha_M), \tag{2}$$

where a subscript o refers to the organic phase and α_M means the side reaction coefficient of a metal ion with a tartrate ion. The indices n and m are the numbers of L^- and HL bound in extracted chelates, respectively. The second acid dissociation constant of tartaric acid, H_2tart, is $10^{-3.94}$,[10] and thus the dianion, tart^{2-}, is exclusively present, when pH $\gg$ 3.94. Under the present experimental conditions, lanthanoid(III) ions are generally present as a ditartrate complex.[11] Hence, the term of α_M can be regarded as being constant, and Eq. 2 is then reduced to a logarithmic form as Eq. 3.

$$\log D_M = \log K'_{ex} + n\mathrm{pH} + (n+m)\log[\mathrm{HL}]_o. \tag{3}$$

Here, K'_{ex} is the conditional extraction constant, which is the product of α_M and the extraction constant (K_{ex}).

Based on Eq. 3, we evaluated extracted species ($\mathrm{ML}_n(\mathrm{HL})_m$) by the slope analysis of equilibrium data. In Fig. 2, plots of $\log D_M$ against pH at a constant concentration of DV-PHACl gave a slope of 3 for lanthanoids(III) and yttrium(III). In addition, plots of ($\log D_M - 3$pH) against $\log[\mathrm{HL}]_o$ exhibited a slope of 6 as shown in Fig. 3. In the extraction with C8-PHACl and PV-PHACl, the slope of ($\log D_M - 3$pH) against $\log[\mathrm{HL}]_o$ were 5. These results indicate that C8-PHACl and PV-PHACl give an $\mathrm{ML_3(HL)_2}$-type chelate, and DV-PHACl gives an $\mathrm{ML_3(HL)_3}$-type chelate. The type of extracted species summarized in Table 2 depend only on branching and not on the halogen substitution. The type of the extracted species and the logarithms of

Table 2. Extracted Species and Logarithmic Extraction Constants ($\log K'_{ex}$) in the Extraction of Lanthanoids(III) and Ytterium(III) with R-PHAs and R-PHACls

Extractant	Extracted species	$\log K'_{ex}$ Pr(III)	Eu(III)	Y(III)	Yb(III)
C8-PHA[a)]	$ML_3(HL)_2$	−12.19	−10.96	−9.85	−9.25
C8-PHACl	$ML_3(HL)_2$	−10.32	−9.33	−8.44	−7.93
PV-PHA[a)]	$ML_3(HL)_2$	−14.44	−13.30	−11.35	−9.85
PV-PHACl	$ML_3(HL)_2$	−12.58	−11.81	−10.42	−9.01
DV-PHA[b)]	$ML_3(HL)_3$	−15.68	−14.78	−13.52	−11.69
DV-PHACl	$ML_3(HL)_3$	−14.09	−12.99	−11.74	−9.95

a) Ref. 2. b) Ref. 1.

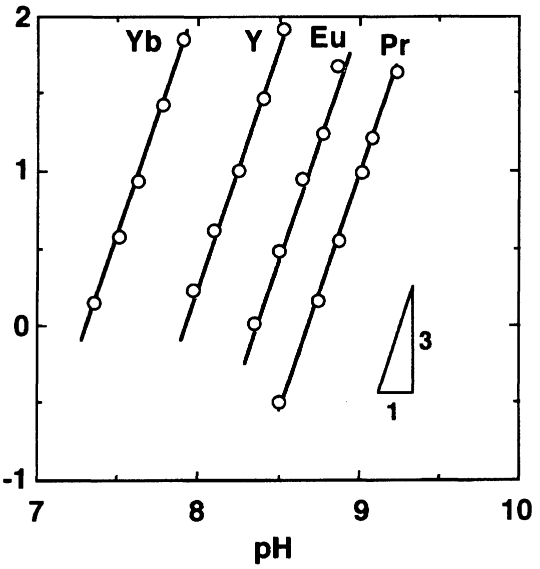

Fig. 2. $\log D_M$ against pH in the extraction of metal ions with DV-PHACl.

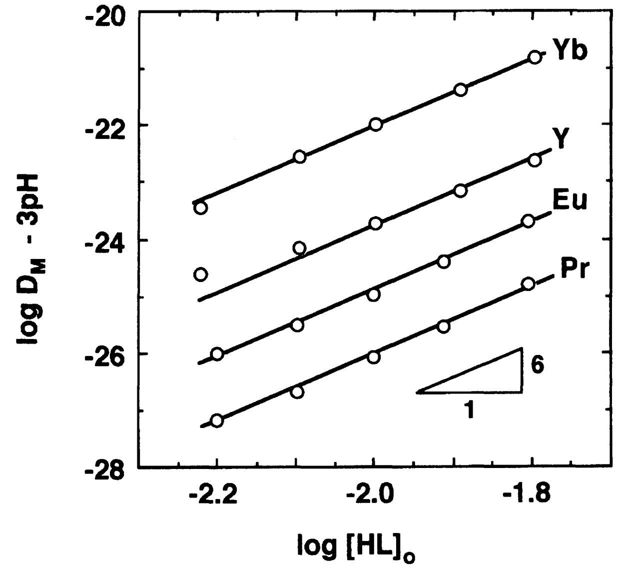

Fig. 3. $\log D_M - 3\mathrm{pH}$ against $\log [\mathrm{HL}]_o$ in the extraction of metal ions with DV-PHACl.

the conditional extraction constants ($\log K'_{ex}$) thus obtained are summarized in Table 2.

Separation Factor. For evaluation of the selectivity of R-PHACls and αBr-PHA, we have compared separation factors for pairs of lanthanoids(III) and yttrium(III). The reason is the fact that the stoichiometric composition of the chelates for DV-PHACl is different from that for C8-PHACl and PV-PHACl. The separation factors are the ratio of K'_{ex} values for a pair of two metal ions as defined by Eq. 4,

$$(\mathrm{SF}) = K'_{ex}(\mathrm{I})/K'_{ex}(\mathrm{II}), \qquad (4)$$

where the indices (I) and (II) refer to two distinct metal ions.

In Table 3, the logarithms of the separations factors are presented along with those reported previously for the corresponding parent R-PHAs. Evidently, there is very slight difference in the separation factors of R-PHACl and R-PHA having the same alkyl structure. It is thus concluded that the *p*-chloro substitution of the phenyl group gives no significant effect on the selectivity.

Extraction pH. In Table 1, the minus logarithmic K_a ($\mathrm{p}K_a$) values of R-PHACls are smaller than those of R-PHAs. Thus, extraction pH for R-PHACls is expected to shift to an acid range. From the plots of $\log D_M$ against pH, we obtained the values of $\mathrm{pH}_{1/2}$ and have summarized them in Table 3, together with those for extraction with the parent R-PHAs. Apparently, the difference in the $\mathrm{pH}_{1/2}$ values for a pair of R-PHAs and R-PHACls having the same alkyl structure is 0.3—0.5. It is apparent that the chloro substituent of the phenyl group shifts the pH values to an acid range, while the separation factors remain unchanged in comparison with R-PHAs.

Then, we have examined the effect of a halogen substituent of the acyl group on the extraction of lanthanoids(III) and yttrium(III). The $\mathrm{p}K_a$ value of αBr-PHA was 5.15, while that of DV-PHA was 10.05. This may suggest a good possibility of lowering the pH values for extraction. However, the logarithmic separation factor of αBr-PHA for a pair of ytterbium(III) and yttrium(III) was 0.45, which was considerably smaller than that of DV-PHA (1.83), as shown in Table 3.

Table 3. Logarithmic Separation Factors (log (SF)) and Half Extraction pH Values ($pH_{1/2}$) in the Extraction of Lanthanoids(III) and Ytterium(III) with R-PHAs and R-PHACls

Extractant	log (SF)			$pH_{1/2}$[c]			
	Eu/Pr	Yb/Y	Yb/Eu	Pr(III)	Eu(III)	Y(III)	Yb(III)
C8-PHA[a]	1.23	1.11	0.51	7.66	7.25	6.85	6.71
C8-PHACl	0.99	0.89	0.51	7.03	6.70	6.41	6.24
PV-PHA[a]	1.14	1.95	1.50	8.41	8.03	7.62	7.13
PV-PHACl	0.77	1.39	1.41	7.79	7.53	7.07	6.60
DV-PHA[b]	0.90	1.29	1.83	9.49	9.19	8.77	8.10
DV-PHACl	1.10	1.25	1.79	8.91	8.59	8.17	7.58

a) Ref. 2. b) Ref. 1. c) $[HL]=1.00\times10^{-2}$ mol dm^{-3}.

In this respect, the substitution at the alkyl group is unsatisfactory. The strong electron-withdrawing character of a bromine atom would be expected to decrease the electron-donation, from the carbonyl oxygen to a metal ion, which is enhanced by branching. This is consistent with our previous results in which the Taft σ^* values of the alkyl groups were inversely correlated with the separation factors that increased on going from a primary to a tertiary alkyl moiety.[2]

The chloro substitution of the phenyl group will also reduce the electron donation of the carbonyl oxygen. However, the selectivity of R-PHACls was the same as that of R-PHAs. It seems likely that the delocalized π electrons of the phenyl group decrease the magnitude of the electron-withdrawing effect of the chloro group on the electron donation of the carbonyl oxygen to lanthanoids(III).

In conclusion, the chloro substituent of the phenyl group of R-PHAs was effective for lowering pH values in the extraction of lanthanoids(III) without any significant effect on the selectivity. On the other hand, the bromo substituent of the acyl group decreased the pH values, but decreased the separation factors. In this respect, the chloro substitution of the phenyl group was a good choice for modifying the acid-base properties of R-PHAs.

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