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Sadanobu Inoue[a]; Qiangbin Zhang[b]; Hirotsugu Minami[a]; Masayuki Uto[a]
[a] Department of Materials Science, Kitami Institute of Technology, Kitami-shi, Hokkaido, Japan [b] Faculty of Natural Resources and Information Technology, Department of Natural Resources and Environment Sciences, China University of Petroleum, Changping, Beijing, China

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Synergistic Extraction of Lanthanides(III) with N-p-Methoxybenzoyl-N-Phenylhydroxylamine and Neutral Nitrogen Donors

Sadanobu Inoue, Masayuki Uto, and Hirotsugu Minami
Department of Materials Science, Kitami Institute of Technology,
Kitami-shi, Hokkaido, Japan

Qiangbin Zhang
Faculty of Natural Resources and Information Technology, Department
of Natural Resources and Environment Sciences, China University of
Petroleum, Changping, Beijing, China

Abstract: We investigated the extraction equilibrium behavior of a series of trivalent lanthanide ions, (M^{3+}), La, Pr, Eu, Ho, and Yb, from tartrate aqueous solutions using a chloroform solution containing N-p-methoxybenzoyl-N-phenylhydroxylamine (Methoxy-BPHA or HL) combined with an adductant, 1,10-phenanthroline (phen) or 2,2′-bipyridyl (bipy). The synergistic species extracted were found to be $\{ML_2(phen)(HL)\}^+(1/2)Tar^{2-}$ and $\{ML_2(bipy)(HL)_2\}^+(1/2)Tar^{2-}$, where Tar^{2-} is the tartrate ion. The stoichiometry, the extraction constants, and the separation factors of these systems were determined. We discuss the extractability and the separation factors in comparison with self-adduct chelates, $ML_3(HL)_{2,(o)}$, which were formed in the absence of phen or bipy.

Keywords: Synergistic extraction, lanthanides, hydroxamic acid, 1,10-phenanthroline, 2,2′-bipyridyl

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Address correspondence to Sadanobu Inoue, Department of Material Science, Institute of Technology, 165 Koen-cho, Kitami-shi, Hokkaido 090-8507, Japan. Fax: 0157-26-4973; E-mail: inouesd@mail.kitami-it.ac.jp

INTRODUCTION

Mixtures of chelating agents and neutral donors have been used extensively in the synergistic extraction of trivalent lanthanides and actinides (1). It can be expected that the formation of mixed ligand chelates involving the chelating extractant and adductants such as 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy) would provide not only better extractability, but also improved separation. N-Benzoyl-N-phenylhydroxylamine (BPHA) and its analogues are known to be powerful extractants, particularly for "hard" metals such as lanthanides and actinides (2). Numerous studies concerning the extractant properties of BPHA with these metal ions have been reported in the literature (3–8). In addition, some data are available on the synergistic extraction of the trivalent actinides Am and Cm, and the trivalent lanthanides Pm and Eu by mixtures of BPHA and tributyl phosphate (TBP), tri-n-octylphosphine oxide (TOPO) or bipy in chloroform, but there is little information available on the extraction mechanism or synergistic effects, and it is not possible to calculate equilibrium constants for the organic phase synergistic reactions (9). We have therefore initiated research on the synergistic extraction of trivalent lanthanides by mixtures of N-p-methoxybenzoyl-N-phenylhydroxylamine (Methoxy-BPHA) and neutral nitrogen donors such as phen and bipy. The present work is concerned with the extraction of the selected lanthanides, La, Pr, Eu, Ho, and Yb, with Methoxy-BPHA/phen/Tar^{2-} and Methoxy-BPHA/bipy/Tar^{2-} systems in chloroform, where Tar^{2-} is tartrate ion.

EXPERIMENTAL PROCEDURES

Apparatus and Reagents

Methoxy-BPHA was synthesized by the reaction of phenylhydroxylamine with p-methoxybenzoyl chloride as previously reported (10), and the crude products were purified by recrystallization from ethanol and water. Methoxy-BPHA was dissolved in chloroform immediately prior to use. Stock solutions containing lanthanides(III) were prepared from chloride salts (Sigma-Aldrich, Milwaukee, WI) and standardized by complexometric titration with ethylenediaminetetraacetic acid (EDTA) using xylenol orange as an indicator. Chloroform of super gradient grade (Wako Pure Chemical Industries, Ltd., Osaka, Japan) was used without further purification and after saturation with water. Buffer solutions containing 0.025 mol dm^{-3} tris(hydroxymethyl)aminomethane (THAM) with small amounts of sodium hydroxide or hydrochloric acid were prepared to cover the pH range from 6.7 to 9.4, and 0.085 mol dm^{-3} sodium tartrate solution was also added in the aqueous phase to prevent hydrolysis of the lanthanides(III). All other reagents were of analytical grade and were used without further purification. A Hitachi Model U-3210 spectrophotometer, Iwaki V-SN shaker and Hitachi-Horiba F-7AD pH meter were used.

Determination of the Distribution Ratio

A 10 cm^3 portion of a buffered lanthanides(III) solution with an initial concentration of 1.92×10^{-5} mol dm^{-3} and containing 0.034 mol dm^{-3} tartrate ions and an equal volume of reagents such as Methoxy-BPHA and phen or bipy in chloroform was equilibrated in a 50-cm^3 vial by vigorous shaking for 1 h, a time period which was found to be adequate for the attainment of equilibrium. The pH at equilibrium was measured after phase separation. An aliquot of the organic phase was shaken with a 0.1 mol dm^{-3} sodium formate-formic acid buffer at pH 4.05. The concentration of the lanthanides(III) back-extracted into the aqueous solution was determined by the Arsenazo III method described previously (11). The lanthanides(III) concentration in the aqueous phase was calculated using material balance. In several experiment, the metal ion concentrations were also obtained in the aqueous phase to check the experimental error of these systems. Distribution ratios calculated from either the organic or aqueous phase composition showed very good agreement.

RESULTS AND DISCUSSION

When an ion associate, $[\mathrm{ML}_x(\mathrm{phen})_y(\mathrm{HL})_z]^{(3-x)+}\{(3-x)/2\}\mathrm{Tar}^{2-}$, is responsible for the extraction of lanthanide ions with Methoxy-BPHA, a neutral donor (S) such as phen or bipy, and tartrate ion, the equilibrium can be written as:

$$\mathrm{MTar}_2^- + (x+z)\mathrm{HL}_{(o)} + y\mathrm{S}_{(o)} \overset{\mathrm{Kex},_{(s)}}{\rightleftharpoons} [\mathrm{ML}_x\mathrm{S}_y(\mathrm{HL})_z]^{(3-x)+}\{(3-x)/2\}\mathrm{Tar}^{2-}_{(o)} + x\mathrm{H}^+ + (x+1)/2\,\mathrm{Tar}^{2-} \qquad (1)$$

with

$$\mathrm{Kex},_{(s)} = \frac{[\{\mathrm{ML}_x\mathrm{S}_y(\mathrm{HL})_z\}^{(3-x)+}\{(3-x)/2\}\mathrm{Tar}^{2-}]_{(o)}[\mathrm{H}^+]^x[\mathrm{Tar}^{2-}]^{(x+1)/2}}{[\mathrm{MTar}^{2-}][\mathrm{HL}]_{(o)}^{(x+z)}[\mathrm{S}]_{(o)}^y} \qquad (2)$$

where the predominant tartrate species is the dianion Tar^{2-} in the pH range studied (6.7–9.5). This gives a constant concentration ($\mathrm{C_T}$) of 0.034 mol dm^{-3}, and lanthanide ion is present in the aqueous phase largely in the form of its ditartrate complexes, MTar_2^- (11). The subscript o refers to concentrations in the organic phase. Accordingly, Eq. (2) can be rewritten as

$$\log \mathrm{Kex},_{(s)} = \log \mathrm{D} - x\,\mathrm{pH} - (x+z)\log[\mathrm{HL}]_{(o)} - y\log[\mathrm{S}]_{(o)} + (x+1)/2\,\log[\mathrm{Tar}^{2-}] \qquad (3)$$

In the present study, we used the traditional slope analysis method, which is based on the variation of the distribution ratio D with relevant experimental variables, in order to clarify both the stoichiometry of the formation of the extractable complexes and its extraction equilibrium constant. The distribution ratios with respect to pH for the trivalent lanthanides(III) La, Pr, Eu, Ho, and Yb are shown in Fig. 1. Slopes of approximately 2 for both the phen and bipy systems were obtained for all lanthanides(III), indicating that two protons were released during the extraction process; thus, x is 2 in Eq. (1). Plots of (log D − 2 pH) values vs. the logarithmic concentration of HL in the organic phase at constant $S_{(o)}$, constant tartrate, and constant hydrogen ion concentrations are shown in Fig. 2. Slopes of approximately 3 for the phen system and of approximately 4 for the bipy system were obtained for each lanthanides(III) solution, indicating that three molecules for the phen

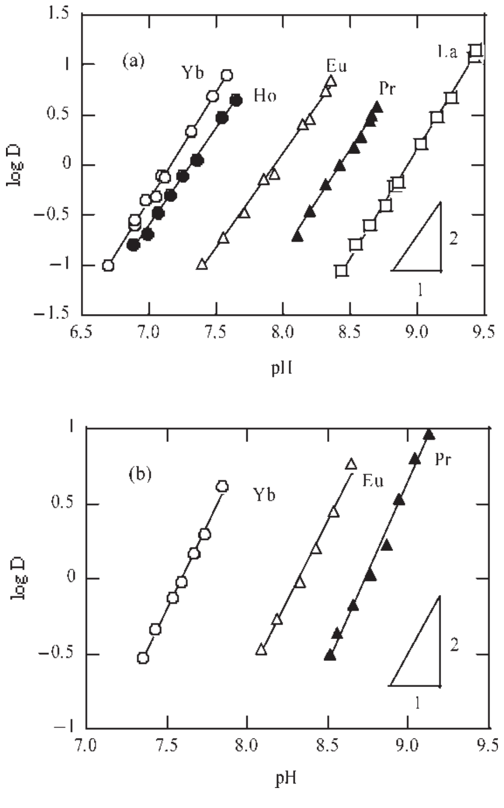

Figure 1. Distribution ratios of lanthanides with mixtures of Methoxy-BPHA and phen (a) or bipy (b) as a function of pH; $[M^{3+}] = 1.92 \times 10^{-5}$ mol dm^{-3}, $[HL]_{(o)} = 10^{-2}$ mol dm^{-3}, $[phen]_{(o)} = 10^{-3}$ mol dm^{-3}, $[bipy]_{(o)} = 3 \times 10^{-2}$ mol dm^{-3}. The aqueous phase includes tartrate ion at a constant concentration of 0.034 mol dm^{-3}.

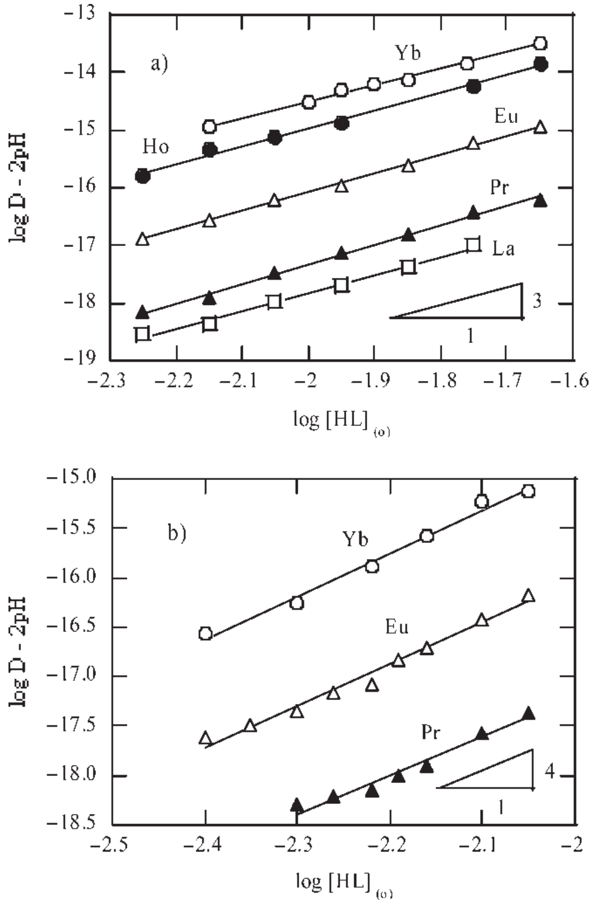

Figure 2. Distribution ratios of lanthanides with mixtures of Methoxy-BPHA and phen (a) or bipy (b) as a function of log $[HL]_{(o)}$; $[M^{3+}] = 1.92 \times 10^{-5}$ mol dm^{-3}, $[HL]_{(o)}$ = varied, $[phen]_{(o)} = 10^{-3}$ mol dm^{-3}, $[bipy]_{(o)} = 3 \times 10^{-2}$ mol dm^{-3}, at a constant pH. The aqueous phase includes tartrate ion at a constant concentration of 0.034 mol dm^{-3}.

system and four molecules for the bipy system were used in the extraction process. These results give $x + z = 3$ and $z = 1$ for the phen system and $x + z = 4$ and $z = 2$ for the bipy system. Plots of (log D − 2 pH) values vs. the logarithmic concentration of S in the organic phase at constant $HL_{(o)}$, constant tartrate and constant hydrogen ion concentrations are shown in Fig. 3. A slope of approximately 1 was obtained for each lanthanides(III) solution for both systems, indicating that one molecule is used in the extraction process. These results also indicate that $y = 1$ for both systems; therefore, the charge of the complex of both systems is assigned to be +1. Thus,

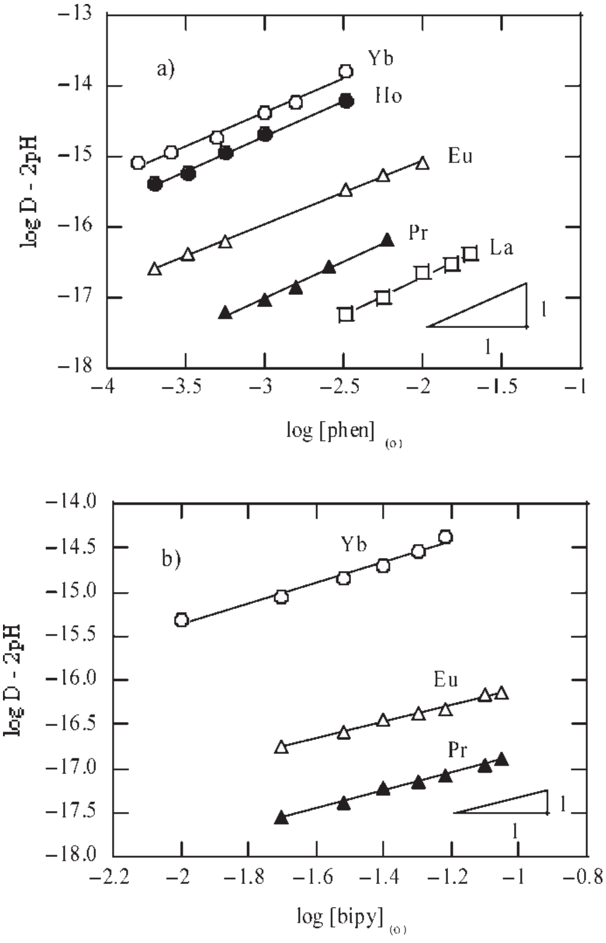

Figure 3. Distribution ratios of lanthanides with mixtures of Methoxy-BPHA and phen (a) or bipy (b) as a function of log $[\mathrm{phen}]_{(o)}$ or log $[\mathrm{bipy}]_{(o)}$; $[M^{3+}] = 1.92 \times 10^{-5}$ mol dm^{-3}, $[\mathrm{HL}]_{(o)} = 10^{-2}$ mol dm^{-3}, $[\mathrm{phen}]_{(o)}$ = varied, $[\mathrm{bipy}]_{(o)}$ = varied, at a constant pH. The aqueous phase includes tartrate ion at a constant concentration of 0.034 mol dm^{-3}.

extracted ion associates contain the cationic chelates $[ML_2(\mathrm{phen})(HL)]^+$ and $[ML_2(\mathrm{bipy})(HL)_2]^+$. The number of tartrate dianions used to extract the chelate into organic phase was then determined. A slope of −1.5 was obtained for plots of (log D − 2 pH) vs. the logarithmic concentration of tartrate ion in the aqueous phase at constant concentrations of $HL_{(o)}$ and $\mathrm{phen}_{(o)}$ or $\mathrm{bipy}_{(o)}$ (Fig. 4), indicating that approximately 1.5 mol of the tartrate ion takes part in the extraction systems, and that x is 2 in Eq. (1).

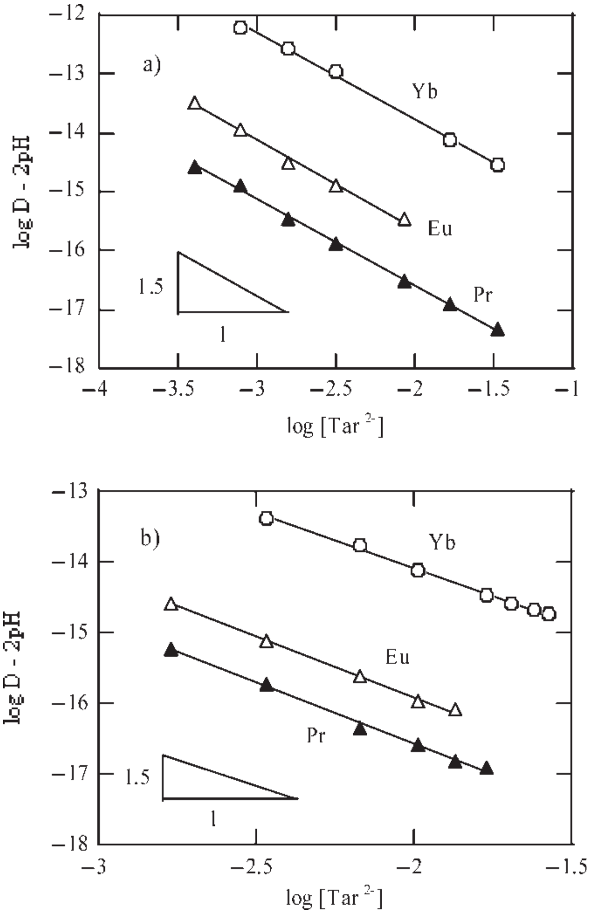

Figure 4. Distribution ratios of lanthanides with mixtures of Methoxy-BPHA and phen (a) or bipy (b) as a function of log [Tar^{2-}]; [M^{3+}] = 1.92×10^{-5} mol dm^{-3}, $[\mathrm{HL}]_{(o)} = 10^{-2}$ mol dm^{-3}, $[\mathrm{phen}]_{(o)} = 10^{-3}$ mol dm^{-3}, $[\mathrm{bipy}]_{(o)} = 3 \times 10^{-2}$ mol dm^{-3}, at a constant pH.

Thus, the extraction equilibrium, Eq. (1), can be written as:

$$\mathrm{MTar}_2^- + (2+z)\mathrm{HL}_{(o)} + \mathrm{S}_{(o)} \overset{\mathrm{Kex},_{(s)}}{\rightleftharpoons} [\mathrm{ML}_2\mathrm{S(HL)}_z]^+(1/2)\mathrm{Tar}^{2-}_{(o)} + 2\mathrm{H}^+ + (3/2)\mathrm{Tar}^{2-} \qquad (4)$$

$$\mathrm{Kex},_{(s)} = \frac{[\{\mathrm{ML}_2\mathrm{S(HL)}_z\}^+(1/2)\mathrm{Tar}^{2-}]_{(o)}[\mathrm{H}^+]^2[\mathrm{Tar}^{2-}]^{3/2}}{[\mathrm{MTar}_2^-][\mathrm{HL}]_{(o)}^{(2+z)}[\mathrm{S}]_{(o)}} \qquad (5)$$

The distribution ratio D of the lanthanide for ion-pair extraction equilibrium (Eq. (5)) is given by

$$D = \mathrm{Kex}_{,(s)} \frac{[\mathrm{HL}]^{(2+z)}{}_{(o)}[\mathrm{S}]_{(o)}}{[\mathrm{H}^+]^2[\mathrm{Tar}^{2-}]^{3/2}} \tag{6}$$

and

$$\log D = \log \mathrm{Kex}_{,(s)} + 2\,\mathrm{pH} + (2+z)\log[\mathrm{HL}]_{(o)} + \log[\mathrm{S}]_{(o)} - (3/2)\log\,[\mathrm{Tar}^{2-}] \tag{7}$$

where z is 1 for the phen system and 2 for the bipy system.

Although lanthanides(III) with Methoxy-BPHA alone (without S) in the organic phase and in the presence of tartrate ion in aqueous phase was extracted as a self-adduct chelate, $\mathrm{LnL_3(HL)_{2,(o)}}$, which is described by the following equation (10),

$$\mathrm{MTar}_2^- + 5\mathrm{HL}_{(o)} \xrightleftharpoons{\mathrm{K'ex}\beta_{2\mathrm{HL}}} \mathrm{ML_3(HL)_{2(o)}} + 3\mathrm{H}^+ + 2\mathrm{Tar}^{2-} \tag{8}$$

Note that Eq. (8) can be written as the following equation when the tartrate ion is absent from the extraction system:

$$\mathrm{M}^{3+} + 5\mathrm{HL}_{(o)} \xrightleftharpoons{\mathrm{Kex}\beta_{2\mathrm{HL}}} \mathrm{ML_3(HL)_{2(o)}} + 3\mathrm{H}^+ \tag{9}$$

where $\beta_{2\mathrm{HL}}$ is the adduct formation constant of the following reaction:

$$\mathrm{ML}_{3,(o)} + 2\mathrm{HL}_{(o)} \xrightleftharpoons{\beta_{2\mathrm{HL}}} \mathrm{ML_3(HL)_{2,(o)}} \tag{10}$$

The conditional extraction constant (K′ex) is related to the extraction constant (Kex) in the following manner:

$$\log \mathrm{Kex} = \log \mathrm{K'ex} + \log(\beta_2 C_T^2) \tag{11}$$

where β_2 is the formation constant of the lanthanide tartrate complex.

It was found that a cationic and mixed chelate, $[\mathrm{ML_2S(HL)}_z]^+$, was formed in the presence of phen or bipy. For this reason, the successive stability constant of the $\mathrm{ML_3}$ chelate, k_3 (= $[\mathrm{ML_3}]/[\mathrm{ML_2^+}][\mathrm{L^-}]$), is presumably smaller than that of the $\mathrm{MS^{3+}}$ chelate, k_1 (= $[\mathrm{MS^{3+}}]/[\mathrm{M^{3+}}][\mathrm{S}]$). The formation of the cationic chelate, $[\mathrm{ML_2S(HL)}_z]^+$, may also be promoted in the presence of tartrate anions in the aqueous phase. We observed a difference between the phen and bipy systems in the number of the coordinated HL in extracted species; specifically, one molecule for the phen system and two for the bipy system. This result may be due to the influence of the interaction

Table 1. Equilibrium extraction parameters

		Extraction constants and $pH_{1/2}$					Separation factors and $pH_{1/2}$ differences				
Extrated species		La	Pr	Eu	Ho	Yb	Pr/Eu	Eu/Yb	Yb/Pr	Conditions	Eq.
Methoxy-BPHA with phen and tartrate ion											
$LnL_2(phen)(HL)^+(1/2)Tar^{2-}$	log $Kex_{,(phen)}$	−11.05	−10.05	−9.08	−7.82	−7.54	0.97	1.54	2.51	$[HL] = 0.01$, $[phen] = 0.001$	(4)
	$pH_{1/2}$	(8.92)	(8.42)	(7.94)	(7.31)	(7.17)	(0.48)	(0.77)	(1.25)	$[Tar^{2-}] = 0.034$	
Methoxy-BPHA with bipy and tartrate ion											
$LnL_2(bipy)(HL)_2^+(1/2)Tar^{2-}$	log $Kex_{,(bipy)}$	—	−10.10	−9.30	—	−7.85	0.80	1.45	2.25	$[HL] = 0.01$, $[bipy] = 0.03$	(4)
	$pH_{1/2}$	—	(8.71)	(8.31)	—	(7.59)	(0.40)	(0.72)	(1.12)	$[Tar^{2-}] = 0.034$	
Methoxy-BPHA alone											
$LnL_3(HL)_2$	$\log(K'ex\beta_{2HL})$	−17.17	−16.53	−15.24	−14.34	−14.05	1.29	1.19	2.48	$[HL] = 0.01$	(8)
	$pH_{1/2}$	(9.06)	(8.84)	(8.41)	(8.11)	(8.02)	(0.43)	(0.39)	(0.82)	$[Tar^{2-}] = 0.034$	
	$\log(Kex\beta_{2HL})$	−13.81	−12.57	−10.78	−10.18	−9.69	1.79	1.09	2.88	$[HL] = 0.01$	(9)
	$pH_{1/2}$	(7.94)	(7.52)	(6.93)	(6.73)	(6.56)	(0.59)	(0.37)	(0.96)	$[Tar^{2-}]$ = none	

of Methoxy-BPHA with neutral donors in chloroform in the following equation:

$$\text{Methoxy-BPHA}_{(o)} + \text{S}_{(o)} \rightleftharpoons \text{Methoxy-BPHA} \cdot \text{S}_{(o)} \qquad (12)$$

The interaction will be higher for neutral donors of higher basicity as corroborated by the association constant values of BPHA with TBP and TOPO (12), and hence the interaction between Methoxy-BPHA and phen ($pKa = 4.92$) (13) is higher than that between Methoxy-BPHA and bipy ($pKa = 4.44$) (13). This gives a higher free neutral Methoxy-BPHA concentration in the bipy system than in the phen system and thus, the observed difference in the number of the coordinated HL.

The extraction constants ($\log Kex_{,(s)}$) and the pH values at half extraction ($pH_{1/2}$) for La, Pr, Eu, Ho, and Yb were calculated under the described experimental conditions, and the obtained values are summarized in Table 1; the extraction constant {log ($Kex\beta_{nHL}$)} and conditional extraction constants {log ($K'ex\beta_{nHL}$)} for lanthanides(III) with Methoxy-BPHA alone, that is, in the absence of phen or bipy, respectively, are also summarized for comparison. The conditional extraction constants for Methoxy-BPHA were calculated by substituting known values of the formation constant β_2 ($=[MTar_2^-]/[M^{3+}][Tar^{2-}]^2$) of the lanthanide tartrate, $MTar_2^-$, i.e., $\log \beta_2 = 6.3$ for La, 6.9 for Pr, 7.4 for Eu, 7.1 for Ho, and 7.3 for Yb (11), along with the values of C_T ($=0.034\ \text{mol dm}^{-3}$) in the experiments using Eq. (11). During the extraction of Pr, Eu, and Yb with Methoxy-BPHA and neutral donors, under identical conditions as in the presence of $0.034\ \text{mol dm}^{-3}$, an increase in extraction was found in comparison with $pH_{1/2}$ values. The extractability with phen, which has a higher basicity than that of bipy, is better than that with bipy. Figure 5 shows the $\log Kex_{,(s)}$ and log ($K'ex\beta_{2HL}$) values as a

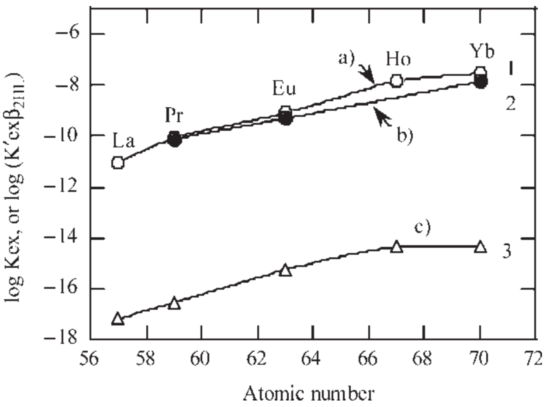

Figure 5. Relationship between $\log Kex_{,(s)}$ or log ($K'ex\beta_{2HL}$) and the atomic numbers of the lanthanides(III); a) for $\log Kex_{,(phen)}$, b) for $\log Kex_{,(bipy)}$ and c) for log ($K'ex\beta_{2HL}$).

function of the atomic number of the lanthanides(III). The log $Kex,_{(s)}$ or log ($K'ex\beta_{nHL}$) values of the lanthanides for each of the extraction systems exhibit the well-known increase with increasing ionic number (7). The relationship is linear up to Ho^{3+} and suggests that the slope may provide a good way of describing the selectivity of the extractants used for the M^{3+} group. The separation factors {log (SFs)} defined as the differences in log $Kex,_{(s)}$, log ($Kex\beta_{nHL}$) and log ($K'ex\beta_{nHL}$) for Pr/Eu, Eu/Yb and Yb/Pr are also summarized in Table 1. Note that the addition of phen or bipy improves the separation of the middle and heavier lanthanides of the Eu/Yb pair although the separation factor of the lighter and middle lanthanides of the Pr/Eu pair is lower than that observed in the case of extraction with Methoxy-BPHA only. The information obtained in the present study will be useful in research on the synergistic extraction of lanthanides(III) and actinides(III) with hydroxamic acid and other neutral donors.

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