Adduct Formation Constants in the Synergistic Solvent Extraction of Several Lanthanoids with Two Chelating Extractants: *β*-Diketone and Bidentate Nitrogen Bases

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The synergistic solvent extraction of La(III), Nd(III), Eu(III), Ho(III), and Lu(III) with a chelating extractant 4-benzoyl-3-phenyl-5-isoxazolone (HPBI) or 2-thenoyltrifluoroacetone (HTTA) and neutral bidentate heterocyclic amines, such as 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy), in $CHCl_3$ was investigated. Synergism was found to be due to formation of the ternary complex, $Ln(PBI)_3 \cdot S$ or $Ln(TTA)_3 \cdot S$, in the organic phase, where S denotes a neutral ligand. On the basis of the experimental data, the values of the equilibrium constants were calculated. The parameters of the extraction process were determined. The influence of the synergistic agent on the extraction process is discussed. The synergistic and separation factors were determined.

Introduction

The phenomenon in which two extractants taken together extract a metal ion species with a much higher efficiency as compared to the normal additive effect of these extractants separately is called synergism. The well-known synergistic effect in solvent extraction involves the enhancement of the extraction of a metal ion with an acidic chelating agent by the addition of a neutral ligand. Many studies have been carried out using a neutral unidentate ligand as the synergistic agent like crown ethers,[1−3] organophosphorus compounds,[4−6] sulfoxides,[7,8] or alkylammonium salts.[9−11] Compared with these, there are a limited number of investigations devoted to the solvent extraction of metals with mixtures involving a neutral bidentate ligand. The formation of synergistic adducts containing a *β*-diketone as the acidic component (acetylacetone, benzoylacetone,[12−14] pivaloyltrifluoroacetone,[15] thenoyltrifluoroacetone,[16−22] LIX 54,[23] and 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone[24]) and bidentate chelating agents, 1,10-phenanthroline and 2,2′-bipyridyl, have been reported for many metals under a variety of conditions. A very high, up to 10^6, synergistic effect was achieved by Kassierer and Kertes[16] using the combination of two bidentate chelating agents, the *β*-diketone and a nitrogen base.

4-Acyl-3-phenyl-5-isoxazolones are representative of an interesting class of *β*-diketones because of their lower pK_a values in comparison with corresponding 4-acylpyrazolones or typical *β*-diketones (such as thenoyltrifluoroacetone). The synthesis, crystal structure, and luminescent properties of solid complexes of Eu(III) with 3-phenyl-4-benzoyl-5-isoxazolone and 2,2′-bipyridine and 1,10-phenanthroline have been published recently.[25] Various isoxazolones have been used several times as chelating agents for the synergistic extraction of lanthanoids,[26−31] but a more detailed investigation involving the bidentate N-donor ligands is desirable.

The object of the present work is to present an investigation on the synergistic solvent extraction of some lanthanoid(III) ions (La, Nd, Eu, Ho, and Lu) with mixtures of 4-benzoyl-3-phenyl-5-isoxazolone (HPBI) or 2-thenoyltrifluoroacetone (HTTA) and bidentate nitrogen bases 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) as synergistic agents in $CHCl_3$ with the goal of elucidating the nature of the extracted complexes in the organic phase, to determine their formation constants as well as to clarify the selectivity between the lanthanoid ions.

Experimental Section

Reagents. The commercial product HPBI with a purity higher than 97 % (Fluka, Switzerland), HTTA (> 99 %, Fluka, Switzerland) 2,2′-bipyridine (Merck, p.a.), and 1,10-phenanthroline (Merck, p.a.) were used as supplied (the structural formulas of the extractants are presented in Figure S1, see Supporting Information). Stock solutions of the lanthanoid ions were prepared from their oxides (Fluka, puriss) by dissolving in concentrated perchloric acid and diluting with distilled water to the required volume. The diluent was $CHCl_3$ (p.a., Merck, Germany). Arsenazo III (Fluka, Switzerland) was of analytical purity as were the other reagents used.

Apparatus. A S-20 spectrophotometer Boeco (Germany) was used for measuring absorbances, and a pH 211 HANNA digital pH meter was used for the pH measurements in the solvent extraction studies.

Solvent Extraction Procedure. Equal volumes (10 cm^3) of each of the aqueous and organic phases were shaken mechanically for 45 min at (22 ± 2) °C, which was sufficient to reach equilibrium. After phase separation, the metal concentration in the aqueous phase was determined spectrophotometrically using Arsenazo III.[32] The acidity of the aqueous phase was measured by a pH meter with a precision of 0.01 pH units. The ionic strength was maintained at 0.1 M with (Na, H)ClO_4. The initial concentration of the metals was $2.5 \cdot 10^{-4}$ $mol \cdot dm^{-3}$ in all experiments.

Results and Discussion

The solvent extraction of the lanthanoid(III) ions with HPBI and HTTA in $CHCl_3$ has been studied previously.[5,31] The extraction process can be described by the equation:

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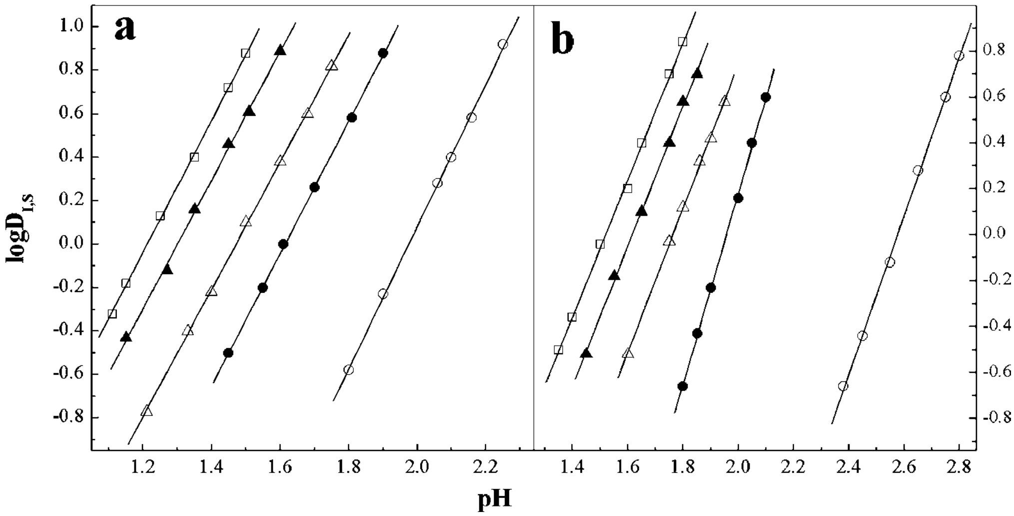

Figure 1. log $D_{I,S}$ vs pH for the extraction of lanthanoid elements with a HPBI-S mixture at [HPBI] = $2.5 \cdot 10^{-3}$ mol·dm^{-3} and [S] = $5 \cdot 10^{-3}$ mol·dm^{-3} in $CHCl_3$ (○, La; ●, Nd; △, Eu; ▲, Ho; □, Lu): (a) 1,10-phen, slopes: (2.92 to 3.04) ± (0.02 to 0.06); (b) 2,2′-bipy, slopes: (2.98 to 3.34) ± (0.03 to 0.05).

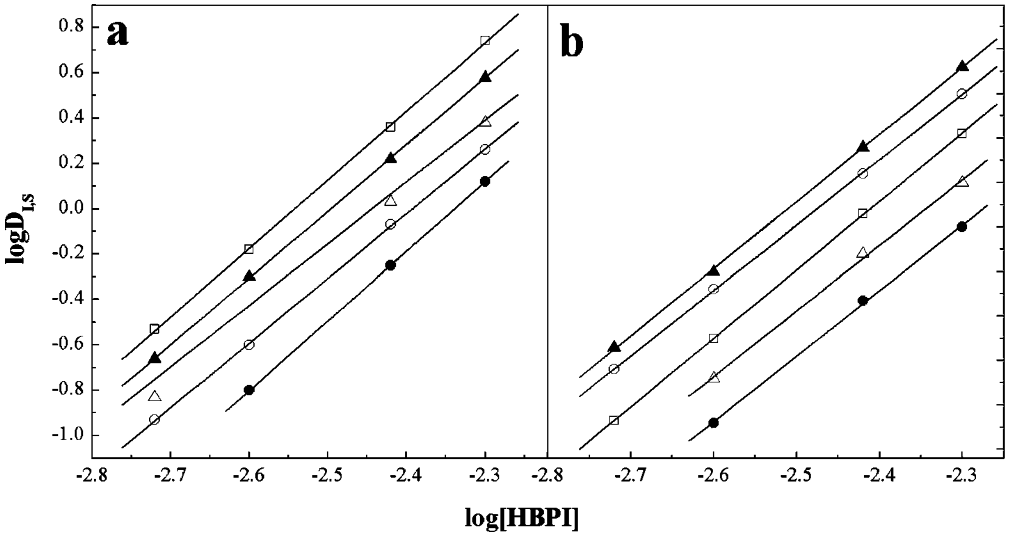

Figure 2. log $D_{I,S}$ vs [HPBI] for the extraction of lanthanoid elements with a HPBI-S mixture at [S] = $5 \cdot 10^{-3}$ mol·dm^{-3} in $CHCl_3$ (○, La; ●, Nd; △, Eu; ▲, Ho; □, Lu): (a) 1,10-phen: La, pH = 1.80; Nd, pH = 1.35; Eu, pH = 1.30; Ho, pH = 1.20; Lu, pH = 1.05. Slopes: (2.71 to 3.06) ± (0.02 to 0.33); (b) 2,2′-bipy: La, pH = 2.50; Nd, pH = 1.75; Eu, pH = 1.55; Ho, pH = 1.55; Lu, pH = 1.35. Slopes: (2.94 to 3.01) ± (0.03 to 0.12).

$$Ln^{3+}_{(aq)} + 3HL_{(o)} \leftrightarrow LnL_{3(o)} + 3H^{+}_{(aq)} \qquad (1)$$

where Ln is the lanthanoid ion, L^- represents the anion of a chelating agent, and the subscripts "aq" and "o" denote the aqueous and organic phases, respectively.

The lanthanoid(III) ion extraction with mixtures of HL-S was studied using the "slope analysis" method. Double logarithmic plots of $D_{I,S}$ or $D_{T,S}$ (the distribution coefficient due to the synergistic effect) versus one of the variables, [H^+], [HL], and [S], keeping the other two constant, indicate the stoichiometry and allow the calculation of the equilibrium constants. If the concentration of the extractants is constant, and the hydrolysis in the aqueous phase as well as the polymerization in the organic phase occurs to a negligible extent only, then the plots will be straight lines, and their slopes will give the number of ligands present in the adducts. As the metal extraction with 1,10-phenanthroline or 2,2′-bipyridine (S) is negligible under the experimental conditions of the present study and the partition of HL (HTTA or HPBI) and S [23] toward the aqueous phase is low, the values of $D_{I,S}$ and $D_{T,S}$ were calculated as $D - D_I$ and $D - D_T$ ($D_{I,S}$ is the distribution coefficient obtained for the metal extraction with mixtures of HPBI and S, and D_I with HPBI alone under the same experimental conditions).

The plots of log $D_{I,S}$ versus pH, log[HPBI], and log[S] (Figures 1 to 3) and the plots of log $D_{T,S}$ versus pH, log[HTTA], and log[S] (Figures S2 to S4, see Supporting Information) represent straight lines close to 3, 3, and 1, respectively.

On the basis of slope analysis, the extraction of the metals with mixtures HPBI-S and HTTA-S can be represented by the following equation:

$$Ln^{3+}_{(aq)} + 3HL_{(o)} + S_{(o)} \leftrightarrow LnL_3 \cdot S_{(o)} + 3H^{+}_{(aq)} \qquad (2)$$

This stoichiometry, that includes one molecule of the synergist, was also established for the extraction of some lanthanoid ions with the combination of HTTA-bipy in C_6H_6.[21] Duyckaerts et al.[18] have also reported the formation of mixed complexes in four diluents, for example, $Eu(TTA)_3 \cdot B$, where B was 2,2′-dipy, 1,10-phen, and its 2,9-dimethyl derivative. All of the rare earth elements were synergistically extracted as $LnA_3 \cdot S$ adducts with the same synergistic agents and the active component of LIX 54, 1-phenyl-3-isoheptyl-1,3-propanedione.[23] When the phen solution was gradually added into EuA_3 solution (A

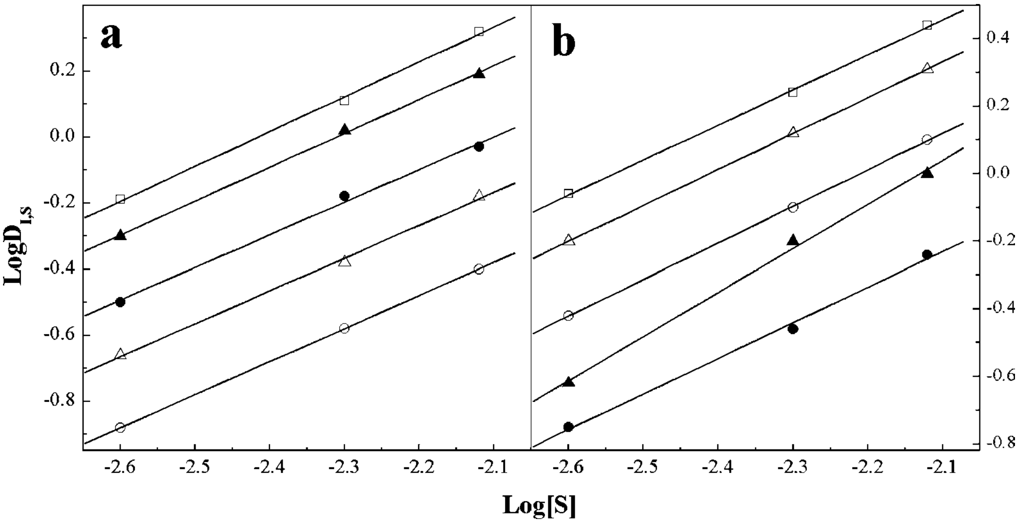

Figure 3. log $D_{I,S}$ vs [S] for the extraction of lanthanoid elements with a HPBI-S mixture at [HPBI] = $2.5 \cdot 10^{-3}$ mol·dm^{-3} in CHCl$_3$ (○, La; ●, Nd; △, Eu; ▲, Ho; □, Lu): (a) 1,10-phen: La, pH = 1.80; Nd, pH = 1.55; Eu, pH = 1.35; Ho, pH = 1.30; Lu, pH = 1.25. Slopes: (0.97 to 1.02) ± (0.03 to 0.08); (b) 2,2′-bipy: La, pH = 2.55; Nd, pH = 1.85; Eu, pH = 1.80; Ho, pH = 1.55; Lu, pH = 1.60. Slopes: (1.03 to 1.30) ± (0.02 to 0.07).

Table 1. Values of the Equilibrium Constants K_I, $K_{I,S}$, and $\beta_{I,S}$ and pH$_{50}$ for the Extraction of Lanthanoid Ions with HPBI and HPBI-S Systems in CHCl$_3$[a]

		log $K_{I,S}$		log $\beta_{I,S}$			pH$_{50}$	
Ln^{3+}	log K_I[31]	HPBI-bipy	HPBI-phen	HPBI-bipy	HPBI-phen	HPBI	HPBI-bipy	HPBI-phen
La	−1.33	2.38	4.23	3.71	5.56	3.04	2.58	1.98
Nd	−0.54	4.24	5.34	4.78	5.88	2.78	1.96	1.61
Eu	0.06	4.80	5.67	4.74	5.61	2.62	1.77	1.47
Ho	0.36	5.25	6.20	4.89	5.84	2.72	1.62	1.30
Lu	0.70	5.55	6.48	4.85	5.78	2.83	1.42	1.21

[a] The values of the equilibrium constants are calculated on the basis of the 42 experimental points; the statistical confidence is 95 %, and the standard deviation is less than ± 0.05.

Table 2. Values of the Equilibrium Constants K_T, $K_{T,S}$, and $\beta_{T,S}$ and pH$_{50}$ for the Extraction of Lanthanoid Ions with HTTA and HTTA-S Systems in CHCl$_3$[a]

		log $K_{T,S}$		log $\beta_{T,S}$			pH$_{50}$	
Ln^{3+}	log K_T[5]	HTTA-bipy	HTTA-phen	HTTA-bipy	HTTA-phen	HTTA	HTTA-bipy	HTTA-phen
La	−11.06	−5.85	−3.95	5.21	7.11	5.08	4.13	3.48
Nd	−10.12	−3.71	−1.78	6.41	8.34	4.77	3.40	2.76
Eu	−8.68	−2.23	−0.43	6.45	8.25	4.29	2.92	2.31
Ho	−8.56	−1.75	0.08	6.81	8.64	4.25	2.74	2.13
Lu	−8.15	−0.96	0.64	7.19	8.79	4.11	2.52	1.95

[a] The values of the equilibrium constants are calculated on the basis of the 42 experimental points; the statistical confidence is 95 %, and the standard deviation is less than ± 0.05.

represents the anion of a pivaloyltrifluoroacetone), a heat change was observed,[15] exothermic in C$_6$H$_6$, CCl$_4$, and hexane, while it was endothermic in CHCl$_3$. The authors suggested that the contribution of organic solvents, such as solvent−solute interactions, was significant in the adduct formation. In all those mixed ligand compounds in solution, with a stoichiometry Ln−diketone−base of 1:3:1, the lanthanoids exhibit octacoordinate properties. On the other hand, the existence of the adducts RE(A)$_3$(S)$_2$ was also observed, having two molecules of phen per adduct (A, benzoylacetone, pivaloyltrifluoroacetone, haxafluoroacetylacetone) for the extraction of trivalent La and Sm.[14]

The equilibrium constants $K_{I,S}$ and $K_{T,S}$ can be determined as:

$$\log K_{L,S} = \log D_{L,S} - 3\log[HL] - \log[S] - 3\,pH \tag{3}$$

The formation of mixed adducts in the organic phase can be expressed by the equation:

$$LnL_{3(o)} + S_{(o)} \leftrightarrow LnL_3 \cdot S_{(o)} \tag{4}$$

The equilibrium constants $\beta_{I,S}$ and $\beta_{T,S}$ for the organic phase reaction can be determined as:

$$\log \beta_{L,S} = \log K_{L,S} - \log K_L \tag{5}$$

The values of log K_I, log $K_{I,S}$, and log $\beta_{I,S}$ are given in Table 1. The corresponding equilibrium values obtained for the mixtures of HTTA and S are given in Table 2. The equilibrium constants measured in this work are concentration constants, and they are based on the assumption that the activity coefficients of the species do not change significantly during the reaction. The data in Tables 1 and 2 show that the values of the equilibrium constants $K_{I,S}$ and $K_{T,S}$ increase with decreasing ionic radii from La to Lu. With increasing atomic number, the ionic radii decrease at constant charge; consequently, the charge densities increase, and the formation of extractable complexes is favored. Thus, an increase of the extraction efficiency is

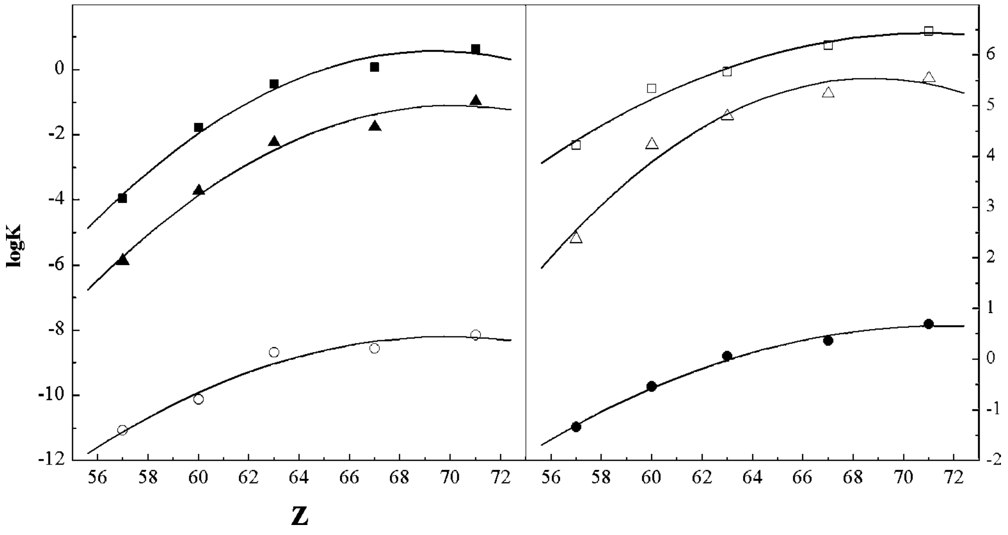

Figure 4. Log $K_L(K_{L,S})$ versus Z. (○, HTTA; ▲, HTTA-bipy; ■, HTTA-phen; ●, HPBI; △, HPBI-bipy; □, HPBI-phen).

observed from La to Lu. The variation of the equilibrium constants K_L and $K_{L,S}$ versus the atomic number Z of the lanthanoids is given in Figure 4. It can be seen that the curves for HTTA and HBPI vary practically in the same manner as those for the corresponding systems including a synergistic agent.

In most cases the values of log $K_{I,S}$ are seven logarithmic units higher than those of log $K_{T,S}$ (Tables 1 and 2). Changing the chelating extractant from HPBI to HTTA, in combination with the same synergistic agent, results in a significant increase of the lanthanoid's extraction. This fact can be explained by taking into account that HTTA is a weaker acid ($pK_a = 6.2^7$) than HPBI ($pK_a = 1.23^{29}$).

To compare the extraction ability of the mixtures HPBI-S and HTTA-S to that of the chelating extractants HPBI or HTTA, the pH_{50} values (i.e., values of pH where log $D = 0$, [HBPI] = $2.5 \cdot 10^{-3}$ mol·dm^{-3}, [HTTA] = $4 \cdot 10^{-2}$ mol·dm^{-3}, and [S] = $5 \cdot 10^{-3}$ mol·dm^{-3}), corresponding to the extraction of the studied lanthanoids in the absence and in the presence of a synergist, are collected in Tables 1 and 2. A difference between the pH_{50} values of approximately 1.5 and 2 pH units is observed for HTTA-2,2′-bipy and HTTA-1,10-phen as well as 1 and 1.5 pH units for HPBI-2,2′-bipy and HPBI-1,10-phen combinations. Another advantage of the extractant mixture including HPBI is that the extraction process is carried out at lower pH values of the aqueous phase.

However, the values of $\beta_{I,S}$ (for the organic phase synergistic reaction) are significantly smaller than the values of log $\beta_{T,S}$.

The comparison of $K_{L,S}$ values obtained for the HL−1,10-phen, and HL−2,2′-bipy combinations shows that the stability of the complexes involving 1,10-phen is higher than those involving 2,2′-bipy, probably because of the higher basicity of the former. A similar trend has been observed in the synergistic extraction of different metals by other investigators also.[16−20,23] The size of the synergistic enhancement can be found by calculation of the synergistic coefficients as: SC = $\log(D_{1,2}/D_1 + D_2)$ where D_1, D_2, and $D_{1,2}$ are the distribution ratios of the lanthanoids between the aqueous and the organic phase with the extractants taken separately and with their mixture. The values of the synergistic coefficients are given in Tables 3 and 4. It can be seen that the synergistic enhancement is found for all five metals and mixtures of extractants (SC > 0). It changes approximately from 10^2 to 10^6. So, the combination of two bidentate ligands, the acidic chelating agent and the Lewis base phenanthroline or bipyridyl, produces a very strong synergistic effect in the solvent extraction of lanthanoids. These data show that the SC obtained for the mixtures including 1,10-phenantroline as a synergistic agent are approximately 2 and 1 order of magnitude higher than that when 2,2′-bipyridyl is used in combination with HTTA and HPBI, respectively. This observation is in confirmation with previous investigations in which, the synergistic effects decrease in the order phen > bipy with differences up to 2 orders of magnitude.[16] The larger synergistic effect with phenanthroline is probably due to its stronger donor properties.[23] The obtained SC in the present study are much higher than that in the cases when diphenylsulfoxide,[7] crown ethers,[3] or calix[4]arenes[5,27,31] were used as a second extractant for the synergistic extraction of Ln^{3+} with a β-diketone.

Table 3. Values of the Synergistic Coefficients ([HPBI = $2.5 \cdot 10^{-3}$ mol·dm^{-3}, [S] = $5 \cdot 10^{-3}$ mol·dm^{-3}; phen: pH = 1.70; bipy: pH = 1.90) and Separation Factors for the Lanthanoid Extraction with HPBI Alone and HPBI-S Systems in $CHCl_3$

	SC			SF		
Ln^{3+}	HPBI-bipy	HPBI-phen		HPBI	HPBI-bipy	HPBI-phen
La	1.41	3.26	Nd/La	6.16	72.44	12.88
Nd	2.48	3.58	Eu/Nd	3.98	3.63	2.13
Eu	2.44	3.31	Ho/Eu	1.99	2.82	3.38
Ho	2.59	3.54	Lu/Ho	2.18	1.99	1.90
Lu	2.55	3.48				

Table 4. Values of the Synergistic Coefficients ([HTTA] = $4 \cdot 10^{-2}$ mol·dm^{-3} and [S] = $5 \cdot 10^{-3}$ mol·dm^{-3}; phen: pH = 2.50; bipy: pH = 3.20) and Separation Factors for the Lanthanoid Extraction with HTTA Alone and HTTA-S Systems in $CHCl_3$

	SC			SF		
Ln^{3+}	HTTA-bipy	HTTA-phen		HTTA	HTTA-bipy	HTTA-phen
La	2.91	4.82	Nd/La	8.70	138.09	147.9
Nd	4.11	6.04	Eu/Nd	27.54	30.19	22.38
Eu	4.15	5.95	Ho/Eu	1.31	3.02	3.23
Ho	4.51	6.34	Lu/Ho	3.54	6.16	3.63
Lu	4.89	6.49				

The separations between the lanthanoids can be assessed using the separation factors (SF), calculated as a ratio of the distribution coefficients of two adjacent lanthanoids. When the metal ions form complexes of the same type (as in the present case), the separation factors can be determined as a ratio of the equilibrium constants $K_{I,S}$ or $K_{T,S}$. Their values are given in Tables 3 and 4. The data of the separation factors and those of the synergistic coefficients show that the addition of S to the chelating extractants HPBI or HTTA not only enhances the extraction efficiency but causes a moderate improvement of the selectivity among the lanthanoids for some pairs (or remains almost the same). This is in contrast to the generally accepted observation that the separation becomes poorer as the extractability increases in the synergistic solvent extraction of metals. It is interesting to compare the separation factors obtained for the extraction of lanthanoids with the same chelating extractants and various synergists, namely, the crown ethers,[3] calix[4]arenes,[5,27,31] diphenylsulfoxide,[7] and bis-2-ethylhexylsulfoxide.[8] Unfortunately, limited comparisons are possible because no data are available for all of the lanthanoids. The separation factors of the pairs Eu/La and Lu/Eu for these systems are listed in Table S1 of the Supporting Information along with data obtained in the present study. It is seen from the separation factors of Table S1 that there is an advantage for the systems HTTA-1,10-phen and HTTA-2,2′-bipy used in the present study for the separation of the 4f metals. The separation factor between La and Lu is approximately $7.76 \cdot 10^4$, for the system HTTA-2,2′-bipy, which is similar to those found for the extraction of the same lanthanoids ($7.08 \cdot 10^4$) in aqueous-benzene medium.[21]

Conclusion

Five lanthanoid(III) ions representative of the 4f-series (La, Nd, Eu, Ho, and Lu) have been extracted as $\mathrm{Ln(PBI)_3 \cdot S}$ and $\mathrm{Ln(TTA)_3 \cdot S}$ species with mixtures containing chelating extractants (HPBI or HTTA) and neutral bidentate heterocyclic amines (S: 1,10-phenantroline or 2,2′-bipyridine). The addition of a synergist to the chelating extractant improves the extraction efficiency of the lanthanoid ions and produces rather large synergistic effects. A very high synergism, up to 6 orders of magnitude, was established for the HTTA−1,10-phen system. The values of the overall equilibrium constants increase with an increase in the atomic number of the lanthanoids as expected from their decreasing atomic radii. The values of log $K_{\mathrm{I,S}}$ are seven logarithmic units higher than those of log $K_{\mathrm{T,S}}$. In the synergistic systems the selectivity among the lanthanoids has been increased upon the change of the chelating extractant HPBI with HTTA.

Supporting Information Available:

Figures S1−S4 and Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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