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Scientific paper

Application of 4,4,4-Trifluoro-1-(Biphenyl-4-yl)Butane-1,3-Dione as a Chelating Extractant in the Solvent Extraction and Separation of Light Lanthanoids in Combination with Phosphine Oxides

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Abstract

The 4,4,4-trifluoro-1-(biphenyl-4-yl)butane-1,3-dione(HL) has been synthesized and its complexation properties in solution was examined. Mixed ligand chelate extraction of light trivalent lanthanoids (La÷Gd) from chloride medium at constant ionic strength $\mu = 0.1$ into C_6H_6 with HL in combination with one of the three phosphine oxide compounds trioctylphosphine oxide(TOPO), tributylphosphine oxide(TBPO) or triphenyphosphine oxide(TPPO) was studied. The composition of the extracted species was established as LnL_3 with HL alone and as LnL_3 2S in the presence of TOPO and TBPO or LnL_3 S with the mixture of HL–TPPO. The 28 values of the overall equilibrium constants were calculated. A synergic effect up to 10^3–10^4 was observed for the extraction of the above-mentioned lanthanoid ions with binary mixtures of extractants. The change of the synergistic agent causes a significant increase of the $K_{L,S}$ values in the order TBPO < TPPO < TOPO. The parameters of the extraction process were determined and the separation factors between two adjacent Ln(III) were calculated.

Keywords: Extraction, lanthanoids, 4,4,4-trifluoro-1-(biphenyl-4-yl)butane-1,3-dione, TOPO, TBPO, TPPO, synergism, separation

1. Introduction

The synergistic effect was observed by Cunningham et al.[1] for the extraction of Pr(III) and Nd(III) by mixtures of 2-thenoyltrifluoroacetone (HTTA) and tributylphosphate (TBP) in kerosene but synergism acquired its name in 1958 when a group of scientists from Oak Ridge laboratory investigated the extraction of U(VI) by combinations of organophosphorus extracting agents.[2] The synergistic effect is often significant but the separation among the metal ions is poorer. A lot of efforts have been made to develop extraction systems containing reagents suitable to separate 4f elements. As the elements are so similar in size and properties, the separation is extremely difficult. Fluorinated substituents have often been introduced into extractants. The acidity of the extracting agent is increased by the electron-withdrawing effect of the fluorinated group, and the extracting agent can be used to extract metal ions from more acidic aqueous solutions.[3] A popular ligand for the solvent extraction of 4f-elements is thenoyltrifluoroacetone used alone and in combination of various synergistic agents.[3] Adduct formation constants have been determined in the thirteen diluents for two types of synergic adducts $Eu(TTA)_3$ S and $Eu(TTA)_3$ 2S (S = TOPO) by Akiba et al.[4] Irving and Edington[5] have established the mixed-adduct complexes of the type $M(TTA)_2(NO_3)$ 2TBPO (M = Am or Eu). The optimum conditions were established when Ln^{3+} were synergistically extracted with hexafluoroacetylacetone and TOPO as mixed ligand complexes with the general formula LnL_3 2TOPO.[6] Considering the interaction reaction between the extractants in cyclohexane, Atalka and Favaro[7] have identified in the organic phase the species $Ln(TTA)_3$ TOPO and $Ln(TTA)_3$ 2TOPO for

La and Yb. The extensive study on the extraction of the whole lanthanoid series, except Pm and Lu, with HTTA and TPPO mixture in benzene from an aqueous perchlorate medium at constant ionic strength of 0.2 M was carried out by Aly et al.[8] It was found that the main extracted adduct contains the lanthanoid chelates together with two TPPO molecules. In the solvent extraction of metal β-diketonates, it is well known that the presence of a Lewis base such as TOPO enhances the extractability, because of adduct formation between the metal chelates and this Lewis base. Such synergism has been widely investigated, but steric hindrance by the terminal groups in the β-diketones has hardly been recognized.[9] No investigations, however, have been published on the extraction of 4f-elements using 4,4,4-trifluoro-1-(biphenyl-4-yl)butane-1,3-dione as well as the evaluation of its complexation properties in combination with organophosphorus extractants.

As a part of a systematic study of the synergistic solvent extraction of the lanthanoids, the present work was undertaken to investigate the extraction of light trivalent ions of the metals of the 4f-series (La÷Gd) (with exception of radioactive Pm) with a mixture of β-diketone with trifluoromethyl group, 4,4,4-trifluoro-1-(biphenyl-4-yl)butane-1,3-dione (HL) and neutral donors, the trialkyl derivatives of phosphine oxides, where alkyl is the butyl (tributylphosphine oxide, (TBPO)), octyl group (trioctylphosphine oxide, (TOPO)) and phenyl group (triphenylphosphine oxide, (TPPO)) (S) in C_6H_6. Our goal is to elucidate the nature of the complexes extracted into the organic phase and to determine the possibilities for separation of the light lanthanoid metals.

2. Materials and Methods

2. 1. Materials

4,4,4-trifluoro-1-(biphenyl-4-yl)butane-1,3-dione (HL) was synthesized according to modified procedure based on the Claisen condensation method[10] as shown in Scheme 1.

A solution of 9.81 g (0.05 mol) 4-acetylbiphenyl and 6.65 g methyl trifluoroacetate (0.052 mol, 5.23 ml) in 70 ml benzene was added to 2.8 g sodium methoxide. The mixture was stirred about 10 minutes and left overnight. The solvent was distilled off under reduced pressure, the solid residue was acidified with HCl solution and then was neutralized with sodium acetate. The crude product was isolated by filtration under vacuum and air dried. Yield 83%, ^{1}H NMR (600MHz, DMSO-d_6) δ (ppm): 8.05 d (1H, ArH), 7.98 d (1H, ArH), 7.83 d (1H, ArH), 7.78–7.35 m (3H, ArH), 7.53–7.49 m (2H, ArH), 7.45–7.40 m (1H, ArH), 2.62 s (2H, -CH_2-). Elemental analysis data: $C_{16}H_{11}F_3O_2$ found / (calculated) % C 65.27/ (65.56), H 3.56 / (3. 79).

The commercial products trioctylphosphine oxide (TOPO), tributylphosphine oxide (TBPO) and triphenylphosphine oxide (TPPO) (Fluka, ≥ 98%) were used as received. The diluent was C_6H_6 (Merck, p.a.) Stock solutions of metals with the concentration 2.5×10^{-3} mol dm^{-3} were prepared from their oxides (Fluka, puriss) by dissolving in concentrated hydrochloric acid and diluting with distilled water to the required volume. Arsenazo III (Fluka) was of analytical grade purity as were the other reagents used.

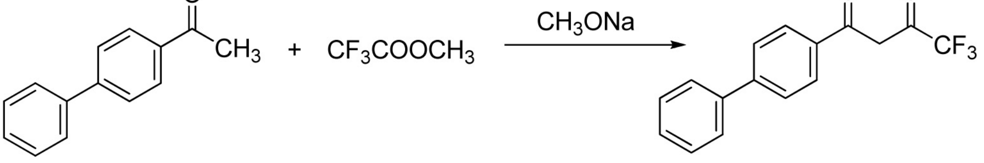
2. 2. Methods

The experiments were carried out using 10 cm^3 volumes of aqueous and organic phases. The samples were shaken mechanically (Orbital Shaker OS-20, Boeco, Germany, 120 rpm) for 55 minutes at room temperature (22 ± 2 °C) which was sufficient to reach equilibrium. After the separation of the phases, the metal concentration in the aqueous phase was determined photometrically (S-20 Spectrophotometer Boeco, Germany) using Arsenazo III.[11] The concentration of the metal ion in the organic phase was calculated by subtraction of the determined amount in the aqueous phase from the total amount present. The acidity of the aqueous phase was measured by a digital pH meter (pH 211 HANNA, USA) with an accuracy of 0.01 pH units. The ionic strength was maintained at 0.1 M with (Na, H)Cl. The initial concentration of the metals was 2.5×10^{-4} mol dm^{-3} in all experiments.

3. Results and Discussion

3. 1. Solvent Extraction of Ln(III) with 4,4,4-trifluoro-1-(biphenyl-4-yl)butane-1,3-dione

Information about major complex for the system under study is usually obtained from the slope analysis. One assumption used in the slope analysis method is constancy



Scheme 1. Synthesis of 4,4,4-trifluoro-1-(biphenyl-4-yl)butane-1,3-dione (HL)

of the activity coefficients, so that concentrations can be used to describe the equilibrium involved in the extraction. The extraction process of lanthanoids with β-diketones[3] can be described by the equation:

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

where Ln^{3+} denote lanthanoid and the subscripts “aq” and “o” indicate the species in the aqueous and organic phase.

The extraction constant, K_L, is defined as

$$K_L = \frac{[LnL_3]_{(o)}[H^+]^3_{(aq)}}{[Ln^{3+}]_{(aq)}[HL]^3_{(o)}} = D_L\,\frac{[H^+]^3_{(aq)}}{[HL]^3_{(o)}} \quad (2)$$

where D_L is the lanthanoid distribution ratio. As seen from Figs.1 and 2 the plots of $\log D_L$ vs pH and log[HL] are linear, with slopes very close to 3, in accordance with eq.1.

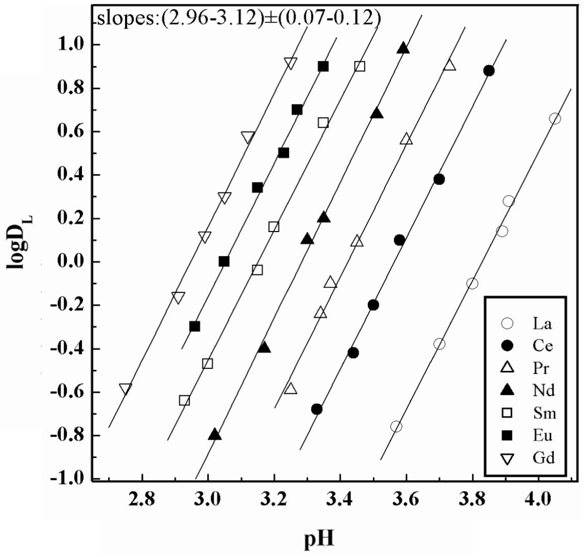


Figure 1. LogD_L vs. pH for the extraction of lanthanoid(III) ions with [HL] = 2 × 10^{-2} mol dm^{-3}.

The equilibrium constants for the extraction of light lanthanoids with 4,4,4-trifluoro-1-(biphenyl-4-yl)butane-1,3-dione were calculated on the basis of eq. 3 and summarized in Table 1.

$$\log K_L = \log D_L - 3pH - 3\log[HL] \quad (3)$$

The experimental data showed that the lanthanoid ions extraction with TBPO, TOPO and TPPO alone is negligible under the experimental conditions of the present study.

3. 2. Synergistic Solvent Extraction of Ln(III) with Mixtures of HL and TOPO, TBPO or TPPO

When an auxiliary reagent, such as TOPO, TBPO and TPPO (S), is added to the extraction system, enhanced extraction results because of the more hydrophobic adduct formation.[4–8] The synergistic solvent extraction of Ln(III) ions with mixture of HL and S can be expressed by the equation:

$$Ln^{3+}_{(aq)} + mHL_{(o)} + nS_{(o)} \leftrightarrow LnL_m\,S_{n(o)} + mH^{+}_{(aq)} \quad (4)$$

It can be shown that

$$\log D_{L,S} = \log K_{L,S} + m\log[HL] + n\log[S] + mpH \quad (5)$$

where $D_{L,S}$ is the distribution ratio due to the synergistic effect and $K_{L,S}$ is the overall equilibrium constant.

If the hydrolysis and complexation in the aqueous phase as well as the polymerization in the organic phase occur to a negligible extent only, then the double logarithmic plots of $D_{L,S}$ vs. one of the variables [HL], [S] and $[H^+]$ keeping the other two constant will be linear and their slopes will give the number of the ligands participating in the formation of the adduct. It can be seen from Figures 3 and 4 (plots of $\log D_{L,S}$ vs $\log[H^+]$ and log[HL] at fixed S concentrations) that three β-diketone moieties are attached to the synergistic species in all studied systems.

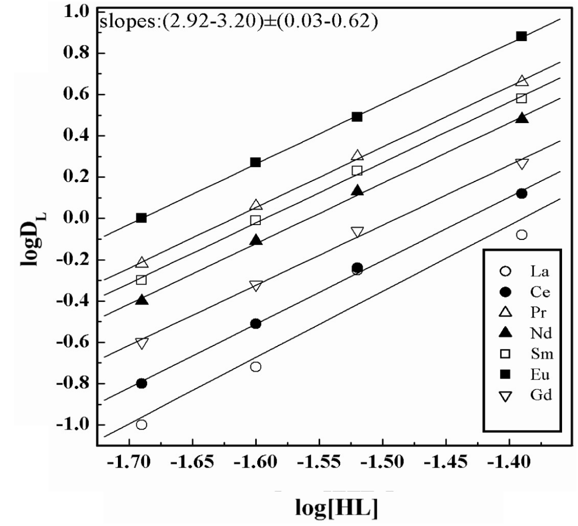


Figure 2. LogD_L vs. log[HL] for the extraction of lanthanoid(III) ions at pH for La, pH = 3.50; Ce, pH = 3.30; Pr, pH = 3.35; Nd, pH = 3.15; Sm, pH = 2.95; Eu, pH = 3.05; Gd, pH = 2.75.

The plots of $\log D_{L,S}$ vs log[S] at fixed HL concentration (Fig. 5) gave slopes of one for TPPO and two for TOPO and TBPO. These results indicate the attachment of only one TPPO molecule and two TOPO or TBPO in these synergistic systems and show the extraction of the synergistic species LnL_3 TPPO, LnL_3 2TBPO and LnL_3 2TOPO in the organic phase. The Indian researchers[12] reported that two synergistic species having one and two oxo-donor molecules are simultaneously extracted ($Eu(TTA)_3$ 2S, $Eu(TTA)_3$ S (S = TPSO, TBP and TOPO))

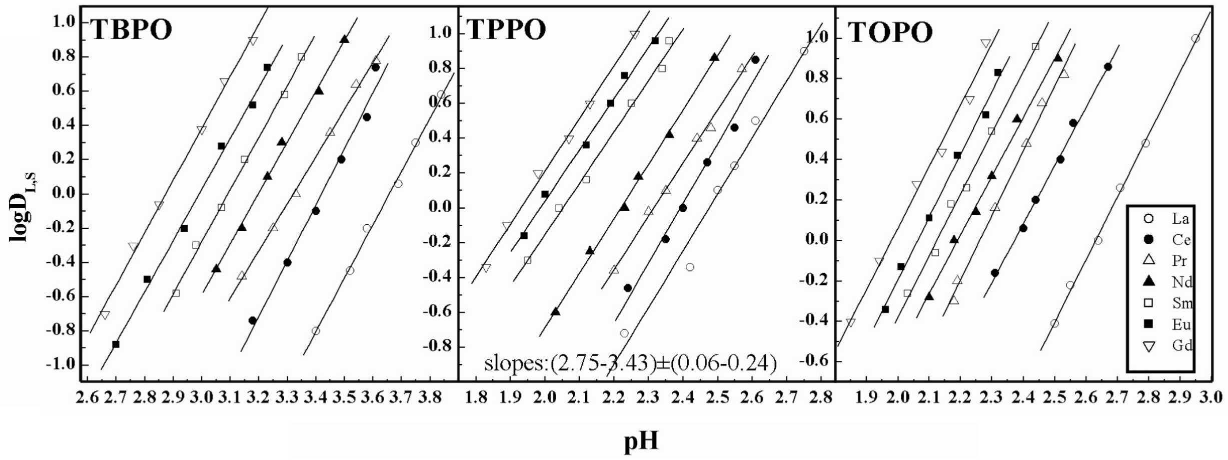


Figure 3. Log$D_{L,S}$ vs. pH for the extraction of lanthanoid(III) ions with mixtures HL–TPPO(TBPO), [HL] = 1 × 10^{-2} mol dm^{-3} and HL–TOPO, [HL] = 2 × 10^{-2} mol dm^{-3} and [S] = 5 × 10^{-3} mol dm^{-3}.

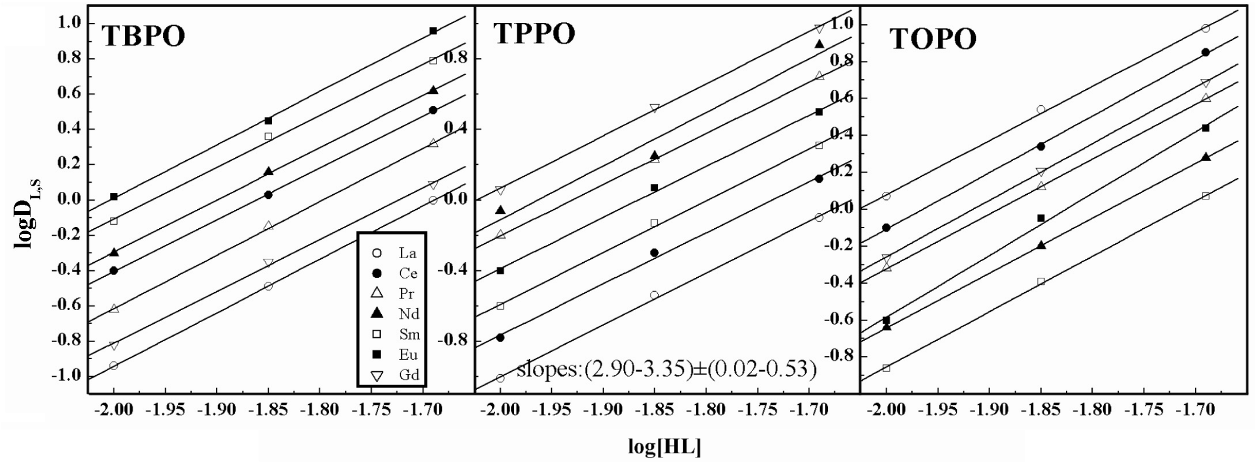


Figure 4. Log$D_{L,S}$ vs. log[HL] for the extraction of lanthanoid(III) ions at [S] = 5 × 10^{-3} mol dm^{-3} and constant pH. TPPO: La, pH = 2.15; Ce, pH = 2.15; Pr, pH = 2.25; Nd, pH = 2.20; Sm, pH = 1.85; Eu, pH = 1.85; Gd, pH = 1.95. TBPO: La, pH = 3.35; Ce, pH = 3.30; Pr, pH = 3.10; Nd, pH = 3.10; Sm, pH = 3.05; Eu, pH = 3.00; Gd, pH = 2.60. TOPO: La, pH = 2.95; Ce, pH = 2.65; Pr, pH = 2.45; Nd, pH = 2.35; Sm, pH = 2.15; Eu, pH = 2.20; Gd, pH = 2.20.

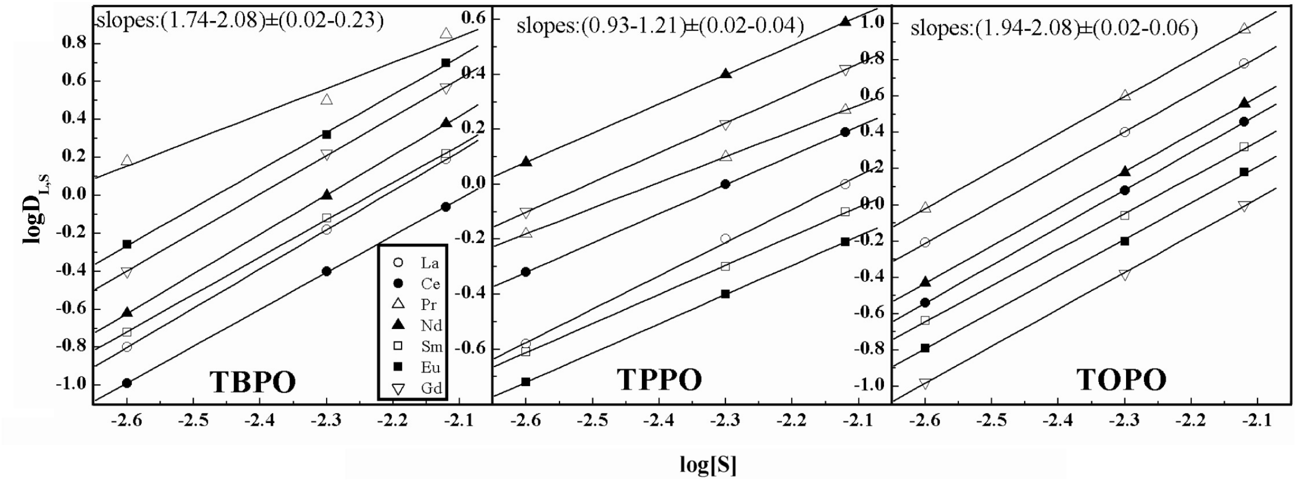


Figure 5. Log$D_{L,S}$ vs log[S] for the extraction of lanthanoid(III) ions with mixtures HL–TPPO(TBPO), [HL] = 1 × 10^{-2} mol dm^{-3} and HL–TOPO, [HL] = 2 × 10^{-2} mol dm^{-3} and constant pH. TPPO: La, pH = 2.40; Ce, pH = 2.40; Pr, pH = 2.35; Nd, pH = 2.35; Sm, pH = 1.95; Eu, pH = 1.85; Gd, pH = 2.00. TBPO: La, pH = 3.60; Ce, pH = 3.30; Pr, pH = 3.50; Nd, pH = 3.20; Sm, pH = 3.05; Eu, pH = 3.10; Gd, pH = 2.95. TOPO: La, pH = 2.75; Ce, pH = 2.40; Pr, pH = 2.45; Nd, pH = 2.25; Sm, pH = 2.10; Eu, pH = 2.00; Gd, pH = 1.85.

in benzene. Kandil and Farah[13] also noted on the basis of the thermodynamic studies that the coordination number of the chelate expands from 6 to 8 to accommodate direct coordination of the adduct to metal in Eu(TTA)$_3$ 2TOPO. The enhanced extraction observed during the calorimetric study by Choppin et al.[14] of the adduct species Nd(TTA)$_3$ 2TOPO was attributed to the decreased hydrophilic character from the loss of water molecules Nd(TTA)$_3$ 2H$_2$O and to the presence of hydrophobic side chains on the coordinated neutral ligand.

On the basis of the slope analysis data, the synergistic extraction of the light lanthanoids can be described by the following reactions:

$$Ln^{3+}_{(aq)} + 3HL_{(o)} + S_{(o)} \leftrightarrow LnL_3\,S_{(o)} + 3H^+_{(aq)} \qquad (6)$$

$$Ln^{3+}_{(aq)} + 3HL_{(o)} + 2S_{(o)} \leftrightarrow LnL_3\,2S_{(o)} + 3H^+_{(aq)} \qquad (7)$$

The overall equilibrium constant $K_{L,S}$ can be determined by the equations:

$$\log K_{L,S} = \log D_{L,S} - 3\log[HL] - \log[S] - 3pH \qquad (8)$$

$$\log K_{L,S} = \log D_{L,S} - 3\log[HL] - 2\log[S] - 3pH \qquad (9)$$

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

$$LnL_{3(o)} + S_{(o)} \leftrightarrow LnL_3\,S_{(o)} \qquad (10)$$

$$LnL_{3(o)} + 2S_{(o)} \leftrightarrow LnL_3\,2S_{(o)} \qquad (11)$$

The equilibrium constant $\beta_{L,S}$ for the organic phase synergistic reaction can be determined as:

$$\log\beta_{L,S} = \log K_{L,S} - \log K_L \qquad (12)$$

The values of $\log K_{L,S}$ and $\log\beta_{L,S}$ are given in Table 1. The equilibrium constant values mentioned here refer only to the concentration quotients which have been calculated on the assumption that the activity coefficients of the species involved do not change significantly under the experimental conditions employed.

The data in Table 1 shown that the values of $K_{L,S}$ increases with decreasing ionic radii of the metal ions. The variation of the equilibrium constants K_L and $K_{L,S}$ versus the atomic number Z of the light lanthanoids is given in Fig. 6.

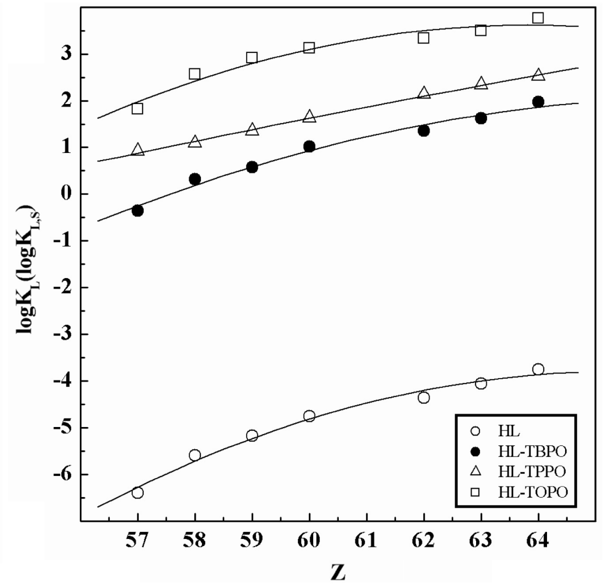


Figure 6. LogK_L($K_{L,S}$) vs. Z.

The overall equilibrium constant $K_{L,S}$ For Ln(III) ions obtained with the synergistic mixture HL–TOPO are approximately 2 orders of magnitude smaller than those obtained with the same synergistic agent and HTTA as a chelating extractant,[7] or with 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone,[15] and eight kinds of ortho-substituted 4-aroylpyrazol-5-ones.[16] This is mainly due to the different acidity of the chelating extractants, the equilibrium constant values increase as the pK$_a$ value decreases.[9,17] The comparison of $K_{L,S}$ values obtained for

Table 1. Values of the equilibrium constants K_L, $K_{L,S}$ and $_{L,S}$ for the Ln^{3+} extraction with HL–S mixtures in C$_6$H$_6$.

Ln^{3+}	logK_L	log$K_{L,S}$			log$\beta_{L,S}$		
		HL–TPPO	HL–TBPO	HL–TOPO	HL–TPPO	HL–TBPO	HL–TOPO
La	–6.40	0.92	–0.36	1.82	7.32	6.04	8.22
Ce	–5.59	1.09	0.32	2.57	6.68	5.91	8.16
Pr	–5.17	1.35	0.58	2.92	6.52	5.75	8.09
Nd	–4.76	1.63	1.02	3.12	6.39	5.78	7.88
Sm	–4.36	2.14	1.35	3.33	3.50	5.71	7.69
Eu	–4.06	2.34	1.62	3.50	6.40	5.68	7.56
Gd	–3.75	2.52	1.97	3.76	6.27	5.72	7.51

Note: The values of the equilibrium constants are calculated on the basis of the 39 experimental points, statistical confidence 95 % and standard deviation ≤ ± 0.05.

HL–TPPO, HL–TBPO and HL–TOPO combinations shows that the stability of the complexes involving TOPO is higher that those involving TBPO or TPPO. A steric hindrance caused by the three phenyl groups would result in the lower stability for LnL_3 TPPO adducts. The change of the synergist causes a significant increase of the $K_{L,S}$ values in the order TBPO < TPPO < TOPO.

The synergistic enhancement obtained for the combination of two extractants can be evaluated calculating the synergistic coefficients (SC) as: $SC = \log(D_{1,2}/D_1 + D_2)$ where $D_{1,2}$, D_1 and D_2 denote the distribution ratio of a metal ion using mixture of extractants ($D_{1,2}$) and the same extractants separately (D_1 and D_2). The values of the synergistic coefficients of the lanthanoid ions for TPPO, TBPO and TOPO used as synergistic agent in combination with 4,4,4-trifluoro-1-(biphenyl-4-yl)butane-1,3-dione are given in Table 2.

Table 2. Values of the synergistic coefficients ($[HL] = 1 \times 10^{-2}$ mol dm^{-3}, $[S] = 5 \times 10^{-3}$ mol dm^{-3}) and separation factors for the Ln^{3+} extraction with mixtures of HL–S in C_6H_6.

Ln^{3+}	S.C.			S.F.			
	HL–TPPO	HL–TBPO	HL–TOPO	HL	HL–TPPO	HL–TBPO	HL–TOPO
La	5.02	1.44	3.62	6.45	1.47	4.78	5.62
Ce	4.38	1.31	3.56	2.63	1.82	1.82	2.23
Pr	4.22	1.15	3.49	2.57	1.90	2.75	1.58
Nd	4.09	1.18	3.28	2.51	3.23	2.13	1.62
Sm	3.80	0.71	3.69	1.99	1.58	1.86	1.47
Eu	4.10	1.08	2.96	2.04	1.51	2.23	1.82
Gd	3.97	1.12	2.91				

It is seen that all Ln(III) ions are extracted synergistically (SC > 0). The addition of S to the chelating extractant improves the extraction efficiency of the Ln(III) ions and produces rather large synergistic effects. The synergistic enhancement decreases from La to Gd for the three phosphine oxides and for a particular lanthanoid ion is larger when TPPO is used as synergistic agent. The last observation is due to the different type of extracted complexes with TPPO. The SC established in the present study are higher (2–8 times) as compared to those found by Atanassova and Dukov in previous investigations dealing with Ln(III) extraction with HP–DB24C8(DB18C6) (HP: 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one),[18] HP(HTTA)–1-(2-pyridylazo)-2-naphtol.[19] The obtained SC values for the system HL–TBPO are approximately the same as those found for the systems HTTA–DPSO (diphenylsulfoxide)[17] and HTTA–phosphorus-containing calix[4]arene.[20] The obtained synergistic effect of TOPO was much greater that that of TBP when complexes EuL_3S_2 have been extracted with five β-diketonate (L: furoyltrifluoroacetone, pivaloyltrifluoroacetone, thenoyltrifluoroacetone, benzoyltrifluoroacetone, heptafluorobutanoylpivaloylmethane).[21]

The separation factors (SF) between the light Ln(III) ions, defined as a ratio of the respective equilibrium constants ($K_{L,S(Z+1)}/K_{L,S(Z)}$) are listed in Table 2. It is generally believed that the synergistic extraction makes the separation of metals worse, compared with the extraction with a chelating ligand only. Such an inclination that the addition of a synergist causes the lowering of separation efficiency is often seen in the synergistic extraction systems. The obtained SF values are higher for the three used systems. The system HL–TPPO exhibits separation for the pair Pr/La which is 3.2, 3.6 and 4.5 times smaller than that when mixtures of HL–TBPO, HPMTFP–TOPO[16] (1-phenyl-3-methyl-4-(trifluoroacetyl)-5-pyrazolone) and HL–TOPO are applied. Akaiwa was also mentioned[22] that the main factors controlling the selectivity in the synergistic extraction are the basicity of the synergist and its structure. The data for the metal separation of the same pair (Pr/La) calculated for the system HL–TOPO is analogous with that obtained by Freiser and Umetani[15] when these metals have been extracted with the mixture HPMTFP–CMPO (octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide) into $CHCl_3$.The calculated SF value of the pair Eu/Nd for the system HL–TBPO (3.98) is approximately the same as those obtained when combinations of HP–phosphorus-containing calix[4]arene[23] and H2SbBP–TOPO[24] or H2SbBP–CMPO[24] (H2SbBP, 4-acylbis(pyrazolones)) were used. In addition this value is 2 times higher that those when mixture HTTA–TPPO[12] was used.

So, the addition of a neutral organophosphorous extractant to the Ln^{3+}–chelate system improves both the extraction efficiency and selectivity among the light Ln(III) ions. The donor ability of the phosphoryl oxygen is the key parameter that determines the increase extraction of lanthanoids with β-diketones in the presence of neutral oxo-donors. [24]

4. Conclusions

The light trivalent ions of the metals of the lanthanoid series were extracted with binary mixtures of a chelating extractant 4,4,4-trifluoro-1-(biphenyl-4-yl)butane-1,3-dione (HL) in combination with phosphine oxides (S

= TBPO, TOPO or TPPO) in C_6H_6. The composition of the extracted species was established as LnL_3, $LnL_3 \cdot 2S$ (TOPO and TBPO) and $LnL_3 \cdot S$ (TPPO). The addition of a synergist to the chelating extractant improves the extraction efficiency of the lanthanoid ions and produces rather large synergistic effect (10^3–10^4). The SF between the adjacent metals are higher for the four systems used.

5. References

1. J. G. Cunningham, D. Scargill, H. H. Willis, Harwell, UKAEA-Research group. AERE-C/M, **1954**, 215.
2. C. A. Blake, C. F. Baes, K. B. Brown, C. F. Coleman, J. C. White, Proc. Intern. Conf. on the Peaceful Uses of Atomic Energy, Geneva, 1958, vol. *28*, IAEA, Vienna, **1959**, 289.
3. K. Binnemans, Rare earth beta-diketonates. In: Handbook on the physics and chemistry of rare earths, vol. *35*, Chapter 225. Eds.Elsevier Science B. V., Amsterdam, **2005**, 107–272.
4. K. Akiba, M. Wada, T. Kanno, *J. Inorg. Nucl. Chem.,* **1981**, *43*, 1031–1034.
5. H. Irving, D. N. Edgington, *J. Inorg. Nucl. Chem.*, **1961**, *21*, 169–180.
6. K. S. R. Murthy, R. J. Krupadam, Y. Aujaneyuly, *Proc. Indian Acad. Sci., Chem. Sci.*, **1998**, *110*(2), 83–92.
7. D. I. T. Favaro, L. T. Atalta, *J. Radioanal. Nucl. Chem. Art*, **1987**, *111*(1), 81–94.
8. H. F. Aly, S. M. Khalifa, N. Zakareia, *Solvent Extr. Ion Exch.,* **1984**, *2*(6), 887–898.
9. K. Sasayama, S. Umetani, M. Matsui, *Anal. Chim. Acta*, **1983**, *149*, 253–258.
10. L. Claisen, A. Claperede, *Ber.* **1881**, *14*, 2460–2468.
11. S. B. Savvin, Arsenazo III. Atomizdat, Moskva, **1966**, 177.
12. J. N. Mathur, S. A. Pai, P. K. Khopkar, M. S. Sumramanian, *J. Inorg. Nucl. Chem.,* **1977**, *39*,653–657.
13. A. T. Kandil, K. Farah, *J Inorg. Nucl. Chem.*, **1980,** *42*, 1491–1494.
14. M. Caceci, G. R. Choppin, Q. Lin, *Solvent Extr. Ion Exch.,* **1985**, *3*(5), 605–621
15. H. Freiser, S. Umetani, *Inorg. Chem.*, **1987**, *26*, 3179–3181.
16. H. Mukai, S. Umetani, Matsui M, *Solvent Extr. Ion Exch.*, **2003**, *21*(1), 73–90.
17. M. Atanassova, I. Dukov, *J. Solut. Chem.*, **2009**, *38*, 289–301.
18. I. L. Dukov, M. Atanassova, *Acta Chim. Slov.,* **2006**, *53*, 457–463.
19. I. L. Dukov, M. Atanassova, *Sep. Purif. Technol.*, **2006**, *49*, 101–105.
20. M. Atanassova, V. Lachkova, N. Vassilev, B. Shivachev, S. Varbanov, I. Dukov, *Polyhedron,* **2008**, 27, 3306–3312.
21. T. Taketatsu, *Anal. Chim. Acta*, **1985**, *174*, 323–326.
22. H. Akaiwa, Int Solv Extr Conf (ISEC'90), July 16–21, Kyoto, Japan (Eds. T. Sekine), 1990, Elsevier Science Publ., **1992**, 441–449.
23. M. Atanassova, V. Lachkova, N. Vassilev, S. Varbanov, I. Dukov, *J. Inclus. Phenom. Macroc. Chem.,* **2007**, *58*, 173–179.
24. R. Pavithran, M. L. P. Reddy, *Anal. Chim. Acta*, **2005**, *536,* 219–226.

Povzetek

Sintetizirali smo 4,4,4-trifluoro-1-(bifenil-4-il)butan-1,3-dion (HL) in raziskali njegove lastnosti kompleksiranja v raztopinah. Študirali smo ekstrakcijo mešanih kelatnih ligandov lahkih trivalentnih lantanoidov (La÷Gd) iz kloridnega medija pri konstantni ionski moči $\mu = 0.1$ v C_6H_6 s HL v kombinaciji s trioktilfosfin oksidom (TOPO), tributilfosfin oksidom (TBPO) ali trifenilfosfin oksidom (TPPO) (S). Sestava ekstrahiranih zvrsti je bila LnL_3, ko smo uporabili samo HL; $LnL_3 \cdot 2S$, ko smo uporabili HL v kombinaciji s TOPO in TBPO in $LnL_3 \cdot S$ v kombinaciji s TPPO. Izračunali smo 28 konstant ravnotežja. Pri ekstrakciji lantanoidnih ionov z mešanicami reagentov je prišlo do pojava sinergije z vrednostmi do 10^3–10^4. Vrednosti konstante $K_{L,S}$ naraščajo v smeri TBPO < TPPO < TOPO. Določili smo parametre procesa ekstrakcije in izračunali separacijske faktorje za lahke Ln(III) ione.