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Scientific paper

Synergistic Solvent Extraction of Lanthanides(III) with Mixtures of 4-Benzoyl-3-Methyl-1-Phenyl-5-Pyrazolone and Phosphoryl-Containing Podands

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Abstract

The solvent extraction of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu from weak acidic chloride solutions into an organic phase containing 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (HP) and phosphoryl-containing podands (L) has been studied. A considerable synergistic effect was observed in the presence of neutral ligands L in the organic phase containing HP. The stoichiometry of the Ln(III) extracted species was determined by slope analysis and the equilibrium constants were calculated. It was found that the lanthanide(III) ions are extracted with mixtures of HP and neutral ligands in toluene from weak acidic solutions as $LnLP_3$ complexes.

Keywords: Lanthanides(III); synergistic extraction; 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone; phosphoryl-containing podands.

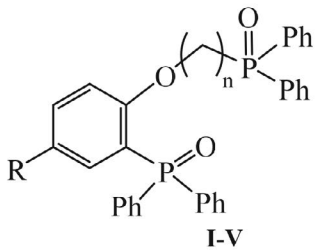
1. Introduction

Solvent extraction is a widely used technique for the separation and preconcentration of lanthanide(III) ions. A synergistic effect, a non-additive increase in the distribution ratios of metal ions, is often used to increase the efficiency of the extraction of metal ions.[1–3] The synergistic effect in solvent extraction systems is due to an increase in the hydrophobicity of extracted species as a result of replacement of water molecules bound to the metal ion by molecules of a synergistic compound.[3] The application of mixtures of an acidic chelating extractant and a neutral donor is one of the most thouroughly studied synergistic extraction processes. During the last few decades, the synergistic extraction of lanthanides(III) with mixtures of acidic chelating extractants such as β-diketones, 4-acylpyrazolones, 4-acyl-5-izoxazolone, etc. and neutral donor extractants (*e.g.* nitrogen-containing compounds,[4–6] sulfoxides,[7,8] crown ethers,[3,9–11] diglycolamides,[12] neutral mono- and polydentate organophosphorus compounds,[13–20] *etc.*) has been studied. Many studies have been carried out using phosphorus-containing calix[*n*]arenes as a synergistic agent at the Ln(III) extraction with various acidic chelating extractants of β-diketone type.[21–26] The introduction of P(O) functional groups in the calixarene architecture leads to a significant increase in the extraction efficiency.[26] The addition of phosphorus-containing calix[6]arene to the chelating extractant, 4-benzoyl-3-

methyl-1-phenyl-5-pyrazolone, improves the Ln(III) extraction and produces very large synergistic effects (more than five orders of magnitude).[25]

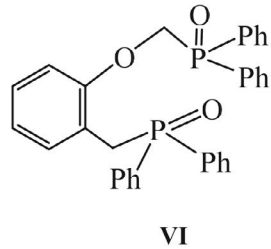
Recently, a great interest has arisen in the use of acyclic analogues of crown ethers (podands), as extractants. The complexation ability of a linear polyether ligand can be markedly increased by replacing its terminal alkyl groups with amide or phosphoryl groups.[27,28] Phosphoryl-containing podands have high extraction abilities for metal ions due to the ability of flexible podand molecules to acquire pseudo-macrocyclic conformation upon complexation.[29] The main factors determining the efficiency of metal ion extraction with phosphoryl-containing podands are the donor ability of phosphoryl oxygen atoms, the length of the polyether chain, and the nature of the moiety linking it to the phosphoryl group.[30]

In this work, we study the effect of structure of phosphoryl-containing podands **I-VII** on the extraction of Ln(III) ions with 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (HP) in organic diluents and determine the composition of the extracted complexes of Ln(III). The extraction behavior of the above ligands is compared with that of 2-(2-(diphenylphosphoryl)phenoxy)-N,N-dioctylacetamide **VIII** and monodentate neutral extractant, triphenylphospine oxide (TPhPO).[31] The structural formulae of the extractants studied are given below.

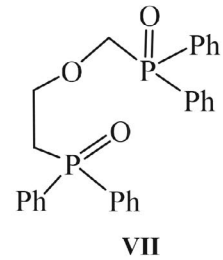


I-V

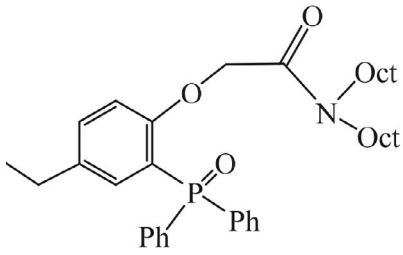
I: R = H, n = 0; **II**: R = H, n = 1;
III: R = Et, n = 1; **IV**: R = Et, n = 2;
V: R = H, n = 3



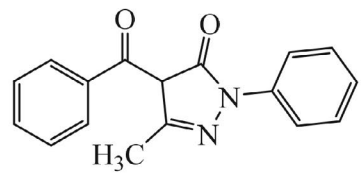
VI



VII



VIII



HP

2. Experimental

2. 1. Materials and Methods

The commercial products triphenylphosphine oxide (purity > 99%, Chemapol) and 4-benzoyl-3-methyl-1-phenyl-5-pyrazone (purity > 99%, Vekton) were used as received. Chemical- and analytical-grade chloroform, 1,2-dichloroethane and toluene were used as diluents. (2-((Diphenylphosphoryl)methoxy)phenyl)diphenylphosphine oxide (**II**), (2-((diphenylphosphoryl)-4-ethylphenoxy)methyl)diphenylphosphine oxide (**III**), (2-(2-(diphenylphosphoryl)-4-ethylphenoxy)ethyl)diphenylphosphine oxide (**IV**), (2-(3-(diphenylphosphoryl) propoxy)phenyl)diphenylphosphine oxide (**V**) and ((2-(diphenylphosphoryl)ethoxy)methyl)diphenylphosphine oxide (**VII**) were synthesized as described.[33–35] Their physical constants and data on elemental analysis and NMR spectra were in agreement with the published data.

2. 2. Synthesis of the Extragents

2-(Diphenylphosphoryl)phenyldiphenylphosphinate (I). A mixture of 6.40 g (21.74 mmol) of (2-hydroxyphenyl)diphenylphosphine oxide,[32] 1.69 g (21.74 mmol) of dry pyridine, 5.12 g (21.74 mmol) of diphenylphosphinic chloride and 50 mL of dry benzene was mixed on magnetic stirrer at the temperature of 80 °C for 6 h. Then the reaction mixture was poured into water, extracted by benzene (4 × 30 mL), the organic extracts were rinsed with 20% HCl solution (3 × 30 mL), water (3 × 30 mL), dried by $MgSO_4$. After evaporation, the residue was crystallized from benzene` – hexane mixture. The yield of **I** was 7.23 g (69%), m.p. 175–177 °C. Anal. Calcd. for $C_{30}H_{24}O_3P_2$ (%): C, 72.87; H, 4.89; P 12.53. Found (%): C, 72.93; H, 4.90; P, 12.56. ^{1}H NMR ($CDCl_3$): δ: 7.01–7.28 (2H, m, Ar-*H*), 7.33–7.56 (12H, m, Ar-*H*), 7.63–7.90 (10H, m, Ar-*H*). ^{31}P

NMR ($CDCl_3$): δ: 28.72, 32.25.

(2-((diphenylphosphoryl)methoxy)benzyl)diphenylphosphine oxide (VI). A mixture of 3.22 g (10.00 mmol) 2-(hydroxybenzyl)diphenylphosphine oxide 3.86 g (10.00 mmol) (diphenylphosphoryl)methyl-4-methylbenzenesulphonate and 2.26 g (10.00 mmol) anhydrous cesium carbonate in 35 mL of dry dioxane was heated and stirred at 100 °C for 8 h.[36] The reaction mixture was diluted by 75 mL of water, acidified by adding concentrated HCl to pH 1, and extracted by $CHCl_3$ (3 × 25 mL). The organic layer was separated, washed with water, and evaporated under reduced pressure to give crude product **VI.** It was purified by column chromatography on silica gel 100–160 mm, the eluents $CHCl_3$ and $CHCl_3$/*i*-PrOH (10:1). The yield of **VI** was 4.04 g (77 %), m.p. 168–169.5 °C. Anal. Calcd. for $C_{32}H_{28}O_3P_2$ (%): C, 73.56; H, 5.40; P 11.86. Found (%): C, 73.40; H, 5.34; P, 11.69. ^{1}H NMR ($CDCl_3$): δ: 3. 81 (2H, d, $^2J_{H-P}$ = 7.10 Hz, ArCH_2P), 4.49 (2H, d, $^2J_{H-P}$ = 5.18 Hz, OCH_2P(O), 7.00–7.32 (2H, m, Ar-*H*), 7.35–7.56 (12H, m, Ar-*H*), 7.61–7.92 (10H, m, Ar-*H*). ^{31}P NMR ($CDCl_3$): δ: 28.15, 32.15.

2. 3. Apparatus

An X-7 mass spectrometer with a quadrupole mass analyzer (Thermo Electron, USA) was used for measurement of lanthanides concentration and pH-150 digital pH meter was used for pH measurements. The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker DXP-200 spectrometer with Fourier transform using tetramethylsilane (^{1}H, internal) and 85% H_3PO_4 (^{31}P, external) as standard. Elemental analyses were performed using a Perkin-Elmer 240C analytical instrument.

2. 4. Solvent Extraction Procedure

Stock solutions of the lanthanide(III) ions were prepared from their oxides by dissolving in concentrated hydrochloric acids and diluting with deinonized water to the required volume. All the lanthanides (III) (except Pm) were present in the initial aqueous phase when simultaneous extraction of Ln(III) was studied. The ionic strength was maintained at 0.1 M with NaCl and HCl. The initial lanthanide ions concentration was 2×10^{-6} M for each element. Extractant solutions in the organic diluents were prepared from precisely weighed amounts of the reagents.

Equal volumes (2 mL) of the aqueous and organic phases were shaken mechanically for 60 min at 22 ± 1 °C, which was sufficient to reach equilibrium. After phase separation, 1 mL of the aqueous solution was taken for further analysis. A portion of the organic phase was transferred to another glass tube, and a specific volume of 1 M HCl solution was added. The mixture was shaken for 30 min and Ln(III) in the organic phase was extracted back into the aqueous phase.

Concentrations of Ln(III) in the initial and equilibrium aqueous solutions after extraction and back-extraction were determined by inductively coupled plasma mass-spectrometry (ICP-MS). The sum of the metal ion concentrations in the two phases agreed well with the initial concentration. The distribution ratios of lanthanides (D_{Ln}) were calculated as the ratio of concentrations in the equilibrium organic and aqueous phases. Triplicate experiments showed that the reproducibility of the D_{Ln} measurements was generally within 5%. The acidity of the aqueous phase was measured by a pH-meter with an accuracy of 0.01 pH units.

3. Results and Discussion

3. 1. Extraction of Lanthanide(III) Ions with Mixtures of HP and Neutral Ligands I–VIII

There have been many reports on solvent extraction of lanthanide(III) ions with 4-acylpyrazolones.[37] The lanthanides(III) extraction with 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (HP) alone in organic diluents was previously studied by Dukov et al.[38,39] They found that the metal ions are extracted as self-adducts LnP_3HP and their extraction can be described by the equation:

$$Ln^{3+}_{(aq)} + 4HP_{(org)} \rightleftharpoons LnP_3HP_{(org)} + 3H^+_{(aq)} \qquad (1),$$

where the subscripts "aq" and "org" denote the aqueous and organic phases, respectively.

The corresponding extraction constant K_P is

$$K_P = D_{Ln}\,[H^+]^3_{(aq)}[HP]^{-4}_{(org)} \qquad (2)$$

Preliminary experiments showed that the lanthanides(III) extraction with compounds **I**–**VII** and TPhPO alone is negligible under the experimental conditions of the present study. However, a considerable enhancement of the Ln(III) extraction with HP in the presence of these compounds in the organic phase was observed.

To compare the extraction efficiency of neutral donor compounds, a simultaneous extraction of Ln(III) ions from aqueous solutions with mixtures of HP and compounds **I**–**VIII** and TPhPO in 1,2-dichloroethane was studied (Figure 1). These experiments showed that the efficiency of Ln(III) synergistic extraction with compounds of phosphine oxide type (**II**–**VII**) is higher than that of compound **I** of phosphinate type. This can be due a weakening donor ability of P(O) group of compound **I** as compared with compounds **II**–**VII**. The efficiency of Ln(III) synergistic extraction with compounds **II**–**VII** is higher than that of monodentate TPhPO (Figure 1). Therefore, an increase of a number of P(O) groups in the compounds **II**–**VII** molecule leads to an increase in the D_{Ln} values.

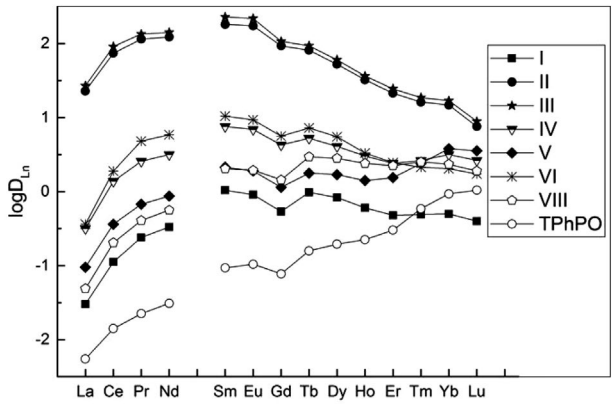


Figure 1. The extraction of lanthanides(III) with HP–compounds **I**–**VIII** and TPhPO mixtures in 1,2-dichloroethane at [HP] = 0.02 M, [L] = 0.005 M and pH = 2.0.

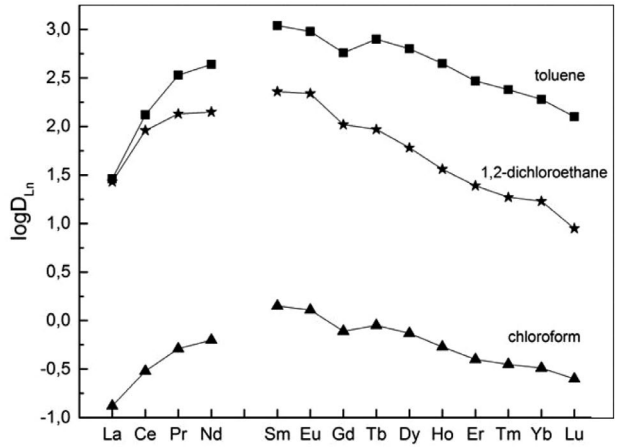


Figure 2. The extraction of lanthanides(III) with HP–compound **III** mixtures in toluene, 1,2-dichloroethane and chloroform at [HP] = 0.02 M, [L] = 0.005 M and pH = 2.0.

The data in Figure 1 suggest that mixtures containing compounds **II** or **III** exhibit the highest synergistic effect. The introduction of ethyl group into the *o*-phenylene fragment of compound **II** is not appreciably influence on the Ln(III) extraction with compound **III**, though is accompanied by an increase of compound **III** hydophobicity. The replacement of $P(O)Ph_2$ group in the molecule of compound **III** by $C(O)NOct_2$ one leads to a decrease of Ln(III) extraction with compound **VIII,** which suggests that the P(O) group has a higher complexation ability than the C(O) group. The replacement of the *o*-phenylene fragment in the compound **II** molecule by a dimethylene one causes a decrease of Ln(III) extraction with compound **VII**. A higher extraction efficiency of compound **II** as compared with that of podand **VII** was explained both by the delocalization of the electron density from the phenylene group to the metal-connected chelate cycle and an increase in the conformational rigidity of compound **II** molecule, which facilitates the formation of a more stable Ln(III) complex.[28] An increase in alkylene bridge between P(O) group and ether oxygen atom (compounds **IV** and **V**) as well as an increase in the distance between the phosphoryl group and the *o*-phenylene fragment (compound **VI**) violates the conditions favorable for the formation of chelate cycles and thus leads to a decrease of the Ln(III) extraction with mixtures of HP and compounds **IV**–**VI** (Figure 1).

It should be noted that the difference in the synergistic efficiency of compounds **II** or **III** and other studied compounds decreases from La(III) to Lu(III), i.e. with an increase of their atomic number (Z). Thus, the ratio D_{Ln}(**I-II**)/D_{Ln}(**VIII**) decreases in the lanthanide series from 467 for La(III) to 4.0 for Lu(III) and the ratio D_{Ln}(**II**)/D_{Ln}(**VII**) decreases from 57 for La(III) to 1.6 for Lu(III). Evidently, the synergistic extraction of light Ln(III) ions is most sensitive to changes in the neutral synergistic structure.

The effect of an organic diluent on the synergistic extraction of Ln(III) ions with mixtures of HP and compound **III** was also studied. The data in Figure 2 show that the extraction efficiency increased in the order: chloroform < 1,2-dichloroethane < toluene. The same tendency was observed at the metal ions extraction with mixtures of acidic chelating extractants and neutral donor compounds.[40]

3. 2. Extraction of Lanthanide(III) Ions with Mixtures of HP and Neutral Ligand III in Toluene

In the extraction systems with compound **III** and HP, the plots of log D_{Ln} vs. pH exhibited a series of straight lines with slopes close to three (Figure 3), which means that three H^+ ions were released in the extraction reaction.

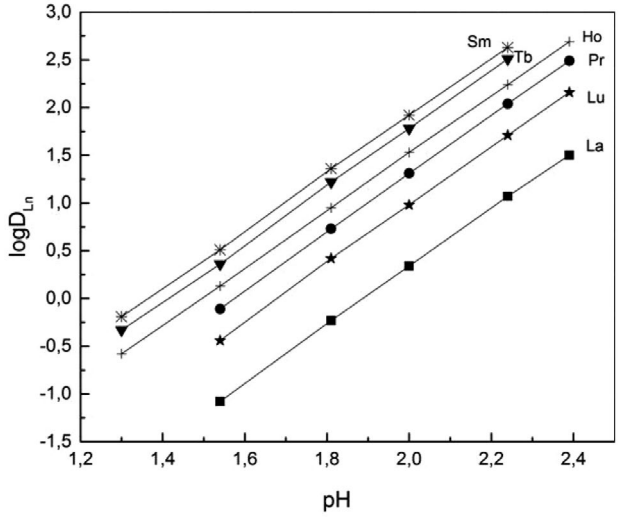


Figure 3. The effect of pH on the extraction of Ln(III) with the mixture of 0.001 M compound **III** and 0.01 M HP in toluene.

The stoichiometry of the Ln(III) extracted complexes in HP–**III** systems was determined by slope analysis. The plots of log D_{Ln} *vs.* log [HP] at a constant pH and neu-

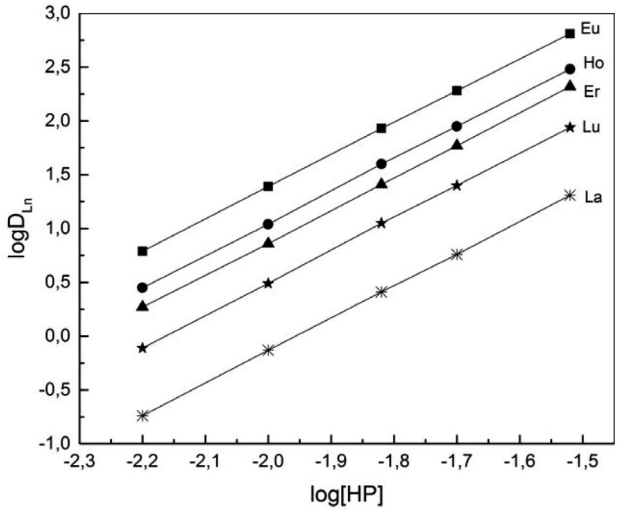


Figure 4. The effect of HP concentration in toluene containing 0.001 M compound **III** on the extraction of lanthanides(III) at pH = 2.0.

tral ligand **III** concentration in the organic phase are straight lines with slopes close to three (Figure 4).

As the Ln(III) extraction from aqueous solutions with compound III and HP alone is negligible (log D_{Ln} < –2) at pH = 2, the values of D_{Ln} obtained experimentally are equal to the distribution ratios due to the synergistic effect. Therefore, the synergistic extraction of Ln(III) ions can be described by the equation:

$$Ln^{3+}_{(aq)} + 3HP_{(org)} + sL_{(org)} \rightleftharpoons LnP_3L_{s(org)} + 3H^+_{(aq)} \quad (3),$$

where s is the metal:L stoichiometric ratio.

The variation of D_{Ln} as a function of the compound **III** concentration in toluene containing HP is shown in Figure 5.

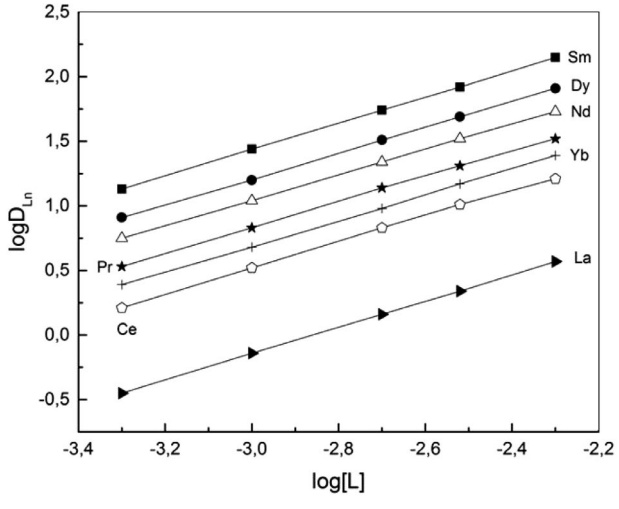


Figure 5. The effect of compound **III** concentration in toluene containing 0.01 M HP on the extraction of lanthanides(III) at pH = 2.0.

The dependence of logD_{Ln} vs. log[L] is linear with a slope of 1 ± 0.02. Hence, one molecule of neutral donor compound **III** is involved in the formation of synergistic Ln(III) complexes. The same stoichiometry of the Ln(III) extracted complexes was observed at the extraction with mixtures of HP and phosphorus-containing calix[6] arene.[31] On the other hand, in the HP – trioctylphosphine oxide (TOPO) system, the formation of LnP_3TOPO complexes at lower TOPO concentrations and $LnP_3(TOPO)_2$ at higher TOPO concentrations was observed.[13]

Assuming that the partition of HP and compound **III** towards aqueous phase is very low and the polymerization in the organic phase as well as the hydrolysis in the aqueous phase occur only to a negligible extent,[37,34] the overall equilibrium constant values $K_{P,L}$ can be determined by the equation:

$$\log K_{P,L} = \log D_{Ln} - 3\log[HP]_{(org)} - \log[L]_{(org)} - 3\,pH \quad (4)$$

The formation of synergistic adducts in the organic phase can be described by the equation:

$$LnP_3HP_{(org)} + L_{(org)} \rightleftharpoons LnP_3L_{(org)} + HP_{(org)} \quad (5)$$

The equilibrium constant $\beta_{P,L}$ for the adducts formation in the organic phase can calculated using the expression:

$$\log \beta_{P,L} = \log K_{P,L} - \log K_P \quad (6)$$

The values of K_P for the lanthanides(III) extraction with HP alone in toluene were obtained in the previous work.[20] The values of the equilibrium constants $K_{P,L}$ and $\beta_{P,L}$ were calculated from the experimental data and are presented in Table 1.Note that these constants are concentration only because they were calculated on the assumption that the activity coefficients of the species involved do not change significantly under the experimental conditions of the present work.

The data presented in Table 1 show that the addition of neutral donor ligand **III** to the system Ln(III)–HP leads to a very large increase of the efficiency of Ln(III) extraction. The synergistic enhancement produced by mixtures of HP and the studied neutral donor extractant can be determined using a synergistic coefficient SC = $D_{L,HP}/(D_L + D_{HP})$, where D_L, D_{HP} and $D_{L,HP}$ are the distribution ratios of the Ln(III) ion with the two extractants taken separately and with their mixture. The values of SC for Ln(III) extraction with mixtures of HP and compound **III** is determined by the stability of Ln(III) adducts and dependent on the concentration of HP and compound **III** in organic phase:

$$\log SC = \log \beta_{P,L} + \log[L]_{(org)} - \log[HP]_{(org)} \quad (7)$$

The data presented in Table 1 show that the extraction ability of HP alone for lanthanide(III) ions increases

Table 1. Values of the equilibrium constants K_P, $K_{P,L}$, log $\beta_{HP,L}$ as well as values of synergistic coefficients SC for Ln(III) extraction with HP-compound **III** mixtures in toluene.

Ln(III)	log K_P [20]	log $K_{P,L}$	log $\beta_{P,L}$	log SC [a)]
La	−5.56 ± 0.03	2.86 ± 0.03	8.42 ± 0.06	8.12
Ce	−4.83 ± 0.03	3.51 ± 0.02	8.34 ± 0.05	8.04
Pr	−4.36 ± 0.03	3.91 ± 0.03	8.27 ± 0.06	7.97
Nd	−4.08 ± 0.04	4.03 ± 0.02	8.11 ± 0.06	7.81
Sm	−3.48 ± 0.03	4.43 ± 0.02	7.91 ± 0.05	7.61
Eu	−3.35 ± 0.03	4.37 ± 0.02	7.72 ± 0.05	7.42
Gd	−3.44 ± 0.04	4.15 ± 0.03	7.59 ± 0.07	7.29
Tb	−3.17 ± 0.03	4.29 ± 0.02	7.46 ± 0.05	7.16
Dy	−3.06 ± 0.04	4.19 ± 0.02	7.25 ± 0.06	6.95
Ho	−3.07 ± 0.03	4.04 ± 0.02	7.11 ± 0.05	6.81
Er	−2.94 ± 0.03	3.86 ± 0.03	6.80 ± 0.06	6.50
Tm	−2.67 ± 0.03	3.77 ± 0.02	6.44 ± 0.05	6.14
Yb	−2.43 ± 0.04	3.67 ± 0.03	6.10 ± 0.07	5.80
Lu	−2.46 ± 0.03	3.49 ± 0.02	5.95 ± 0.05	5.65

[a)] [HP] = 0.01 M, [**III**] = 0.005 M and pH = 2.0

with the increasing atomic number of lanthanides. This can be connected with an increase of the stability of Ln(III) complexes with hard ligands as the Ln^{3+} ions charge density increase owing to decrease of their ionic radii when Z rises. In the lanthanides series, the $K_{P,L}$ values increases from La(III) to Sm(III) and then non-monotonic decrease in $K_{P,L}$ values is observed due to tetrad effect upon the Ln(III) extraction.[41] The same character of the $K_{P,L}$–Z dependency was observed at the Ln(III) extraction with mixtures of HP and dibutyl-(*N,N*-dibutylcarbamoylmethoxy)phosphine oxide.[20]

The data presented in Table 1 show that the values of $\beta_{P,L}$ as well as SC decrease from La(III) to Lu(III). A similar tendency was observed for the adduct formation of LnP_3 with trioctylphospine oxide,[13] phosphorus-containing calix[6]arene and dibutyl-(*N,N*-dibutylcarbamoylmethoxy) phosphine oxide.[25,20] On the other hand, an increase of the β values from La(III) to Lu(III) was observed by Atanassova and Dukov in the HP–1-(2-pyridylazo)-2-naphtol synergistic system.[42]

4. Conclusions

Synergetic solvent extraction of lanthanide (III) ions with mixtures of 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone and neutral phosphoryl-containing podands has been studied. The structure of phosphoryl-containing podands has a considerable effect on their extraction efficiency. In combination with HP, compounds **II** and **III** exhibit the highest synergistic effect. A remarkably large synergistic effect (more than 5–8 order of magnitude) was observed for the Ln(III) ions extraction with mixtures of HP and **III** in toluene from weak acidic HCl solutions. This effect is associated with the replacement of HP in self-adducts LnP_3HP by neutral donor ligand **III**. The stoichiometry of the Ln(III) extracted complexes in the HP–**III** system was determined by slope analysis and the equilibrium constants were calculated.

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Povzetek

Proučevali smo ekstrakcijo La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, in Lu ionov iz šibko kisle raztopine s kloridnimi ioni v organsko fazo, ki vsebuje 4-benzoil-3-metil-1-fenil-5-pirazolon (HP) in fosforil-vsebujoče podande (L). Opažen je bil izrazit sinergistični efekt ob prisotnosti nevtralnega liganda L v organski fazi, ki vsebuje HP. Stehiometrijo Ln(III) ekstrahiranih zvrsti smo določili iz naklonskega kota premic v diagramih ter izračunali ravnotežno konstanto. Lantanidni(III) ioni se ekstrahirajo v toluen s prisotnima HP in nevtralnim ligandom iz šibko kisle raztopine kot $LnLP_3$ kompleksi.