

Synergistic Solvent Extraction of Trivalent Lanthanoids with Mixtures of 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone and Crown Ethers

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Abstract

The synergistic solvent extraction of 14 trivalent lanthanoids (except Pm) with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HP) and dibenzo-18-crown-6 (DB18C6) or dibenzo-24-crown-8 (DB24C8) in 1, 2-dichloroethane has been studied. It was found that in the presence of HP alone the lanthanoids have been extracted as $\text{LnP}_3\cdot\text{HP}$ and in the presence of mixtures of HP and crown ethers (S) – as $\text{LnP}_3\cdot\text{S}$. On the basis of the experimental data, the values of the equilibrium constants as well as the values of the synergistic coefficients and the separation factors have been calculated. The addition of crown ethers to the system Ln^{3+} – HP improves both the extraction efficiency and the selectivity among the lanthanoid(III) ions.

Keywords: synergistic solvent extraction, 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone, dibenzo-18-crown-6, dibenzo-24-crown-8, lanthanoids, separation factors.

1. Introduction

During the last years various crown ethers have been frequently used as synergistic agents in combination with β -diketones such as thenoyltrifluoroacetone, thiothenoyltrifluoroacetone, benzoylacetone, 4-acyl-5-pyrazolones¹⁻¹⁵ as well as with 4-acyl-5-isoxazolones¹⁶⁻¹⁸ for the extraction of lanthanoids and actinoids. Formation of mixed adducts containing one or two crown ether molecules have been reported. It was suggested that in the last case complexes of a sandwich type having one crown ether ligand on either side of the metal chelate have been extracted.⁴ It was also noted that the various 4-acyl-5-pyrazolones can extract the lanthanoids from relatively strong acidic solutions due to their lower pK_a values in comparison with thenoyltrifluoroacetone as well as that the complexation and extraction behaviour of the acylpyrazolones depend on the nature of the substituent in the fourth position.¹³

The reviews of Bond et al.^{19,20} have summarized much of the studies dealing with the synergistic extraction of metals using crown ethers as synergists. Unfortunately, the synergistic extraction of the lanthanoids of the whole series have been studied rarely. Kitatsuji et al.⁸ have studied the lanthanoids extraction with thenoyltrifluoroacetone and 18-crown-6 or dicyclohexano-18-crown-6 and Atanassova and Dukov¹⁵ have used a combination of thenoyltrifluoroacetone and dibenzo-18-crown-6 or dibenzo-24-crown-8.

The object of the present work is to study the synergistic solvent extraction and separation of the metals of the entire lanthanoid series (with exception of Pm) using 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HP) and dibenzo-18-crown-6 (DB18C6) or dibenzo-24-crown-8 (DB24C8) in 1, 2-dichloroethane.

2. Experimental

2.1. Reagents

1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (HP) (purity, >99%), dibenzo-18-crown-6 (DB18C6) and dibenzo-24-crown-8 (DB24C8) (purity, >98%) were obtained from Fluka, Switzerland and were used as received. The diluent was 1, 2-dichloroethane (Merck, p.a.). Arsenazo III (Fluka) was of analytical grade purity. All other chemicals used were of AR grade too.

2.2. Apparatus

A pH 211 HANNA digital pH-meter (USA) was used for the pH measurements and S-20 Spectrophotometer Boeco, (Germany) for spectrophotometric measurements.

2.3. Procedure

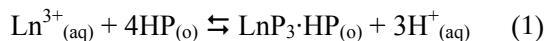
The experiments were carried out in stoppered glass vials containing 10 cm³ volumes of aqueous and organic phases. The samples were shaken for 45 minutes at $22 \pm 1^\circ\text{C}$ in a mechanical shaker. After the separation

of the phases, the metal concentration in the aqueous phase was determined spectrophotometrically using Arsenazo III [21]. The concentration of the metal ions in the organic phase was obtained by material balance. These concentrations were used to calculate the distribution coefficient, D , as a ratio of the metal content in the equilibrium organic and aqueous phases. The acidity of the aqueous phase was measured by a pH meter with an accuracy of 0.01 pH unit. 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/dm³ in all experiments.

3. Results and Discussion

3.1. Solvent extraction of Ln³⁺ ions with HP or crown ethers alone

The extraction behaviour of the lanthanoid ions using HP in 1,2-dichloroethane was studied as a function of pH and [HP]. The plots of $\log D_p$ (D_p is the distribution coefficient for the extraction with HP alone) vs. pH and $\log[HP]$ were linear with slopes 3 ± 0.10 and 4 ± 0.04 . (These plots are not shown in the figures.) The slope 3 observed in the plots of $\log D_p$ vs. pH indicates the release of three hydrogen ions by the interaction of one Ln³⁺ ion with four molecules HP (slope 4 in the plot of $\log D_p$ vs. $\log[HP]$). So, the extraction of Ln³⁺ ions can be described by equation:



The formation of self-adducts when acylpyrazolone is used as extractant has been reported by several authors^{4,5,22,23,26-28} but in other studies^{11,13,29,30} extraction of LnP₃ chelates has been found. The extraction complexes of different type could be due to the different experimental conditions as well as of the various acylpyrazolone derivatives used.

As the partition of HP towards the aqueous phase is very low²⁴, the relationship between the distribution coefficient D_p and the equilibrium constant K_p can be expressed as

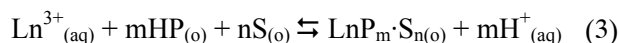
$$\log K_p = \log D_p - 4\log[HP] - 3\text{pH} \quad (2)$$

The values of the equilibrium constant K_p are given in Table 1. It is seen that they increase with decreasing radii of the Ln³⁺ ions. The increase in the extractability across the lanthanoid series can be due to the increase in electrostatic interaction between the cation and the ligand with decrease in the ionic radii.²⁵

The experimental data showed that the lanthanoids(III) extraction with both DB18C6 and DB24C8 alone is negligible under the experimental conditions of the present study.

3.2. Solvent extraction of Ln³⁺ ions with mixtures of HP and DB18C6 or DB24C8

The synergistic solvent extraction of Ln³⁺ ions with mixtures of HP and DB18C6 or DB24C8 (S) can be expressed by the equation:



It may be shown easily that

$$\log D_{p,S} = \log K_{p,S} + m\log[HP] + n\log[S] + mp\text{H} \quad (4)$$

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

As the lanthanoid extraction with the crown ethers is negligible under the experimental conditions of the present study, the values of the distribution coefficient D obtained experimentally is the sum of $D_{p,S}$ and D_p . So, the values of $D_{p,S}$ can be calculated as $D - D_p$.

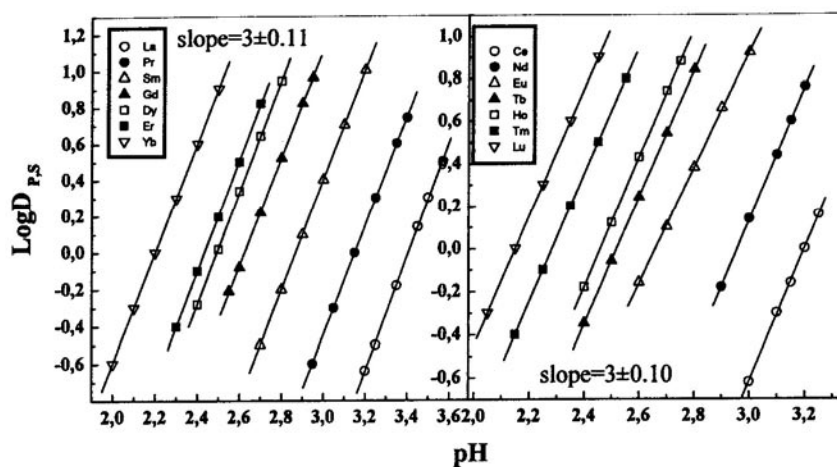


Figure 1. $\log D_{p,S}$ vs. pH for the extraction of lanthanoid(III) ions with HP – DB24C8 mixture at $[\text{HP}] = 3 \times 10^{-2}$ mol/dm³ and $[\text{DB24C8}] = 5 \times 10^{-3}$ mol/dm³.

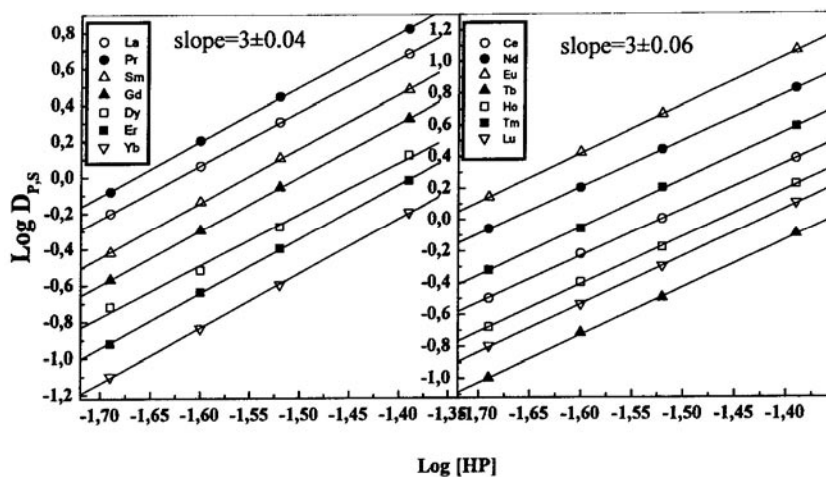


Figure 2. $\text{Log}D_{\text{PS}}$ vs. $\text{log}[\text{HP}]$ for the extraction of lanthanoid(III) ions with mixture HP – DB24C8 at $[\text{DB24C8}]=5 \times 10^{-3} \text{ mol/dm}^3$. (La, pH=3.50; Pr, pH=3.30; Sm, pH=2.90; Gd, pH=2.60; Dy, pH=2.40; Er, pH=2.30; Yb, pH=2.00; Ce, pH=3.20; Nd, pH=3.10; Eu, pH=2.90; Tb, pH=2.35; Ho, pH=2.40; Tm, pH=2.35; Lu, pH=2.05).

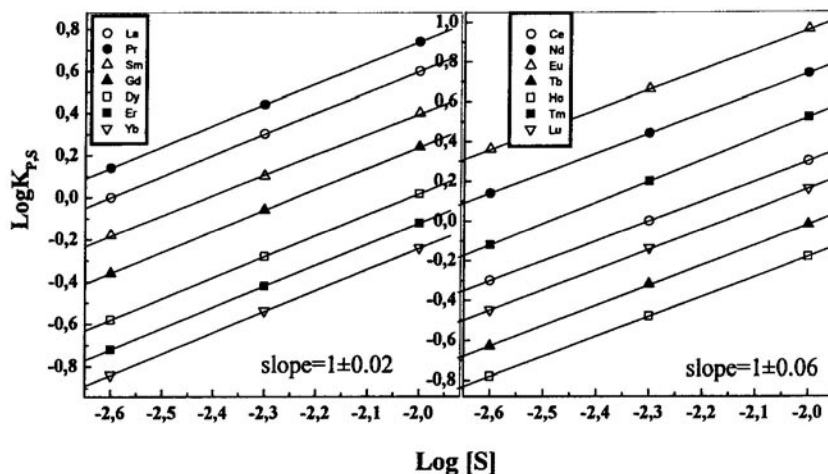


Figure 3. $\text{Log}K_{\text{PS}}$ vs. $\text{log}[\text{DB24C8}]$ for the extraction of lanthanoid(III) ions with HP – DB24C8 at $[\text{HP}]=3 \times 10^{-2} \text{ mol/dm}^3$. (La, pH=3.50; Pr, pH=3.30; Sm, pH=2.90; Gd, pH=2.60; Dy, pH=2.40; Er, pH=2.30; Yb, pH=2.10; Ce, pH=3.20; Nd, pH=3.10; Eu, pH=2.90; Tb, pH=2.40; Ho, pH=2.30; Tm, pH=2.35; Lu, pH=2.10).

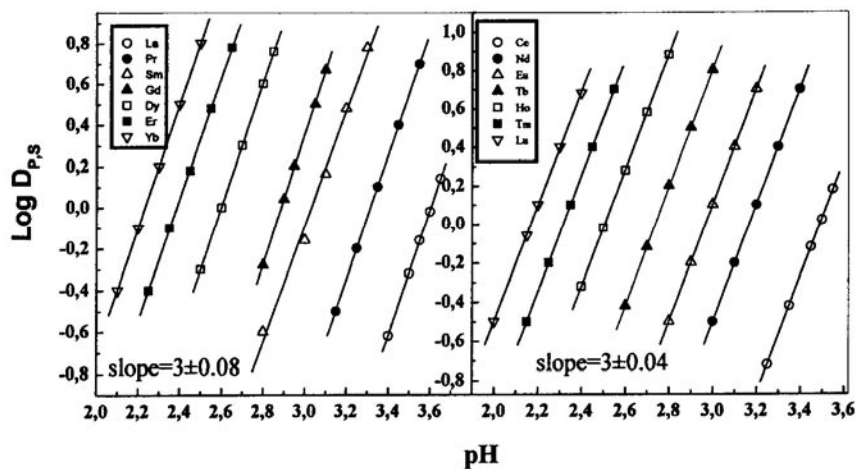


Figure 4. $\text{Log}D_{\text{PS}}$ vs. pH for the extraction of lanthanoid(III) ions with HP – DB18C6 mixture at $[\text{HP}]=3 \times 10^{-2} \text{ mol/dm}^3$ and $[\text{DB18C6}]=5 \times 10^{-3} \text{ mol/dm}^3$.

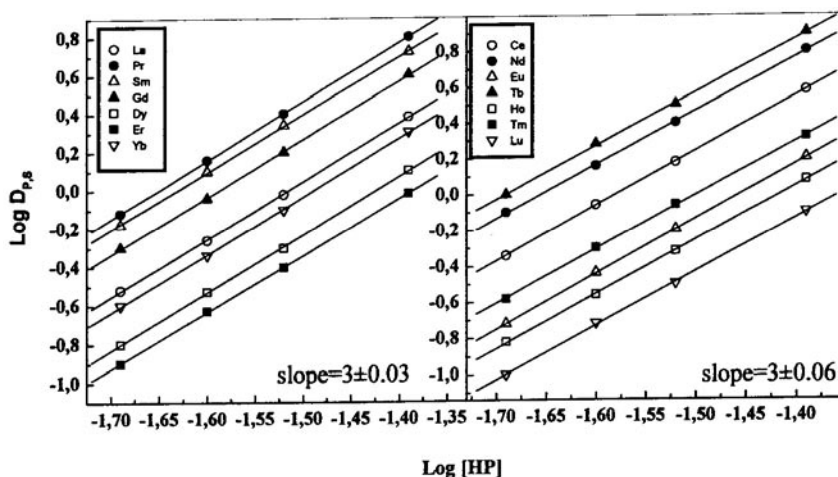


Figure 5. $\text{Log}D_{\text{PS}}$ vs. $\text{log}[\text{HP}]$ for the extraction of lanthanoid(III) ions with HP – DB18C6 mixture at $[\text{DB18C6}] = 5 \times 10^{-3} \text{ mol/dm}^3$. (La, $\text{pH} = 3.60$; Pr, $\text{pH} = 3.45$; Sm, $\text{pH} = 3.15$; Gd, $\text{pH} = 2.95$; Dy, $\text{pH} = 2.50$; Er, $\text{pH} = 2.25$; Yb, $\text{pH} = 2.20$; Ce, $\text{pH} = 3.55$; Nd, $\text{pH} = 3.30$; Eu, $\text{pH} = 2.90$; Tb, $\text{pH} = 2.90$; Ho, $\text{pH} = 2.40$; Tm, $\text{pH} = 2.30$; Lu, $\text{pH} = 2.00$).

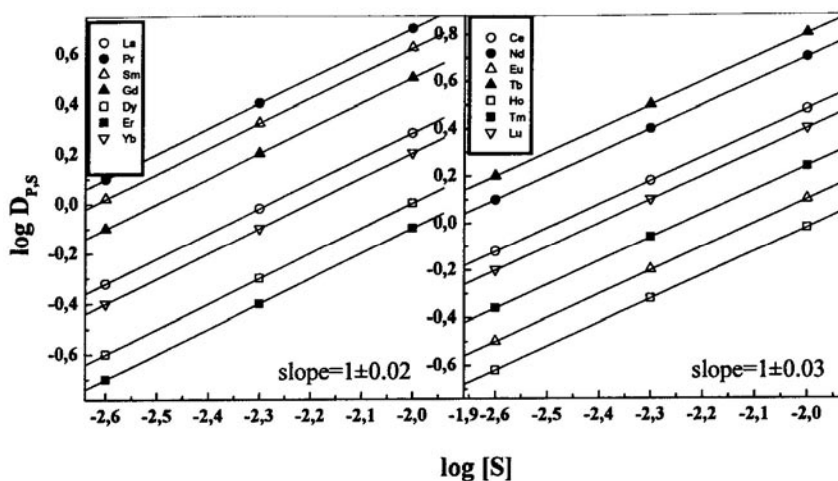
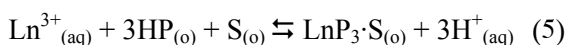


Figure 6. $\text{Log}D_{\text{PS}}$ vs. $\text{log}[\text{DB18C6}]$ for the extraction of lanthanoid(III) ions with HP – DB18C6 mixture at $[\text{HP}] = 3 \times 10^{-2} \text{ mol/dm}^3$. (La, $\text{pH} = 3.60$; Pr, $\text{pH} = 3.45$; Sm, $\text{pH} = 3.15$; Gd, $\text{pH} = 2.95$; Dy, $\text{pH} = 2.50$; Er, $\text{pH} = 2.25$; Yb, $\text{pH} = 2.20$; Ce, $\text{pH} = 3.55$; Nd, $\text{pH} = 3.30$; Eu, $\text{pH} = 2.90$; Tb, $\text{pH} = 2.90$; Ho, $\text{pH} = 2.40$; Tm, $\text{pH} = 2.30$; Lu, $\text{pH} = 2.20$).

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_{PS} vs. one of the variables $[\text{HP}]$, $[\text{DB18C6}]$ (DB24C8) and $[\text{H}^+]$ 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.

The experimental data for the extraction of the lanthanoids with mixtures of HP and DB18C6 or DB24C8 are shown in Figs. 1–6. The plots of $\text{log} D_{\text{PS}}$ vs. pH and $\text{log}[\text{HP}]$ are linear with slopes of 3 ± 0.11 and the plots of $\text{log} D_{\text{PS}}$ vs. $\text{log}[\text{S}]$ exhibit slopes equal to 1 ± 0.03 .

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



The overall equilibrium constant K_{PS} can be determined by the equation:

$$\text{log}K_{\text{P,S}} = \text{log}D_{\text{P,S}} - 3\text{log}[\text{HP}] - \text{log}[\text{S}] - 3\text{pH} \quad (6)$$

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



The equilibrium constant β_{PS} for the organic phase synergistic reaction can be determined as

$$\text{log}\beta_{\text{P,S}} = \text{log}K_{\text{P,S}} - \text{log}K_{\text{P}} \quad (8)$$

The values of $\text{log}K_{\text{PS}}$ and $\text{log}\beta_{\text{PS}}$ (along with the values of $\text{log}K_{\text{P}}$) are given in Table 1. The equilibrium constants are based on the assumption that the activity coefficients of the species do not change significantly under the experimental conditions.

Table 1. Values of the equilibrium constants K_p , K_{ps} and β_{ps} for the extraction of lanthanoid ions with HP – DB24C8 and HP – DB18C6 mixtures in 1,2-dichloroethane.

Ln ³⁺	logK _p	logK _{p,s}		logβ _{p,s}	
		DB24C8	DB18C6	DB24C8	DB18C6
La	-4.90± 0.02	-3.35± 0.03	-3.90± 0.03	1.55± 0.05	1.00± 0.05
Ce	-4.62± 0.02	-2.75± 0.04	-3.60± 0.04	1.87± 0.06	1.02± 0.06
Pr	-4.18± 0.02	-2.60± 0.04	-3.10± 0.03	1.58± 0.06	1.08± 0.05
Nd	-3.62± 0.02	-2.00± 0.02	-2.58± 0.03	1.62± 0.04	1.04± 0.05
Sm	-3.28± 0.02	-1.74± 0.02	-2.27± 0.04	1.54± 0.04	1.01± 0.06
Eu	-3.12± 0.02	-1.16± 0.02	-2.04± 0.02	1.96± 0.04	1.08± 0.04
Gd	-2.86± 0.04	-1.02± 0.02	-1.80± 0.04	1.84± 0.06	1.06± 0.08
Tb	-2.45± 0.04	-0.70± 0.03	-1.35± 0.03	1.76± 0.07	1.10± 0.07
Dy	-2.42± 0.02	-0.60± 0.03	-0.95± 0.03	1.82± 0.05	1.47± 0.05
Ho	-2.39± 0.02	-0.52± 0.04	-0.66± 0.02	1.86± 0.06	1.73± 0.04
Er	-2.35± 0.02	-0.43± 0.02	-0.30± 0.02	1.91± 0.04	2.06± 0.04
Tm	-2.30± 0.02	0.01± 0.02	-0.10± 0.02	2.31± 0.04	2.20± 0.04
Yb	-2.28± 0.02	0.26± 0.03	0.16± 0.02	2.54± 0.05	2.44± 0.04
Lu	-2.26± 0.02	0.41± 0.03	0.36± 0.03	2.67± 0.05	2.62± 0.05

Notes: The values of the equilibrium constants are calculated on the basis of the 36 experimental points, statistical confidence 95%.

The data in Table 1 show that the values of K_{ps} and β_{ps} increases with decreasing ionic radii of the metal ions. The comparison of K_{ps} values obtained for HP–DB24C8 and HP–DB18C6 combinations show that the stability of the complexes involving DB24C8 is higher than those involving DB18C6. It could be explained by the fact that the electron density at the oxygen atoms adjacent to the benzene rings is less than those at the other oxygens.⁵ So, the oxygen atoms with higher electron density can come nearer to the metal ion and the result is a stronger bonding. As the number of the oxygen atoms in DB24C8 is greater, the stability of the complex with its participation is higher too. However, the difference between the values of K_{ps} (and β_{ps} too) obtained with HP–DB18C6 and HP–DB24C8 mixtures for a particular metal ion decreases from La to Lu. This fact can be explained by sterical hindrances due to the decreasing ionic radii.

The synergistic enhancement obtained for the combination of two extractants can be evaluated calculating the synergistic coefficients (SC) as proposed by Mathur³¹:

$$SC = \log(D_{12} / D_1 + D_2) \quad (9)$$

where D_{12} , D_1 and D_2 denote the distribution coefficient of a metal ion using mixture of extractants (D_{12}) and using the same extractants separately (D_1 and D_2).

The values of the synergistic coefficients of the lanthanoid ions for DB18C6 and DB24C8 used as synergistic agents in combination with HP are given in

Table 2. The synergistic enhancement increases from La to Lu for both crown ethers and for a particular lanthanoid ion it is larger when DB24C8 is used as synergistic agent.

The separation factors (SF) between the Ln³⁺ ions, defined as a ratio of the respective equilibrium constants ($K_{ps(Z+1)}/K_{ps(Z)}$) are listed in Table 2. The addition of DB18C6 or DB24C8 to the Ln³⁺ – HP system improves the separation. So, the synergistic mixtures used in the present study combine the higher extraction efficiency with the improved selectivity as compared to HP.

Reddy et al.¹¹⁻¹³ have studied the synergistic solvent extraction of Nd, Eu and Tm with chelating extractants such as 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone (HPMTFP)¹¹, 4,4,4-trifluoro-1-phenyl-1,3-butanedione (HBTFA)¹², 1-phenyl-3-methyl-4-pyvaloyl-5-pyrazolone (HPMP)¹³ and various crown ethers including DB18C6. It has been established that the separation factors of the pair Eu/Nd found for mixtures of the above chelating extractants and DB18C6 (21.4¹¹, 20.2¹² and 49.7¹³) are much higher than those of the pair Tm/Eu (3.6¹¹, 5.1¹² and 13.4¹³).

The comparison of these results with the data found in the present study for the system HP–DB18C6 as well as with the data in our recent study¹⁵ for the system thenoyltrifluoroacetone (HTTA)–DB18C6 show an opposite tendency. The separation factors of the pair Eu/Nd (3.5 (present study) and 3.7¹⁵) are several times lower than those of the pair Tm/Eu (87 (present study) and 17¹⁵).

Table 2. Values of the synergistic coefficients ($[HP]=3\times 10^{-2}$ mol/dm³, $[DB24C8 (DB18C6)]=5\times 10^{-3}$ mol/dm³ and pH=3.50) and the separation factors for the lanthanoid extraction with HP alone, HP – DB24C8 and HP – DB18C6 in 1,2-dichloroethane.

Ln ³⁺	S. C.			S.F.		
	HP–DB24C8	HP–DB18C6	Pair	HP	HP–DB24C8	HP–DB18C6
La	0.78	0.23	Ce/La	1.91	3.98	2.00
Ce	1.10	0.25	Pr/Ce	2.75	1.41	3.16
Pr	0.81	0.31	Nd/Pr	3.63	3.98	3.31
Nd	0.84	0.26	Sm/Nd	2.18	1.82	2.04
Sm	0.78	0.25	Eu/Sm	1.44	3.80	1.69
Eu	1.19	0.31	Gd/Eu	1.82	1.38	1.73
Gd	1.07	0.29	Tb/Gd	2.57	2.08	2.81
Tb	0.99	0.33	Dy/Tb	1.07	1.25	2.51
Dy	1.09	0.70	Ho/Dy	1.07	1.20	1.94
Ho	1.10	0.96	Er/Ho	1.09	1.23	2.29
Er	1.15	1.29	Tm/Er	1.12	2.75	1.58
Tm	1.54	1.43	Yb/Tm	1.04	1.77	1.82
Yb	1.79	1.67	Lu/Yb	1.04	3.13	1.58
Lu	1.90	1.87				

4. Conclusions

The lanthanoid(III) ions are synergistically extracted with HP – DB18C6 and HP – DB24C8 mixtures as LnP₃·S. The addition of DB18C6 and DB24C8 to HP improves both the extraction efficiency and the selectivity among the lanthanoid ions. The values of the equilibrium constants as well as those of the synergistic coefficient are higher when DB24C8 is used as synergistic agent but the difference between these values for the two crown ethers decreases with increasing atomic number. This effect is attributed to the sterical hindrances due to the decreasing lanthanoid radii.

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Povzetek

Raziskovali smo sinergijo ekstrakcije 14 trovalentnih lantanoidov (razen Pm) z različnimi topili: 1-fenil-3-metil-4-benzoil-5-pirazonom (HP), dibenzo-18-crown-6 (DB18C6), dibenzo-24-crown-8 (DB24C8) ter 1,2-diklorethanom. Ugotovili smo, da ekstrakcija lantanoidov s čistim HP poteka preko tvorbe kompleksa $\text{LnP}_3 \cdot \text{HP}$, z mešanico HP in crown etrov (S) pa kot $\text{LnP}_3 \cdot \text{S}$. S pomočjo eksperimentalnih podatkov smo določili tako vrednosti ravnotežnih konstant kot tudi sinergistične koeficiente in separacijske faktorje. Ugotovili smo, da dodatek crown etra v sistem $\text{Ln}^{3+} - \text{HP}$ izboljša tako učinkovitost kot tudi selektivnost.