

## Solvent extraction and separation of lanthanoids with mixtures of chelating extractant and 4-(2-pyridylazo)-resorcin

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Received 21 September 2006

**Abstract.** The solvent extraction of trivalent lanthanoids (La, Nd, Eu, Ho, and Lu) with mixtures of the chelating extractant 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (thenoyltrifluoro-acetone, HTTA) or 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-on (HP) and 4-(2-pyridylazo)-resorcin (PAR, S) in  $\text{CHCl}_3$  was studied. It was found that in the presence of 4-(2-pyridylazo)-resorcin the lanthanoids were extracted as  $\text{Ln}(\text{TTA})_3 \cdot \text{S}$  and  $\text{LnP}_3 \cdot \text{S}$ . On the basis of the experimental data, the values of the equilibrium constants were calculated. A synergistic effect was observed for the extraction of the above-mentioned ions with the binary mixture of extractants. The separation of the lanthanoids with synergistic mixtures was higher than those obtained with HTTA or HP alone. In most cases an enhancement of the separation of metal ions was observed upon the change of the chelating extractant HP with HTTA.

**Key words:** lanthanoids; synergistic extraction; 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione; 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-on; 4-(2-pyridylazo)-resorcin; separation factors.

### INTRODUCTION

The term “synergism” is used to describe cases where the extractive capability of a mixture of extractants is greater than the sum of their individual extractive capabilities. Significant effort has been devoted to the study of synergistic extractions over the last decades as the very nature of synergism offers interesting possibilities of research into both the chemistry of these extractants and their practical applications. The chemistry of synergic systems generally, and also of those making use of chelating extractants, is highly diverse as the variety of extracting agents and their possible combinations are numerous. The synergistic extraction of trivalent actinoids and lanthanoids is of great interest

because of the high extraction efficiency of these metal ions in the presence of a chelating agent and a neutral donor [1–7]. The separation of the lanthanoids and actinoids has also been discussed [8–12]. Thenoyltrifluoroacetone and a large number of 4-acyl-5-pyrazolones have been extensively used as extractants for lanthanoids and other elements separately and in combination with various synergistic agents [2–4, 13–16]. Several researchers have used 4-(2-pyridylazo)-resorcin (further abbreviated as PAR or S) for the extraction of metals [17–19].

The object of the present work is to investigate the synergistic solvent extraction of the metals of the lanthanoid series (La, Nd, Eu, Ho, and Lu) with a mixture of the chelating extractant 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (HTTA) or 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-on (HP) and PAR in  $\text{CHCl}_3$  and to determine the possibilities for the separation of the metals. The conditions of the extraction experiment, the probable mechanism of the extraction process, as well as the composition of the metal complexes being transferred into the organic phase are specified.

## EXPERIMENTAL

### Reagents

The commercial products HTTA (purity >99%, Fluka), HP (purity >99%, Fluka) and PAR (p.a., Fluka) were used as received. The diluent was  $\text{CHCl}_3$  (p.a., Merck). Stock solutions of the metals were prepared from their oxides (Fluka, puriss.). Arsenazo III (Fluka) as well as the other reagents used were of analytical grade purity.

### Procedure

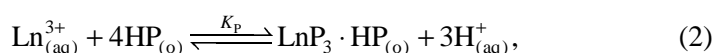
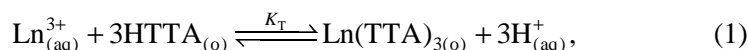
The experiments were carried out using  $10 \text{ cm}^3$  volumes of aqueous and organic phases. The samples were shaken mechanically for 45 min at room temperature, which was sufficient to reach equilibrium. After the separation of the phases, the metal concentration in the aqueous phase was determined photometrically using Arsenazo III [20]. The acidity of the aqueous phase was measured with a pH-meter with an accuracy of 0.01 pH unit. The ionic strength was maintained at  $0.1 \text{ mol/dm}^3$  with (Na, H)Cl. The initial concentration of the metals was  $2.5 \times 10^{-4} \text{ mol/dm}^3$  in all experiments.

The distribution coefficients of the lanthanoids were determined in three series of experiments:

- with fixed HTTA(HP) and PAR concentrations and varied pH,
- with fixed pH and PAR concentrations and a varied HTTA(HP) concentration,
- with fixed pH and HTTA(HP) and a varied PAR concentration.

## RESULTS AND DISCUSSION

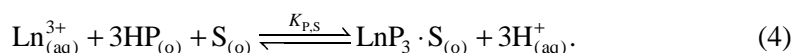
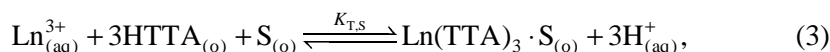
The solvent extraction of the lanthanoid(III) ions with HTTA and HP alone in  $\text{CHCl}_3$  has been studied previously [21, 22]. It was found that the metal extraction can be represented by the following equations:



where  $\text{Ln}^{3+}$  denotes a lanthanoid ion, the subscripts “aq” and “o” denote aqueous and organic phases, respectively, and  $K_T$  and  $K_P$  are equilibrium constants.

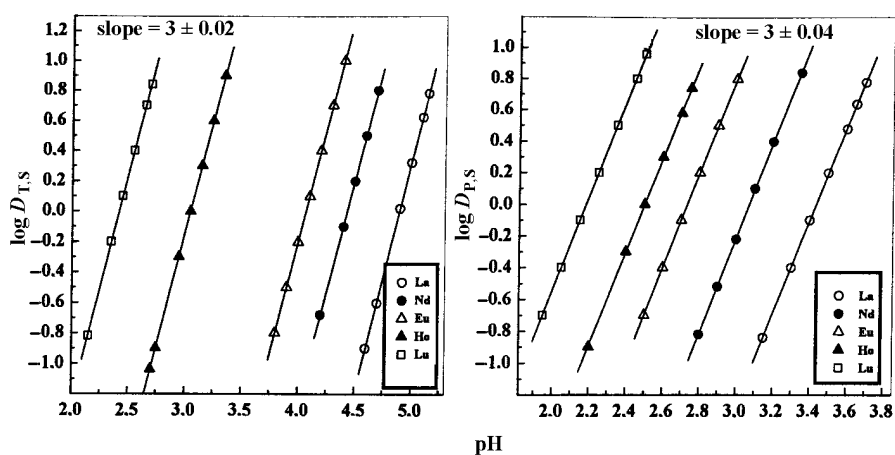
The synergistic solvent extraction of the lanthanoids was studied using a traditional and effective means of obtaining both stoichiometric and equilibrium constant information about extraction processes, called “slope analysis”. It is based on an examination of the variation of  $D_{T,S}$  or  $D_{P,S}$  (the distribution coefficient due to the synergistic effect) as a function of the relevant experimental variables. As the lanthanoids extraction with PAR alone is negligible under the experimental conditions of the present study, the values of the distribution coefficient  $D$  obtained experimentally are the sum of  $D_{T,S}$  and  $D_T$  or  $D_{P,S}$  and  $D_P$  ( $D_T$  and  $D_P$  are the distribution coefficients due to the lanthanoid extraction with HTTA or HP alone under the same experimental conditions). So, the values of  $D_{T,S}$  ( $D_{P,S}$ ) were calculated as  $D - D_T$  ( $D_P$ ). A log–log plot of  $D_{T,S}$  ( $D_{P,S}$ ) vs. one of the variables  $[\text{H}^+]$ ,  $[\text{HTTA}(\text{HP})]$ , or  $[\text{PAR}, \text{S}]$  keeping the other two constant, indicates the stoichiometry of the extractable complex, and thus leads to the derivation of a suitable equilibrium expression and then to the calculation of the equilibrium constant. If the concentration of the extractants is constant and the hydrolysis in the aqueous phase as well as the polymerization in the organic phase occur to a negligible extent only, then the plots will be straight lines and their slopes will give the number of the ligands of the adducts.

The experimental data for the extraction of the lanthanoid metals with a mixture of HTTA–PAR and HP–PAR are given in Figs 1–3. The plots of  $\log D_{T,S}$  ( $D_{P,S}$ ) vs. pH and  $\log[\text{HTTA}(\text{HP})]$  are linear with the slope close to three and the plots of  $\log D_{T,S}$  and  $\log(D_{P,S})$  vs.  $\log[\text{S}]$  with the slope close to one. Therefore, in the presence of HTTA–PAR and HP–PAR the lanthanoid extraction can be expressed by the following equations:

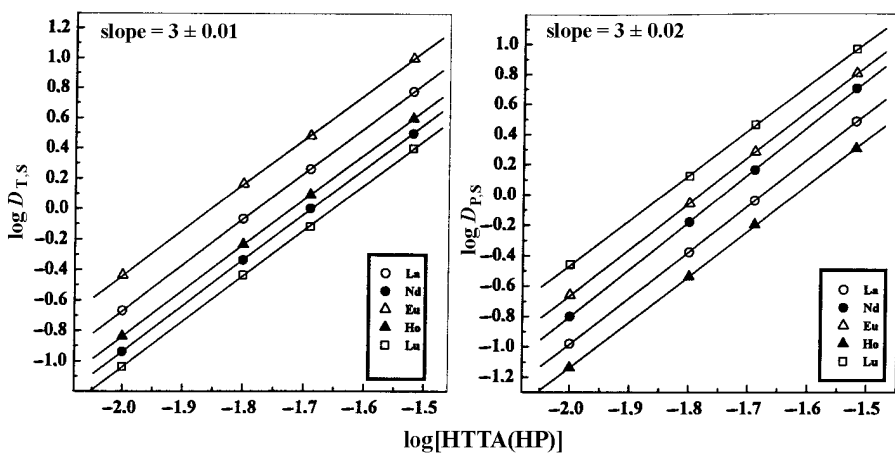


The formation of the species  $\text{Ln}(\text{TТА})_3 \cdot \text{S}$  or  $\text{LnP}_3 \cdot \text{S}$  is in accordance with the statement of Marcus & Kertes [23, p. 853] that a combination of one weak

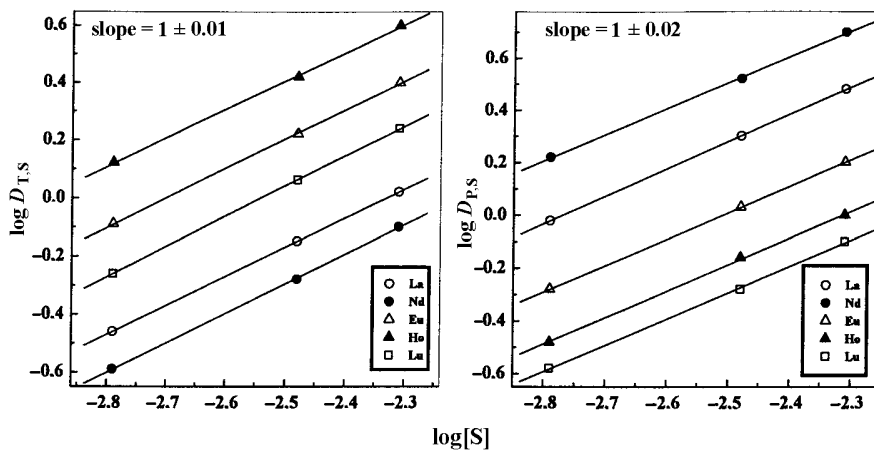
and one strong  $\beta$ -diketone can produce the extraction of a mixed adduct accompanied by a synergistic effect as well as with the statement of Hala [24] that the weaker acid is involved in the mixed adduct as a neutral molecule (the pKa values of HTTA, HP, and PAR are 6.2 [15], 3.95 [14] and 6.9 [17] respectively).



**Fig. 1.** Values of  $\log D_{T,S}$  and  $\log D_{P,S}$  vs. pH for the extraction of lanthanoid elements with HTTA-PAR and HP-PAR mixtures at  $[\text{HTTA}] = 3 \times 10^{-2} \text{ mol/dm}^3$ ,  $[\text{HP}] = 3 \times 10^{-2} \text{ mol/dm}^3$ , and  $[\text{PAR}] = 4.86 \times 10^{-3} \text{ mol/dm}^3$ .



**Fig. 2.** Values of  $\log D_{T,S}$  and  $\log D_{P,S}$  vs.  $\log[\text{HTTA, HP}]$  for the extraction of lanthanoid elements with HTTA-PAR and HP-PAR mixtures at  $[\text{PAR}] = 4.86 \times 10^{-3} \text{ mol/dm}^3$ . HTTA-PAR: La, pH = 5.15; Nd, pH = 4.60; Eu, pH = 4.0; Ho, pH = 3.25; Lu, pH = 2.55. HP-PAR: La, pH = 3.60; Nd, pH = 3.30; Eu, pH = 3.00; Ho, pH = 2.60; Lu, pH = 2.50.



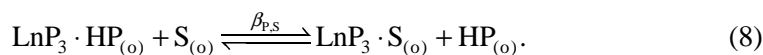
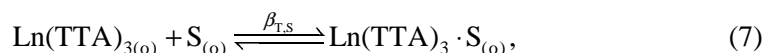
**Fig. 3.** Values of  $\log D_{T,S}$  and  $\log D_{P,S}$  vs.  $\log [\text{PAR}]$  for the extraction of lanthanoid elements with HTTA-PAR and HP-PAR mixtures at  $[\text{HTTA}] = 3 \times 10^{-2} \text{ mol/dm}^3$ ,  $[\text{HP}] = 3 \times 10^{-2} \text{ mol/dm}^3$ . HTTA-PAR: La, pH = 4.90; Nd, pH = 4.40; Eu, pH = 4.20; Ho, pH = 3.25; Lu, pH = 2.50. HP-PAR: La, pH = 3.60; Nd, pH = 3.30; Eu, pH = 2.80; Ho, pH = 2.50; Lu, pH = 2.15.

Taking into account that the partition of HP [14], HTTA [15], and PAR [17] toward the aqueous phase is very low and on the basis of the slope analysis data, the overall equilibrium constants  $K_{T,S}$  and  $K_{P,S}$  can be determined by the equations:

$$\log K_{T,S} = \log D_{T,S} - 3 \log [\text{HTTA}] - \log [\text{S}] - 3\text{pH}, \quad (5)$$

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

The formation of mixed complexes in the organic phase can be described by the equations:



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

$$\log \beta_{T,S} = \log K_{T,S} - \log K_T, \quad (9)$$

$$\log \beta_{P,S} = \log K_{P,S} - \log K_P. \quad (10)$$

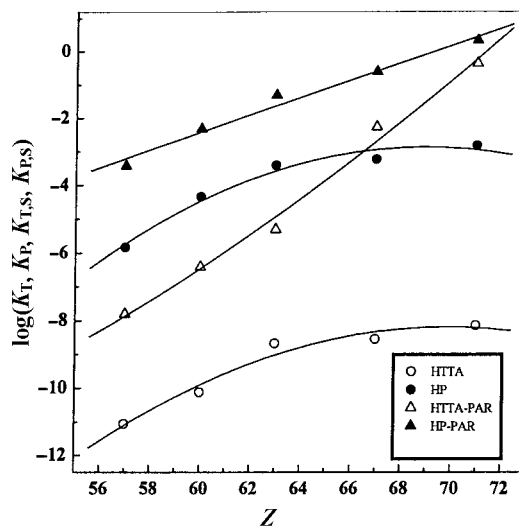
The values of the equilibrium constants  $K_{T,S}$ ,  $K_{P,S}$ , and  $\beta_{T,S}$ ,  $\beta_{P,S}$  calculated from the experimental data are given in Table 1. The equilibrium constants are based on the assumption that the activity coefficients of the species do not

change significantly under the experimental conditions, so they are concentration constants. The data in Table 1 show that the values of the equilibrium constants  $K_{T,S}$ ,  $K_{P,S}$ ,  $\beta_{T,S}$ , and  $\beta_{P,S}$  increase from La to Lu. In most cases the values of  $\log K_{P,S}$  are 2–3 orders higher than those of  $\log K_{T,S}$ . The variation of the equilibrium constants  $K_T$ ,  $K_P$ ,  $K_{T,S}$ , and  $K_{P,S}$  versus the atomic number  $Z$  of the representative lanthanoids is given in Fig. 4. It can be seen that the curves of HTTA and HP vary practically in the same manner as those including a synergistic agent. In addition, the heavier lanthanoids are extracted more effectively with a binary mixture HTTA–PAR than with HP alone although HTTA is a weaker acid than 4-acylpyrazolones. It is well known that the acidity of the extractant is one of the predominant factors governing extractability.

**Table 1.** Values of the equilibrium constants  $K_T$ ,  $K_P$ ,  $K_{T,S}$ ,  $K_{P,S}$ ,  $\beta_{T,S}$ , and  $\beta_{P,S}$  for the  $\text{Ln}^{3+}$  extraction with HTTA–PAR and HP–PAR mixtures in  $\text{CHCl}_3$

$\text{Ln}^{3+}$	$\log K_T$ [21]	$\log K_P$ [22]	HTTA–PAR		HP–PAR	
			$\log K_{T,S}$	$\log \beta_{T,S}$	$\log K_{P,S}$	$\log \beta_{P,S}$
La	–11.06	–5.84	–7.81	3.26	–3.43	2.41
Nd	–10.12	–4.35	–6.43	3.69	–2.34	2.0
Eu	–8.68	–3.42	–5.33	3.35	–1.33	2.09
Ho	–8.56	–3.24	–2.28	6.28	–0.63	2.61
Lu	–8.15	–2.83	–0.38	7.77	0.32	3.15

Note: Error limits in the range  $\leq \pm 0.06$ .



**Fig. 4.** Values of  $\log(K_T, K_P, K_{T,S}, \text{ and } K_{P,S})$  vs.  $Z$ .

However, the values of  $\beta_{p,s}$  (for the organic phase synergistic reaction) are significantly smaller than the values of  $\log \beta_{T,S}$ . This fact can be explained taking into account the formation of self-adducts  $\text{LnP}_3 \cdot \text{HP}$  when HP alone is used as extractant [25]. The structure of these complexes could be compared with those of the mixed synergistic complexes. The neutral HP molecule acts as a synergist displacing water molecules and rendering the self-adducts less hydrophilic. It is known that the major factor in synergism is an increase in the hydrophobic character of the extracted metal complex upon addition of the synergistic agent [26, 27]. So, the transformation of the self-adduct into the mixed complex  $\text{LnP}_3 \cdot \text{S}$  according to Eq. (8) cannot contribute to a large increase in its stability in the organic phase as neither  $\text{LnP}_3 \cdot \text{HP}$  nor  $\text{LnP}_3 \cdot \text{S}$  contains water molecules in the coordination sphere. Then, the equilibrium constants  $K_p$  and  $K_{p,S}$  will not differ to a large extent, and  $\beta_{p,S}$  calculated according to Eq. (10) will not be large either. On the other hand, the formation of the complex  $\text{Ln}(\text{TTA})_3 \cdot \text{S}$  in the organic phase (Eq. (7)) is connected with the replacement of all water molecules from the coordination sphere of the complex  $\text{La}(\text{TTA})_3(\text{H}_2\text{O})_n$  [28]. This results in a much higher stability of the mixed complex  $\text{Ln}(\text{TTA})_3 \cdot \text{S}$  (as compared to the chelate  $\text{Ln}(\text{TTA})_3$ ). Therefore, the difference between  $K_{T,S}$  and  $K_T$  will be higher than that between  $K_{p,S}$  and  $K_p$ , and the values of  $\beta_{T,S}$  calculated from Eq. (9) will be higher than  $\beta_{p,S}$ , which is confirmed by the data in Table 1.

The synergistic enhancement produced by HTTA–PAR and HP–PAR mixtures can be determined using the synergistic coefficients (S.C.). They were calculated according to the equation:  $\text{S.C.} = \log(D_{1,2}/(D_1 + D_2))$ , where  $D_1$ ,  $D_2$ , and  $D_{1,2}$  are the distribution coefficients of the metal with the two extractants taken separately and with their mixture [29]. The values of the synergistic coefficients are listed in Table 2. It is evident that all lanthanoids are extracted synergistically ( $\text{S.C.} > 0$ ). The synergistic coefficients increase from La to Lu for both HTTA–PAR and HP–PAR combinations but the synergistic enhancement is much higher for the couple HTTA–PAR, especially for the heavier lanthanoids.

**Table 2.** Values of the synergistic coefficients ( $[\text{HP}] = 3 \times 10^{-2} \text{ mol/dm}^3$ ,  $[\text{PAR}] = 4.89 \times 10^{-3} \text{ mol/dm}^3$ ,  $\text{pH} = 3.00$ ;  $[\text{HTTA}] = 3 \times 10^{-2} \text{ mol/dm}^3$ ,  $[\text{PAR}] = 4.89 \times 10^{-3} \text{ mol/dm}^3$ ,  $\text{pH} = 3.00$ ) and separation factors for the  $\text{Ln}^{3+}$  extraction with mixtures of HTTA–PAR and HP–PAR in  $\text{CHCl}_3$

$\text{Ln}^{3+}$	Synergistic coefficients		Separation	Factors			
	HP–PAR	HTTA–PAR		HP	HTTA	HP–PAR	HTTA–PAR
La	1.64	0.94	Nd/La	30.91	8.70	12.30	24.76
Nd	1.23	1.38	Eu/Nd	8.51	27.54	10.23	12.60
Eu	1.31	1.04	Ho/Eu	1.52	1	5.01	1122.1
Ho	1.83	3.97	Lu/Ho	2.53	3.54	8.91	79.43
Lu	2.37	5.46					

The separation of the lanthanoids using HTTA–PAR and HP–PAR mixtures can be assessed by the separation factors calculated as a ratio of the distribution coefficients of two adjacent lanthanoids (the heavier and the lighter one). 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  $K_{T,S}$  or  $K_{P,S}$ . Their values are given in Table 2. The separation factors and the synergistic coefficients (given also in Table 2) show that the addition of PAR to the chelating extractants HTTA and HP not only enhances the extraction efficiency but improves the selectivity among the lanthanoids as well although it has been generally believed that synergistic extraction makes the separation of metals worse, compared with the extraction with a chelating ligand only. In the Hpta (pivaloyltrifluoroacetone) and Hhfa (hexafluoroacetylacetone) systems [30] involving the bidentate neutral ligand 1,10-phenantroline, the separation factor was improved by the synergistic extraction of rare earths (La, Sm, Tb, and Lu). The values of both synergistic coefficients and separation factors obtained for the extraction of lanthanoids with HTTA–PAR mixtures are higher than those for their extraction with HP–PAR mixtures. It has to be pointed out that the separation factors of the heavier lanthanoids found in the present study are rather high (4–5 times higher) as compared to those found in other synergistic systems including the same chelating extractants and various synergistic agents (crown ethers, quaternary ammonium salt in perchlorate form, 1-(2-pyridylazo)-2-naphthol [3, 4, 11, 22, 31, 32]. This suggests a further possibility of synergism in separation science.

## CONCLUSIONS

The synergistic solvent extraction of representative trivalent lanthanoid metals (La, Nd, Eu, Ho, and Lu) with binary mixtures HTTA–PAR and HP–PAR was investigated. The weaker acid is involved in the mixed adducts as a neutral molecule  $\text{Ln}(\text{TTA})_3 \cdot \text{S}$  and  $\text{LnP}_3 \cdot \text{S}$ . The equilibrium constants of the synergistic species were found to increase monotonically with the decrease in ionic radii of the metal ions. The addition of a synergist to the chelating extractant improves the extraction efficiency of the lanthanoid ions and produces rather large synergistic effects. In the synergistic systems the selectivity among the lanthanoids has been increased upon the change of the chelating extractant HP with HTTA.

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## **Solvendi ekstraksioon ning lantanoidide eraldamine kelaativate ekstrahentide segude ja 4-(2-püridüülaso)resortsiiniga**

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On uuritud lantanoidide (La, Nd, Eu, Ho ja Lu) ekstraksiooni kelaativate ekstrahentide 1-(2-tienüül)-4,4,4-trifluoro-1,3-butaandiooni (tenoüültrifluoroatsetooni, HTTA) ja 4-bensoüül-3-metüül-1-fenüül-2-pürasoliin-5-ooniga (HP), kasutades neid segus 4-(2-püridüülaso)resortsiiniga (PAR, S) CHCl<sub>3</sub> lahuses. Katsetulemuste põhjal on määratud vastavate tasakaalukonstantide väärtused. Eelmainitud ionide ekstraheerimisel ekstrahentide binaarse seguga on täheldatud sünergilist efekti. Lantanoidide eraldusaste on sünergiliste segude puhul kõrgem kui üksnes HTTA või HP kasutamisel. Kelaativa ekstrahendi HP asendamisel HTTA-ga on enamikul juhtudest täheldatud metalliioonide eraldamise paranemist.