

# Synergistic Solvent Extraction of Lanthanides with Mixtures of 1-Phenyl-3-methyl-4-benzoyl-pyrazol-5-one and Aliphatic Amines: Influence of the Ammonium Salt Ions

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**Summary.** The synergistic solvent extraction of Pr, Gd, and Yb with mixtures of 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one (HP) and tridodecylammonium (TDAHA), trioctylammonium (TOAHA), and dioctylammonium (DOAHA) salts ( $A^- = \text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{ClO}_4^-$ ) in  $\text{C}_6\text{H}_6$  has been studied. The composition of the extracted species has been determined as  $\text{AmH}^+[\text{LnP}_4]^-$  ( $\text{AmH}^+$ : ammonium salt cation). The values of the equilibrium constant have been calculated. The influence of the ammonium salt ions on the extraction process is discussed.

**Keywords.** Aliphatic amines; Lanthanides; 1-Phenyl-3-methyl-4-benzoyl-pyrazol-5-one; Synergistic extraction.

## Synergetische Extraktion von Lanthaniden mit Mischungen aus 1-Phenyl-3-methyl-4-benzoyl-pyrazol-5-on und aliphatischen Aminen: Einfluß der Ammoniumsalzionen

**Zusammenfassung.** Die synergetische Extraktion von Pr, Gd und Yb mit Mischungen aus 1-Phenyl-3-methyl-4-benzoyl-pyrazol-5-on (HP) und Tridodecylammonium-(TDAHA), Trioctylammonium-(TOAHA) und Dioctylammoniumsalzen (DOAHA) ( $A^- = \text{Cl}^-$ ,  $\text{NO}_3^-$  und  $\text{ClO}_4^-$ ) in  $\text{C}_6\text{H}_6$  wurde untersucht. Die Zusammensetzung der Extraktionskomplexverbindungen wurde zu  $\text{AmH}^+[\text{LnP}_4]^-$  bestimmt; die Gleichgewichtskonstanten wurden berechnet. Der Einfluß der Ionen des Ammoniumsalzes auf die Extraktion wird diskutiert.

## Introduction

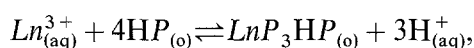
The synergistic solvent extraction of lanthanides with mixtures of 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one (HP) and the ammonium salts  $\text{TOAHCl}$ ,  $\text{TDAHCl}$ ,  $\text{TDAHNO}_3$ , and  $\text{TDAHClO}_4$  ( $\text{TOA}$  = trioctylamine;  $\text{TDA}$  = tridodecylamine) has been studied by Dukov *et al.* [1–3]. The formation of anionic mixed complexes of the composition  $\text{TOAH}^+[\text{LnP}_4]^-$  or  $\text{TDAH}^+[\text{LnP}_4]^-$  has been observed. Anionic complexes ( $\text{AmHML}_3$ ) have also been found when divalent metals (Co, Ni, Cu, Zn, Cd) were synergistically extracted with mixtures of acylpyrazolones and trioctylammonium or dodecylammonium salts [4–9]. It has been assumed

that – according to the experimental conditions – the synergist could be either the ammonium salt or the ion pair  $AmH^+P^-$  obtained as a result of the interaction between the extractants.

In the course of systematic investigations on synergistic solvent extractions of lanthanides, the influence of the ions of the ammonium salts on the extraction of Pr, Gd, and Yb with mixtures of HP and chloride, nitrate, and perchlorate salts of tridodecylamine (*TDA*), trioctylamine (*TOA*), and dioctylamine (*DOA*) in  $C_6H_6$  have been studied.

## Results and Discussion

The solvent extraction of lanthanides with HP alone has been studied earlier [11]. It was found that the metal extraction can be expressed by the equation



where  $Ln = Pr, Gd,$  and  $Yb$ , and the subscripts “aq” and “o” denote the aqueous and organic phase, respectively. Self-adduct species formation for La, Eu, and Lu extraction with HP has recently been reported by Indian scientists [12].

The lanthanide extraction with ammonium salts alone was negligible under the experimental conditions of the present study. The synergistic extraction of the lanthanides was studied using the traditional procedure called “slope analysis”. It is based on an examination of the variation of  $D_{p,s}$  (the distribution coefficient due to the synergistic effect) with relevant experimental variables. A double logarithmic plot of  $D_{p,s}$  vs. one of the variables  $pH$ ,  $[HP]$  and  $[AmHA]$  (the amine salt concentration), keeping the other two constant, indicates the stoichiometry of the extracted complex and leads to the derivation of a suitable equilibrium expression and subsequently to the calculation of the equilibrium constant. It was found that the plots of  $\log D_{p,s}$  vs.  $\log [HP]$  and  $pH$  are linear with slopes close to four; plots of  $\log D_{p,s}$  vs.  $\log [AmHA]$  exhibit slopes close to one. The experimental data for the metal extraction with mixtures of HP and perchlorate ammonium salts are given in Figs. 1–3.

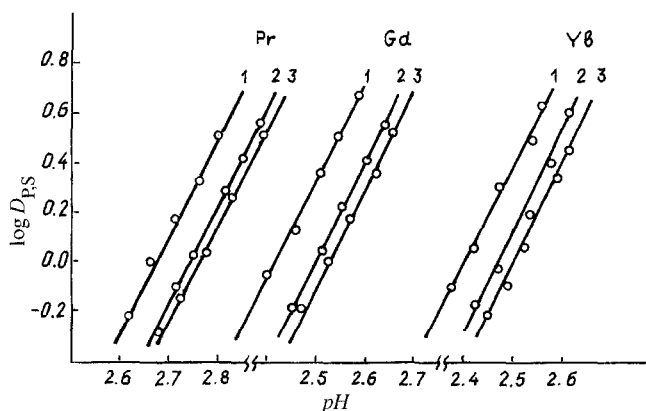
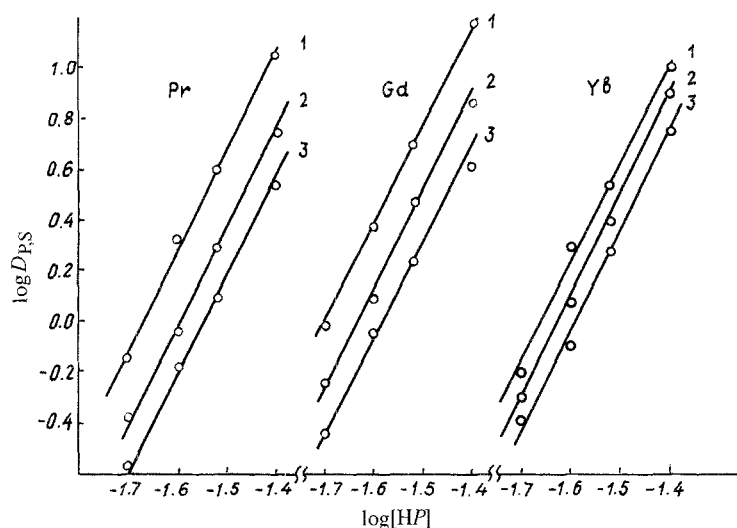
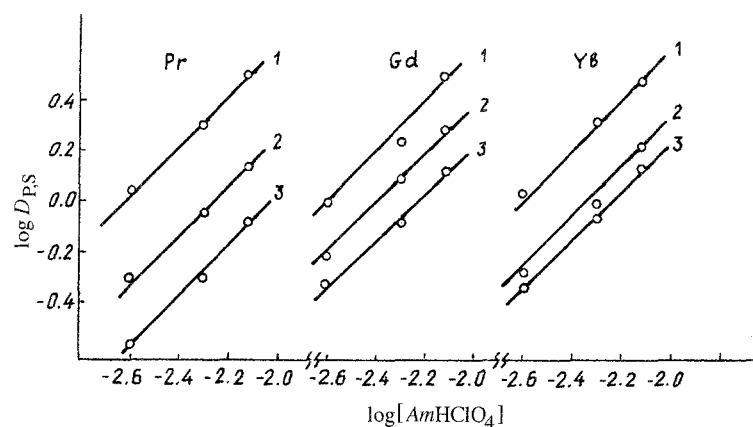


Fig. 1.  $\log D_{p,s}$  vs.  $pH$  for Pr, Gd, and Yb extraction with mixtures of HP and ammonium perchlorates at  $[HP] = 2.5 \times 10^{-2} \text{ mol/dm}^3$  and  $[AmHClO_4] = 5 \times 10^{-3} \text{ mol/dm}^3$ ; 1)  $DOAHClO_4$ ; 2)  $TOAHClO_4$ ; 3)  $TDAHClO_4$ .

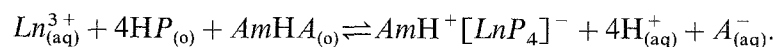


**Fig. 2.**  $\log D_{P,S}$  vs.  $\log[HP]$  for Pr, Gd, and Yb extraction with mixtures of HP and ammonium perchlorates at  $[AmHClO_4] = 5 \times 10^{-3} \text{ mol/dm}^3$ ; Pr: 1)  $DOAHClO_4$ ,  $pH = 2.75$ ; 2)  $TDAHClO_4$ ,  $pH = 2.75$ ; 3)  $TOAHClO_4$ ,  $pH = 2.70$ ; Gd: 1)  $TOAHClO_4$ ,  $pH = 2.60$ ; 2)  $TDAHClO_4$ ,  $pH = 2.55$ ; 3)  $DOAHClO_4$ ,  $pH = 2.40$ ; Yb: 1)  $TDAHClO_4$ ,  $pH = 2.55$ ; 2)  $DOAHClO_4$ ,  $pH = 2.40$ ; 3)  $TOAHClO_4$ ,  $pH = 2.45$



**Fig. 3.**  $\log D_{P,S}$  vs.  $\log[AmHClO_4]$  for Pr, Gd, and Yb extraction with mixtures of HP and ammonium perchlorates at  $[HP] = 2.5 \times 10^{-2} \text{ mol/dm}^3$ ; Pr: 1)  $DOAHClO_4$ ,  $pH = 2.75$ ; 2)  $TDAHClO_4$ ,  $pH = 2.75$ ; 3)  $TOAHClO_4$ ,  $pH = 2.70$ ; Gd: 1)  $TOAHClO_4$ ,  $pH = 2.60$ ; 2)  $TDAHClO_4$ ,  $pH = 2.55$ ; 3)  $DOAHClO_4$ ,  $pH = 2.40$ ; Yb: 1)  $TDAHClO_4$ ,  $pH = 2.55$ ; 2)  $DOAHClO_4$ ,  $pH = 2.40$ ; 3)  $TOAHClO_4$ ,  $pH = 2.45$

On the basis of slope analysis, the metal extraction can be represented by the following equation:



The overall equilibrium constant  $K_{P,S}$  can be determined as

$$\log K_{P,S} = \log D_{P,S} - 4\log[HP] - \log[AmHA] - 4pH + \log[A^-].$$

**Table 1.** Values of the equilibrium constant  $K_{p,s}$  for Pr, Gd, and Yb extraction with mixtures of HP and ammonium salts

Metal	Extractants	$\log K_{p,s}$		
		Chloride	Nitrate	Perchlorate
Pr	HP-TDA	$-1.56 \pm 0.03$ [3]	$-2.30 \pm 0.02$ [2]	$-3.35 \pm 0.02$ [2]
	HP-TOA	$-1.54 \pm 0.06$ [1]	$-2.62 \pm 0.06$	$-3.30 \pm 0.02$
	HP-DOA	$-1.84 \pm 0.03$	$-3.06 \pm 0.06$	$-3.04 \pm 0.03$
Gd	HP-TDA	$-0.39 \pm 0.02$ [3]	–	$-2.48 \pm 0.05$
	HP-TOA	$-0.40 \pm 0.03$ [1]	–	$-2.41 \pm 0.04$
	HP-DOA	$-0.97 \pm 0.04$	–	$-2.03 \pm 0.03$
Yb	HP-TDA	$-0.22 \pm 0.02$ [3]	–	$-2.23 \pm 0.06$
	HP-TOA	$-0.25 \pm 0.04$ [1]	–	$-2.14 \pm 0.06$
	HP-DOA	$-0.47 \pm 0.04$	–	$-1.87 \pm 0.03$

The values of the equilibrium constant are given in Table 1. The equilibrium constant  $K_{p,s}$  is concentration independent *i.e.* it is assumed that the activity coefficients of the species do not change significantly under the experimental conditions. It can be seen from Table 1 that the lanthanide extraction is significantly influenced by the ammonium salt anion. The cation (at a given anion) of the tertiary amines used in this study does not noticeably influence the lanthanide extraction. The metal extraction decreases when secondary ammonium salts ( $DOAHCl$  and  $DOAHNO_3$ ) are used as synergists, but it surprisingly increases a little in comparison with  $TOAHClO_4$  and  $TDAHClO_4$  when  $DOAHClO_4$  is used. As the ammonium salts can be considered as ion pairs [13], the above facts could be explained by the influence of the cation and the anion on the stability of the ammonium salt in the organic phase. This is important because the formation of mixed anionic complexes is connected with the breaking of the bond between the cation and the anion [2]. The attraction between the cation and the anion increases with decreasing number of carbon chains at the cation. As a result of the more favourable steric conditions, the stability and the bond energy of the ammonium salts decrease in the order primary > secondary > tertiary. It is clear that the secondary salts ( $DOAHCl$  and  $DOAHNO_3$ ) will be more stable than the respective tertiary ones. The higher stability of the secondary salts is the reason for the lower values of the equilibrium constant  $K_{p,s}$  when the metals are extracted with HP- $DOAHCl$  or  $DOAHNO_3$  mixtures. The influence of the anion on the stability of the salts is due to the different free hydration energy ( $\Delta G_h$ ) of these anions as well as to the anion radius. The radii and the values of  $\Delta G_h$  of  $Cl^-$ ,  $NO_3^-$ , and  $ClO_4^-$  are 0.181, 0.189, and 0.236 nm and  $-330.5$ ,  $-288.7$ , and  $-234.3$  kJ/mol, respectively [13, p. 63]. It is clear that the stability of the ammonium salt in the organic phase increases with increasing anion radius because of the easier transfer of the larger anions from aqueous into organic phase. On the other hand, the larger anion radius causes a decrease of the bond energy which is proportional to the expression  $e^2/r$  ( $e$ : charge;  $r = r^+ + r^-$ : sum of the cation and anion radii). Thus, the decrease is larger for the secondary than for the

tertiary salts, the influence of  $r^-$  on the bond energy being higher when  $r^+$  is smaller. This effect is most pronounced when the largest anion ( $\text{ClO}_4^-$ ) forms a salt with the smallest cation ( $\text{DOAH}^+$ ). In this case, the stability of  $\text{DOAHClO}_4$  probably becomes a little lower than those of  $\text{TOAHClO}_4$  or  $\text{TDAHClO}_4$ . Therefore,  $\text{DOAHClO}_4$  is a more effective synergist than  $\text{TOAHClO}_4$  and  $\text{TDAHClO}_4$ . On the other hand, because of their smaller radii, the chloride and nitrate anions exert a weaker effect on the bond energy. This fact, combined with the more favourable steric conditions is the reason for the greater stability of  $\text{DOAHCl}$  and  $\text{DOAHNO}_3$ , *i.e.* the chlorides and nitrates of the tertiary amines (in contrast with the perchlorates) are more effective synergists than the chloride and nitrate of  $\text{DOA}$ .

The values of the equilibrium constant  $K_{P,S}$  do not give a clear notion about the synergistic enhancement obtained as a result of the use of mixtures of the extractants. This enhancement can be found by calculating the synergistic coefficients (SC) as defined by *Taube and Siekierski* [14] as

$$\text{SC} = \log(D_{1,2}/D_1 + D_2)$$

where  $D_1$ ,  $D_2$ , and  $D_{1,2}$  are the distribution coefficients of the lanthanides between the aqueous and organic phases with the extractants taken separately and with their mixture. The values of  $D_{1,2}$  were taken from the experimental data of this study. The values of  $D_1$  (for lanthanide extraction with  $\text{HP}$  alone) were taken from Ref. [11]. The values of  $D_2$  (for lanthanide extraction with ammonium salts) were negligibly small under the experimental conditions. The values of the synergistic coefficient are given in Table 2. It can be seen that synergistic enhancement is found for all metals and mixtures of extractants ( $\text{SC} > 0$ ). It changes approximately from  $10^4$  to  $10^2$ . The values of the synergistic coefficient decrease in the order  $\text{Pr} > \text{Gd} > \text{Yb}$  and chlorides  $>$  nitrates  $>$  perchlorates.

**Table 2.** Values of the synergistic coefficient for Pr, Gd, and Yb extraction with mixtures of  $\text{HP}$  and ammonium salts in  $\text{C}_6\text{H}_6$  at  $[\text{HP}] = 3 \times 10^{-2} \text{ mol/dm}^3$ ,  $[\text{AmHA}] = 5 \times 10^{-3} \text{ mol/dm}^3$ , and  $\text{pH} = 3.00$

Metal	Extractants	Synergistic Coefficient		
		Chloride	Nitrate	Perchlorate
Pr	HP-TDA	4.22	3.48	2.43
	HP-TOA	4.24	3.16	2.48
	HP-DOA	3.94	2.72	2.74
Gd	HP-TDA	4.35	–	2.26
	HP-TOA	4.34	–	2.33
	HP-DOA	3.77	–	2.71
Yb	HP-TDA	3.60	–	1.59
	HP-TOA	3.57	–	1.68
	HP-DOA	3.35	–	1.95

## Experimental

HP (Pharmachim Sofia, *p.a.*), TDA (Merck-Schuchardt), TOA, and DOA (Fluka) were used as supplied. The oxides  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Gd}_2\text{O}_3$ , and  $\text{Yb}_2\text{O}_3$  (Fluka, *puriss.*) were used to prepare the stock solutions of the metals. The other reagents used were of analytical grade.

Equal volumes ( $10\text{ cm}^3$  each) of aqueous and organic phases were shaken mechanically for 60 min at room temperature which was sufficient to reach equilibrium. After phase separation, the metal concentration in the aqueous phase was determined photometrically using Arsenazo III [10]. The acidity of the aqueous phase was measured by a *pH* meter with an accuracy of 0.01 *pH* units. The ionic strength was maintained at 0.1 M with (Na, H)Cl,  $\text{NO}_3$ , and  $\text{ClO}_4$ . The initial metal concentration was  $2.5 \times 10^{-4}\text{ mol/dm}^3$  in all experiments.

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