

Peculiarities of the Synergistic Solvent Extraction of Lanthanides with Mixtures of Chelating Extractants and Tridodecylamine

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Summary. The synergistic solvent extraction of Pr, Gd, and Yb with mixture of thenoyltrifluoroacetone (*HTTA*) or 1-phenyl-3-methyl-benzoyl-pyrazol-5-one (*HP*) and tridodecylammonium chloride (*TDAHCl*) in C_6H_6 has been studied. The composition of the extracted complexes has been determined as $Ln(TTA)_3TDAHCl$ and $TDAH^+[LnP_4]^-$. The values of the equilibrium constants have been calculated. Some peculiarities of the synergistic extraction process are discussed.

Keywords. Lanthanides; 1-Phenyl-3-methyl-4-benzoyl-pyrazol-5-one; Synergistic extraction; Thenoyltrifluoroacetone; Tridodecylamine.

Einige Eigenschaften der synergetischen Extraktion von Lanthaniden mit Mischungen aus chelatbildenden Extrahenten und Tridodecylamin

Zusammenfassung. Es wurde die synergetische Extraktion von Pr, Gd und Yb mit Mischungen aus Thenoyltrifluoroacetone (*HTTA*) oder 1-Phenyl-3-methyl-4-benzoyl-pyrazol-5-on (*HP*) und Tridodecylamin (*TDA*) untersucht. Die Zusammensetzung der Extraktionskomplexverbindungen $Ln(TTA)_3TDAHCl$ und $TDAH^+[LnP_4]^-$ wurde bestimmt und die Gleichgewichtskonstanten wurden berechnet. Die Eigenschaften der synergetischen Extraktion werden diskutiert.

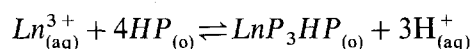
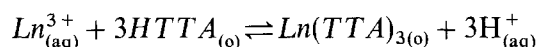
Introduction

In the last years, mixtures of chelating extractants and high molecular weight amines have frequently been used in the extraction of lanthanides as well as of other metals. Thenoyltrifluoroacetone (*HTTA*) or 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one (*HP*) as chelating extractants and trioctylamine (*TOA*) or tribenzylamine (*TBA*) as synergistic agents have often been used. Synergistic extraction of trivalent lanthanides [1, 3, 4, 10] and divalent transition or alkaline earth metals [2, 5–9] have been reported. Formation of anionic mixed complexes or amine adducts has been observed when the metals were extracted with *HP* or *HTTA* and long chain amines. The influence of the temperature on the synergistic extraction was also

studied [11–12]. In the present work, the synergistic extraction of Pr, Gd, and Yb with mixtures of *HTTA* or *HP* and tridodecylammonium chloride (*TDAHCl*) was investigated.

Results and Discussion

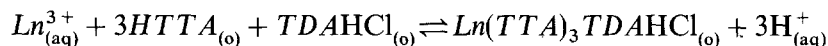
The solvent extraction of Pr, Gd, and Yb with solutions of *HTTA* or *HP* was studied earlier [14, 15]. The metal extraction can be represented by the equations



where $\text{Ln} = \text{Pr, Gd, and Yb}$, and “aq” and “o” denote aqueous and organic phase, respectively.

The synergistic extraction of the metals was studied by the determination of the distribution coefficients $D_{\text{T,S}}$ or $D_{\text{P,S}}$ ($D_{\text{T,S}}$ and $D_{\text{P,S}}$ are the distribution coefficients for the extraction of the metals with *HTTA* – *TDAHCl* or *HP* – *TDAHCl* mixtures) as a function of one of the variables pH , $[\text{HTTA}]$ ($[\text{HP}]$), and $[\text{TDAHCl}]$, keeping the other two constant. The experimental data for the extraction of Pr, Gd, and Yb with mixtures of *HTTA* and *TDAHCl* or *HP* and *TDAHCl* in C_6H_6 are shown in Figs. 1–6. The plots of $\log D_{\text{T,S}}$ vs. pH and $\log[\text{HTTA}]$ are linear with slopes close to three; the plots of $\log D_{\text{T,S}}$ vs. $\log[\text{TDAHCl}]$ show a slope close to one. On the other hand, the plots of $\log D_{\text{P,S}}$ vs. pH and $\log[\text{HP}]$ are linear with slopes close to four; the plots of $\log D_{\text{P,S}}$ vs. $\log[\text{TDSHCl}]$ again show a slope close to one.

On the basis of the slope analysis data the synergistic extraction of the metals can be represented by the equations



and

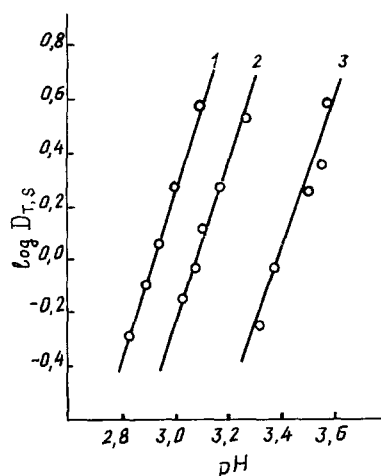
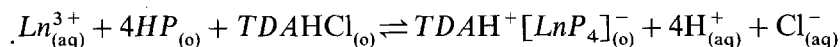


Fig. 1. $\log D_{\text{T,S}}$ vs. pH for Pr, Gd, and Yb extraction at $[\text{HTTA}] = 6 \times 10^{-2} \text{ mol/dm}^3$ and $[\text{TDAHCl}] = 5 \times 10^{-3} \text{ mol/dm}^3$; 1: Yb; 2: Gd; 3: Pr

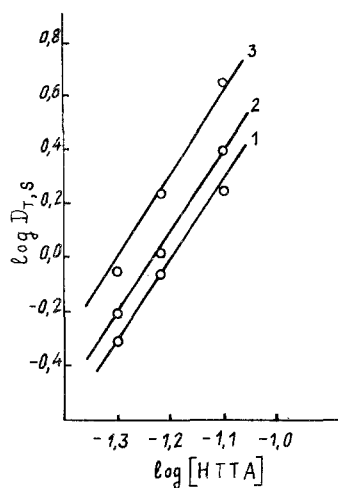


Fig. 2. $\log D_{T,S}$ vs. $\log [HTTA]$ for Pr, Gd, and Yb extraction at $[TDAHCl] = 5 \times 10^{-3}$ mol/dm³; 1: Pr, $pH = 3.40$; 2: Gd, $pH = 3.10$; 3: Yb, $pH = 3.00$

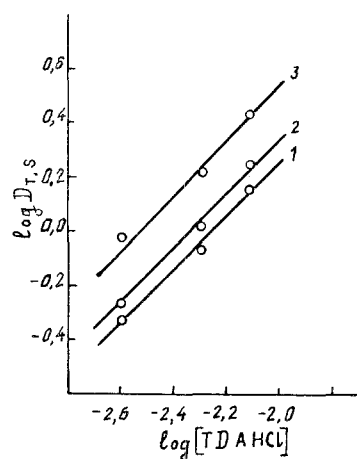


Fig. 3. $\log D_{T,S}$ vs. $\log [TDAHCl]$ for Pr, Gd, and Yb extraction at $[HTTA] = 6 \times 10^{-2}$ mol/dm³; 1: Pr, $pH = 3.40$; 2: Gd, $pH = 3.10$; 3: Yb, $pH = 3.00$

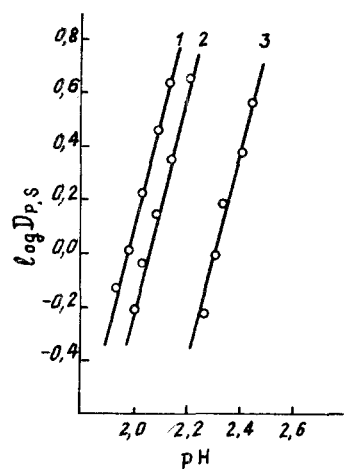


Fig. 4. $\log D_{P,S}$ vs. pH for Pr, Gd, and Yb extraction at $[HP] = 2.5 \times 10^{-2}$ mol/dm³ and $[TDAHCl] = 5 \times 10^{-3}$ mol/dm³; 1: Yb; 2: Gd; 3: Pr

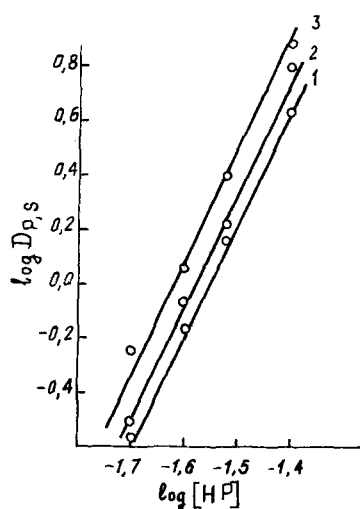


Fig. 5. $\log D_{P,S}$ vs. $\log[HP]$ for Pr, Gd, and Yb extraction at $[TDAHCl] = 5 \times 10^{-3} \text{ mol/dm}^3$; 1: Yb, $pH = 1.95$; 2: Pr, $pH = 2.30$; 3: Gd, $pH = 2.05$

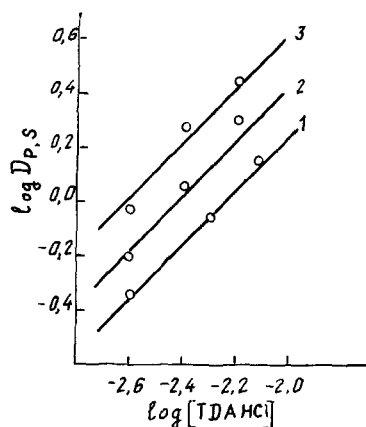


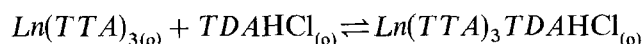
Fig. 6. $\log D_{P,S}$ vs. $\log[TDAHCl]$ for Pr, Gd, and Yb extraction at $[HP] = 2.5 \times 10^{-2} \text{ mol/dm}^3$; 1: Pr, $pH = 2.30$; 2: Gd, $pH = 2.05$; 3: Yb, $pH = 2.05$

The equilibrium constants $K_{T,S}$ and $K_{P,S}$ can be determined as

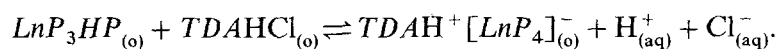
$$\log K_{T,S} = \log D_{T,S} - 3\log[HTTA] - \log[TDAHCl] - 3pH;$$

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

The formation of mixed adducts in the organic phase can be expressed by the equations



and



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

$$\log \beta_{T,S} = \log K_{T,S} - \log K_T \quad \text{and} \quad \log \beta_{P,S} = \log K_{P,S} - \log K_P.$$

The values of $\log K_{T,S}$ and $\log \beta_{T,S}$ are given in Table 1 and the values of $\log K_{P,S}$ and $\log \beta_{P,S}$ in Table 2. These equilibrium constants are concentration constants; they are based on the assumption that the activity coefficients of the species do not change significantly under the experimental conditions of the present study.

It can be seen from the experimental data that the lanthanides form different complexes with *HTTA*–*TDAHCl* and *HP*–*TDAHCl* mixtures: adduct chelates and anionic mixed complexes. Analogous results were obtained earlier for the lanthanide extraction with *HTTA*–*TOA* and *HP*–*TOA* mixtures [3, 10]. This is probably due to the rather large difference in the pK_a values of the two chelating extractants (pK_a is equal to 6.2 for *HTTA* [16] and 3.95 for *HP* [17]). Besides, the *HTTA*–*TDAHCl* mixture cause a smaller synergistic effect than a *HP*–*TDAHCl* mixture. It can be seen from the data in Table 3 that the values of pH_{50} for the mixtures of *HTTA* and *TDAHCl* are approximately one pH unit higher than those for *HP*–*TDAHCl* (pH_{50} is the pH value at which 50% of the metal is extracted).

Table 1. Values of the equilibrium constants for the extraction of Pr, Gd, and Yb with *HTTA*–*TDAHCl* mixtures in C_6H_6

Metal	$\log K_T$ [14]	$\log K_{T,S}$	$\log \beta_{T,S}$
Pr	-9.02 ± 0.03	-4.25 ± 0.02	4.77 ± 0.05
Gd	-7.72 ± 0.03	-3.33 ± 0.02	4.39 ± 0.05
Yb	-6.70 ± 0.03	-2.79 ± 0.02	3.91 ± 0.05

Table 2. Values of the equilibrium constants for the extraction of Pr, Gd, and Yb with *HP*–*TDAHCl* mixtures in C_6H_6

Metal	$\log K_P$ [15]	$\log K_{P,S}$	$\log \beta_{P,S}$
Pr	-4.08 ± 0.05	-1.56 ± 0.03	2.52 ± 0.08
Gd	-3.04 ± 0.04	-0.39 ± 0.02	2.65 ± 0.06
Yb	-2.13 ± 0.04	-0.22 ± 0.01	1.91 ± 0.05

Table 3. Values of pH_{50} for the extraction of Pr, Gd, and Yb with *HTTA*–*TDAHCl* and *HP*–*TDAHCl* mixtures

Metal	pH_{50}		ΔpH_{50}
	<i>HTTA</i> – <i>TDAHCl</i>	<i>HP</i> – <i>TDAHCl</i>	
Pr	3.40	2.30	1.10
Gd	3.10	2.02	1.08
Yb	2.92	1.98	0.94

Mixed anionic complexes were also found by french workers for the extraction of di- and trivalent metals with mixtures of various acylpyrazolones and *TOA* or dodecylamine [6–9]. The authors assume that the pyrazolones can react with the amine salts forming an ion pair, *e.g.* $TOAH^+P^-$, and according to the experimental conditions, the synergist can be the amine salt or the ion pair. They pointed out that the two mechanisms describing the synergistic extraction are thermodynamically equivalent and the extracted species are identical. Analogous ideas were first proposed by *Newman* and *Klotz* [1] for the synergistic extraction of Ce(III) with *HTTA* and *TOA*. They found that in the presence of HCl in the aqueous phase the extractants form the compounds *TOAHCl*, *TOAHClHTTA*, and *TOAHTTA*; all of them contribute equally to the synergistic effect. In our opinion, these concepts cannot be accepted without reservation. It was pointed out by *Baes et al.* [18] that the use of the slope analysis method is complicated if a complex is formed between the two extractants; however, the method can be used if one of the extractants is consumed completely during the reaction. The chelating extractant is usually in excess, and the amine salt should react completely. If this is always true, the synergistic extraction process should not be influenced by the anion of the salt. However, our experimental data demonstrate the important role of the anion in the extraction of lanthanides with *HP* and tridodecylammonium salt in their chloride, nitrate, and perchlorate forms as well as with *HTTA* and the quaternary ammonium salt Aliquat 336 as chloride, nitrate, and perchlorate. The change from the chloride anion to nitrate and perchlorate causes a considerable reduction of the equilibrium constants [19, 20]. This effect can be explained with the fact that the synergistic agent is the amine salt and that the anionic complex formation is connected with the breaking of the bond between the cation and the anion of the salt. Taking into consideration that the bond energy increases from the chloride to the nitrate and perchlorate forms of the tridodecylammonium salt [21], it is clear that the values of the equilibrium constants will decrease in that order.

Experimental

HTTA (Merck, p.a.), *HP* (Pharmachim Sofia, p.a.), and *TDA* (Merck-Schuchardt) were used as supplied. The oxides Pr_6O_{11} , Gd_2O_3 , and Yb_2O_3 (Fluka, puriss.) were used to prepare the stock solutions of the metals. The other reagents used were of analytical reagent grade.

Equal volumes (10 cm³ 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 [13]. 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 metal concentration was 2.5×10^{-4} mol/dm³ in all experiments.

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