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Synergic Solvent Extraction of Some Lanthanides with Mixtures of Thenoyltrifluoroacetone and Benzo-15-crown-5

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Summary. The synergic solvent extraction of Pr, Gd, and Yb with mixtures of thenoyltrifluoroacetone (*HTTA*) and a crown ether benzo-15-crown-5 (*B15C5*) in CCl_4, C_6H_6 and $CHCl_3$ has been studied. The composition of the extracted species has been determined as $Ln(TTA)_3 \cdot 2B15C5$ ($Ln =$ Pr, Gd, and Yb). The values of the equilibrium constants have been calculated.

Keywords. Benzo-15-crown-5; Lanthanides; Synergic extraction; Thenoyltrifluoroacetone.

Synergetische Extraktion von Lanthaniden mit Thenoyltrifluoraceton und Benzo-15-crown-5

Zusammenfassung. Es wurde die synergetische Extraktion von Pr, Gd und Yb mit Mischungen aus *HTTA* und Benzo-15-crown-5 in CCl_4, C_6H_6 und $CHCl_3$ untersucht. Die Zusammensetzung der Extraktionskomplexverbindungen $Ln(TTA)_3 \cdot 2B15C5$ ($Ln =$ Pr, Gd und Yb) wurde bestimmt, und die Gleichgewichtskonstanten wurden berechnet.

Introduction

During last years crown ethers have been used many times as synergistic agents in the extraction of lanthanides as well as of other metals. Synergistic extraction of trivalent lanthanides and actinides [1–9], divalent transition metals, alkali and alkaline earth metals [10–12] with mixtures of chelating extractants and various crown ethers have been reported. Mixtures of organophilic sulfonic, phosphoric and carboxylic acids and crown ethers have also been used for synergistic extraction of lanthanides and some other divalent metals [13–18]. Linear polyethers have been used as synergists as well [6, 12].

In the present work the synergic extraction of Pr, Gd and Yb with mixtures of thenoyltrifluoroacetone (*HTTA*) and benzo-15-crown-5 (*B15C5*, *S*) in CCl_4, C_6H_6, and $CHCl_3$ was studied.

Experimental Part

HTTA (Merck p.a.) and *B15C5* (Fluka, puriss.) 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 reagent used were of analytical reagent grade.

Equal volumes (10 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 [19]. The acidity of the aqueous phase was measured using a *pH*-meter with an accuracy of 0.01 *pH* unit. The ionic strength was maintained at 0.1 with (Na, H)Cl. The initial metal concentration was 2.5×10^{-4} mol/dm^3 in all experiments.

Results and Discussion

The solvent extraction of Pr, Gd, and Yb with solutions of *HTTA* was studied earlier [20]. The metal extraction can be represented by the equation

$$Ln^{3+}_{(aq)} + 3HTTA_{(o)} \rightleftharpoons Ln(TTA)_{3(o)} + 3H^+_{(aq)}$$

where Ln = Pr, Gd, and Yb and "*aq*" and "*o*" denote aqueous and organic phase, respectively.

The values of the equilibrium constant K_T for the formation of the metal chelates are given in Table 1.

The metal extraction with *B15C5* was negligibly small under the experimental conditions of the present study.

The synergic extraction of the metals was studied by the determination of the distribution coefficients $D_{T,S}$ as a function of one of the variables *pH*, [*HTTA*] and [*B15C5*], keeping the other two constant. The experimental data for the extraction of Pr, Gd, and Yb with mixtures of *HTTA* and *B15C5* in CCl_4, C_6H_6, and $CHCl_3$ are shown in Figs. 1–3. The plots of log $D_{T,S}$ vs. *pH* and log [*HTTA*] are linear of slopes close to three and the plots of log $D_{T,S}$ vs. log [*B15C5*] of slope close to two.

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

$$Ln^{3+}_{(aq)} + 3HTTA_{(o)} + 2S_{(o)} \rightleftharpoons Ln(TTA)_3 2S_{(o)} + 3H^+_{(aq)}.$$

The equilibrium constant $K_{T,S}$ for the synergistic complex formation can be determined as

$$\log K_{T,S} = \log D_{T,S} - 3\log[HTTA] - 2\log[S] - 3pH.$$

Table 1. Values of the equilibrium constants for the extraction of Pr, Gd, and Yb

Metal	Diluent	$\log K_T$[20]	$\log K_{T,S}$	$\log \beta_{T,S}$
Pr	CCl_4	−9.81±0.03	−1.68±0.02	8.13±0.05
	C_6H_6	−9.02±0.03	−2.50±0.03	6.52±0.06
	$CHCl_3$	−9.61±0.06	−4.03±0.01	5.58±0.07
Gd	CCl_4	−8.64±0.06	−0.44±0.01	8.20±0.07
	C_6H_6	−7.72±0.03	−1.18±0.02	6.54±0.05
	$CHCl_3$	−8.35±0.06	−2.75±0.01	5.60±0.07
Yb	CCl_4	−7.45±0.07	0.20±0.02	7.65±0.09
	C_6H_6	−6.70±0.03	−0.28±0.01	6.42±0.04
	$CHCl_3$	−7.30±0.04	−1.64±0.01	5.66±0.05

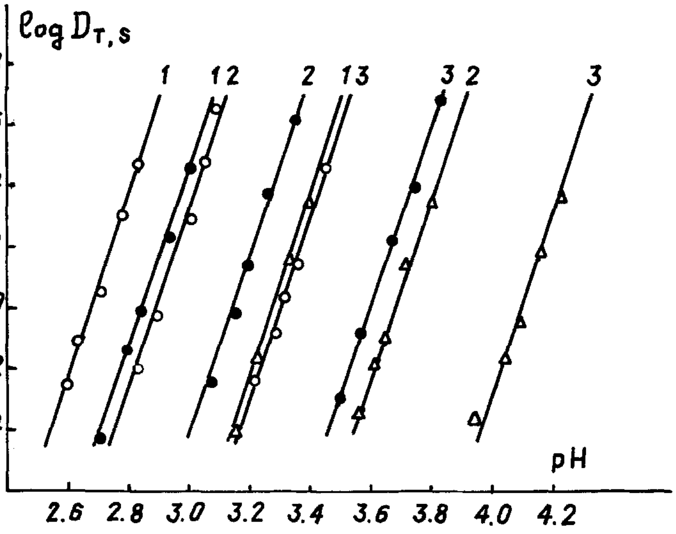

Fig. 1. Log $D_{T,S}$ vs. pH for Pr, Gd, and Yb extraction at $[HTTA] = 6 \times 10^{-2}$ mol/dm^3 and $[B15C5] = 5 \times 10^{-3}$ mol/dm^3. 1) Yb; 2) Gd; 3) Pr. Open circles – CCl_4; closed circles – C_6H_6; triangles – $CHCl_3$

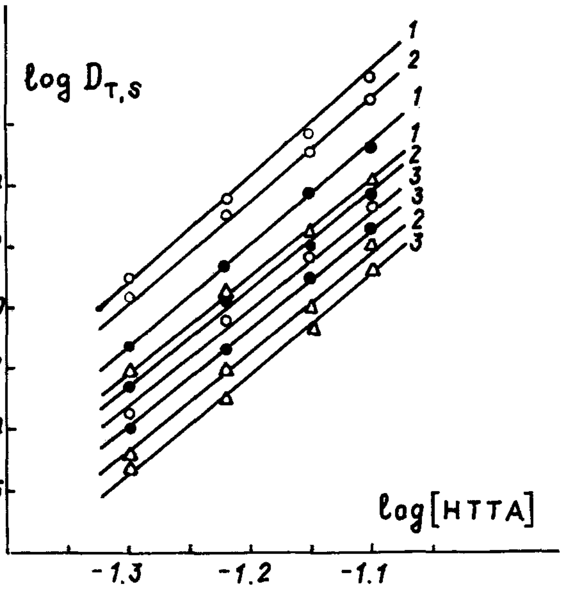

Fig. 2. Log $D_{T,S}$ vs. log $[HTTA]$ for Pr, Gd, and Yb extraction at $[B15C5] = 5 \times 10^{-3}$ mol/dm^3. 1) Yb; open circles – CCl_4, $pH = 2.80$; closed circles – C_6H_6, $pH = 2.90$; triangles – $CHCl_3$, $pH = 3.30$. 2) Gd; open circles – CCl_4, $pH = 3.00$; closed circles – C_6H_6, $pH = 3.15$; triangles – $CHCl_3$, $pH = 3.60$. 3) Pr; open circles – CCl_4, $pH = 3.30$; closed circles – C_6H_6, $pH = 3.55$; triangles – $CHCl_3$, $pH = 4.10$

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

$$Ln(TTA)_{3(o)} + 2S_{(o)} \rightleftharpoons Ln(TTA)_3 2S_{(o)}.$$

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

$$\log \beta_{T,S} = \log K_{T,S} - \log K_T.$$

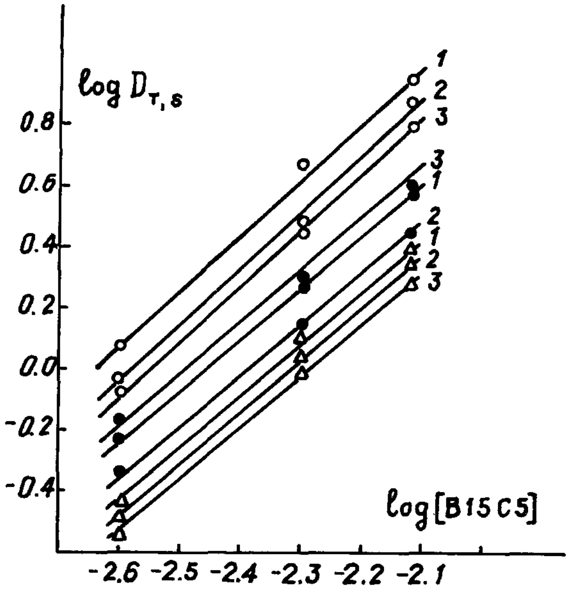

Fig. 3. Log $D_{T,S}$ vs. log [*B15C5*] for Pr, Gd, and Yb extraction at [*HTTA*] = 6×10^{-2} mol/dm^3. 1) Yb; open circles – CCl_4, *pH* = 2.90; closed circles – C_6H_6, *pH* = 2.95; triangles – $CHCl_3$, *pH* = 3.35. 2) Gd; open circles – CCl_4, *pH* = 3.10; closed circles – C_6H_6, *pH* = 3.20; triangles – $CHCl_3$, *pH* = 3.70. 3) Pr; open circles – CCl_4, *pH* = 3.50; closed circles – C_6H_6, *pH* = 3.70; triangles – $CHCl_3$, *pH* = 4.10

The values of log $K_{T,S}$ and log $\beta_{T,S}$ are given in Table 1. The equilibrium constants measured in this work are concentration constants and they are based on the assumption that the activity coefficients of the species do not change significantly during the reaction.

The values of log $K_{T,S}$ increase with increasing atomic number of the metals but the values of log $\beta_{T,S}$ for a definite diluent do not practically depend on the metal. With the change of the diluent the extraction of Pr, Gd, and Yb increases in the order: $CHCl_3 < C_6H_6 < CCl_4$.

Formation of the same adducts viz. $Ln(TTA)_3 2S$ was found by Aly et al. [1] for the extraction of Eu, Tm, and Yb with mixtures of *HTTA* and 15-crown-5 (*15C5*) in $CHCl_3$ but the values of the equilibrium constants differ significantly from those found in the present work. On the other hand Ensor and Shah [5, 6] have found formation of $Ln(TTA)_3S$ complexes for the extraction of trivalent lanthanides and actinides with mixtures of *HTTA* and nitrogen containing crown ethers *222BB* and *K22DD* or *15C5*.

Mathur and Khopkar [2] has accepted that not all oxygen atoms of the crown ether are coordinated to the metal. On the basis of thermodynamic studies [3] it is suggested that *B15C5* is bound to the metal only through the three oxygen atoms and that $LnP_3 2B15C5$ (*P* is 1-phenyl-3-methyl-4-trifluoroacetyl-pyrazol-5-one) is a sandwich type complex. It is possible that $Ln(TTA)_3 2B15C5$ is a sandwich type complex also.

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