Monatshefte für Chemie 130, 865–871 (1999)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

High Molecular Weight Amines as Synergistic Agents in the Solvent Extraction of Lanthanides with Thenoyltrifluoroacetone

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Summary. The synergistic solvent extraction of Pr, Gd, and Yb with mixtures of thenoyltrifluoroacetone (*HTTA*) and chlorides and perchlorates of methyldioctylamine (*MDOA*), trioctylamine (*TOA*), and tridodecylamine (*TDDA*) in C_6H_6 was studied. The composition of the extracted species was determined as $Ln(TTA)_3B\mathrm{H}A$ ($B = MDOA$, TOA, $TDDA$; $\mathrm{A} = \mathrm{Cl}^-$, ClO_4^-). The values of the equilibrium constants and the separation factors were calculated. The effect of the ammonium salts on the extraction process and the separation of the lanthanides is discussed.

Keywords. Synergistic extraction; Lanthanides; Thenoyltrifluoroacetone; Aliphatic amines; Separation factors.

Hochmolekulare Amine als synergetische Reagentien bei der Extraktion von Lanthaniden mit Thenoyltrifluoroaceton

Zusamenfassung. Es wurde die synergetische Extraktion von Pr, Gd und Yb mit Mischungen aus Thenoyltrifluoroaceton (H*TTA*) und Methyldioctylamin (*MDOA*), Trioctylamin (*TOA*) und Tridodecylamin (*TDDA*) (Chlorid- und Perchloratform) in C_6H_6 untersucht. Die Zusammensetzung der Extraktionskomplexverbindungen $Ln(TTA)_3B\mathrm{H}A$ ($B = MDOA$, TOA, $TDDA$; $A = \mathrm{Cl}^-$, ClO_4^-) wurde bestimmt und die Gleichgewichtskonstanten wurden berechnet. Die Eigenschaften der synergetischen Extraktion werden diskutiert.

Introduction

In the last years, high molecular weight amines have often been used as synergistic agents in combination with β-diketones. The synergistic extraction of trivalent Lanthanides [1–9], divalent transition, alkaline, and alkaline earth metals [10–17], and actinides [18, 19] with mixtures of thenoyltrifluoroacetone (H*TTA*) or acetylacetone (H*ACAC*) and various amines has been studied. It has been found that the metals can be extracted synergistically with considerable enhancement. Formation of mixed adducts $M^{n+}L_n mB\mathrm{H}A$, where L is the chelating extractant and

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*B*H*A* is the ammonium salt, has been established. The extraction mechanism has been discussed in the papers of *Newman* and *Klotz* [1] and *Ke* and *Li* [10].

The present work deals with the synergistic solvent extraction of representative trivalent lanthanides (Pr, Gd, and Yb) with mixtures of H*TTA* and tertiary ammonium chlorides or perchlorates.

Results and Discussion

The solvent extraction of Pr, Gd, and Yb with solutions of H*TTA* has been studied earlier [4]. The metal extraction can be expressed as

$$Ln^{3+}_{(aq)} + 3\mathrm{H}TTA_{(o)} \overset{K_\mathrm{T}}{\rightleftharpoons} Ln(TTA)_{3(o)} + 3\mathrm{H}^{+}_{(aq)}$$

where $Ln = \mathrm{Pr}$, Gd, and Yb and the subscripts *aq* and *o* denote the aqueous and organic phase, respectively. The lanthanide extraction with the chlorides and perchlorates of *TDDA*, *TOA*, and *MDOA* was negligible under the experimental conditions of the present study.

The synergistic extraction of the metals was studied by an examination of the variation of $D_\mathrm{T,S}$ (the distribution coefficient due to the synergistic effect) with relevant experimental variables. As the metal extraction with the ammonium salts was negligible, the values of the distribution coefficient *D* obtained for the metal extraction with mixtures of H*TTA* and ammonium salts *B*H*A* ($B = MDOA$, *TOA*, *TDDA*; $A = \mathrm{Cl}^-$, ClO_4^-) are given by the sum of $D_\mathrm{T,S}$ and D_T (due to the extraction with H*TTA* alone under the same experimental conditions). So, the values of $D_\mathrm{T,S}$ were calculated as D–D_T. Double logarithmic plots of $D_\mathrm{T,S}$ *vs.* one of the variables *pH*, [H*TTA*], and [*B*H*A*] keeping the other two constant indicate the stoichiometry of the extractable complex and lead to the derivation of a suitable equilibrium expression and after that to the calculation of the equilibrium constant. It was found that the plots of log$D_\mathrm{T,S}$ *vs.* *pH* and log[H*TTA*] were linear with slopes close to three and the plots of log$D_\mathrm{T,S}$ *vs.* log[*B*H*A*] had slopes close to one. The experimental data for the extraction of Pr, Gd, and Yb with mixtures of H*TTA* and *MDOA*H*A* are shown in Figs. 1–3. On the basis of the slope analysis data, the synergistic extraction of the metals can be described by

$$Ln^{3+}_{(aq)} + 3\mathrm{H}TTA_{(o)} + B\mathrm{H}A_{(o)} \overset{K_\mathrm{T,S}}{\rightleftharpoons} Ln(TTA)_3B\mathrm{H}A_{(o)} + 3\mathrm{H}^{+}_{(aq)}$$

The overall equilibrium constant $K_\mathrm{T,S}$ can be determined as

$$\log K_\mathrm{T,S} = \log D_\mathrm{T,S} - 3\log[\mathrm{H}TTA] - \log[B\mathrm{H}A] - 3pH$$

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

$$Ln(TTA)_{3(o)} + B\mathrm{H}A_{(o)} \overset{\beta_\mathrm{T,S}}{\rightleftharpoons} Ln(TTA)_3B\mathrm{H}A_{(o)}$$

The equilibrium constant $\beta_\mathrm{T,S}$ can be determined as

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

where K_T is the equilibrium constant for the metal extraction with H*TTA* alone.

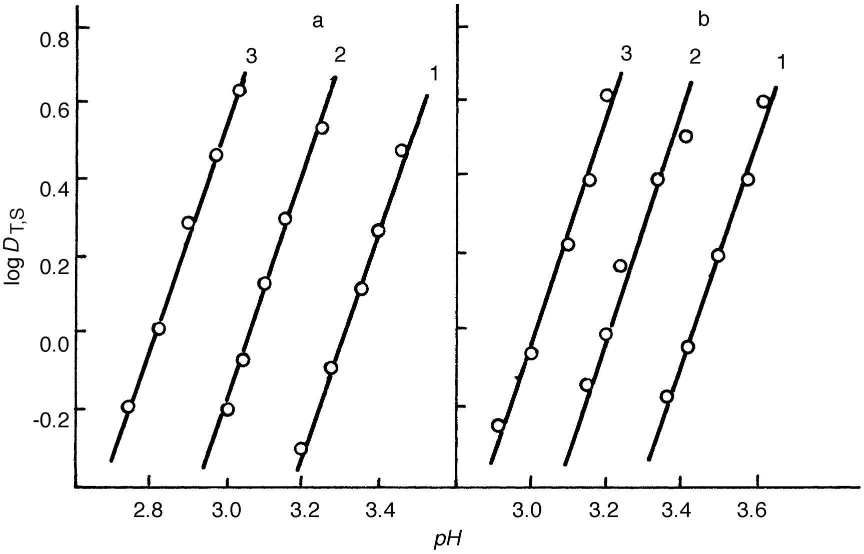

Fig. 1. log$D_{T,S}$ *vs.* *pH* for Pr, Gd, and Yb extraction with H*TTA*-*MDOA*HA mixtures at [H*TTA*] = 6×10^{-2} mol/dm^3 and [*MDOA*HA] = 5×10^{-3} mol/dm^3; a) chloride medium: 1: Pr; 2: Gd, 3: Yb; b) perchlorate medium: 1: Pr; 2: Gd, 3: Yb

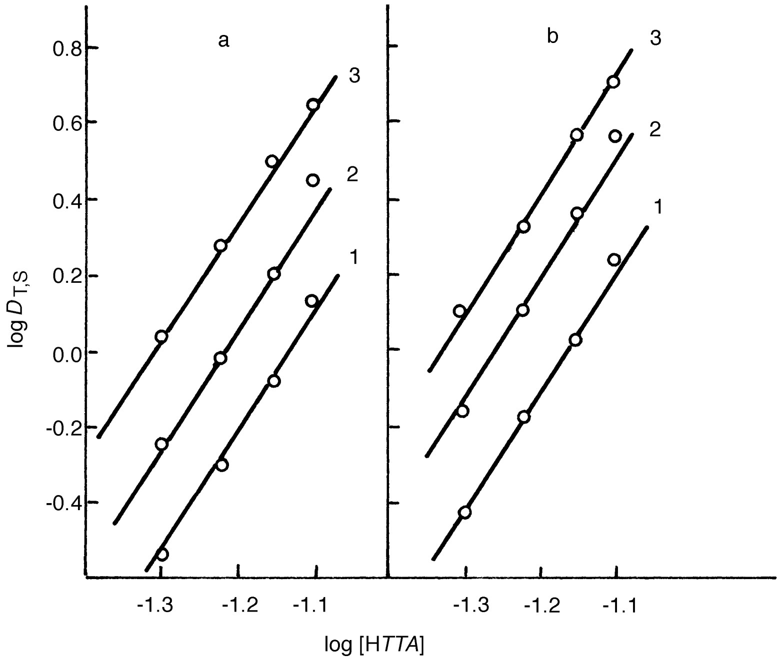

Fig. 2. log$D_{T,S}$ *vs.* log[H*TTA*] for Pr, Gd, and Yb extraction with H*TTA*-*MDOA*HA mixtures at [*MDOA*HA] = 5×10^{-3} mol/dm^3; a) chloride medium: 1: Pr, *pH* = 3.20, 2: Gd, *pH* = 3.05, 3: Yb, *pH* = 2.90; b) perchlorate medium: 1: Pr, *pH* = 3.35, 2: Gd, *pH* = 3.20, 3: Yb, *pH* = 3.10

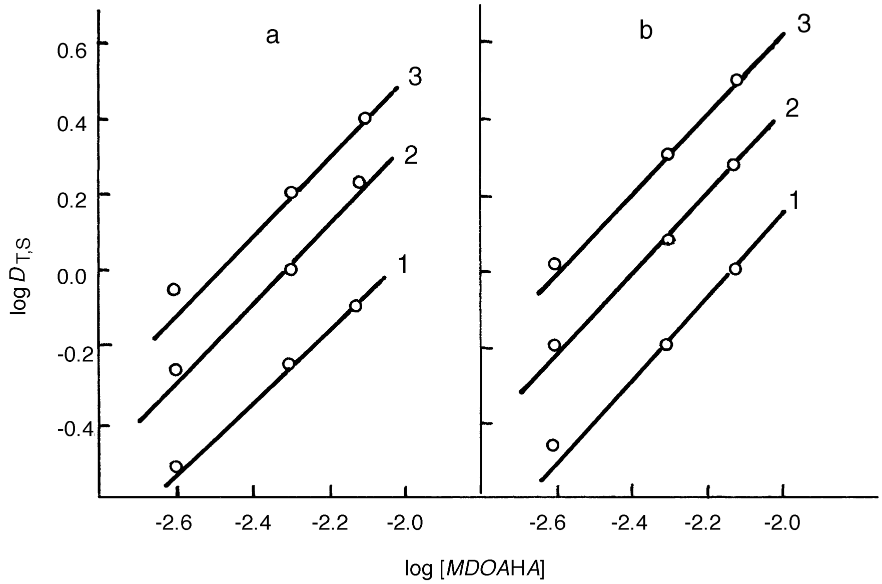

Fig. 3. log$D_{T,S}$ *vs.* log[*MDOA*HA] for Pr, Gd, and Yb extraction with H*TTA*-*MDOA*H*A* mixtures at [H*TTA*] = 6×10^{-2} mol/dm^3; a) chloride medium: 1: Pr, *pH* = 3.20, 2: Gd, *pH* = 3.05, 3: Yb, *pH* = 2.90; b) perchlorate medium: 1: Pr, *pH* = 3.35, 2: Gd, *pH* = 3.20, 3: Yb, *pH* = 3.10

The values of K_T, $K_{T,S}$, and $\beta_{T,S}$ 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, *i.e.* they are concentration constants.

The data in Table 1 show that the length of the carbon chains of the ammonium salt does not play a significant role in the synergistic extraction of the lanthanides. Approximately the same values of $K_{T,S}$ were found when primary ammonium salts (tridecylammonium chloride and perchlorate) were used as synergistic agents in combination with H*TTA* [5]. These results can be explained by the fact that the ammonium salt is bound to the metal through its anion [10]. As the metal radii decrease with increasing atomic number (lanthanide contraction), the larger anion (ClO_4^-) causes a larger decrease of the $K_{T,S}$ values for Yb than for Gb and Pr because of steric hindrances. The data in Table 2 confirm these explanations. The $\Delta\log K_{T,S}$ values were calculated as a difference of the equilibrium constant values for H*TTA*-*B*HCl and H*TTA*-*B*HClO$_4$ systems. Previous investigations [21] have shown that when Pr, Gd, and Yb were extracted synergistically with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (H*P*) and the same ammonium chlorides and perchlorates, the change of the anion affected the lanthanides extraction to a greater extent. The values of $\Delta\log K_{P,S}$ are several times larger than those of $\Delta\log K_{T,S}$. This is due to the fact that the formation of anionic complexes *B*H[*LnP*$_4$], as observed when H*P* is used as chelating extractant, is connected with the breaking of the bond between the cation and the anion of the salt.

The metal separation can be assessed using separation factors. They can be calculated as a ratio of the equilibrium constant $K_{T,S}$ for two metals when they

Table 1. Values of the equilibrium constants K_{T}, $K_{\mathrm{T,S}}$, and $\beta_{\mathrm{T,S}}$ for Pr, Gd, and Yb extraction with H*TTA*-*B*H(Cl,ClO$_4$) mixtures

Metal	Extractants	logK_{T}(4)	log$K_{\mathrm{T,S}}$	log$\beta_{\mathrm{T,S}}$
Pr	H*TTA*	−9.02±0.03	–	–
	H*TTA*-*MDOA*HCl	–	−4.00±0.05	5.02±0.06
	H*TTA*-*MDOA*HClO$_4$	–	−4.24±0.05	4.78±0.08
	H*TTA*-*TOA*HCl	–	−4.09±0.04	4.93±0.07
	H*TTA*-*TOA*HClO$_4$	–	−4.35±0.03	4.67±0.06
	H*TTA*-*TDDA*HCl	–	−4.25±0.02 [5]	4.77±0.05 [5]
	H*TTA*-*TDDA*HClO$_4$	–	−4.32±0.02 [5]	4.70±0.05 [5]
Gd	H*TTA*	−7.72±0.03	–	–
	H*TTA*-*MDOA*HCl	–	−3.16±0.02	4.56±0.05
	H*TTA*-*MDOA*HClO$_4$	–	−3.48±0.03	4.24±0.06
	H*TTA*-*TOA*HCl	–	−3.02±0.02	4.70±0.05
	H*TTA*-*TOA*HClO$_4$	–	−3.48±0.03	4.24±0.06
	H*TTA*-*TDDA*HCl	–	−3.33±0.02	4.39±0.05
	H*TTA*-*TDDA*HClO$_4$	–	−3.65±0.03	4.07±0.06
Yb	H*TTA*	−6.70±0.03	–	–
	H*TTA*-*MDOA*HCl	–	−2.46±0.02	4.24±0.05
	H*TTA*-*MDOA*HClO$_4$	–	−3.04±0.05	3.66±0.08
	H*TTA*-*TOA*HCl	–	−2.50±0.03	4.20±0.06
	H*TTA*-*TOA*HClO$_4$	–	−3.13±0.02	3.57±0.05
	H*TTA*-*TDDA*HCl	–	−2.79±0.02	3.91±0.05
	H*TTA*-*TDDA*HClO$_4$	–	−3.29±0.04	3.41±0.07

Table 2. Values of Δlog$K_{\mathrm{T,S}}$ for Pr, Gd, and Yb extraction with mixtures of H*TTA* and alkylammonium chlorides and perchlorates

Metal	Δlog$K_{\mathrm{T,S}}$			
	H*TTA*-*MDOA*	H*TTA*-*TOA*	H*TTA*-*TDDA*	H*TTA*-*TDA* [5]
Pr	0.24	0.26	0.07	0.14
Gd	0.32	0.46	0.32	0.38
Yb	0.58	0.63	0.50	0.61

form the same type of complexes with a given combination of extractants (Table 3). The data in the table show that the chelating extractants alone afford better lanthanide separation. The separation factors for the pair Gd/Pr are larger than those for the pair Yb/Gd not only for H*TTA* but for all combinations of extractants too. The same tendency was found when mixtures of H*P* and ammonium salts were used for Pr, Gd, and Yb extraction [22]. It has to be noted that the separation with H*P* alone is worse than that with H*TTA* alone, but the separation factors of the lighter lanthanides are larger for synergistic mixtures containing H*P* instead of H*TTA*. The opposite is true for the heavier lanthanides. Besides, the H*TTA*-*B*HClO$_4$ systems show a lower separation of the lanthanides than H*TTA*-*B*HCl systems. This

Table 3. Separation factors for Pr, Gd, and Yb with H*TTA*-alkylammonium salt

Extractants	Separation Factor	
	Gd/Pr	Yb/Gd
H*TTA*	19.9	10.5
H*TTA*-*MDOA*HCl	6.9	5.0
H*TTA*-*MDOA*$HClO_4$	6.3	2.6
H*TTA*-*TOA*HCl	11.7	3.3
H*TTA*-*TOA*$HClO_4$	7.4	2.2
H*TTA*-*TDDA*HCl	8.3	3.5
H*TTA*-*TDDA*$HClO_4$	4.7	2.3

effect could be explained by the faster decrease of the equilibrium constant $K_{T,S}$ values with decreasing atomic number of the lanthanides when perchlorate salts were used as synergistic agents. Thus, the separation factors (the ratio of the equilibrium constant $K_{T,S}$ for two metals) will be lower for H*TTA*-*B*$HClO_4$ systems.

Experimental

H*TTA* (Merck, p.a.), tridodecylamine (*TDDA*, Merck-Schuchardt), trioctylamine (*TOA*), and methyldioctylamine (*MDOA*, Fluka, purum) were used as supplied. Pr_6O_{11}, Gd_2O_3, and Yb_2O_3 (Fluka, puriss.) were used to prepare the stock solutions. Benzene (Merck, p.a.) was used as diluent. The other reagents were of analytical grade.

Equal volumes (10 cm^3 each) of aqueous and organic phases were shaken mechanically for 60 minutes 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 [20]. 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 mol/dm^3 with (Na,H)Cl,ClO_4. The initial metal concentration was 2.5×10^{-4} mol/dm^3 in all experiments.

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Received November 10, 1998. Accepted (revised) December 28, 1998