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Some Tendencies of the Synergistic Extraction of Lanthanides with Mixtures of Thenoyltrifluoroacetone and Trioctylamine

Short Communication

Ivan L. Dukov *, **Georgi I. Kassabov**, and **Afaf F. Al-Nimri**

Department of Inorganic Chemistry, Higher Institute of Chemical Technology,
1156 Sofia, Bulgaria

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Solvent extraction of Pr, Gd and Yb with mixtures of H*TTA* and *TOA* has been investigated. The values of the synergistic equilibrium constant have been calculated. Some tendencies of the synergistic extraction of lanthanides have been discussed.

(Keywords: Diluents; Lanthanides; Synergistic extraction; Thenoyltrifluoroacetone; Trioctylamine)

Einige Tendenzen in der synergistischen Extraktion von Lanthaniden mit einer Mischung aus Thenoyltrifluoraceton und Trioctylamin (Kurze Mitteilung)

Es wurde die synergistische Extraktion von Pr, Gd und Yb mit einer Mischung aus H*TTA* und *TOA* untersucht. Die synergistischen Gleichgewichtskonstanten wurden berechnet und die Auswirkungen spezifischer Versuchsbedingungen auf das Extraktionsgleichgewicht diskutiert.

Mixtures of chelating extractants and highmolecular weight amines have been used in several cases for synergistic extraction of lanthanides[1–6]. The influence of the factors that affect the extraction equilibrium have been studied[1,2,4,6] but these studies still lack details on specific tendencies of the lanthanide synergistic extraction.

Studies of the extraction of lanthanides (Pr, Gd and Yb) with solutions of thenoyltrifluoroacetone (H*TTA*) and Trioctylamine (*TOA*) in $CHCl_3$, C_6H_6, CCl_4 and C_8H_{18} from aqueous phase containing HCl,

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HNO_3 and $HClO_4$ have been undertaken now to elucidate the effect of both diluents and acids.

The synergistic extraction of metals may be expressed by the equation

$$M^{n+}_{(aq)} + n\,HTTA_{(org)} + m\,S_{(org)} \rightleftharpoons M\,(TTA)_n\,S_{m(org)} + n\,H^{+}{}_{(aq)}$$

where M is the metal and S is the synergist. It may be shown easily that

$$\log D = \log K + n\,pH + n \log[HTTA] + m \log[S]$$

where D is the distribution coefficient, K is the synergistic equilibrium constant and n, m are stoichiometric coefficients.

The extraction of the metals with $HTTA$ and TOA separately was not studied because it is negligible at these experimental conditions[8,9].

If the concentration of the extractants is constant i. e. $[HTTA]$ and $[TOA] \gg [Ln^{3+}]$ and the polymerization in the organic phase, and hydrolysis and complexation in the aqueous phase occur to a negligible extent, the plots of $\log D$ vs. pH, $\log D$ vs. $\log[HTTA]$, and $\log D$ vs. $\log[S]$ will be linear. The values of n and m can be determined from the slopes. The values of n and m were found to be approximately 3 and 1 respectively. Almost in all cases the experimental points fit a linear relationship with a correlation coefficient of 0.997 or better and so the indicated composition of the extracted species is $Ln(TTA)_3S$. The values of the synergistic equilibrium constant as well of pH_{50} (pH at which 50% from the metal is extracted) and the slopes are given in Table 1.

It was found that the metal extraction increase in the order $CHCl_3 < C_6H_6 < CCl_4 < C_8H_{18}$ and in the order $HClO_4 < HNO_3 < HCl$ for diluents and acids. The diluents with high solvation ability stabilize the polar amine salts (in which the amine is transformed easily in the presence of acids in the aqueous phase[10,11]) so that the formation of the synergistic adducts is hindered more when such diluents are used and the values of the equilibrium constant are the lowest. On the other hand, the differences between these values—when synergists are TOA salts of various acids—are the highest for $CHCl_3$ which is the diluent with the highest solvation ability and they are the lowest for the most inert diluent (C_8H_{18}). This is due to differencies in the solvation of the amine salts.

The tendencies of the synergistic extraction may be understood better if our earlier studies[6] are taken into consideration. It was found that using relatively active diluents as C_6H_6 and CCl_4 results in the amine salt acting as synergist but when inert diluents as octane and cyclohexane are used both the amine salt and the amine act as

Table 1. *Extraction of lanthanides with* $HTTA/TOA$ *mixtures*: $\log D$ *vs.* pH *relationships.* $[HTTA] = 4 \cdot 10^{-2} M$ for C_8H_{18} and $8 \cdot 10^{-2} M$ for the other diluents. $[TOA] = 5 \cdot 10^{-3} M$ in all experiments

Metal	Diluent	HCl			HNO_3			$HClO_4$		
		$\log K$	pH_{50}	slope	$\log K$	pH_{50}	slope	$\log K$	pH_{50}	slope
Pr	C_8H_{18}	—2.99	3.17	2.75	—3.10	3.20	2.99	—3.22	3.23	3.16
	CCl_4	—3.35	3.00	2.75	—3.75	3.11	2.78	—3.96	3.18	3.30
	C_6H_6	—3.75	3.12	2.77	—4.25	3.28	3.04	—4.45	3.34	3.30
	$CHCl_3$	—4.54	3.38	3.07	—5.06	3.56	2.73	—5.27	3.61	3.14
Gd	C_8H_{18}	—2.00	2.85	3.00	—2.11	2.89	3.10	—2.35	2.95	3.01
	CCl_4	—2.50	2.73	2.95	—2.74	2.78	2.83	—2.82	2.80	2.89
	C_6H_6	—2.82	2.81	2.87	—3.13	2.91	3.22	—3.35	2.97	2.95
	$CHCl_3$	—3.91	3.17	2.94	—4.20	3.26	3.09	—4.41	3.36	3.29
Yb	C_8H_{18}	—1.50	2.68	2.82	—1.62	2.72	3.01	—1.86	2.80	3.04
	CCl_4	—1.98	2.53	2.90	—2.08	2.56	3.02	—2.29	2.63	3.11
	C_6H_6	—2.28	2.63	3.10	—2.55	2.72	3.08	—3.04	2.87	2.96
	$CHCl_3$	—3.27	2.96	3.01	—3.58	3.05	3.12	—4.13	3.24	3.04

synergists, i.e. the amine salt participates in the formation of one part of the adducts and the amine in the remaining part. It is clear that the formation of those adducts in which the amine is synergist is not so affected: neither by the diluent because of the weak interaction of the almost nonpolar *TOA* with the inert diluent[10], nor by the acid used; this contributes additionally for smaller differencies between the values of the equilibrium constant.

Experimental

HTTA (Merck) and *TOA* (Fluka) were used as supplied. The solutions of the metals were prepared from the oxides Pr_6O_{11}, Gd_2O_3 and Yb_2O_3 (Fluka, puriss.). Arsenazo III (Fluka) was p.a. Other reagents used were of A.R. quality.

10 ml each of the aqueous phase and organic phase were shaken mechanically. Equilibrations were reached within 1 h. The concentration of the metals was determined photometrically using Arsenazo III[7]: an aliquote part of the analyzed solution with pH 2-3 was poured into a 25 ml flask with 5 ml 0.01% Arsenazo III and 10 ml buffer solution ($pH = 3$). A volume of 25 ml was adjusted with water. The absorbance was measured at the wavelength 665 nm against Arsenazo III solution as a reference.

The aqueous phase acidities were measured by a pH-meter with an accuracy of 0.01 pH unit. The ionic strength was maintained at 0.1 with (Na, H) Cl, NO_3, ClO_4.

The initial concentration of the metals was $2.5 \cdot 10^{-4} M$ in all experiments.

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