Monatshefte für Chemie 116, 737—743 (1985)

Monatshefte für Chemie
Chemical Monthly

Temperature Effect on the Solvent Extraction of Some Lanthanides with Thenoyltrifluoroacetone

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

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

(Received 7 June 1984. Accepted 6 July 1984)

The solvent extraction of Pr, Gd and Yb with thenoyltrifluoroacetone solutions in C_6H_6, $CHCl_3$ and CCl_4 at 288 K, 298 K, 308 K and 318 K has been investigated. The values of the equilibrium constant have been calculated as well as the values of the thermodynamic parameters ΔH, ΔS and ΔG. The temperature effect on the solvent extraction of lanthanides with thenoyltrifluoroacetone is discussed.

(Keywords: Lanthanides; Solvent extraction; Temperature effect; Thenoyltrifluoroacetone)

Einfluß der Temperatur auf die Extraktion einiger Lanthanoide mit Thenoyltrifluoraceton

Es wurde die Extraktion von Pr, Gd und Yb mit Lösungen von Thenoyltrifluoraceton in C_6H_6, $CHCl_3$ und CCl_4 bei 288 K, 298 K, 308 K und 318 K untersucht. Es wurden die Gleichgewichtskonstanten für die untersucht3n Metalle, Lösungsmittel und Temperaturen sowie die Werte der thermodynamischen Parameter ΔH, ΔS und ΔG berechnet. Der Einfluß der Temperatur auf die Extraktion von Lanthaniden wird diskutiert.

Introduction

Chelating extractants are used often for the solvent extraction of metals[1—3] but the temperature effect on the extraction process has not been studied extensively so far, although some investigations for the extraction of Co, Zn, Cd, Eu, Tb with thenoyltrifluoroacetone (H*TTA*) have been done[4—14,17]. Recently, data on the temperature effect on the extraction of Zn with *LIX 34* (8-alkarylsulfonamidoquinoline) were published[15].

The present work was undertaken to give more information about the influence of temperature on the solvent extraction of Pr, Gd and Yb with solutions of H*TTA* in C_6H_6, $CHCl_3$ and CCl_4.

Experimental

H*TTA* (Merck) and Arsenazo III (Fluka) were p.a. The metal solutions were prepared from the oxides Pr_6O_{11}, Gd_2O_3 and Yb_2O_3 (Fluka, p.a.). All other reagents used were of A.R. quality.

The metal extraction was studied at 288 K, 298 K, 308 K and 318 K. The temperature was measured with an accuracy of 0.1°. The ionic strength was maintained at 0.1 *M* with (Na, H) Cl. The aqueous phase acidities were measured with an accuracy of 0.01 *pH* unit.

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

The procedures were identical to those used in our previous study[16].

Results and Discussion

It is well known[3] that the extraction of lanthanides with H*TTA* can be expressed by the equation

$$Ln^{3+}_{(aq)} + 3\,\mathrm{H}TTA_{(org)} \rightleftharpoons Ln(TTA)_{3(org)} + 3\,\mathrm{H}^{+}{}_{(aq)}$$

where *Ln* = Pr, Gd, Yb, aq. and org. are aqueous and organic phase. It may be shown easily that

$$\log D = \log K + 3 \log [\mathrm{H}TTA] + 3pH$$

where *D* is the distribution coefficient and *K* is the equilibrium constant.

If the concentration of the extractant is constant i.e. $[\mathrm{H}TTA] \gg [\mathrm{Ln}]$ and the polymerization in the organic phase as well as hydrolysis and complexation in the aqueous phase occur to a negligible extent, the plots of log *D* vs. *pH* will be straight lines of slope 3. The experimental data for the extraction of Pr, Gd and Yb with solutions of H*TTA* in C_6H_6, $CHCl_3$ and CCl_4 at 288 K, 298 K, 308 K and 318 K are shown in Figs. 1–3. The plots represent straight lines of slope 3. This proves that the composition of the extracted species really is $Ln(TTA)_3$. The values of the equilibrium constant of the metals at various temperatures were calculated from the experimental data. They are given in Table 1. The increase of the temperature leads to an increase of the extraction. The same effect of temperature was found for the formation of some other lanthanide chelates[11,14]. The values of ΔH and ΔS can be determined from the values of the equilibrium constant at various temperature taking into account the equation $\ln K = -\Delta H/RT + \Delta S/R$. Plotting ln *K* vs. $1/T$ should result in a straight line with a slope of $-\Delta H/R$ and an intercept of $\Delta S/R$, as is shown in Fig. 4. The equations for the best fits of the plots of ln *K* vs. $1/T$ along with the correlation coefficients and the values of ΔH and ΔS are given in Table 2. The values of ΔG are obtained from the equation ΔG

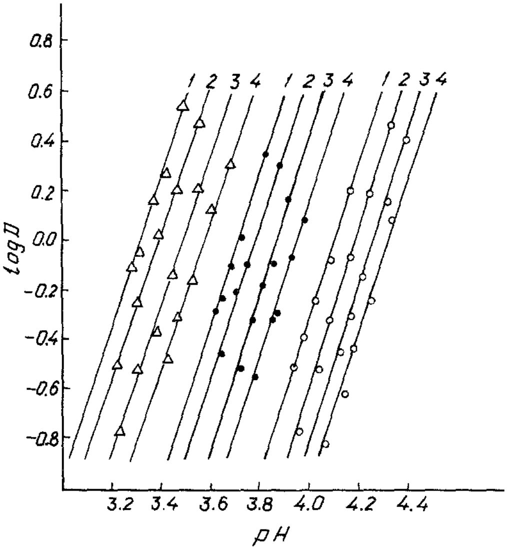

Fig. 1. log*D* vs. *pH* for the extraction of Pr, Gd and Yb with H*TTA* in CCl_4. *1*, 318 K; *2*, 308 K; *3*, 298 K; *4*, 288 K. *Pr* opened circles; *Gd* closed circles; *Yb* triangles

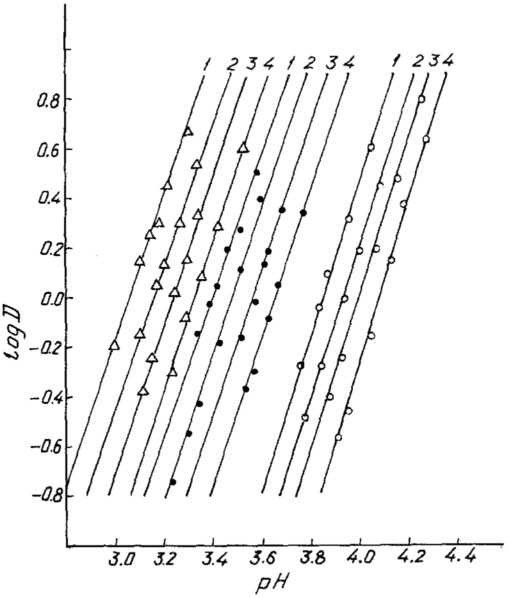

Fig. 2. log*D* vs. *pH* for the extraction of Pr, Gd and Yb with H*TTA* in C_6H_6. *1*, 318 K; *2*, 308 K; *3*, 298 K; *4*, 288 K. *Pr* opened circles; *Gd* closed circles; *Yb* triangles

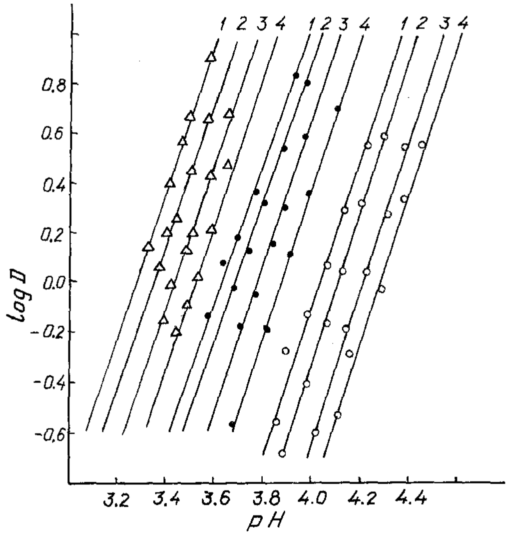

Fig. 3. log*D* vs. *pH* for the extraction of Pr, Gd and Yb with H*TTA* in $CHCl_3$. *1,* 318 K; *2,* 308 K; *3,* 298 K; *4,* 288 K. *Pr* opened circles; *Gd* closed cirles; *Yb* triangles

Table 1. *Values of the equilibrium constant for the extraction of* Pr, Gd *and* Yb *with* H*TTA in* C_6H_6, $CHCl_3$ *and* CCl_4 *at various temperatures*

Metal	Diluent	log *K*			
		288 *K*	298 *K*	308 *K*	318 *K*
Pr	C_6H_6	—9.28 ± 0.08	—9.02 ± 0.03	—8.83 ± 0.02	—8.52 ± 0.02
	$CHCl_3$	—9.81 ± 0.06	—9.61 ± 0.06	—9.31 ± 0.06	—9.06 ± 0.07
	CCl_4	—10.04 ± 0.06	—9.81 ± 0.03	—9.59 ± 0.05	—9.30 ± 0.03
Gd	C_6H_6	—7.96 ± 0.06	—7.72 ± 0.03	—7.43 ± 0.08	—7.23 ± 0.06
	$CHCl_3$	—8.60 ± 0.03	—8.35 ± 0.06	—8.07 ± 0.03	—7.87 ± 0.06
	CCl_4	—8.88 ± 0.06	—8.64 ± 0.06	—8.35 ± 0.03	—8.15 ± 0.06
Yb	C_6H_6	—6.98 ± 0.03	—6.70 ± 0.03	—6.46 ± 0.03	—6.20 ± 0.06
	$CHCl_3$	—7.54 ± 0.06	—7.30 ± 0.04	—7.03 ± 0.03	—6.81 ± 0.03
	CCl_4	—7.70 ± 0.04	—7.45 ± 0.07	—7.16 ± 0.03	—6.96 ± 0.06

$= -RT\ln K$ at 298 K. The values of the thermodynamic parameters are based on the concentrations rather than activities of the species in the solution. However, it is known that "the behaviour of such systems closely approaches ideality"[1]. So it can be expected that these parameters will not vary considerably from those calculated using activities.

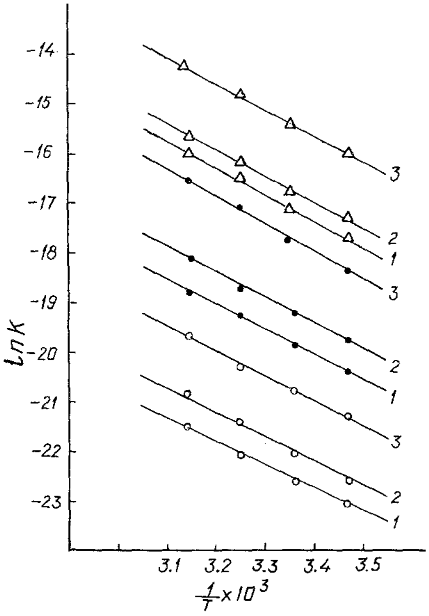

Fig. 4. ln *K* vs. 1/*T* for the extraction of Pr, Gd and Yb with H*TTA* in C_6H_6, $CHCl_3$ and CCl_4. *1*, CCl_4; *2*, $CHCl_3$; *3*, C_6H_6. *Pr* opened circles; *Gd* closed circles; *Yb* triangles

It is seen from the data given in Table 2 that the values of ΔH are positive and practically equal for all metals. The positive values of ΔH were expected because the formation of chelate complexes not only of lanthanides but of some other metals is an endothermic process[4—6]. It is accepted that water molecules from the inner coordination sphere of the metal ion in the aqueous phase are replaced by the chelating extractant. It is noted however, that the replacement of water molecules from the hydrated lanthanide ions with composition $Ln(H_2O)_x$ where $x = 8$ or 9 should cause a positive entropy change which has not been found by the author[11].

Our data show that the values of ΔS are negative for Pr and Gd and positive for Yb. Probably, the variation of the sign is due to a difference in the hydration numbers of the metals. Such a difference between the lighter and the heavier lanthanide ions has been pointed out[18].

The values of the thermodynamic parameters for some lanthanides (Eu mainly) were given earlier[11,13,14]. The data for Gd obtained in the present work have the same signs and similar values as those for Eu obtained by *Bhatti*[11] and *Kandil*[14].

Table 2. *Equations, ΔH, ΔS, ΔG, and correlation coefficient values for the variable temperature extraction of* Pr, Gd *and* Yb *with* H*TTA in* C_6H_6, $CHCl_3$, *and* CCl_4

Metal	Diluent	Eq. for ln *K*	Correlation coefficient	ΔH^a kJ/mol	ΔS^b J/mol·deg	ΔG^c kJ/mol
Pr	C_6H_6	$= \frac{5239.7}{T} - 3.20$	0.997	43.6	—26.6	51.5
	$CHCl_3$	$= \frac{5417.7}{T} - 3.84$	0.997	45.0	—31.9	54.6
	CCl_4	$= \frac{5166.3}{T} - 5.22$	0.998	43.0	—43.4	55.9
Gd	C_6H_6	$= \frac{5266.1}{T} - 0.06$	0.999	43.8	—0.5	44.0
	$CHCl_3$	$= \frac{5247.0}{T} - 1.58$	0.999	43.6	—13.2	47.6
	CCl_4	$= \frac{5256.3}{T} - 2.21$	0.998	43.7	—18.3	49.2
Yb	C_6H_6	$= \frac{5465.7}{T} + 2.91$	1.000	45.4	24.2	38.2
	$CHCl_3$	$= \frac{5217.6}{T} + 0.74$	1.000	43.4	6.2	41.5
	CCl_4	$= \frac{5311.9}{T} + 0.71$	0.998	44.2	5.9	42.3

[a] Estimated standard deviation $\leqslant 2.3$ kJ/mol.
[b] Estimated standard deviation $\leqslant 7.4$ J/mol·deg.
[c] Estimated standard deviation $\leqslant 0.4$ kJ/mol.

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