Monatshefte für Chemie 119, 693—698 (1988)

Monatshefte für Chemie
Chemical Monthly

The Influence of Different Salting-out Agents on the Extraction of Ce, Eu, Gd, Tb Using Tri-*n*-butyl Phosphate

Marek Majdan

Institute of Chemistry, Marie Curie Skłodowska University,
PL-20-031 Lublin, Poland

(Received 6 May 1987. Accepted 29 May 1987)

The extraction enthalpies ΔH° of Ce, Eu, Gd, Tb nitrates using *TBP* in the presence of different salting-out agents in aqueous phase were determined. It was established that the extraction process is the most exothermic in the case of $LiNO_3$.

(Keywords: Lanthanide nitrates; Tri-n-butyl phosphate; Salting-out agent; Extraction enthalpy)

Der Einfluß verschiedener Aussalzmittel auf die Extraktion von Ce, Eu, Gd *und* Tb *mit Tri-n-butylphosphat*

Es wurden die Extraktionsenthalpien ΔH° von Ce-, Eu-, Gd- und Tb-Nitrat unter Verwendung von *TBP* in Gegenwart verschiedener Aussalzmittel in wäßriger Phase bestimmt. Es wurde festgestellt, daß der Extraktionsprozeß im Fall von $LiNO_3$ am meisten exotherm verläuft.

Introduction

Tri-*n*-butyl phosphate is still one of the most convenient extraction agents used for the separation of lanthanides and actinides [1–6]. The extraction is carried out from solutions with high HNO_3 concentration or neutral [7]. In the latter case it is necessary to use salting-out agents which increase the concentration of NO_3^- on one hand and cause dehydration of the lanthanide cation on the other hand to make the extraction process easier. We can formulate the whole process as follows:

$$Ln(H_2O)^{3+}_{x\,aq} \leftrightarrows Ln^{3+}_{aq} + x\,H_2O_{aq} \tag{1}$$

$$Ln^{3+}_{aq} + 3\,NO^-_{3\,aq} + 3\,TBP_0 \leftrightarrows Ln(NO_3)_3 \cdot 3\,TBP_0 \tag{2}$$

The first stage refers to the dehydration of the lanthanide cation. The lower the water activity, the more advanced is the dehydration of the Ln^{3+} cation. The second stage should not depend on the water activity.

Therefore the whole enthalpy of the extraction at constant *TBP* concentration depends on the course of the first stage. The aim of this paper was to show the influence of the different salting-out agents on the enthalpy for the extraction of Ce, Eu, Gd, Tb nitrates using *TBP*.

Experimental

$Ce(NO_3)_3$ was a product of Polskie Odczynniki Chemiczne (99% purity); Gd_2O_3, Eu_2O_3, Tb_2O_3 produced by Johnson Matthey (spectral purity); *TBP* Merck (analytically pure); HNO_3, C_6H_6 Polskie Odczynniki Chemiczne (analytically pure); $LiNO_3$, NH_4NO_3, $NaNO_3$ Polskie Odczynniki Chemiczne (pure).

To determine the extraction enthalpy the extraction of the lanthanides in the range 10–50 °C in the following systems was performed:

$$Ln(NO_3)_3 - 6\,M\ NH_4NO_3 - 1\,M\ TBP$$
$$Ln(NO_3)_3 - 6\,M\ NaNO_3 - 1\,M\ TBP$$
$$Ln(NO_3)_3 - 5.2\,M\ LiNO_3 - 1\,M\ TBP$$

The measurements of the distribution coefficients were performed using the following isotopes (with the different half-periods given in bracket): ^{141}Ce(32 d), ^{152}Eu(13 y), ^{153}Gd(200 d), ^{160}Tb(73 d). The radioisotopes were obtained as the result of the neutron activation of the respective oxides or nitrates (in the case of Ce). A 1 *M* solution of *TBP* in benzene was used as the organic phase. As the aqueous phase the solutions of Li, Na, and NH_4NO_3 were used. These were prepared by the dissolution of the appropriate amount of the salt in 0.1 *M* HNO_3 to prevent the hydrolysis of the lanthanides. The extraction was carried out in a separatory funnel connected through a water jacket with the thermostat. The temperature was controlled using a thermometer immersed in the solution. Equal volumes (50 cm^3) of both phases were used during extraction. Few drops of active solution of lanthanide nitrate (prepared by dissolution of the active oxide in 0.1 *M* HNO_3) were introduced into the separation funnel before each extraction. After shaking both phases for 10 minutes and separation of the phases, the precise volumes of both phases were taken and the content of the separation funnel was adjusted to the next temperature. At least three sets of measurements for five temperatures were performed. The activity of γ-emitters was measured with the aid of a NaI(Tl) scintillation counter. Three samples were taken from each phase and transferred to the special cells where their activities were measured in a period of 1 minute 3–5 times. The distribution coefficient was calculated from the ratio of the activities in the organic and aqueous phases. The typical set of the activities of Gd is given in Table 1.

Result and Discussion

It is easy to notice that the temperature change of the distribution coefficients is the quickest one in the case of $LiNO_3$ and the slowest in the case of NH_4NO_3 (see Figs. 1–4). Table 2 lists the values of extraction enthalpies calculated from the following relationships:

$$\Delta H^\circ = \frac{-\,\mathrm{d}\ln K}{\mathrm{d}(1/T)} \cdot R \qquad (3)$$

Table 1. *The typical set of the activities of* Gd *for the extraction in the system:* $Gd(NO_3)_3$—NH_4NO_3—*TBP*

Temp.	Activity of the organic phase imp/min			Activity of the aqueous phase imp/min			Background	Distribution coefficient D
	I	II	III	I	II	III		
10 °C	31 562	31 292	31 493	32 401	32 657	32 849	679	0.9735
	31 735	31 217	32 225	32 611	32 348	32 485		
	31 706	31 605	31 750	32 229	32 148	32 439		
17 °C	29 252	29 337	29 101	34 750	33 738	32 239	769	0.8686
	29 159	29 576	29 307	33 968	34 188	33 144		
	29 936	29 342	29 614	34 493	33 628	33 523		
25 °C	25 246	25 264	25 883	37 884	36 632	36 783	826	0.6873
	25 451	25 644	26 197	37 079	36 790	36 630		
	25 428	25 673	26 377	37 786	37 384	36 443		
35 °C	24 233	24 083	24 180	40 692	41 332	40 384	740	0.5796
	24 456	23 426	23 771	41 006	41 202	40 446		
	24 454	23 492	23 521	40 471	40 835	40 818		
50 °C	19 993	20 130	20 344	43 342	42 631	43 649	788	0.4570
	20 430	20 162	20 313	43 121	43 410	43 176		
	20 472	19 929	20 343	43 655	42 891	44 014		

Table 2. *Extraction enthalpies of* Ce, Eu, Gd, Tb *for different salting-out agents*

Salting-out agent	$LiNO_3$ 5.2 M				$NaNO_3$ 6 M				NH_4NO_3 6 M		
Lanthanide	Ce	Eu	Gd	Tb	Ce	Eu	Gd	Tb	Eu	Gd	Tb
$\Delta H°$ J/mol	31 710 ± 682	30 309 ± 883	32 372 ± 1 096	33 112 ± 423	20 447 ± 1 247	23 016 ± 657	20 891 ± 567	20 928 ± 515	13 652 ± 803	14 857 ± 853	15 238 ± 561

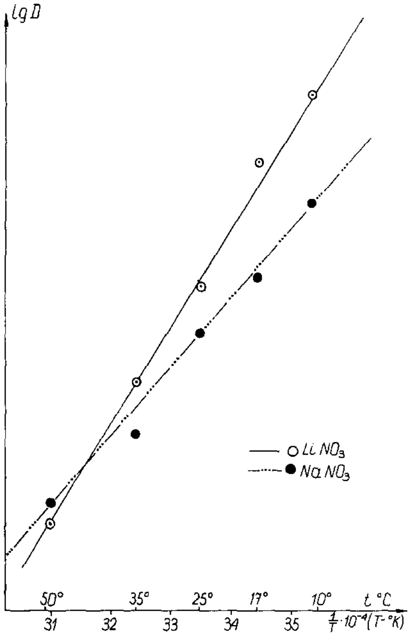

Fig. 1

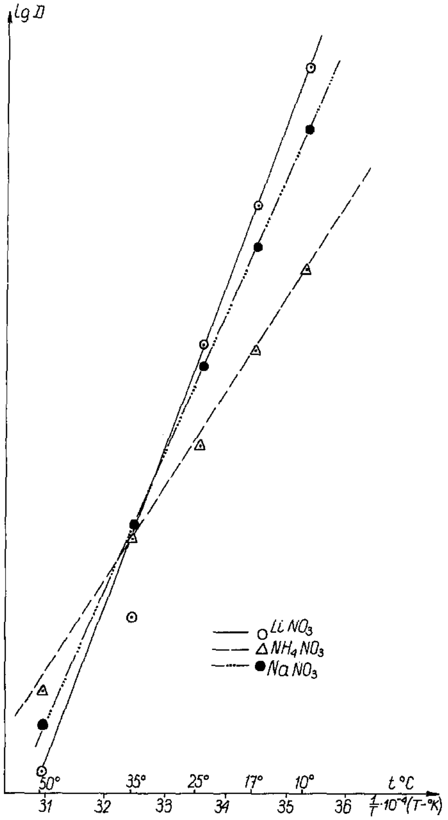

Fig. 2

Fig. 1. The change of the distribution coefficient of Ce with temperature (6 M $NaNO_3$: t °C = 10, 17, 25, 35, 50; $\lg D = -0.063, -0.156, -0.254, -0.410, -0.520$; 5.2 M $LiNO_3$: t °C = 10, 17, 25, 35, 50; $\lg D = 1.12, 0.97, 0.77, 0.62, 0.39$)

Fig. 2. The change of the distribution coefficient of Gd with temperature (5.2 M $LiNO_3$: t °C = 10, 17, 25, 35, 50; $\lg D = 1.63, 1.49, 1.33, 1.15, 0.89$; 6 M NH_4NO_3: t °C = 10, 17, 25, 35, 50; $\lg D = 0.005, -0.071, -0.150, -0.225, -0.350$; 6 M $NaNO_3$: t °C = 10, 17, 25, 35, 50; $\lg D = 0.610, 0.512, 0.421, 0.298, 0.137$)

$$\frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)} = \frac{\mathrm{d}\ln D}{\mathrm{d}(1/T)} \tag{4}$$

where ΔH° is the extraction enthalpy, K the equilibrium constant of the extraction reaction, D the distribution coefficient, R the gas constant, and T the absolute temperature.

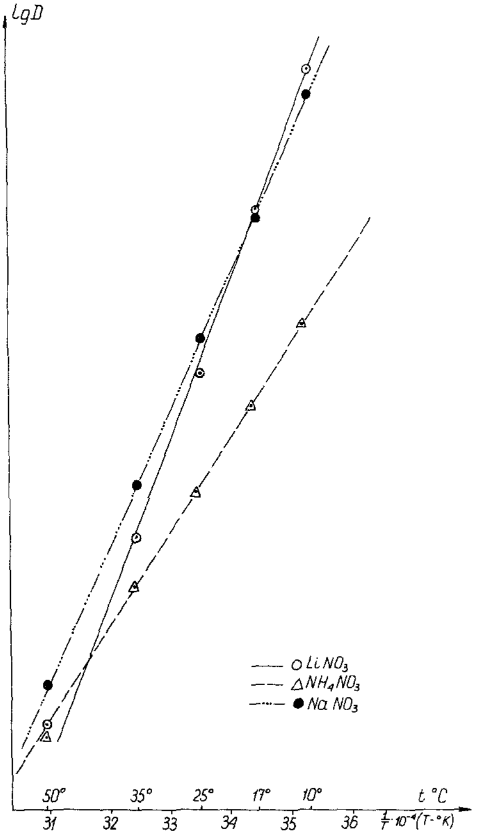

Fig. 3

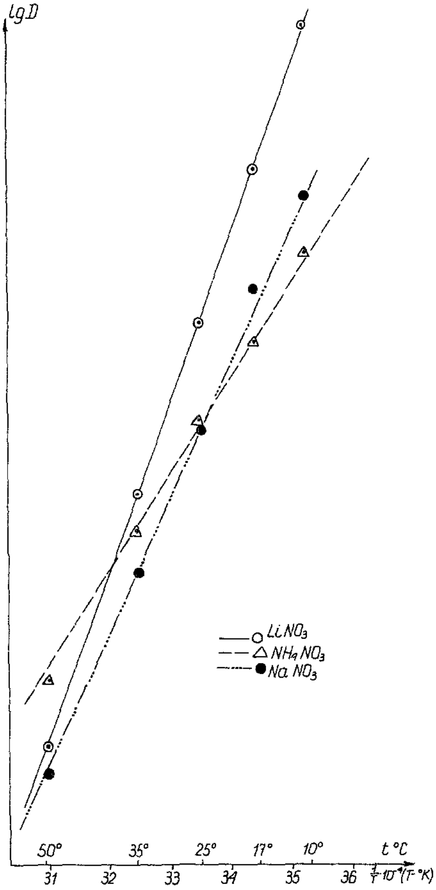

Fig. 4

Fig. 3. The change of the distribution coefficient of Eu with temperature (5.2 *M* $LiNO_3$: t °C = 10, 17, 25, 35, 50; lg$D$ = 1.55, 1.41, 1.23, 1.06, 0.86; 6 *M* NH_4NO_3: t °C = 10, 17, 25, 35, 50; lg$D$ = 0.018, − 0.050, − 0.120, − 0.196, − 0.316; 6 *M* $NaNO_3$: t °C = 10, 17, 25, 35, 50; lg$D$ = 0.65, 0.55, 0.45, 0.33, 0.18)

Fig. 4. The change of the distribution coefficient of Tb with temperature (5.2 *M* $LiNO_3$: t °C = 10, 17, 25, 35, 50; lg$D$ = 1.73, 1.57, 1.41, 1.22, 0.96; 6 *M* NH_4NO_3: t °C = 10, 17, 25, 35, 50; lg$D$ = 0.15, 0.073, 0.004, − 0.085, − 0.202; 6 *M* $NaNO_3$: t °C = 10, 17, 25, 35, 50; lg$D$ = 0.73, 0.65, 0.54, 0.42, 0.26)

It was possible to apply this relationships assuming no change of the activity coefficients of Ln^{3+} with temperature. The absolute value of the extraction enthalpy is the highest in the case of $LiNO_3$ and the lowest in the case of NH_4NO_3 for all lanthanides. This means that in the case of low water activity the lanthanide ions occur probably in the more dehydrated form [$Ln(H_2O)_x^{3+}$ with $x < 9$], contrary to the situation when high water activity favours the full hydration of the lanthanide ion [formation of $Ln(H_2O)_9^{3+}$ is possible].

References

[1] *Chun-hui Huang, Bautista RG* (1983) Sep Sci Technol 18: 1667–1683
[2] *Rossmanith K* (1977) Monatsh Chem 108: 681–688
[3] *Rossmanith K* (1974) Monatsh Chem 105: 1025–1029
[4] *Rossmanith K, Mecl R* (1980) Monatsh Chem 111: 693–702
[5] *Choppin G, Rydberg J* (1980) Nuclear chemistry; theory and application. Pergamon Press, New York
[6] *Gschneider KA* (1981) Speciality inorganic chemicals. The Royal Society of Chemistry, London
[7] *Majdan M* (1980) The influence of the different salting-out agents on the separation of Y, La and lanthanides during extraction using TBP. Ph.D. thesis, Lublin UMCS