

The Influence of Methanol and Ethanol on the Efficiency of Extraction of Lanthanides(III) with 1-(2-Pyridylazo)-2-naphthol (PAN) in Carbon Tetrachloride

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The efficiency of extraction of microquantities of Eu(III), Sm(III) and Gd(III) from water — 50% (v/v) methanol phase or water — 50% (v/v) ethanol phase with PAN solutions in CCl₄ was examined. Separation factors for the following pairs of lanthanides(III) were determined: Eu—Sm, Eu—Gd, Sm—Gd, as well as Eu—Ln, Sm—Ln and Gd—Ln, where: Ln = Tb, Ho, or Lu; their changes with respect to the composition of the polar phase were also estimated.

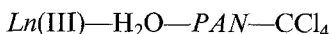
[Keywords: Extraction; Lanthanides; 1-(2-Pyridylazo)-2-naphthol (PAN); Lanthanide separation factor]

Der Einfluß von Methanol und Ethanol auf die Effektivität der Extraktion der Lanthaniden mit Lösungen von 1-(2-pyridylazo)-2-naphthol (PAN) in Tetrachlorkohlenstoff

Die Effektivität der Extraktion von Mikromengen Eu(III), Sm(III) und Gd(III) aus der Wasser-Methanol- und Wasser-Ethanol-Phase (50 vol. %), mit Hilfe von PAN-Lösungen in CCl₄ wurde untersucht. Die Trennfaktoren für nachstehende Lanthaniden(III)-Paare: Eu—Sm, Eu—Gd, Sm—Gd und Eu—Ln, Sm—Ln, Gd—Ln (Ln = Tb, Ho oder Lu) wurden berechnet und ihre Änderungen in der Abhängigkeit von der polaren Phase geschätzt.

Introduction

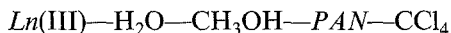
Thus far, results of studies in lanthanide(III) extraction efficiency with the use of PAN solutions in CCl₄ have been presented in the following system:



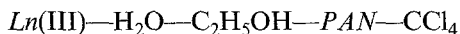
where Ln(III) = La, Ce, Pr, Nd, Sm, Gd¹, Eu, Tb⁵, Dy, Yb², and Lu⁷.

In the above extraction system, separation factors have been determined for some pairs of lanthanides(III)^{1,5}.

In the present work, the effect of the presence of methanol and ethanol in the aqueous phase on the values of separation factors have been studied for the following pairs of lanthanides(III): Eu—Sm, Eu—Gd, Sm—Gd as well as Eu—*Ln*, Sm—*Ln*, and Gd—*Ln*, where *Ln* = Tb, Ho, Lu. For this purpose, the efficiency of extraction of microquantities of lanthanides(III) with *PAN* solutions in CCl_4 has been investigated within the following systems:



where $\text{Ln(III)} = \text{Sm, Eu, Gd}$
and



where $\text{Ln(III)} = \text{Sm, Eu}$.

The results of the efficiency of the extraction of Tb(III), Ho(III) and Lu(III) from water—methanol and water—ethanol solutions have already been described^{4–6}.

Experimental

Aqueous solutions of lanthanide(III) perchlorates were prepared from adequate oxides of 99.9% purity (Sm_2O_3 —Inter. Enzym. Limit., Eu_2O_3 , Gd_2O_3 —Serva)¹. Both the methodology and the remaining reagents were described in earlier studies^{1–4}.

Since in the course of extraction of the studied lanthanides a suspension on the phase boundary appeared, inferences concerning the efficiency of extraction were made on the basis of the lanthanide content in the organic phase.

The efficiency of the extraction of a given lanthanide (% E_{Ln}) was calculated as

$$\% E_{Ln} = \frac{g_{(0)}}{g_{in}} \cdot 100 \quad (1)$$

where $g_{(0)}$ is the lanthanide content in the organic phase in the equilibrium state and g_{in} the initial lanthanide content in the polar phase.

The efficiency of extraction of Sm(III), Eu(III), and Gd(III) with *PAN* solutions in CCl_4 from water—alcohol phases was studied with the initial constant concentration of a lanthanide amounting to 50 mg/dm^3 , the constant ionic strength of the solution being $\mu = 0.1 \text{ mol/dm}^3$ and equal initial phase volumes. The concentration of alcohol in the polar phase was 50% of the volume. The pH^* of the water—alcohol phase ($pH^* = -\lg [\text{H}^+]$ in water—alcohol solutions⁸) was adjusted with ammonia solutions and measured with ± 0.02 unit accuracy. On the account of the change in the phase volume in the course of extraction from water—alcohol solutions, the initial *PAN* concentration in CCl_4 was purposely matched, so that its equilibrium concentration in the organic phase would be constant ($1.00 \cdot 10^{-2} \text{ mol/dm}^3$).

The studied lanthanides were found not to be extracted with pure CCl_4 from water—methanol or water—ethanol solutions.

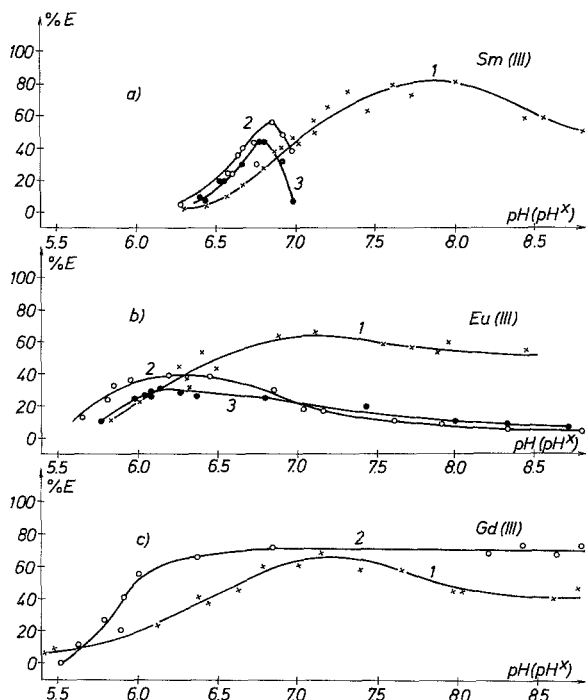


Fig. 1. Efficiency of solvent extraction of Sm(III), Eu(III) and Gd(III) by PAN in CCl_4 , the equilibrium concentration being $1.00 \cdot 10^{-2}$ mol/dm³. 1 from aqueous phase^{1,5}; 2 from water—50% (v/v) methanol phase; 3 from water—50% (v/v) ethanol phase

The efficiency of Sm(III), Eu(III) and Gd(III) extraction, dependent upon the pH^* of the water—alcohol phase and upon the kind of alcohol is shown in Fig. 1. For the purpose of direct comparison of methanol or ethanol influence on the efficiency of extraction of the lanthanides, Fig. 1 also presents the previously obtained curves indicating %E dependence of those ions upon the pH of aqueous solutions^{1,5}.

In the present work, the separation factor for lanthanide pair equals the quotient of factors of individual lanthanide decontamination from the water—alcohol solution^{1,9}:

$$S_{Ln_1}^{Ln_2} = \frac{g_{2,in}/g_{2(p)}}{g_{1,in}/g_{1(p)}} = \frac{100 - \% E_{Ln_1}}{100 - \% E_{Ln_2}} \quad (2)$$

where $S_{Ln_1}^{Ln_2}$ is the separation factor of a lanthanide pair ($\% E_{Ln_2} > \% E_{Ln_1}$), $g_{1,in}$ and $g_{2,in}$ are initial Ln_1 and Ln_2 lanthanide contents in the polar phase, and $g_{1(p)}$ and $g_{2(p)}$ are equilibrium Ln_1 and Ln_2 lanthanide contents in the polar phase.

Based on our previous studies¹ as well as on literature data^{10,11} we assumed that the presence of two lanthanides in microquantities in the polar phase does not mutually affect the efficiency of individual lanthanide extraction.

Results and Discussion

The presence of methanol or ethanol in the polar phase shifts the pH^* range securing maximum efficiency of lanthanide extraction towards values of pH^* that are lower in comparison with the ones obtained in the process carried out from the aqueous phase under the same conditions (Fig. 1). A similar dependence had been observed previously for Tb(III)⁵, Ho(III)⁴, Yb(III)^{3,4} and Lu(III)⁶.

In the case of Sm(III) extraction from water—50% (v/v) methanol or water—50% (v/v) ethanol solutions within a pH^* range from about 6.3 to 6.9, the occurrence of a synergistic effect was observed (Fig. 1 a).

The presence of 50% methanol volume in the polar phase during Eu(III) extraction yields a synergistic effect within a pH^* range of 5.6–6.3. The addition of 50% ethanol volume to the aqueous phase does not change the efficiency of Eu(III) extraction if pH^* is not higher than 6.2. For higher pH^* values of water—alcohol solutions, significant decrease in the percentage of Eu(III) extraction was observed, in comparison with the process carried out from the aqueous phase (Fig. 1 b).

In the case of Gd(III) extraction from water—50% (v/v) methanol phase, a synergistic effect occurred practically within the whole studied pH^* range (Fig. 1 c).

Values of separation factors for given pairs of lanthanides, determined on the basis of equation (2), are dependent upon the polar phase pH^* value. Fig. 2 shows for instance changes in separation factor values for the separation of Eu(III) from Sm(III) and from Gd(III), as well as from the previously studied Tb(III)⁵, Ho(III)⁴, and Lu(III)⁶, in relation to pH^* of water—50% (v/v) methanol solutions. The dependence of the separation factor vs. pH^* of the polar phase shows a maximum, which makes it possible to estimate the optimum pH^* range for the separation process of a given lanthanide pair. Table 1 presents calculated maximum $^{max}S_{L_1}^{L_2}$ values and the corresponding pH^* values of the polar phase for the extraction carried out from water—50% (v/v) methanol or ethanol solutions. These factors were compared with $^{max}S_{L_1}^{L_2}$ values determined for the process carried out from the aqueous phase. It follows from these data that for most of the studied lanthanide pairs the highest $^{max}S_{L_1}^{L_2}$ values were obtained in the course of extraction from water—50% (v/v) methanol solutions. Considerable (3–4 times) increase of $^{max}S_{Sm}^{Ho}$, $^{max}S_{Sm}^{Lu}$, and $^{max}S_{Eu}^{Ho}$ values is significant in comparison with corresponding factors determined for the aqueous phase extraction. It is caused by the occurrence of greater differences in the efficiency of light and heavy lanthanide extraction when the process is carried out from the water-methanol phase in comparison with the aqueous phase extraction.

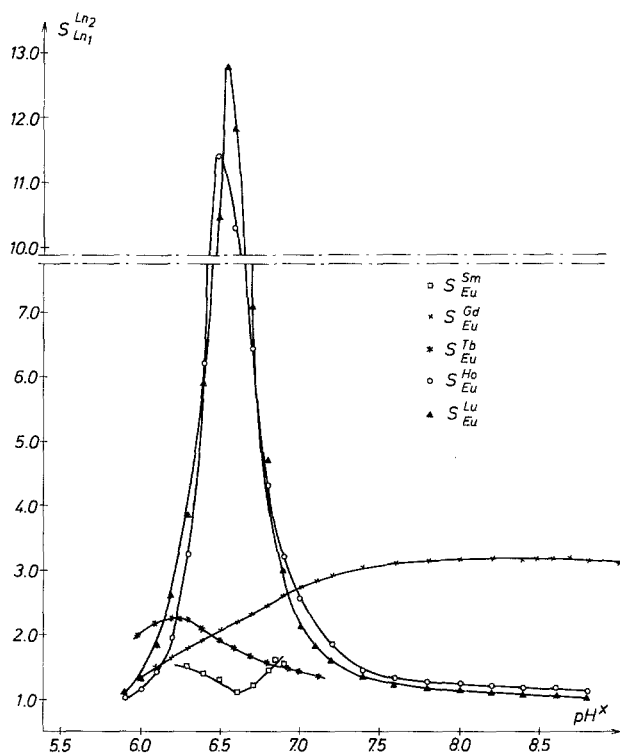


Fig. 2. Factors of Eu(III) separation from respective lanthanides(III), in relation to pH^* of the water—50% (v/v) methanol phase; the extractant was *PAN* in CCl_4 , the equilibrium concentration being $1.00 \cdot 10^{-2} \text{ mol/dm}^3$

The extraction coefficient $D_{Ln}^{12,13}$ of a given lanthanide can be represented as:

$$D_{Ln} = \frac{g_{(0)}/V_{(0)}}{g_{(p)}/V_{(p)}} \quad (3)$$

where $g_{(0)}$ and $g_{(p)}$ is the content of the lanthanide in the equilibrium state of the system, in the organic and polar phases, respectively; $V_{(0)}$ and $V_{(p)}$ are the volumes of the organic and polar phases, respectively, in the equilibrium state of the system. Considering that $g_{(0)} = g_{in} - g_{(p)}$ (g_{in} is the initial content of the lanthanide in the polar phase), and having determined $V_{(0)}/V_{(p)} = r$, we obtain the relationship:

$$\frac{g_{in}}{g_{(p)}} = D_{Ln} \cdot r + 1 \quad (4)$$

Table 1. *Maximum values of separation factors for particular pairs of lanthanides(III) $\max S_{Ln_1}^{Ln_2}$ and corresponding values of the polar phase pH (pH^*). The extractant was PAN solution in CCl_4 , the equilibrium concentration being $1.00 \cdot 10^{-2}$ mol/dm³*

$Ln_1 - Ln_2$	Extraction from phase					
	water		water—50% (v/v) methanol		water—50% (v/v) ethanol	
	$\max S_{Ln_1}^{Ln_2}$	pH	$\max S_{Ln_1}^{Ln_2}$	pH^*	$\max S_{Ln_1}^{Ln_2}$	pH^*
Sm—Gd	1.66	6.80	2.71	6.40		
Sm—Tb	3.35	7.00	3.36	6.30	2.66	6.40
Sm—Ho	3.70	7.10	14.64	6.50		
Sm—Lu	5.33	7.40	15.30	6.55	6.38	6.65
Eu—Sm	2.25	7.90	1.62	6.85	1.30	6.80
Eu—Gd			3.20	8.70		
Eu—Tb	2.18	7.10	2.25	6.25	2.07	6.50
Eu—Ho	2.67	7.10	11.45	6.50		
Eu—Lu	6.42	7.40	12.80	6.55	6.73	6.70
Gd—Eu	1.14	6.60				
Gd—Tb	2.20	7.00				
Gd—Ho	2.67	7.10	5.63	6.50		
Gd—Lu	6.67	7.40	6.10	6.55		
Tb—Gd			2.96	8.20		

Substituting relationship (4) in equation (2) respectively for Ln_1 and Ln_2 , and taking into account that the conventional separation factor $\alpha_{Ln_1}^{Ln_2} = D_{Ln_2}/D_{Ln_1}$ (where $D_{Ln_2} > D_{Ln_1}$), we get:

$$S_{Ln_1}^{Ln_2} = \frac{\alpha_{Ln_1}^{Ln_2} + \frac{1}{D_{Ln_1} \cdot r}}{1 + \frac{1}{D_{Ln_1} \cdot r}} \quad (5)$$

From relationship (5) it follows that factor $S_{Ln_1}^{Ln_2}$ is generally lower than $\alpha_{Ln_1}^{Ln_2}$, and only in the case of $D_{Ln_1} \cdot r \gg 1$, $S_{Ln_1}^{Ln_2} \approx \alpha_{Ln_1}^{Ln_2}$.

Table 2 presents the maximum values of the separation factor $S_{Ln_1}^{Ln_2}$ and the values of the separation factor $\alpha_{Ln_1}^{Ln_2}$ calculated for two lanthanide pairs (Dy—Yb, Er—Lu) in the process of solvent extraction with PAN solutions in CCl_4 from the aqueous phase. In the course of solvent extraction of these lanthanides no suspension at the phase boundary was observed.

The values of $\alpha_{Ln_1}^{Ln_2}$ factors were calculated from the equilibrium constants of the extraction reaction of individual lanthanides $K_{ex, Ln}^{2,7}$ ($\alpha_{Ln_1}^{Ln_2} = K_{ex, Ln_2}/K_{ex, Ln_1}$).

From the correlation of the values of $^{max}S_{Ln_1}^{Ln_2}$ and $\alpha_{Ln_1}^{Ln_2}$ factors one can assume that the maximum value of the $S_{Ln_1}^{Ln_2}$ factor for a given pair $Ln_1 - Ln_2$ may be the measure of the possibility of separating these elements, similarly to the value of the $\alpha_{Ln_1}^{Ln_2}$ factor.

Table 2. Comparison of separation factors $^{max}S_{Ln_1}^{Ln_2}$ and $\alpha_{Ln_1}^{Ln_2}$ in the process of the aqueous phase extraction

Extractant	Lanthanide pair ($Ln_1 - Ln_2$)					
	Sm—Gd	Eu—Gd	Gd—Tb	Gd—Lu	Dy—Yb	Er—Lu
	Separation factor $^{max}S_{Ln_1}^{Ln_2}$					
PAN in CCl_4	1.66	1.14*	2.20	6.67	2.33	1.38
	Separation factor $\alpha_{Ln_1}^{Ln_2}$					
PAN in CCl_4					2.69	1.45
TBP ¹⁴	2.33	1.41	2.19	14.08	3.65	2.63
HTTA ¹⁵ in CCl_4	1.90	1.41	1.51	25.70	6.92	5.89
HPMBP ¹⁶ in $CHCl_3$	2.40	1.23	2.50	8.12	3.71	2.04

* S_{Gd}^{Eu}

Analogous correlations between the values of $^{max}S_{Ln_1}^{Ln_2}$ and $\alpha_{Ln_1}^{Ln_2}$ have been also found for the extraction process from water—methanol and water—ethanol phases.

In Table 2 the values of $^{max}S_{Ln_1}^{Ln_2}$ for some other pairs of lanthanides, calculated for the extraction process from aqueous phase, have been compiled. They are compared with $\alpha_{Ln_1}^{Ln_2}$ separation factors given in the literature and also established in the process of aqueous phase extraction with the use of tri-*n*-butyl phosphate (TBP)¹⁴, 2-thenoyltrifluoroacetone (HTTA)¹⁵ and 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP)¹⁶.

It may be concluded from this comparison that the possibilities of separating the discussed pairs of lanthanides in the studied system approximate those obtained with the use of HPMBP as an extractant.

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