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Extraction of Chlorides of Some Lanthanoides by Tricaprylylmethylammonium Pelargonate

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Summary. The extraction of some lanthanoides by tricaprylylmethylammonium pelargonate has been investigated in the system of $LnCl_3 - Na(H)Cl - R_4NB - CCl_4$ at constant ionic strength $\mu = 0.1$. A mechanism of the extraction process is suggested, which explains the simultaneous extraction of HCl and $LnCl_3$.

Keywords. Binary extraction; Tricaprylylmethylammonium pelargonate; Distribution coefficient; Lanthanoides.

Extraktion von Chloriden einiger Lanthanoiden mittels Tricaprylylmethylammonium-Pelargonat

Zusammenfassung. Es wurde die Extraktion von Lanthanoiden mittels Tricaprylylmethylammonium-Pelargonat in dem System $LnCl_3 - Na(H)Cl - R_4NB - CCl_4$ bei konstanter Ionenstärke $\mu = 0.1$ untersucht. Ein Mechanismus des Extraktionsprozesses wird vorgeschlagen, der die gemeinsame Extraktion von HCl und $LnCl_3$ erklärt.

Introduction

The binary extractants, which are salts of organic acids and bases, are a relatively new class of compounds making possible the complete passage of the inorganic compound (salt, acid or base) into the organic phase. The course of the extraction processes with neutral extractants is similar, but in the case of binary extraction the cationic and anionic parts of the inorganic substance pass into the organic phase in a stoichiometric ratio, whereby a double ion-exchange process takes place. Binary extractants have been used in investigating the extraction of salts of various metals [1–9] and also of some inorganic acids [10–12]. The present paper examines the possibilities offered by this class of extractants for extracting the salts of rare-earth metals.

Experimental

The necessary salts (chlorides of praseodymium, gadolinium and ytterbium) were obtained by dissolving Ln_2O_3 (Koch Light Laboratory, 99.9% purity) in HCl. The accurate concentration of the metals in the initial phase (abt. $2.5 \cdot 10^{-3}$ mol dm^{-3}) was determined complexometrically. The constant ionic strength of the aqueous phase, $\mu = 0.1$, was maintained by Na(H)Cl, while the variation of the acidity of the aqueous phase was obtained by varying the ratio between HCl and NaCl. The salting-out reagent used in some of the experiments was NaCl (analytically pure).

The binary extractant, tricaprylylmethylammonium pelargonate, was obtained by a known method [1, 3, 5, 11] involving the mixing of equimolar amounts (0.5 mol dm^{-3} in CCl_4) of pelargonic acid (Merck, $C_8H_{17}COOH$ or $R''COOH$, zur Synthese) and tricaprylylmethylammonium chloride (Fluka, $R_3R'NCl$, Aliquat-336), followed by washing with a slight excess of sodium hydroxide. After separation of the phases, the organic one containing 0.25 mol dm^{-3} binary extractant tricaprylylmethylammonium pelargonate – $(R_3R'N)R''COO$, further on referred to as R_4NB – was washed several times with distilled water for removing the sodium and chloride ions.

The extraction was carried out by shaking equal volumes (10 cm^3) of aqueous and organic phases for half an hour at room temperature. After separation of the phases the aqueous one was analyzed photocolorimetrically with Arsenaso III [13] for establishing the content of the respective lanthanoide; the *pH* was determined by the high-precision *pH*-meter Radelkis OP-208/1. The Cl^- content was determined by a method described in [14]. The content of the lanthanoide in the organic phase was calculated as the difference of its content in the initial and in the equilibrium aqueous phases.

Results and Discussion

A survey of the changes in the distribution coefficients (*D*) of the lanthanoides established that, at a constant concentration of the extractant, the extraction depends on the *pH* of the aqueous phase. The *pH* is changed by changing the ratio between HCl and NaCl in the initial aqueous phase. Since the concentration of the lanthanoides in the initial solutions is low ($2.5 \cdot 10^{-4}$ mol dm^{-3}), the conditions are not suited only for the extraction of the metals. The distribution coefficients within the entire interval of investigation (from the beginning of the extraction to the point of complete extraction) depend on the concentration of hydrogen ions. This means that within a certain interval of acidity of the aqueous phase there is a process of simultaneous extraction of the inorganic acid (HCl) and of the respective lanthanoide, which may be described by the expressions

$$x\,H^+_{(aq)} + x\,Cl^-_{(aq)} + x\,R_4NB_{(o)} = x\,R_4NCl_{(o)} + x\,HB_{(o)}, \qquad (1)$$

$$Ln^{3+}_{(aq)} + 3\,Cl^-_{(aq)} + 3\,R_4NB_{(o)} = 3\,R_4NCl_{(o)} + LnB_{3(o)}. \qquad (2)$$

Parallel with these processes it is possible to assume also extraction of the lanthanoides by the organic acid obtained as a result of the first reaction

$$Ln^{3+}_{(aq)} + 3\,HB_{(o)} = LnB_{3(o)} + 3\,Hs^+_{(aq)}. \qquad (3)$$

The process of simultaneous extraction of HCl and of the lanthanoides can be described by the summary equation

$$\begin{aligned} 2\,Ln^{3+}_{(aq)} &+ (3+x)\,Cl^-_{(aq)} + (3+x)\,R_4NB_{(o)} + (3-x)\,HB_{(o)} \\ &= (3+x)\,R_4NCl_{(o)} + 2\,LnB_{3\,(o)} + (3-x)\,H^+_{(aq)}. \qquad (4) \end{aligned}$$

The (aq) and (o) indices are related to the aqueous and organic phases, respectively.

The extraction constant of the process is given by the expression

$$K = \frac{[R_4NCl]_{(o)}^{(3+x)}\,[LnB_3]_{(o)}^2\,[H^+]_{(aq)}^{(3-x)}}{[Ln^{3+}]_{(aq)}^2\,[Cl^-]_{(aq)}^{(3+x)}\,[R_4NB]_{(o)}^{(3+x)}\,[HB]_{(o)}^{(3-x)}}. \qquad (5)$$

If we introduce the distribution coefficient of the cation of the respective lanthanoide

$$D = \frac{[LnB_3]_{(o)}}{[Ln^{3+}]_{(aq)}},$$

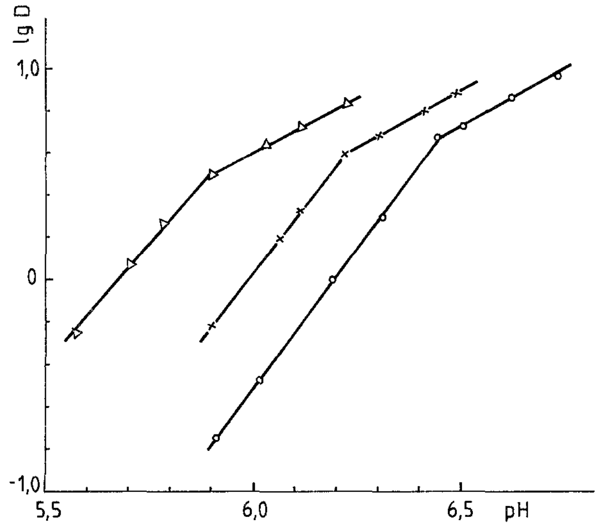

Fig. 1. Dependence of the distribution coefficients of Pr (○), Gd (×) and Yb (△) on *pH*. Initial concentrations: lanthanoides $2.5 \cdot 10^{-4}$ mol dm^{-3}; extractant 0.1 mol dm^{-3}; $\mu = 0.1$

the expression for the extraction constant may be transformed into

$$K = \frac{D^2 [R_4\mathrm{NCl}]_{(\mathrm{o})}^{(3+x)} [\mathrm{H}^+]_{(\mathrm{aq})}^{(3-x)}}{[\mathrm{Cl}^-]_{(\mathrm{aq})}^{(3+x)} [R_4\mathrm{N}B]_{(\mathrm{o})}^{(3+x)} [\mathrm{H}B]_{(\mathrm{o})}^{(3-x)}}. \tag{6}$$

In the presence of a considerable excess of the binary extractant in relation to the lanthanoide and to the binary and the inorganic acid, it may be assumed that its concentration is constant and, after taking the logarithm of expression (6), we shall obtain

$$\log D = \frac{1}{2} \log K' + n pH, \tag{7}$$

where $n = (3-x)/2$.

The experimentally established dependences of log *D* on the *pH* of the equilibrium aqueous phases for praseodymium, gadolinium and ytterbrium are shown in Fig. 1. Clearly outlined for each one of the investigated metals are two regions, in one the straight line has a gradient of $n = 2.5$, while in the other region $n = 1$. There is no real meaning for "x" in the first region ($x < 0$). It may be assumed that decomposition of a part of the binary extractant takes place under these conditions and that extraction is performed by pelargonic acid under a typical cation-exchange mechanism. At higher *pH* values, which are different for the different lanthanoides, the gradient of the curve is 1.0, and a value of unity is also obtained for "x".

Consequently, in the extraction system examined it is neither possible to attain conditions where the extraction does not depend on the *pH* of the aqueous phase, nor to analyze the distribution of the metals due only to extraction with the binary extractant.

In some publications [1, 6] it has been indicated that under conditions of constant activity of the components in the organic phase and in the absence of a salting-out reagent, regardless of the type of the salt subject to extraction, the tangent of the gradient angle of the isotherm of the extraction in the logarithmic coordinates is equal to unity, i.e. the distribution depends in a first degree on the

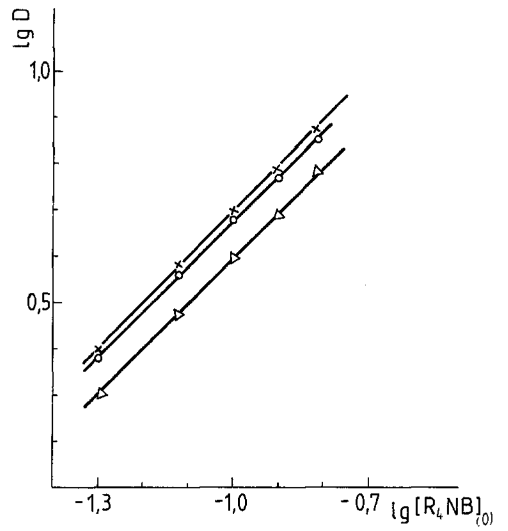

Fig. 2. Dependence of the distribution coefficients of Pr (○) at *pH* = 6.5, of Gd (×) at *pH* = 6.3, and of Yb (△) at *pH* = 5.9 on the concentration of the extractant; diluent CCl_4

concentration of the extractant. To obtain some confirmation for that, a series of experiments was carried out on the extraction of lanthanoides with variable concentrations of the binary extractant from 0.05 to 0.25 mol dm^{-3}. It was established that at a concentration of 0.2 mol dm^{-3} the extraction of the lanthanoides coincides with the data on extraction with 0.1 mol dm^{-3}. This fact may be explained if we assume that in the organic phase there is a process of dimerization of the extractant, which leads to a decrease in its active concentration. Provided that: $[Cl^-]_{(aq)} = 2\,[Ln^{3+}]_{(aq)}$ and $[R_4NCl]_{(o)} = 2\,[Ln^{3+}]_{(o)}$, Eq. (6) is transformed into

$$K = \frac{D^4\,[H^+]^2}{[R_4NB]_{(o)}\,[HB]^2_{(o)}}. \tag{8}$$

Upon constant concentration of the hydrogen ions and of the organic acid we obtain:

$$\log D = \frac{1}{4}\log K'' + \log\,[R_4NB]_{(o)}. \tag{9}$$

Fig. 2 shows the dependences of log *D* on the intitial concentration of the binary extractant at selected *pH* values for each lanthanoide. The straight lines obtained have a gradient of unity, in corroboration for the assumed mechanism of extraction.

It has been established that at the binary extraction of salts it is possible to influence the distribution of the cation by changing the anion concentration and vice versa [6]. This is a process analogous to salting-out upon extraction with neutral extractants. In the investigated system we tested the salting-out action of NaCl on the distribution of the lanthanoides. With constant concentration of the hydrogen ions, the dependence of the distribution coefficient (*D*) on the change in the concentration of the chloride ions is presented in Fig. 3. The salting-out action of Cl^- is most markedly manifested at the extraction of Yb, and is insignificant in the case of Pr.

The investigation undertaken in the extraction system $LnCl_3-Na(H)Cl-R_4NB-CCl_4$ points to the possibility of using the binary extractant for the extraction of lanthanoides. The processes may be carried out at a higher acidity of

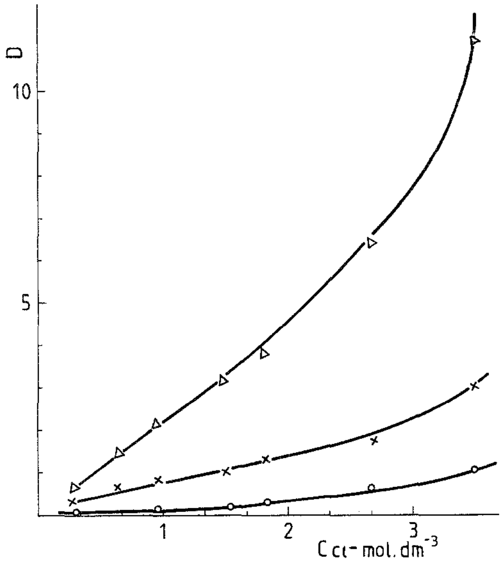

Fig. 3. Dependence of the distribution coefficients of Pr (○), Gd (×) and Yb (△) on the concentration of Cl^- ions. Extractant concentration 0.1 mol dm^{-3}, $pH = 5.80$

the initial aqueous phase, compared to extraction with pelargonic acid only (unpublished data). The experimental results bear confirmation for the joint extraction of HCl and $LnCl_3$, which is compatible to the proposed mechanism.

References

[1] Davis J. C., Grinstead R. R. (1970) J. Phis. Chem. **74**: 147
[2] Navtanovich M. L., Kheifec V. L., Mayslish R. S. (1974) Zh. Prikl. Khim. **47**: 1524
[3] Navtanovich M. L., Kheifec V. L. (1975) Zh. Obshch. Khim. **45**: 413
[4] Navtanovich M. L., Senina N. N., Kheifec V. L. (1978) Zh. Obshch. Khim. **48**: 1441
[5] Sato T., Yamamoto M., Watanabe H. (1980) Proc. Int. Solv. Extr. Conf. Liege **2**: 178
[6] Kholkin A. I., Kusmin V. I. (1984) Sb. Khimiya Ekstrakcii. Nauka, Novosibirsk, p. 53
[7] Kholkin A. I., et al. (1987) Tzvetnie Metali **1**: 19
[8] Kholkin A. I., et al. (1988) ISEC' 88 **3**: 215
[9] Georgiev G., Zakharieva M., Genov L. (in press) God. Vissh. Khim. Tekhnol. Inst. (Sofia)
[10] Kholkin A. I., Kuzmin V. I., Protasova N. V. (1986) Zh. Neorgan. Khim. **31**: 1245
[11] Belova V. V., Novicova T. I., Perevoznicova L. N., Kholkin A. I. (1986) Izv. SO Akad. Nauk. SSSR, Ser. Khim. Nauk. **1**: 25
[12] Georgiev G., Zakharieva M., Genov L. (in press) God. Vissh. Khim. Tekhnol. Inst. (Sofia)
[13] Sawin S. B. (1966) Arsenazo III. Atomizdat, Moscow
[14] Williams W. J. (1982) Opredelenie Anionov. Khimia, Moscow

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