EXTRACTION OF SELECTED LANTHANOIDS AND SCANDIUM WITH BIS(2-ETHYLHEXYL)HYDROGENPHOSPHATE IN 1,1,2,2-TETRACHLORODIFLUOROETHANE

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A study was made of the extraction of Ce, Pm, Eu, Tm and Sc(III) from aqueous into organic medium of 1,1,2,2-tetrachlorodifluoroethane (CFC-112) using bis(2-ethylhexyl)hydrogenphosphate (HDEHP) as extracting reagent. On the basis of earlier work which demonstrated the usefulness of using this type of solvent for extractions with dibutylhydrogenphosphate (HDBP) and also the possibility of using CFC-112 for converting the metal chelates formed to the solid phase, the work was concentrated particularly on the dependence of the extraction of selected lanthanoids on the analytical concentration of HDEHP and also on the $[H^+]$ concentration. In addition the dimerization and distribution constants were determined for this reagent in a mixture of CFC-112 with benzene and the extraction constants were determined for the individual metals.

On the basis of earlier works[1,2], demonstrating the suitability and usefulness of the organic solvents CFC-113 ($Cl_2FC-CClF_2$) and CFC-112 ($Cl_2FC-CCl_2F$) for the extraction of some lanthanoids and scandium using dibutylhydrogenphosphate (HDBP), a study was carried out of the analogous use of bis(2-ethylhexyl)hydrogenphosphate (HDEHP) for the extraction of Ce, Pm, Eu, Tm and Sc. It was found, not only that CFC-112 exhibits a higher K_{ex} value than that obtained when HDEHP was employed with the formerly used organic solvents, but also that it is possible to convert the organic phase including the extracted complex to the solid state.

This work was carried out in order to test the use of CFC-112 for the extraction of these metals using HDEHP as an extracting agent, to find the optimum conditions for the quantitative extraction and to compare the results obtained with those given in the literature.

EXPERIMENTAL

Chemicals and Instrumentation

The HDEHP employed, pure (Koch–Light, England), was purified by the published procedure[3]. CFC-112 (Spolek pro chemickou a hutní výrobu, Ústí nad Labem) was purified by column distillation: the temperature of the collected fraction was 91 – 93 °C. CFC-113 was of p.a. purity (Merck, F.R.G.). The benzene employed was of p.a. purity (Lachema Brno), as were the inorganic salts and acids. The specific activities and concentrations of the radioactive isotopes in the stock solutions of ^{144}Ce, ^{147}Pm, and ^{155}Eu (ÚVVVR, Prague) were equal to 5.72 MBq g^{-1} (1.8 . 10^{-3} mol l^{-1}), 5.4 MBq g^{-1} (6.4 . 10^{-8} mol l^{-1}) and 4.7 MBq g^{-1} (1.9 . 10^{-7} mol l^{-1}). The specific activities and concentrations of ^{170}Tm and ^{46}Sc (Poland) were equal to 87.5 GBq g^{-1} (1.3 . 10^{-4} mol l^{-1}) and 445.5 MBq g^{-1} (2 . 10^{-6} mol l^{-1}). The radioactive isotopes were stored in 0.1M-HNO_3 solutions. The relative gamma activity of the aqueous and organic phases was measured using a NKQ 322 scintillation detector with a NaI(Tl) type SKW scintillator. The relative beta activity was measured using an NKQ 321 scintillation detector with a type SPF plastic scintillator. Measurements were carried out on a NZQ 601 spectrometric unit with recorder (all from Tesla Liberec). The pH was measured using a combined electrode with a type OP-208/1 pH-meter (Radelkis, Hungary). The electrode was calibrated using phthalate and oxalate buffers.

Procedure

The extraction was carried out using a rotating extractor and test-tube with glass stopper. The organic and aqueous phases (each 5 ml) were mixed together for 60 min and then left to stand for 30 min for phase separation; it was assumed that the distribution of the total analytical concentration of the reagent c_{HA} between the two phases after establishment of extraction equilibrium is given by the equation

$$c_{HA} = c_{HA,w} + c_{HA,org} , \qquad (1)$$

where symbol c corresponds to the concentrations of all the chemical forms of the reagent in the given phase. Symbols in square brackets were employed to describe the equilibrium concentrations of concrete forms, i.e.

$$c_{HA,w} = [HA] + [A^-] \qquad (2)$$

and

$$c_{HA,org} = [HA]_{org} + [H_2A_2]_{org} , \qquad (3)$$

where index "org" refers to the organic phase and symbols without an index refer to the aqueous medium.

The temperature was maintained during the extractions using a thermostat at 20 °C ± 1 °C and, when using CFC-112 alone, at 26 °C ± 1 °C. To measure the relative activities of the aqueous and organic phases for the Sc, Ce and Eu isotopes, volumes of 2 ml were transferred to glass ampoules and measured in 4π geometry. Samples containing Pm and Tm isotopes with the same volume were transferred to Petri dishes, evaporated and measured in 2π geometry. Constant measuring conditions were maintained during measurements on the organic and aqueous phases and the relative activity of the sample was corrected for the background in the calculation of the distribution ratios D. The values of constants K_{ex}, K_D(HA) and K_2 were determined experimentally according to the literature procedure[2,4].

RESULTS AND DISCUSSION

On the basis of the earlier results[2] on the extraction of similar metals using HDBP and aqueous medium of 0.1M-HNO_3 into CFC-112, a study was made of the suitability of using this solvent and 10 : 1 mixtures of this solvent with benzene (decreasing the melting point from 26 °C to 0 °C) for extraction using HDEHP. In order to be able to compare the extraction properties of the two reagents, the dependence of the extraction of Tm on the initial analytical concentration of the reagent was first measured. The extraction was carried out using CFC-112, CFC-112 + benzene or CFC-113 as the organic phase. It can be seen from the extraction curves, given in Fig. 1, that the addition of benzene (1 : 10) to CFC-112 leads to a decrease in the $\log D_{\mathrm{Tm}}$ value by about 0.6 for both HDBP and HDEHP. However, in contrast to HDBP, HDEHP with Tm were extracted best into CFC-113 organic medium. It follows from comparison of the two reagents in the test organic system that higher distribution ratio values are obtained for the complexes of HDBP with Tm than for HDEHP. Some of the extraction constants for the extraction of Tm using HDEHP into various organic solvents[5], especially those based on chlorinated hydrocarbons, are given in Table I. The constants for the CFC-112 and CFC-113 systems were calculated on the basis of the expected mechanism, see Eq. (*4*), using Eq. (*5*), where $n = 1$.

$$M^{3+} + (3 + n)\,(HA)_{org} \leftrightarrow (MA_3(HA)_n)_{org} + 3\,H^+ \qquad (4)$$

$$K_{ex} = \frac{[MA_3(HA)_n]_{org}\,[H^+]^3}{[HA]_{org}^{3+n}\,[M^{3+}]} = D_M \frac{[H^+]^3}{[HA]_{org}^{3+n}} \qquad (5)$$

It followed from the dependence of the kinetics of extraction of Tm, Eu and Sc using HDEHP into the test organic medium that extraction equilibrium is attained within 15 min. An extraction time of 60 min was selected for the experiments.

To determine the effect of $[H^+]$ in the aqueous medium, a study was carried out of the extraction of Ce, Pm, Eu, Tm and Sc on the pH at constant ionic strength $I = 0.1$,

TABLE I

Values of constant K_{ex} for the extraction of Tm using HDEHP from aqueous medium ($I = 0.1$) into various organic solvents

Org. phase	$\log K_{ex}$	Org. phase	$\log K_{ex}$
CFC-112	6.12	CCl_4	2.15
CFC-112[a]	5.58	Chloroform	-0.07
CFC-113	6.40	Bromoform	1.14
Chlorobenzene	0.96	n-Heptane	3.69
Cl_2CH_2	0.27	Benzene	0.70

[a] Mixture with benzene in a volume ratio of 10 : 1.

where the pH was adjusted by a combination of 0.1 mol l^{-1} solutions of HNO_3 and $LiNO_3$. The curves for the individual extractions are given in Fig. 2. It follows that the

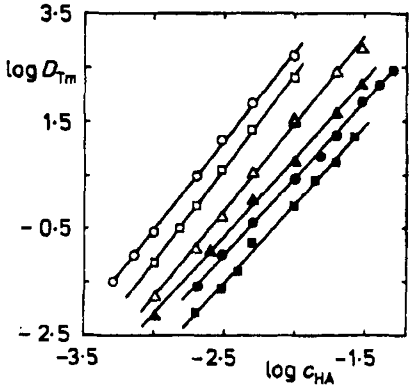

FIG. 1
Extraction of Tm using HDEHP (full circles) and HDBP (empty circles) in CFC-112 (○), a mixture of CFC-112 with benzene (□) and CFC-113 (Δ); I = 0.1 (0.1M-HNO_3), t_{ex} = 60 min, c_{Tm} = 1.7 . 10^{-7} mol l^{-1}

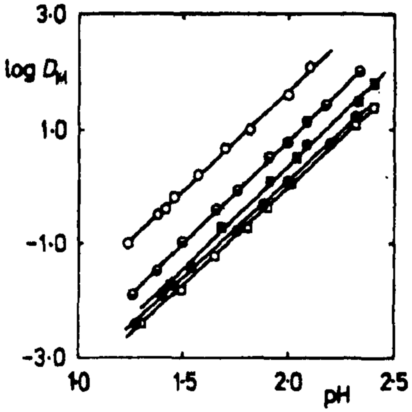

FIG. 2
Dependence of the extraction of Ce (●), Pm (□), Eu (■), Tm (⊖) and Sc (○) using HDEHP into CFC-112 with benzene (10 : 1) on the pH at constant ionic strength I = 0.1; t_{ex} = 60 min, T = 20 °C. c_{HA}, mol l^{-1}: Sc 1.9 . 10^{-5}, Tm 1 . 10^{-3}, Ce 5 . 10^{-2}, Eu, Pm 1.9 . 10^{-2}

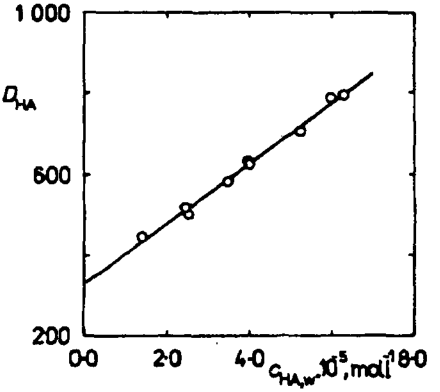

FIG. 3
Dependence of the distribution ratio of the reagent D_{HA} on its analytical concentration in the aqueous phase $c_{HA,w}$, 0.1M-HNO_3; determined using Sc, c_{Sc} = 8 . 10^{-9} mol l^{-1}

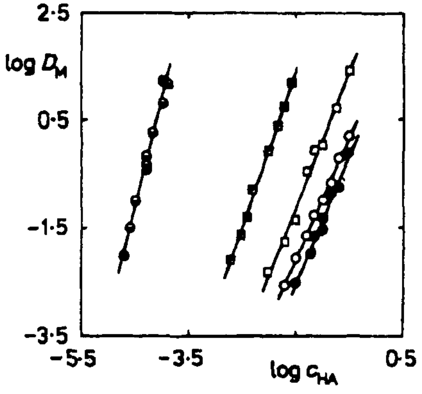

FIG. 4
Effect of the initial reagent concentration c_{HA} on the distribution ratio value for Ce (●), Pm (○), Eu (□), Tm (■) and Sc(⊖) in extraction using HDEHP into a mixture of CFC-112 with benzene (10 : 1); 0.1M-HNO_3, t_{ex} = 60 min, T = 20 °C. c_M, mol l^{-1}: Sc 8 . 10^{-9}, Tm 1.3 . 10^{-6}, Pm 1.3 . 10^{-8}, Eu 3 . 10^{-9}, Ce 5.6 . 10^{-7}

metals are extracted as trivalent cations according to Eq. (*4*), corresponding to the slopes of the linear parts of the curves, equal to 3 ± 0.1, in agreement with the results of similar works[1,6]. The distribution constants $K_D(HA)$ and dimerization constants K_2 of the reagent in the organic phase employed, i.e. for a 10 : 1 mixture of CFC-112 and benzene, were also determined. These constants were determined on the basis of the dependence of the distribution ratio of the reagent D_{HA} on its equilibrium concentration in the aqueous phase $c_{HA,w}$, using the calibration curves for the extraction of Sc, see ref.[2]. Constants K_2 and $K_D(HA)$ for HDEHP in the given extraction system were calculated from the shape of this dependence, given in Fig. 3. These values are given in Table II. For comparison, the constants for HDEHP in some other solvents are also given.

A study was also carried out of the extraction of Ce, Pm, Eu and Sc from aqueous medium of 0.1M-HNO_3 into a mixture of CFC-112 with benzene in dependence on the analytical concentration of the reagent c_{HA} and on the equilibrium concentration of the reagent in the organic phase $[HA]_{org}$. Figures 4 and 5 depict the extraction straight lines for these metals. At analytical concentrations c_{HA} greater than 0.3 mol l^{-1}, the extraction process is affected by the decreased solubility of the extraction reagent in the organic system. For this reason, higher values of $\log D$ are not given in the dependence in Fig. 4 for Ce and Pm. The following relationship as employed to convert the values of the analytical concentration of the reagent c_{HA} to the equilibrium concentration in the organic phase $[HA]_{org}$.

$$[HA]_{org} = \frac{-B + [(B)^2 + 8K_2 c_{HA}]^{1/2}}{4K_2}, \qquad (6)$$

where $B = (1/K_D + K_a/K_D[H^+] + 1)$ and c_{HA} is the overall analytical concentration of the reagent. The K_a value for HDEHP at an ionic strength of $I = 0.1$ is equal to 0.039, see

TABLE II
Values of constants K_2 and $K_D(HA)$ for HDEHP in some organic solvents, $I = 0.1$

Org. phase	$\log K_2$	$\log K_D$	Ref.
CFC-112[a]	1.52	2.67	
CFC-113	1.14	3.07	1
$CHCl_3$	1.38	0.29	7
CCl_4	1.17	0.49	7
Benzene ($I = 0.2$)	2.90	1.30	8
n-Octane	4.47	3.44	9

[a] Mixture with benzene in a volume ratio of 10 : 1.

ref.[9]. The slopes of the extraction curves for the test metals are equal to 4 ± 0.3. For the given extraction equilibrium conditions and for the given metals, their shape indicates the formation of chelates of the $MA_3(HA)$ type. Equation (*4*) can then be rearranged for Ce to yield

$$Ce^{3+} + 4\,HA \leftrightarrow CeA_3(HA) + 3\,H^+ \,. \tag{7}$$

The extraction constants were calculated from the experimental dependences on the basis of Eq. (*5*). The calculated $\log K_{ex}$ values for the individual metals are given together with the expected type of extracted complex in Table III. The values of the logarithms of the separation factors $\log \alpha$ are also given for the individual pairs of test lanthanoids, calculated on the basis of the relationship

$$\log \alpha = \log \frac{D_{M1}}{D_{M2}} = \log D_{M1} - \log D_{M2}\,, \tag{8}$$

where D_{M1} and D_{M2} are the values of the distribution ratios of the compared metals, determined by graphical analysis of the extraction curves in Fig. 5.

For orientative comparison of the extraction abilities of HDEHP for the group of lanthanoids based on the K_{ex} values, Fig. 6 depicts the $\log K_{ex}$ dependences on the atomic number Z for the test metals for organic medium of CFC-112 with benzene and toluene[8]. For comparison, the extraction curve for HDBP and a mixture of CFC-112 with benzene is also given. It follows that the curve is similar to that for HDEHP which, however, exhibits lower K_{ex} values.

It follows from comparison of these results with the conclusions of earlier works that the tested organic phases exhibit good solvation properties for extraction with HDEHP. The K_{ex} values for the test metals attain higher values than, for example, when using

TABLE III

Values of K_{ex} for the test metals during extraction using HDEHP into a mixture of CFC-112 with benzene (10 : 1), I = 0.1 and the separation factors for lanthanoids (log α)

Metal	Type of complex	$\log K_{ex}$	log α	
Ce	CeA_3 (HA)	1.67	Ce–Pm	0.26
Pm	PmA_3 (HA)	2.00	Ce–Eu	1.50
Eu	EuA_3 (HA)	3.10	Ce–Tm	3.62
Tm	TmA_3 (HA)	5.58	Pm–Eu	1.23
Sc	ScA_3 (HA)	13.9	Pm–Tm	3.35
			Eu–Tm	2.12

benzene, toluene, n-heptane, tetrachloromethane or other commonly used organic solvents. These favourable properties of CFC-112 and CFC-113 are a consequence primarily of their nonpolar character and thus also low relative permittivity values (for CFC-112, $\varepsilon_r = 2.25$ and for CFC-113, $\varepsilon_r = 2.41$; all values at $t = 25$ °C)[10]. The dependence in Fig. 7 is given for comparison of the polarities of some organic solvents commonly employed in solvent extraction, along with the values of the extraction constants $\log K_{ex}$ HDEHP for the extraction of Tm into these solvents. The relative absorption energies of the various solvents on aluminium oxide[11] are given as the polarity values ε^0. The straight line obtained confirm the expected dependences of the

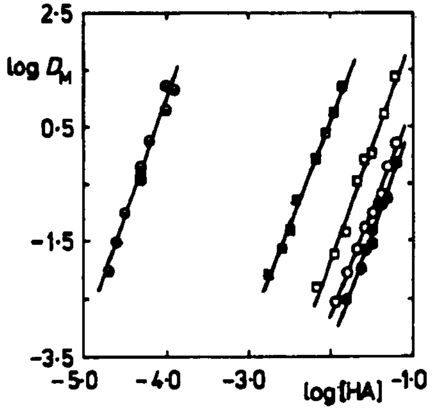

Fig. 5

Effect of the equilibrium concentration of reagent in the organic phase $[HA]_{org}$ on the value of the distribution ratio of Ce (●), Pm (○), Eu (□), Tm (■) and Sc (○) for extraction with HDEHP into a mixture of CFC-112 with benzene (10 : 1); other conditions as in Fig. 4

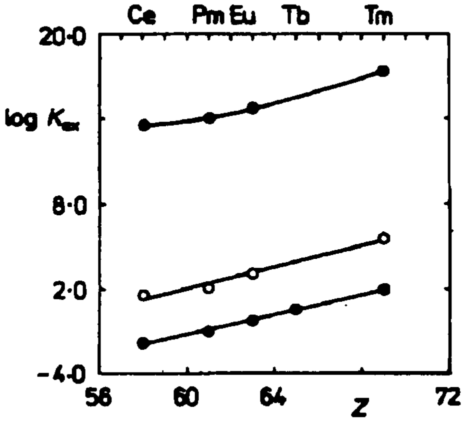

Fig. 6

Dependence of $\log K_{ex}$ on the atomic number (Z) of the lanthanoids extracted using HDEHP into CFC-112 mixed with benzene (○), toluene (●) and using HDBP into CFC-112 with benzene (⊖) at an ionic strength of $I = 0.1$, 0.1M-HNO_3

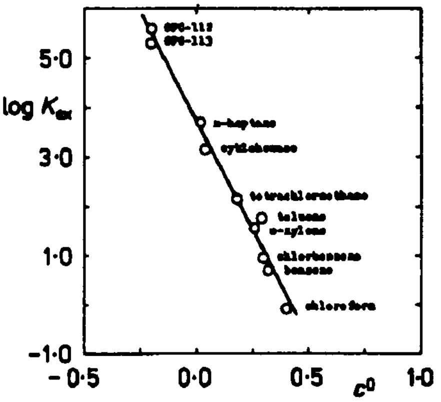

Fig. 7

The effect of the polarity of the organic phase ε^0 on the K_{ex}(Tm) value for extraction using HDEHP from aqueous medium with ionic strength $I = 0.1$

compared quantities. When CFC-112 alone was employed, which differed negligibly from the mixture with benzene in the extraction of the individual metals[2], use can be made of the ability to convert the extracted complex in the organic phase into a solid on the basis of cooling of the extraction system below 25 °C. This factor can simplify subsequent operations with the organic phase.

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