EXTRACTION OF Ce, Pm, Eu, Tm AND Sc USING DI-n-BUTYLHYDROGEN-PHOSPHATE IN 1,1,2,2-TETRACHLORODIFLUOROETHANE

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A study was carried out of the extraction of Ce, Pm, Eu, Tm and Sc from aqueous HNO_3 medium into an organic phase of 1,1,2,2-tetrachlorodifluoroethane (CFC-112, Ledon-112) using di-n-butylhydrogen-phosphate (HDBP) as extracting reagent. The organic solvent was studied from the point of view of some of its interesting properties that can be utilized in practical applications of liquid extraction. Especially the dependence of the extraction of selected lanthanoids on the HDBP concentration and pH was studied and constants K_2 and $K_D(HA)$ were found for this reagent in CFC-112 and mixtures of this solvent with benzene.

On the basis of earlier studies of the extraction of the complexes of some lanthanoids into organic solvent CFC-113 (FCl_2C–$CClF_2$)[1–3], a study was carried out of the use of CFC-112 (Cl_2FC–CCl_2F) because of its higher boiling point and very good solvation properties, as well as because of its relatively lower activity for ozone[4]. Its physical constants were also considered interesting. The tested favourable properties of this type of solvent include its chemical and thermal stability and inflammability.

This work was carried out in order to test the use of CFC-112 for the liquid extraction of selected lanthanoids using di-n-butylhydrogenphosphate (HDBP) as extracting reagent, to find the optimum conditions for quantitative extraction and compare the results obtained with those in the literature.

EXPERIMENTAL

Chemicals and Instruments

The HDBP, pure (Koch–Light, England) was repurified according to the published procedure[5]. CFC-112 (intermediate in the production of CFC-13, SPCHV, Ústí nad Labem) was redistilled on a column, and the 92 °C fraction was collected. The benzene was of p.a. purity (Lachema, Brno), as were the inorganic salts and acids. The specific activities and concentrations of the radioactive solutions of isotopes ^{144}Ce, ^{147}Pm and ^{155}Eu (ÚVVVR, Prague) were 5.72 MBq g^{-1} ($1.8 \cdot 10^{-3}$ mol l^{-1}), 5.4 MBq g^{-1} ($6.4 \cdot 10^{-8}$ mol l^{-1}) and 4.7 MBq g^{-1} ($1.9 \cdot 10^{-7}$ mol l^{-1}). The specific activities and concentrations of the isotopes ^{170}Tm and ^{46}Sc (Poland) were 87.5 GBq g^{-1} ($1.3 \cdot 10^{-4}$ mol l^{-1}) and 445.5 MBq g^{-1} ($2 \cdot 10^{-6}$ mol l^{-1}). The radioactive isotopes were dissolved in 0.1M-HNO_3.

The gamma relative activities of the aqueous and organic phases were measured using a NKQ 322 scintillation detector with a type SKW NaI(Tl) scintillator. The relative beta activity was measured using a NKQ 321 scintillation detector with a type SPF plastic scintillator. The evaluation apparatus was a NZQ 601 spectrometric unit with recorder (Tesla Liberec). The pH was measured using a combined electrode and a type OP-208/1 pH meter (Radelkis, Hungary). The electrode was calibrated using borate and phthalate buffers. The melting point of the CFC-112 mixture was measured using a laboratory MK-70 ultracryostat (F.R.G.) with ethanol filling.

Procedure

Extractions were carried out using a rotating extractor and test tubes with glass stoppers. The organic and aqueous phases (ratio of volumes 5/5 ml) were mixed for 60 min, followed by a 30 min rest period for phase separation. 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 the distribution constants $K_D(\mathrm{HA})$ and dimerization constants $K_2(\mathrm{HDBP})$ were determined by graphical analysis using the functional dependence of the distribution ratio of the reagent D_{HA} on its equilibrium concentration in the aqueous phase $c_{\mathrm{HA,w}}$. After establishment of the extraction equilibrium between the two phases, it was considered that the distribution of the total analytical concentration of the reagent c_{HA} between the two phases is given by the equation

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

where symbols c refer to the concentration 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.

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

and

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

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

The determination procedure using a microcomputer has already been described[6]. The values of the equilibrium concentrations of the reagent in the aqueous [HA] or organic phase $[\mathrm{HA}]_{\mathrm{org}}$ were determined on the basis of the calibration dependence log D_{Sc} vs log c_{HA} using the $^{46}\mathrm{Sc}$ isotope in 0.1M-$\mathrm{HNO_3}$. The K_2 and $K_D(\mathrm{HA})$ values were calculated using the relationship

$$D_{\mathrm{HA}} = \frac{K_D(\mathrm{HA})}{\varphi} + \frac{2K_2 K_D(\mathrm{HA})^2}{\varphi^2} c_{\mathrm{HA,w}} \,, \qquad (1)$$

where $K_D(\mathrm{HA}) = [\mathrm{HA}]_{\mathrm{org}}/[\mathrm{HA}]$, $K_2 = [\mathrm{H_2A_2}]_{\mathrm{org}}/[\mathrm{HA}]^2_{\mathrm{org}}$ and $\varphi = (1 + K_a/[\mathrm{H^+}])$, where dissociation constant K_a is given by $K_a = [\mathrm{H^+}][\mathrm{A^-}]/[\mathrm{HA}]$. The extraction constants K_{ex} were found using the relationship

$$K_{ex} = \frac{[MA_n]_{org}\,[H^+]^n}{[M^{n+}]\,[HA]^n_{org}}, \tag{2}$$

where the equilibrium concentration of the monomer forms of the reagent in the organic phase $[HA]_{org}$ can be expressed for this type of equilibrium by the expression

$$[HA]_{org} = \frac{-B + [(B)^2 + 8K_2\,c_{HA}]^{1/2}}{4K_2}, \tag{3}$$

where $B = (1/K_D + K_a/K_D\,[H^+] + 1)$ and c_{HA} is the overall analytical concentration of the reagent.

RESULTS AND DISCUSSION

On the basis of study of the extraction dependence $\log D_{Tm}$ vs $\log c_{HDBP}$, CFC-112 was found to have very good solvation properties for the given purpose. It follows from the extraction curves in Fig. 1 that the extraction efficiency of HDBP for Tm is greater than that obtained using CFC-113, benzene, n-heptane, CCl_4, 1,2-dichloroethane, di-n-butyl ether (DBE) and chloroform. Some extraction constants K_{ex} are given in Table I.

Because of the suitable properties of CFC-112 for liquid extraction, a study was carried out of the utilization of its melting point (25 °C) for conversion of the organic phase from a liquid into a solid. This factor can simplify some practical applications, liquid extractions, e.g. during separations, re-extractions, etc, especially when the volume of the organic phase is less than that of the aqueous phase. A change of state can be brought about, e.g. by cooling the extraction system with water. The solid organic phase with the extracted metal can then be simply separated from the aqueous phase, decanted or otherwise treated for the subsequent procedure.

To determine the conditions for quantitative extraction, the kinetics of the extraction of Tm were first studied. For purposes of comparison, this dependence was studied in CFC-112, CFC-113 and benzene and is depicted in Fig. 2. It follows from the curves that the extraction equilibrium in the HDBP system in CFC-112 is attained in approx. 15 min, similar to the results obtained in similar works[2,3].

TABLE I
Values of constant K_{ex} for the extraction of Tm using HDBP in various organic solvents

Org. phase	Conditions	$\log K_{ex}$	Ref.
CFC-112	I = 0.1 (HNO_3)	19.1	
CFC-113	I = 0.1 (HNO_3)	18.0	
DBE	I = 1 (HNO_3)	6.2	5
Toluene	I = 1 (HNO_3)	4.6	5
Benzene	I = 0.1 ($HClO_4$)	6.2	7

The behaviour of HDBP in CFC-112 was also studied in dependence on the use of various types of inorganic acids and their ionic strengths. The extraction of Tm was carried out using HDBP into CFC-112 from aqueous medium of $HClO_4$, HNO_3, HCl and H_2SO_4. The results are depicted in Fig. 3. The course of the extraction curves indicate that the $\log D_{\mathrm{Tm}}$ values are very similar in the concentration interval 0.1 – 1 mol l^{-1}. In the further study of the extraction dependences, 0.1M-HNO_3 was employed as the aqueous phase, taking into consideration a number of additional factors, such as sorption of the isotopes on the glass, etc.

The ability to convert the organic phase after extraction into a solid was tested for selected lanthanoids and scandium using HDBP in 0.1M-HNO_3. The most suitable volume ratio for working with the solid organic phase in this system was found to be a phase ratio of $V_{\mathrm{org}}/V_{\mathrm{w}}$ of 0.5/5 ml. The extraction curves for selected lanthanoids and scandium using HDBP in CFC-112 alone are given in Fig. 4. For comparison with the other dependences, the values of the percent extraction E, including unequal phase ratios, were recalculated to $\log D$ according to the relationship

$$\log D = \frac{E\,V}{V_{\mathrm{org}}} - \log(100 - E)\,. \qquad (4)$$

If CFC-112 is to be used in classical liquid extraction, the necessity for an elevated temperature during the extraction (above 25 °C) can be eliminated through the addition of some other organic solvent. The solubilities of some extraction reagents can be similarly increased. For these purposes, a study was carried out of the dependence of the

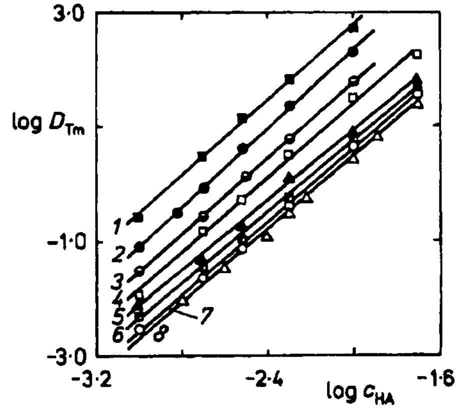

FIG. 1

Extraction of Tm using HDBP into various organic solvents. ■ CFC-112, ● CFC-113, ⊖ n-heptane, □ CCl_4, ▲ mixture of CFC-113 with benzene (1 : 2), ◪ dichloroethane, ○ benzene, Δ chloroform; $I = 0.1$, $t_{\mathrm{ex}} = 60$ min, $c_{\mathrm{Tm}} = 1.7 \,.\, 10^{-7}$ mol l^{-1}

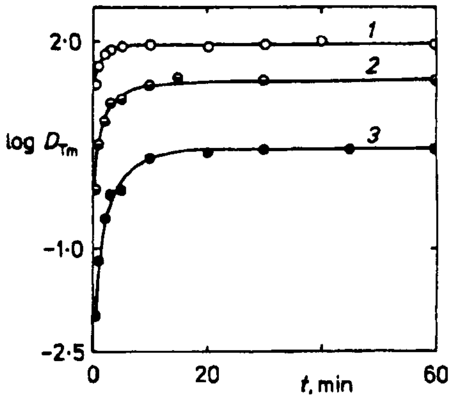

FIG. 2

Kinetics of the extraction of Tm into HDBP in ○ CFC-112, ⊖ CFC-113 and ● benzene; $I = 0.1$, $c_{\mathrm{HDBP}} = 5 \,.\, 10^{-3}$ mol l^{-1}, $c_{\mathrm{Tm}} = 3.5 \,.\, 10^{-8}$ mol l^{-1}

melting point of CFC-112 in mixtures with CFC-113 and benzene, in various ratios. This dependence is given in Fig. 5.

On the basis of these dependences, further extractions were carried out using a mixture of CFC-112 and benzene in a ratio of 10 : 1, with a m.p. of about 0 °C. The extraction ability of HDBP for selected elements using this mixture, see Fig. 6, is very good (cf. Fig. 4). The slopes of the log D vs log $[HA]_{org}$ curves for the studied metals depicted in Figs 4 and 6 for Ce, Pm, Eu and Tm are approximately equal to 5, while that for Sc is approx. equal to 4; thus it can be expected that complexes of the $MA_3(HA)_2$ type are extracted according to the equation

$$Ce^{3+} + 5\,(HA)_{org} \longleftrightarrow [CeA_3(HA)_2]_{org} + 3\,H^+ \qquad (D)$$

which is also valid for Eu, Pm and Tm. For the extraction of scandium, the shape of the curve indicates that a complex of the type $ScA_3(HA)$ is extracted, i.e.

$$Sc^{3+} + 4\,(HA)_{org} \longleftrightarrow [ScA_3(HA)]_{org} + 3\,H^+\,. \qquad (E)$$

Constant K_{ex} was calculated from the linear portions of the curves for the extraction of the individual metals using HDBP into CFC-112 and a mixture of this solvent with benzene. It follows from the K_{ex} values, given in Table II that both CFC-112 and its mixture with benzene are suitable organic phases for this type of extraction. The K_{ex} values for the test metals are higher than for a number of organic solvents, such as benzene (see Table II), toluene, dibutyl ether, etc. For comparison of the extraction

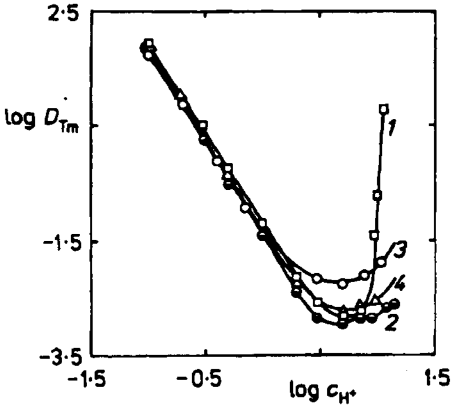

FIG. 3

Effect of the initial concentration of inorganic acid on log D_{Tm} using HDBP in CFC-112; □ $HClO_4$, ◒ HNO_3, ○ HCl, Δ H_2SO_4; c_{Tm} = 1.4 . 10^{-8} mol l^{-1}, c_{HDBP} = 5 . 10^{-3} mol l^{-1}, t_{ex} = 60 min, T = 26 °C

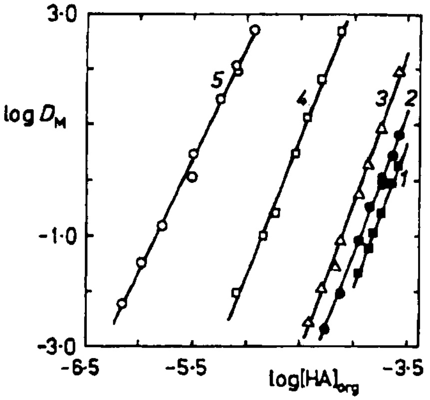

FIG. 4

Extraction ■ Ce, ● Pm, Δ Eu, □ Tm and ○ Sc with HDBP in CFC-112, I = 0.1. 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}. T = 26 °C, t_{ex} = 60 min ability of HDBP in various organic solvents and expression of the dependence of log K_{ex} on the extractability of the individual metals, Fig. 7 depicts the dependence of log K_{ex} on the ionic radius of the metal. It also follows from these curves that HDBP will tend to exhibit higher separation factors for lanthanoids with higher proton numbers.

A study was also carried out of the determination of constants K_D(HA) and K_2 for HDBP in an aqueous phase of 0.1M-HNO_3 and organic phase of *a*) CFC-112 and *b*)

TABLE II

Extraction constants K_{ex} for the extraction of selected metals into HDBP in CFC-112, a mixture of CFC-112 with benzene (10 : 1) and benzene[8] (B), I = 0.1

Metal	Type of complex	log K_{ex}		
		CFC-112	CFC-112 + B	B
Ce	$CeA_3(HA)_2$	15.1	13.6	2.0
Pm	$PmA_3(HA)_2$	15.7	14.1	2.54
Eu	$EuA_3(HA)_2$	16.5	14.8	3.11
Tm	$TmA_3(HA)_2$	19.1	17.2	6.2
Sc	$ScA_3(HA)$	18.6	18.1	–

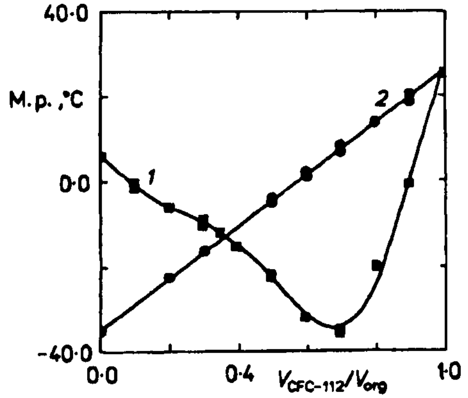

FIG. 5

Dependence of the melting point of CFC-112 on the volume fraction in a mixture with ■ benzene and ● CFC-113

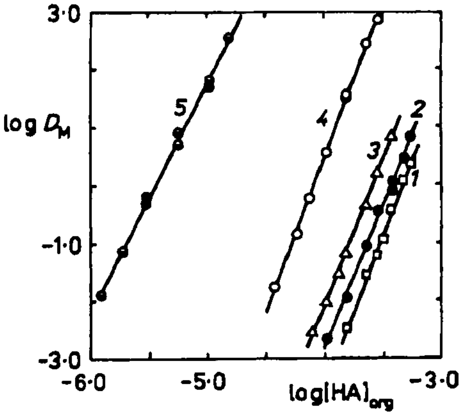

FIG. 6

Dependence of the distribution ratio of □ Ce, ● Pm, Δ Eu, ○ Tm and ⊖ Sc on the initial concentration of HDBP in a mixture of CFC-112 with benzene (10 : 1), I = 0.1, t_{ex} = 60 min, t = 20 °C, other conditions as in Fig. 4

a mixture of CFC-112 with benzene (10 : 1). The calculated values are given in Table III and the graphical plot of D_{HA} vs $c_{HA,w}$ for the calculation of these constants is depicted in Fig. 8. It follows from these dependences and calculated values that HDBP behaves similarly as in the CF-113 and CCl_4 extraction systems. For clarity, Table III also gives the values for a number of other organic solvents. In connection with a study of the extraction of these metals using HDBP with a change in the reagent concentration, the effect of the equilibrium [H^+] concentration or pH was also followed at constant ionic

TABLE III
Dimerization and distribution constants for HDBP in some solvents at an ionic strength of the aqueous phase of I = 0.1

Organic phase	$\log K_2$	$\log K_D$	Ref.
CFC-112	5.83	-1.13	
CFC-112 + benzene (10 : 1)	5.18	-0.87	
CFC-113	5.62	-1.44	2
$CHCl_3$	4.41	-2.00	7
CCl_4	6.49	-1.44	9
Benzene (I = 1)	4.88	-0.42	10

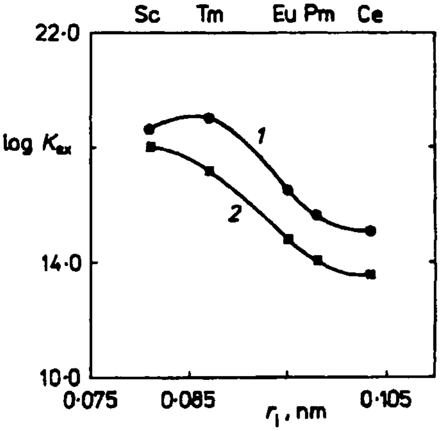

FIG. 7
Dependence of the log K_{ex} value of the test metals on the ionic radius during extraction using HDBP into ● CFC-112 and ■ CFC-112 + benzene

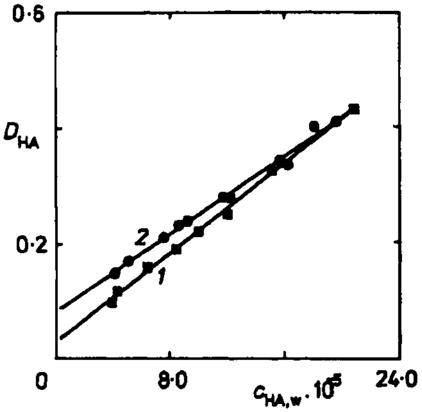

FIG. 8
Dependence of the distribution ratio D_{HA} of the reagent HDBP on its equilibrium concentration in the aqueous phase; c_{Sc} = 8 . 10^{-9} mol l^{-1}, I = 0.1, t_{ex} = 60 min, ■ CFC-112 (T = 26 °C), ● CFC-112 + benzene (10 : 1)

strength I = 0.1, see Fig. 9. The slopes of the linear portions of these curves are approximately equal to 3, corresponding to the expected extraction of the metal as the trivalent ion Ce^{3+}, Pm^{3+}, Eu^{3+}, Tm^{3+}, and Sc^{3+}, see Eqs (D), (E).

It has thus been demonstrated that 1,1,2,2-tetrachlorodifluoroethane (CFC-112) can be used as an organic solvent in extraction using HDBP in a liquid–liquid system. This solvent has very good solvation properties, that increase the extraction efficiency, i.e. the log K_{ex} value were above those so far measured for commonly used organic solvents. Some of its physical properties are also useful in the practical application of liquid extraction.

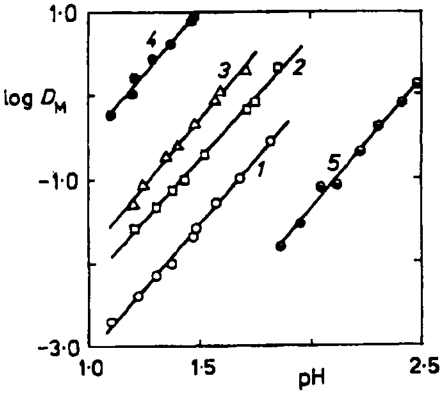

FIG. 9

Effect of the pH of the aqueous phase on the distribution ratio ○ Ce, □ Pm, △ Eu, ● Tm and ◒ Sc in extraction with HDBP in CFC-112 + benzene, I = 0.1, t_{ex} = 60 min, T = 20 °C. c_{HA}, mol l^{-1}: 1.9 . 10^{-5} (Sc), 1.9 . 10^{-3} (Tm), 5 . 10^{-2} (Ce), 1.9 . 10^{-2} (Eu, Pm)

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