

EXTRACTION OF SCANDIUM, CERIUM, PROMETHIUM, AND EUROPIUM WITH DIBUTYLPHOSPHORIC, BIS(2-ETHYLHEXYL)-PHOSPHORIC, AND DIOCTYLPHOSPHORIC ACIDS IN FREON 113

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The extraction of Sc, Ce, Pm, and Eu from aqueous solutions of HClO₄ and HNO₃ into organic phases constituted by solutions of dialkylphosphoric acids in Freon 113 was studied. The effects of the kind of inorganic acid, concentration of hydrogen ions in the aqueous phase and concentration of the extracting agent in the organic phase were examined. Based on the dependences of the distribution ratios of the metals on the above variables, the compositions of the extractable complexes were determined and the extraction constants calculated. The dimerization constants and distribution constants of the monomer were also determined for dibutylphosphoric and bis(2-ethylhexyl)phosphoric acids.

Although considerable attention has been paid to liquid-liquid extraction of Sc, Ce, Pm, and Eu with dialkylphosphoric acids¹, practically only CCl₄ has been employed as a nonflammable organic phase. The possibility of using Freon 113 (CCl₂F₂·CClF₂) as the nonflammable organic medium has been indicated by us in our previous work² dealing with the extraction of some rare earth elements, cobalt, zinc, and hafnium with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone, where we observed that a 2 : 1 mixture of Freon 113 with benzene was still virtually nonflammable.

With a view to gaining a better insight into metal extraction into this nonflammable organic phase, we centered now on the partition of scandium, cerium, promethium, and europium between an aqueous phase containing HClO₄ or HNO₃ and solutions of di-n-butylphosphoric acid (HDBP), bis(2-ethylhexyl)phosphoric acid (HDEHP) or di-n-octylphosphoric acid (HDOP) in Freon 113. For HDBP and HDEHP we also determined the dimerization constants and distribution constants of the monomers. The extraction constants of the metals were obtained by conventional graphical analysis and computer processing of the extraction curves.

EXPERIMENTAL

Chemicals and Apparatus

HDEHP and HDOP were synthesized and purified at the Institute of Nuclear Research in Řež. HDBP of reagent grade purity was a commercial chemical of Koch-Light, U.K., the remaining

chemicals were reagent grade products supplied by Lachema, Brno, Freon 113 (Du Pont, U.S.A.) was distilled prior to use. The solutions of the extracting agents in the organic phase were prepared by weighing. The radioactive metals used were converted to perchlorates; their analytical concentrations (mol l^{-1}) and specific activities ($\text{s}^{-1} \text{cm}^{-3}$) in the aqueous phase before the extraction were as follows: ^{46}Sc (Poland) $2.2 \cdot 10^{-10}$, $2.7 \cdot 10^5$; ^{144}Ce (Poland) $3.1 \cdot 10^{-11}$, $2.6 \cdot 10^3$; ^{147}Pm (U.S.S.R.) $4.3 \cdot 10^{-11}$, $1.5 \cdot 10^3$; $^{152+154}\text{Eu}$ (Poland) $6.1 \cdot 10^{-10}$, $2.5 \cdot 10^3$. The purity of the radioactive preparations was tested spectrometrically with an ICA-70 4096-channel analyzer (KFKI, Hungary) using a Ge-Li detector at 1 keV/channel.

The pH of the samples after the extraction was measured with an OP-208 pH-meter (Radelkis, Budapest) equipped with a glass indicator electrode and a calomel reference electrode. The cell was calibrated prior to each measurement using phthalate and borate buffers. The gamma radioactivity of the samples was measured scintillometrically with an SKW 1D NaI/Tl well crystal 45×50 mm using a 61 PK 412 photomultiplier, the pulse counts were recorded with an NZQ 714 measuring system employing a VN 31 external high-voltage supply, and the beta radioactivity of ^{147}Pm was measured with an NAQ 221 probe interfaced to an NZQ 727 T measuring system (all Tesla, Liberec).

Procedure

The extractions were performed by agitating the two phases (10 ml each) in thermostated glass test tubes with polyethylene stoppers at $20 \pm 1^\circ\text{C}$ on a homemade rotary shaking machine. The extraction time, which was 8 h for Sc, Eu and Pm and 24 h for Ce, was chosen based on the study of the kinetic curves of extraction. After the extraction and phase separation (after the establishment of the radioactive equilibrium for Ce), 2 ml aliquots of each phase were taken and their gamma activity was measured for each of the metals except for Pm, for which the beta activity of the evaporation residue on a dish was determined. The measurement geometry was held constant and the relative standard deviation never exceeded 2%. The pH of the aqueous phase was also measured on 5 ml aliquots.

For determining the dimerization and distribution constants of HDBP and HDEHP, the equilibrium concentration of the acid (HA) in the aqueous phase was measured indirectly. After the partition of HA between the two phases, an aliquot of the aqueous phase was taken, adjusted to pH 1, and shaken with pure Freon. Virtually all HA passed into the organic phase because the distribution ratio D_{HA} at this pH, as was found by tentative experiments, is greater than 100. To this solution of HA in Freon was then added the same volume of solution of radioactive hafnium in 1M-HCl or of radioactive scandium in 0.1M-HCl, and their partition was examined. The initial equilibrium concentration of HA in the aqueous phase was obtained by comparison with calibration curves.

The acidity of the aqueous phase was adjusted with $\text{HClO}_4 + \text{NaClO}_4$ or $\text{HNO}_3 + \text{LiNO}_3$ solutions so that the ionic strength was constant, except for experiments where the dependences of the distribution ratios of the metals on the initial concentrations of the mineral acids were investigated.

Computer Handling of Extraction Curves

The extraction constants were calculated by using the program EXLET^{3,4}. The input data were the total analytical concentrations of the components, pH, log D values, encoded compositions of the complexes formed, and initial parameter estimates. The calculations relied on the minimization of the sum of squares of differences between the observed (D_{obs}) and calculated (D_{calc}) distribution ratios of the metal, $U = \sum_1 (\log D_{\text{obs}} - \log D_{\text{calc}})^2$. The pK of the extracting agent,

its dimerization constant in the organic phase and the distribution ratio of its monomer were considered as known parameters. It was also usually assumed that the sole complex formed and extracted is $M(HA)_nA_p$ type; in view of this, the values of the constants obtained are to be considered as a first approximation.

The calculations using the program EXLET (104 K) were performed on an EC 1033 computer at the Institute of Computer Instrumentation, Purkyně University in Brno.

RESULTS AND DISCUSSION

Determination of Dimerization and Distribution Constants of HA

The dimerization and distribution constants of HDBP and HDEHP were determined based on the relations used previously⁵. The values, along with those obtained in CCl_4 (refs^{6,7}), are given in Table I; they indicate that the extent of dimerization of the two substances in CCl_4 and in Freon is of the same order of magnitude. The distribution constant of the monomeric HDEHP, on the other hand, is more than two orders of magnitude higher in the Freon–aqueous phase ($I = 0.1$) system than in the CCl_4 –water system. For HDOP the dimerization and distribution constants were not determined because the solubility of this agent in water is too low for reliable experimental measurements.

Effect of Initial Concentration of Inorganic Acid on Metal Extraction

The dependences of the distribution ratios of the metals on the initial concentrations of $HClO_4$ and HNO_3 indicate that for all the metals and dialkylphosphoric acids studied, the extraction mechanism alters as the acid concentration is increased. The curves for HDBP are shown in Figs 1 and 2, those for HDOP and HDEHP are alike. The extraction curves display minima, which are very marked with $HClO_4$ and less marked with HNO_3 . The initial ion exchange extraction mechanism in the

TABLE I

Distribution (K_D) and dimerization (K_2) constants of HDBP and HDEHP at an ionic strength of the aqueous phase of $I = 0.1$

Substance	Organic phase	$\log K_D$	$\log K_2$
HDBP	Freon	−1.44	5.62
	CCl_4^a	−1.44	6.49
HDEHP	Freon	3.07	1.14
	CCl_4^b	0.49	1.17

^a Ref. 6; ^b ref. 7.

less acidic region is replaced by the solvation mechanism. This effect has been observed for the extraction of the majority of trivalent metal cations from the above mineral acids with acidic organophosphorus agents in various organic solvents; it is very pronounced with perchloric acid, whereas with nitric acid the extraction of the $(HA)_x(HNO_3)_y$ species, competing with the metal extraction, must be taken into account. The distribution ratios of the metals do not change in the strongly acid region of the aqueous phase on replacing the mineral acids by their sodium or lithium salts (Figs 1 and 2, curves 4).

Effect of Hydrogen Ion Concentration

The dependences of the distribution ratios of the metals on the hydrogen ion concentration in the aqueous phase at a constant ionic strength of $I = 0.1$ for Ce, Eu and Pm at pH 1–3 and $I = 1.0$ for Sc at c_{HClO_4} or $c_{HNO_3} = 0.1–1 \text{ mol l}^{-1}$ are linear with a slope of 3.00 ± 0.15 in all cases, which implies that at low acidities of the aqueous phase, where the ion exchange mechanism is assumed, three protons are exchanged according to the equation

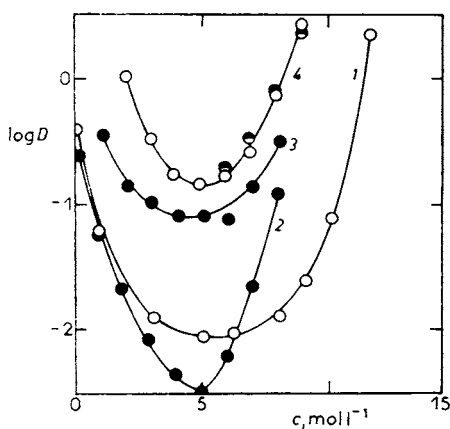


FIG. 1

Effect of initial concentration of perchloric acid (c) on the metal distribution between the aqueous phase and solutions of HDBP in Freon. Element, c_{HDBP} (mmol l^{-1}): 1 Ce, 10; 2 Eu, 5; 3 Pm, 25; 4 Sc, 0.1; Points ●: $c_{H^+} = \text{const} = 6 \text{ mol l}^{-1}$, ○: $c \equiv c_{ClO_4^-}$

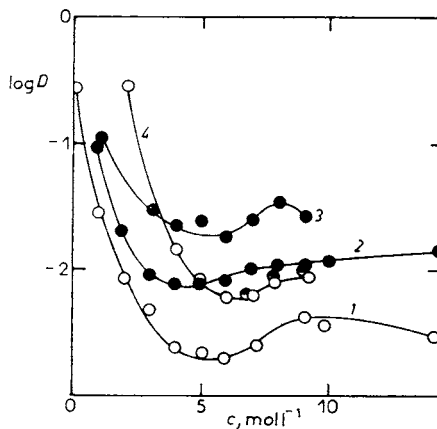


FIG. 2

Effect of initial concentration of nitric acid (c) on the metal distribution between the aqueous phase and solutions of HDBP in Freon. Element, c_{HDBP} (mmol l^{-1}): 1 Ce, 50; 2 Eu, 50; 3 Pm, 25; 4 Sc, 0.1. Points ●: $c_{H^+} = \text{const} = 6 \text{ mol l}^{-1}$, ○: $c \equiv c_{NO_3^-}$

where the subscript org refers to the organic phase and the unlabelled species are those in the aqueous phase; HA is the monomer of the dialkylphosphoric acid.

Effect of Initial Concentration of Dialkylphosphoric Acid

Figs 3 and 4 show the dependences of the distribution ratios of the metals on the equilibrium concentration of the monomeric form of HDBP or HDEHP in the organic phase, $[HA]_{org}$, at $c_{HClO_4} = 0.1 \text{ mol l}^{-1}$ for Ce, Eu and Pm and 1.0 mol l^{-1} for Sc. The $[HA]_{org}$ values were calculated based on the known dissociation (K_a), distribution (K_D) and dimerization (K_2) constants of the agents using the relations

$$c_{HA} = [HA] + [A^-] + [HA]_{org} + 2[H_2A_2]_{org} \quad (1)$$

$$c_{HA} = [HA]_{org} \{ 1/K_D + K_a/(K_D[H^+]) + 1 \} + 2[HA]_{org}^2 K_2 \quad (2)$$

$$[HA]_{org} = \left\{ -[1/K_D + K_a/(K_D[H^+]) + 1] + \left\{ [1/K_D + K_a/(K_D[H^+]) + 1]^2 + 8K_2c_{HA} \right\}^{1/2} \right\} / 4K_2, \quad (3)$$

where c_{HA} is the initial concentration of the agent. The K_a values were taken from ref¹.

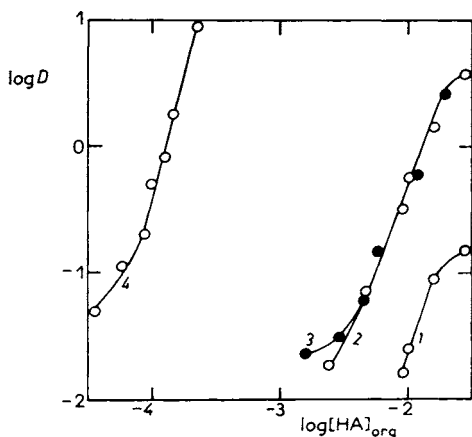


FIG. 3

Effect of equilibrium concentration of HDBP monomer on the metal distribution between the aqueous phase at an ionic strength of $I = 0.1$ (1.0 for Sc) and solutions of HDBP in Freon. Curves: 1 Ce, 2 Pm, 3 Eu, 4 Sc

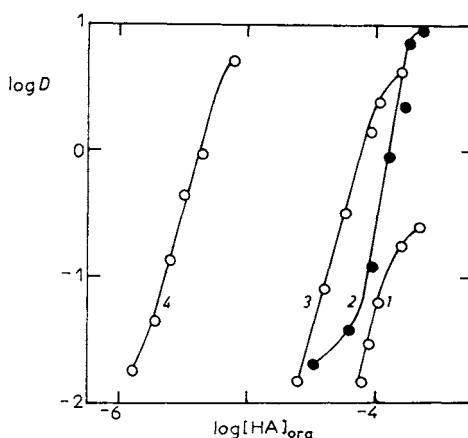


FIG. 4

Effect of equilibrium concentration of HDEHP monomer on the metal distribution between the aqueous phase at an ionic strength of $I = 0.1$ (1.0 for Sc) and solutions of HDEHP in Freon. Curves: 1 Ce, 2 Eu, 3 Pm, 4 Sc

The slope of the linear segments of the curves shown in Fig. 3 for HDBP is 4.0 ± 0.2 for all the metals followed except for Pm, where the slope is 6. For HDEHP (Fig. 4) the slope is 3.0 ± 0.3 , only for Sc it is 4.0 ± 0.2 . For HDOP the dependences could not be established because the K_D and K_2 values were unknown for reasons mentioned above.

Based on these data, the extraction constants of the complexes conforming to equilibrium (A) could be calculated as

$$K_{ex} = [MA_3(HA)_n]_{org} [H^+]^3 / ([HA]_{org}^{3+n} [M^{3+}]) = D_M ([H^+]^3 / [HA]_{org}^{3+n}). \quad (4)$$

The data, along with the numbers of reacting monomeric HA particles, are given in Table II; they were obtained by graphical analysis and, for HDBP, also by computer handling of the extraction curves. For a comparison, the extraction constants of scandium and some rare earth elements determined previously^{8,9} using benzene or n-octane as the organic phase are also given.

It can be concluded that Freon 113 suits well as a nonflammable phase for extractions with dialkylphosphoric acids. It does not differ markedly in its properties

TABLE II

Extraction constants K_{ex} and numbers of reacting monomeric particles $m = 3 + n$ at an ionic strength of $I = 0.1$

Metal	Organic phase	HDBP			HDEHP	
		m	$\log K_{ex}$		m	$\log K_{ex}$
			graphical analysis	computer handling		
Ce	Freon	4	11.7	11.3	3	1.4
	benzene ^a	6	17.0	—	—	—
Eu	Freon	4	13.3	11.8	3	2.6
	benzene ^a	6	17.3	—	—	—
Pm	Freon	6	20.3	20.1	3	2.6
Tb	benzene ^a	6	18.3	—	—	—
Tm	benzene ^a	6	19.3	—	—	—
Sc ^b	Freon	4	21.4	21.4	4	15.6
	benzene ^c	6	25.6	—	6	26.8

^a Ref.⁸; ^b $I = 1.0$; ^c n-octane for HDEHP; both ref.⁹.

from tetrachloromethane. As compared with benzene, the number of reacting monomeric HDBP or HDEHP particles in it is lower. This implies that the free ligand is not present preferentially in the dimeric HA_2^- form; instead, the A^- species rather predominates. In the examined region of initial HA concentrations, the $\text{CeA}_3(\text{HA})$, $\text{EuA}_3(\text{HA})$, $\text{ScA}_3(\text{HA})$, and $\text{PmA}_3(\text{HA})_3$ complexes are extracted into Freon with HDBP, whereas the CeA_3 , EuA_3 , PmA_3 , and $\text{ScA}_3(\text{HA})$ complexes are extracted with HDEHP. The number of complexes examined was too low to enable us to arrive at an explanation of the different composition of the complexes with promethium; the computer processing, however, suggests that in the aqueous phase the presence of the PmA^{2+} species with a reasonably high stability ($\log \beta_1 \approx 3.5$) should be taken into account. On the whole, Table II demonstrates that there is a fairly good agreement between the results of graphical analysis and computer handling of the extraction curves in connection with the calculation of the extraction constants.

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