EXTRACTION OF PROMETHIUM COMPLEX WITH 4-BENZOYL-5--METHYL-2-PHENYL-2,4-DIHYDRO-3*H*-PYRAZOL-3-ONE INTO FREON 113 AND ITS MIXTURES WITH BENZENE

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A study of the dependence of distribution of Pm(III) between aqueous phase (perchlorate medium) and Freon 113 (or a Freon 113–benzene mixture 2 : 1) on pH and pA has shown that the complex PmA_3 is extracted into the organic phase with the extraction constant $\log K_{ex} = -4\cdot35$. The stability constant β_n of the complex PmA_3 has been calculated by the Leden method.

Although the liquid extraction of important lanthanoids with application of 4-benzoyl-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (BEP) has been paid adequate attention (for a survey see refs[1,2]), no reports exist about the extraction of Pm(III) with this reagent in available literature. The extraction with Freon as the organic solvent in this system is described in ref.[3] for the first time. In spite of general aversion to applications of Freons they are advantageous for the liquid–liquid extraction systems because of their temperature and chemical resistance, low toxicity, and incombustibility.

The aim of the present communication is to find conditions for quantitative extraction of Pm(III) in the title systems and compare them with those of the lanthanoids already investigated.

EXPERIMENTAL

Chemicals and Apparatus

4-Benzoyl-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (BEP) was prepared and purified in the known way[4]. Freon 113 (du Pont) was distilled before use as solvent for preparation of the organic phase. Benzene for mixtures with Freon was of p.a. purity grade (Lachema) and so were also the perchloric acid and sodium perchlorate used for adjusting the ionic strength. The radioactive ^{147}Pm (U.S.S.R.) was transformed into the corresponding perchlorate; its analytical concentration in aqueous phase before the extraction was $4\cdot3 \,.\, 10^{-11}$ mol dm^{-3}, the specific activity being $1\cdot5 \,.\, 10^{3}$ Bq cm^{-3}. The beta radioactivity of ^{147}Pm samples was measured with a NAQ 221 probe, the counting rate being recorded by means of a laboratory measuring set NZQ 727 T (Tesla Liberec). The pH of samples after the extraction was measured by means of a Radelkis OP-208 apparatus (Hungary) using a glass and a calomel electrodes. The cell was calibrated with phthalate and borate buffers before each measurement.

Procedure

The extractions were carried out by mixing the aqueous and organic phases (10 cm^3 each) for 8 h using a rotation shaker of our own construction and glass test tubes with polyethylene stopper in a thermostat at 20 ± 1°C. After the extraction was finished and the phases were separated, samples were taken from both phases (2 cm^3 for each), and their evaporation residues were measured in a constant geometrical arrangement, the relative standard deviation of all the measurements being less than 2%. For the pH measurements of aqueous phase 5 cm^3 samples were taken. The value of partition coefficient D was calculated from the ratio of impulse numbers (s^{-1}) of the isotope measured in the organic and aqueous phases (2 cm^3) corrected with respect to the background.

The values of the partition constant of the BEP reagent $K_D(HA) = [HA]_{org}/[HA]$ were taken from ref.[3] for both the systems, viz. aqueous phase (ionic strength 0·1) — Freon 113 ($\log . K_D(HA) = 2{\cdot}84 \pm 0{\cdot}10$), and aqueous phase (ionic strength 0·1) — mixture Freon 113–benzene in the ratio of 2 : 1 ($\log K_D(HA) = 3{\cdot}39 \pm 0{\cdot}15$). From these values it is seen that BEP is better soluble in benzene than in Freon. In neat Freon 113 it is possible to prepare the solution of the reagent at a concentraion of $1 . 10^{-2}$ mol dm^{-3}. However, the 2 : 1 mixture of Freon 113 and benzene, which is incombustible, is well applicable to the extraction, the attainable reagent concentration being $3 . 10^{-2}$ mol dm^{-3}.

RESULTS AND DISCUSSION

The dependence studied (the pH range ca from 2 to 6) with four various reagent concentrations in Freon 113 and one concentration in Freon 113–benzene mixture (2 : 1) is given in Fig. 1. The ionic strength was adjusted by means of $HClO_4$ and $NaClO_4$. The dependence of the partition coefficient on the ligand concentration $[A^-]$ in aqueous phase, expressed in the form $\log D = f(pA)$, is presented in Fig. 2 from which it can be seen that this function has the same course for all the reagent concentrations used.

From the shape of the extraction curve (Fig. 1) it is obvious that the quantitative extraction of Pm(III) is reached at pH > 4 with the maximum reagent concentrations $1 . 10^{-2}$ and $3 . 10^{-2}$ mol dm^{-3} in Freon and Freon–benzene (2 : 1), respectively. The slope of ascending sections of extraction curves is approximately equal to three.

Hence from the experimental results it can be stated that the complexes formed in aqueous phase are of the types PmA^{2+}, PmA_2^+, and PmA_3, the last type being extracted into the organic phase. The Leden method was used for calculations of the stability constants β_n of the PmA_3 complex, and these constants are given in Table I along with the values of partition constant $K_D(PmA_3)$ and extraction constant. The corresponding values for the cognate elements Ce(III) and Eu(III) taken from ref.[3] are given for comparison, too.

The extraction constants given in Table I were calculated from the ascending sections of the extraction curves with the presumption that the extraction follows

TABLE I

The distribution constants (K_D), extraction constants (K_{ex}), and stability constants (β_n) of the complexes (Pm, Ce, Eu) A_3. Ionic strength 0·1, temperature 20°C, organic phases: A Freon 113, B Freon 113–benzene (2 : 1), C benzene (or toluene)

Metal	log $K_D(MeA_3)$			log K_{ex}			log β_1	log β_2	log β_3
	A	B	C	A	B	C			
Pm(III)	1·7	1·7	—	−4·35	−4·45	—	6·0	11·7	16·0
Ce(III)	0·9	0·9	2·8[a]	−4·85	−4·98	−2·28[a]	4·8	9·8	15·0
Eu(III)	1·9	2·0	3·15[a]	−4·84	−5·21	−3·96	4·7	9·4	14·1

[a] Toluene.

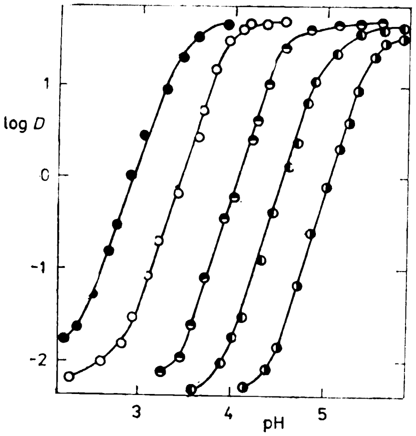

FIG. 1

Effect of pH of the aqueous phase on the distribution ratio (*D*) of promethium between the aqueous phase (1 . 10^{-1} mol dm^{-3} (H, Na)ClO_4) and the organic phase formed by solutions of BEP in Freon 113 (concentrations of BEP in mol dm^{-3}; ○ 1 . 10^{-2}, ◒ 5 . 10^{-2}, ◐ 1 . 10^{-3}, ◑ 5 . 10^{-4}) or BEP in Freon–benzene 2 : 1 (● 3 . 10^{-2} mol . . dm^{-3} BEP)

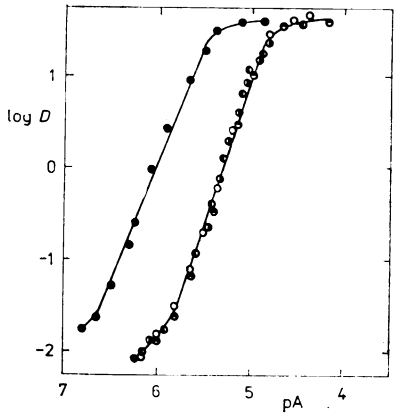

FIG. 2

Dependence of the distribution ratio (*D*) of promethium on the equilibrium concentration of free ligand BEP. The aqueous phase: 1 . 10^{-1} mol dm^{-3} (H, Na)ClO_4. The starting concentration of BEP in Freon 113 (in mol dm^{-3}): ○ 1 . 10^{-2}, ◒ 5 . 10^{-2}, ◐ 1 . 10^{-3}, ◑ 5 . 10^{-4}, or in Freon 113–benzene 2 : 1 (● 3 . 10^{-2} mol dm^{-3} BEP) the scheme: $Pm^{3+} + 3\,HA_{org} \rightleftarrows (PmA_3)_{org} + 3\,H^+$ for which the extraction constant is $K_{ex} = [PmA_3]_{org}[H^+]^3/[Pm^{3+}][HA]^3_{org}$.

A comparison with the extractions of Ce(III) and Eu(III) in benzene or toluene is carried out in ref.[3]. The extraction constants with Freon as the organic phase are lower by 1 order of magnitude (at least) in both the cases. As the extraction of Pm(III) with the BEP reagent is not described in available literature, it is impossible to carry out a comparison with possible applications of other types of solvents.

The values of extraction constants found for Pm(III) agree in order of magnitude with those for Ce(III) and Eu(III). The ratio of the stepwise constants of stability of the chelate of Pm(III) with BEP is greater than 1 in accordance with theoretical presumptions.

It can be concluded that the found values of quantitative constants of Pm(III) correspond well with the theoretical presumption of extraction of this element in the extraction system investigated, if they are compared with the cognate Ce(III) and Eu(III).

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