Di-(n-BUTOXYETHYL)PHOSPHORIC ACID
AS AN EXTRACTION AGENT

O. NAVRÁTIL

Department of Inorganic Chemistry,
J. E. Purkyně University, 611 37 Brno

The distribution of di-(n-butoxyethyl)phosphoric acid (HA) between benzene and 2M-(H, Na). .ClO_4 or 2M-(H, Na)Cl was studied and the corresponding dissociation, dimerization and distribution constants were determined for HA. It follows from the study of the Hf(IV) distribution that the $HfA_4.2$ HA complex is extracted into the organic phase from 2M mineral acid; in strongly acidic aqueous media (above 5M-HCl or $HClO_4$) the ion-exchange mechanism is replaced by a solvation mechanism. Eu(III) is extracted from a weakly acidic aqueous medium with an ionic strength of 0.1 to 1.0 as complex $EuA_3(HA)_x$, $x = 0-2$, the extraction curves exhibiting perceptible maxima in a pH range of 1.5—2.0.

During the study of the effect of the structure of some dialkylphosphoric acids (HA) on the extractability of metal cations, attention was also paid to derivatives containing oxygen in the middle of an alkyl chain. It has been found that these are perspectively useful reagents, especially for the extraction of tervalent lanthanoids and actinoids[1−3]. The study of the extraction of Eu(III) using di-(n-hexoxyethyl)-phosphoric acid has shown that complexes with the composition $EuA_3.2$ HA pass preferentially into the organic phase from 0.25M-$HClO_4$ (ref.[1]); analogously, the species $EuA_3.3$ HA is extracted with HA from a medium of 0.16M-HNO_3 + + 0.84M-$NaNO_3$ (ref.[3]).

In the present work, the distribution of di-(n-butoxyethyl) phosphoric acid (further denoted as HA) between the aqueous and organic phase was studied in order to obtain the corresponding values of the dissociation, dimerization and distribution constants of HA and the distribution ratios for Hf and Eu.

EXPERIMENTAL

Chemicals and Apparatus

HA was prepared in the Nuclear Research Institute, Řež, according to the procedure described earlier[3]. The other chemicals, apparatus and the experimental procedure were described in our previous work[4]. The ionic strength equalled $I = 2.0$ except for the study of the Eu complexes, where it was 0.1 or 1.0. A stock solution of $^{152+154}$Eu was prepared from radioactive

Eu_2O_3 by dissolving it in HNO_3; its activity and concentration in the aqueous phase amounted to $480 \, s^{-1} \, ml^{-1}$ and $5 \cdot 10^{-8} M$, respectively.

RESULTS AND DISCUSSION

Determination of the Dissociation, Dimerization and Distribution Contants of HA

The dissociation constant, $K_a = [H^+][A^-][HA]^{-1}$, dimerization constant $K_2 = [H_2A_2]_{org}[HA]_{org}^{-2}$ and distribution constant $K_D = [HA]_{org}[HA]^{-1}$ of the reagent were determined using the relationship, $D_{HA} = K_D/\varphi + 2K_2K_D^2 c_{aq}/\varphi^2$, discussed in detail in our earlier work[4]; the symbol HA denotes the reagent monomeric molecule and the square brackets, the equilibrium concentrations. The organic phase is denoted by subscript org, while the aqueous phase is without a subscript, $\varphi = (1 + K_a[H^+]^{-1})$. The distribution of HA between benzene and $2M$-(H, Na)ClO_4 or $2M$-(H,Na)Cl in dependence on the pH of the aqueous phase is given in Fig. 1. The pK_a value, determined by the intercept of the asymptotes on the linear parts of the curves, equals 0.80 ± 0.10. The dimerization and distribution constants for HA were determined analogously from the dependence $D = f(c_{aq})$ for the benzene organic phase; their values are given in Table I. From these values it follows that the properties of HA are similar to those of di-n-butylphosphoric acid, especially the K_D value.
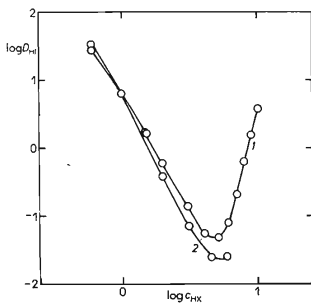

FIG. 1

HA Distribution between $2M$-(H, Na)ClO_4 and $2M$-(H, Na) Cl and Benzene in Dependence on the Aqueous Phase pH

1 $2M$-(H, Na)ClO_4, $c_{HA} = 7 \cdot 10^{-4} M$; *2* $2M$-(H,Na)Cl, $c_{HA} = 1 \cdot 10^{-3} M$.
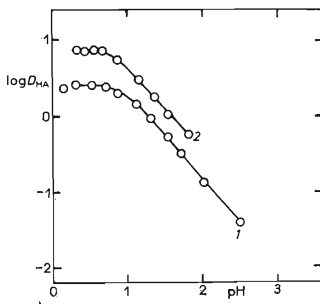

FIG. 2

The Effect of the Hydrochloric and Perchloric Acid (HX) Initial Concentration on the Hf Distribution between the Aqueous Phase and $3 \cdot 10^{-4} M$-HA in Benzene

1 HCl, *2* $HClO_4$.

Study of Complex Compounds of HA with Hafnium

It follows from the distribution of hafnium in dependence on the hydrogen ion concentration in the aqueous phase at a constant ionic strength of 2·0 that the extraction of Hf obeys the relationship, $\log D_{Hf} = \log (\text{const. } [H^+]^{-4})$, in 1—2M-HCl or $HClO_4$; the hydrolysis of hafnium must be considered for $c_H < 1M$. The dependence of the Hf distribution ratio on the hydrogen ion concentration in the aqueous phase for $3 . 10^{-4}$M-HA in benzene and a HCl medium is shown in Fig. 2, curve *1*. It is evident that, similar to di-n-alkylphosphoric acids[8], the extraction mechanism changes into a solvation mechanism in 4—5M-HCl. The shape of this dependence in a $HClO_4$

TABLE I
Dissociation (K_a), Dimerization (K_2) and Distribution (K_D) Constants for HA
Organic phase, benzene.

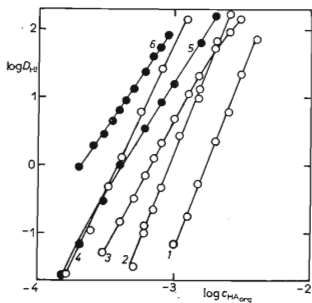| Reagent	pK_a	$\log K_2$	$\log K_D$	Medium	Ref.
HA	$0·80 \pm 0·10$	$4·56 \pm 0·15$	$-0·68 \pm 0·10$	1M-$HClO_4$	this paper
Di-n-octylphosphoric acid	1·48	3·13	4·90	1M-(H, Na)NO_3	5
Di-n-butylphosphoric acid	0·80	4·74	$-0·09$	0·1M-HNO_3 + + 0·9M-NaNO_3	6
		4·88	$-0·42$	1M-HNO_3	7

FIG. 3

Dependence of the Hf Distribution on the Analytical Concentration of Some Acidic Organophosphoric Reagents in Organic Solvents

Aqueous phase: 2M-$HClO_4$. Curve *1—4* di-n-(butoxyethyl)phosphoric acid, *1* n-octane, *2* cyclohexane, *3* chloroform, *4* benzene; *5* di-n-butylphosphoric acid, benzene; *6* di-n-octylphosphoric acid, benzene.

medium (curve 2) is analogous up to $c_{HClO_4} \leqq 4M$; at higher concentrations, sorption of hafnium on glass or in the interface occurs. It follows from Fig. 3 showing the dependence of the logarithm of the Hf distribution ratio on the initial HA concentration in the organic phase that the extractability of Hf increases along the series, n-octane > cyclohexane > CHCl$_3$ > benzene. Further it can be stated that Hf passes into benzene using virtually the same analytical concentrations as those employed with di-n-butylphosphoric and di-n-octylphosphoric acids. Employing knowledge of constants K_a, K_D and K_2, the dependence, log D_{Hf} = f(log [HA]$_{org}$), can be calculated[4] for the benzene organic phase; a linear dependence with a slope of $6 \cdot 0 \pm 0 \cdot 1$ is obtained.

Hence it can be concluded that extraction of Hf with HA into benzene (for $c_{Hf} \leqq \leqq 4 . 10^{-7}M$) is described by the scheme,

$$Hf^{4+} + 6(HA)_{org} \rightleftharpoons (HfA_4.2\,HA)_{org} + 4\,H^+ , \qquad (1)$$
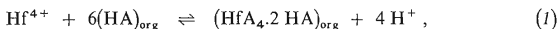
where

$$K_{ex} = [HfA_4.2\,HA]_{org}[H^+]^4/[Hf][HA]_{org}^6 \quad \text{equals} \quad 10^{27,1} .$$

Study of HA Complex Compounds with Europium

The dependence of the logarithm of the Eu distribution ratio on the aqueous phase pH for an ionic strength of $0 \cdot 1$ (perchlorate medium, curve $1-4$) and of $1 \cdot 0$ (chloride medium, curve 5) is shown in Fig. 4. It can be concluded from these curves and dependences log D_{Eu} = f(log [HA]$_{org}$), obtained by recalculation similar to the hafnium complexes discussed above, that the extraction of Eu into benzene in an interval of $c_{HA} = 3 . 10^{-3} - 2 . 10^{-2}M$ and pH $1 \cdot 0 - 1 \cdot 9$ obeys the scheme,
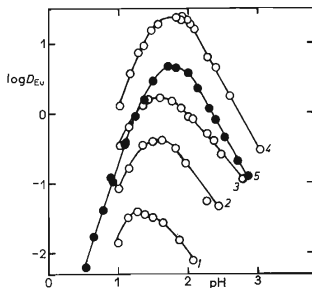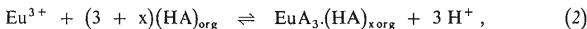

FIG. 4

The Effect of the Aqueous Phase pH on the Europium Distribution between Solutions of HA in Benzene and $0 \cdot 1M$-(H, Na)ClO$_4$ or $1 \cdot 0M$-(H, Na)Cl

$0 \cdot 1M$-(H, Na)ClO$_4$, c_{HA}: 1 $3 . 10^{-3}M$ 2 $5 . 10^{-3}M$, 3 $1 . 10^{-2}M$, 4 $2 . 10^{-2}M$; $1 \cdot 0M$-(H, Na)Cl, 5 $c_{HA} = 1 . 10^{-2}M$.

$$Eu^{3+} + (3 + x)(HA)_{org} \rightleftharpoons EuA_3.(HA)_{x\,org} + 3\,H^+ , \qquad (2)$$

where x equals 0 to 2 depending on the aqueous phase acidity and the initial HA concentration. For pH $1·4$ and $c_{HA} = 5 . 10^{-3} - 2 . 10^{-2}$M, $x = 2$; the corresponding extraction constant, $K_{ex} = [EuA_3.2\,HA]_{org}[H^+]^3/[Eu][HA]_{org}^5$, equals $10^{19,1}$.

The formation of the maxima on the extraction curves caused by a decrease in the Eu distribution ratio with increasing aqueous phase pH, can be explained either by a decrease in the HA equilibrium concentration in the organic phase due to HA dissociation in the aqueous phase or by the formation of poorly extractable negatively charged complexes EuA_4^- or by the simultaneous effect of the two processes.

REFERENCES

1. Peppard D. F., Mason G. W., Giffin G.: J. Inorg. Nucl. Chem. 27, 1683 (1965).
2. Mason G. W., Bollmeier A. F., Peppard D. F.: J. Inorg. Nucl. Chem. 29, 1103 (1967).
3. Kolařík Z., Dražanová S., Chotívka V.: J. Inorg. Nucl. Chem. 33, 1125 (1971).
4. Navrátil O.: This Journal 40, 1711 (1975).
5. Kolařík Z., Hejná J., Pánková H.: J. Inorg. Nucl. Chem. 30, 253 (1968).
6. Kolařík Z., Hejná J., Pánková H.: J. Inorg. Nucl. Chem. 30, 2795 (1968).
7. Hardy C. J., Scargill D.: J. Inorg. Nucl. Chem. 11, 128 (1959).
8. Navrátil O.: J. Inorg. Nucl. Chem. 30, 1605 (1968).

Translated by M. Štulíková.