APPLICATION OF METHYLPHOSPHONIC ACID MONOALKYL ESTERS TO THE EXTRACTION OF SOME METALS

Oldrich NAVRATIL and Petr SLADEK

Department of Special Chemistry,
The Military College of Ground Forces, 682 03 Vyskov, The Czech Republic

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The distribution between aqueous nitric acid and benzene was examined for methylphosphonic acid monoalkyl esters where the alkyl was a methyl, propyl, butyl, isobutyl, pentyl, 2-methylbutyl, cyclohexyl or 1,2,2-trimethylpropyl group. The extraction of complexes of these reagents with Ag, Co, Zn, Sc, Yb, Eu and Hf was also investigated. The esters do not dimerize in benzene. The pK_a and K_D values of the reagents and the corresponding extraction constants were determined. Derivatives containing five and more carbon atoms in the alkyl groups were found practically applicable to the extraction.

Monoalkyl esters of methylphosphonic acid, $RO(CH_3)P(O)OH$ (henceforth HA), have found application as precursors of some chemical war substances (the nerve-paralyzing substances soman and sarin) and herbicides. 1-(Dimethyl)propyl methylphosphonate can be applied to the separation of cerium[1], zirconium[2] and thorium with uranium[3] by solvent extraction from the aqueous phase into benzene. The composition of the extracted complex $Ce(NO_3)A_2(HA)_2$ has been examined[1] at an ionic strength of $I = 0.5$ (nitrate medium, $c_{HA} = 0.1$ to 0.5 mol l^{-1}). The composition of the extracted complexes $ZrOA_2$, ThA_4 and UO_2A_2 has been identified[2,3] at $I = 2.0$.

The group of alkyl esters of the analogous phenylphosphonic acid has found considerably wider application. In this case, the 2-ethylhexyl and 1-methylheptyl groups are most widespread[4], although the normal alkyls: octyl[5], hexyl, and decyl[6] are used as well. As is the case with acid dialkyl(aryl) phosphates[7], this group of reagents also exhibits apparent dimerization in the organic phase. Alkylphenylphosphonic acids dimerize in benzene the better, the shorter their normal alkyl group. The distribution constants of their monomers in benzene decrease in that order[6].

The present paper deals with the distribution of some monoalkyl esters with R = methyl (Me), propyl (Pr), butyl (Bu), isobutyl (iBu), pentyl (Pen), 2-methylbutyl (iPen), cyclohexyl (cHex) or 1,2,2-trimethylpropyl (iHex) and of their complexes with some metals existing in various oxidation states, viz. silver, cobalt, zinc, scandium, europium, ytterbium and hafnium, between aqueous solutions of nitric acid and benzene.

EXPERIMENTAL

Chemicals and Apparatus

The reagents were synthesized at Army Factory 072 in Zemianske Kostolany (The Slovak Republic) following refs[8,9]. Their purity was checked by ^{31}P NMR spectroscopy. Stock solutions were prepared by dissolution of precisely weighed-in amounts in benzene. The other chemicals used were of reagent grade purity (Lachema, Brno, and VEB Apolda, Germany).

Radioactive isotopes (Poland) were added to the aqueous phase as their nitrates. Their concentrations (in $\mu mol\ l^{-1}$) and specific activities (in $kBq\ ml^{-1}$) in the working solutions were as follows: ^{110m}Ag 0.3, 1; ^{60}Co 40, 3.5; ^{65}Zn 2, 2; ^{46}Sc 1, 30; ^{152}Eu 1.5, 25; ^{169}Yb 0.4, 10; $^{175+181}Hf$ 8, 15.

An NA 3601 Gammaautomat (Tesla, Liberec, The Czech Republic) equipped with an NaI(Tl) well detector was used to measure the gamma activity of the solutions used. The pH of the aqueous phase was measured with an OP-208/1 pH-meter fitted with an OP-0808P combined glass electrode (Radelkis, Hungary). Phthalate and citrate buffers were used for calibration. ^{31}P NMR spectra of 50 wt.% solutions of HA in $CDCl_3$ were recorded on a WP 80 SY instrument (Bruker, Germany) using H_3PO_4 as the external standard.

Procedure

Extractions were performed on a homemade rotary extractor using test tubes with glass stoppers. The organic and aqueous phases (8 + 8 ml) were agitated for 60 min at 20 ± 1 °C. Preliminary experiments gave evidence that the agitation period was sufficient for the extraction equilibrium to establish. After phase separation, the pH of the aqueous phase was determined, and 2 ml aliquots of either phase were pipetted into glass vials and their gamma activity was measured. The pulse frequency of the well detector was adjusted so that the mean square error of the individual measurements did not exceed 2%.

The dissociation, distribution and dimerization constants were determined as described in refs[5,6]. The concentrations of HA in the organic and aqueous phases (in the latter, only in the presence of 1 M HNO_3 for the investigation of the reagent dimerization) were determined after its distribution between the two phases under defined conditions. A 5 ml aliquot of the organic phase was taken, 5 ml of radioactive hafnium solution in 1 M HNO_3 (c_{Hf} = 0.035 to 0.70 $\mu mol\ l^{-1}$) were added, extraction was carried out, and the equilibrium concentration of the reagent in the organic phase was determined based on calibration extraction curves of hafnium. For quantitating unknown concentrations of HA in the aqueous phase, 5 ml of the phase were taken, 0.05 ml of radioactive hafnium solution in 1 M HNO_3 and 5.05 ml of benzene were added, extraction was carried out, and the equilibrium concentration of HA in the aqueous phase was determined as above. The relatively high concentration of HNO_3, 1 $mol\ l^{-1}$, was chosen for the hafnium solutions based on preliminary experiments, in order to prevent hydrolysis and polymerization of hafnium and to suppress dissociation of the reagent.

RESULTS AND DISCUSSION

The Reagents

The methylphosphonic monoalkyl esters investigated are weak or moderately strong monobasic acids (HA). Their ^{31}P NMR spectra exhibit a single peak at 26.7 – 28.0 ppm. The dissociation constants $pK_a = [H^+][A^-]/[HA]$, distribution constants of the monomer

$K_D = [HA]_o/[HA]$ in the aqueous/benzene system and dimerization constants in benzene $K_2 = [H_2A_2]_o/[HA]_o^2$ were determined from their distribution equilibria. We have

$$D_{HA} = 2\,[H_2A_2]_o \; + \; [HA]_o/([HA] + [A^-]) = \; K_D/q \; + \; 2\,K_2K_D^2([HA] + [A^-])/q^2 \,, \quad (1)$$

where D_{HA} is the reagent distribution ratio, the brackets denote the equilibrium concentrations, the subscript o refers to the organic phase whereas the quantities with no subscript refer to the aqueous phase, and $q = 1 + K_a/[H^+]$.

If the dimerization in the organic phase is negligible, Eq. (*1*) simplifies to

$$D_{HA} \; = \; [HA]_o/([HA] + [A^-]) \; = \; K_D/q \; . \qquad (2)$$

The $D_{HA} = f([HA] + [A^-])$ dependence was first examined with respect to Eq. (*1*) in order to assess whether dimerization takes place in the organic phase (if the straight line has a nonzero slope) and to determine the K_2 and K_D values (the latter, by extrapolation of D_{HA} to a zero value of the sum ($[HA] + [A^-]$). The reagents possessing five and more carbon atoms in the ester group, i.e. the Pen, iPen, cHex and iHex esters, were subject to examination, using benzene as the organic phase and 1 M HNO_3 as the aqueous phase. Fifteen experimental points were measured for each reagent over the region of initial concentrations of 0.1 to 10 mmol l^{-1} in benzene. The slopes were all zero, hence, the four reagents, over the region of initial concentrations not exceeding 50 mmol l^{-1}, do not dimerize. Since the remaining reagents, with the Pr, Bu and iBu groups, are assumed to be even better soluble in water than the above four, only 5 experimental points of the dependence were measured for initial concentrations of 1 to 10 mmol l^{-1}. The Me reagent could not be examined in this manner: the hafnium calibration curves did not enable that. The K_D values, along with the confidence intervals[10], for benzene as the organic phase are given in Table I. The values are seen to decrease with increasing length of the alkyl chain in the –OR group, in agreement with the data in ref.[6].

After the dimerization of the reagents in benzene was found to be negligible, the pK_a values could be determined by employing Eq. (*2*). The plot of log K_D vs log c_{H^+} of the aqueous phase was examined (Fig. 1). The acidity was adjusted for this by using 0.1 M HNO_3 and $LiNO_3$; only HNO_3 was employed at pH < 1 (the pH was measured down to 0.7). Strictly speaking, the pK_a value for ionic strength $I = 0.1$ only holds for the cHex and Hex reagents, for the remaining reagents the data refer to $I = 0.1$ to 1, but the changes in the reagent distribution ratios D_{HA} across that ionic strength region are negligible. The corresponding pK_a values (along with the confidence intervals) are also given in Table I. The data increase with increasing aliphatic chain length in the –OR group; chain branching, on the other hand, has no marked effect. Both the K_D and pK_a values suggest that one should be circumspect in the ensuing experiments: for instance, when the log D_M vs c_{HA} dependence is examined using 0.1 M HNO_3, the pH of the aqueous phase should be measured after the extraction because this quantity can also vary with varying initial reagent concentration, thereby distorting the results.

Reagent–Metal Complexes

The log D_M vs c_{HA} plots (D_M is the metal distribution ratio, c_{HA} is the analytical concentration of the reagent) for Sc, Yb, Eu and Hf are shown in Figs 2 and 3. Scandium and hafnium are seen to be well extracted from 0.1 M HNO_3 (hafnium, from 1 M HNO_3)

TABLE I
Distribution of reagents HA and their metal complexes between aqueous nitric acid (0.1 mol l^{-1}) and benzene

HA	pK_a	K_D(HA)	log K_{ex}		
			$ScA_3(HA)_2$	YbA_3	EuA_3
Pr	0.53 ± 0.15	0.05 ± 0.02	10.5	–	–
Bu	0.75 ± 0.10	0.14 ± 0.05	13.0	–	–
iBu	0.77 ± 0.10	0.10 ± 0.03	13.3	–	–
Pen	0.82 ± 0.10	0.24 ± 0.04	15.7	4.1	1.2
iPen	0.85 ± 0.05	0.13 ± 0.04	16.4	4.6	1.6
CH	1.08 ± 0.10	0.14 ± 0.04	15.3	4.3	1.1
iHex	1.48 ± 0.10	0.59 ± 0.08	14.1	2.3	0.1

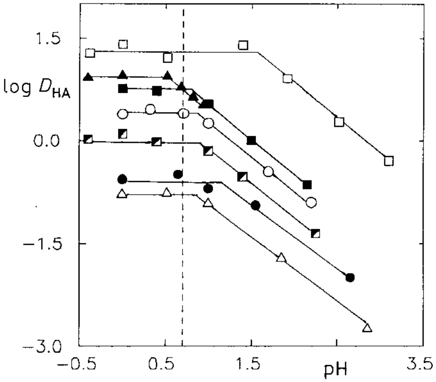
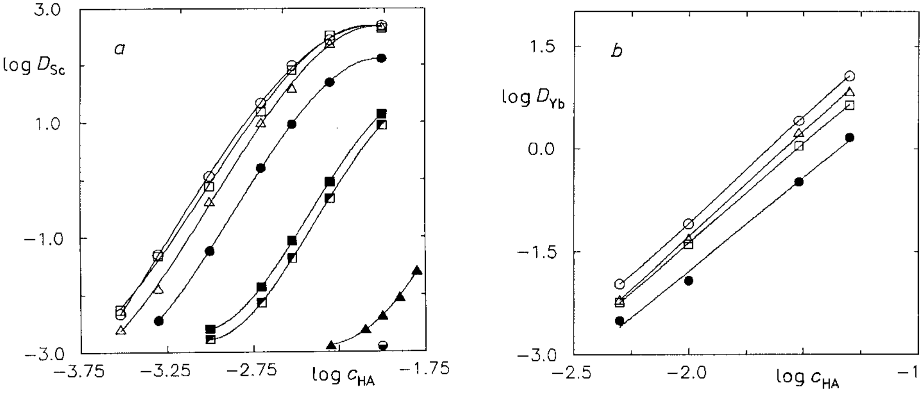


FIG. 1
Effect of pH on the distribution ratio of HA between benzene and aqueous 1 M HNO_3 (c_{Hf} = 7.9 μmol l^{-1}); alkyl: ❍ Pen, ❐ iHex, Δ iPen, ● cHex (all c_{HA} = 3 mmol l^{-1}), ■ Bu, ❐ iBu (both 30 mmol l^{-1}), ▲ Pr 465 mmol l^{-1}

into benzene, whereas the rare earth elements are extracted to a considerably lower degree. For the trivalent metals and hafnium, the extractability generally increases with increasing aliphatic chain length (Me < Pr < Bu < Pen) and decreases with chain branching (Pen > iPen, Bu > iBu). (The dependences were not examined for silver, cobalt or zinc because their distribution ratios, using solutions up to 50 mM HA in benzene, did not reach 0.05). The dependences of the metal distribution ratios on the aqueous phase acidity also indicate that uncharged complexes of the $MA_n(HA)_x$ type pass into the organic phase, obeying the equilibrium

$$M^{n+} + (n+x)\,(HA)_o \rightleftharpoons \{MA_n\,(HA)_x\}_o + n\,H^+ \qquad (A)$$



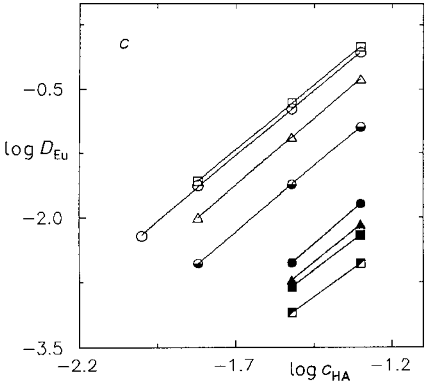


FIG. 2

Effect of analytical concentration of HA on the metal distribution ratio for benzene and 0.1 M HNO_3; *a* scandium (c_{Sc} = 1.08 µmol l^{-1}), *b* ytterbium (c_{Yb} = 0.43 µmol l^{-1}), both ❍ Pen, ❐ iHex, Δ iPen, ● cHex, ■ Bu, ❐ iBu, ▲ Pr, ❍ Me; *c* europium (c_{Eu} = 1.5 µmol l^{-1}), ● Pen, ■ iHex, ▲ iPen, ❐ cHex, medium of 0.1 M HNO_3 + $LiNO_3$, pH 1.63, ❐ iHex, ❍ Pen, Δ iPen, ❍ cHex for which the extraction constant K_{ex} can be formulated as

$$K_{ex} = \frac{[MA_n\,(HA)_x]_o\,[H^+]^n}{[M^{n+}]\,[HA]_o^{n+x}} = D_M\,\frac{[H^+]^n}{[HA]_o^{n+x}} \qquad (3)$$

and the n and x values can be determined by slope analysis from the log $D_M = f(\mathrm{pH})$ and log $D_M = f([HA]_o)$ plots. Figures 2 – 4 indicate that x is 2 for scandium and 0 for the remaining metals. The quantity n is 3 for Yb, Eu and Sc. The dependence of the distribution ratio of hafnium of the aqueous phase acidity indicates that D_{Hf} is independent of the analytical concentration of HNO_3 within the region of 0.3 to 3 mol l^{-1}. Hence, the extraction of hafnium does not occur by the ion exchange mechanism (*A*) within that region, and some different reaction must be assumed. This problem was beyond the scope of the present study.

The extraction constants calculated for the metals by Eq. (*3*) are given in Table I. The data increase with increasing number of carbon atoms in the linear part of the aliphatic chain in the –OR group. They are different to the extent that separation of not only the Sc–rare earth element group but also of the Eu–Yb pair may be practicable.

In conclusion, only those methylphosphonic acid monoalkyl esters having five and more carbon atoms in the alkyl chain in the –OR group are applicable to separation of metals by solvent extraction using benzene as the organic phase. Moreover, tentative

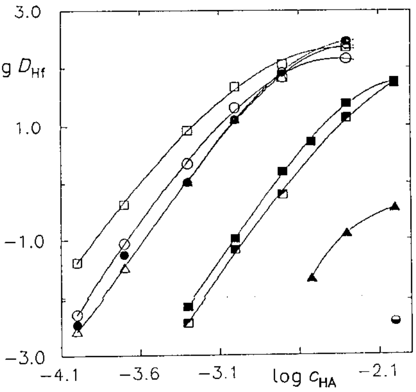


FIG. 3
Effect of analytical concentration of HA on the distribution ratio of hafnium (c_{Hf} = 8.5 μmol l^{-1}) between benzene and 1.0 M HNO_3; ❍ Pen, ❐ iHex, Δ iPen, ● cHex, ■ Bu, ❐ iBu, ▲ Pr, ❍ Me

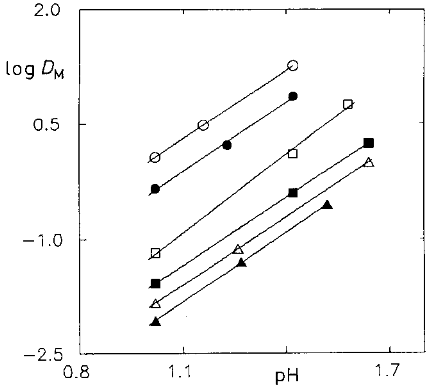


FIG. 4
Effect of pH on the distribution ratios of metals D_M between benzene and aqueous phase using the Pen and iPen esters of methylphosphonic acid; c_{HA} (mmol l^{-1}), c_M (μmol l^{-1}): ❍, ● Sc, 1.0, 1.08; Δ, ▲ Eu, 50, 1.5; ❐, ■ Yb, 10, 0.43

experiments showed that chloroform and 1,1,2,2-tetrachloroethane will suit better than benzene.

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