

Studies of the Complex Formation between Di-2-ethylhexylphosphate (HDEHP) and Tributylphosphate (TBP) or Trioctylamine (TOA) in Toluene

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The distribution of di-2-ethylhexylphosphate (= HDEHP = HA) between 0.10 M (Na,H)ClO₄ and toluene in the presence of tributylphosphate or trioctylamine (= B) has been studied using ³²P-labelled HDEHP. The distribution data have been computer-analyzed using the DISTR-program,¹ a version of the LETAGROP program for distribution data, and the formation of the following species are indicated: (1) HA(org), H₂A₂(org) and HA, A⁻, H₂A₂ in the aqueous phase, (2) with B=TBP, HAB(org), (3) with B=TOA, HAB(org) and (BH⁺ClO₄⁻)₂(org). At C_A < 5 × 10⁻⁴ M and -log[H⁺] < 3, the data also indicate the formation of the species H₂A⁺(aq) and HA.HClO₄(org). A summary of the equilibrium constants for the formation of the various HA-B species is given in Table 5.

Previous work^{2,20} in this laboratory has shown that dialkylphosphate (= HA) in organic solvents forms mixed complexes (HA)_pB_q with neutral organophosphorus compounds (= B), of the type tributylphosphate (TBP) or trioctylphosphineoxide (TOPO). It was shown that the use of a combination of HA and B as extractant can give either synergistic or antagonistic effects in the extraction of metal ions.^{3,4} Further, to understand these effects quantitatively and to determine the formation constants of the metal species extracted, one needs to know the constant for the formation of the various (HA)_pB_q complexes. The preliminary results of distribution studies of HDEHP in different organic solvents by the present author have already been reported,⁵ but as will be explained below some, before now, unknown radioactive impurity present in the ³²P-labelled HDEHP used seems to make the conclusions drawn in that preliminary report somewhat uncertain. The sample of radioactive HDEHP used in the distribution experiments leading to the preliminary results, which was purchased from the Radiochemical Centre, Amersham, was later shown in the laboratory of the Radiochemical Centre (Monks⁶) by the use of another chromatographic system (isopropyl alcohol/water/0.880 M

ammonia (75:24:1) on silica gel G) to contain some unknown radioactive impurity. This impurity could not be detected with the previously used paper chromatography (isopropyl alcohol/0.880 M ammonia, 3:1) and thin-layer chromatography (hexane/acetone, 4:1, on silica gel G); both methods revealed only one radioactive component. In the new chromatographic system this unknown radioactive impurity was found to have an R_F -value intermediate between those of mono- and di-2-ethylhexylphosphates and could not be separated from di-2-ethylhexylphosphate by usual extraction procedure. It was found later, that this impurity, upon further and continued reaction with excess of 2-ethylhexyl alcohol, can be destroyed with the apparent formation of equal quantities of mono- and di-2-ethylhexylphosphate- ^{32}P .

In the present work the distribution, protonation and complex formation of HDEHP and tributylphosphate or trioctylamine were studied in the system toluene/0.10 M (Na,H)ClO₄ using a new sample radioactive HDEH ^{32}P , which is free from the radioactive impurity mentioned above. Distribution studies of HDEHP were also reported by Uljanov and Sviridova,^{7,8} Szabó and Szabon,⁹ Kolařík,¹⁰ and Yagodin and Tarasov.¹² Their results, however, show many disagreements and indicate the need of further investigations.

The equilibrium constants for the formation of the HDEHP-TOA species have been used in the computer treatment of the extraction data of Hf(IV) in the system Hf(IV)-1 M H₂SO₄/HDEHP-TOA-toluene.^{13,14}

EXPERIMENTAL

Reagents. The HDEHP, (C₈H₁₇O)₂P(=O)OH, purchased from Albright and Wilson, London, with a purity of approximately 95 %, was further purified by a procedure similar to that described previously for the purification of HDBP.¹⁵ Potentiometric titrations of the purified HDEHP in 0.10 M NaClO₄ ethanol-water solution (and evaluation of the data with the Gran II method¹⁸ for the detecting of equivalence points) indicated that the product was free from mono-2-ethylhexylphosphate and at least 99 % pure. The radioactive HDEH ^{32}P was purchased from the Radiochemical Centre, Amersham, England. The HDEH ^{32}P -toluene solutions were washed 4–5 times with equal volumes of 0.10 M HClO₄ solution before use, to wash away small amounts of water soluble radioactive impurities, probably HMEH ^{32}P , present. Shaking the HDEH ^{32}P -toluene solution with 0.1 M NaOH solution removed all radioactivity which shows that the sample was free from radioactive impurities in the form of neutral organophosphorus compounds such as tri-ethylhexylphosphate- ^{32}P . Tributylphosphate, TBP, (Kebo) was purified as described previously.¹⁵ Trioctylamine, TOA, (Eastman Kodak) was used without further purification.

The toluene was of analytical grade (Merck) with at least 99 % purity from gas chromatographical analysis, and was used without further purification.

Distribution experiments. Equal volumes of 0.10 M (Na,H)ClO₄ solutions and HDEHP-TBP or HDEHP-TOA toluene solutions (10 ml each) in glass-stoppered centrifuge tubes were equilibrated by tilting the tubes in a rotating rack for at least 2 h. The equilibrated solutions were then centrifuged to separate the two phases. The distribution of HDEHP was determined by measuring the β -radioactivities in 5 ml samples of the aqueous and organic phases with a Tracerlab P-20 DWB beta well detector connected with a Tracerlab SC-70 Compu/Matic V or a SC-81 Versa/Matic II spectrometer.

In some of the experiments the distribution of HDEHP was determined by measuring the Cerenkov effect produced in the two phases with a Tracerlab Coru/Matic 100 AES/SC 535 AL liquid scintillation counter.

The numbers of impulses, I_{aq} and I_{org} , were corrected for the different absorptions of β -particles in the aqueous and organic phases (factor $\lambda = 0.95$).

At $-\log[\text{H}^+] > 2$ the aqueous solutions, which had a calculated ionic strength $I = 0.10$ M, were buffered with 0.01 M sulfanilic acid or 0.01 M Na_2HPO_4 . The $[\text{H}^+]$ in the aqueous phase was determined with a Wilhelm-type saltbridge arrangement: RE/0.10 M NaClO_4 /equilibrated solution/GE.

RE = Ag, AgCl/0.10 M AgClO_4 and GE = glass electrode.

A Beckman blue glass electrode type 40498 was used in conjunction with a digital-voltmeter type DM2022S (Dynamco Instruments, England). The correction for liquid junction potential was determined in a separate E_0 -titration¹⁷ and the measured emf was found to follow the relationship:

$$E = E_0 + 59.155 \log[\text{H}^+] + 580[\text{H}^+] \text{ mV}$$

The E_0 value was always determined before and after each series of measurements using 0.100 M (Na,H)ClO₄ standard buffer solution with $[\text{H}^+] = 0.010$ M. All experiments were carried out in thermostated rooms at 25°C.

SYMBOLS AND EQUILIBRIUM CONSTANTS

- HA = di-(2-ethylhexyl)phosphoric acid $(\text{CH}_3 - (\text{CH}_2)_3 - \overset{\text{C}_2\text{H}_5}{\underset{\text{H}}{\text{C}}} - \text{CH}_2\text{O})_2\text{P} \begin{matrix} \text{O} \\ // \\ \text{OH} \end{matrix}$
(HDEHP) (or other dialkylphosphate)
- B = tributylphosphate ($n\text{-C}_4\text{H}_9\text{O}$)₃P=O, (TBP), or trioctylamine ($n\text{-C}_8\text{H}_{17}$)₃N, (TOA)
- [] = equilibrium concentration in the aqueous phase
[]_{org} = equilibrium concentration in the organic phase
 C_A = initial total concentration of HA in the organic phase in mol/l
 C_B = initial total concentration of B in the organic phase in mol/l
 D_{exp} = $A_{\text{org}}/A_{\text{aq}}$ experimental net distribution ratio of HA
 K_a = $[\text{H}^+][\text{A}^-]/[\text{HA}]$ stoichiometric acid dissociation constant
 K_d = $[\text{HA}]_{\text{org}}/[\text{HA}]$ distribution constant of the monomers
 K_2 = $[\text{H}_2\text{A}_2]_{\text{org}}/[\text{HA}]_{\text{org}}^2$ dimerization constant in the organic phase
 K_{pq} = $[(\text{HA})_p\text{B}_q]_{\text{org}}/[\text{HA}]_{\text{org}}^{-p}[\text{B}]_{\text{org}}^{-q}$ formation constant of the complex $(\text{HA})_p\text{B}_q$ in the organic phase
 $K_{2\text{aq}}$ = $[\text{H}_2\text{A}_2]/[\text{HA}]^2$ dimerization constant in the aqueous phase
 K_{d2} = $[\text{H}_2\text{A}_2]_{\text{org}}/[\text{H}_2\text{A}_2]$ distribution constant of the dimers
 A_{org} = total concentration of HA in the organic phase, free or bound
 A_{aq} = total concentration of HA in the aqueous phase, free or bound
 D_{calc} = calculated net distribution ratio of HA, assuming the set of species $\text{H}_p(\text{HA})_q$ in the aqueous phase and $(\text{H})_p(\text{HA})_q\text{B}_r$ in the organic phase with a given set of equilibrium constants
- $U = \sum_1^{Np} (\log D_{\text{calc}} - \log D_{\text{exp}})^2$, error-square sum to be minimized for Np experimental points (in the DISTR program correspond to $val=1$)
- $\sigma(y)$ = standard deviation for y and $y = \log D$ in case when $val=1$ is used.

CHEMICAL MODEL

The species in the two-phase system may be represented by the general formula $(H)_p(HA)_qB_r$, leaving out complex formation with H_2O , Na^+ , ClO_4^- and species from the buffer added. We now make the reasonable assumptions that in the aqueous phase we only have $(H)_p(HA)_q$ species, *i.e.* $r=0$, and that we may assume that only uncharged species are extracted in the organic phase, *i.e.* for values of $p > 0$ the uncharged extracted species are $(H^+X^-)_p(HA)_qB_r$, where $X^- = ClO_4^-$ or some other inorganic anion. The $(-1,1,0)$ complex in the aqueous phase thus represents the ion A^- and the $(0,1,1)$ species in the organic phase the extracted HAB complex. The concentration of a (p,q,r) complex in the organic phase is thus given as:

$$[(H)_p(HA)_qB_r]_{org} = C_{pqr}(org) = K_{pqr}^{org}[H^+]^p[HA]^q[B]_{org}^r \quad (1)$$

The concentration of a $(p,q,0)$ complex in the aqueous phase may be expressed as:

$$[(H^+)_p(HA)_q] = C_{pq0}(aq) = K_{pq0}^{aq}[H^+]^p[HA]^q \quad (2)$$

For $V_{aq} = V_{org}$ (*i.e.* $V_{fak} = 1$) the mass balance for HA and B gives the following relationship:

$$C_A = A_{org} + A_{aq} = \sum q[(H)_p(HA)_qB_r]_{org} + \sum q[(H)_p(HA)_q] = \sum qK_{pqr}^{org}[H^+]^p[HA]^q[B]_{org}^r + \sum qK_{pq0}^{aq}[H^+]^p[HA]^q \quad (3)$$

$$C_B = \sum r[(H^+)_p(HA)_qB_r]_{org} = \sum rK_{pqr}^{org}[H^+]^p[HA]^q[B]_{org}^r \quad (4)$$

Using (1) and (2) we may express the distribution ratio for HA as:

$$D_{calc} = A_{org}/A_{aq} = \frac{\sum qK_{pqr}^{org}[H^+]^p[HA]^q[B]_{org}^r}{\sum qK_{pq0}^{aq}[H^+]^p[HA]^q} \quad (5)$$

Given the values of C_A , C_B , $[H^+]$, K_{pqr}^{org} and K_{pq0}^{aq} we may from (3) and (4) calculate $[HA]$ and $[B]_{org}$ and, from (5) D_{calc} can now be calculated.

COMPUTER CALCULATIONS OF THE DATA

The distribution data were computer analyzed using a new version of the LETAGROPVRID computer program for distribution data. The program, called DISTR,¹ calculates from data on the distribution of a component B between two phases, the "best" values of the constant for the formation of complexes with two, three, or four components. In the present work it calculates the set of constants $K_1, K_2 \dots K_N$ for the formation of the $(H)_p(HA)_qB_r$ species in the aqueous and in the organic phase which will, *e.g.*, minimize the error-square sum $U = \sum_1^{Np} (\log D_{calc} D_{exp}^{-1})^2$. The input data to the computer were: (1) $\log[H^+]$, (2) C_A , initial total concentration of HA in the organic phase, (3) C_B , initial total concentration of B in the organic phase, (4) I_{aq} in cpm (³²P-activity in the aqueous phase), (5) I_{org} in cpm (³²P-activity in the organic phase).

RESULTS

Distribution equilibria of di-(2-ethylhexyl)phosphate (HDEHP = HA) with $C_{\text{TBP}} = 0$. The distribution of HDEHP (=HA) between toluene and 0.10 M (Na,H)ClO₄ was studied as a function of the initial total concentration of HDEHP in the organic phase ($C_A = 0.926 - 5.871 \times 10^{-5}$ M) and the hydrogen ion concentration ($[\text{H}^+] = 10^{-1} - 10^{-7}$ M) of the aqueous phase.

Table 1. The distribution of HDEHP at 25°C between toluene and 0.10 M (Na,H)ClO₄ for different initial total concentrations of HDEHP and $[\text{H}^+]$. Data given as C_A M, $-\log[\text{H}^+]$, $\log D_{\text{exp}}$, $\log(D_{\text{calc}}D_{\text{exp}}^{-1})$. The aqueous phase was buffered with 0.01 M sulfanilic acid or 0.01 M Na₂HPO₄. $V_{\text{org}} = V_{\text{aq}} = 10$ ml. In Table 1A the values of $\log(D_{\text{calc}}D_{\text{exp}}^{-1})$ have been calculated assuming the $(\text{H}^+)_p(\text{HA})_q$ species and equilibrium constants given in Table 6 (model VII), while the values given in Table 1B were calculated assuming the set of species and equilibrium constants in Table 6 (model VIII).

Table 1A:

0.9262,	3.915,	+1.733,	+0.044;	0.6947,	4.039,	+1.740,	+0.036;
0.5789,	4.317,	+1.751,	+0.021;	0.4632,	4.628,	+1.740,	+0.023;
0.2316,	5.266,	+1.736,	-0.054;	0.2292,	5.323,	+1.659,	+0.010;
0.2006,	5.386,	+1.655,	-0.008;	0.1719,	5.474,	+1.607,	+0.004;
0.1433,	5.591,	+1.549,	+0.005;	0.1146,	5.720,	+1.457,	+0.015;
8.607×10^{-2} ,	5.882,	+1.336,	+0.006;	5.739×10^{-2} ,	6.055,	+1.162,	-0.006;
2.874×10^{-2} ,	6.295,	+0.845,	-0.027;	2.301×10^{-2} ,	6.303,	+0.783,	-0.019;
1.155×10^{-2} ,	6.425,	+0.514,	-0.026;	5.818×10^{-3} ,	6.518,	+0.249,	-0.031;
2.953×10^{-3} ,	6.603,	-0.048,	-0.022;	2.380×10^{-3} ,	6.638,	-0.158,	-0.021;
1.234×10^{-3} ,	6.694,	-0.447,	-0.013;	6.611×10^{-4} ,	6.766,	-0.747,	-0.025;
3.746×10^{-4} ,	6.804,	-0.989,	-0.017;	3.446×10^{-4} ,	6.821,	-1.027,	-0.031;
2.300×10^{-4} ,	6.826,	-1.179,	+0.006;	1.997×10^{-4} ,	3.123,	+1.868,	+0.017;
1.727×10^{-4} ,	6.834,	-1.303,	+0.050;	1.440×10^{-5} ,	6.843,	-1.334,	+0.029;
8.806×10^{-5} ,	5.269,	+0.657,	-0.011;	8.806×10^{-5} ,	6.806,	-1.291,	-0.051;
4.596×10^{-4} ,	3.649,	+1.837,	-0.062;	4.596×10^{-4} ,	3.718,	+1.801,	-0.038;
4.596×10^{-4} ,	3.790,	+1.785,	-0.035;	4.596×10^{-4} ,	3.879,	+1.777,	-0.045;
4.596×10^{-4} ,	3.983,	+1.725,	-0.017;	4.596×10^{-4} ,	4.097,	+1.690,	-0.014;
4.596×10^{-4} ,	4.237,	+1.524,	+0.105;	4.596×10^{-4} ,	4.453,	+1.436,	+0.101;
4.596×10^{-4} ,	4.830,	+1.217,	+0.095;	4.596×10^{-4} ,	3.588,	+1.729,	+0.055;
4.596×10^{-4} ,	5.738,	+0.465,	+0.030;	6.895×10^{-4} ,	7.001,	-1.212,	+0.066.

Table 1B:

5.871×10^{-5} ,	1.000,	+2.749,	+0.111;	8.806×10^{-5} ,	1.000,	+2.879,	-0.020;
1.997×10^{-4} ,	1.772,	+2.626,	+0.063;	1.154×10^{-4} ,	2.004,	+2.505,	+0.113;
4.596×10^{-4} ,	1.000,	+3.032,	-0.186;	4.596×10^{-4} ,	1.097,	+2.797,	+0.040;
4.596×10^{-4} ,	1.222,	+2.856,	-0.036;	4.596×10^{-4} ,	1.398,	+2.787,	-0.012;
4.596×10^{-4} ,	1.654,	+2.618,	+0.025;	4.596×10^{-4} ,	1.699,	+2.588,	+0.022;
4.596×10^{-4} ,	1.803,	+2.546,	-0.019;	4.596×10^{-4} ,	1.971,	+2.378,	+0.002;
4.596×10^{-4} ,	2.000,	+2.393,	-0.039;	4.596×10^{-4} ,	2.212,	+2.248,	-0.065;
4.596×10^{-4} ,	2.606,	+2.080,	-0.107.				

The distribution data given in Tables 1A and 1B ($Np = 55$ points) were analyzed with the DISTR program (=LETAGROP version for treatment of liquid-liquid distribution data) for different assumptions for the formation of the species $(\text{H}^+)_p(\text{HA})_q$. Table 6 summarizes the results of the computer analysis for the various chemical models tried, giving the values of the minimized error-square sum $U = \sum_1^{55} (\log D_{\text{calc}} - \log D_{\text{exp}})^2$, the standard

Table 2. The distribution of HDEHP at 25°C between toluene and 0.10 M (Na,H)ClO₄ aqueous solutions for different initial total concentrations of HDEHP (C_A) and at different constant values of TBP (C_B). The aqueous phase was buffered with 0.01 M sulfanilic acid or 0.01 M Na₂HPO₄. Data given as C_A M, $-\log [H^+]$, $\log D_{\text{exp}}$ and $\log (D_{\text{calc}}D_{\text{exp}}^{-1})$, which have been calculated assuming the set of $(H^+)_p(HA)_qB_r$ species and equilibrium constants given in Table 5. $V_{\text{org}} = V_{\text{aq}} = 10$ ml.

$C_B = 0.1998$ M

0.5790,	4.028,	+1.763,	+0.033;	0.4632,	4.472,	+1.743,	+0.048;
0.2317,	5.079,	+1.654,	+0.092;	0.1160,	5.553,	+1.476,	+0.113;
5.750×10^{-2} ,	5.915,	+1.246,	+0.062;	2.885×10^{-2} ,	6.185,	+0.971,	+0.011;
2.026×10^{-2} ,	6.288,	+0.833,	-0.007;	1.166×10^{-2} ,	6.427,	+0.623,	-0.031;
5.930×10^{-3} ,	6.548,	+0.369,	-0.020;	3.065×10^{-3} ,	6.633,	+0.173,	-0.015;
1.633×10^{-3} ,	6.708,	+0.027,	-0.025;	2.205×10^{-3} ,	6.923,	-0.120,	-0.090;
1.997×10^{-4} ,	6.808,	-0.213,	+0.006;	1.255×10^{-3} ,	6.977,	-0.222,	-0.096;
7.728×10^{-4} ,	7.009,	-0.294,	-0.084;	4.863×10^{-4} ,	7.029,	-0.372,	-0.044;
1.997×10^{-4} ,	7.050,	-0.459,	+0.005.				

$C_B = 0.4990$ M

0.3475,	4.553,	+1.765,	+0.064;	0.2317,	4.910,	+1.688,	+0.126;
2.885×10^{-2} ,	6.149,	+1.067,	+0.035;	1.576×10^{-2} ,	6.343,	+0.842,	+0.003;
8.795×10^{-3} ,	6.515,	+0.625,	-0.017;	5.930×10^{-3} ,	6.590,	+0.522,	-0.027;
3.065×10^{-3} ,	6.680,	+0.380,	-0.024;	1.632×10^{-3} ,	6.815,	+0.156,	+0.033;
1.997×10^{-4} ,	6.727,	+0.259,	-0.012;	1.997×10^{-4} ,	7.051,	-0.144,	+0.066;
1.776×10^{-3} ,	6.965,	+0.117,	-0.080;	1.059×10^{-3} ,	6.995,	+0.042,	-0.048;
7.728×10^{-4} ,	7.007,	+0.036,	-0.059;	4.863×10^{-4} ,	7.029,	-0.024,	-0.027.

deviation $\sigma(\log D)$ and the equilibrium constants for the formation of the $(H^+)_p(HA)_q$ species. Table 6 shows that out of the different models tried, model IV seems to give the lowest value for the error-square sum $U_{\text{min}} = 0.153$ ($\sigma(\log D) = 0.056$). The analysis of the distribution data thus indicates that the distribution of HDEHP between the two-phase system 0.10 M

Table 3. Distribution of HDEHP between toluene and 0.10 M (Na,H)ClO₄ aqueous solutions at 25°C for different concentrations of TBP (C_B) in the organic phase and different constant values of initial total concentrations of HDEHP (C_A). Data given as C_B M, $-\log [H^+]$, $\log D_{\text{exp}}$ and $\log (D_{\text{calc}}D_{\text{exp}}^{-1})$, which have been calculated assuming the set of $(H^+)_p(HA)_qB_r$ species and equilibrium constants given in Table 5. The aqueous phase was buffered with 0.01 M Na₂HPO₄. $V_{\text{org}} = V_{\text{aq}} = 10$ ml.

$C_A = 1.997 \times 10^{-4}$ M

1.5979,	6.786,	+0.593,	+0.090;	1.3982,	6.791,	+0.562,	+0.058;
0.8988,	6.800,	+0.378,	+0.045;	0.9987,	6.797,	+0.424,	+0.046;
0.7990,	6.807,	+0.336,	+0.029;	0.5992,	6.807,	+0.231,	+0.013,
0.3995,	6.815,	+0.068,	-0.002;	0.1997,	6.542,	+0.029,	+0.037.

$C_A = 1.154 \times 10^{-4}$ M

0.5815,	6.838,	+0.161,	+0.038;	0.1454,	6.845,	-0.370,	-0.007;
7.269×10^{-2} ,	6.854,	-0.647,	+0.003;	5.820×10^{-2} ,	6.850,	-0.699,	-0.017;
2.910×10^{-2} ,	6.840,	-0.928,	+0.011;	1.455×10^{-2} ,	6.848,	-1.108,	+0.019;
7.275×10^{-3} ,	6.849,	-1.209,	+0.006;	5.826×10^{-3} ,	6.848,	-1.239,	+0.011;
2.913×10^{-3} ,	6.847,	-1.296,	+0.011;	1.456×10^{-3} ,	6.853,	-1.343,	+0.018;
7.282×10^{-4} ,	6.855,	-1.386,	+0.041.				

(Na,H)ClO₄/toluene may be satisfactorily described by the formation of the (H⁺)_p(HA)_q species: (0,1)=HA(aq), (1,1)=H₂A⁺(aq), (-1,1)=A⁻(aq), (2,2)=H₂A₂(aq) and the species (0,1)=HA(org), (0,2)=H₂A₂(org) and (1,1)=HA.HClO₄(org). Addition of the species HA₂⁻(aq) or A₂²⁻ (models V and VI) did not improve the *U*-value, since the β values for the formation of these species were reduced to zero during the calculation.

Furthermore, it can be shown that the formation of the species H₂A⁺(aq) and HA.HClO₄(org) seems to be important only for distribution data at -log [H⁺] < 3 and C_A < 5 × 10⁻⁴ M (*Np* = 15 points; Table 1B). This may be concluded from the result of analysis for the set of distribution data with values of -log [H⁺] > 4 (*Np* = 40 points, Table 1A) given in Table 6, model VII, (*U*_{min} = 0.072, σ(log *D*) = 0.045), indicating that for this set of data a satisfactory fit was found by only assuming the formation of HA(aq), H₂A₂(aq), A⁻(aq), HA(org), and H₂A₂(org). However, for the data with -log [H⁺] < 3, C_A < 5 × 10⁻⁴ M (Table 1B) a satisfactory fit may only be obtained when the additional complexes H₂A⁺(aq) and HA.HClO₄(org) are included in the set of (H⁺)_p(HA)_q species found previously (Table 6, model VIII).

It should, however, be noted that the distribution data in Table 1B consist only of experimental points with rather high values of distribution ratio *D*, which thus may be expected to be less accurate than the data in Table 1A with lower *D* values. Considering this experimental uncertainty and also the

Table 4. The distribution of HDEHP at 25°C between toluene and 0.10 M (Na,H)ClO₄ aqueous solutions in the presence of trioctylamine (TOA). Data given as the initial total concentration of TOA in the organic phase C_B M, initial total concentration of HDEHP C_A M, -log [H⁺], log *D*_{exp}, log (*D*_{calc}/*D*_{exp}⁻¹). The aqueous phase was buffered with 0.01 M Na₂HPO₄. *V*_{org} = *V*_{aq} = 10 ml. In Table 4A the values of log (*D*_{calc}/*D*_{exp}⁻¹) have been calculated assuming the set of (H⁺)_p(HA)_qB_r(ClO₄)_s species and equilibrium constants given in Table 5, while the values given in Table 4B were calculated using log *K* = 17.62 for the formation of (BHClO₄)₂ and log *K* = 10.68 for HAB(org) (see text).

Table 4A:

0.1003,	4.596 × 10 ⁻⁴ ,	7.165,	+1.688,	+0.071;
8.024 × 10 ⁻² ,	4.596 × 10 ⁻⁴ ,	7.150,	+1.659,	+0.049;
4.012 × 10 ⁻² ,	4.596 × 10 ⁻⁴ ,	7.122,	+1.563,	-0.014;
2.006 × 10 ⁻² ,	4.596 × 10 ⁻⁴ ,	7.105,	+1.446,	-0.061;
1.003 × 10 ⁻² ,	4.596 × 10 ⁻⁴ ,	7.092,	+1.254,	-0.040;
8.024 × 10 ⁻³ ,	4.596 × 10 ⁻⁴ ,	7.089,	+1.220,	-0.063;
4.012 × 10 ⁻³ ,	4.596 × 10 ⁻⁴ ,	7.089,	+1.014,	-0.044;
2.006 × 10 ⁻³ ,	4.960 × 10 ⁻⁴ ,	7.074,	+0.739,	+0.011;
1.003 × 10 ⁻³ ,	4.596 × 10 ⁻⁴ ,	7.070,	+0.355,	+0.139;
7.021 × 10 ⁻⁴ ,	6.895 × 10 ⁻⁴ ,	7.055,	+0.212,	+0.015;
3.009 × 10 ⁻⁴ ,	6.895 × 10 ⁻⁴ ,	7.046,	-0.214,	-0.030;
2.006 × 10 ⁻⁴ ,	6.895 × 10 ⁻⁴ ,	7.016,	-0.364	(-0.354) ^a , -0.058 (-0.068) ^a ;
1.003 × 10 ⁻⁴ ,	6.895 × 10 ⁻⁴ ,	7.005,	-0.651	(-0.628) ^a , -0.024 (-0.047) ^a .

Table 4B:

0.8022,	4.596 × 10 ⁻⁴ ,	7.388,	+2.071	(+2.049) ^a ,	+0.069	(+0.091) ^a ;
0.4011,	4.596 × 10 ⁻⁴ ,	7.310,	+1.987	(+1.853) ^a ,	+0.001	(+0.135) ^a ;
0.2006,	4.596 × 10 ⁻⁴ ,	7.225,	+1.722,	+0.115.		

^a Distribution ratio determined by measurement of the Cerenkov light.

Table 5. Equilibrium constant $^a \log \beta_{pqr}$ for formation of $(H^+)_p(HA)_qX_rB_t$ species (HA = HDEHP or HDOP, X = inorganic anion) in various two-phase systems.

System	Reaction components	$(H^+)_p(HA)_qX_rB_t$ species	Ref.
HDEHP-toluene/0.1 M (Na,H)ClO ₄	HA(aq), H ⁺	A ⁻ (aq), -0.47 ± 0.05; HA(org), 4.79 ± 0.09	This work
HDEHP-TOA-toluene/0.1 M (Na,H)ClO ₄	HA(org)	H ₂ A ₂ (org), 5.10 ± 0.09	This work
	H ₂ A ₂ (org)	H ₂ A ₂ (aq), -1.78 ± 0.10	
	HA(org), B(org), H ⁺ ClO ₄ ⁻	HAB(org), 5.71 (max. 5.98) (BHClO ₄) ₂ (org), 17.07 (max. 17.49)	
HDEHP-TBP-toluene/0.1 M (Na,H)ClO ₄	HA(org), B(org)	HAB(org), 2.00 ± 0.13	This work 7 (10)
	HDEHP-octane/0.1 M (Na,H)ClO ₄	HA(aq), H ⁺	
HDOP-heptane/1 M (Na,H)NO ₃	HA(aq), H ⁺	HA(org), 3.98; A ⁻ (aq), -1.48	11
	HA(org)	H ₂ A ₂ (org), 3.48	
	HA(aq)	HA(org), 4.78	
HDOP-toluene/1 M (Na,H)NO ₃	HA(aq)	H ₂ A ₂ (org), 3.21	11
	HA(org)	HA(org), 4.90	
HDOP-benzene/1 M (Na,H)NO ₃	HA(aq)	H ₂ A ₂ (org), 3.13	11
	HA(org)	HA(org), 4.78	
HDOP-butylether/1 M (Na,H)NO ₃	HA(aq)	H ₂ A ₂ (org), 2.39	11
	HA(org)	HA(org), 5.82	
HDOP-methylisobutylketone/ 1 M (Na,H)NO ₃	HA(aq)	H ₂ A ₂ (org), -0.2	11
	HA(aq)		
HDOP-cyclohexane/1 M (Na,H)NO ₃	HA(aq)	HA(org), 4.19	11
	HA(org)	H ₂ A ₂ (org), 3.47	
HDOP-CHCl ₃ /1 M (Na,H)NO ₃	HA(aq)	HA(org), 5.37	11
	HA(org)	H ₂ A ₂ (org), 2.36	
HDOP-CHBr ₃ /1 M (Na,H)NO ₃	HA(aq)	HA(org), 4.55	11
	HA(org)	H ₄ A ₄ (org), 7.30	
HDOP-CCl ₄ /1 M (Na,H)NO ₃	HA(aq)	HA(org), 4.96	11
	HA(org)	H ₃ A ₃ (org), 4.72	
HDOP-chlorobenzene/1 M (Na,H)NO ₃	HA(aq)	HA(org), 4.56	11
	HA(org)	H ₂ A ₂ (org), 3.19	
HDOP-nitrobenzene/1 M (Na,H)NO ₃	HA(aq)	HA(org), 4.34	11
	HA(org)	H ₂ A ₂ (org), 2.70	
HDOP-octane/0.1 M (Na,H)ClO ₄	HA(aq), H ⁺	A ⁻ (aq), -1.2 (-1.3)	8 (10)
	HA(org)	HA(org), 3.98 (3.8)	
	HA(aq), H ⁺	H ₂ A ₂ (org), 3.54 (3.5)	
HDEHP-(Na,H)X (X = ?)	HA(aq), H ⁺	A ⁻ (aq), -2.85	9
HDEHP-CCl ₄ /0.2 M HClO ₄	HA(aq)	HA(org), 1.22	9 ^b
	HA(org)	H ₂ A ₂ (org), 1.98	
HDEHP-benzene/0.2 M HClO ₄	HA(aq)	HA(org), 1.30	9 ^b
	HA(org)	H ₂ A ₂ (org), 2.90	
HDEHP-TBP-benzene/0.2 M HClO ₄	HA(org), B(org)	HAB(org), 0.78	9
HDEHP-TBP-CCl ₄ /0.2 M HClO ₄	HA(org), B(org)	HAB(org), 1.12	9
HDEHP-TOPO-octane	H ₂ A ₂ (org), B(org)	H ₂ A ₂ B(org), 2.0	19

^a The equilibrium constant $\beta_{pqr} = [(H^+)_p(HA)_qX_rB_t] / [H^+]^p[(HA)_{n_i}]^{-q} [X]^{-r} [B]_{org}^{-t}$, where the subscript *i* refers to the organic or aqueous phase as given in the reaction and *n* = 1 or 2 is the degree of association for HA. The limits given correspond approximately to $\log(\beta \pm 3\sigma(\beta))$ and if $\sigma(\beta) > 0.2\beta$ the maximum value $\log(\beta + 3\sigma(\beta))$ is given.

^b Cf. comments in Discussion (p. 202).

Table 6. The equilibrium constants β_{pq} of different sets of complexes $(H^+)_p(HA)_q$ in the two-phase system 0.10 M (Na,H)ClO₄/toluene, which give the lowest error-square sum $U = \sum_1^{55} (\log D_{\text{calc}} - \log D_{\text{exp}})^2$

Model	$(H^+)_p(HA)_q$ (aq)	$(H^+)_p(HA)_q$ (org)	U_{min}	$\sigma(\log D)$
I	(-1,1) -3.67, max. -3.30	(0,2) 8.03, max. 8.55	17.431	0.574
II	(-1,1) 0.24, max. 0.60; (1,1) $\beta=0$, max. 4.71; (0,2) 13.45, max. 14.08	(0,1) 5.98, max. 6.41; (0,2) 15.59 \pm 0.18	3.677	0.263
III	(-1,1) 0.06, max. 0.57; (0,2) 13.51, max. 14.25	(0,1) 5.59, max. 6.11; (1,1) 7.43, max. 7.97; (0,2) 15.52; max. 16.25	2.516	0.224
IV	(-1,1) -0.48, max. -0.07; (1,1) 5.18, max. 5.61; (0,2) 12.89, max. 13.50	(0,1) 4.77, max. 5.20; (1,1) 8.04, max. 8.46; (0,2) 14.66, max. 15.28	0.153	0.056
V	(-1,1) -0.48, max. -0.07; (1,1) 5.18, max. 5.61; (0,2) 12.89, max. 13.50; (-1,2) $\beta=0$	(0,1) 4.77, max. 5.20; (1,1) 8.04, max. 8.46; (0,2) 14.66, max. 15.28	0.153	0.056
VI	(-1,1) -0.48, max. -0.07; (1,1) 5.18, max. 5.61; (0,2) 12.89, max. 13.50; (-2,2) $\beta=0$, max. 0.77	(0,1) 4.77, max. 5.20; (1,1) 8.04, max. 8.46; (0,2) 14.66, max. 15.28	0.153	0.056
VII	(-1,1) -0.47 \pm 0.05; (0,2) 12.90 \pm 0.10	(0,1) 4.79 \pm 0.09; (0,2) 14.68 \pm 0.09	0.072 ^b	0.045
VIII	^c (-1,1) -0.47 \pm 0.05; ^c (0,2) 12.90 \pm 0.10; (1,1) 5.19 \pm 0.15	^c (0,1) 4.79 \pm 0.09; ^c (0,2) 14.68 \pm 0.09; (1,1) 8.05 \pm 0.09	0.153	0.054

^a The limits of the equilibrium constants correspond approximately to $\log(\beta_{pq} \pm 3\sigma(\beta_{pq}))$ and if $\sigma(\beta_{pq}) > 0.2\beta_{pq}$ the maximum value $\log(\beta_{pq} + 3\sigma(\beta_{pq}))$ is given.

^b Calculated value for $Np=40$ points (data in Table 1A).

^c The value of the equilibrium constant is not varied during the course of the computer calculation.

rather limited number of experimental points in Table 1B used for the analysis, the conclusions drawn on the formation of the species H_2A^+ (aq) and $HA \cdot HClO_4$ (org) in this work should not be considered as conclusive, but rather as indicative. We thus conclude that the "best" description for the distribution of HDEHP between 0.10 M (Na,H)ClO₄ and toluene at the experimental conditions studied (data in Table 1A) is by assuming the formation of the set of $(H^+)_p(HA)_q$ species with the equilibrium constants given in Table 6, model VII, and summarized in Table 5.

Distribution of HDEHP in the presence of TBP. To study the complex formation between HDEHP (=HA) and TBP (=B) the distribution of HDEHP between toluene and 0.10 M (Na,H)ClO₄ was studied in the presence of TBP. In Fig. 1 the distribution of HDEHP is given as $\log D = f(\log A_{\text{aq}})$ for different constant values of C_B (0.1998 M and 0.4990 M), and in Fig. 2 as $\log D[H^+]^{-1}$ versus $\log C_B$ for constant values of C_A (1.154×10^{-4} and 1.997×10^{-4} M). Computer analysis of the data ($Np=50$ points) indicates that a good fit can be obtained by assuming the formation of the species HAB (org),

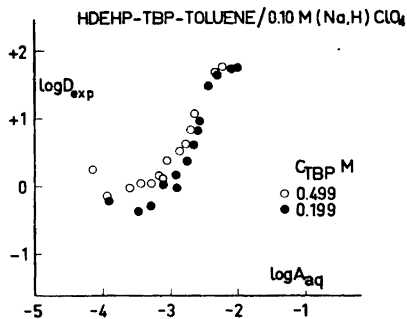


Fig. 1. The distribution of HDEHP between 0.10 M (Na,H)ClO₄ and toluene as a function of the total concentration of HDEHP in the aqueous phase for different constant initial concentrations of TBP in the organic phase: 0.199 M (●), 0.499 M (○). The distribution data are given in Table 2.

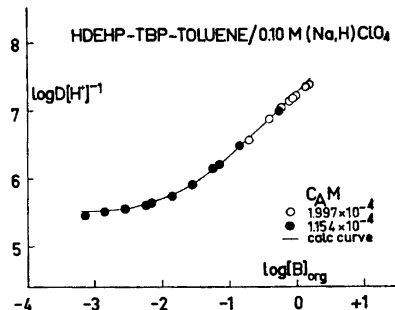


Fig. 2. The distribution of HDEHP between 0.10 M (Na,H)ClO₄ and toluene as a function of the concentration of TBP in the organic phase for different constant initial total concentration of HDEHP: 1.997×10^{-4} M (○), 1.154×10^{-4} M (●). The line is calculated assuming the HDEHP-TBP species and equilibrium constants given in Table 5. The distribution data are given in Table 3.

B(org), HA(org), H₂A₂(org), HA(aq), H₂A₂(aq), and A⁻(aq) ($U_{\min} = 0.127$, $\sigma(\log D) = 0.050$ for $Np = 50$ points). Addition of H₂A₂B species in the organic phase to the set of (H⁺)_p(HA)_qB_r species mentioned above gave no improvement in the value of U_{\min} found previously, since its β value was reduced to zero. The equilibrium constant for the formation of HAB(org) was calculated as:

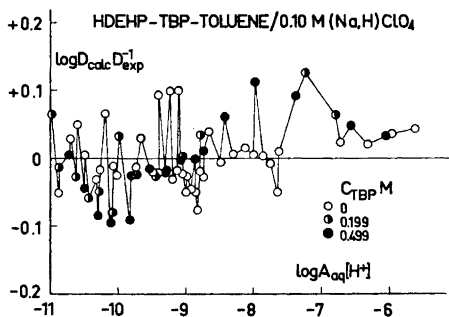
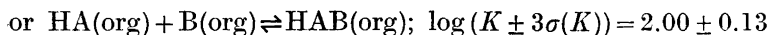
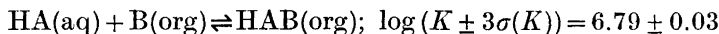


Fig. 3. The minimized error $\log(D_{\text{calc}}D_{\text{exp}}^{-1})$ as a function of $\log(A_{\text{aq}}[\text{H}^+])$ for the two-phase system HDEHP-TBP-toluene/0.10 M (Na,H)ClO₄, assuming the (H⁺)_p(HA)_qB_r species and equilibrium constants given in Table 5. The distribution data are given in Table 1A and 2.

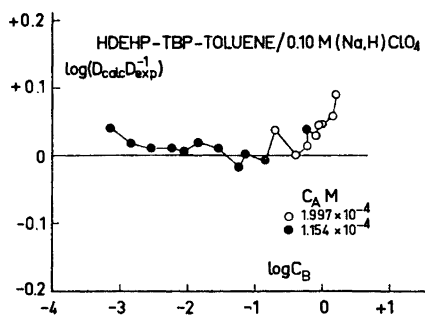


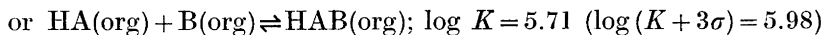
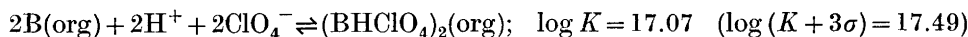
Fig. 4. The minimized error $\log(D_{\text{calc}}D_{\text{exp}}^{-1})$ as a function of the initial concentration of TBP in the organic phase for the two-phase system HDEHP-TBP-toluene/0.10 M (Na,H)ClO₄, assuming the HDEHP-TBP species and equilibrium constants given in Table 5. The distribution data are given in Table 3.

During the analysis the values of the constants for the formation of the $(\text{H}^+)_p(\text{HA})_q$ species found previously (Table 6, model VII) were not varied. In Fig. 3 the values of the minimized error $fel[1] = \log(D_{\text{calc}}D_{\text{exp}}^{-1})$ are plotted as a function of $\log(A_{\text{aq}}[\text{H}^+])$, and in Fig. 4 as a function of C_{B} .

Distribution of HDEHP in the presence of trioctylamine (TOA). The complex formation between HA and B in the organic phase may be expected to be influenced by the nature of B, such that a more basic character of B will give a stronger complex formation with HA.²⁰ It was shown² that in hexane and in CCl_4 , di-butylphosphoric acid forms a stronger HAB complex with trioctylphosphineoxide (TOPO) ($\log K_{11} = 4.88$ (hexane); 4.36 (CCl_4)) than with TBP ($\log K_{11} = 2.94$ (hexane); 2.65 (CCl_4)). Trioctylamine (TOA) being a more basic extractant than TBP and TOPO, might thus be expected to form yet stronger complexes with HA.

The complex formation between HDEHP (=HA) and trioctylamine (=TOA=B) was studied from the distribution of HDEHP at different constant values of C_{A} ($= 4.596 \times 10^{-4}$, 4.960×10^{-4} and 6.895×10^{-4} M) and varying concentration of TOA ($C_{\text{B}} = 1.003 \times 10^{-4} - 0.8022$ M).

The distribution data with $C_{\text{B}} \leq 0.1003$ M in Table 4A ($Np = 15$ points) were computer-analyzed assuming the formation of $(\text{H}^+)_p(\text{HA})_q$ species with the equilibrium constants found previously (Table 6, model VII), which were not varied during the calculation, and the formation of additional $(\text{H})_p(\text{HA})_q\text{B}$, species. A good fit to the data was found ($U = 0.050$ and $\sigma(\log D) = 0.062$) by assuming the formation of the species $\text{B}(\text{org})$, $(\text{BHClO}_4)_2(\text{org})$ and $\text{HAB}(\text{org})$. Adding the trimeric species $(\text{BHClO}_4)_3(\text{org})$ to the set of species mentioned above did not improve the value of U , since its β value was reduced to zero. The formation of the species $(\text{BHClO}_4)_2$ and HAB may be described by the following equilibria:



Including the data with $C_{\text{B}} > 0.2$ M (5 points) in Table 4B, the data may also satisfactorily be explained, within the experimental error, by assuming the same set of $(\text{H}^+)_p(\text{HA})_q\text{B}_r(\text{ClO}_4^-)_s$ species as found previously ($U = 0.125$, $\sigma(\log D) = 0.084$ for $Np = 20$ points). However, the values found for the constant for the formation of $(\text{BHClO}_4)_2$ ($\log K = 17.62$, max. 18.21) and HAB ($\log K = 10.68$, max. 11.06) show rather significant difference from those found previously, especially for the formation of the TOA dimers. This difference in the values of the constant of formation found may indicate a non-ideal behaviour of the organic solution at higher TOA concentrations ($C_{\text{B}} > 0.2$ M). The limited amount of data available in this work certainly do not suffice for drawing any definitive conclusion on this matter. One may, however, in the present stage of this work assume that the equilibrium constants calculated from data in Table 4A with $C_{\text{B}} < 0.1003$ M are probably closer to the "truth".

The monomeric TOA species may exist as the base form $\text{B}(\text{org})$ and as the salt from $\text{BHClO}_4(\text{org})$. The available data with practically constant pH do not permit us to distinguish the two species from each other. However,

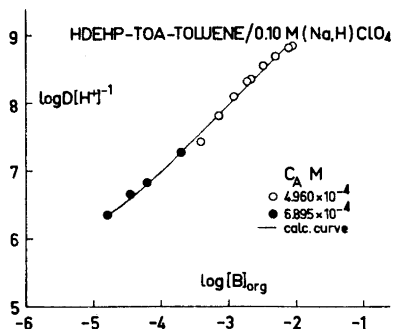


Fig. 5. The distribution of HDEHP between 0.10 M (Na,H)ClO₄ and toluene as a function of the concentration of TOA in the organic phase for different constant initial total concentration of HDEHP: 4.960×10^{-4} M (○), 6.895×10^{-4} M (●). The line is calculated assuming the HDEHP-TBP species and equilibrium constants given in Table 5. The distribution data are given in Table 4A.

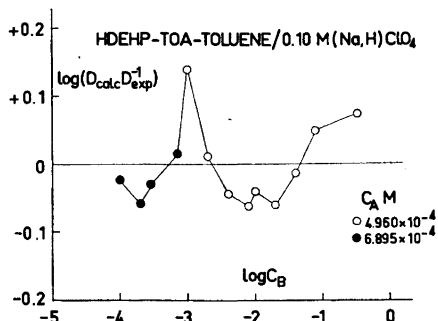


Fig. 6. The minimized error $\log(D_{\text{calc}}D_{\text{exp}}^{-1})$ as a function of the initial concentration of TOA in the organic phase for the two-phase system HDEHP-TOA-toluene/0.10 M (Na,H)ClO₄, assuming the $(\text{H}^+)_p(\text{HA})_q\text{B}_r$ species and equilibrium constants given in Table 5. The distribution data are given in Table 3.

in the extraction conditions studied ($-\log[\text{H}^+] \approx 7$), we may assume that the base form B(org) will be the predominant one (*cf.* Högfeldt¹⁸).

In Fig. 5 the distribution of HDEHP is plotted as $\log(D[\text{H}^+]^{-1})$ versus $\log[\text{B}]_{\text{org}}$. The drawn line has been calculated assuming the formation of the set of $(\text{HA})_p\text{B}_q$ species with the equilibrium constants found in the present work. In Fig. 6 the minimized error $\text{fel}[1] = \log(D_{\text{calc}}D_{\text{exp}}^{-1})$ is plotted versus $\log C_{\text{B}}$.

DISCUSSION

The value found in the present work for the acid constant $\text{p}K_{\text{a}} \pm 3\sigma = 0.47 \pm 0.05$ indicates that di-2-ethylhexylphosphoric acid is a rather strong acid, compared with $\text{p}K_{\text{a}} \pm 3\sigma = 0.75 \pm 0.08$ for diethylphosphoric acid and 1.00 for dibutylphosphoric acid found previously.²⁰ Szabó and Szabon⁹ reported the value for $\text{p}K_{\text{a}} = 2.85$ from potentiometric titration studies. Kolařík *et al.*¹¹ reported the value 1.42 in 0.1 M (Na,H)ClO₄ medium, which was calculated from extraction data of ⁹⁵Zr + ⁹⁵Nb with HDEHP, and the value 1.48 for HDOP from distribution studies with ³²P-labelled HDOP. The disagreements between the values reported are striking and can hardly be explained from the effect of ionic medium or different branching of the octyl-group. The result of the present work indicates that the increasing effect on the value of $\text{p}K_{\text{a}}$ when the length of the alkyl-group in $(\text{RO})_2\text{P}(=\text{O})\text{OH}$ is increased may not apply beyond a certain length of the alkyl-group.

The results further indicate the strong tendency of di-2-ethylhexylphosphate to form dimers even in polar solvents as water. The value found for $K_{2\text{aq}} = [\text{H}_2\text{A}_2][\text{HA}]^{-2} = 10^{12.90 \pm 0.10} \text{ M}^{-1}$ is unexpectedly large compared with the

value found for HDBP in 0.10 M H_2SO_4 ($K_{2\text{aq}} = 10^{2.40} \text{ M}^{-1}$), which must be interpreted as an indication of the unstable nature of the undissociated monomer HA.

The value found for the distribution constant of HDEHP, $\log(K_d \pm 3\sigma(K_d)) = 4.79 \pm 0.09$, may be compared with the value 4.78 for HDOP-toluene/1.0 M (Na,H) NO_3 and the value 4.90 for HDOP-benzene/1 M (Na,H) NO_3 reported by Kolarik *et al.*¹¹ The value of $\log K_d = 1.30$ for HDEHP-benzene/0.2 M HClO_4 reported by Szabó and Szabon⁹ seems to be too low and might be caused by the same sort of radioactive impurity found in the HDEH³²P ordered from Amersham before April 1968.⁶

The results further indicate that HDEHP-TBP and HDEHP-TOA in toluene only form the 1:1 complex HAB. No improvement of the U value was found by adding the species $\text{H}_2\text{A}_2\text{B}$, which for HDBP-TBP was found in hexane and CCl_4 , and for HDBP-TOPO in hexane. This absence of indications of the formation of the $\text{H}_2\text{A}_2\text{B}$ species in the distribution system studied, may in part be due to the steric hindrance found in the bulky structure of HDEHP dimers.

The interaction between HDEHP and TOA in toluene has been studied in a broad range of the concentration of TOA ($C_B = 7 \times 10^{-4} - 0.8022 \text{ M}$), and as was found from the computer-analysis of the data, that within the experimental error, the data may be described by assuming the formation of the species HAB and $(\text{BHClO}_4)_2$.

The formation of HAB(org) may be expressed as a reaction with HA(org): $K = [\text{HAB}]_{\text{org}}[\text{HA}]_{\text{org}}^{-1}[\text{B}]_{\text{org}}^{-1} = 10^{5.71} \text{ M}^{-1}$, which thus indicates that HDEHP forms stronger complex with TOA than with TBP or TOPO.² The value of the equilibrium constant found for the formation of the dimeric TOA species $K = [(\text{BHClO}_4)_2]_{\text{org}}[\text{B}]_{\text{org}}^{-2}[\text{H}^+]^{-2}[\text{ClO}_4^-]^{-2} = 10^{17.07} \text{ M}^{-5}$ may be compared with the value $K = 10^{14.12} \text{ M}^{-5}$ reported by Högfeldt¹⁸ for the system TOA-*o*-xylene/1 M (Li,H) ClO_4 . This significant difference in the values of the constants could, in part, be caused by the ionic strength of the aqueous medium. However, a greater part must be attributed to the organic solvent effect, which was found by Högfeldt¹⁸ to be important for amine acid equilibria. A general discussion on the complex formation of dialkylphosphoric acids with non-acidic complexing agents, such as tributylphosphate, and their use as combined extractants in the extraction of several metal ions is given in Ref. 20.

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