Extraction of Sulphuric Acid by Methyl Diphenyl Phosphate and Tributyl Phosphate

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The extraction equilibria in the sulphuric acid–methyl diphenyl phosphate–water and sulphuric acid–tributyl phosphate–water systems were investigated. The activities of methyl diphenyl phosphate and tributyl phosphate were calculated in the range of aqueous 0—10M-H_2SO_4, with the aid of the Gibbs–Duhem relationship. The experimental data found are consistent with the formation of the $[H(H_2O)_3(MePh_2PO_4)_4^+][HSO_4^-]$ complex with the equilibrium constant $K = 2 \times 10^{-3}$ (mol/kg $MePh_2PO_4$)$^{-1}$. At higher acid concentrations complete miscibility of $MePh_2PO_4$ and H_2SO_4 is observed. At low concentrations of H_2SO_4, the acid is extracted by tributyl phosphate in the form of $H_2SO_4(H_2O)_6(Bu_3PO_4)_3$ with $K = 20$ (mol/kg Bu_3PO_4)$^{-3}$. Some summarizing remarks on the extraction of HNO_3, HCl, and H_2SO_4 by $MePh_2PO_4$ and Bu_3PO_4 are also given.

THIS work is a continuation of our investigations [1-3] on extraction equilibria in the systems containing mineral acids and neutral organophosphates. The present paper deals mainly with extraction of sulphuric acid by methyl diphenyl phosphate ($MePh_2PO_4$). In order to calculate the activities of tributyl phosphate (Bu_3PO_4) in the H_2SO_4–Bu_3PO_4–H_2O system, supplementary data to those previously published [1] are given. Sulphuric acid, the phosphates, water, and complexes in the organic phase are denoted by the subscripts H, S, W, and C,

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[1] A. Apelblat, *J. Chem. Soc.* (*A*), 1970, 1271.

[2] A. Apelblat, in 'Solvent Extraction Research,' ed. A. S. Kertes and Y. Marcus, Wiley, New York, 1969, p. 101.

[3] A. Apelblat, *J. Chem. Soc.* (*A*), 1971, 3459.

respectively. The quantities of the organic phase are marked with the bar.

Materials and experimental techniques were described.[1,2]

RESULTS AND DISCUSSION

$MePh_2PO_4$–H_2SO_4–H_2O.—The equilibrium distribution of sulphuric acid between the aqueous phase and methyl diphenyl phosphate, and the water content in the organic phase, are shown in Figure 1 (curves 1 and 2). The dissolved (unbonded) water, $\overline{[H_2O]}_{diss}$, was calculated.[1] The phase diagrams (Figure 2) of the $MePh_2PO_4$–H_2SO_4–H_2O (1) and the Bu_3PO_4–H_2SO_4–H_2O (2) systems differ from the corresponding diagrams involving HNO_3 and HCl.[3] In the former, complete miscibility is relatively easily obtained at high concentrations of H_2SO_4. The progressive disappearance of the two-phase region is clearly seen on the extraction isotherm (Figure 1) where the solubility of the acid in the organic phase at *ca.* 15—16M-H_2SO_4 increases steeply. Some of the tie-lines in Figure 2 are omitted for clarity.

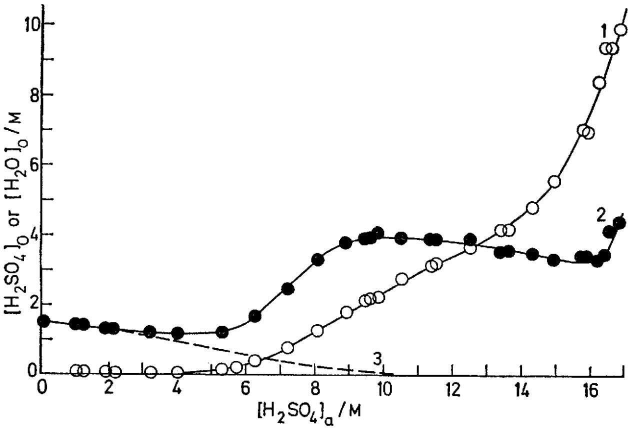

FIGURE 1 Solubility of 1, sulphuric acid; 2, total water; and 3, water dissolved in $MePh_2PO_4$ as a function of sulphuric acid concentration in the aqueous phase

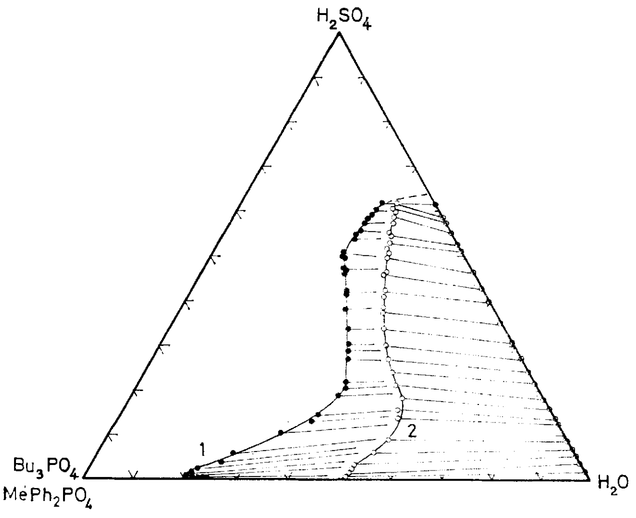

FIGURE 2 Phase diagrams of the 1, $MePh_2PO_4$–H_2SO_4–H_2O and 2, Bu_3PO_4–H_2SO_4–H_2O systems (in mol fraction units)

Figure 3 includes the organic phase densities of the H_2SO_4, HNO_3, HCl–H_2O–$MePh_2PO_4$, and Bu_3PO_4 systems. With the aid of these density data and equilibrium concentrations in both phases, the activities of methyl diphenyl phosphate were calculated from the Gibbs–Duhem relationship by assuming the aqueous phase to be a two-component (acid + water) system[1] (1)

$$\ln a_S/a_S^\circ = \int_0^{a_H} F \, da_H$$

$$F \equiv \frac{M_S}{1000 a_H}\left[\frac{\bar{m}_W m_H}{55{\cdot}51} - \bar{m}_H\right] \qquad (1)$$

where M_S denotes the molecular weight of the phosphate and m_i and $\bar{m}_i$ denote the molalities of the component i in the aqueous and the organic phases, respectively. The activities of the water-saturated phosphates are $a_S^\circ = 0{\cdot}80$ for $MePh_2PO_4$, and $a_S^\circ = 0{\cdot}515$ for Bu_3PO_4. The integrand F was calculated with the aid of Gazith's[4] values for the activities of aqueous solutions of H_2SO_4, $a_H = 4(m_H\gamma_\pm)^3$. The integral (1) was evaluated graphically in the range aqueous 0—10M-H_2SO_4. The smoothed activities of methyl diphenyl phosphate referring to pure anhydrous $MePh_2PO_4$ as the standard state are presented in the Table. Up to aqueous *ca.* 5·5M-H_2SO_4 the organic phase is practically a two-component system; therefore, according to the Gibbs–Duhem relationship with $(\partial a_W/\partial C_H)_T$ negative, $(\partial a_S/\partial C_H)_T$ must be positive, *i.e.*, a_S increases with increasing C_H ($\overline{[H_2O]} \approx \overline{[H_2O]}_{diss}$ decreases; Figure 1, curve 3). At higher concentrations of sulphuric acid, the acid in the $MePh_2PO_4$ phase cannot be neglected and a_S decreases sharply with C_H.

As in the HCl–$MePh_2PO_4$–H_2O system,[3] analysis of the partition data of the H_2SO_4–$MePh_2PO_4$–H_2O system leads to the conclusion that the sulphuric acid complex is partly dissociated (2) in the organic phase. The solvation number $q = 4$ was found from the dilution experiments with benzene as diluent. The hydration number $h = 3$ was obtained from the slope[3] $d\overline{[H_2O]}_{bond}/d\bar{C}_H = h$. The equilibrium constant for the complexation reaction (2) is (3).

$$H_2SO_4 + hH_2O + q\overline{MePh_2PO_4} \xrightleftharpoons{K} \overline{H^+(H_2O)_h(MePh_2PO_4)_q} + \overline{HSO_4^-} \qquad (2)$$

$$K = \frac{(\bar{m}_c\bar{\gamma}_\pm)^2}{a_S^4 a_W^3 a_H} \qquad (3)$$

The values of $K/\bar{\gamma}_\pm^2$ as a function of m_H were plotted from equation (3), and the value of $K = (2 \pm 0{\cdot}5) \times 10^{-3}$ (mol/1000 g $MePh_2PO_4$)$^{-1}$ was estimated from the extrapolation to zero m_H ($\bar{\gamma}_H \longrightarrow 1$ when $\bar{m}_H \longrightarrow 0$).

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[4] M. Gazith, Israel Atomic Energy Commission Reports, IA-1004, 1964, IA-1009, 1965.

By use of this value of K, the activity coefficients of the complex $\bar{\gamma}_{\pm}$ were calculated (Table). The very slight concentration-dependence of $\bar{\gamma}_{\pm}$, especially in the concentration region up to aqueous *ca.* 5·5M-H_2SO_4 supports the suggested mechanism of the extraction.

Activities of methyl diphenyl phosphate and tributyl phosphate, and activity coefficients of the complex in the H_2SO_4–H_2O–$MePh_2PO_4$ and in the H_2SO_4–H_2O–Bu_3PO_4 systems at 25 °C (the activities of pure phosphates are unity)

Aqueous molar concn. of H_2SO_4	$MePh_2PO_4$		Bu_3PO_4	
	a_S	$\bar{\gamma}_{\pm}$	a_S	$\bar{\gamma}_c$
0·0	0·800	1·00	0·515	1·00
0·1	0·800	1·00	0·516	1·03
0·2	0·801	1·00	0·518	1·07
0·3	0·802	1·00	0·519	1·17
0·5	0·804	1·00	0·523	1·21
0·7	0·806	1·00	0·526	1·29
1·0	0·809	1·00	0·531	1·57
1·5	0·814	1·02	0·538	2·10
2·0	0·820	1·04	0·545	2·66
2·5	0·829	1·06	0·550	3·07
3·0	0·838	1·10	0·548	3·35
3·5	0·850	1·14	0·529	3·23
4·0	0·861	1·18	0·495	2·83
4·5	0·872	1·27	0·453	2·41
5·0	0·888	1·38	0·406	2·01
5·5	0·882	1·64	0·352	1·51
6·0	0·875	2·00	0·298	0·86
7·0	0·821	3·5	0·195	0·20
8·0	0·659	6·8	0·116	
9·0	0·544	13·5	0·0616	
10·0	0·334	44·0	0·0284	

Bu_3PO_4–H_2SO_4–H_2O.—The extraction of sulphuric acid by tributyl phosphate alone or diluted has been widely studied.[5-9] Hansen and Patel[10] pointed out that in the low concentration region, hydrated trisolvate $H_2SO_4(H_2O)_{5.5}(Bu_3PO_4)_3$ is the predominant species and when the acidity increases $Bu_3PO_4(H_2SO_4)_2(H_2O)_{2.35}$ is formed. As can be seen, the ratio between Bu_3PO_4 and H_2SO_4 in the complexes decreases as acidity increases.

Partition data for the Bu_3PO_4–H_2SO_4–H_2O system have been published.[1] Additional and more accurate data (Figures 2—4) permit a thermodynamic analysis of the system. These data agree well with those in the literature for partition of acid[10] and water.[8] The activities of Bu_3PO_4 were calculated according to equation (1) (Table).

The formation of trisolvate at low acid concentrations is generally accepted.[8,9] However, analysis of the water partition data is difficult, because $\overline{[H_2O]}_{\text{bond}}$ decreases continuously with $\bar{C}_H$ and the limit of $d\overline{[H_2O]}_{\text{bond}}/d\bar{C}_H = h$ when $\bar{C}_H \longrightarrow 0$ cannot be determined accurately. Our results confirm the formation of hexahydrate, which was suggested previously by Brauer and Högfeldt.[7] From the complex stoicheiometry and the fact that the solubility of water in Bu_3PO_4 can be *formally* considered as formation of a *weak* Bu_3PO_4–H_2O complex, the extraction equilibrium in the low concentration region can be written as (4) and (5) where reaction (6) has the equilibrium constant $K_W = 1{\cdot}751\,\text{mol}^{-1}$.

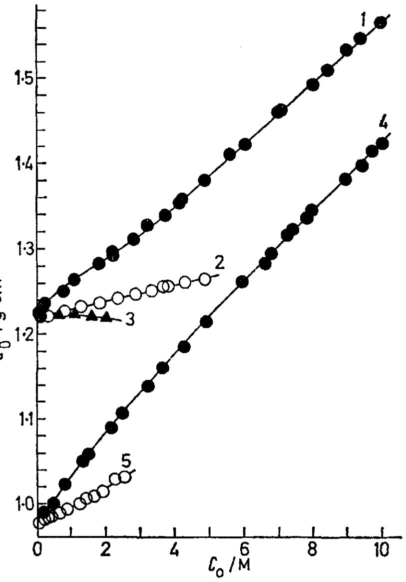

FIGURE 3 Densities of the organic phase in 1, $MePh_2PO_4$–H_2SO_4–H_2O; 2, $MePh_2PO_4$–HNO_3–H_2O; 3, $MePh_2PO_4$–HCl–H_2O; 4, Bu_3PO_4–H_2SO_4–H_2O; and 5, Bu_3PO_4–HCl–H_2O systems

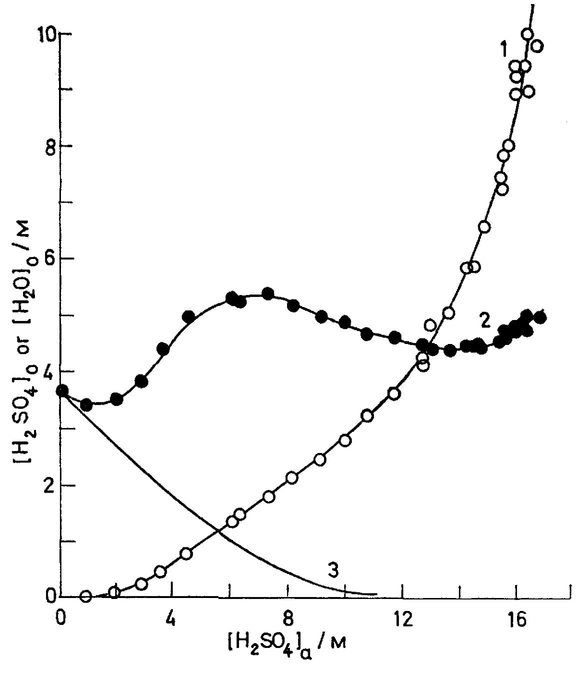

FIGURE 4 Solubility of 1, sulphuric acid; 2, total water; and 3, water dissolved in Bu_3PO_4 as a function of sulphuric acid concentration in the aqueous phase

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[5] E. Hesford and H. A. C. McKay, *J. Inorg. Nuclear Chem.*, 1960, **13**, 156.

[6] K. Naito and T. Suzuki, *J. Phys. Chem.*, 1962, **66**, 983.

[7] E. Brauer and E. Högfeldt, *J. Inorg. Nuclear Chem.*, 1961, **23**, 115.

[8] P. Biddle, A. Coe, H. A. C. McKay, J. H. Miles, and M. J. Waterman, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2615.

[9] S. Nishimura, R. Mitamura, Y. Kondo, and N. C. Li, *J. Inorg. Nuclear Chem.*, 1968, **30**, 3033.

[10] C. Hansen and A. N. Patel, *J. Appl. Chem.*, 1969, **19**, 20.

The degree of ionization of sulphuric acid at low concentration in Bu_3PO_4 does not exceed *ca.* 0·05, as estimated from measurements of electrical conductivity

$$3\overline{Bu_3PO_4\text{–}H_2O} + H_2SO_4 + 6H_2O \overset{K}{\rightleftharpoons} \overline{(Bu_3PO_4)_3H^+(H_2O)_6HSO_4^-} + 3H_2O \quad (4)$$

$$K = \frac{\bar{m}_H\,\bar{\gamma}_c}{K_W a_W^6 a_S^3 a_H} \quad (5)$$

$$\overline{Bu_3PO_4} + H_2O \overset{K_W}{\rightleftharpoons} \overline{Bu_3PO_4\text{–}H_2O} \quad (6)$$

and viscosity,[8] so that to a first approximation the dissociation of the trisolvate can be neglected. From the plot $KK_W/\bar{\gamma}_c$ as a function of C_H the value of $K = 20 \pm 1$ (mol/1000 g $Bu_3PO_4)^{-3}$ was derived ($\bar{\gamma}_c \longrightarrow 1$ when C_H or $\bar{C}_H \longrightarrow 0$). The standard free energy change $\Delta G^\circ = -RT \ln K = -1{\cdot}8$ kcal mol^{-1} is negative, so the direct reaction in equation (4) is preferred. The activity coefficients of the trisolvate $\bar{\gamma}_c$ were calculated by use of K (Table). The weak concentration dependence of $\bar{\gamma}_c$ in the low concentration region indicates that the trisolvate is formed predominantly in this region.

Mineral Acid–Organophosphate Extraction Equilibrium.—Extraction of HCl, HNO_3, and H_2SO_4 by $MePh_2PO_4$ and Bu_3PO_4 was analysed[1–3] in terms of the mass action law (7). The activity of the phosphate, a_S, can

$$\bar{a}_c = K a_H a_W^h a_S^q \quad (7)$$

be evaluated from equation (1) where a_S° is obtained from vapour pressure or solubility data.[11] The activity of the acid $a_H = \nu_1^{\nu_1}\nu_2^{\nu_2}(m\gamma_\pm)^\nu$ ($\nu_1 + \nu_2 = \nu$), and the activity of water are known.[4] The hydration number is obtainable from[3] $h = d[\overline{H_2O}]_{bond}/d\bar{C}_H$ and the solvation number q from careful analysis of dilution experiments.

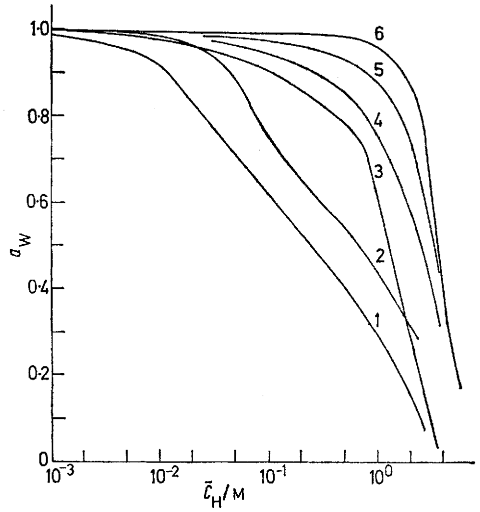

FIGURE 5 Activity of water, a_W as a function of the acid concentration in the organic phase: 1, $MePh_2PO_4$–H_2SO_4–H_2O; 2, $MePh_2PO_4$–HCl–H_2O; 3, Bu_3PO_4–H_2SO_4–H_2O; 4, Bu_3PO_4–HCl–H_2O; 5, $MePh_2PO_4$–HNO_3–H_2O; and 6, Bu_3PO_4–HNO_3–H_2O

The extraction isotherm given by equation (7) can be simplified in the low concentration region ($\bar{C}_H < 0{\cdot}1$M) because $[\overline{H_2O}]_{bond}$ is usually negligible and $[\overline{H_2O}] \simeq [\overline{H_2O}]_{diss}$, where the concentration of dissolved water,[3] $[\overline{H_2O}]_{diss}$ decreases slowly with decreasing a_W. In this region the water activity plays an important role only for highly hydrated complexes (HCl and H_2SO_4 complexes of $MePh_2PO_4$; Figure 5) and the activity of the phosphate is almost constant: $a_S \simeq a_S^\circ$ (Figure 6). Equation (7) becomes $\bar{a}_c \sim a_H$ or $\bar{a}_c \sim a_H a_W^h$ (or frequently even $\bar{C}_H \sim a_H$, *i.e.*, $\bar{C}_H$ is proportional to m_H^ν).

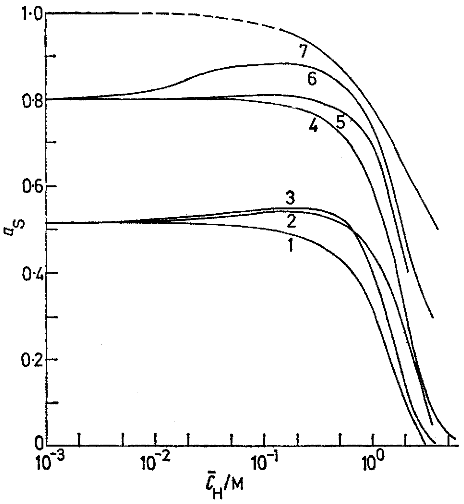

FIGURE 6 Activity of phosphate, a_S, as a function of the acid (water) concentration in the organic phase: 1, $MePh_2PO_4$–HNO_3–H_2O; 2, $MePh_2PO_4$–H_2SO_4–H_2O; 3, $MePh_2PO_4$–HCl–H_2O; 4, Bu_3PO_4–HNO_3–H_2O; 5, Bu_3PO_4–HCl–H_2O; 6, Bu_3PO_4–H_2SO_4–H_2O; and 7, Bu_3PO_4–H_2O

In the Bu_3PO_4–H_2O[1] and in the Bu_3PO_4–HNO_3–H_2O[1,2] systems the dissolved water plays a dominant role in the high concentration region (Figure 6). Here the activity of the phosphate a_S can be correlated linearly with $\bar{C}_H$; $a_S \sim a_S^\circ - B\bar{C}_H$, where the constant B changes from one system to another. The value $B = 0{\cdot}25$ gives a good approximation for all the systems considered except for Bu_3PO_4–H_2O and Bu_3PO_4–HCl–H_2O where B is smaller ($B = 0{\cdot}16$). A similar relationship was observed for the water activity; $a_W \simeq 1 - B'\bar{C}_H$. B' is not common to all systems.

The functional form of the equilibrium relations in the mineral acid–$MePh_2PO_4$ and –Bu_3PO_4 systems is typical of many non-electrolyte–electrolyte systems. This was observed in the $Th(NO_3)_4$–$C_6H_{13}OH$–H_2O,[12] $Th(NO_3)_4$–$C_7H_{15}OH$–H_2O, $UO_2(NO_3)_2$–$MePh_2PO_4$–H_2O, and $Th(NO_3)_4$–$MePh_2PO_4$–H_2O systems.[13]

I thank Miss P. Edelman for technical assistance.

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[11] A. Apelblat, *J. Chem. Soc.* (*B*), 1969, 1293.

[12] A. Apelblat and I. Michaeli, *J. Inorg. Nuclear Chem.*, 1970, **32**, 239.

[13] A. Apelblat, *J.C.S. Faraday I*, in the press.