Extraction of Zinc and Copper Nitrates by Methyl Diphenyl Phosphate

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Extraction equilibria in the zinc nitrate–water–methyl diphenyl phosphate ($MePh_2PO_4$) and copper nitrate–water–$MePh_2PO_4$ systems have been investigated. The data found are consistent with formation of partially dissociated $[Zn(NO_3)_2(H_2O)_2(MePh_2PO_4)_3]$ and $[Cu(NO_3)_2(H_2O)_3(MePh_2PO_4)_3]$ complexes. In the case of zinc, the equilibrium constant for complex formation $K = (3{\cdot}6 \pm 0{\cdot}7) \times 10^{-6}$ (mol kg^{-1} $MePh_2PO_4$)$^{-1}$.

THIS work is a continuation of our investigations on extraction equilibria in systems involving $MePh_2PO_4$.[1-5] Thermodynamic analysis of partition data in the ternary zinc nitrate–water–methyl diphenyl phosphate ($MePh_2PO_4$) and copper nitrate–water–methyl diphenyl phosphate systems is discussed.

EXPERIMENTAL

The salts $Zn(NO_3)_2$ and $Cu(NO_3)_2$, supplied by Merk, were used without further purification. The partition and density measurements have already been described.[6] The Zn^{2+} and Cu^{2+} cations were determined by ethylenediaminetetra-acetic acid (H_4edta) titration or by spectrophotometry.[7]

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[1] A. Apelblat, *J. Chem. Soc.* (*B*), 1969, 175.

[2] A. Apelblat, *J. Chem. Soc.* (*B*), 1970, 1459.

[3] A. Apelblat, *Proc. Internat. Solvent Extraction Conf.*, 1971, eds. J. G. Gregory, B. Evans, and P. C. Weston, Society of Chemical Industry, London, 1971, vol. 2, pp. 1208—1210.

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

[5] A. Apelblat, *J.C.S. Dalton*, 1973, 1198.

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

[7] F. J. Welcher, 'The Analytical Use of E.D.T.A.,' D. Van Nostrand, 1958.

RESULTS AND DISCUSSION

$Zn(NO_3)_2$–H_2O–$MePh_2PO_4$ *System.*—The extraction of nitrates by neutral organophosphates can usually be presented as reaction (1) (M = Zn or Cu), where it is

$$M^{2+} + 2NO_3^- + q\overline{MePh_2PO_4} + hH_2O \overset{K}{\rightleftharpoons} \overline{M(NO_3)(MePh_2PO_4)_q(H_2O)_h^+} + \overline{NO_3^-} \qquad (1)$$

assumed that the complex in the organic phase is partially dissociated; q and h are solvation and hydration numbers, respectively, and species in the organic phase are marked by a bar. The equilibrium constant of the reaction is given by equation (2), where the activity

$$K = \bar{a}_c/a_M a_W^h \bar{a}_S^q \qquad (2)$$

of the complex $\bar{a}_c = (\bar{m}_M\bar{\gamma}_\pm)^2$ and that of the nitrate $a_M = 4(m_M\gamma_\pm)^3$ (m = molality). The activity of water, a_W, and activity coefficients of the nitrates, $\gamma_\pm$, are known.[8] The activity of methyl diphenyl phosphate, $\bar{a}_S$, equilibrium constant, K, stoicheiometry (q and h), and activity coefficients of the complex, $\bar{\gamma}_\pm$, were determined in this work from partition and density data.

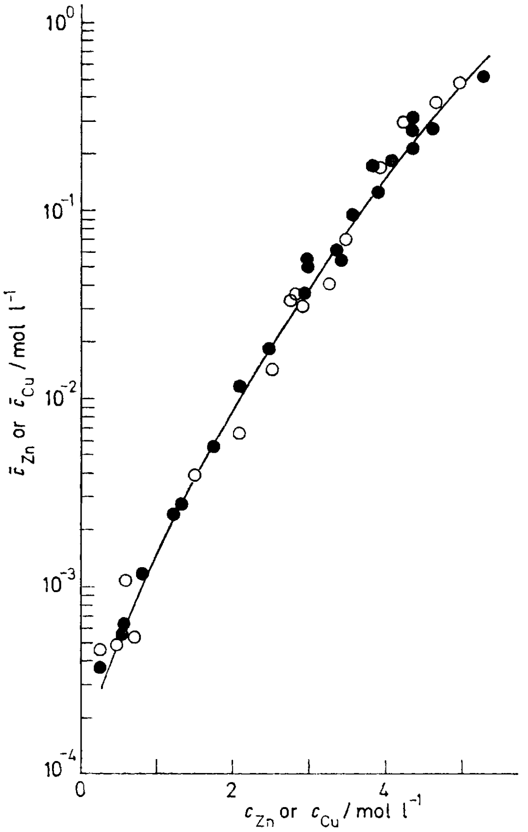

FIGURE 1 Equilibrium distribution of zinc nitrate (○) and copper nitrate (●)

The equilibrium distribution of zinc nitrate between the aqueous phase and $MePh_2PO_4$ is shown in Figure 1 and the total water content of the organic phase, $\overline{[H_2O]} = \bar{c}_W$, in Figure 2. The solvation number was found to be $q = 3$ ($q = d\ln D/d\ln\overline{[MePh_2PO_4]}$; $D = \bar{m}_M/m_M$) from a dilution experiment with benzene ($MePh_2PO_4$–C_6H_6 is an almost ideal mixture). Determination of the hydration number $h = 2$ has also been described[4] ($h = d\overline{[H_2O]}_{bound}/d\bar{c}_{Zn}$, where $\overline{[H_2O]}_{bound} = \bar{c}_W - \overline{[H_2O]}_{diss.}$). In the case of independent dissolution and complexing of water, $\overline{[H_2O]}_{diss.}$ is given by the distribution of water in the $MePh_2PO_4$–H_2O system [equation (3)],[1] where the activity of water, a_W, in zinc

$$\ln a_W = \ln\overline{[H_2O]}_{diss.} - 0{\cdot}2323\overline{[H_2O]}_{diss.} - 0{\cdot}0488 \qquad (3)$$

nitrate solutions is known.[8] This is the Setchenov equation, $\ln a_W/\bar{c}_W = \lambda\bar{c}_W + k$, where λ and k are constants. The total water content was plotted in the form $\bar{c}_W = f(a_W)$ [Figure 3, curve (3)], obtained by eliminating c_{Zn} from $\bar{c}_W = f(c_{Zn})$ (Figure 2) and from $a_W = f(c_{Zn})$.[8] As can be seen [Figure 3, curves (1) and (3)], the water content of the organic phase closely obeys equation (3) (*i.e.* $\overline{[H_2O]} \simeq \overline{[H_2O]}_{diss.}$) as long as the concentration of nitrates in the organic phase is low.

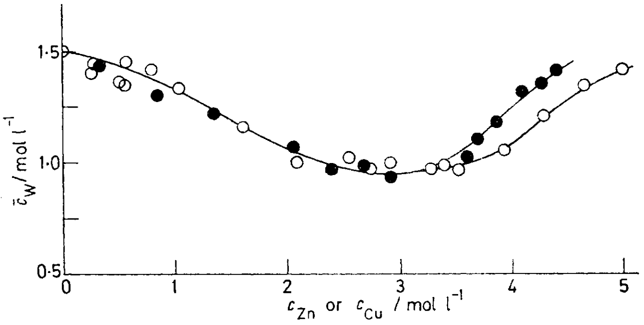

FIGURE 2 Water content of the organic phase, $\bar{c}_W$, as a function of aqueous zinc nitrate (○) and copper nitrate (●) concentrations

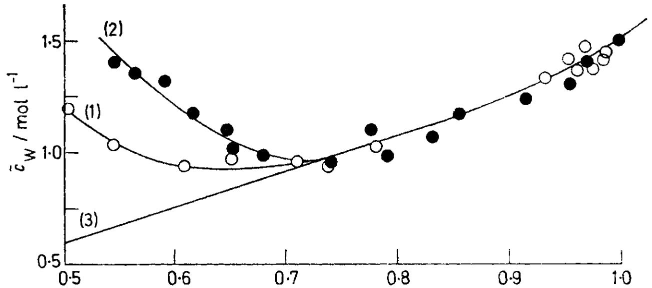

FIGURE 3 Water content of the organic phase, $\bar{c}_W$, as a function of water activity in zinc nitrate (1) and copper nitrate (2) solutions, and as calculated [curve (3)] from equation (3)

Activities of $MePh_2PO_4$, $\bar{a}_S$, were calculated from equation (4),[6] where M_S denotes the molecular weight

$$\ln(\bar{a}_S/\bar{a}_S^W) = \int_0^{a_M} F\,d\ln a_M;$$

$$F = \frac{M_S}{1000}\left(\frac{\bar{m}_W m_M}{55{\cdot}51} - \bar{m}_M\right) \qquad (4)$$

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[8] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' 2nd edn., Butterworths, London, 1959, pp. 487, 499—500.

of the phosphate; the activity of methyl diphenyl phosphate saturated with water, $\bar{a}_S{}^W$, is 0·80. The integral (4) was evaluated by a computer. Smoothed activities of $MePh_2PO_4$ in the form $\bar{a}_S = f(c_{Zn})$ are given in the Table. Knowledge of the complex stoicheiometry, $q = 3$, and $h = 2$, and the activities a_W, a_M, and $\bar{a}_S$ permits evaluation of $K/\bar{\gamma}_\pm{}^2 = f(c_{Zn})$ from equation (2). The value of K can be calculated from the extrapolation $c_{Zn} \longrightarrow 0$ (or $\bar{c}_{Zn} \longrightarrow 0$). The infinitely dilute complex in $MePh_2PO_4$ saturated with water was chosen as the standard state (*i.e.* $\bar{\gamma}_\pm \longrightarrow 1$ as $\bar{c}_{Zn} \longrightarrow 0$).

Activities of methyl diphenyl phosphate in the $Zn(NO_3)_2$–H_2O–$MePh_2PO_4$ and $Cu(NO_3)_2$–H_2O–$MePh_2PO_4$ systems at 25 °C; the activity of pure methyl diphenyl phosphate is unity

Aqueous molar concentration of $Zn(NO_3)_2$ or $Cu(NO_3)_2$	$\bar{a}_S$	
	In $Zn(NO_3)_2$	In $Cu(NO_3)_2$
0·0	0·800	0·800
0·1	0·802	0·802
0·2	0·803	0·803
0·3	0·805	0·805
0·4	0·807	0·806
0·5	0·808	0·807
0·6	0·810	0·809
0·7	0·811	0·810
0·8	0·813	0·812
0·9	0·815	0·814
1·0	0·817	0·816
1·2	0·821	0·819
1·4	0·825	0·822
1·6	0·829	0·827
1·8	0·834	0·830
2·0	0·841	0·839
2·2	0·845	0·840
2·4	0·849	0·844
2·6	0·852	0·848
2·8	0·855	0·851
3·0	0·857	0·853
3·2	0·859	0·854
3·4	0·858	0·854
3·6	0·855	0·852
3·8	0·849	0·849
4·0	0·837	0·843
4·2	0·822	0·833
4·4	0·804	0·819

Analysis of the $(K/\bar{\gamma}_\pm{}^2)$ curve showed that from $c_{Zn} \geqslant$ 0·001M $(c_{Zn} \geqslant 1M)$ onward $(K/\bar{\gamma}_\pm{}^2)$ is almost constant. The extrapolation from this concentration region gives $K = (3{\cdot}6 \pm 0{\cdot}7) \times 10^{-6}$ (mol kg^{-1} $MePh_2PO_4)^{-1}$ and activity coefficients, $\bar{\gamma}_\pm$, do not exceed 1·1 for the aqueous 1—5M-$Zn(NO_3)_2$ range. This fact supports the proposed extraction mechanism [equation (1)]. At lower concentration of zinc nitrate in the organic phase ($\bar{c}_{Zn} < 0{\cdot}001M$) a gradual change occurs in the partition mechanism. The picture would probably be clearer if distribution data for zinc nitrate were extended to at least $\bar{c}_{Zn} = 10^{-5}M$. This would necessitate a different analytical approach than that used for this work. Summarizing, extraction of macroscopic quantities of zinc nitrate by $MePh_2PO_4$ can adequately be described by formation of the partially dissociated complex $[Zn(NO_3)_2(MePh_2PO_4)_3(H_2O)_2]$.

$Cu(NO_3)_2$–H_2O–$MePh_2PO_4$ *System*.—The partition data of the salts $Cu(NO_3)_2$ and $Zn(NO_3)_2$ (Figure 1) are identical but the water content is different, especially in the presence of macroscopic quantities of copper in the organic phase (Figures 2 and 3). This is shown by the different hydration number, $h = 3$. Formation of the partially dissociated $[Cu(NO_3)_2(MePh_2PO_4)_3$-$(H_2O)_3]$ complex is postulated analogous to zinc. However, evaluation of the equilibrium constant, K, from extrapolation to zero of $\bar{c}_{Cu}$ was not as accurate as for zinc and the best tentative value found is *ca.* 4×10^{-6} (mol kg^{-1} $MePh_2PO_4)^{-1}$. The activity coefficients of the copper complex, $\bar{\gamma}_\pm$, increase with c_{Cu} (and with $\bar{c}_{Cu}$), but this concentration dependence is not strong (*e.g.* for the highest concentration $c_{Cu} = 4{\cdot}4M$, $\bar{\gamma}_\pm \simeq 2{\cdot}5$). Activities of methyl diphenyl phosphate, $\bar{a}_S$, were evaluated as those for zinc nitrate (Table 1). In both systems under consideration $\bar{a}_S > \bar{a}_S{}^W$ in the entire concentration region, *i.e.* the effect of nitrates is only secondary and the systems behave like typical binary (H_2O–$MePh_2PO_4$) mixtures. The activity of water, a_S, decreases with increasing $\bar{c}_M$ and that of the phosphate, $\bar{a}_S$, increases in accordance with the Duhem–Gibbs relation.

We thank Mrs. Y. Keren for experimental assistance.

[3/2602 *Received, 28th December*, 1973]