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Solvent Extraction Chemistry of Dialkyldithiophosphates. IV. Formation and Partition of Zinc Bis(dibutyldithiophosphate) in the Carbon Tetrachloride and Heptane–1 M $(Na,H)ClO_4$ Systems

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The extraction of zinc from acidic perchlorate solutions was studied with dibutyldithiophosphoric acid as the chelating extractant. It was confirmed that zinc is extracted as the complex $Zn[S_2P(OC_4H_9)_2]_2$ (or ZnA_2) when carbon tetrachloride and heptane are used as organic solvents. In strongly acidic solutions the extraction may formally be explained by the reaction

$$Zn^{2+} + 2(HA)_{org} \rightleftarrows (ZnA_2)_{org} + 2H^+$$

with the equilibrium constants $\log K_{ex} = 1.67$ and 1.85 for CCl_4 and n-C_7H_{16}, respectively. The formation constant of the complex ZnA_2 was determined to $\log \beta_2 = 2.27$.

A great deal is known about the coordination chemistry of the dialkyldithiophosphates.[1] However, this information mainly concerns the properties of isolated complexes such as molecular structure and spectral characteristics,[2] whereas comparatively little is known about the complex formation equilibria of these ligands. The scanty data presently available have almost exclusively been obtained in homogeneous organic-aqueous systems.[3–5] This is surprising considering the interest shown for dialkyldithiophosphoric acids (HD(R)DTP) as solvent extraction reagents for metals.[1,6,7] Only the zinc bis(dibutyldithiophosphate) complex has been studied thoroughly in an aqueous system by Handley *et al.*,[8] who employed the extraction method. Since then further studies[9,10] have been performed on HD(R)DTP in solvent extraction systems which have given results diverging from earlier work.

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EXPERIMENTAL

Chemicals: ^{65}Zn ($t_{1/2}$ 253 d) was purchased from Amersham Radiochemical Center in the form of a 0.1 HCl solution. It was used after dilution about 1:1000 by the ionic medium (1 M $NaClO_4$). The radioisotopic purity was checked by measurement with a Ge(Li) detector attached to a multichannel analyzer.

Dibutyldithiophosphoric acid (HDBDTP = HA) was synthesized and purified as described previously;[9] its purity was at least 99.8 %. A 0.1 M stock solution of NaA in 0.9 M $NaClO_4$ was prepared by neutralization of HDBDTP with NaOH. All other chemicals were of reagent grade and were used without further purification.

Procedure. The distribution experiments were carried out in 10 ml test tubes sealed with polyethylene stoppers. Appropriate amounts of reagent stock solutions in organic solvent, acid or 0.1 M NaA, ionic medium and ^{65}Zn stock solution were pipetted into each tube. The phases were equilibrated in a Griffin shaker for 1 h. Preliminary experiments had shown that equilibrium was reached within less than half this time. The equilibration was performed at 25 ± 1 °C in a thermostated room. After centrifugation, aliquots of both phases were taken with dispensible plastic pipettes of the Eppendorf type. Utmost care was exercised not to contaminate the aqueous phase; this was especially required when heptane was used as the organic solvent. The use of a semiautomatic pipetter with dispensable plastic tips was found to be superior to glass pipettes both with regard to ease of handling and against contamination. The samples were measured in the well NaI crystal of a Picker Autowell II sample changer. For samples with low aqueous activity the measuring time could reach 1 hour. The background was counted for at least 2 h.

Net counting rates were corrected for measuring geometry due to the use of different sample volumes. (A 10 ml sample only had 60 % of the net counting rate of a 0.1 ml sample with the same activity.)

RESULTS

Organic solvent CCl_4. The distribution of Zn with carbon tetrachloride as the organic solvent was measured as a function of hydrogen ion concentration at different reagent concentrations. Measurement of equilibrium hydrogen ion concentration with a glass electrode was not feasible, because these experiments were performed in strongly acidic solutions (p*h* 0 – 2). Since HDBDTP is a strong acid ($pk_a \approx 0$)[10] the free hydrogen ion concentration (h) is given with good accuracy by eqn. (1) where h_0 is the initial hydrogen ion con-

$$h = h_0 + [A] \tag{1}$$

centration and [A] is the free concentration of dithiophosphate anion. Since the partition constant k_d of HA is $\gg 1$, [A] for equal phase volumes is given by eqn. (2),[9] where $\bar{C}_{HA}$ is the initial concentration of HA in the organic phase and k_a is the protolysis constant of HA. $\log k_d k_a^{-1}$ is "the apparent pk_a" of HA in the two phase system; $k_d k_a^{-1}$ had been determined earlier by two phase titrations[9] and distribution measurements[10] to be 1.01×10^3 and 0.96×10^3 M^{-1} for 0.1 M and 0.01 M HA in CCl_4, respectively. Combination of eqns. (1) and (2) (thereby eliminating h) gives [A] as a solution to a second degree equation.

$$[A] = \frac{\bar{C}_{HA}}{k_d k_a^{-1} h + 1} \tag{2}$$

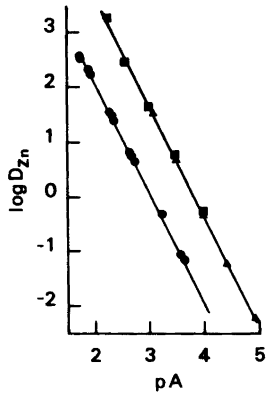

Fig. 1. Distribution of zinc between 1 M (Na,H)ClO_4 and CCl_4 (■,▲) and heptane (●) as a function of free ligand concentration. Initial concentrations of HDBDTP in the organic phase are: 0.100 M (■); 0.0103 M (▲) and 0.030 M (●). The CCl_4 curve corresponds to an equilibrium p*h* range of 0 – 2 and for heptane of 1 – 3.

The distribution ratio of zinc is denoted D_{Zn}; a plot of $\log D_{Zn}$ *vs.* pA ($= -\log[A]$) is shown in Fig. 1. The points corresponding to different total concentrations of HA in the organic phase fall on a single line thereby indicating the absence of any self adduct formation between the extracted complex and HA. It must be observed that when $\log k_d k_a^{-1}$ is rather small, the equilibrium concentration of HA in the organic phase ($[\overline{HA}]$) should be kept approximately constant. This was one reason for using low p*h* values in these measurements; $[\overline{HA}]$ did not change more than about 5 %. The absence of self adducts in an inert solvent like CCl_4 also eliminates the possibility for such phenomena occurring in any solvent. The reason is simply that the tendency for adduct formation with other species than the solvent decreases with the solvation ability of the solvent.

A straight line was fitted to the experimental data using a least squares procedure, see Fig. 1. It was found that the slope of the line is 1.99 ± 0.03,* which confirms that the extraction of zinc may be explained by the reaction (3).

$$Zn^{2+} + 2A^- \rightleftarrows \overline{ZnA_2} \tag{3}$$

In the absence of metal hydrolysis, self adduct formation and formation of anionic complexes, the liquid-liquid distribution of a bivalent metal (Zn) is given by the relation (4), where β_1 and β_2 are the

$$D_{Zn} = \frac{\lambda_2 \beta_2 [A]^2}{1 + \beta_1 [A] + \beta_2 [A]^2} \tag{4}$$

formation constants of ZnA^+ and ZnA_2, respectively, and λ_2 is the partition constant of the neutral complex ZnA_2. When Zn^{2+} is the predominating metal species in the aqueous phase, the extraction is seen to be described by eqn. (3) with $\lambda_2 \beta_2$ as the equilibrium constant. Thus the straight line in Fig. (1) corresponds to the equation (5).

* The error limits denoted in this work correspond to ± one standard deviation ($\pm\sigma$).

$$\log D_{Zn} = \log \lambda_2\beta_2 - 2pA \quad (5)$$

The value of $\log \lambda_2\beta_2$ was determined from the intercept of the least squares fitted line for $\log D_{Zn}=0$; this gave $\log \lambda_2\beta_2 = 7.63 \pm 0.02$.

In the region of high acidities the extraction of zinc may formally be described by the heterogeneous reaction

$$Zn^{2+} + 2\overline{HA} \rightleftarrows \overline{ZnA_2} + 2H^+$$

with the equilibrium quotient K_{ex} given by eqn. (6).

$$\log K_{ex} = \log \lambda_2\beta_2 - 2\log k_d k_a^{-1} \quad (6)$$

When $\log k_d k_a^{-1}$ determined from two phase titrations (2.98) is used, eqn. (6) gives $\log K_{ex} = 1.67 \pm 0.02$.

Attempts to increase [A] in order to reach the "plateau" of the distribution curve corresponding to λ_2 were futile. The $\log D_{Zn}$ values exceeding about 3.5 were severely scattered and did not show any significant tendency to level off. This is in disagreement with earlier work;[8] see further the discussion below.

Organic solvent n-C_7H_{16}. In order to determine separate values of λ_2 and β_2 an inert solvent with a smaller solubility parameter than CCl_4 had to be used. For this purpose heptane was found to be suitable. The distribution measurements were carried out with a low and almost constant equilibrium concentration of HA in the organic phase ($[\overline{HA}] \approx 0.02-0.03$ M). On the other hand, the composition of the ionic medium changed considerably, from 1 M $HClO_4$ to 0.1 M NaA + 0.9 M $NaClO_4$. Therefore p*h* measurements were not practical,[9] but [A] could be calculated from the initial amounts of HA, $HClO_4$ and NaA present in each sample. For $k_d \gg 1$ ($k_d \approx 10^2$ for heptane) and equal phase volumes eqns. (7) and (8) for the balance of A^- and H^+ in the two phases hold, where C_A is the

$$\bar{C}_{HA} + C_A \simeq k_d k_a^{-1} h[A] + [A] \quad (7)$$

$$\bar{C}_{HA} + h_0 \simeq k_d k_a^{-1} h[A] + h \quad (8)$$

initial concentration of NaA in the aqueous phase. From eqns. (7) and (8) [A], *h* and $[\overline{HA}]$ ($= k_d k_a^{-1} h[A]$) were obtained.

A plot of the straight line part of the distribution curve $\log D_{Zn}$ *vs.* p*A* is shown in Fig. 1. For that part of the data that corresponds to $\log D_{Zn} \lesssim 2.5$ a linear regression analysis according to eqn. (5) gave a slope $= 2.002 \pm 0.024$ and $\log \lambda_2\beta_2 = 6.046 \pm 0.021$. With $\log k_d k_a^{-1}$ for heptane $= 2.097$ (from two phase titrations[9]) $\log K_{ex} = 1.85 \pm 0.02$.

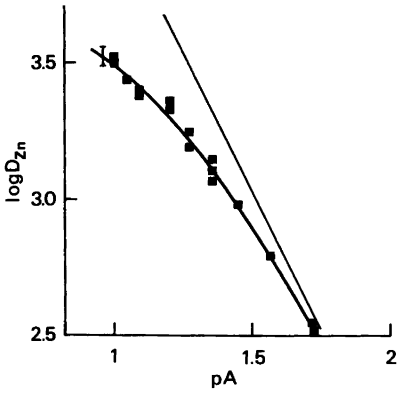

Fig. 2. Distribution of zinc between 1 M $NaClO_4$ and heptane. Initial concentration of HDBDTP in the organic phase = 0.030 M. p*A* is varied by the concentration of NaDBDTP in the aqueous phase. The curve is drawn according to the calculated constants; the vertical length of the line shown on its upper part gives the standard deviation in $\log D_{Zn}$ estimated by radiometric measurements in this region.

The distribution curve for $\log D_{Zn} \gtrsim 2.5$ is shown in Fig. 2. The bending of the curve indicates that formation of the complexes ZnA^+ and ZnA_2 takes place in the aqueous phase for $pA \lesssim 2$. The data represented in Fig. 2 were linearized by means of the relation (9) (*cf.* eqn. (4)). Least squares fitting

$$(\lambda_2\beta_2[A]^2 D_{Zn}^{-1} - 1)[A]^{-1} = \beta_1 + \beta_2[A] \quad (9)$$

according to this equation gave $\beta_1 = 8 \pm 3$ and $\beta_2 = 185 \pm 25$ M^{-1} or $\log \beta_1 = 0.90 \pm 0.15$ and $\log \beta_2 = 2.27 \pm 0.06$. The partition constant for the neutral zinc complex may now be calculated from $\log \lambda_2\beta_2$ and $\log \beta_2$. This gives $\log \lambda_2 = 5.37 \pm 0.06$ and 3.78 ± 0.06 for CCl_4 and n-C_7H_{16}, respectively.

DISCUSSION

The results of this investigation deviate considerably from those reported by Handley *et al.*[8] for the CCl_4/1 M (Na,H)Cl system. Thus Handley gives (the present results are given within parenthesis): $\log K_{ex} = 1.22$ (1.67); $\log \lambda_2\beta_2 = 6.57$ (6.05); $\log \lambda_2 = 2.77$ (5.37) and $\log \beta_2 = 3.81$ (2.27). For

K_{ex} the difference might be explained by the use of another ionic medium, but this is certainly not so for λ_2 and β_2. The cloride complexes of zinc are too weak[11] ($\log\beta_n<0$) to have such a strong influence on the extraction. The same method was used as in this study, but much higher metal concentrations were employed, $\approx 10^{-2}$ M as opposed to $10^{-5}-10^{-4}$ M in this study. In neither case was the metal concentration found to have any influence on extraction. On the other hand, very high partition constants might be expected for ligands comprising large alkyl groups and the slightly polar sulfur groups such as HDBDTP.

The large standard deviations found in the present work for β_1 and β_2 are, of course, due to the use of extremely high distribution ratios and to the fact that the plateau value of $\log\lambda_2$ was never reached. Some trial experiments to measure the distribution at still higher ligand concentrations up to 1 M failed; the scattering was so severe that inclusion of these data would have given even higher uncertainties. Moreover, there is another reason for not going beyond a higher value of [A] than about 0.1 M. When [A]=1 M, about 25 % of the water in the aqueous phase has been exchanged for the bulky ligand molecules, which would have a strong influence on aqueous activity coefficients. In keeping the ionic medium as near 1 M $NaClO_4$ as possible, a more credible result for the complex formation in that medium has been obtained.

The employed evaluation method may only be used when a slope of the $\log D_{Zn}$ *vs.* p*A* curve corresponding to the charge of the metal ion is ascertained. About the same values (within the given standard deviations) for the formation constants were obtained by a non-linear regression analysis. However, the previous results were retained, since $\lambda_2\beta_2$ was determined more precisely by the first method. The observed deviation of this constant (± 0.02 in log units) had no significant influence on the β_2 value. On the other hand, the larger deviations given for β_1 reflects the statistical error of $\log\lambda_2\beta_2$.

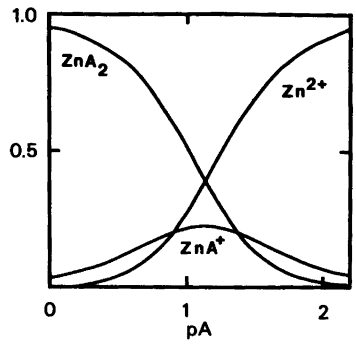

Fig. 3. $[ZnA_i]/[Zn]_{tot}$ as a function of p*A*.

The complex fraction ($=[ZnA_i]/[Zn]_{tot}$) as a function of p*A* is given as an illustration in Fig. 3. There is little doubt that the dialkyldithiophosphates form chelate complexes,[1] but it is evident that they are unusually weak. In regard to their redox properties they are referred to as *pseudohalogenides.*[12] This similarity does, in fact, also seem to describe their ability to form complexes. Any further comparison with other (pseudo-) halogenides is made difficult by the chelate effect.

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