Solvent Extraction Chemistry of Dialkyldithiophosphates. III.

A Spectrophotometric Study of the Protolysis and Distribution

Equilibria of Dibutyldithiophosphoric Acid in the Systems Carbon

Tetrachloride – 1 M (Na,H)ClO$_4$ and – 1 M (Na,H)Cl

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The distribution of dibutyldithiophosphoric acid (HDBDTP) between carbon tetrachloride and the ionic media 1 M (Na,H)ClO$_4$ or 1 M (Na,H)Cl was studied by spectrophotometric determination of the dithiophosphate in the aqueous phase. The protolysis of HDBDTP may be described by assuming pk_a = – 0.24 and – 0.09 for the two ionic media when the variation of activity coefficients is neglected. At low hydrogen ion activities the results are in excellent agreement with the data reported previously from two phase titrations.

In the studies of metal complexation by solvent extraction methods an accurate knowledge of ligand behaviour in the two-phase system is needed. The free ligand concentration ([A$^-$]=[A]) in the aqueous phase is given by

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

where
$\bar{C}_{HA}$ = initial concentration of the reagent (HA) in the organic phase, M.
k_d = the conditional partition constant of HA (valid for specified ionic medium)
θ = phase volume ratio, organic/aqueous
k_a = conditional protolysis constant of HA, M
h = hydrogen ion concentration, M

From eqn. (1) follows that separate values of k_d and k_a are not needed when $k_d \gg \theta^{-1}$. In this case

$(k_d + \theta^{-1})k_a^{-1} \simeq k_d k_a^{-1}$ may be determined by, for example, two-phase titrations.[1] The most suitable conditions for this method have been described earlier.[2]

The formation and partition constants of dialkyldithiophosphoric acids have been studied by Zucal et al.,[3] who found these acids to be really quite strong with p$k_a \approx$ 0. They also reported log k_d for dibutyldithiophosphoric acid (HDBDTP) to be 2.52 in the system CCl$_4$/1 M (Na,H)Cl. The condition $k_d \gg 1$ is therefore fulfilled for this reagent as has also been confirmed in the analysis of two-phase titration data.[2] However, in view of the discrepancies found between those two studies, it would still be of interest to redetermine an accurate value of k_d, because one may then find correlations for the very high partition constants of metal complexes with this ligand.[4]

Provided that the absorption spectrum of the acid and base forms are sufficiently different, the spectrophotometric method is generally regarded as the best available technique for determination of formation constants of strong acids. Jørgensen[5] has reported that the >P(S)S$^-$ chromophore has its first absorption band at 44.5 kK = 225 nm, but he does not mention anything about changes in spectrum due to formation of >P(S)SH. The UV absorption spectrum of a 7×10^{-5} M solution of DBDTP$^-$ in 1 M NaClO$_4$ is shown in Fig. 1. It was found in this work that the absorbance at this wavelength showed a slight but significant decrease at increased acidity. However, this change was not
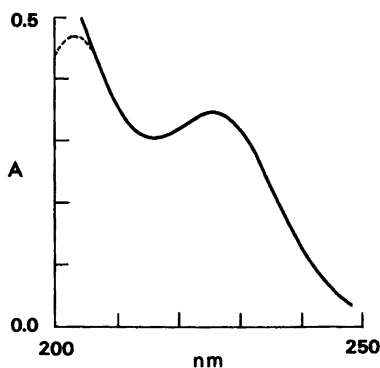
Fig. 1. UV spectrum of a *ca.* 7×10^{-5} M solution of NaDBDTP in 1 M $NaClO_4$.

Table 1. Apparent extinction coefficient (ε') at 225 nm of HDBDTP at different initial acidities (h_0) in the ionic medium 1 M $(Na,H)ClO_4$.

h_0 M	ε' M^{-1} cm^{-1}
1.03	4039
0.72	4062
0.31	4097
0.185	4116
0.103	4130
0	4152

large enough for an accurate determination of k_a. Instead, spectrophotometry was employed as a selective analytical method in distribution measurements.

Apart from the previously[3] used iodometric method, an obvious alternative would have been the use of radioactively labeled $DBDTP^-$. However, even minute amounts of radioisotopic impurities would have caused serious difficulties with the large distribution factors expected in the actual case. It is known that the usual synthesis route for HDBDTP gives rise to a considerable number of by-products[6] and this approach was therefore not attempted.

EXPERIMENTAL

Chemicals. HDBDTP of at least 99.8 % purity was prepared as previously described.[2] All other chemicals were of *p.a.* quality.

Procedure. The distribution experiments were performed with 10 ml of each phase in sealed glass ampoules. The added organic phase was about 0.1 M with respect to HDBDTP and the aqueous phase contained accurately known concentrations of H^+ at 1 M ionic strength. Equilibrium was achieved by shaking for 30 minutes. Preliminary experiments had shown that equilibrium was reached within this time. After centrifuging, an aliquot of the aqueous phase was diluted with pure ionic medium and the absorbance spectrum obtained on a Beckmann DB spectrophotometer connected to a recorder. The experiments were performed in a thermostated room at 25 ± 1 °C.

EVALUATION METHODS AND RESULTS

The absorbance at the 225 nm shoulder (*cf.* Fig. 1) was found to follow Beer's law up to an absorbance $A \leq 0.6$. Commonly the A readings employed in the evaluation fell within 0.15 to 0.5. (The dashed "peak" at 205 nm is due to instrumental limitations; the correct spectrum is indicated by the solid line in Fig. 1.)

Extinction coefficients were determined by measurements on a series of total $DBDTP^-$ concentrations at varying acidities. Results for 1 M $(Na,H)ClO_4$ are shown in Table 1. The observed change in apparent extinction coefficient (ε') with acidity indicates clearly different extinctions of the acid and base forms at this wavelength. It can be shown (eqn. (2)) that

$$\varepsilon' = \frac{\varepsilon_{HA}k_a^{-1}h + \varepsilon_A}{k_a^{-1}h + 1} \tag{2}$$

where ε_{HA} and ε_A are the true extinction coefficients of the acid and base, respectively. This equation may be rearranged (eqn. (3))

$$\varepsilon' = \varepsilon_{HA}k_a^{-1}h - k_a^{-1}\varepsilon'h + \varepsilon_A \tag{3}$$

thus permitting an evaluation of ε_{HA}, ε_A and k_a by least squares fitting of experimental data to a linear equation of the form $z = ax + by + c$. The obtained results are: $\varepsilon_{HA} \simeq 3.9 \times 10^3$ M^{-1} cm^{-1}, $\varepsilon_A = 4.15 \times 10^3$ M^{-1} cm^{-1} and $k_a \simeq 1.2$ M. ε_{HA} and k_a are inevitably inaccurate due to the very small variation in ε'. On the other hand, ε_A is of much higher accuracy as it is the limiting value for $h = 0$, which may also be determined directly in the actual 1 M ionic medium. Within experimental accuracy the same result was obtained in 1 M $(Na,H)Cl$.

The calculation of k_a from the distribution experiments was done as follows. Due to the small total concentration of DBDTP$^-$ in the aqueous phase ($c_A = [HA] + [A^-]$) the equilibrium aqueous concentration of H$^+$ is given by $h = h_0 + [A^-] \simeq h_0 + c_A$, where h_0 is the initial hydrogen ion concentration. This is a good approximation since in the actual case either $[HA] \ll [A^-]$ or $h_0 \gg c_A$. Measurements with a glass electrode would not have been practical in the actual ph range. The value c_A is obtained from spectrophotometric measurements on the aqueous phase diluted f_{dil} times with pure ionic medium (1 M NaClO$_4$ or 1 M NaCl): cf. eqn. (4) where k'_a denotes the approximative value

$$c_A = \frac{k'^{-1}_a h + f_{dil}}{\varepsilon_{HA} k'^{-1}_a f^{-1}_{dil} h + \varepsilon_A} A \qquad (4)$$

of the protolysis constant found in the calibration procedure. A is the net absorbance at 225 nm (corrected for absorbance from the minute amounts of organic solvent present in the aqueous phase). The phase volumes being equal, the equilibrium organic phase concentration of HA ($= [\overline{HA}]$) is simply given by difference: $[\overline{HA}] = \bar{C}_{HA} - c_A$. This is permissible, because the distribution ratio D_A ($= [\overline{HA}]/c_A$) was always greater than 10.

The apparent two-phase formation constant $k_d k_a^{-1}$ is determined by the standard method of plotting $1/D_A$ vs. $1/h$ (cf. Fig. 2), which gives a
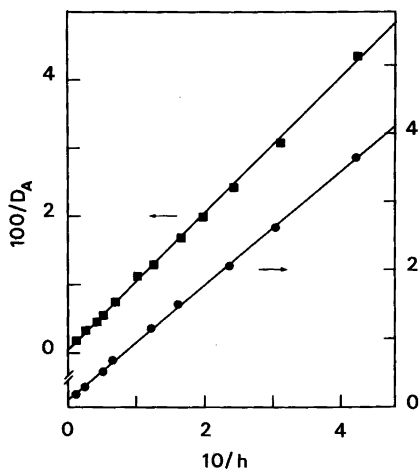
straight line with slope k_a/k_d and intercept $1/k_d$, according to eqn. (5).

$$1/D_A = 1/k_d + (k_a/k_d)(1/h) \qquad (5)$$

However, for numerical reasons, this intercept value of k_d is not highly precise. Instead, the $k_d k_a^{-1}$ found by least squares analysis is used for experimental data in the range $0.1 < h \leq 1$ according to

$$k_d k_a^{-1} h/D_A - 1 = k_a^{-1} h \qquad (6)$$

Thus, a plot of the left hand side of eqn. (6) vs. h should give a straight line with slope $= k_a^{-1}$ through the origin. This is found to be the case; cf. Fig. 3.

The experimental data used for calculations are given in Tables 2 and 3. The resulting values of $k_d k_a^{-1}$ are 1.01×10^3 and 1.14×10^3 for the perchlo-
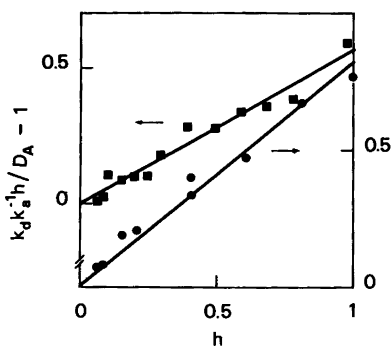

Fig. 3. Plot of $k_d k_a^{-1} h/D_A - 1$ vs. h for the systems CCl$_4$/1 M (Na,H)ClO$_4$ (■) and 1 M (Na,H)Cl (●). Note the shift of ordinate scales.

Fig. 2. Plot of $1/D_A$ vs. $1/h$ for the systems CCl$_4$/1 M (Na,H)ClO$_4$ (■) and 1 M (Na,H)Cl (●). Note the shift of ordinate scales.

Table 2. Experimental data for distribution of DBDTP in the system CCl$_4$/1 M (Na,H)ClO$_4$. $\bar{C}_{HA} = 0.0976$ M.

h	f_{dil}	A	h	f_{dil}	A
0.974	3.33	0.194	0.147	12.5	0.237
0.876	3.33	0.229	0.0985	12.5	0.356
0.779	3.33	0.211	0.0791	14.3	0.358
0.682	3.33	0.233	0.0600	16.7	0.400
0.584	3.33	0.273	0.0506	16.7	0.471
0.487	5	0.208	0.0412	20	0.478
0.390	5	0.262	0.0321	25	0.479
0.293	5	0.321	0.0235	50	0.337
0.244	10	0.180	0.0153	67.7	0.345
0.195	10	0.224	0.0088	100	0.365

Table 3. Experimental data for distribution of DBDTP in the system $CCl_4/1$ M $(Na,H)Cl$. $\bar{C}_{HA} = 0.1009$ M. The asterisk (*) denotes experiments where the phases were equilibrated for 2 h instead of 30 min.

h	f_{dil}	A	h	f_{dil}	A
1.010	3.33	0.220	0.0820	14.3	0.334
1.010	3.33	0.190*	0.0621	20	0.311
0.808	3.33	0.225	0.0425	20	0.424
0.606	5	0.177	0.0425	20	0.432*
0.404	5	0.252	0.0329	25	0.427
0.404	5	0.240*	0.0329	33.3	0.322
0.203	10	0.217	0.0237	50	0.294
0.152	11.1	0.257	0.0156	100	0.227
0.102	12.5	0.352	0.0156	100	0.228*

rate and chloride systems, respectively. For k_a the corresponding values are 1.8 ± 0.1 and 1.2 ± 0.05. Of course the given standard deviations are not a measure of overall accuracy but rather an indication of internal consistency and numerical precision. The scattering of data as shown in Fig. 3 is quite normal for high distribution ratios. In fact, these plots are extreme magnifications of a data range normally presented in log-log-diagrams. Plots of log D_A vs. ph are shown in Fig. 4 for comparison.

DISCUSSION

Because $k_d k_a^{-1}$ is evaluated from the slope of D_A^{-1} vs. h^{-1}, it is not sensitive to scatter in the region $ph < 1$; cf. Fig. 2. For the same reason these
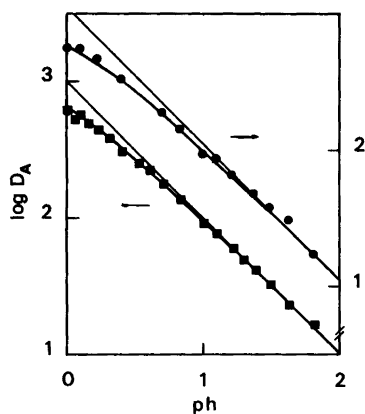

Fig. 4. Plot of log D_A vs. ph for the systems $CCl_4/1$ M $(Na.H)ClO_4$ (■) and 1 M $(Na,H)Cl$ (●).

Table 4. Comparison of $\log k_d k_a^{-1}$ as obtained by two phase titrations[2] and by the method of this work. The estimated uncertainty $(\pm \sigma)$ is about ± 0.005 log units for both methods.

Ionic medium	Ref. 2	This work
1 M $(Na,H)ClO_4$	2.984	3.005
1 M $(Na,H)Cl$	3.047	3.058

values may be assumed to be only slightly affected by the change of ionic medium at high acidities. Thus, it might be expected that these $k_d k_a^{-1}$ should compare very well with $(k_d + 1)k_a^{-1} \simeq k_d k_a^{-1}$ as determined by two-phase titrations, see Table 4. Clearly, the agreement is excellent and provides a strong indication of the accuracy of both methods. The small discrepancies $(\Delta \log k_d k_a^{-1} \approx 0.01 - 0.02)$ may be explained by the non-ideal behaviour of the organic phase. For a non-dimerizing solute like HDBDTP it is found with the Scatchard-Hildebrand equation[7] that the change in $k_d k_a^{-1}$ with $[\overline{HA}]$ is given by eqn. (7)

$$\Delta \log k_d k_a^{-1} = \frac{v_{HA}(\delta_{HA} - \delta_S)^2}{RT \ln 10}\left[1 - (1 - \frac{[\overline{HA}]v_{HA}}{1000})^2\right]$$

(7)

where
$v_{HA} = 226$ cm^3 = molal volume of HA[8]
$\delta_{HA} = 20.7$ J$^{1/2}$ cm$^{-3/2}$ = solubility parameter of HA[9]
$\delta_S = 17.49$ J$^{1/2}$ cm$^{-3/2}$ = solubility parameter of CCl_4[10]

Eqn. (7) gives the change of log $k_d k_a^{-1}$ compared to the value of infinite dilution ($[\overline{HA}] = 0$), and might be expected to hold up to $[\overline{HA}] \approx 0.5$ M. For $[\overline{HA}] \simeq 0.1$ M in comparison to $[\overline{HA}] \simeq 0.02$ M during the two phase titrations, $\Delta \log k_d k_a^{-1}$ obtained from eqn. (7) is 0.015, which explains the observed discrepancies to within the experimental accuracy.

The values of pk_a determined in this work are -0.24 and -0.09 for the perchlorate and chloride media, respectively. These values do not correlate well with data reported in the literature. Thus, Curtui et al.[11] give $pk_a = 0.28$ for the perchlorate system, and Zucal, Handley and Dean[3] report $pk_a = 0.22$ for 1 M $(Na,H)Cl$. In the latter work it is not clear whether the pk_a refers to a "mixed activity-concentration constant" k_a, or if it is defined, as in

this work, as a concentration quotient. Furthermore, taking the overall scatter of data into account only two experimental points (out of 15) are significant for the determination of pk_a. It also seems that Zucal et al. have drawn the $\log D_A$ vs. ph curve for HDBDTP more or less parallel to similar curves for other HD(R)DTP's, where a "plateau" value (corresponding to $\log k_d$) was reached outside the 1 M ionic medium. Thus, $\log k_d$ for the diiso-butylester was obtained at 4.5 and 10 M HCl.

The same criticism may also be raised against the more recently determined pk_a in the perchlorate medium. First, there is strong evidence for a difference in ph scale from this work by almost one unit.[2] Secondly, only one experimental point within the 1 M ionic medium (and one at ≈ 2.5 M $HClO_4$) can be used for the estimation of pk_a. These experimental data cannot be fitted to any reasonable $\log D_A$-ph relationship.

The high value of k_a determined in this work indicates that the species HDBDTP is to be considered as an ion pair in the aqueous phase. This view is also supported by the very slight change in absorption spectrum observed at high acidities. There is a close agreement between k_a found by both methods of this work, spectro-photometric and distribution measurements.

It should be recalled that severe problems are encountered in attempts to determine very small formation or complex constants and also in the interpretation of results from such measurements. Some of these problems might have been solved by the use of a higher ionic strength, say 3 M, but information gained in such a system would be of little use in the 1 M media commonly chosen for metal extraction studies. It is not satisfactory to give k_a without any comment on its significance. Here k_a is defined as a concentration quotient. Thus it includes the acidity dependence of unknown activity coefficients. There is no reason to a priori assume a constant quotient of these activity coefficients. Thus one may only state that the distribution of HDBDTP is described formally by the determined constants $k_d k_a^{-1}$ and k_a.

Finally, it must be concluded that since the $ph = pk_a$ is not reached within the ionic medium, one should not rely too much on k_d from these measurements. However, as a crude estimate, $\log k_d$ for HDBDTP may be taken to be $\simeq 3.2$ for both systems CCl_4/1 M (Na,H)ClO_4 and 1 M (Na,H)Cl.

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