

Solvent Extraction Chemistry of Dialkyldithiophosphates.

I. Potentiometric Two-phase Titration Studies of Dibutyl- and Methylheptyldithiophosphoric Acids

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In studies of metal complexation by chelating extraction reagents, the free ligand concentration of the aqueous phase is primarily governed by “the effective extraction constant” of the reagent, defined as $(k_d + 1)k_a^{-1}$, where k_d is the partition constant and k_a the acidity constant of the reagent. For dialkyldithiophosphoric acids these constants are very difficult to determine separately. In this study $(k_d + 1)k_a^{-1}$ has been determined for dibutyl- and methylheptyldithiophosphoric acids by a series of potentiometric two-phase titrations with different non-polar organic solvents; the data have been evaluated by a linearized Gran-function.

The dialkyldithiophosphates, $(RO)_2P(S)^-$, have attracted considerable interest as soft chelating ligands, capable of forming extractable complexes with the heavy metals even in strongly acidic solutions. Busev¹ and coworkers pioneered in the development of their use as precipitation and colorimetric reagents in the analysis of metal ions some thirty years ago. Bode² then drew attention to the use of these reagents and he also examined their possibilities for extractive separation of metals. Busev and Bode studied only the diethyldithiophosphate but Handley^{3,4} extended the studies to longer chained alkyl groups such as isopropyl, butyl and isobutyl. Handley also examined the distribution of the corresponding dialkyldithiophosphoric acids (HD(R)DTP) in solvent extraction systems.⁵ More recent work on the basic extraction chemistry of these compounds has been performed by a Romanian group.⁶

Higher homologues of dialkyldithiophosphoric acids, notably the di-(2-ethylhexyl) ester

(HDEHDTP), have been thoroughly investigated as selective extraction reagents for hydrometallurgical purposes by Levin and coworkers.⁷ However, due to the low stability of these compounds against oxidation (to the disulfide) or hydrolysis (to the sulfide), the corresponding interest from industry is lacking – at least outside the USSR.

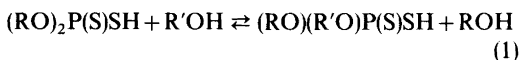
The coordination chemistry of dialkyldithiophosphates has been explored, for instance, by Jørgensen⁸ and Fernando *et al.*⁹ A review on this topic has been presented by Wasson *et al.*,¹⁰ covering 460 references. The vivid interest in these ligands can to some extent be explained by their important industrial uses, for example, as intermediates in the production of organophosphorus insecticides, lubricant additives and flotation agents.^{11,14}

The work described in this paper was partly initiated by the search for an extraction reagent capable of recovering nickel from strongly acidic industrial waste solutions. It was found that several HD(R)DTP met this purpose, but they proved to be unstable, and thus the original idea was abandoned. However, the features of dialkyldithiophosphates seemed quite extraordinary for chelating extraction reagents. Together with some apparent discrepancies in the extraction behaviour as reported in the literature this justified a closer study.

One of the prime requirements for the understanding of a metal chelate extraction system is a knowledge of the behaviour of the reagent, notably its constants for acid protolysis (k_a) and partition (k_d). It is easily derived (see below), and it is also extensively recognized that when $k_d \gg 1$ (say $\log k_d \geq 2$), these constants may not have to be deter-

mined separately, because it is then the product $k_d k_a^{-1}$ which is required for the analysis of metal extraction equilibria. In the actual case it was known that dialkyldithiophosphoric acids are quite strong with pK_a around 0. Therefore, it would in fact be impossible to determine k_a separately by potentiometric titrations in a one-phase aqueous system. On the other hand, when $k_d \geq 100$, the "apparent pK_a " = $\log k_d k_a^{-1}$ in a two-phase system could be determined with an appreciable accuracy. This requirement was found to be met only for the dibutyl ester (HDBDTP) and higher homologues. However, the higher homologues ($\geq C_5$) could not be synthesized in sufficiently high purity. Zucal *et al.*⁵ studied the distribution equilibria of HDBDTP by an iodometric method for the determination of the reagent in both phases. Bode² examined different such methods but did not use them in his work, evidently. Thereby he confirmed¹² that the ordinary route for such a method (by oxidation in acidic medium) is not satisfactory, because the redox potentials of iodine and dithiophosphate are close to each other¹⁵ (*cf.* also Ref. 13), giving a negative systematic error of several percent. This problem may not be significant when the oxidation is performed in alkaline medium. It is not clear, which of these methods was employed by Zucal.⁵ At any rate, low concentrations would, in fact, be very difficult to determine with high accuracy, especially in the presence of reducing impurities. A reexamination of the distribution equilibria for dibutylthiophosphoric acids with other methods, therefore, seemed inevitable.

Very little is known¹⁰ of the properties of *unsymmetrically* substituted dialkyldithiophosphates, primarily due to difficulties in the synthesis of sufficiently pure compounds. However, in a patent by Carpenter¹⁶ it was shown how such compounds could be made in high yields by transesterification,



where elimination of ROH by distillation at reduced pressure will drive the reaction to completion. For this method to be successful R must be methyl through hexyl and R'OH heptanol or a higher homologue. It would be of considerable interest to examine the solvent extraction behaviour of such an unsymmetrical ester, and especially one with just as many aliphatic carbons as HDBDTP. The most

exciting choice would be methylheptyldithiophosphoric acid (HMHpDTP), which was also included in this study.

EXPERIMENTAL PROCEDURE

Chemicals

Dibutylthiophosphoric acid (HDBDTP) was synthesized by alcoholysis of analytical grade butanol (Fluka) with P_4S_{10} (Riedel de Haen). In order to make a sufficiently pure compound, the method described in the literature¹⁸ had to be somewhat modified. The reaction was performed under nitrogen atmosphere at 50–60 °C and with the alcohol diluted to 50 vol-% with benzene. The raw product contained about 75 % HDBDTP, the rest being unreacted alcohol and a wide range of by-products.¹⁹ The acid was then converted to an aqueous solution of the Na salt by neutralization with NaOH with 25 % deficit of the acid content. This solution (*ca.* 1.5 M NaDBDTP) was washed twice with benzene and the acid was regenerated by addition of an equivalent amount of 6 M HCl. After addition of benzene to make up a 50 v/v-% solution of the acid, this organic phase was washed twice with equal volumes of 1 M NaCl. The washed benzene solution was then dried with Na_2SO_4 , and after removal of benzene on a rotating thin film evaporator the HDBDTP (purity about 96 %) was further purified by vacuum distillation (0.7 mmHg, 92–96 °C) on a boiling water bath. The intermediate extractive purification step could be excluded, but then the final product was slightly coloured and of highly disagreeable odour. The purity of the final, uncoloured, product was ascertained by acidimetric titration and PMR, and was found to be at least 99.8 %. It could be stored in tightly stoppered bottles in a refrigerator at 0 °C for several months without decomposing noticeably.

Dimethylthiophosphoric acid (HDMDTP) was synthesized by the reaction of methanol with P_4S_{10} , as described for HDBDTP. Distillation at reduced pressure (8–10 mmHg, 72 °C) gave a product of 95 % purity.

Methylheptyldithiophosphoric acid (HMHpDTP) was prepared by the reaction of equimolar amounts of HDMDTP and reagent grade heptanol (Fluka) at 50 °C and a pressure of 30 mmHg. Attempts to purify HMHpDTP by vacuum distillation failed at the lowest pressure available (≈ 1 mmHg); when the temperature rose above 100 °C nearly quantitative decomposition was caused. One batch of raw HMHpDTP was analyzed by a two-phase titration and was found to contain about 15 mol-% of the diheptyl ester (HDHpDTP). The formation of

HDHpDTP clearly indicates that the reaction according to eqn. (1) had gone too far. However, since the difference in $\log k_d$ between the two esters would certainly be more than 3, an extractive separation, as described for HBDTP above, was employed. The acidimetric purity of the final product was 97%. Since PMR showed the remaining impurity to be benzene, this material was considered to be of sufficient purity for the actual purpose. However, in a careful analysis of data from the subsequent two-phase titrations some HDHpDTP was still found to be present. The acid could, therefore, not be used for distribution studies of metals, where such an impurity certainly would have been unacceptable.

All other chemicals and solvents were of reagent grade or equivalent.

Titration procedure

All titrations were performed in a 400 ml cylindrical glass vessel with a tightly closing lid. The lid was provided with ground joints for the connection of a thermometer, sample inlet, glass electrode and burette PTFE tubings. The vessel was placed on a magnetic stirrer and surrounded by a jacket connected to a thermostated bath. The temperature was kept at 25 ± 0.2 °C. (The use of an inert protecting gas against CO_2 was not considered necessary since pH never exceeded 5 during the titrations.) 100 ml of the ionic medium (1 M NaClO_4 or NaCl) was pipetted into the vessel, followed by addition of 75 ml of the actual organic solvent. Then 2 ml of 1 M HClO_4 (or HCl, where appropriate) was added. A Gran calibration titration was next performed by addition of 0.1 M NaOH + 1 M NaClO_4 (or NaCl) from a Metrohm burette. (The presence of organic solvent during the calibration was justified, because in some cases the solvent was found to influence slightly the electrode potential.) After each addition the magnetic stirrer was started and the phases thoroughly mixed (without excessive splashing) for at least 2 min or until no drift in the EMF value could be noted during the same time. Then the phases were allowed to separate and the EMF was read off on a Radiometer PHM 64 potentiometer to within ± 0.1 mV. The electrode system consisted of a standard Radiometer combination glass-calomel electrode. For the perchlorate systems the inner solution of the reference half cell had been replaced by 1 M NaClO_4 .

When the equivalence point of the calibration titration had been reached, 25 ml of a solution of HD(R)DTP in the actual organic solvent was added. This solution had previously been shaken three times with portions of ionic medium in order to remove traces of an acidic impurity, which was

found to be formed at prolonged storage of HD(R)DTP. The two phase titration was then performed to the equivalence point by additions of standardized 0.1 M NaOH in 0.9 M of the actual ionic medium, just as described for the calibration. The total amounts of added HD(R)DTP ranged between 1.5 and 4 mmol, corresponding to 15–40 ml 0.1 M NaOH.

EVALUATION METHOD

The determination of the equilibrium quotient ratio k_d/k_a by two-phase titrations is well known and was originally developed by Dyrssen.²⁰ However, a further analysis of the basic assumptions behind such a method should be of considerable interest.

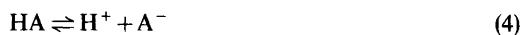
At the moment it will be assumed that (i) the organic acid HA is *not* dimerized in either phase, and (ii) the "apparent $\text{p}k_a$ " = $\log k_d k_a^{-1}$ is not higher than 5, thus allowing us to disregard the influence of water protolysis. The material balances for the A^- and the H^+ ions during a two-phase titration is then given by eqns. (2) and (3), respectively, where

$$n_A = (V_o + v)([\text{HA}] + [\text{A}^-]) + \bar{V}_o[\overline{\text{HA}}] \quad (2)$$

$$n_H - vt_{\text{OH}} = (V_o + v)([\text{HA}] + h) + \bar{V}_o[\overline{\text{HA}}] \quad (3)$$

n_A = number of mmol of A^- added to the system; n_H = total initial amount of H^+ in the system, mmol; V_o = initial volume of aqueous phase, ml; v = added volume of alkaline solution, ml; \bar{V}_o = volume of organic phase, ml; t_{OH} = hydroxyl ion concentration in alkaline titrant solution, M; $[\text{A}^-]$ = actual free concentration of A^- , M; h = actual free hydrogen ion concentration, M. (The bars denote quantities relevant to the organic phase.)

The involved equilibria are the protolysis in the aqueous phase [eqn. (4)] and partition of the acid



between the phases [eqn. (5)].



The thermodynamic equilibrium constants for these reaction are defined as in eqns. (6) and (7), respectively, where the y 's denote the appropriate activity

$$k_a^\circ = y_o[\text{HA}]/y_{\text{H}^+}h[\text{A}^-] \quad (6)$$

$$k_d^\circ = \bar{y}[\overline{\text{HA}}]/y_0[\text{HA}] \quad (7)$$

coefficients on the molar scale. At high, constant ionic strength the activity coefficient quotient of eqn. (6) has been shown to vary very little, even for appreciable changes in ionic medium due to increase in $[\text{A}]$.²¹ One may, therefore, use the conditional concentration quotient k_a , defined by eqn. (8).

$$k_a = k_a^\circ y_{\pm}^{-2} y_0 \quad (8)$$

Unfortunately there are no possibilities to *a priori* assume a similar constant activity coefficient quotient in eqn. (7) during a two-phase titration. Only by keeping the change of ionic medium small enough, say a few percent, one may quite safely use the conditional partition constant k_d , defined according to eqn. (7) as

$$k_d = k_d^\circ y_0 \bar{y}^{-1} \quad (9)$$

Finally, if the A^- and H^+ ions are assumed to be added to the system simultaneously as the acid HA, it follows that $n_{\text{A}} = n_{\text{H}} = n_{\text{HA}}$. Thereby eqns. (2) and (3) may be rearranged to

$$(k_d + \frac{V_0 + v}{V_0}) k_a^{-1} = \frac{n_{\text{HA}} - (V_0 + v)[\text{A}]}{V_0 h [\text{A}]} \quad (10)$$

where $[\text{A}]$ is known from

$$[\text{A}] = \frac{v t_{\text{OH}}}{V_0 + v} + h \quad (11)$$

From eqn. (10) it is seen that a two-phase titration primarily gives the quantity $(k_d + 1)k_a^{-1}$, provided that phase volume ratio θ , ($= \bar{V}_0 / (V_0 + v)$), is kept constant = 1. This approach has been used extensively by Skytte-Jensen.²² It is also clear that when $k_d \gg 1$ and $\theta \approx 1$, any imaginable change of θ during the titration will be of negligible importance and $(k_d + \theta^{-1})k_a^{-1} \approx k_d k_a^{-1}$. On the other hand, when k_d is of about the same order of magnitude as θ , eqn. (10) permits a precise determination of $(k_d + 1)k_a^{-1}$ by extrapolation of $(k_d + \theta^{-1})k_a^{-1}$ to $\theta = 1$. This method will only operate for quite weak acids, when $k_a \lesssim 10^{-2}$. The significant feature of a two-phase titration of a metal extraction reagent is that $(k_d + 1)k_a^{-1}$ is often the only quantity that is needed to calculate the free ligand concentration $[\text{A}]$ of the aqueous phase. Separate values of k_d

and k_a are only necessary when k_d is low and θ is not kept equal to 1 in a series of extraction experiments.

However, the use of eqn. (10) for every single titration point is highly sensitive to the accuracy of the total amount of added HA ($= n_{\text{HA}}$). Careful weighing in of the acid is not sufficient, when the available substance is of limited purity.

Dyrssen²⁰ partly circumvented this problem by using a modified Gran method for determination of the equivalence volume. In his description, the Gran function for a two-phase titration of an acid with strong base is not given, but it can be shown to be eqn. (12), where E is the measured EMF of

$$\psi = \frac{v}{V_0 + v} \times 10^{-E/S} \sim (v_c - v) \quad (12)$$

the glass-reference electrode pair. $S =$ the slope of E vs. $pH = (\eta RT \ln 10)/F$, η being the electrode sensitivity or reversibility. However, ψ is not linear enough to permit any numerical evaluation by linear regression of the equivalence volume v_c . Thus it was found necessary in this work to develop a more elaborate method that permits simultaneous determination of $(k_d + 1)k_a^{-1}$ and v_c from a "linearized" form of eqn. (12).

The free hydrogen ion concentration h is given by the relation (13) where $E_0 =$ standard EMF of

$$E = E_0 + \Delta E_j + \eta \frac{RT \ln 10}{F} \log(y_{\text{H}^+} \cdot h) \quad (13)$$

the electrode pair, V ; $\Delta E_j =$ the change in liquid junction potential of the reference electrode due to variations in ionic medium, V ; $y_{\text{H}^+} =$ activity coefficient of hydrogen ion.

E_0 and the electrode sensitivity η were determined by a standard Gran titration of the strong acid corresponding to the ionic medium (HClO_4 or HCl) followed by a least squares fitting of E vs. $\log h$. The constant term from this evaluation is $E_0' = E_0 + S \log y_{\text{H}^+}$, because y_{H^+} may be regarded as constant²³ for the low h employed for calibration ($h < 5 \times 10^{-3}$ M). η ranged in the interval 0.995–1.005. The liquid junction potential changes almost linearly with the change of ionic medium during the two-phase titrations. In preliminary experiments this change was shown to be given approximately by $\Delta E_j = e_j [\text{A}]$, where $e_j = -10$ to -15 mV M⁻¹ for the actual electrode systems and $[\text{A}] \lesssim 0.1$ M.

Due to the small range of $[A]$ (typically <0.03 M), the influence of E_j on the final result was found to be just barely significant. It may also be noted that the observed change of E_j incorporates the expected but minor variation of y_{H^+} with $[A]$ at constant ionic strength. In the evaluation of $(k_d + 1)k_a^{-1}$ as described below $e_j = -13$ mV M^{-1} was used. h was thereby evaluated by an iterative procedure applied to eqns. (11) and (13).

In a more general case than that discussed above, water protolysis and acid dimerization in the organic phase might be incorporated. Thus eqns. (2) and (3) are replaced by eqns. (14) and (15), respectively. These equations can be combined to give

$$n_A = n_{HA} = (V_o + v)([HA] + [A]) + \bar{V}_o([\overline{HA}] + 2[\overline{(HA)}_2]) \quad (14)$$

$$n_{HA} - vt_{OH} = (V_o + v)([HA] + h - [OH^-]) + \bar{V}_o([\overline{HA}] + 2[\overline{(HA)}_2]) \quad (15)$$

eqn. (16), where k_2 is the dimerization constant and

$$(V_o + v)[A] = n_{HA} - \bar{V}_o \times \left\{ k_d(1 + 2k_2k_dk_a^{-1}h[A]) + \frac{V_o + v}{\bar{V}_o} \right\} k_a^{-1}h[A] \quad (16)$$

$[A]$ this time is given more generally by eqn. (17), where k_w is the dissociation constant of water in the

$$[A] = \frac{vt_{OH}}{V_o + v} + h - k_w h^{-1} \quad (17)$$

actual ionic medium. However, in this work h always was $>10^{-5}$ M and the corresponding term could, therefore, be neglected (*cf.* eqn. 11). A plot of the factor within braces times k_a^{-1} in eqn. (16) *vs.* $h[A]$ (*cf.* eqn. 10) never showed any significant trend, confirming that the dimerization of dialkyl-dithiophosphoric acids is negligible^{5,24} even in nonpolar solvents. Thus eqn. (16) could be simplified to

$$(V_o + v)[A] = n_{HA} - \bar{V}_o(k_d + \theta^{-1})k_a^{-1}h[A] \quad (18)$$

This relation is, of course, the same as given by eqn. (10), but here it is clearly seen that when $(V_o + v)[A]$ is plotted *vs.* $\bar{V}_o h[A]$, a straight line with slope $-(k_d + \theta^{-1})k_a^{-1}$ and intercept n_{HA} is obtained, provided that either $k_d \gg \theta^{-1}$ or θ is constant during the titration. In this work the former

requirement was fulfilled, the most critical case having a k_d at least 50 times as great as θ^{-1} . This quantity varied from about 1.2 to 1.5, but no trend in $(k_d + \theta^{-1})k_a^{-1}$ according to eqn. (10) was ever noted. A similar approach for determination of pK_a 's in single phase systems has been described by Briggs and Steuhr.²⁵

RESULTS

Examples of plots $(V_o + v)[A]$ *vs.* $\bar{V}_o h[A]$ are shown in Figs. (1) and (2). Data for one titration of HBDTP in the system $CCl_4/1$ M $NaClO_4$ are given in Table 1. Least squares fitting of these data according to eqn. (18) gave $(k_d + \theta^{-1})k_a^{-1} = 958 \pm 2$ M^{-1} and $n_{HA} = 3.219 \pm 0.003$ mmol ($\pm \sigma$). Values of $(k_d + \theta^{-1})k_a^{-1}$ for two other titrations were 970 ± 1 and 964 ± 3 M^{-1} . Final result is 964 ± 6 M^{-1} . A summary of the final results is presented in Table 2.

The precision of each titration, as given by the standard deviation of $(k_d + 1)k_a^{-1}$ obtained from the least squares fitting, is certainly not a measure of the total precision. Comparison of several

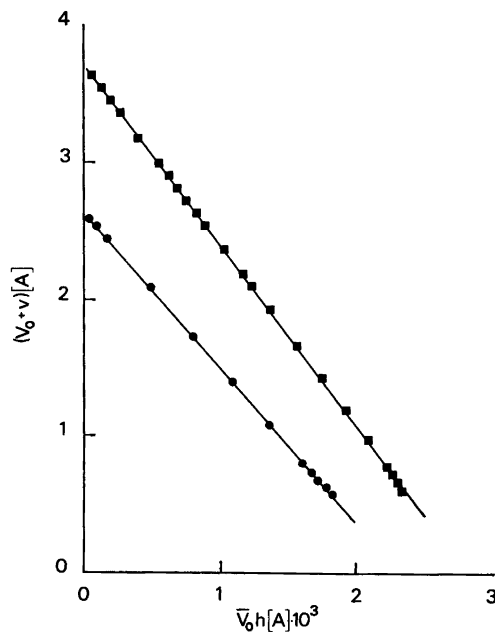


Fig. 1. $(V_o + v)[A]$ *vs.* $\bar{V}_o h[A]$ from titrations of HBDTP (\square) and HMHpDTP (\circ) in the system toluene/1 M $NaClO_4$.

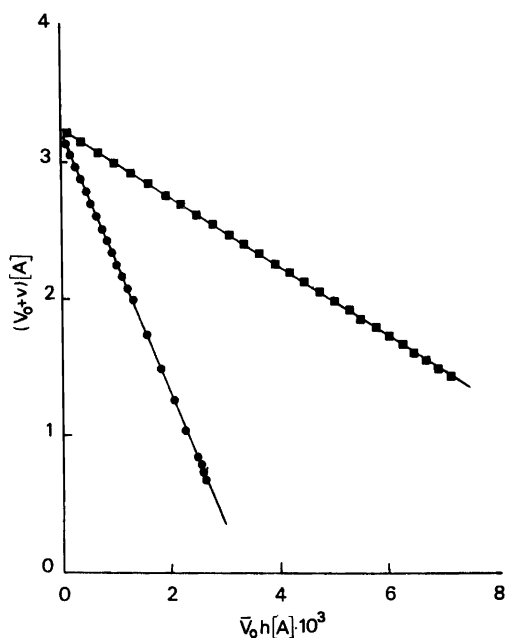


Fig. 2. $(V_0 + v)[A]$ vs. $\bar{V}_0 h[A]$ from titrations of HDBDTP in the systems CCl_4 (O) and $\text{c-C}_6\text{H}_{12}$ (□)/1 M NaClO_4 .

titrations showed good agreement and gave error limits more reasonable as a measure of precision. However, when data from a single titration were evaluated by eqn. (10) with n_{HA} taken from the regression analysis, the standard deviation for the mean $(k_d + 1)k_a^{-1}$ was empirically found to be almost the same as that obtained from the mean of $(k_d + 1)k_a^{-1}$ from different titrations. The single titration precision of $(k_d + 1)k_a^{-1}$ ranged from 0.14 to 0.66 % with a mean of 0.3 %, and the estimated total precision ranged from 0.41 to 2.9 % with a mean of 0.9 %.

In some cases, experimental data for the first few milliliters of the titration showed some scatter in comparison to the expected linear relationship of eqn. (18). These minor discrepancies are probably due to the kinetic behaviour of the system in a state of low buffering capacity. Comparison of several titrations showed no significant influence on the calculated $(k_d + 1)k_a^{-1}$, whether this effect was present or not.

A careful analysis of titration data for HMHpDTP showed that this substance contained an acidic impurity (1–2 mol %) with considerably higher

Table 1. Primary data for a titration of HDBDTP in the system CCl_4 /1 M NaClO_4 . $V_0 = 122.1$ ml, $t_{\text{OH}} = 0.09825$ M, $\bar{V}_0 = 100$ ml, $E'_0 = 366.40$ mV and $\eta = 0.99851$. A plot of $(V_0 + v)[A]$ against $\bar{V}_0 h[A]$ is shown in Fig. (2).

v , ml	E , mV	$\bar{V}_0 h[A] \times 10^3$	$(V_0 + v)[A]$
0.9	229.3	2.644	0.679
1.9	227.0	2.583	0.732
2.9	224.8	2.538	0.789
3.9	222.5	2.474	0.848
6.9	215.6	2.271	1.042
9.9	208.7	2.049	1.258
12.9	201.7	1.807	1.490
15.9	194.5	1.556	1.735
18.9	186.8	1.293	1.988
19.9	184.1	1.206	2.074
20.9	181.1	1.110	2.161
21.9	178.0	1.017	2.247
22.9	174.8	0.926	2.335
23.9	171.5	0.840	2.424
24.9	167.6	0.743	2.512
25.9	163.2	0.644	2.601
26.9	158.6	0.553	2.691
27.9	153.0	0.456	2.780
28.9	146.3	0.360	2.870
29.9	137.6	0.263	2.960
30.9	125.4	0.167	3.051
31.9	103.0	0.072	3.142

Table 2. Summary of results from two-phase titrations of HDBDTP and HMHpDTP.

Organic solvent	$k_d k_a^{-1} \pm \sigma$ M^{-1}	$\log k_d k_a^{-1} \pm \sigma$
HDBDTP; 1 M NaClO_4		
$\text{C}_6\text{H}_5\text{CH}_3$	1313(9)	3.118(6)
CCl_4	964(6)	2.984(6)
$\text{c-C}_6\text{H}_{12}$	251(3)	2.400(10)
C_7H_{16}	125(1)	2.097(10)
$\text{C}_{12}\text{H}_{26}$	87.2(25)	1.94(2)
HDBDTP; 1 M NaCl		
CCl_4	1115(5)	3.047(4)
HMHpDTP; 1 M NaClO_4		
$\text{C}_6\text{H}_5\text{CH}_3$	1133(6)	3.054(4)
CCl_4	779(5)	2.891(6)
C_7H_{16}	93.5(6)	1.971(6)
HMHpDTP; 1 M NaCl		
CCl_4	752(6)	2.876(8)

$\log(k_d + 1)k_a^{-1}$, almost certainly HDHpDTP (*cf.* the experimental procedure). However, the evaluation method employed in this work allows such impurities to be present, just as when ordinary Gran titrations of mixtures of acids are performed. The only provision is a sufficiently great difference in the "apparent pK_a " of the two acids. For HMHpDTP and HDHpDTP, $\Delta \log k_d$ is larger than 3 units and only the last one or two milliliters of the titrations (out of 20–35) were influenced by the presence of HDHpDTP. These data were of course excluded from the evaluation.

Inspection of eqn. (18) shows \bar{V}_o and $(k_d + 1)k_a^{-1}$ to be inversely covariant. This means that the value of \bar{V}_o and its constancy during a titration is very critical. When the molal volume of HDBDTP and HMHpDTP are taken into account, ($\approx 226 \text{ cm}^3 \text{ }^{26}$) \bar{V}_o is found to decrease 0.5 to 0.7 % during a titration. This effect is partially compensated for by the fact that the increase in aqueous phase volume during the titration has the opposite effect on the $(k_d + \theta^{-1})$ factor by the same order of magnitude. A trial calculation incorporating this source of systematic error gave no significant change in the final results. The evaporation of organic solvent may be considered as negligible, due to the use of an almost hermetically sealed titration vessel. The maximum error of h in the ph range of the two phase titrations could be estimated from the calibration procedure to be within $\pm 0.002 \text{ } ph$ units, or corresponding to $\pm 0.1 \text{ mV}$. The accepted total standard deviations may, therefore, be taken as a measure of overall accuracy.

DISCUSSION

Before the work described in this paper was performed, only one study of a similar system was reported in the literature by Zucal, Handley and Dean⁵ in 1963. They studied the distribution of HDBDTP between CCl_4 and a 1 M (Na,H)Cl ionic medium at 25 °C. In order to make a direct comparison possible, this system was included in the present work. These workers report $\log k_d k_a^{-1} \approx \log(k_d + 1)k_a^{-1} = 2.70$ to be compared with the present result of 3.05. However, this great discrepancy may be because Zucal *et al.* evidently used another ph - (or rather pH -) scale in their study.

After the experimental part of this work was completed, a study on the systems HD(R)DTP in benzene (and butanol)/1 M(Na,H)ClO₄ at 22–23 °C

was published by Curtui *et al.*⁶ The value of $\log k_d k_a^{-1}$ for HDBDTP in the benzene system was reported to be 2.38. This is highly surprising, because $\log k_d k_a^{-1}$ for benzene ought to be *higher* than the value for toluene, which in this study was found to be 3.12. However, this discrepancy may again be due to a different choice of concentration-activity relationship for the hydrogen ion: Curtui *et al.* evidently equalled the readings on a pH-meter with $\log h$; no information of the calibration of the pH-scale in the perchlorate medium is presented. (The distribution of HDBDTP was determined by the same method as employed by Zucal *et al.*)

The method used in the present study has given results of considerably higher accuracy than can be obtained by distribution measurements, and with a well-defined thermodynamic reference scale for ionic activities and concentrations.

The constant $(k_d + 1)k_a^{-1}$ might be considered as the "effective extraction constant" of the reagent in a metal chelate extraction system. Its use is, of course, thereby in the calculation of the aqueous free ligand concentration (tracer amount of metal assumed) according to eqn. (19), where \bar{C}_{HA} is the

$$[A] = \frac{\bar{C}_{HA}}{(k_d + \theta^{-1})k_a^{-1}h + \theta^{-1}} \quad (19)$$

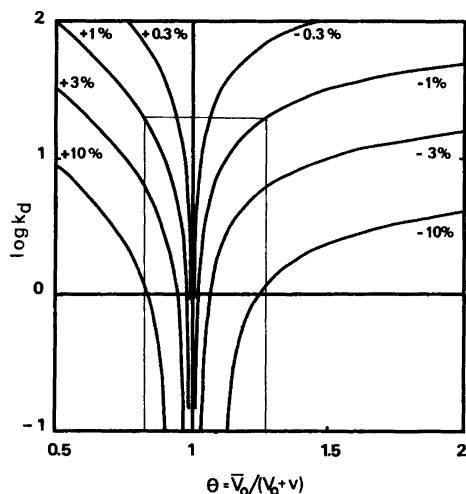


Fig. 3. Lowest permissible $\log k_d$ as a function of θ for several allowed maximum errors in $[A]$ (*cf.* eqn. 20). Example shown: $\log k_d$ is known to be about 1.3. With a maximum allowed error of 1 % in $[A]$, $(k_d + 1)k_a^{-1}$ may still be used, provided θ is kept in the range 0.87 to 1.27

initial molarity of HA in the organic phase. When metal extraction experiments are consistently performed with $\theta=1$, no systematic error is of course to be expected from the use of $(k_d+1)k_a^{-1}$ instead of separate values of k_d and k_a according to eqn. (19).

In titration experiments — using devices like the AKUFVE²⁷, for example — θ may vary considerably during a run. Since $(k_d+1)k_a^{-1}$ is determined more exactly than k_d , one might prefer to use the former value even for cases when k_d is small ($<10^2$). When $(k_d+\theta^{-1})$ is substituted by (k_d+1) in eqn. (19), the relative percentage error in $[A]$ ($\% r_A$) is given by eqn. (20).

$$\% r_A = \frac{100(1-\theta)k_a^{-1}h}{\theta(k_d+1)k_a^{-1}h+1} \quad (20)$$

The maximum error is obtained in the acidic region, where $ph < pk_a$. In Fig. (3) the lowest permissible $\log k_d$ is shown as a function of θ for several allowed maximum errors. It is also seen that for $\log k_d > 2$, the maximum error is always less than 1% for $0.5 \leq \theta < 2$, an interval seldom exceeded in AKUFVE experiments.

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