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Behavior of Dialkyl Phosphorodithioic Acids in Liquid Extraction Systems

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▶ The solubility and acidity of the diethyl, diisopropyl, di-*n*-butyl, and diisobutyl esters of phosphorodithioic acid in water and the distribution of each between CCl_4, methyl isobutyl ketone, or *n*-amyl acetate and HCl-NaCl solutions have been studied. From the data, the acid dissociation constants and the partition coefficients were calculated. No evidence was found for dimerization of dialkyl phosphorodithioic acids in the organic phase. These constants are discussed, together with data for the dialkyl phosphates. The acid dissociation constant is somewhat larger and the partition coefficient is much larger when comparing di-*n*-butyl phosphorodithioic acid with di-*n*-butyl phosphate.

DIALKYL phosphorodithioic acids have been screened in acid media for their selectivity in extraction of metal ions (*7*), but little is known about extractants which contain thiono and thiolo phosphorus groups. Hence, the principal objective of this investigation was to establish the general behavior of several individual esters of this class of reagents. The use of liquid-liquid partition to investigate the equilibria of dialkylphosphorodithioic acids in solution seemed most applicable among methods which have been employed to study similar equilibria in view of the strength of these acids and the ultimate employment of the information to metal extraction systems.

EXPERIMENTAL

Special Reagents. Dialkyl phosphorodithioic acids. Methods for preparation and purification have been described, and commercial sources of the reagents listed (*7*).

Methyl isobutyl ketone, technical grade, was distilled before use.

Apparatus. Extractions were performed with a Burrell wrist-action shaker. pH measurements were made with a Beckman Model G pH meter which had been calibrated with a phthalate buffer (pH = 4.01 at 25° C.) and checked against a 0.1*N* HCl buffer (pH = 1.10) which contained an appropriate quantity of NaCl to adjust the ionic strength.

Titrations were performed with microsyringe pipets, 0.5- and 1.0-ml. capacity.

Procedure. Equal volumes, 5 ml., of both phases were contacted for a period of 2 hours at 25° C. Phase separation was assisted by centrifugation at 2000 r.p.m. for 10 minutes. The acid concentration in the aqueous phase was determined from a pH measurement or, when $[H^+] > 0.1M$, by an alkalimetric titration. An extractive two-phase method was employed with the organic phase. The concentration of phosphorodithioic acid was determined by an iodometric titration (*3*, *4*).

The change in volume due to mutual solubility of the solvents can be neglected for the system CCl_4–water and, although it is about 5% for methyl isobutyl ketone–water and *n*-amyl acetate–water, corrections were not attempted.

Reagent Solubility in Aqueous Media. The solubility of di-*n*-butyl phosphorodithioic acid as a function of HCl or NaCl concentration was obtained by saturating the aqueous phase with the pure reagent during a shaking period of 1 hour at 30° C. Results are shown in Figure 1. The solubility of the diisobutyl ester was determined also in HCl medium; results superimposed essentially on the curve for the di-*n*-butyl ester.

Dependency of Distribution Ratio on Concentration of Reagent in Organic Phase. Two methods were suggested by Dyrssen (*5*) to establish whether dimerization of the reagent occurred in the organic phase and, incidentally, to determine the partition coefficient, $P_r = [HR]_o/[HR]$ of the reagent between the aqueous and organic phases when the acid dissociation constant is known. The subscript *o* signifies the organic phase.

In one case, the hydrogen ion concentration established by the reagent distributing between an organic solvent and an aqueous solution of a univalent salt of a strong acid is plotted as a function of reagent concentration in the organic phase, C_{org}. For such a system,

$$C_{org} = 2\ K_2\ (P_r/K_a)^2([H^+][R^-])^2 + (P_r/K_a)[H^+][R^-]$$

where K_2 is the dimerization constant of the reagent in the organic phase and K_a is the acid dissociation constant in water saturated with the organic solvent. A plot of log C_{org} *vs.* log $[H^+][R^-]$ is shown in Figure 2 for solutions of di-*n*-butyl phosphorodithioic acid shaken with an equal volume of 1*M* NaCl. For each of the organic solvent–water systems the points fell reasonably close to the straight line drawn with a slope equal to one although considerable scatter prevailed. A slope of one implies that the reagent exists only as a monomer in the organic phase and the term involving the dimerization constant may be neglected. Subsequent data will lend further support.

In the second case, the distribution ratio, *D*, of the reagent between the particular organic solvent and an aqueous solution of HCl was studied as a function of total reagent concentration. For such a system,

$$D = 2\ K_2\ (P_r/\phi)^2\ C_{aq} + P_r/\phi$$

where $\phi = 1 + K_a/[H^+]$. On double logarithmic coordinates, a plot of *D vs.* the equilibrium concentration of reagent in the aqueous phase, C_{aq}, for a series of fixed HCl concentrations, gives a series of horizontal lines as shown

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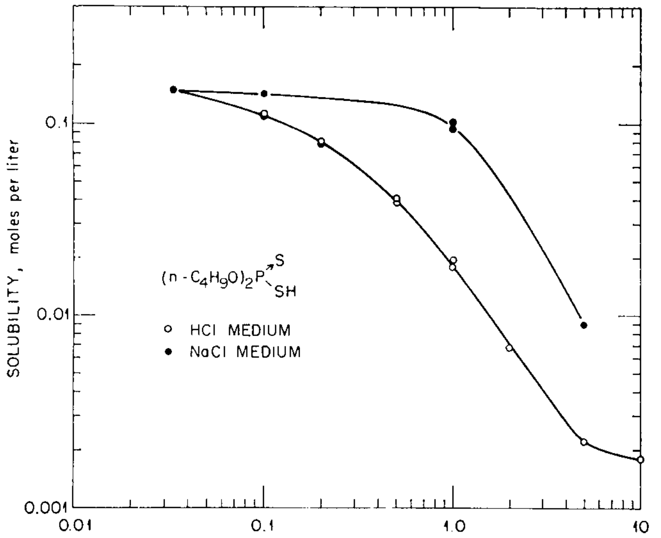

Figure 1. Solubility of di-*n*-butyl phosphorodithioic acid in HCl and NaCl media at 30° C.

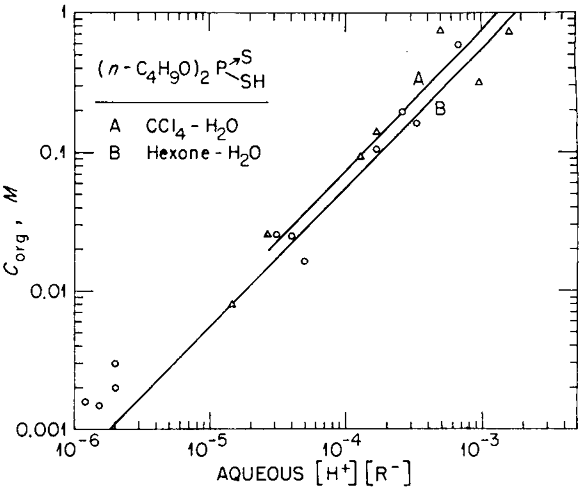

Figure 2. Distribution of di-*n*-butyl phosphorodithioic acid between an organic solvent and an aqueous solution 1.0*M* in NaCl

Solvent pairs: A, CCl_4–water; B, methyl isobutyl ketone–water

in Figure 3. The distribution ratio is independent of C_{aq} which once again indicates that no perceptible dimerization occurs in the organic phase for the di-*n*-butyl ester.

Acid Dissociation Constant and Partition Coefficient. For systems in which only one associated molecular species is formed and partitions, and no higher species are formed in either phase, the equilibria involved are the acid dissociation constant and the partition coefficient of the molecular species. The distribution ratio is given by:

$$D = [HR]_o([HR] + [R^-])^{-1}$$

and by appropriate substitution:

$$1/D = 1/P_r + K_a/P_r[H^+] \text{ or}$$
$$D = P_r(1 + K_a/[H^+])^{-1}$$

A plot of $1/D$ *vs.* $1/[H^+]$ is shown in Figure 4 for the diethyl ester. For the longer chain esters the intercepts become very small values and involve a long graphical extrapolation, an indication that the partition coefficients are large numbers.

On double logarithmic coordinates, a plot of D *vs.* $[H^+]$ provided two limiting conditions. On the plateau, $D = P_r$. Extrapolation of the two linear branches of the curve to their intersection gives K_a. In addition, the ratio P_r/K_a is given by $1/[H^+]$ when $D = 1$ and $P_r >> 1$. Data for the diethyl, diisopropyl, di-*n*-butyl, and diisobutyl esters are shown in Figure 5 for the system, CCl_4–water. Data for the di-*n*-butyl ester in two additional solvent systems are shown in Figure 6. The solid line drawn through each set of points represents the distribution ratio with the values of K_a and P_r from Table II inserted in the above expression.

Influence of Salt Concentration. Certain peculiarities observed in metal extraction systems when high concentrations of electrolytes were present in weakly acid solutions prompted a study of the influence of NaCl upon the distribution ratio of the di-*n*-butyl phosphorodithioic acid. Results are shown in Table I for the system CCl_4–0.05*M* HCl. Comparable data were obtained with the methyl isobutyl ketone–aqueous HCl system. Low concentrations of sodium chloride, 0.2*M*, depressed significantly the distribution ratio of the reagent for all reagent concentrations, whereas higher concentrations increased markedly the

Table I. Influence of Electrolyte Concentration on Distribution Ratio of Di-*n*-butyl Phosphorodithioic Acid

[HR] total, *M*	[HCl], *M*	[NaCl], *M*	Distribution ratio
0.90	0.05	...	35
	0.05	0.2	22
	0.05	2.0	120
0.20	0.05	...	27
	0.05	0.2	9
	0.05	2.0	85
0.045	0.05	...	18
	0.05	0.2	4
	0.05	2.0	73
0.0052	0.05	...	10
	0.05	0.2	0.9
	0.05	2.0	58
0.00064	0.05	...	28
	0.05	0.2	0.5
	0.05	2.0	100
0.172	None	1.0	14
	None	2.0	21
	None	5.0	94

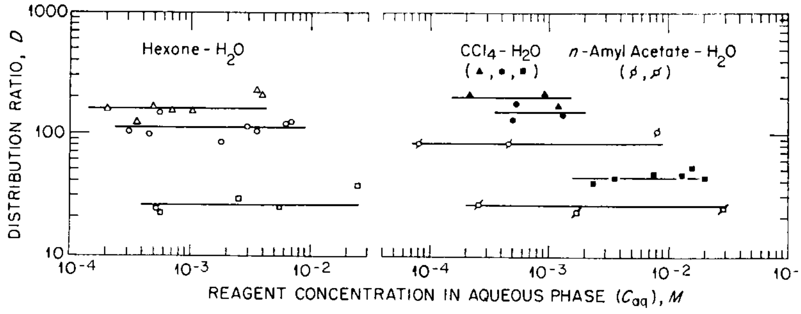

Figure 3. Distribution ratio of di-*n*-butyl phosphorodithioic acid between different pairs of solvents as a function of HCl concentration in the aqueous phase

Triangles, 1.0*M* HCl; circles, 0.5*M* HCl; squares, 0.1*M* HCl

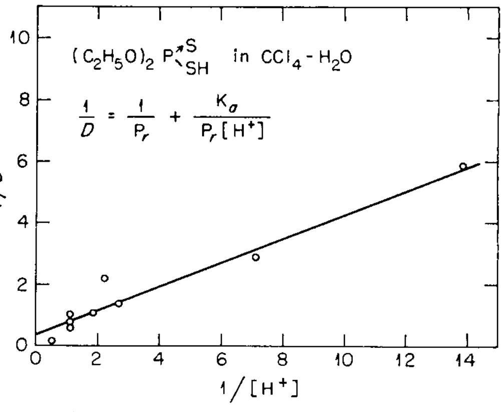

Figure 4. Distribution of diethyl phosphorodithioic acid in CCl_4–water system

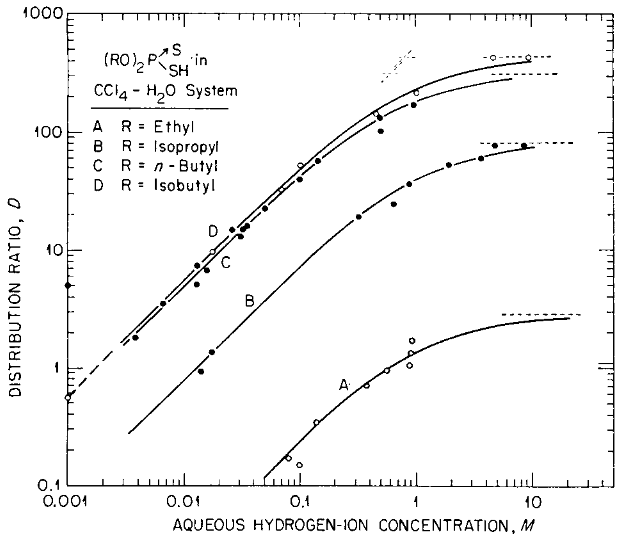

Figure 5. Distribution ratio of various dialkyl phosphorodithioic acids between CCl$_4$ and water as a function of hydrogen ion concentration in the aqueous phase

Curve A, diethyl ester; curve B, diisopropyl ester; curve C, di-*n*-butyl ester; curve D, diisobutyl ester

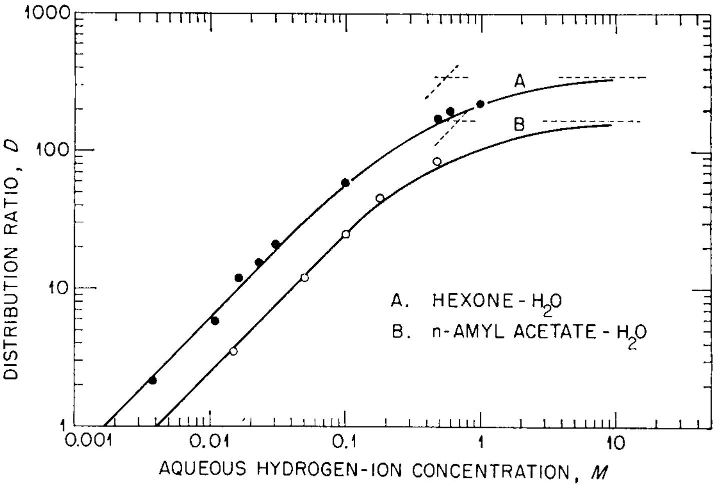

Figure 6. Distribution ratio of di-*n*-butyl phosphorodithioic acid between solvents as a function of hydrogen-ion concentration in aqueous phase

Curve A, methyl isobutyl ketone-water; curve B, *n*-amyl acetate-water

distribution ratio. As the reagent concentration decreased, the effect of increased salt concentration became more marked. Results would indicate extensive solvation of the reagent by water molecules in the aqueous phase and, in fact, Bode and Arnswald (*3*) reported a stable trihydrate sodium salt.

DISCUSSION

The dialkyl phosphorodithioic acids are quite strong acids. Because of this fact, it was impossible to maintain a constant, but low, ionic strength in the aqueous phase. At high concentrations of hydrogen ion the experimental points showed some scatter. However, the use of three different solvent systems provided a check upon the experimental value of the acid dissociation constant. From the data shown in Figures 2 through 6, values for K$_a$ and P$_r$ were selected which provided the most coherent fit with the experimental data. These values are collected in Table II. Because we are dealing with two phases at equilibrium, the values of the acid dissociation constants refer to an aqueous phase which has been saturated with an organic solvent; similarly, the partition coefficient of the reagent refers to the ratio of the concentration of HR in an organic phase saturated with an aqueous phase to the concentration of HR in an aqueous phase saturated with an organic phase. This stipulation must be borne in mind when comparing values obtained in different pairs of solvent. The more accurate measurements of the distribution ratio are naturally those for which *D* equals, or is not far removed from, unity. Thus, values of *D* = 1 (denoted pH$_{1/2}$ in metal extraction systems) are more readily determinable than the individual values of P$_r$ or K$_a$ to which it is related by the expression:

$$\mathrm{pH}_{1/2} = \mathrm{pK}_a + \log \mathrm{P}_r$$

Fortunately, it is the ratio P$_r$/K$_a$ which is actually required in expressions dealing with metal extraction systems.

Perusal of Table II indicates only a small change in the acid dissociation constant among the several dialkyl esters, but a very large change in the partition coefficients. Each increases in the order: diethyl < diisopropyl < di-*n*-butyl < diisobutyl. From the limited number of esters studied, it appears that chain branching among isomers brings about an increase in the value of the partition coefficient and the acid dissociation constant. Among the solvent pairs employed, CCl$_4$–water and methyl isobutyl ketone–water behaved alike; but in *n*-amyl acetate–water the reagent shows a slightly smaller value for the partition coefficient.

Table II. Characteristic Constants for Dialkyl Phosphorodithioic Acids

(Ionic strength = 1.0 except when [H$^+$] > 1*M*)

Alkyl group	Solvent system	pH$_{1/2}$	log P$_r$	pK$_a$
Ethyl	CCl$_4$-water	0.35	0.45	−0.10
Isopropyl	CCl$_4$-water	1.89	1.90	0.00
n-Butyl	CCl$_4$-water	2.70	2.52	0.22
	Methyl isobutyl ketone–water	2.77	2.54	0.25
	n-Amyl Acetate–water	2.40	2.23	0.18
Isobutyl	CCl$_4$-water	2.74	2.63	0.10

The dialkyl phosphorodithioic acids are somewhat stronger than are the dialkyl phosphates. Dyrssen (*5*) reported pK$_a$ = 1.00 for di-*n*-butyl phosphate as compared with 0.22 for the dithioic acid ester. On comparing the partition coefficients for the two classes of reagents, wherein Dyrssen and Liem (*6*) reported for the dibutyl phosphate a value log P$_r$ = 0.34 in CHCl$_3$ and log P$_r$ = 1.36 in methyl isobutyl ketone, the partition coefficients for the dithioic acids are an order of magnitude larger, a major difference between the two classes of reagents.

No evidence for dimerization in the organic phase was detected in this study, a second major difference. Hydrogen bonding involving the thiol group has been reported from infrared studies in concentrated solutions of dithioic acids in CCl$_4$ (*1*). However, frequencies assigned to the P → S group remain constant only if the immediate environment of the phosphorus atom or thiono group does not change. Dyrssen and Liem (*6*) pointed out that an increase in the partition coefficient seems to be combined with a decrease in the dimerization constant for di-*n*-butyl phosphate. Many solvents conform to the relationship, K$_2$P$_r^2$ = 5 × 10^3. If true here, K$_2$ ≤ 0.08 (methyl isobutyl ketone) and ≤ 0.05 (CCl$_4$). If association does occur, it must be slight in the dilute solutions employed. Furthermore, the degree of association of dialkyl phosphates has been found to exceed that of dialkyl phosphorothioates (*8*). According to cryoscopic data (*2*, *9*), the molecular weight of diethyl and di-*n*-butyl phosphorodithioic acids in benzene does not depend on concentration, in the range permitted by the method, and agrees with the theoretical value of the monomer.

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