

The Liquid Distribution of Diethyl Phosphate (DEP)

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The distribution of diethyl phosphate, DEP (= HA), between a number of organic solvents and perchlorate solutions of different compositions was studied with ³²P-labelled DEP at 25°C.

By variation of [H⁺] in the aqueous phase we determined with methylisobutylcarbinol (hexol) as the organic phase: $\log K_a = \log [H^+][A^-]/[HA] = -0.73$ for both 0.1 M and 1 M (H,Na)ClO₄; $\log K_d = \log [HA]_{org}/[HA] = 0.35$ for 0.1 M and 0.41 for 1 M (H,Na)ClO₄.

From a similar study with methylisobutylketone we obtained, using $\log K_a = -0.73$, $\log K_d = -0.67$ for 0.1 M and -0.56 for 1 M (H,Na)ClO₄.

By variation of the concentration of DEP we obtained the following dimerization constants, $K_2 = [H_2A_2]_{org}[HA]_{org}^{-2}$, and distribution constants, K_d (aq. phase 1 M (H,Na)ClO₄): isopropyl ether ($\log K_2 = 2.19$; $\log K_d = -1.75$), chloroform (4.46; -2.05), nitrobenzene (3.61; -2.14). For benzene we could only obtain $\log K_2 K_d^2 = -0.49$.

From a study of the distribution of DEP between carbon tetrachloride and 0.1 M HClO₄ as a function of [B]_{org}, we calculated $\log K_B K_d = \log [HAB]_{org}/[B]_{org}[HA] = -0.91$ for B = tributylphosphate (TBP) and -0.75 for B = hexol.

The present data are compared with previous work¹⁻³ on dibutylphosphate (DBP) and it is found that K_2 is about the same for both acids, but K_d is 70-250 times smaller for DEP depending on the solvent. The effect of CH₂ groups on the distribution of acids is discussed.

The study of complex formation reactions between H₃PO₄ and metal ions in acid solutions is often obscured by the fact that both polynuclear and acidic complexes may be formed. The equilibria should be less complicated if one or two of the hydrogens in H₃PO₄ are replaced by alkyl groups. In this paper we studied the distribution and acid-base properties of diethylphosphoric acid, (C₂H₅O)₂POOH (DEP). We hope to use this acid for later studies dealing with the formation of metal complexes.

The investigation was conducted in a manner similar to our previous studies^{1,2} on dibutylphosphate, (C₄H₉O)₂POOH (DBP). The dimerization, distri-

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bution, and dissociation constants were determined in the same media as employed with DBP in order to see whether there is a effect on the different equilibria by changing the alkyl group.

EXPERIMENTAL

The quality of most chemicals has been described before.^{1,2} The benzene (Merck-Darmstadt) and nitrobenzene (Stockholms Gasverk) were of analytical grade and were not further purified.

The radioactive DEP labelled with ³²P was purchased from the Radiochemical Centre Amersham, England. It contained about 1 % of non-acidic radioactive material, which was detected by carrying out the extraction with the different solvents at pH 6 where practically no DEP is extracted. Corrections were made for this contamination.

The inactive DEP was kindly provided by Docent Lennart Larsson at the Swedish Research Institute of National Defence, Dept 1, Sundbyberg 4. It was obtained by controlled hydrolysis of diethyl phosphoryl chloride with NaOH. The result was a neutral solution of 1 M DEP (sodium salt) containing 1 M of NaCl. The chloride was removed by precipitation with AgClO₄. The molarity of the DEP solution was checked by determining [Cl⁻] as AgCl and [Na⁺] by filtering a known volume of the solution through a cation-exchange in hydrogen form and taking [A⁻] as 2[H⁺] - [Cl⁻] = 0.983 M.

All experiments were carried out at 25°C as described in our previous papers.^{1,2} In most cases, however, [H⁺] was calculated from the known amount of HClO₄ added.

RESULTS

Determination of pK_a. The pK_a of DBP was determined previously² by measuring the distribution of DB³²P between chloroform or hexone and 0.1 M or 1 M (H,Na)ClO₄ solutions as a function of [H⁺]. Since the distribution constant, K_d, of HA was found to be much lower for DEP it was considered more favorable to choose methylisobutylcarbinol (hexol) for the organic layer. Our results are given in Table 1 and plotted in Fig. 1 as log q against log [H⁺].

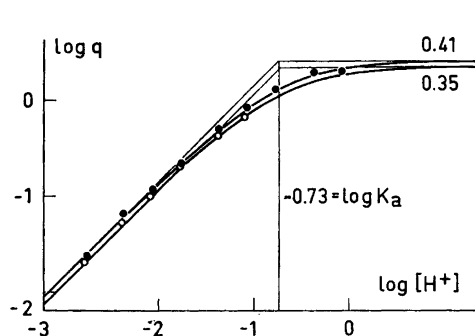


Fig. 1. Distribution of DEP between hexol and 1 M (Na,H)ClO₄ (●) or 0.1 M (Na,H)ClO₄ (○) as a function of the acidity. The normalized curve $Y = -\log(1 + v)$, $X = -\log v$ has been fitted to the data. The point of intersection of the asymptotes gives log K_a and log K_d (cf. Fig. 7, Ref.²). The data are given in Table 1.

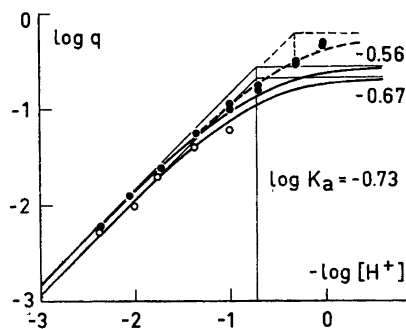


Fig. 2. Distribution of DEP between hexone and 1 M (Na,H)ClO₄ (●) or 0.1 M (○) as a function of the acidity. The normalized curve $Y = -\log(1 + v)$, $X = -\log v$ is fitted to the data using pK_a = 0.73 from the experiments with hexol. The dashed lines refer to a fit discussed in the text.

Table 1. Distribution of DEP between hexol and 1 M or 0.1 M (H,Na)ClO₄ solutions. Initial conc. of DEP in the aqueous layer was 1.89×10^{-5} M. Data are given as $\log q(-\log [H^+])$.

1 M: 0.301 (0.07), 0.286 (0.36), 0.119 (0.76), -0.066 (1.06), -0.304 (1.36), -0.648 (1.75), -0.920 (2.06), -1.176 (2.36), -1.621 (2.75).
 0.1 M: -0.170 (1.09), -0.365 (1.37), -0.688 (1.78), -0.987 (2.08), -1.270 (2.38), -1.669 (2.77).

Table 2. Distribution of DEP between hexone and 1 M or 0.1 M (H,Na)ClO₄ solutions. Initial conc. of DEP in the aqueous layer was 1.89×10^{-5} M. Data are given as $\log q(-\log [H^+])$.

1 M: -0.298, -0.322 (0.01), -0.498, -0.530 (0.30), -0.761, -0.798 (0.70), -0.950, -0.991 (1.00), -1.264 (1.36), -1.619 (1.75), -1.910 (2.06) -2.222 (2.36).
 0.1 M: -1.221 (1.01), -1.404 (1.38), -1.703 (1.77), -2.014 (2.01), -2.288 (2.38)

As before² the normalized curve $Y = -\log(1 + v)$, $X = -\log v$ was fitted to the data giving at the point of intersection of the asymptotes to the curve: $\log K_d = 0.35$ for 0.1 M and 0.41 for 1 M (H,Na)ClO₄ and $-\log [H^+] = 0.73 = -pK_a$ for both media.

Using this value of pK_a we could not obtain a good fit for the distribution of DEP between hexone and 1 M (H,Na)ClO₄ in the cases where most of the Na⁺ was replaced by H⁺ (see Fig. 2; the data are given in Table 2). In fact if only these data had been available we would have calculated a pK_a of 0.32 (dashed fit in Fig. 2), a value which does not at all agree with conductometric work.^{4,5} We therefore assumed that the hexol data were correct and that the hexone data for 1 M ClO₄⁻ were only reliable when $[H^+] \leq 0.1$ M. The fit with $pK_a = 0.73$ then gave $\log K_d = -0.67$ for 0.1 M and -0.56 for 1 M (H,Na)ClO₄.

Determination of K_d and K_2 . The values of the distribution constants K_d and the dimerization constants K_2 were determined by measuring the distribution of DE³²P at different total concentrations of DE³²P + inactive DEP. The aqueous phase was 1 M (H,Na)ClO₄. The primary data for the solvents isopropylether, chloroform, nitrobenzene are given in Table 3.

Table 3. Distribution of DEP at 25°C between various solvents and 1 M (H,Na)ClO₄ aqueous solutions for different initial concentrations of DEP in the aqueous layer (C_A). Equal volumes (15 ml) of both phases.

Isopropylether: $\log C_A (\log q, \log [H^+])$: -2.862(-1.826, -0.01), -2.365(-1.820, -0.01), -2.170(-1.817, -0.02), -1.870(-1.844, -0.02), -1.569(-1.772, -0.04), -1.172(-1.718, -0.07), -0.871(-1.659, -0.15).

Chloroform: $\log C_A (\log q, \log [H^+])$: -4.547(-2.167, -0.32), -4.547(-2.154, -0.01), 2.862(-1.920, -0.01), -2.565(-1.721, -0.01), -2.170(-1.602, -0.02), -1.870(-1.309, -0.02), -1.569(-1.091, -0.03), -1.171(-0.759, -0.07), -0.871(-0.498, -0.15).

Nitrobenzene: $\log C_A (\log q, \log [H^+])$: -2.842(-2.164, -0.03) -2.554(-2.160, -0.03), -2.260(-2.119, -0.03) -2.166(-2.156, -0.03), -1.868(-1.923, -0.05), -1.569(-1.853, -0.06) -1.171(-1.643, -0.10), -0.870(-1.376, -0.18)

Benzene: $\log C_A (\log q, \log [H^+])$: -2.260(2.622, -0.03), -1.868 (-2.298, -0.05), -1.569(-1.967, -0.06), -1.171(-1.572, -0.10), -0.871 (-1.236, -0.18)

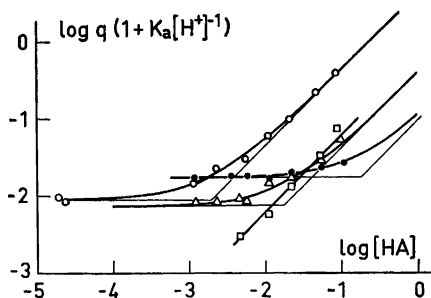


Fig. 3. Determination of $\log K_d$ and $\log K_a$ for DEP and the following organic solvents: chloroform (O), benzene (\square), nitrobenzene (\triangle) and isopropyl ether (\bullet). The curves and lines are explained in the text. The primary data are given in Table 3.

As previously shown for DBP, the net distribution ratio of DEP is

$$q = \frac{2[\text{H}_2\text{A}_2]_{\text{org}} + [\text{HA}]_{\text{org}}}{[\text{HA}] + [\text{A}^-]} = \frac{2K_2K_d^2[\text{HA}] + K_d}{1 + K_a[\text{H}^+]^{-1}}$$

As $[\text{H}^+]$ was not constant in the present experiments we plotted $\log q(1 + K_a[\text{H}^+]^{-1})$ against $\log [\text{HA}]$ in Fig. 3; with equal phase volumes (15 ml) $[\text{HA}]$ was calculated from the known initial concentration of DEP in the aqueous phase (C_A):

$$[\text{HA}] = C_A (1 + q)^{-1}(1 + K_a[\text{H}^+]^{-1})^{-1}$$

The normalized curve, $Y = \log(1 + v)$, $X = \log v$, was fitted to the data as in the same manner as with DBP, and the values of $\log q(1 + K_a[\text{H}^+]^{-1})$ and $\log [\text{HA}]$ at the point of the intersection between the two asymptotes to the curve, $Y = 0$ and $Y = X$, gave $\log K_d$ and $-\log 2K_2K_d$.

From Fig. 3 we obtained the following values:

Organic solvent	$\log K_d$	$\log 2K_2K_d$
Isopropylether	-1.75	+ 0.74
Chloroform	-2.05	+ 2.71
Nitrobenzene	-2.14	+ 1.77

For benzene we could only determine $\log 2K_2K_d^2 = -0.19 \pm 0.07$. The values of q at lower $[\text{HA}]$ were too small and thus unreliable, in part because of the correction that was made for the non-acidic radioactive impurity present.

Determination of $K_B K_d$ for TBP or hexol in carbon tetrachloride. In our previous work ^{1,2} we showed that TBP (tributylphosphate) and DBP formed a 1:1 complex in carbon tetrachloride or chloroform at low concentrations of DBP. From a study ⁶ of the influence of hexol on the extraction of Y^{3+} with DBP in chloroform it was further concluded that hexol and DBP form a 1:1 complex.

Using the same technique as previously, we studied the distribution of DE^{32}P between solutions of TBP or hexol in carbon tetrachloride and 0.1 M HClO_4 as a function of the concentration of TBP or hexol (denoted in the formulas as B) in the organic layer. The data are given in Table 4.

Table 4. Distribution of DEP between CCl_4 and 0.0985 M HClO_4 for different concentrations of TBP or hexol in the organic layer. The initial conc. of DEP in the aqueous layer was 4.72×10^{-5} M. The data are given as $\log q(\log[\text{TBP}]_{\text{org}}$ or $\log[\text{hexol}]_{\text{org}})$.

TBP: $-3.179(-1.876)$, $-2.651(-1.477)$, $-2.558(-1.176)$, $-2.319(-0.876)$, $-2.116(-0.699)$, $-1.877(-0.477)$, $-1.527(-0.176)$, $-1.300(0)$
 Hexol: $-3.130(-1.908)$, $-2.802(-1.480)$, $-2.431(-1.176)$, $-2.010(-0.873)$, $-1.829(-0.699)$, $-1.456(-0.477)$, $-1.012(-0.176)$, $-0.857(0)$

As the concentration of DEP was low in both phases (the initial value in the aqueous layer was 4.72×10^{-5} M) we assumed that there were no dimeric species (H_2A_2) present with $[\text{B}]_{\text{org}} > 0.001$ M. The experiments show that $\log q/[\text{B}]_{\text{org}}$ was practically constant except for concentrations of hexol above 0.3 M, where $q/[\text{B}]_{\text{org}}$ was somewhat larger (HAB_2 might be formed). This indicated that the distribution ratio could be expressed as

$$q = \frac{[\text{HAB}]_{\text{org}}}{[\text{HA}] + [\text{A}^-]} = K_{\text{B}}K_{\text{d}}[\text{B}]_{\text{org}}(1 + K_{\text{a}}[\text{H}^+]^{-1})^{-1}$$

or at $[\text{H}^+] = 0.1$ M

$$\log q/[\text{B}]_{\text{org}} = K_{\text{B}}K_{\text{d}} - 0.46$$

From the data in Table 4 we calculated for TBP: $\log K_{\text{B}}K_{\text{d}} = -0.91 \pm 0.05$ and for hexol: -0.75 ± 0.08 ; the difference in $\log K_{\text{B}}$, 0.16 ± 0.10 is small. Unfortunately $\log K_{\text{d}}$ for CCl_4 was too small to be measured with any accuracy.

DISCUSSION

The value of pK_{a} . Our values of pK_{a} in 0.1 M NaClO_4 are 0.73 for DEP and 1.00 for DBP. We have recalculated conductometric data of Drushel and Felty⁴ using the Onsager relation $\Lambda = \Lambda^\circ - (59.86 + 0.2277 \Lambda^\circ)\sqrt{c}$ to correct for the influence of the ionic concentration on the conductance. Furthermore, as the dialkyl phosphoric acids are rather strong acids, $\Lambda^\circ = 380$ was obtained by extrapolation of Λ against \sqrt{c} . The following data were obtained by successive approximations:

	$(\text{CH}_3\text{O})_2\text{POOH}$	$(\text{C}_2\text{H}_5\text{O})_2\text{POOH}$	$(\text{C}_3\text{H}_7\text{O})_2\text{POOH}$
$C = 1/8$ M			
$[\text{H}^+] = [\text{A}^-]$	0.00985	0.0879	0.0839
$[\text{H}^+][\text{A}^-]/[\text{HA}]$	0.366	0.208	0.171
pK_{a}°	0.61	0.86	0.94
$C = 1/16$ M			
$[\text{H}^+] = [\text{A}^-]$	0.0526	0.0493	0.0479
$[\text{H}^+][\text{A}^-]/[\text{HA}]$	0.280	0.184	0.157
pK_{a}°	0.70	0.88	0.95

K_{a}° are the dissociation constants corrected to zero ionic strength by using activity factors given by Kielland.⁷ The corresponding pK_{a}° values determined from our data are 0.90 (DEP) and 1.17 (DBP). As seen from Fig. 4

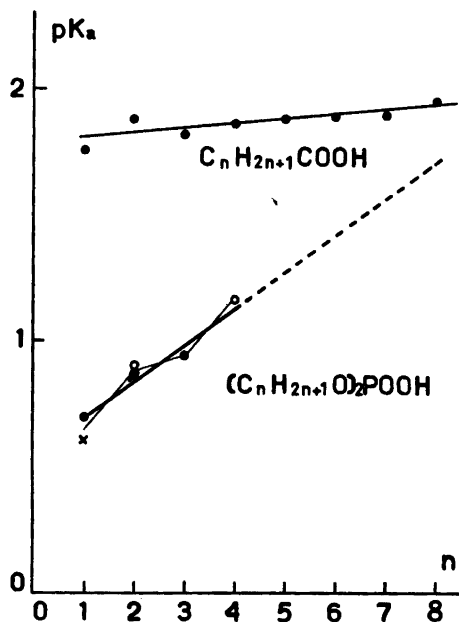


Fig. 4. Values of pK_a° for dialkyl phosphoric acids and $pK_a^\circ - 3$ for fatty acids as a function of the number of carbon atoms in the alkyl groups. pK_a° for HCOOH is 3.751 and for H_3PO_4 2.124.

the agreement between these sets of data is acceptable. Conductometric measurements of DEP by van Hove⁵ seem to be less accurate than the determinations by Drushel and Felty.⁴ Values of pK_a by Kumler and Eiler⁸ seem definitely to be too high.

Dippy has measured pK_a° conductometrically for many carboxylic acids. In Fig. 4 we have plotted his data¹⁰ for the fatty acids as a function of the number of carbon atoms attached to the COOH groups. The influence of the *n*-alkyl groups on pK_a° is larger for the dialkyl phosphoric acids.

The values of $\log K_a$ and $\log K_2$. If the distribution curves for DEP in Fig. 3 and for DBP in Fig. 1 in Ref.¹ are compared, it is obvious that the curves for DEP lie in a much less favorable region of $\log q$. It was thus not possible to obtain any reliable data for hexane, and $\log K_a$ could not be determined for carbon tetrachloride and benzene with any accuracy. Neither could the $\log K_2$ be determined in hexone.

However, data collected in Table 5 show that $\log K_a$ is considerably lower for DEP than DBP, but that $\log K_2$ is not altered very much if the butyl groups are replaced by ethyl groups.

The effect of CH_2 groups on distribution of acids. It was shown previously² for the distribution of fatty acids between chloroform and water that K_a was increased approximately by a factor of 4 for each CH_2 -group added. An increase of the hydrocarbon chain with 4 CH_2 -groups should then increase $\log K_a$ by 2.40. We obtained 2.39 for DEP and DBP (Table 5) and conclude therefore that *irrespective of whether the hydrocarbon chain is attached to the aqueous lattice through a COOH group or a POOH group, $\Delta \log K_a$ (chloroform/water) = 0.6*

Table 5. Distribution and dimerization constants for DBP and DEP.

Organic solvent	(RO) ₂ POOH	log K _d	log K ₂	log K ₂ K _d ²	aq. phase	Ref.	Δlog K _d	Δlog K ₂	Δlog K ₂ K _d ²
Hexol	DBP	2.21	<-1	-	0.1 M HNO ₃	1	1.86	-	-
	DEP	0.35	-	-	0.1 M (Na ₂ H)ClO ₄	this work			
	DEP	0.41	-	-	1 M "				
Hexone	DBP	1.36	1.19	3.91	0.1 M (Na ₂ H)ClO ₄	2	2.03	-	-
	DBP	1.49	-	-	1 M "	2	2.05	-	-
	DEP	-0.67	-	-	0.1 M "	this work			
	DEP	-0.56	-	-	1 M "	" "			
	DEP	-0.52	2.29	3.33	0.1 M HNO ₃	1	2.27	0.10	4.64
Isopropylether	DBP	-1.75	2.19	-1.31	1 M (Na ₂ H)ClO ₄	this work			
	DEP								
Chloroform	DBP	0.34	4.48	5.16	0.1 M (Na ₂ H)ClO ₄	2	2.39	0.15	4.73
	DBP	0.34	4.21	4.89	0.1 M HClO ₄	9			
	DBP	0.34	-	-	1 M (Na ₂ H)ClO ₄	2			
	DBP	0.28	4.36	4.92	1 M HClO ₄	9			
	DBP	0.24	4.61	5.09	0.1 M HNO ₃	1			
	DEP	-2.05	4.46	0.36	1 M (Na ₂ H)ClO ₄	this work			
	DEP								
Nitrobenzene	DBP	-0.14	3.55	3.27	1 M HNO ₃	9	2.00	-0.06	3.94
	DEP	-2.14	3.61	-0.67	1 M (Na ₂ H)ClO ₄	this work			
Benzene	DBP	-0.42	4.88	4.04	1 M HNO ₃	9	-	-	4.53
	DEP	-	-	-0.49	1 M (Na ₂ H)ClO ₄	this work			

per CH₂ added. The free energy for distortion of the aqueous lattice around one CH₂-group may, however, be taken as 1.364 × 0.6 kcal/mole only if the attraction of the CH₂-group to the chloroform and water molecules due to van der Waals forces are comparable. The volume of the CH₂-groups should not be very different from the volume of a H₂O molecule.

For isopropylether we obtained $\Delta \log K_d = 2.27 \approx 4 \times 0.57$ for DBP—DEP which is not very different from the value for chloroform. Using diethyl ether Collander¹¹ found $\Delta \log K_d = 0.57$ per CH_2 -group for acetic acid to hexoic (caproic) acid. For the dicarboxylic acids, which can be attached to the aqueous lattice at two different points, Collander¹¹ found that $\Delta \log K_d$ increased with the length of the hydrocarbon chain from practically zero to 0.56 for azelaic acid ($\text{HOOC}(\text{CH}_2)_7\text{COOH}$) and sebacic acid ($\text{HOOC}(\text{CH}_2)_8\text{COOH}$).

The value of $\Delta \log K_d = 1.86 = 4 \times 0.465$ (Table 5) for hexol was considerably lower than for the other solvents. This is understandable as alcohols are associated liquids even if the hydrogen bonding is not so intense as in water. This result agrees also with work of Collander¹² on isobutanol. He found $\Delta \log K_d = 0.45$ per CH_2 -group for acetic acid to caproic acid ($\text{CH}_3\text{CH}_2)_4\text{COOH}$).

The $\Delta \log K_d$ values (DBP—DEP) for hexone (2.04) and nitrobenzene (2.00) lie between those of hexol and isopropylether.

The energy needed to make a hole in the aqueous lattice should influence the molar solubility (S) of hydrocarbons in water as well. In Table 6 we have collected data for $n\text{-C}_5\text{H}_{12}$, $n\text{-C}_6\text{H}_{14}$, $n\text{-C}_7\text{H}_{16}$ and $n\text{-C}_8\text{H}_{18}$ from the Handbook of Chemistry and Physics, 40th Ed. The addition of a CH_2 -group causes a decrease in $\log S$ of 0.49 to 0.59 units. The values of $\log MS^{-1}$ in Table 6 can be regarded as the distribution constant between the solvent itself and water; $\Delta \log MS^{-1}$ is here 0.44 to 0.59. However, if the solubilities are corrected to the same vapor pressure (mm) with Henry's law (*cf.* Hildebrand and Scott¹³), *i.e.* to the same fugacity, there remains no large and regular differences in $\log S$ (*cf.* values of $\log Sp^{-1}$ in Table 6).

Table 6. Solubility of normal hydrocarbons in water.

	Pentane	Hexane	Heptane	Octane
Molarity (M)	8.67	7.65	6.82	6.16
Solubility in water (S) mM	4.98	1.60	0.52	0.13
Temp. °C	16	15.5	15.5	16
Vapor pressure at this temp (p) mm	360	100	270	80
$\log S$	-2.30	-2.80	-3.29	-3.88
$\Delta \log S$		0.50	0.49	0.59
$\log MS^{-1}$	3.24	3.68	4.12	4.67
$\Delta \log MS^{-1}$		0.44	0.44	0.55
$\log Sp^{-1}$	-4.86	-4.80	-4.72	-4.79

If we compare the distribution constants for DEP, $(\text{C}_2\text{H}_5\text{O})_2\text{POOH}$ ($\log K_d = -2.05$) and valeric acid, $\text{C}_4\text{H}_9\text{COOH}$ (+ 0.32) between chloroform and water it is obvious that the POOH-group is much more effectively attached to the aqueous layer than the COOH-group. We might also compare the distribution constant for DBP, $(\text{C}_4\text{H}_9\text{O})_2\text{POOH}$, between hexane and water ($\log K_d = -2.34$) and the value of $\log MS^{-1} = +4.67$ in Table 6 for octane, C_8H_{18} . As the hydrophobic parts are equal in size, this indicates that the POOH-group is bound to the aqueous lattice with an energy of about 11 kcal/mole at 15–25°C as compared with the solvation in the organic layer.

The values of $K_B K_d$. It was shown previously^{1,2} that the value of $K_B = [\text{HAB}]_{\text{org}}[\text{HA}]_{\text{org}}^{-1}[\text{B}]_{\text{org}}^{-1}$ for HA = DBP and B = TBP was considerably lower in chloroform ($\log K_B = 1.40$) than in carbon tetrachloride ($\log K_B = 2.84$). Furthermore, from other experiments⁶ we concluded that in chloroform K_B was larger for hexol than TBP ($\log K_B = 2.21$). In the present work we found that for DEP in carbon tetrachloride there is very little difference between the values for hexol and TBP ($\Delta \log K_B = 0.16 + 0.10$). This is understandable if one recalls that TBP forms a complex with chloroform.²

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