The Liquid Distribution of Diethyl Phosphate (DEP)

DAVID DYRSSEN*, SOLVEIG EKBERG and DJIET HAY LIEM

Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm 70, Sweden

The distribution of diethyl phosphate, DEP (= HA), between a number of organic solvents and perchlorate solutions of different compositions was studied with $^{31}P$-labelled DEP at 25°C.

By variation of $[H^+]$ in the aqueous phase we determined with methylisobutylcarbinol (hexol) as the organic phase:

\[ \log K_a = \log \frac{[H^+][A^-]/[HA]}{[H^+]_a} = -0.73 \text{ for both } 0.1 \text{ M and } 1 \text{ M } \text{(H,Na)ClO}_4; \]
\[ \log K_d = \log \frac{[HA]_\text{org}/[HA]}{[H^+]_a} = 0.35 \text{ for } 0.1 \text{ M and } 0.41 \text{ for } 1 \text{ M } \text{(H,Na)ClO}_4. \]

From a similar study with methylisobutylketone we obtained, using

\[ \log K_a = -0.73, \log K_d = -0.67 \text{ for } 0.1 \text{ M and } -0.56 \text{ for } 1 \text{ M } \text{(H,Na)ClO}_4. \]

By variation of the concentration of DEP we obtained the following dimerization constants, $K_s = \frac{[H_3A]_\text{org}/[HA]_\text{org}^2}$, and distribution constants, $K_d$ (aq.phase 1 M (H,Na)ClO$_4$):

- Isopropyl ether: $K_s = 2.19; \log K_d = -1.75$,
- Chloroform: $4.46; -2.05$,

For benzene we could only obtain $\log K_sK_d = -0.49$.

From a study of the distribution of DEP between carbon tetrachloride and 0.1 M HClO$_4$ as a function of $[B]_\text{org}$, we calculated $K_{pK_d} = \log \frac{[HAB]_\text{org}/[B]_\text{org}[HA]}{[HA]} = -0.91$ for $B$ = tributylphosphate (TBP) and $-0.75$ for $B$ = hexol.

The present data are compared with previous work on dibutylphosphate (DBP) and it is found that $K_s$ is about the same for both acids, but $K_d$ is 70–250 times smaller for DEP depending on the solvent. The effect of CH$_2$ groups on the distribution of acids is discussed.

The study of complex formation reactions between H$_3$PO$_4$ 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 H$_3$PO$_4$ are replaced by alkyl groups. In this paper we studied the distribution and acid-base properties of diethylphosphoric acid, (C$_3$H$_7$O)$_2$POOH (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 on dibutylphosphate, (C$_4$H$_9$O)$_2$POOH (DBP). The dimerization, distr-
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. 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 in-active 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 AgCl. 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. In most cases, however, [H^+] was calculated from the known amount of HClO_4 added.

RESULTS

Determination of pK_a. The pK_a of DBP was determined previously by measuring the distribution of DB^{32}P between chloroform or hexone and 0.1 M or 1 M (H,Na)ClO_4 solutions as a function of [H^+]. Since the distribution constant, K_a, 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^+].

\begin{itemize}
  \item Fig. 1. Distribution of DEP between hexol and 1 M (Na,H)ClO_4 (●) or 0.1 M (Na,H)ClO_4 (○) as a function of the acidity. The normalized curve \( Y = -\log (1 + \epsilon), X = -\log \epsilon \) 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).
  \item The data are given in Table 1.
\end{itemize}
LIQUID DISTRIBUTION OF DEP

Table 1. Distribution of DEP between hexol and 1 M or 0.1 M (H,Na)ClO₄ solutions. Initial concn. of DEP in the aqueous layer was 1.89 × 10⁻⁵ M. Data are given as
\[
\log q (\log [\text{H}^+])
\]
1 M: 0.301 (0.07), 0.288 (0.36), 0.119 (0.06), 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 concn. of DEP in the aqueous layer was 1.89 × 10⁻⁴ M. Data are given as
\[
\log q (\log [\text{H}^+])
\]
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 before \(^2\) 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: \(\log K_a = 0.35\) for 0.1 M and 0.41 for 1 M (H,Na)ClO₄ and \(-\log [\text{H}^+] = 0.73 = pK_a\) 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 hexone data were correct and that the hexone data for 1 M ClO₄⁻ were only reliable when \([\text{H}^+] \leq 0.1\) M. The fit with \(pK_a = 0.73\) then gave log \(K_a = -0.67\) for 0.1 M and \(-0.56\) for 1 M (H,Na)ClO₄.

**Determination of \(K_a\) and \(K_a^2\).** The values of the distribution constants \(K_a\) and the dimerization constants \(K_a^2\) were determined by measuring the distribution of DEP at different total concentrations of DEP + 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 \([\text{H}^+]\)): -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 \([\text{H}^+]\)): -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 \([\text{H}^+]\)): -2.842 (-2.164, -0.03), -2.554 (-2.160, -0.03), -2.260 (-2.119, -0.03), -2.166 (-2.156, -0.03), -1.888 (-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 \([\text{H}^+]\)): -2.290 (2.622, -0.03), -1.868 (-2.298, -0.05), -1.569 (-1.967, -0.06), -1.171 (-1.372, -0.10), -0.871 (-1.236, -0.18).

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

\[ q = \frac{2[H_2A_3]_{\text{org}} + [HA]_{\text{org}}}{[HA] + [A^-]} = \frac{2K_aK_d^2[HA] + K_d}{1 + K_a[H^+]^{-1}} \]

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

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

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 \(\log q (1 + K_a[H^+]^{-1})\) and \(\log [HA]\) at the point of the intersection between the two asymptotes to the curve, \(Y = 0\) and \(X = X\), gave \(\log K_d\) and \(-\log 2K_aK_d\).

From Fig. 3 we obtained the following values:

<table>
<thead>
<tr>
<th>Organic solvent</th>
<th>(\log K_d)</th>
<th>(\log 2K_aK_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropylether</td>
<td>-1.75</td>
<td>+ 0.74</td>
</tr>
<tr>
<td>Chloroform</td>
<td>-2.05</td>
<td>+ 2.71</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>-2.14</td>
<td>+ 1.77</td>
</tr>
</tbody>
</table>

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

**Determination of \(K_BK_d\) 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 DEP\(^{3+}\)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.

*Acta Chem. Scand.* 18 (1964) No. 1
LIQUID DISTRIBUTION OF DEP

Table 4. Distribution of DEP between CCl₄ and 0.0985 M HClO₄ for different concentrations of TBP or hexol in the organic layer. The initial conc. of DEP in the aqueous layer was $4.72 \times 10^{-5}$ M. The data are given as log $q$; log[TBP]ₐrg or log[hexol]ₐrg.

**TEB:** $-3.176(-1.876)$, $-2.651(-1.477)$, $-2.558(-1.176)$, $-2.319(-0.876)$, $-2.116(-0.699)$, $-1.877(-0.477)$, $-1.527(-0.176)$, $-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 $4.72 \times 10^{-5}$ M) we assumed that there were no dimeric species ($H_2A_2$) present with [B]ₐrg $> 0.001$ M. The experiments show that log $q/[B]$_ₐrg was practically constant except for concentrations of hexol above 0.3 M, where $q/[B]$_ₐrg was somewhat larger ($HAB_2$ might be formed). This indicated that the distribution ratio could be expressed as

$$q = \frac{[HAB]_{org}}{[HA][A^-]} = K_BK_d[B]_{org}(1 + K_a[H^+])^{-1}$$

or at [$H^+] = 0.1$ M

log $q/[B]$_ₐrg $= K_BK_d - 0.46$

From the data in Table 4 we calculated for TBP: log $K_BK_d = -0.91 \pm 0.05$ and for hexol: $-0.75 \pm 0.08$; the difference in log $K_B$, $0.16 \pm 0.10$ is small. Unfortunately log $K_d$ for CCl₄ was too small to be measured with any accuracy.

DISCUSSION

The value of $pK_a$. Our values of $pK_a$ in 0.1 M NaClO₄ are 0.73 for DEP and 1.00 for DBP. We have recalculated conductometric data of Drushel and Felty using the Onsager relation $\Lambda = \Lambda^0 + (59.86 + 0.2277 \Lambda^0)\sqrt{c}$ to correct for the influence of the ionic concentration on the conductance. Furthermore, as the dialkyl phosphoric acids are rather strong acids, $\Lambda^0 = 380$ was obtained by extrapolation of $\Lambda$ against $\sqrt{c}$. The following data were obtained by successive approximations:

<table>
<thead>
<tr>
<th>C</th>
<th>(CH₂O)₂POOH</th>
<th>(C₈H₁₇O)₂POOH</th>
<th>(C₃H₇O)₂POOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[H^+] = [A^-]$</td>
<td>0.00985</td>
<td>0.0879</td>
<td>0.0839</td>
</tr>
<tr>
<td>$[H^+] [A^-] /[HA]$</td>
<td>0.366</td>
<td>0.208</td>
<td>0.171</td>
</tr>
<tr>
<td>$pK_a^\circ$</td>
<td>0.61</td>
<td>0.86</td>
<td>0.94</td>
</tr>
</tbody>
</table>

$C = 1/16$ M

| $[H^+] = [A^-]$ | 0.0526 | 0.0493 | 0.0479 |
| $[H^+] [A^-] /[HA]$ | 0.280 | 0.184 | 0.157 |
| $pK_a^\circ$ | 0.70 | 0.88 | 0.95 |

$pK_a^\circ$ are the dissociation constants corrected to zero ionic strength by using activity factors given by Kielland. The corresponding $pK_a^\circ$ values determined from our data are 0.90 (DEP) and 1.17 (DBP). As seen from Fig. 4

*Acta Chem. Scand.* 18 (1964) No. 1
the agreement between these sets of data is acceptable. Conductometric measurements of DEP by van Hove\textsuperscript{8} seem to be less accurate than the determinations by Drushel and Felty.\textsuperscript{4} Values of $pK_a$ by Kumler and Eiler\textsuperscript{8} seem definitely to be too high.

Dippy has measured $pK_a^0$ conductometrically for many carboxylic acids. In Fig. 4 we have plotted his data\textsuperscript{10} 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 $pK_a^0$ is larger for the dialkyl phosphoric acids.

The values of log $K_d$ and log $K_2$: If the distribution curves for DEP in Fig. 3 and for DBP in Fig. 1 in Ref.\textsuperscript{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 $K_d$ 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 $K_d$ 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 previously\textsuperscript{2} for the distribution of fatty acids between chloroform and water that $K_d$ 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 $K_d$ 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, $\Delta \log K_d$ (chloroform/water) $= 0.6$
Table 5. Distribution and dimerization constants for DBP and DEP.

<table>
<thead>
<tr>
<th>Organic solvent</th>
<th>(RO)$_2$POOH</th>
<th>log $K_d$</th>
<th>log $K_s$</th>
<th>log $K_dK_s$</th>
<th>aq. phase</th>
<th>Ref.</th>
<th>$\Delta$log $K_d$</th>
<th>$\Delta$log $K_s$</th>
<th>$\Delta$log $K_dK_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexol</td>
<td>DBP</td>
<td>2.21</td>
<td>$&lt;-1$</td>
<td>--</td>
<td>0.1 M HNO$_3$</td>
<td>1</td>
<td>1.86</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>DEP</td>
<td>0.35</td>
<td>--</td>
<td>--</td>
<td>0.1 M (Na, H)ClO$_4$</td>
<td>this work</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DEP</td>
<td>0.41</td>
<td>--</td>
<td>--</td>
<td>1 M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexone</td>
<td>DBP</td>
<td>1.36</td>
<td>1.19</td>
<td>3.91</td>
<td>0.1 M (Na, H)ClO$_4$</td>
<td>2</td>
<td>2.03</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>DEP</td>
<td>1.49</td>
<td>--</td>
<td>--</td>
<td>1 M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DEP</td>
<td>-0.07</td>
<td>--</td>
<td>--</td>
<td>0.1 M</td>
<td>this work</td>
<td>2.05</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>DEP</td>
<td>-0.56</td>
<td>--</td>
<td>--</td>
<td>1 M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopropyl ether</td>
<td>DBP</td>
<td>0.52</td>
<td>2.29</td>
<td>3.33</td>
<td>0.1 M HNO$_3$</td>
<td>1</td>
<td>2.27</td>
<td>0.10</td>
<td>4.64</td>
</tr>
<tr>
<td></td>
<td>DEP</td>
<td>-1.75</td>
<td>2.19</td>
<td>-1.31</td>
<td>1 M (Na, H)ClO$_4$</td>
<td>this work</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>DBP</td>
<td>0.34</td>
<td>4.48</td>
<td>5.16</td>
<td>0.1 M (Na, H)ClO$_4$</td>
<td>2</td>
<td>2.39</td>
<td>0.15</td>
<td>4.73</td>
</tr>
<tr>
<td></td>
<td>DBP</td>
<td>0.34</td>
<td>4.21</td>
<td>4.89</td>
<td>0.1 M HClO$_4$</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DBP</td>
<td>0.34</td>
<td>--</td>
<td>--</td>
<td>1 M (Na, H)ClO$_4$</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DBP</td>
<td>0.28</td>
<td>4.36</td>
<td>4.92</td>
<td>1 M HClO$_4$</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DBP</td>
<td>0.24</td>
<td>4.61</td>
<td>5.09</td>
<td>0.1 M HNO$_3$</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DEP</td>
<td>-2.05</td>
<td>4.46</td>
<td>0.36</td>
<td>1 M (Na, H)ClO$_4$</td>
<td>this work</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>DBP</td>
<td>-0.14</td>
<td>3.55</td>
<td>3.27</td>
<td>1 M HNO$_3$</td>
<td>9</td>
<td>2.00</td>
<td>-0.06</td>
<td>3.94</td>
</tr>
<tr>
<td></td>
<td>DEP</td>
<td>-2.14</td>
<td>3.61</td>
<td>-0.07</td>
<td>1 M (Na, H)ClO$_4$</td>
<td>this work</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>DBP</td>
<td>-0.42</td>
<td>4.88</td>
<td>4.04</td>
<td>1 M HNO$_3$</td>
<td>9</td>
<td></td>
<td></td>
<td>4.53</td>
</tr>
<tr>
<td></td>
<td>DEP</td>
<td>--</td>
<td>--</td>
<td>-0.49</td>
<td>1 M (Na, H)ClO$_4$</td>
<td>this work</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 Collander\(^{11}\) found \( \Delta \log K_d = 0.57 \) per \( \text{CH}_2 \)-group for acetic acid to hexoic (caproic) acid. For the dicarboxylic acids, which can be attached to the aqueous lattice at two different points, Collander\(^{11}\) found that \( \Delta \log K_d \) increased with the length of the hydrocarbon chain from practically zero to 0.56 for azelaic acid \( \text{HOOC(CH}_2\text{)}_7\text{COOH} \) and sebacic acid \( \text{HOOC(CH}_2\text{)}_9\text{COOH} \).

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 Collander\(^{13}\) on isobutanol. He found \( \Delta \log K_d = 0.45 \) per \( \text{CH}_2 \)-group for acetic acid to caproic acid \( \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \).

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 \( \langle S \rangle \) of hydrocarbons in water as well. In Table 6 we have collected data for \( n\text{-C}_3\text{H}_8\), \( n\text{-C}_5\text{H}_{14} \), \( n\text{-C}_7\text{H}_{16} \) and \( n\text{-C}_8\text{H}_{18} \) from the Handbook of Chemistry and Physics, 40th Ed. The addition of a \( \text{CH}_2 \)-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 Scott\(^{19}\)), 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>
<thead>
<tr>
<th>Table 6. Solubility of normal hydrocarbons in water.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
</tr>
<tr>
<td>Molarity ((M))</td>
</tr>
<tr>
<td>Solubility in water ((S)) mM</td>
</tr>
<tr>
<td>Temp. °C</td>
</tr>
<tr>
<td>Vapor pressure at this temp ((p)) mm</td>
</tr>
<tr>
<td>( \Delta \log S )</td>
</tr>
<tr>
<td>( \log MS^{-1} )</td>
</tr>
<tr>
<td>( \Delta \log MS^{-1} )</td>
</tr>
<tr>
<td>( \log Sp^{-1} )</td>
</tr>
<tr>
<td>( \log Sp^{-1} )</td>
</tr>
</tbody>
</table>

If we compare the distribution constants for DEP, \((C_2H_5O)_2\text{POOH}\) (log \( K_d = -2.05 \) and valeric acid, \( C_4H_9\text{COOH} \) (+ 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, \((C_4H_9\text{O})_2\text{POOH}\), 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 $K_B K_A$. It was shown previously$^{1,2}$ that the value of
$K_B = [HAB]_{org}[HA]_{org}^{-1}[B]_{org}^{-1}$ for $HA = DBP$ and $B = TBP$ was consider-
ably lower in chloroform ($\log K_B = 1.40$) than in carbon tetrachloride ($\log K_B = 2.84$). Furthermore, from other experiments$^6$ 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 differ-
ence 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.$^3$

Acknowledgements. We have had the pleasure to discuss the manuscript with the head
of the department, professor L. G. Sillén. The work has been supported by Statens råd för
atomforskning (Swedish Council for Atomic Research). The English has been revised by
Dr. Leonard Newman.

REFERENCES


Received September 26, 1963.