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The Distribution of Benzene and Its Monosubstituted Derivatives between Hexane and Water

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The liquid-liquid distribution equilibria of benzene and its eight monosubstituted derivatives have been investigated in order to study the effect of the substituted atom or atom group on the distribution behavior. The results are compared with the solubilities of the materials in water.

Experimental

All of the reagents used were of a reagent grade. The purity was checked by spectrometry and, in some cases, by gas chromatography. All of the procedures were carried out in a thermostatted room at 25±0.3°C. A weighed portion of the material was dissolved in hexane. The concentration of aniline was further checked by titration with a standard acid solution.

The distribution experiments were done as follows. A portion of a hexane solution of the material and a portion of water (in the case of benzoic acid, 0.03M perchloric acid in order to prevent dissociation) were placed in a stoppered glass vessel. The two phases were shaken vigorously by hand for three minutes, and then the hexane phase was transferred into a stoppered glass tube and centrifuged. When the distribution ratio was too high, a portion of this aqueous phase was also shaken with a portion of hexane, and then this hexane phase was transferred into another glass tube and centrifuged. The concentration of the material in the hexane phase was determined by spectrometry.

Results and Discussion

The distribution ratio of the material, M, was defined as follows:

$$D=\frac{[\mathrm{M}]_{\mathrm{org,total}}}{[\mathrm{M}]_{\mathrm{total}}} \tag{1}$$

The subscript "org" denotes the species in the organic phase, while the absence of a subscript denotes that in the aqueous phase.

The distribution ratios of all these materials except benzoic acid were independent of their concentrations. Thus, it was concluded that these materials undergo no dissociation in the aqueous phase and that there is no association in the organic phase under these experimental conditions.

For this reason, the distribution constant;

$$\mathrm{M} \rightleftharpoons \mathrm{M}_{(\mathrm{org})}\,,\quad K_{\mathrm{D}}=\frac{[\mathrm{M}]_{\mathrm{org}}}{[\mathrm{M}]} \tag{2}$$

for these materials is identical with the distribution ratio. The constants obtained are listed in Table 1.

The distribution ratio of benzoic acid is given in Fig. 1 as a function of its concentration in the aqueous phase. Since the aqueous phase is 0.03M perchloric acid, the dissociation of benzoic acid ($\mathrm{p}K_a=4.0$[1] $\mu=$ 0.1 25°C)) is negligible. Furthermore, this distribution ratio was unaffected by perchloric acid within the concentration range from 0.003M to 0.03 M.

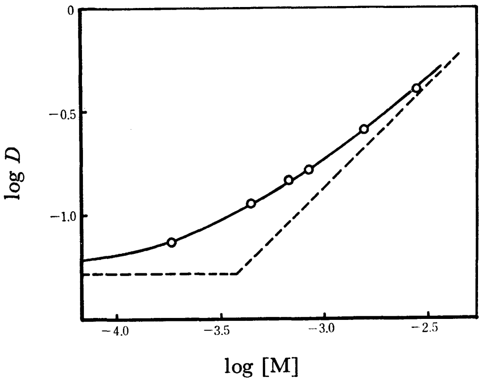

Fig. 1. Distribution ratio of benzoic acid which is denoted by M, between hexane and 0.03 M HClO$_4$ as a function of the solute concentration in the aqueous phase. The solid curve represents:
$\log D=\log(K_{\mathrm{D}}+2K_{\mathrm{dim(org)}}K_{\mathrm{D}}^2[\mathrm{M}])$
$=\log(5.13\times10^{-2}+1.32\times10^{2}[\mathrm{M}])$
The two dotted lines represent the asymptotes for the extraction curve.

Thus, the distribution ratio of benzoic acid can be written as;

$$D=\frac{[\mathrm{M}]_{\mathrm{org}}+2[(\mathrm{M})_2]_{\mathrm{org}}}{[\mathrm{M}]} \tag{3}$$

The dimerization constant in the organic phase can be written as;

$$2\mathrm{M}_{(\mathrm{org})} \rightleftharpoons (\mathrm{M})_{2(\mathrm{org})},\quad K_{\mathrm{dim(org)}}=[(\mathrm{M})_2]_{\mathrm{org}}/[\mathrm{M}]^2_{\mathrm{org}} \tag{4}$$

By introducing the distribution constant and this dimerization constant, Eq. (3) can be rewritten as;

$$D=K_{\mathrm{D}}+2K_{\mathrm{dim(org)}}K_{\mathrm{D}}^2[\mathrm{M}] \tag{5}$$

The K_{D} and $2K_{\mathrm{dim(org)}}K_{\mathrm{D}}^2$ values can be determined by a curve-fitting method.[2] The value of $K_{\mathrm{dim(org)}}$ obtained from these values is listed in Table 1. The table also lists the solubilities of these materials reported in the literature.[3]

The solubility in water has sometimes been employed as an index of the aquophilic tendency of molecular substances; when a molecule has an aquophilic group, it is usually estimated to be more soluble in water than those which have no such group. However, this is only a rough approximation, because the introduction of such a group into a nonpolar molecule increases

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[1] M. Yasuda, K. Yamasaki, and H. Ohtaki, This Bulletin, **33**, 1067 (1960).

[2] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants" McGraw-Hill, New York (1961).

[3] H. Stephen and T. Stephen, "Solubility of Inorganic and Organic Compounds" Vol. I, Pergamon Press, Oxford (1963).

TABLE 1. DISTRIBUTION CONSTANTS BETWEEN HEXANE AND WATER (25°C) AND OTHER PROPERTIES OF BENZENE AND ITS MONOSUBSTITUTED DERIVATIVES

Material	Distribution (25°C)		Solubility (30°C)	
	K_D[a]	$K_D/K_D(C_6H_6)$	S[b] (M)	$S(C_6H_6)/S$
Benzene	2.8×10^2	1	2.4×10^{-2}	1
Toluene	9.7×10^2	3.5	6.2×10^{-3}	3.9
Fluorobenzene	3.0×10^2	1.1	1.6×10^{-2}	1.5
Chlorobenzene	9.5×10^2	3.4	4.3×10^{-3}	5.6
Bromobenzene	1.2×10^3	4.5	2.8×10^{-3}	8.6
Nitrobenzene	3.1×10	1.1×10^{-1}	1.7×10^{-2}	1.4
Aniline	9.0×10^{-1}	3.3×10^{-3}	4.1×10^{-1}	5.9×10^{-2}
Phenol	1.3×10^{-1}	4.9×10^{-4}	9.8×10^{-1}	2.4×10^{-2}
Benzoic acid[c]	5.1×10^{-2}	1.9×10^{-4}	3.4×10^{-1}	7.1×10^{-2}

a) The values for benzoic acid, *cf.* Fig. 1. b) The values of solubility by wt% are summarized in Ref. 3. They are converted into molarity assuming that the density of the solution at this temperature is 1.0. c) The dimerization constant in Eq. (4) was obtained to be 2.5×10^4 in hexane.

not only the interaction between the solute and water molecules in the solution, but also the interaction among the molecules in the pure solute phase. For example, as can be seen from Table 1, the solubility of nitrobenzene in water in the molar units is even lower than that of benzene; this is probably caused by the strong interaction among the molecules in the water-saturated nitrobenzene phase.

The increase in the distribution ratio of toluene may mainly be attributed to the increase in the molecular volume. It was reported by Collander[4] that the distribution ratio of organic compounds between diethyl ether and water increases by a factor of from two to four for each new CH_2 group introduced into the molecule in a homologous series. The solubility of normal aliphatic alcohols in water was found by Kinoshita, Ishikawa, and Shinoda[5] to decrease by a factor of four when a CH_2 group is added to the hydrocarbon chain; an increase in the distribution ratio of aliphatic alcohols between benzene and the aqueous phase by a factor of around four was also reported by Tanaka and Kojima.[6] The increase in the distribution ratio by a factor of 3.5 by the replacement of a hydrogen atom of benzene with a methyl group in the present study is quite similar to these previous results.

The effect on the distribution of the replacement of a hydrogen atom with a halogen atom is not very clear. However, the effect of the replacement with one of the four aquophilic atom groups, $-NO_2$, $-NH_2$, $-OH$, and $-COOH$, seems to be very clear. The replacement increases the molecular volume, but it also increases the interaction with water very much, and the distribution ratio is very much decreased by the latter.

Since the interaction between the solute molecules in the pure solute phase has no effect on the distribution ratio, the effect of the replacement on the distribution is not parallel with that on the solubility, as may be seen from Table 1; the introduction of an aquophilic group does not so increase the solubility into water as it increases the distribution into the aqueous phase.

The dimerization of benzoic acid in the organic phase is very important for its distribution. As can be seen from Fig. 1 and from the value of K_D, the effect of the dimerization becomes negligible only when the concentration is very low.

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[4] A. A. Collander, *Acta Chem. Scand.*, **3**, 717 (1949).

[5] K. Kinoshita, H. Ishikawa, and K. Shinoda, This Bulletin, **31**, 1081 (1958).

[6] M. Tanaka and I. Kojima, *J. Inorg. Nucl. Chem.*, **27**, 1769 (1967).