THE MOLECULAR ASSOCIATION OF PHENOL IN BENZENE AND WATER.

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It has already been discussed by many investigators(1) that the partition coefficient of phenol between benzene and water is not constant but varies with its concentration, although the problem has not yet been solved. H. Hirobe(2) studied the partition of phenol between chlorobenzene and water, and reached the conclusion that in chlorobenzene there exists the chemical equilibrium,

$$3C_6H_5OH \rightleftarrows (C_6H_6O)_3,$$

while in water only the monomolecular phenol is present. As benzene is very similar in chemical natures to chlorobenzene, we may expect the same conclusion in the case of benzene. Following experiments were undertaken from this point of view.

I. Partition of Phenol between Benzene and Water at 25°C.

The measurements of the partition coefficient were carried out at 25° in the usual manner. Specially purified phenol and benzene were employed. Phenol was determined by the bromine method which was tested and found very satisfactory. The results are shown in Table 1, where W and B represent the molar concentrations of phenol calculated as C_6H_5OH in the aqueous and in the benzene layer respectively.

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(1) Rothmund and Wilsmore, *Zeit. physik. Chem.*, **40** (1902) 611.
W. Vaubel, *J. prakt. Chem.*, **67** (1903) 473.
James C. Philip and C.H. Douglas Clark, *J. Chem. Soc.* **127** (1925) 1274.

(2) H. Hirobe, *J. Coll. Science Imp. Univ. Tokyo*, **25** (1908) Art. 12.

TABLE 1.

Molar Concentrations of Phenol in		Partition Coeff.
Benzene Layer B	Aqueous Layer W	$P=\frac{W}{B}$
1.0442	0.2372	0.2272
0.7803	0.2052	0.2630
0.5437	0.1645	0.3026
0.2422	0.0934	0.3855
0.1177	0.0501	0.4256

Thus the values of P decrease with increasing concentration, as other investigators have already found.

At first, we assume that the following equilibrium is established in the benzene layer,

$$3C_6H_5OH \rightleftharpoons (C_6H_6O)_3$$

while only single molecules of phenol are present in the aqueous layer. Let c_1 and c_3 represent the molar concentrations in benzene of C_6H_5OH and $(C_6H_6O)_3$ respectively, then by the law of mass action,

$$Kc_1^3=c_3,$$

where K denotes the association constant. Moreover, there is the relation,

$$B=c_1+3c_3=c_1+3Kc_1^3.$$

Now by the law of partition the ratio of c_1 and W is to be constant; so

$$\gamma W=c_1$$

where γ is the real partition coefficient of C_6H_5OH between benzene and water.

Then, $$B=\gamma W+3\gamma^3KW^3 \cdots\cdots\cdots(1)$$

or $$B/W=1/P=\gamma+3\gamma^3KW^2 \quad (2)$$

If we plot $1/P$ as ordinate and W^2 as abscissa, then we must obtain a straight line, providing our assumption is correct. Figure 1 which shows quite a straight line, has been drawn in such a manner. The equation (2), therefore, is correct and consequently our assumption is right.

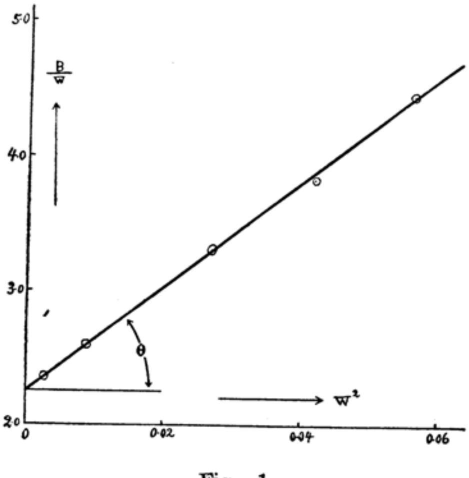

Fig. 1.

In the next place, we can find the values of γ and K from Fig. 1, thus

$$(1/P)_{W=0}=\gamma=2.25$$

and

$$\tan\theta=\frac{d(1/P)}{d(W^2)}=3\gamma^3K=37.77$$

I have calculated these values more exactly by the method of the least squares and obtained

$$3\gamma^3K=37.71 \quad \text{and} \quad \gamma=2.272$$

Then $K=1.072.$

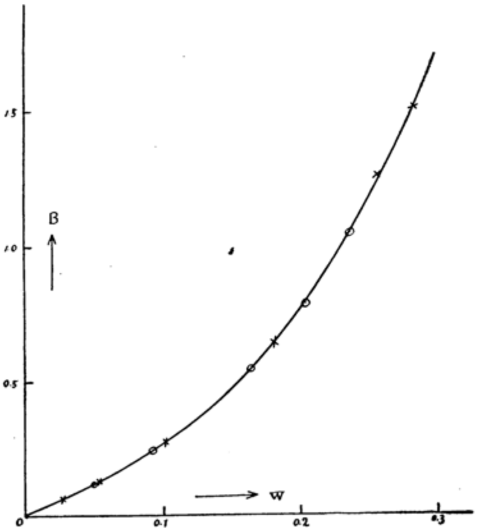

Fig. 2.

So the equation (1) becomes

$$B=2.272\,W+37.71\,W^3 \quad \cdots\cdots\cdots\cdots\cdots(3)$$

The curve in Fig. 2 has been drawn by the equation (3) and the circlets denote the points observed by the author, and the crosses by Rothmund and Wilsmore. The agreement between the theory and the experiment is quite satisfactory.

II. Depression of the Freezing Point of the Aqueous Phenol Solution.

The cryoscopic experiments were also done in order to determine the molecular states of phenol in water. The experiments were carried out on a larger scale than the ordinary cryoscopic method to get the greater accuracy. About 500 cc. of solution have been used each time. The results are shown in Table 2, where C denotes the molar concentration of phenol calculated as C_6H_5OH.

They are also shown graphically in Fig. 3, which represents a d–C curve. If the Raoult's law holds, d–C curve must be a straight line represented by the equation $d=kC$, $(k=1.86)$. But as we see in Fig. 3, it is not a straight line, though the deviation is not large. It shows a regular downward deviation which suggests that there occurs an association of phenol

TABLE 2.

Weight of Water in gram w.	Weight of Phenol in gram g.	$C=\frac{1000g}{94.048w}$	Depression of Freez. Pt. in degree d.
499.4	18.8698	0.4016	0.676
499.4	14.2540	0.3034	0.524
499.4	10.7330	0.2284	0.407
499.3	8.4313	0.1795	0.325
499.4	5.7585	0.1226	0.228
499.4	4.0364	0.0859	0.165
499.4	2.6503	0.0564	0.110
499.3	2.4515	0.0522	0.101

in a small degree in concentrated solutions. Generally, the degree of association decreases with the elevation of the temperature. So at 0°C. the association of phenol is perceptible when the molar concentration is greater than 0.2, while in more dilute solutions it can safely be assumed that there is no association as has been stated in the partition experiment.

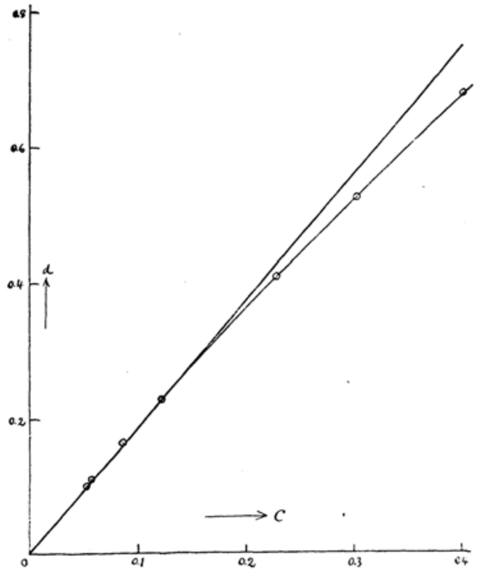

Fig. 3.

Now we will assume

$$3C_6H_5OH \rightleftarrows (C_6H_6O)_3$$

in aqueous solution at 0'C. If c_1' and c_3' denote the molar concentrations of C_6H_5OH and $(C_6H_6O)_3$ respectively, then

$$K'c_1'^3=c_3',$$

where K' is the association constant of phenol in water. The analytical concentration C becomes

$$C=c_1'+3c_3',$$

and the depression of freezing point must be expressed by

$$d=k(c_1'+c_3').$$

Therefore, $$C-\frac{d}{k}=2c_3' \quad \text{or} \quad c_3'=\frac{1}{2}\left(C-\frac{d}{k}\right)\cdots\cdots(4)$$

and
$$c_1'=\frac{d}{k}-c_3' \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(5)$$

By using these two equations we can calculate c_1' and c_3' from Fig. 3 or directly from the observed data. We can also calculate the value of $K'=c_3'/c_1'^3$.

As we see in Fig. 3 the experimental points at concentrations lower than $C=0.2$ almost coincide with the theoretical line of Raoult, so this part has been excluded from the calculation. The results are shown in Table 3.

TABLE 3.

C	d	d/k	c_3'	c_1'	K'
0.4000	0.673	0.3618	0.0191	0.3427	0.47
0.3500	0.596	0.3204	0.0148	0.3056	0.52
0.3000	0.519	0.2814	0.0093	0.2721	0.46
0.2500	0.441	0.2371	0.0065	0.2306	0.53
0.2000	0.359	0.1930	0.0035	0.1895	0.51
				Mean $K'=0.50$	

The constancy of K' is satisfactory.

Summary.

1. From the measurement of the partition coefficient of phenol between benzene and water, it has been proved that phenol is in the state of chemical equilibrium

$$3\text{C H}_5\text{OH} \rightleftarrows (\text{C}_6\text{H}_6\text{O})_3$$

in the benzene layer at 25°C.

2. From the measurement of the freezing point of the aqueous phenol solution, it has also been proved that phenol is in the chemical equilibrium similar to the above in the aqueous solution at 0°C.

It is to be emphasized that phenol associates itself in tripple molecules and not in double molecules.

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