THE ACTIVITY OF PHENOL IN AQUEOUS SALT SOLUTIONS(3)

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The fact, that the solubility of non-electrolytes is lowered by the presence of neutral salts, is well known(4) under the term "salt action" or "salting out." For the study of this problem, partition experiments are

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(3) Read before the Chemical Society of Japan, February, 1925.

(4) Rothmund, "Löslichkeit."

often made. In my previous work⁽¹⁾ the molecular states of phenol in benzene and in water were determined by the partition experiments. In the present paper the studies of salt action on phenol will be described.

Partition of Phenol between Benzene and Aqueous Solutions of Neutral Salts. The measurements were carried out at 25°C. in the same manner as described in the previous paper. All the salt used were purifed by recrystallisation. The results are shown in the following tables, where *B* and *C* represent the molar concentrations of phenol in the benzene and in the aqueous layer respectively, while *S* represents the moler concentration of the added salt.

TABLE 1.

Salt	Conc. of salt. mols (*S*)	Liquids. *B* = Benzene layer. *C* = Water layer.	Conc. of phenol. mols.				
NaCl	2.0	*B*	1.5142	0.7590	0.4383	0.2052	—
		C	0.1282	0.0912	0.0656	0.0379	—
	1.0	*B*	1.4573	0.7187	0.4126	0.1913	—
		C	0.1851	0.1316	0.0913	0.0518	—
	0.5	*B*	1.4180	0.6946	0.3948	0.1839	—
		C	0.2244	0.1557	0.1091	0.0593	—
NaBr	2.589	*B*	0.9316	0.6444	0.4186	—	—
		C	0.0883	0.0738	0.0562	—	—
	1.2945	*B*	0.8842	0.6077	0.3916	0.1937	—
		C	0.1357	0.1106	0.0832	0.0498	—
	0.6472	*B*	0.8513	0.5825	0.3734	—	—
		C	0.1686	0.1357	0.1014	—	—
$NaNO_3$	3.0	*B*	1.1931	0.9045	0.6256	0.2872	0.1399
		C	0.1159	0.1023	0.0827	0.0484	0.0280
	2.0	*B*	1.1583	0.8756	0.6029	0.2757	0.1334
		C	0.1507	0.1313	0.1050	0.0599	0.0344
	1.0	*B*	1.0911	0.8205	0.5757	0.2604	0.1257
		C	0.1902	0.1651	0.1326	0.0752	0.0421
	0.5	*B*	1.0697	0.8025	0.5614	0.2519	0.1225
		C	0.2117	0.1830	0.1469	0.0837	0.0453
	0.25	*B*	1.0559	0.7907	0.5535	0.2437	0.1198
		C	0.2251	0.1949	0.1547	0.0882	0.0481
Na_2SO_4	1.007	*B*	1.3138	0.8178	0.6493	0.3419	—
		C	0.1008	0.0820	0.0689	0.0453	—
	0.5166	*B*	1.1606	0.6111	0.3193	—	—
		C	0.1505	0.1071	0.0684	—	—
	0.2583	*B*	1.1210	0.5851	0.3812	0.1380	—
		C	0.1901	0.1331	0.1004	0.0451	—
	0.1292	*B*	1.0978	0.5698	0.3705	0.1342	—
		C	0.2133	0.1484	0.1112	0.0489	—

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(1) K. Endo, this journal, 1 (1926), 25.

Salt	Conc. of salt. mols.	Liquids. B=Benzene layer. C=Water layer.	Conc. of phenol. mols.				
KCl	2.0990	B	1.4956	0.7445	0.4302	0.2012	—
		C	0.1468	0.1058	0.0771	0.0419	—
	0.9917	B	1.4399	0.7083	0.4043	0.1887	—
		C	0.2025	0.1420	0.0996	0.0544	—
KBr	2.3533	B	0.8331	0.5215	0.2767	—	—
		C	0.1165	0.0885	0.0568	—	—
	1.1766	B	0.7978	0.4957	0.2597	—	—
		C	0.1518	0.1143	0.0738	—	—
	0.5883	B	0.8372	0.5726	0.3667	0.1804	—
		C	0.1827	0.1457	0.1081	0.0630	—
KNO_3	2.0007	B	1.4505	0.7159	0.4094	0.1910	—
		C	0.1919	0.1344	0.0945	0.0521	—
	0.9989	B	1.4127	0.6897	0.3927	0.1828	—
		C	0.2297	0.1606	0.1112	0.0603	—
K_2SO_4	0.50305	B	1.1489	0.6033	0.3951	0.1442	—
		C	0.1622	0.1149	0.0866	0.0389	—
	0.25136	B	1.2083	0.7396	0.3774	0.1369	—
		C	0.2063	0.1601	0.1043	0.0462	—

The data for NaCl in Table 1 are shown graphically in Fig. 1, which represents three B–C curves (namely $S=2$, $S=1$ and $S=0.5$), in comparison with the theoretical curve of $S=0$ drawn according to the equation⑴

$$B = 2.272C_0 + 37.71C_0^3$$

where C_0 denotes the molar concentration of phenol in the aqueous layer without any salt. As we see in the figure, all the B–C curves deviate leftward from the theoretical curve of $S=0$ and the deviation increases with the amount of the salt added. Obviously this shows the decrease of phenol concentration in the aqueous layer and the increase in the benzene layer by the addition of sodium chloride, that is, salting out. The degree of salting out increases with the increase of the salt concentration. The same can be stated as to other salts. Curves are here omitted.

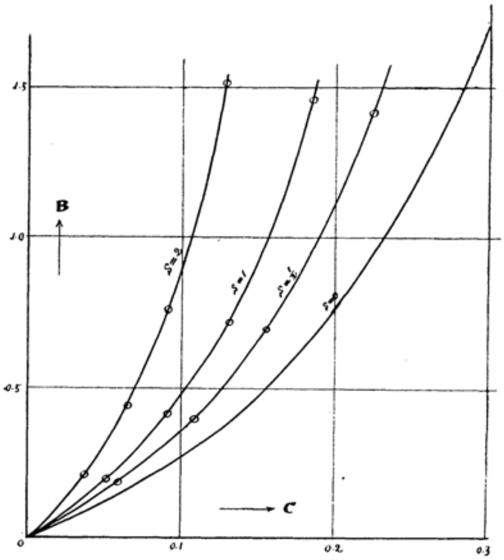

Fig. 1.

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(1) Endo, loc. cit.

Thorne(1), studying the solubility of ether in the aqueous solution of sodium chloride, confirmed that the oldest empirical law of Setschenow is valid in his case, namely,

$$\frac{1}{S}\log\frac{\eta_0}{\eta}=k \quad \text{or} \quad \eta=\eta_0 e^{-kS},$$

where η_0 and η denote the solubilities of non-electrolytes in pure water and in aqueous salt solutions respectively, while k is a constant.

Now in the present case, I have also found this logarithmic formula quite valid. For example the case of sodium chloride is shown in Table 2, where the calculations were made with regard to the three horizontal lines (namely $B=1.0$, $B=0.7$ and $B=0.4$) in Fig. 1.

TABLE 2.

		$B=1.0$		
S	C	$\log C$	$\log C_0-\log C$	$\frac{1}{S}\log\frac{C_0}{C}=\beta$
0	$0.2320=C_0$	$\bar{1}.3655$	—	—
0.5	0.1905	$\bar{1}.2799$	0.0856	0.1712
1.0	0.1570	$\bar{1}.1959$	0.1696	0.1696
2.0	0.1060	$\bar{1}.0253$	0.3402	0.1701
		$B=0.7$		
0	$0.1913=C_0$	$\bar{1}.2817$	—	—
0.5	0.1560	$\bar{1}.1931$	0.0886	0.1772
1.0	0.1290	$\bar{1}.1106$	0.1711	0.1711
2.0	0.0870	$\bar{2}.9395$	0.3422	0.1711
		$B=0.4$		
0	$0.1345=C_0$	$\bar{1}.1287$	—	—
0.5	0.1100	$\bar{1}.0414$	0.0873	0.1746
1.0	0.0895	$\bar{2}.9518$	0.1769	0.1769
2.0	0.0612	$\bar{2}.7867$	0.3420	0.1710
		mean $\beta=0.172$		

Thus the constancy of β is satisfactory. Similarly the values of β for other salts are constant. They are shown in Table 3, where their differences are also indicated.

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(1) Thorne, *J. Chem. Soc.*, **119** (1921), 262.

TABLE 3.

The values of β and their differences.

Anions Cations	Cl'	Cl'-NO_3'	NO_3'	Br'-NO_3'	Br'	$\frac{1}{2}SO_4''$-Br'	$\frac{1}{2}SO_4''$
$Na^{\cdot}$	0.172	0.059	0.113	0.042	0.155	0.055	0.210
$Na^{\cdot}$-$K^{\cdot}$	0.039	—	0.033	—	0.044	—	0.030
$K^{\cdot}$	0.133	0.053	0.080	0.031	0.111	0.069	0.180

We see in this table that β is an additive property.

Next we will consider the thermodynamical meanig of this law. Let X represent the chemical potential of phenol in the aqueous salt solution and Z be that quantity for unit concentration. Then

$$X = Z + RT \ln C$$

where T denotes the absolute temperature and R is the gas constant. If these corresponding quantities in the absence of salt are indicated by suffix 0, then

$$X_0 = Z_0 + RT \ln C_0.$$

Along a horizontal line in Fig. 1,

$$X = X_0 = \text{constant},$$

therefore

$$Z - Z_0 = RT(\ln C_0 - \ln C) = RT \ln \frac{C_0}{C}$$

From the above observation

$$\frac{1}{S} \log \frac{C_0}{C} = \beta \quad \text{or} \quad \frac{1}{S} \ln \frac{C_0}{C} = 2.303\ \beta.$$

Hence

$$\frac{Z - Z_0}{S} = \alpha.$$

where $\alpha = 2.303\ \beta RT$, which is constant for a constant temperature.

Thus the elevation of the chemical potential of phenol for unit concentration by the addition of a neutral salt is proportional to the salt concentration.

Now we can obtain the equation of B–C curves in Fig. 1. As indicated already,

$$B = 2.272\ C_0 + 37.71\ C_0^3,$$

while

$$\log \frac{C_0}{C} = \beta S \quad \text{or} \quad C_0 = 10^{\beta S} C.$$

Therefore

$$B = 2.272 \times 10^{\beta S} C + 37.71 \times 10^{3\beta S} C^3 \quad \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

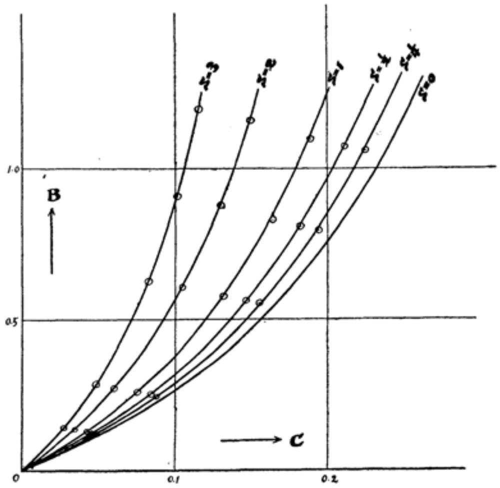

Fig. 2.

This equation (1) is found quite valid. For example, the case of $NaNO_3$ is shown in Fig. 2, where the curves have been drawn according to the equation (1) and the observed points are denoted by circlets.

The Effect of Sodium Nitrate on the Depression of Freezing Point of Aqueous Phenol Solution. In the first place, the measurements on the depression of freezing point of the aqueous solution of sodium nitrate alone were made in the same manner as described in my previous paper, although on this same topic there are sevaral previous reports of experiments which are sometimes not accurate. The results are shown in Table 4, whereafter the molar concentrations are calculeted in mol per 1000 grams of water.

TABLE 4.

Depression of freezing point of the aqueous solution of $NaNO_3$.

Water gr.	$NaNO_3$ gr.	Molar concentrations of $NaNO_3$ S	Depressions of freez. pt. by $NaNO_3$ in degree. D_S.
499.4	2.3105	0.0542	0.189
499.4	4.6406	0.1093	0.373
499.4	8.5151	0.2006	0.670

In the next place, the cryoscopic measurements of the aqueous solution of both phenol and sodium nitrate were made, the result of which are shown in Table 5.

TABLE 5.

Depression of freezing point when both phenol and $NaNO_3$ are simultaneously dissolved in water.

Water gr.	Phenol gr.	Molar conc. of phenol (C)	$NaNO_3$ gr.	Molar conc. of $NaNO_3$ (S)	Depression of freez. pt. in degree. D_{P+S}
499.5	10.198	0.217	0.	0.	$0.388 = D_P$
499.5	10.198	0.217	3.7495	0.0883	0.695
499.5	10.198	0.217	6.9650	0.1640	0.952
499.5	10.198	0.217	9.9715	0.2348	1.185

Subtracting the depression of phenol alone (D_P), from that by the combination of the two solutes (D_{P+S}) in Table 5, the depression apparently due to sodium nitrate is obtained as shown in Table 6, provided that the depression is the additive property of solutes.

TABLE 6.

Portions of depression apparently due to $NaNO_3$ when $C=0.217$.

S	$D_{P+S}-D_P$
0	0
0.0883	0.307
0.1640	0.564
0.2348	0.794

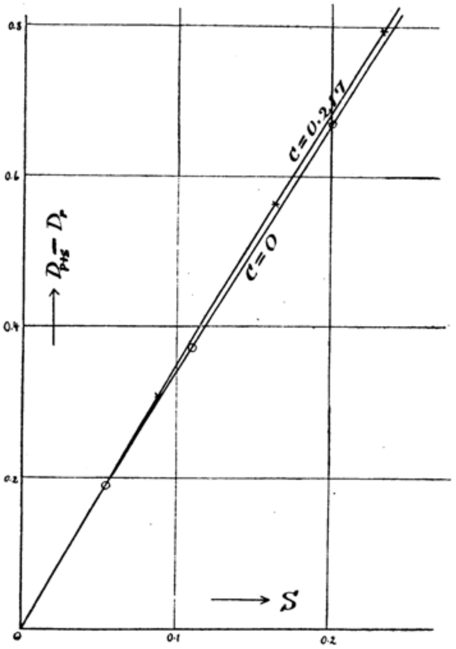

Fig. 3.

These depressions in Table 6 and those in Table 5, which are really due to sodium nitrate, are compared graphically in Fig. 3.

If the additivity holds in this case as assumed, the two curves must coincide, but we see a small discrepancy in the concentrated part. In the first section of this paper, I reached the conclusion that the chemical potential of phenol can be expressed in the following formula,

$$X = Z_0 + aS + RT \ln C$$

or

$$X = Z_0 + RT \ln \left(e^{\frac{a}{TR}S} C\right).$$

Now, as $e^{\frac{a}{RT}S}$ is so-called "activity coefficient," the activity of phenol and consequently, the depression of freezing point due to phenol must increase when a salt is added (that is, $S>0$). And so the above discrepancy of the curves should become perceptible when S is sufficiently great. Actually the curve $C=0.217$ deviates upwards from the curve $C=0$ and the deviation gradually increases with the concentration of sodium nitrate. Therefore, Fig. 3 offers a qualitative proof for the above equation obtained from the study of partition.

However, when the concentration of salt is small, owing to the small value of $\frac{a}{RT}$, the activity coefficient is nearly equal to unity and the effect of salt is negligible. That is why we cannot perceive the discrepancy at the dilute part in Fig. 3.

Summary.

1. From the measurements on the partition of phenol between benzene and the aqueous solutions of neutral salts, it has been found that the following logarithmic law practically holds,

$$\frac{1}{S}\log\frac{C_0}{C}=\beta$$

Applying this to the equation of the chemical potential of phenol it becomes

$$\frac{Z-Z_0}{S}=a.$$

We have also obtained an equation of phenol distribution between benzene and water in the presence of neutral salts at 25°C :

$$B=2.272\times10^{\beta S}C+37.71\times10^{3\beta S}C^3.$$

2. From the measurements of the freezing points of the aqueous phenol solutions in the presence of a neutral salt, it has qualitatively been proved that the chemical potential of phenol can be expressed in the following formula,

$$X=Z_0+aS+RT\ln C$$

and the activity coefficient of phenol is, therefore, to be expressed as

$$e^{\frac{a}{RT}S}.$$

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