THE FORMATION OF A COMPLEX ION IN THE AQUEOUS SOLUTION OF SILVER NITRATE AND PHENOL.

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In the study⁽¹⁾ of the salting out effects of neutral salts on the aqueous phenol solution, the silver nitrate has been found to be an exception in that it showed the opposite effect. It is natural to think this "salting in" effect as due to some chemical combinations between phenol and silver nitrate in the aqueous solution. The following studies were made to solve this problem.

I. The Effect of Silver Nitrate on the Partition of Phenol between Benzene and Water. The experiments on the partition of phenol between benzene and the aqueous solution of silver nitrate were carried out at 25°C. in the same manner as described in the previous paper.⁽²⁾ The results are shown in Table 1, where B and C represent the molar concentrations of phenol in the benzene and in the aqueous layer respectively and S denotes that of silver nitrate.

Table 1.

Partition of phenol between benzene and water in the presence of $AgNO_3$.

Mol. conc. o $AgNO_3$ S	2.0		1.0		0.5		0.25	
Molar concentration of phenol in	benzene layer B	aqueous layer C	benzene layer B	aqueous layer C	benzene layer B	aqueous layer C	benzene layer B	aqueous layer C
	0.8213	0.8517	1.1136	0.5966	0.9177	0.3637	0.9561	0.3092
	0.5688	0.6965	0.7675	0.5139	0.6716	0.3139	0.6429	0.2303
	0.[illegible]647	0.5049	0.5665	0.4190	0.3905	0.2181	0.4189	0.1866
	0.2836	0.4129	0.3862	0.3197	0.1982	0.1303	0.2111	0.1174
	0.1229	0.2056	0.1697	0.1588	0.0963	0.0680	0.1079	0.0564
	0.0615	0.0988	0.0813	0.0829				

Plotting B-C curves, we obtain Fig. 1, where the observed points are denoted by circlets. In Fig. 1, the most left-sided curve, which represents the case without silver nitrate, is taken from the previous paper.⁽²⁾ As we see in the figure, the curve moves to the right as the concentration of silver

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(1) K. Endo, *J. Chem. Soc. Japan*, **47** (1926), 374; This Journal, **2** (1927), 124.

(2) K. Endo, This Journal, **1** (1926), 25.

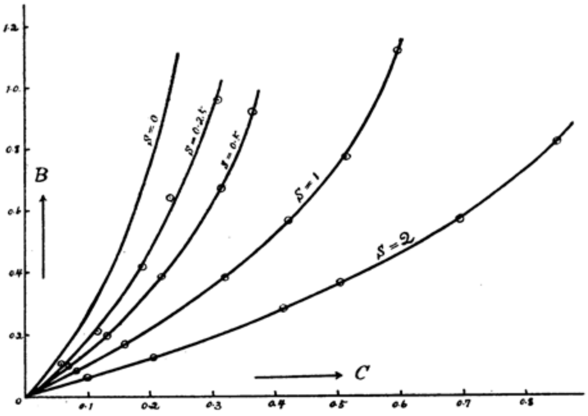

Fig. 1.

nitrate increases, that is, the solubility of phenol in the aqueous layer increases by the addition of silver nitrate. Obviously this effect is in the sense opposite to those of many other normal salts, namely, opposite to "salting out." The reason for this may be easily understood if we assume that some chemical combinations between phenol and silver nitrate (such as, the formation of a complex ion) occur in the aqueous layer. To solve this problem, I have studied, in the next place, the depression of freezing point of the aqueous solution of these substances.

II. The Effect of Silver Nitrate on the Depression of Freezing Point of the Aqueous Phenol Solution. The experiments were carried out in the similar manner as described in the previous paper. The results are shown in the following tables, where D_{P+A}, D_P and D_A represent the depressions of freezing point of the aqueous solutions of phenol in addition to silver nitrate, of phenol alone, and of silver nitrate alone, respectively.

TABLE 2.

Depression of freezing point of the aq. solution of $AgNO_3$.

Water gr.	$AgNO_3$ gr.	Molar conc. of $AgNO_3$ S	Depression (in degree) D_A
499.4	2.1370	0.0252	0.088
499.4	5.2475	0.0619	0.215
499.3	8.1625	0.0962	0.325
499.3	13.0165	0.1535	0.506
499.3	20.2700	0.2384	0.751

The data in Table 2 are also shown graphically by the curve $C=0$ in Fig. 2.

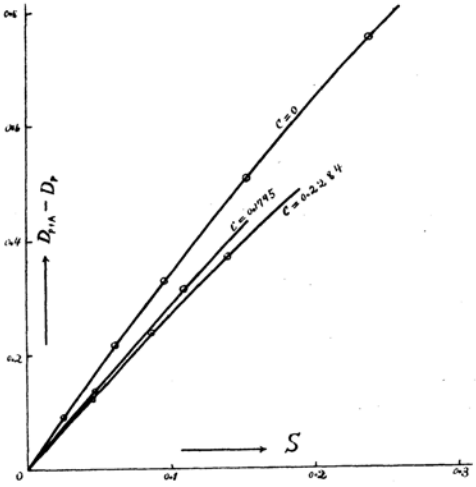

Fig. 2.

TABLE 3.

Depression of freezing point when both phenol and silver nitrate are dissolved simultaneously in water.

Water gr.	$AgNO_3$ gr.	Phenol gr.	D_{P+A} (in degree)
499.5	5.8815	2.4515	0.327
499.4	8.0345	5.7585	0.513
499.3	3.9570	8.4313	0.461
499.3	9.2870	8.4313	0.638
499.4	3.8176	10.7330	0.530
499.4	7.3333	10.7330	0.645
499.4	11.8433	10.7330	0.777

The data of Table 3 are compared in Table 4 with the summe of the individual depressions by phenol and by silver nitrate, which are obtained graphically, the former from Fig. 3 in the previous paper⁽¹⁾ and the latter from Fig. 2 in the present paper.

TABLE 4.

C	S	D_{P+A}	D_P	D_A	D_P+D_A
0.0522	0.0693	0.327	0.101	0.240	0.341
0.1226	0.0947	0.513	0.228	0.321	0.549
0.1795	0.0467	0.461	0.325	0.161	0.486
0.1795	0.1095	0.638	0.325	0.368	0.693
0.2284	0.0450	0.530	0.407	0.155	0.562
0.2284	0.0864	0.645	0.407	0.295	0.702
0.2284	0.1396	0.777	0.407	0.463	0.870

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(1) K. Endo. This Journal, **1** (1926), 28.

Here does not hold the additivity. This is shown more clearly in Fig. 2, where the ordinate denotes $D_{P+A}-D_P$ and the abscissa the molar concentration of silver nitrate. These deviations, as in the case of partition, are in the direction opposite to those of normal cases (e. g. sodium nitrate(1)) and are moreover far greater than the latter. Such a decrease of depression must be considered as being due to the decrease of the number of dissolved particles by some chemical combinations, while all the ionised particles, on the other hand elevate(2) the activity of phenol.

III. Determination of the Chemical Equation. The aqueous solution of silver nitrate and phenol is neutral and colourless, and as no compound between these substances can be separated out in any solid state, we can not determine its formula by chemical analysis. So we are obliged to rely upon the cryoscopic method for this purpose. The observations were made in the following two extreme cases.

a) When the concentration of silver nitrate is very small compared with that of phenol:—In this case we may assume that the whole of silver nitrate combines with phenol. As phenol associates in triple molecules(3) in a small degree, there holds the following relation in the non-combined portion of phenol,

$$c_3 = Kc_1^3,$$

where c_1 and c_3 represent the molar concentrations of monomolecular and trimolecular phenol respectively and K the association constant. Although the initial concentration of phenol (C) is great compared to that of silver nitrate (x), its absolute value is not great. And moreover the value of K is small, so we can put

$$c_3 = KC^3$$

without introducing any serious error, because here we need only the approximate estimation and not the exact evaluation for our purpose. Thus the following depressions of freezing point are expected corresponding to the respective assumed equations.

(1) Let the aquation be

$$\mathrm{AgNO_3 + C_6H_5OH = [Ag.C_6H_6O]^{\cdot} + NO_3'},$$

then the depression of freezing point is to be expressed by

$$D_{P+A}/k = c_1 + c_3 + C_{[\mathrm{Ag.C_6H_6O}]^{\cdot}} + C_{\mathrm{NO_3'}},$$

where $C_{[\mathrm{Ag.C_6H_6O}]^{\cdot}}$ and $C_{\mathrm{NO_3'}}$ denote the ionic concentrations of $\mathrm{[Ag.C_6H_6O]^{\cdot}}$

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(1) See the first foot-note of this paper.

(2) Ditto.

(3) K. Endo, This Journal, 1 (1926), 25.

and NO_3' respectively, and $k=1.86$. Here small correction terms due to the change of activities⁽¹⁾ by the presence of ions are also neglected.

Now $C = c_1+3c_3+C_{[Ag.C_6H_6O]^{\cdot}}$, and $C_{[Ag.C_6H_6O]^{\cdot}}=C_{NO_3'}=x$.

So $D_{P+A}/k = C-2c_3+x = C(1-2KC^2)+x.$

Hence $\left(\dfrac{\partial D_{P+A}}{\partial x}\right)_{x=0} = k.$

Therefore, the $D_{P+A}-x$ curve must have a tangent k at $x=0$.

(2) $AgNO_3+C_6H_5OH = C_6H_5OAg+H^{\cdot}+NO_3'$,

then, by the treatment similar to (1), we obtain the following results,

$$D_{P+A}/k = C(1-2KC^2)+2x$$

and $\left(\dfrac{\partial D_{P+A}}{\partial x}\right)_{x=0} = 2k.$

If C_6H_5OAg dissociates further in two ions,

$$\left(\frac{\partial D_{P+A}}{\partial x}\right)_{x=0} = 3k.$$

(3) $AgNO_3+2C_6H_5OH = [Ag.(C_6H_6O)_2]^{\cdot}+NO_3'$,

then $D_{P+A}/k = C(1-2KC^2)$, and $\left(\dfrac{\partial D_{P+A}}{\partial x}\right)_{x=0} = 0.$

(4) $AgNO_3+3C_6H_5OH = [Ag.(C_6H_6O)_3]^{\cdot}+NO_3'$,

then $\left(\dfrac{\partial D_{P+A}}{\partial x}\right)_{x=0} = -k.$

And so forth.

Now these are tested by observations, the results of which are shown in Table 5.

TABLE 5.

Depression of freez. pt. when the conc. of $AgNO_3$ is very small compared with that of phenol.

Water gr.	Phenol gr.	$AgNO_3$ gr.	x Molar conc. of $AgNO_3$	$D_{P+A}-D_P$ in degree
455.3	27.29	0.679	0.0088	0.017
455.3	27.29	1.352	0.0175	0.033
455.3	27.29	2.172	0.0281	0.051

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(1) loc. cit.; Debye & Hückel, *Phys. Z.* **24** (1924), 185.

From Table 5 we obtain Fig. 3 by plotting $D_{P+A}-D_P$ against x, which becomes, as we see, a straight line represented by an equation

$$D_{P+A}-D_P = kx.$$

Its tangent is therefore

$$\left(\frac{\partial D_{P+A}}{\partial x}\right) = k.$$

which agrees whith the case of (1).

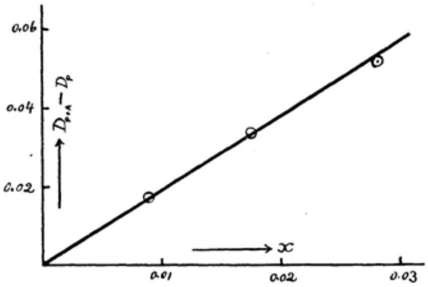

Fig. 3.

b) *When the concentration of phenol is very small compared with that of silver nitrate:*—The chemical equation,

$$AgNO_3+C_6H_5OH = [Ag.C_6H_6O]^{\cdot}+NO_3'$$

which has been proved in the last case, is tested also in this case, where we can assume that the whole of phenol combines with silver nitrate.

According to the conductivity experiments of Werner,⁽¹⁾ the complex salts are to be considered strong electrolytes, while according to Debye and Hückel,⁽²⁾ all strong electrolytes make the perfect dissociation in the aqueous solution and the activity coefficient f_i (for the i-th ion) due to the electric field of ions is given by

$$f = e^{-Az^2\sqrt{\Sigma z_i^2 C_i}},$$

where z_i and C_i denote, respectively, the valency and the concentration of the i-th ion and A is a constant for a constant temperature. Thus,

$$D_{P+A} = k(f_1 C_{Ag^{\cdot}}+f_2 C_{NO_3'}+f_3 C_{[Ag.C_6H_6O]^{\cdot}}).$$

As to the valencies of these ions,

$$z_1 = z_2 = z_3 = 1$$

and moreover there is the relation with regard to the analytical concentration (S) of silver nitrate,

$$\Sigma C_i = C_{Ag^{\cdot}}+C_{NO'_3}+C_{[Ag.C_6H_6O]^{\cdot}} = 2S.$$

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(1) Werner, „Neuere Anschauungen auf dem Gebiete der anorganischen Chemie."

(2) loc. cit.

So, $$f_1 = f_2 = f_3 = e^{-A\sqrt{2S}} = f.$$

Hence, $$D_{P+A}/k = f(C_{\mathrm{Ag}^{\cdot}} + C_{\mathrm{NO}_3'} + C_{[\mathrm{Ag.C_5H_6O}]^{\cdot}}) = 2fS.$$

Consequently, $$\left(\frac{\partial D}{\partial x}\right)_{x=0} = 0$$

where x represents the molar concentration of the added phenol. The experimental results are shown in Table 6 and are depicted in Fig. 4, where a straight line, given by

$$D_{P+A} - D_A = kx,$$

is also drawn for the sake of comparison.

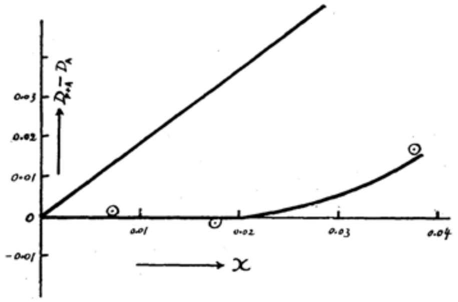

Fig. 4.

TABLE 6.

Depression of freez. pt. when the conc. of phenol is very small compared with that of silver nitrate.

AgNO gr.	Water gr.	Phenol gr.	x	$D_{P+A} - D_A$
5	35.602	0.0245	0.0073	0.001
5	35.602	0.0585	0.0175	0.002
5	35.602	0.1257	0.0375	0.017

In the vicinity of the origin, Fig. 5 shows actually a horizontal line in good agreement with our theory,

$$\left(\frac{\partial D_{P+A}}{\partial x}\right)_{x=0} = 0.$$

Thus the above chemical equation has been confirmed in the both extreme cases.

IV. Calculation of the Equilibrium Constant. As we have proved in the extreme cases that the chemical reaction,

$$\mathrm{AgNO_3 + C_6H_5OH = [Ag.C_6H_6O]^{\cdot} + NO_3'}$$

occurs in the aqueous solution, we shall next calculate the equilibrium constant in the intermediate cases (Table 3).

The association of phenol and the increase of activity of phenol due to the added salt are all negrected in the following calculations and the theory of strong electrolytes for dilute solutions by Debye and Hückel is applied, for here we treat dilute solutions in the cryoscopic measurements. For the calculation of the equilibrium constant, the following ionic equation has been used,

$$C_6H_5OH + Ag^{\cdot} = [Ag.C_6H_6O]^{\cdot}.$$

As to the analytical concentrations of silver nitrate (S) and phenol (C), the following relations hold,

$$S = C_{\mathrm{NO_3'}} = C_{\mathrm{Ag^{\cdot}}} + C_{[\mathrm{Ag.C_6H_6O}]^{\cdot}},$$
$$C = C_P + C_{\ \mathrm{Ag.C_6H_6O}]^{\cdot}},$$

where C_P denotes the non-combined portion of phenol. For the depressions of freezing point by S moles of silver nitrate (D_A) and by C moles of phenol plus S moles of silver nitrate (D_{P+A}), respectively,

$$D_A = k(f_1 C'_{\mathrm{A}\ \cdot} + f_2 C_{\mathrm{NO_3'}}) = 2kfS,$$
$$D_{P+A} = k(f_1 C_{\mathrm{A}\ \cdot} + f_2 C_{\mathrm{NO_3'}} + f_3 C_{[\mathrm{Ag.C_6H_6O}]^{\cdot}} + C_P) = 2kfS + kC_P.$$

Then
$$(D_{P+A} - D_A)/k = C_P{}^{(1)}$$
$$C - C_P = C_{[\mathrm{Ag.C_6H_6O}]^{\cdot}}$$
$$S - C_{[\mathrm{Ag.C_6H_6O}]^{\cdot}} = C_{\mathrm{Ag^{\cdot}}}.$$

By these three equations, we can obtain the equilibrium constant K_0 at 0°C as follows,

$$K_0 = \frac{C_P f C_{\dot{\mathrm{Ag}}}}{f C_{[\mathrm{Ag.C_6H_6O}]^{\cdot}}} = \frac{C_P C_{\dot{\mathrm{Ag}}}}{C_{[\mathrm{Ag.C_6H_6O}]^{\cdot}}}.$$

Table 7 has been calculated from the data given in Table 4.

TABLE 7.

Calculation of the equilibrium constant.

S	C	D_{P+A}	D_A	C_P	$C_{[\mathrm{Ag.C_6H_6O}]^{\cdot}}$	$C_{\mathrm{Ag^{\cdot}}}$	K_0
0.0693	0.0522	0.327	0.240	0.0445	0.0077	0.0616	0.36
0.0947	0.1226	0.513	0.321	0.1010	0.0216	0.0731	0.33
0.0467	0.1795	0.461	0.161	0.1646	0.0149	0.0318	0.35
0.1095	0.1795	0.638	0.368	0.1470	0.0325	0.0770	0.35
0.0450	0.2284	0.530	0.155	0.2095	0.0189	0.0261	0.29
0.0864	0.2284	0.645	0.295	0.1943	0.0341	0.0523	0.30
0.1396	0.2284	0.777	0.463	0.1730	0.0554	0.0342	0.26
						Mean K_0 = 0.32	

In spite of several neglections, the constancy of K_0 is satisfactory.

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(1) In the actual calculation C_P was determined graphically from the experimental D_P-C_P curve. (loc. cit.)

Summary.

1. From the measurement of partition of phenol between benzene and the aqueous solution of silver nitrate, it was found that the silver nitrate elevates considerably the solubility of phenol in the aqueous solution contrary to the salting out effects of other ordinary salts.

2. From the measurements of the depression of freezing point of the aqueous solutions of these substances, it has been proved that the "salting in" action of silver nitrate is due to the formation of a complex ion, $[Ag.C_6H_6O]^{\cdot}$, in the aqueous solution and the chemical equilibrium,

$$\dot{Ag} + C_6H_5OH = [Ag.C_6H_6O]^{\cdot},$$

is established there.

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