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Equilibrium Solubilities of Benzene, Toluene, Ethylbenzene, and Propylbenzene in Silver Nitrate Solutions

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Synopsis. By making use of the solute vapor, the equilibrium solubilities of benzene and three alkylbenzenes in $AgNO_3$ solutions have been measured. The complex formation constants of silver ions are estimated for each solute, and the results are compared with literature values.

It is well known that silver ions form complexes with a wide variety of organic compounds having C–C double bond(s). The formation constants for some aromatic hydrocarbons have been determined by measuring aqueous solubilities of the solutes in the presence of Ag^+ ions.[1–3]

We have reported a method of preparing aqueous solutions saturated with a solute such as aromatic hydrocarbons and iodine.[4,5] The technique involves introducing the solute vapor which is in equilibrium with a liquid or a solid solute, into water and circulating it in a closed system. Here we have applied the method to silver nitrate solutions to determine complex formation constants of Ag^+ with benzene and alkylbenzenes, and the results will be compared with the literature values.

Experimental

All the electrolytes and the nonelectrolytes used were of an analytical reagent grade. Deionized redistilled water was used to prepare silver nitrate solutions, an ionic strength of which was adjusted to 1.00 by adding a suitable amount of the KNO_3 stock solution. The concentration of Ag^+ in the $AgNO_3$ stock solution was determined in advance by the Fajans method. The experimental procedure and the apparatus employed in this work have been previously described in detail.[4] After the solubility equilibrium had been attained (*ca.* 10 min), definite portions of the aqueous phase were withdrawn, and the solute concentrations were determined by extraction with chloroform, followed by spectrophotometric measurements.

Results and Discussion

The complex formations of Ag^+ with aromatic hydrocarbons have been shown as follows:[1] $Ag^+ + \phi = Ag^+ \cdot \phi^+$, K_1, and $Ag^+ + Ag \cdot \phi^+ = Ag_2 \cdot \phi^{2+}$, K_2, where ϕ denotes hydrocarbon molecule, K_1 and K_2 being stepwise complexation constants. The total concentration of hydrocarbon, C_ϕ, and that of silver ions, C_{Ag}, present in the solution, are expressed as follows;

$$C_\phi = [\phi]_{eq}(1+K_1[Ag^+]_{eq} + K_1K_2[Ag^+]^2_{eq}) \tag{1}$$

$$C_{Ag} = [Ag^+]_{eq}(1+K_1[\Phi]_{eq} + 2K_1K_2[\Phi]_{eq}[Ag^+]_{eq}) \tag{2}$$

where the subscript means the equilibrium concentration. Let, in the absence and presence of Ag^+ ions, the hydrocarbon solubility in 1.00 mol dm^{-3} KNO_3 be S_o and S_{obsd}, respectively. Then, $[\phi]_{eq}$ and C_ϕ are equal to S_o and S_{obsd}, respectively, since the hydrocarbon molecules in the aqueous phase free from complexation with Ag^+ are also equilibrated with the solute in the vapor phase. The solubilities of hydrocarbons are small, and even K_1 which is larger than K_2, exhibits no more than a single figure for each hydrocarbon. Hence $[Ag^+]_{eq}$ can be made equal to C_{Ag}. Then, Eq. 1 becomes

$$S_{obsd}/S_0 = 1 + K_1C_{Ag} + K_1K_2C_{Ag}^2. \tag{3}$$

The results of the solubility measurements for each hydrocarbon in KNO_3 solutions containing Ag^+ ions up to 0.5 mol dm^{-3} are listed in Table 1. The K_1 and K_2 values have been determined with the aid of Eq. 3 by a curve-fitting method, and the results are summarized in Table 2 together with the literature values. The magnitude of our K_1 value is in the order of benzene<toluene>ethylbenzene>propylbenzene. It has been suggested that the K_1 value decreases due to a

TABLE 1. SOLUBILITIES OF BENZENE AND THE ALKYLBENZENES IN SILVER NITRATE SOLUTIONS AT 25 °C[a)]

C_{Ag}[b)]	Solubilities of[c)]			
	Benzene	Toluene	Ethylbenzene	Propylbenzene
mol dm^{-3}	10^{-2} mol dm^{-3}	10^{-3} mol dm^{-3}	10^{-3} mol dm^{-3}	10^{-4} mol dm^{-3}
0	1.54(1.00)	3.43(1.00)	1.02(1.00)	2.39(1.00)
0.02	1.62(1.05)	3.60(1.05)	1.07(1.05)	
0.04	1.68(1.09)	3.81(1.11)	1.12(1.10)	
0.05				2.66(1.11)
0.06	1.75(1.14)	4.04(1.18)	1.18(1.16)	
0.08	1.82(1.18)	4.23(1.23)	1.24(1.22)	
0.10	1.89(1.23)	4.39(1.28)	1.29(1.27)	2.95(1.23)
0.15				3.35(1.40)
0.20	2.26(1.47)	5.46(1.59)	1.56(1.53)	3.60(1.51)
0.30	2.65(1.72)	6.51(1.90)	1.87(1.83)	4.46(1.87)
0.40	3.02(1.99)	7.79(2.27)	2.18(2.14)	5.30(2.22)
0.50	3.50(2.27)	9.30(2.71)	2.52(2.47)	6.43(2.69)

a) Ionic strength was adjusted with KNO_3 to be 1.00. b) The toltal concentration of silver ions present in the aqueous solution. c) The S_{obsd}/S_o ratio is indicated in the parentheses.

TABLE 2. COMPLEX FORMATION CONSTANTS OF SILVER IONS WITH BENZENE AND THE ALKYLBENZENES AT 25 °C

Hydrocarbon	K_1/dm^3 mol^{-1}		K_2/dm^3 mol^{-1}	
	This work	Literature	This work	Literature
Benzene	2.30	2.41[a)]	0.349	0.212[a)]
Toluene	2.79	2.95[a)]	0.675	0.214[a)]
Ethylbenzene	2.57	2.7[b)]	0.341	0.15[b)]
Propylbenzene	2.16	2.9[b)]	1.18	

a) Ref. 1. b) Ref. 3.

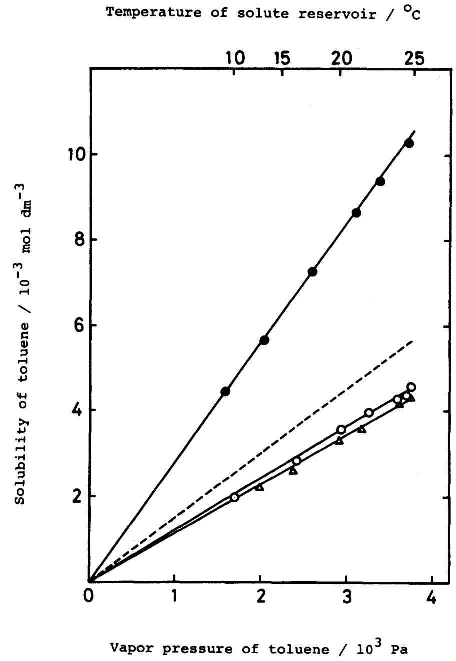

Fig. 1. Equilibrium solubilities of toluene in KNO_3 solutions at 25.00 °C *vs.* vaper pressure.
Pure water (dotted line), 1.00 mol dm^{-3} KNO_3 (△), 0.0197 mol dm^{-3} $AgNO_3$ in 1.00 mol dm^{-3} KNO_3 (○), 0.492 mol dm^{-3} $AgNO_3$ in 1.00 mol dm^{-3} KNO_3 (●).

steric hindrance as the carbon number of a homologous series increases.[1,3,6] With this view, the K_1 value reported in the literature seems to be overestimated for propylbenzene. Our K_2 values are considerably larger than the literature ones, but there is no criterion to judge which is more adequate. In order to determine the K_2 values with a minimum uncertainty, the solubility measurements should be made under higher Ag^+ concentrations. Such conditions, however, cause another uncertainty. In general, the aqueous solubility of a nonelectrolyte depends not only on the concentration, but also on the type of an electrolyte present in the solution, which is referred to the salting (-out or -in) effect. This effect may differ with Ag^+ and K^+, the latter having been added to keep the ionic strength constant, and the difference is to be pronounced at higher Ag^+ concentrations. It should be noted that the literature K_2 values have been determined at relatively higher Ag^+ concentrations up to 1.000 mol dm^{-3}.[1,3]

The present method of preparing aqueous solutions saturated with solute vapor is useful to see whether the solubility obeys Henry's law or not.[4] The solubility of toluene vapor obeys Henry's law in KNO_3 solutions (Fig. 1). This is also the case for the other alkylbenzenes studied here. In sharp contrast, the solubility of benzene vapor has been found to deviate from the law (Fig. 2). Though the reason for the deviation observed for benzene is not clear at present time, a plausible interpretation is that benzene molecules dissolved in KNO_3 solutions associate with each other to dimerize. There have been reported two opposite observations in the literature, one supporting dimerization of benzene,[7] the other not.[8] If dimerization does occur due to hydrophobic interaction between benzene molecules in water,[7] the presence of electrolytes in the solution may be expected to promote dimerization owing to their hydration. It is to be noted that if benzene molecules dissolved in KNO_3 solutions exist as a dimer to an appreciable extent, the K_1 value for benzene determined by us and by others might have been underestimated. If we consider the steric effect to be a main factor as for alkylbenzenes, it seems likely that the K_1 of benzene is rather larger than that of toluene, though the larger K_1 value of toluene has been explained in terms of an inductive effect of the methyl substituent.[1]

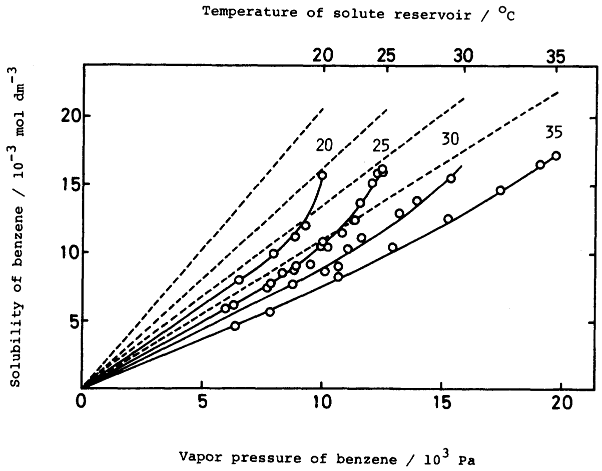

Fig. 2. Equilibrium solubilities of benzene in KNO_3 solutions *vs.* vapor pressure.
Pure water (dotted line), 1.00 mol dm^{-3} KNO_3 (solid line).
The figure near each line indicates the temperature of aqueous solution.

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