[CONTRIBUTION FROM THE HAYDEN MEMORIAL LABORATORIES OF NORTHEASTERN UNIVERSITY]

The Solubility of Tetraethylammonium Iodide in Benzene–Ethylene Dichloride Mixtures

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Introduction

As part of the program to study solubility effects in solvents of low dielectric constant, it was decided to determine the effect of dielectric constant on the solubility of tetraethylammonium iodide. Investigation has shown that in solvents of dielectric constant higher than ten the single ion concentration is high enough so that within certain limits a common-ion effect can be observed. To study the effect in liquids with lower dielectric constant, the system benzene–ethylene dichloride is useful: data for this have been published by Vernon, Wyman and Avery.[1] Tetraethylammonium iodide was selected for the solute since it has a reasonable solubility in ethylene dichloride.

Experimental

Materials.—C. P. thiophene-free benzene, after standing for several days over anhydrous calcium chloride, was distilled from activated alumina, the first and last fifth portions being discarded. The refractive index was 1.4978 at 25.2°; the "International Critical Tables" value is 1.49779 at 25.2°.

Ethylene dichloride was dried over anhydrous calcium chloride to an index of refraction of 1.4422 at 25.2° as compared with the "International Critical Tables" value of 1.44225 at 25.2°.

Tetraethylammonium iodide was prepared by mixing equimolar quantities of ethyl iodide (Merck) and triethylamine (Eastman Kodak Co.) and allowing to stand overnight. The crude product was dried, washed with petroleum ether, dissolved in boiling 95% ethyl alcohol, and treated with alcoholic potassium hydroxide until pink to phenolphthalein. The mixture was then cooled in an ice-bath, the solid filtered off and recrystallized twice from 95% ethyl alcohol. Finally, the pure product was dried in a vacuum desiccator. Since decomposition of the pure solid occurred at 280°, no melting point could be obtained; the analysis of the material for iodine gave 49.61% as compared with the theoretical iodine per cent. of 49.63.

Procedure.—Excess solute was added to 600 cc. of a benzene–ethylene dichloride mixture in a bottle with a ground glass cap which was wired on and coated with paraffin. The bottles were rotated in a water-bath at 35° for twenty-four hours and then at 25 ± 0.02° long enough to establish equilibrium. For the 93,5% ethylene dichloride, rotation at 25° for one hundred and twenty hours gave essentially the same solubility as rotation for twenty-four hours at 35° followed by seventy-two hours at 25°.

After the required rotation time, the bottles and a calibrated 500-cc. volumetric flask were supported in the water-bath at 25 ± 0.02°. The solution, after settling, was forced out by dry air through a glass wool filter into a volumetric flask. Then the solution was poured into a beaker and the flask was washed out with 95% ethyl alcohol, the wash solution being added to the benzene–ethylene dichloride solution. Silver iodide was precipitated by adding excess silver nitrate solution, stirred for five minutes, allowed to settle four hours in the dark, filtered into a Gooch crucible, and dried at 120° to constant weight. This method applied to known amounts of solute was shown to be consistently accurate to within 1.9%.

Results

The solubility results given in Table I are the averages of two or more determinations as shown.

TABLE I

SOLUBILITY OF TETRAETHYLAMMONIUM IODIDE IN ETHYLENE DICHLORIDE–BENZENE MIXTURES AT 25°

Ethylene dichloride, %	Dielectric constant	No. of detns.	Moles per liter of iodide × 10⁴
35.5	3.85	4	0.865 ± 0.009
48.0	4.55	3	2.18 ± .02
56.6	5.20	6	3.80 ± .04
68.0	6.07	5	8.51 ± .08
80.0	7.26	2	18.06 ± .14
85.0	8.01	2	30.6 ± .3
93.5	9.02	4	55.6 ± .3
100.0	10.36	5	91.9 ± .2

The average deviation of the individual determinations from the mean is no greater than 1.05% for any solvent mixture. Figure 1 shows a plot of the log of solubility against the log of the dielectric constant.

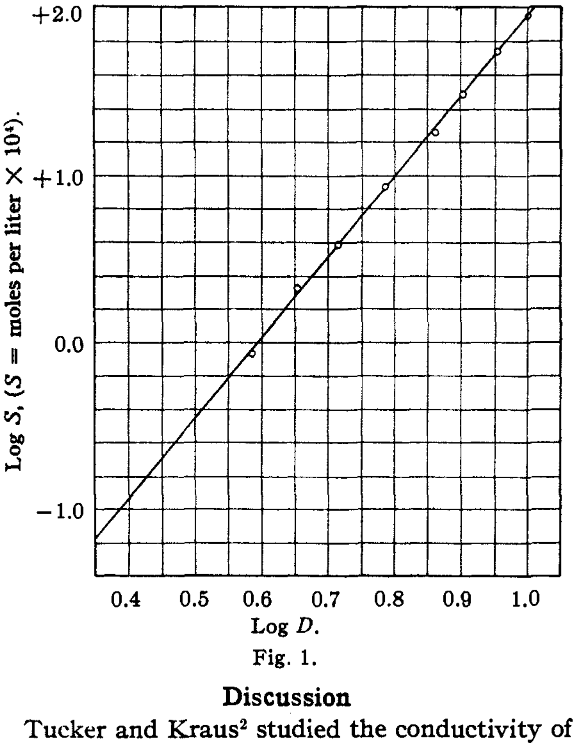

Fig. 1.

Discussion

Tucker and Kraus[2] studied the conductivity of tetraethylammonium picrate in ethylene dichloride at 25° and found that triple ion formation became important at 3.4×10^{-4} N. Luder, Kraus, Kraus and Fuoss[3] found this effect to be significant

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(1) Vernon, Wyman and Avery, THIS JOURNAL, **67**, 1422 (1945).

(2) Tucker and Kraus, *ibid.*, **69**, 454 (1947).

(3) Luder, Kraus, Kraus and Fuoss, *ibid.*, **58**, 255 (1946).

at 1×10^{-5} N for tetrabutylammonium perchlorate in benzene at 25°. For tetraethylammonium iodide the triple ion formation should take place at a lower concentration than for the above reported salts since such an effect increases with decrease in ion size. The solubilities here reported are of the order of 10^{-2} N in pure ethylene dichloride and 10^{-4} N in 35.5% ethylene chloride. Therefore, it seems likely that multiple ion formation exists in all the solutions studied; straight line extrapolation to pure benzene is justified if such conditions continue to exist down to a dielectric constant of 2.274. Extrapolation of Fig. 1 gives a solubility of 6.918×10^{-6} mole per liter for the solubility of tetraethylammonium iodide in benzene at 25°. At this solubility, triple ions may reasonably be expected to exist. Further evidence of ion association would be obtainable from studies of the effect of a common ion upon the solubilities reported in this paper. It is planned to study this as well as the solubility relation in solvents of higher dielectric constant.

Ricci and Davis[4] proposed an empirical equation to relate solubility to dielectric constant of the solvent which showed that a plot of log S against log D should be a straight line with a slope of three. This equation assumed that the Debye–Hückel limiting law applied and that the activity coefficient of an electrolyte at saturation is a constant independent of the dielectric constant of the solvent medium. They further showed that approximate equality of activity coefficients could be expected between solvent dielectric constants of 80 and 40. This, together with the evidence of triple ion formation, seems to indicate that a slope of 3 should not be expected with our data. The explanation of the slope of 5 of Fig. 1 will have to wait until more data are available.

The dielectric constant of benzene is 2.274 and log $D = 0.3568$. By extrapolation of Fig. 1, assuming a straight line relation, a value of log S of -1.160 is obtained. This gives 6.918×10^{-6} mole per liter for the solubility of tetraethylammonium iodide in benzene at 25°.

Summary

The solubility of tetraethylammonium iodide in pure ethylene dichloride and ethylene dichloride–benzene mixtures has been determined. A plot of log S *versus* log D follows closely a straight line with a slope of 5 in contrast to the value of 3 found in solvents with higher dielectric constant.

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[4] Ricci and Davis, This Journal, **62**, 407 (1940).

[Contribution from the Department of Sanitary Engineering, Harvard Graduate School of Engineering]

Equilibrium Studies on N-Chloro Compounds. I. The Ionization Constant of N-Chloro-*p*-toluenesulfonamide[1]

By J. Carrell Morris, J. Alfredo Salazar[2] and Margaret A. Wineman

The N-chloro compounds, those substances in which it may be considered that one or more chlorine atoms in the +1 oxidation state are bound to nitrogen, are of considerable interest because of the widespread use of a number of them as disinfecting agents. In many cases it is believed that their efficiencies as disinfecting agents are related to the magnitudes of their hydrolytic and other equilibrium reactions in water solution, but quantitative data on the equilibria with which disinfection results might be compared are available for only one or two isolated systems. The present series of papers is therefore concerned with the quantitative evaluation of equilibrium relationships for water solutions of certain important N-chloro compounds and with the use of the equilibrium constants so determined for predicting the disinfectant power of solutions of the N-chloro compounds under various conditions.

The system selected for primary study was that in which the substances Dichloramine-T, and Chloramine-T are participants. These two substances are, respectively, N,N-dichloro-*p*-toluenesulfonamide (I) and sodium N-chloro-*p*-toluenesulfonamide, the latter being the sodium salt of N-chloro-*p*-toluenesulfonamide (II). A number of equilibria are established in solutions of these materials, which can be described most conveniently in terms of the following processes:

I. The hydrolysis equilibrium for Dichloramine-T

$$\underset{\text{(I)}}{C_7H_7SO_2NCl_2} + H_2O = \underset{\text{(II)}}{C_7H_7SO_2NHCl} + HOCl \quad (1)$$

for which the equilibrium constant equation is[3]

$$K_h = \frac{(HOCl)(C_7H_7SO_2NHCl)}{(C_7H_7SO_2NCl_2)} \quad (1a)$$

II. The exchange or disproportionation reaction

$$\underset{\text{(II)}}{2C_7H_7SO_2NHCl} = \underset{\text{(I)}}{C_7H_7SO_2NCl_2} + C_7H_7SO_2NH_2 \quad (2)$$

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[1] This work was carried out under a research contract with the Office of the Quartermaster General, U. S. Army.

[2] Now with the West Virginia State Department of Health, Charleston, W. Va.

[3] In all of the equations of this paper parentheses, except when they are used just to set off mathematical terms, indicate molar activities of the substances concerned and square brackets indicate molar concentrations. For non-ionic substances the two are assumed to be the same within the experimental accuracy of the determinations.