

Procedure.—The individual experiments were performed essentially as described previously.¹ All experiments were conducted at 25°.

Summary

α -Pinene, in dilute solution, adds hydrogen

bromide and chloride rapidly from non-donor solvents and slowly from donor solvents. As shown previously¹ coordination of halogen halides with a solvent lessens their effectiveness for addition to an olefinic linkage.

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[CONTRIBUTION FROM THE HAYDEN MEMORIAL LABORATORIES OF NORTHEASTERN UNIVERSITY]

The Solubility Effect in Solvents of Low Dielectric Constant. I. The Solubility of Tetrabutylammonium Iodide in Benzene in the Presence of Tetrabutylammonium Picrate and Nitrate

BY ARTHUR A. VERNON, W. F. LUDER AND MARIO GIELLA

I. Introduction

Attacking the problem from three angles, Kraus and Fuoss have been remarkably successful in explaining the properties of electrolytic solutions in solvents of any dielectric constant.¹ Using conductance, freezing point and dielectric constant measurements, they have shown that, where acid-base reactions are not involved, the properties of such solutions depend primarily upon the dielectric constant of the solvent. These properties have been accounted for on the basis of coulomb forces between ions, ion pairs and triple ions.

Higher association is observed in solvents of very low dielectric constant, such as benzene and dioxane. However, the behavior of such solutions is so complex that no quantitative theory is yet available for any but very dilute solutions, and the accumulation of more data will be necessary before an adequate one can be proposed. One approach to the problem in addition to those employed by Kraus and Fuoss seems to be that of an investigation of the effect of a second salt on the solubility of a salt dissolved in solvents of low dielectric constant.

Some work already has been done on the solubility effect in non-aqueous solvents.² That of most interest in connection with the present investigation has been done by Seward,^{2g} and Seward and Hamblet.^{2f} They used ethylene dichloride and acetic acid as solvents. Solvents of

higher dielectric constant than about ten are of little interest since the concentration of single ions is high enough in such solvents so that the familiar solubility effects are observed: namely, a decrease in solubility with a common ion and an increase when no common ion is present.

An investigation is now under way in this Laboratory to obtain data for solvents of dielectric constants varying from that of benzene (2.28) to that of ethylene dichloride (10.23).³ This paper is the first of a series and presents preliminary results and a discussion of the problem. In solvents of sufficiently low dielectric constant, association is such that the proportion of single ions to ion pairs and higher multiples is exceedingly small. Therefore, it is to be expected that the solubility effects will be different from those usually observed in solvents of higher dielectric constant. This is strikingly demonstrated by the results herewith presented. Even though a common ion is involved, the solubility of tetrabutylammonium iodide in benzene *increases* rapidly as tetrabutylammonium picrate or nitrate is added.

II. Experimental

Materials.—C. p. thiophene free benzene was distilled from calcium oxide onto sodium, the first and last quarters being discarded. It was redistilled from this sodium onto fresh sodium and stored with moisture proof seals.

The salts were prepared and recrystallized according to the method of Cox, Kraus and Fuoss.⁴

The melting points were: for tetrabutylammonium iodide, 148°; for the picrate, 89.5°; for the nitrate, 120°.

(1) Kraus and Fuoss, *THIS JOURNAL*, **55**, 21 (1933), and following papers on properties of electrolytic solutions.

(2) (a) Robinson, *J. Phys. Chem.*, **32**, 1089 (1928); (b) Kraus and Seward, *ibid.*, **32**, 1294 (1928); (c) Williams, *THIS JOURNAL*, **51**, 1112 (1929); (d) Hansen and Williams, *ibid.*, **52**, 2759 (1930); (e) Seward and Schumb, *ibid.*, **52**, 3962 (1930); (f) Seward and Hamblet, *ibid.*, **54**, 554 (1932); (g) Seward, *ibid.*, **56**, 2610 (1934).

(3) Benzene and ethylene dichloride form a thermodynamically ideal solution. One method of obtaining the desired values of dielectric constant will be to choose various proportions of the two liquids. In doing this, the effect of the addition of ethylene dichloride dipoles on the solubility of salts in benzene will also be noted.

(4) Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

Procedure.—The method was that of Kraus and Seward.^{2b} Known amounts of the solvent salt and an excess of tetrabutylammonium iodide were put in the saturation bottle. To this was added 750 cc. of benzene and, after sealing, the mixture was rotated in a thermostat for twenty-four hours at 30° and for twenty-four hours at 25°. The lower temperature was controlled to $\pm 0.01^\circ$; 500 cc. of solution was then forced out through a filter into a calibrated volumetric flask. This solution removed was then transferred to a beaker; 100 cc. of 95% ethyl alcohol was added, and the iodide precipitated by adding 20 to 30 cc. of 0.1 *N* alcoholic silver nitrate. The precipitate was allowed to age for twenty-four hours and was then filtered, dried and weighed. The tests made with known amounts of tetrabutylammonium iodide in benzene showed that this method of analysis is accurate within 0.5%. Since the minimum increase in solubility of the iodide with the added salt was about 15%, this method of analysis is satisfactory.

Results.—The results of the measurements are given in Table I. All concentrations are expressed as moles per liter of benzene and are the averages of duplicate measurements except in the case of pure benzene solution where triplicate measurements were made.

TABLE I

SOLUBILITY OF TETRABUTYLAMMONIUM IODIDE IN THE PRESENCE EITHER OF TETRABUTYLAMMONIUM PICRATE OR NITRATE IN BENZENE AT 25°

Concn. picrate $\times 10^4$	Solubility of iodide $\times 10^4$	Concn. nitrate $\times 10^4$	Solubility of iodide $\times 10^4$
0.00	3.36 \pm 0.08	0.00	3.36 \pm 0.08
1.42	3.88 \pm .03	4.36	6.78 \pm .03
2.84	5.39 \pm .02	8.73	9.30 \pm .18
11.33	8.28 \pm .02	21.82	14.79 \pm .25
28.40	16.51 \pm .82	43.64	19.99
56.80	30.55 \pm .56		

III. Discussion

The rapid increase in solubility shown in the accompanying figure confirms the conclusion of Kraus and Fuoss that solutions of salts in solvents of very low dielectric constant are associated at the concentrations given. If single ions were primarily involved, the solubility of the iodide would decrease rather than increase with the addition of a common ion.

In ethylene dichloride ($D = 10.23$) there are enough single ions present so that the solubility effect is "normal".^{2g} In acetic acid ($D = 6.25$)^{2b} the effect seems to be about midway between those observed in ethylene dichloride and benzene. The solubility change is slight when a common ion is added, increasing in one case and decreasing in the other of two given by Seward and Hamblet.^{2f} Evidently in acetic acid, association to

higher multiples is beginning to predominate over the ion-ion pair equilibrium. When the solvent is benzene, the presence of single ions is not detectable at the measured concentrations.

The work of Seward and Hamblet was done before the clarification of the problem by Kraus and Fuoss, and it is now apparent that the use of the Gronwall, LaMer and Sandved equation was not justified for solutions of dielectric constants as low as those of acetic acid and ethylene chloride. Dissociation is not complete in such solvents in the range of concentration investigated, and the equation does not take into account the degree of dissociation.

An attempt to estimate the number of single ions in solutions of acetic acid and ethylene chloride might be made using the method of Kraus and Fuoss,¹ but this cannot be done for solutions in benzene. Conductance and freezing point measurements indicate that in the concentration range of our measurements there are very few simple ions, and that association to triple ions, quadri-poles, and even higher multiples is typical of this region. For example, the freezing point measurements of Rothrock and Kraus⁵ indicate that for tetrabutylammonium perchlorate in benzene the average molecular weight is from three times to six times the formula weight in the concentration range from 0.001 *N* to 0.014 *N*. The polarization curve of the same salt falls with increasing concentration⁶ which also indicates the building

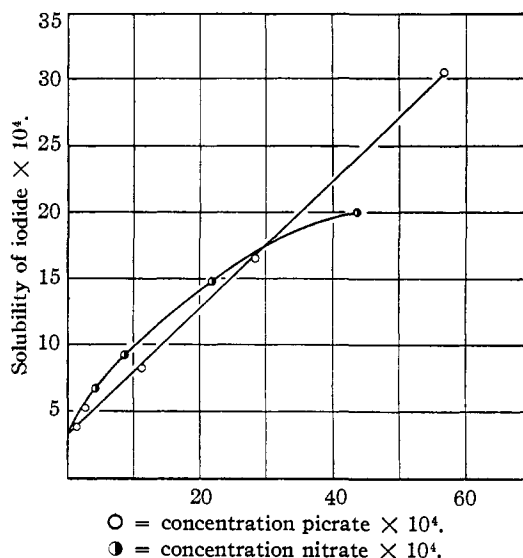


Fig. 1.

(5) Rothrock and Kraus, *THIS JOURNAL*, **59**, 1699 (1937).

(6) Geddes and Kraus, *Trans. Faraday Soc.*, **32**, 585 (1936).

up of dipoles to high aggregates. These results are confirmed by conductance measurements.⁷ The minimum occurs at $1 \times 10^{-5} N$, with the conductance slowly rising as the concentration is increased. The behavior of salts in benzene is exceedingly complex and no quantitative theory can be proposed as yet, but it seems certain that at the concentrations of our solubility measurements the effect of simple ions is negligible.

An adequate explanation of the observed solubility increase must await the accumulation of more data. Addition of other salts increases the dielectric constant,⁸ but since the effect is small and the solubility changes observed in this work are too large to be ascribed to a dielectric constant effect, it seems likely that association is the primary factor. This appears to be supported by the fact that the solubility of the iodide increases more rapidly at first upon addition of the nitrate than with the picrate. Association, according to the work of Kraus and Fuoss, is higher when symmetrical ions are involved and the difference in the

(7) Luder, P. B. Kraus, C. A. Kraus and Fuoss, *THIS JOURNAL*, **58**, 255 (1936).

(8) C. A. Kraus, *Trans. Electrochem. Soc.*, **66**, 201 (1934).

two solubility curves may be in line with corresponding differences in the conductance curves for symmetrical and unsymmetrical salts.

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IV. Summary

The solubility of tetrabutylammonium iodide in benzene in the presence of tetrabutylammonium picrate and nitrate has been measured and found to increase rapidly with the concentration of added salt. These measurements are the first in a series of investigations of the solubility effect in solvents of low dielectric constants in an attempt to secure more information about the complex behavior of electrolytes in such solvents. A discussion of the nature of the problem and of proposed research has been given.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GEORGIA SCHOOL OF TECHNOLOGY]

The Hydrolysis of Methyl Acetate in a Non-Aqueous Solvent¹

BY HAROLD B. FRIEDMAN AND GLENN V. ELMORE

Introduction

In 1883, Ostwald² first studied the velocity of the hydrolysis of methyl acetate: $\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$. This reaction is stoichiometrically second order but due to the relative constancy of the water concentration the velocity follows a first order course. Ostwald ignored the reverse reaction, which was small during the period in which he made his measurements.

Griffith and Lewis³ determined the velocity of the hydrolysis in the presence of hydrochloric acid and trichloroacetic acids and with varying initial concentrations of the ester. Schreiner⁴ compiled the earlier data on the analogous reaction of ethyl

acetate catalyzed by hydrochloric acid. Harned and Pfanstiel⁵ calculated the velocity constant for the ethyl acetate hydrolysis in aqueous solution, in which they ignored neither the reverse reaction nor the slight change in the water during the reaction.

More recently, Harned and Samaras,⁶ using varying amounts of organic solvents, studied the hydrolysis of ethyl orthoformate with acetic acid-sodium acetate buffers. Other work involving hydrolysis in low dielectrics includes that of Tommila and Hinshelwood,⁷ who studied the hydrolysis in aqueous acetone of a large number of substituted esters, in order to determine the effect of the substituents. Poethke⁸ was able to detect only a slight hydrolysis of ethyl acetate in aqueous solution using no catalyst.

(1) Constructed from a thesis presented to the department of Chemistry, Georgia School of Technology, June, 1940, by Glenn V. Elmore in partial fulfillment of the requirements of the degree of Master of Science in Chemistry.

(2) Ostwald, *J. prakt. Chem.*, **28**, 449 (1883).

(3) Griffith and Lewis, *J. Chem. Soc.*, **109**, 67 (1916).

(4) Schreiner, *Z. anorg. Chem.*, **116**, 102 (1921).

(5) Harned and Pfanstiel, *THIS JOURNAL*, **44**, 2193 (1922).

(6) Harned and Samaras, *ibid.*, **54**, 1 (1932).

(7) Tommila and Hinshelwood, *J. Chem. Soc.*, 1801 (1938).

(8) Poethke, *Ber.*, **68B**, 1031 (1935).