[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XIV. The Dielectric Constant of Some Solutions of Electrolytes in Benzene[1]

BY GILMAN S. HOOPER AND CHARLES A. KRAUS

I. Introduction

When the problem of electrolytic solutions in solvents of low dielectric constant was undertaken in this Laboratory several years ago, it was felt that properties other than the conductivity needed to be measured if the results were to be interpreted with any degree of assurance. The results of freezing point measurements have already been reported in THIS JOURNAL.[2] In the present paper we report the results of some measurements of the dielectric constant of solutions of tetraisoamylammonium picrate, triisoamylammonium picrate, tetraisoamylammonium bromide and silver perchlorate in benzene.

If ions associate to form ion-pairs in solution, as is indicated by conductance[3] and cryoscopic measurements, then such electrical dipoles should exhibit high polar moments. Moreover, if the dipoles associate to form more complex aggregates,[2,4] the molecular polarization should diminish with increasing concentration, the effect being the greater, the greater the degree of aggregation.

In view of the low concentration at which aggregation effects appear, it seemed obvious that if dielectric data were to be interpreted at all, the measurements would have to be carried to much lower concentration than is usually the case. It was anticipated that measurements, to be of value, would have to be carried out in the region 10^{-4} to 10^{-3} N.

The only earlier observations on the dielectric constant of solutions of an electrolyte are due to Williams and Allgeier[5] who carried out measurements with silver perchlorate in benzene. Their lowest concentration was in the neighborhood of 0.1 N and they obtained for the molecular polarization of the salt, a value of 461 cc., which is of the same order of magnitude as that of ordinary polar molecules. It was anticipated that, at lower concentrations, higher values would be found for the molecular polarization, which proved to be the case.

The dielectric constants of a number of pure liquids were measured and are recorded below.

II. Method and Materials

Method.—To determine the dielectric constants of the various solutions, a resonance method was adopted which was substantially the same as that of Wyman.[6] The method consists, essentially, in determining the frequency of a rigid resonator immersed in the medium whose dielectric constant is to be determined. Knowing the frequency of the resonator in air, the dielectric constant is given by the relation $D = \omega_0^2/\omega^2$ where ω_0 and ω are the frequencies in air and in the medium, respectively.

To determine the frequency of the resonator, a variable frequency oscillator is employed, whose frequency is adjusted to resonance with that of the resonator, resonance being indicated by the current in the plate circuit of the variable oscillator. The frequency of the variable oscillator is obtained by tuning to one of the harmonics of a crystal oscillator of fixed frequency. In general, the frequency of the resonator will fall between a pair of harmonics of the crystal oscillator, in which case the precise frequency of the resonator may be obtained by interpolating between the harmonics. This is accomplished by introducing a small cylindrical condenser into the circuit of the variable oscillator. The outer cylinder is mounted on the carriage of a micrometer screw and a displacement of approximately 1 cm. of the micrometer screw, or 10,000 divisions of the micrometer head, serves to vary the frequency from one harmonic of the crystal oscillator to the next. The frequency of the variable oscillator was very closely a linear function of the setting of the micrometer.

The method of carrying out the measurements, therefore, is to introduce the resonator into pure benzene, determine the micrometer setting corresponding to one adjacent harmonic, then the setting corresponding to resonance with the resonator and, finally, the setting corresponding to resonance with the other adjacent harmonic. Knowing the adjacent harmonic numbers (determined by means of a wave-meter), the frequency of the resonator in terms of harmonic numbers of the crystal is obtained by simple interpolation. Having similarly determined the harmonic number of the same resonator in air, the dielectric constant of the solution is given by the relation, $D = h_0^2/h^2$, where h_0 and h are the harmonic numbers corresponding to the air and the medium frequencies of the resonator, respectively. Having determined the dielectric constant of pure benzene, the desired amount of solute is added and the dielectric constant of the solution is determined as has just been described.

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[1] This paper is, in part, the subject matter of a thesis submitted to the Graduate School in Brown University by Gilman S. Hooper in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Kraus and Vingee, THIS JOURNAL, **56**, 511 (1934); Batson and Kraus, *ibid.*, **56**, 2017 (1934).

[3] Fuoss and Kraus, *ibid.*, **55**, 1019 (1933).

[4] Fuoss and Kraus, *ibid.*, **55**, 3014 (1933).

[5] Williams and Allgeier, *ibid.*, **49**, 2416 (1927).

[6] Wyman, *Phys. Rev.*, **33**, 623 (1930).

The medium whose dielectric constant was to be determined, together with the resonator, was contained in a glass tube which was brought to temperature in a thermostat and transferred to a Dewar tube, the measurements being carried out as quickly as possible. Probably temperature variations constituted one of the major sources of error in these measurements. The crystal oscillator had a frequency of 868 kilocycles and the resonator used in benzene had an air frequency of 89 megacycles. Other resonators of appropriate frequencies were used in solvents of higher dielectric constant. The specific conductance of the solutions was always less than 1 × 10^{-8} mho.

Materials.—Thiophene-free benzene was purified in the usual way by treatment with sulfuric acid, repeated fractional distillation from sodium-lead alloy (NaPb), and final fractional crystallization. Tetraisoamylammonium bromide, tetraisoamylammonium picrate and triisoamylammonium picrate were samples of salts prepared by Dr. Raymond M. Fuoss.[3,4]

The silver perchlorate used was the sample prepared by Mr. P. B. Kraus[7] and was recrystallized from benzene. With the exception of silver perchlorate, all the solutions were made up by weighing the salt directly into the cell; the perchlorate was weighed in as solution.

The pure solvents for which data are given were all purified by appropriate means.

Densities.—The densities of the solutions were determined at concentrations higher than those at which the dielectric constant measurements were carried out. In calculating the molecular polarization, the densities were interpolated linearly. The density data are given in Table I.

TABLE I

DENSITIES OF SOLUTIONS OF ELECTROLYTES IN BENZENE

(t = 25.00°)

Salt	Concentration	Density
Tetraisoamylammonium picrate	1.875 × 10^{-2}	0.8750
Triisoamylammonium picrate	2.119 × 10^{-2}	.8759
Tetraisoamylammonium bromide	1.930 × 10^{-2}	.8745
Silver perchlorate ($AgClO_4$)	8.851 × 10^{-2}	.8901
Benzene	....	.8732

III. Results

In the following tables are given values for the increase of the dielectric constants, over that of pure benzene, for solutions of tetraisoamylammonium picrate, tetraisoamylammonium bromide, triisoamylammonium picrate and silver perchlorate at 25.00°. The molecular polarization is given in the last column. In Table III are given the dielectric constants of a number of pure solvents.

IV. Discussion

The dielectric constants of the solutions are shown graphically in Fig. 1, the dielectric constant changes due to the electrolytes being plotted as ordinates against concentrations as abscissas. The most striking feature of the results is the high value obtained for the dielectric constant increase. For 0.001 N solutions, the dielectric constant changes amount approximately to 0.03, 0.02, 0.01 for tetraisoamylammonium picrate, triisoamylammonium picrate and silver perchlorate, respectively; for ordinary polar molecules at the same concentrations, it would amount to about 0.002. In other words, the effect of electrolytes on the dielectric constant of a non-polar

TABLE II

DIELECTRIC CONSTANT CHANGE OF SOLUTIONS IN BENZENE

$N \times 10^4$	ΔD	P_2
A. Tetraisoamylammonium Picrate		
1.83	0.0073	6710
2.97	.0112	6360
4.70	.0169	6030
7.41	.0243	5530
10.17	.0328	5390
B. Tetraisoamylammonium Bromide		
1.16	0.00213	3090
2.01	.00345	2900
3.87	.00471	2080
5.11	.00539	1810
8.39	.00687	1420
12.60	.00820	1150
C. Triisoamylammonium Picrate		
1.67	0.00345	3430
2.37	.00496	3520
3.97	.0080	3390
5.71	.0115	3380
8.83	.0165	3330
9.16	.0168	2990
16.52	.0280	2860
D. Silver Perchlorate		
2.04	0.00278	2220
3.18	.00371	1900
4.83	.00573	1930
9.47	.0091	1560
11.45	.0104	1470
30.4	.0190	1000
54.5	.0269	783
64.9	.0309	756
80.7	.0365	715
99.1	.0419	664
199.7	.0701	546

TABLE III

DIELECTRIC CONSTANTS OF PURE LIQUIDS

Liquid	t	D
Cyclohexane	25.00	2.012
Dioxane	25.00	2.181
Benzene	25.00	2.267
n-Butyl ether	25.00	3.045
Anisole	25.00	4.289
Ethylene bromide	25.00	4.756
Ethylene chloride	25.00	10.235
Ammonia	−33.35	22.38

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(7) P. B. Kraus, Thesis, Brown University, 1933.

medium is approximately ten times as great as that of ordinary polar molecules.

Not only the magnitude of the effect, but, also, the form of the curve depends upon the size and constitution of ions. The effect is greatest for electrolytes with the largest ions; the dielectric constant curves are the straighter the greater the electrical asymmetry of the ions. Thus, triisoamylammonium picrate, with two unsymmetrical ions, yields a comparatively linear curve, tetraisoamylammonium picrate and silver perchlorate yield curves that exhibit marked deviations from linearity, while tetraisoamylammonium bromide yields a curve whose deviation from linearity is extreme.

The deviations from linearity are accounted for by the formation of multipoles due to association of dipoles (ion-pairs). As has been pointed out in earlier papers of this series, electrolytes with electrically unsymmetrical ions exhibit much less tendency to form multipoles than do electrolytes with symmetrical ions. The freezing point curves of tetraisoamylammonium picrate and of silver perchlorate are very nearly identical at low concentrations; the deviations of the dielectric constant curves from linearity for these two electrolytes have practically the same percentage value, although they differ greatly in absolute value. The great deviation observed in the case of tetraisoamylammonium bromide closely parallels the corresponding deviation in the freezing point curve of tetraisoamylammonium thiocyanate in benzene and tetraisoamylammonium nitrate in dioxane. Similar parallel relations hold in the case of conductance.

The measurements have not been carried to sufficiently low concentrations to determine the limiting value of the molecular polarization with precision, particularly in the case of tetraisoamylammonium bromide. In the case of the other three electrolytes, a lower limiting value may be approximated. Assuming the limiting tangents to coincide with the curves at the lowest experimental concentration, which corresponds to a linear change of the dielectric constant between the lowest concentration measured and zero concentration, values of the limiting tangent have been estimated and, using the known values of the density of the solutions as obtained by interpolation, limiting values have been calculated for the molecular polarization of the solute molecules. The results are given in Table IV. The limiting polarizations are given in the second column, the polar moments in the third column, and values of a, the distance between centers of charge (obtained by dividing the polar moment by the charge) in the last column. Values of P_0 have not been corrected for deformation polarization since this correction (100–200 cc.) comes within the limit of error of the P_0 values.

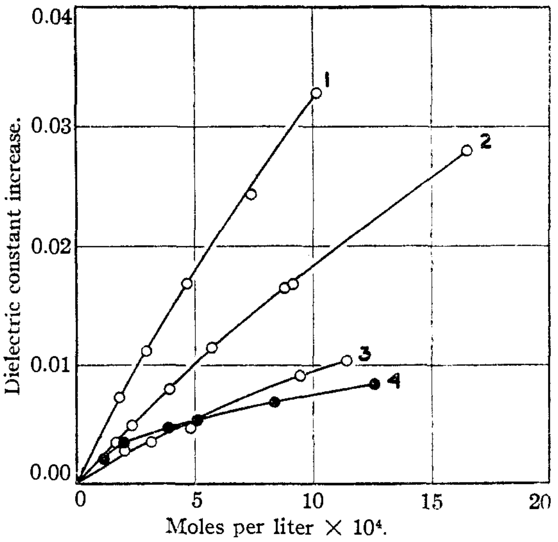

Fig. 1.—Dielectric constant increase due to electrolytes in benzene solution.

TABLE IV

CONSTANTS OF ELECTROPOLAR MOLECULES

Electrolyte	P_0	$\mu \times 10^{18}$	$a \times 10^8$
Tetraisoamylammonium picrate	7800	19.4	4.06
Triisoamylammonium picrate	4000	13.9	2.91
Silver perchlorate	2400	10.7	2.25
Tetraisoamylammonium bromide	>4000	>14	>2.9

As stated, the values appearing for the molecular polarization in the above table are probably lower limits, and an extension of the measurements to lower concentrations may be expected to lead to somewhat larger values. It is evident that the molecular polarization of an electrolyte dissolved in a non-polar medium is of a higher order of magnitude than that of ordinary polar molecules. This result is in harmony with the view that at low concentrations electrolytes exist in the form of ion-pairs. The values that we have obtained are of much the same order of magnitude as those arrived at by Wyman[8] for certain amino acids in water. The value obtained for the distance between charges does not

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[8] Wyman, This Journal, **56**, 536 (1934). References to earlier work are given by Wyman.

differ greatly (somewhat smaller) from that obtained from conductance measurements. There is a close parallelism between the values obtained for the distance between charges from dielectric constant measurements and the strength of the electrolyte as indicated by conductance. Tetraisoamylammonium picrate is a much stronger electrolyte than triisoamylammonium picrate, although the latter is a slightly weaker electrolyte than silver perchlorate.[7] It would seem, therefore, that the phenomena occurring in solutions of electrolytes in a non-polar solvent are, in the main, controlled by coulomb forces. Under the action of these forces, the ions, existing predominantly free in extremely dilute solutions, associate to form, first, ion-pairs, and then more complex structures, neutral as well as charged, depending upon whether oppositely charged ions are present in equivalent amount. In the case of electrolytes having large symmetrical ions, the tendency to build up highly complex neutral structures is very pronounced.

Summary

Results of measurements are recorded for benzene solutions of tetraisoamylammonium picrate, triisoamylammonium picrate, tetraisoamylammonium bromide and silver perchlorate, chiefly between 10^{-4} and 10^{-3} N.

The limiting molecular polarization of these compounds is about ten times that of ordinary polar molecules, 2400 to 7800 cc.

The molecular polarization decreases rapidly with increasing concentration for salts with two electrically symmetrical ions and only slowly for salts with unsymmetrical ions.

The relation between the dielectric and other properties of these solutions is discussed.

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Ketene. III. Heat of Formation and Heat of Reaction with Alcohols

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Our first attempts to measure the heat of formation of ketene were by means of the reaction with water to form acetic acid. We found, however, that when ketene was passed into a calorimeter containing water, the initial rapid rise in temperature was followed by a slow rise, which continued for more than half an hour after the ketene had been passed in. This slow rise, which constituted from 5 to 10% of the total increase in temperature, is evidence of one or more side reactions. Ketene appears to react relatively slowly with cold water: apparently some of the ketene polymerizes to cyclobutadione-1,3 before it reacts with the water. We found acetone, which is one of the products of the hydrolysis of cyclobutadione-1,3, in the reaction mixture, and a quantitative estimation by Messinger's method[1] indicated that approximately 5% of the ketene had polymerized. Evidently the reaction between ketene and water is relatively slow and it is not surprising, therefore, that amino acids in aqueous solution can be acetylated with ketene.[2]

On the other hand, when ketene is passed into dilute aqueous sodium hydroxide in a calorimeter the final temperature is attained very rapidly and an estimate of the acetone present showed that only 1–2% of the ketene had polymerized. Since both the polymerization and hydrolysis of the polymer are exothermic reactions, the error from this source should be less than one per cent. We decided, therefore, to measure the heat of the reaction between dilute sodium hydroxide and ketene and use the value obtained for calculating the heat of formation of this compound.

Our calorimeter was of the Dewar type which has been described frequently.[3] A few modifications were necessary since we were studying the heat of the reaction between a gas and a liquid. At the beginning of an experiment the calorimeter contained a known amount of standard caustic soda at 0°. The Dewar flask containing this solution was surrounded by a coil of Pyrex glass and the whole was then packed in powdered ice. The ketene gas was first passed through this coil and then into the solution in the calorimeter. At the end of the experiment we titrated an aliquot portion of the solution, and

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[1] Messinger, *Ber.*, **21**, 3366 (1888).

[2] Bergmann and Stern, *ibid.*, **63**, 437 (1930).

[3] Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1931. Chapter VI, p. 290.