

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXI. The Conductance of Tributylammonium Picrate in Ethylene Chloride at 25°BY DARWIN J. MEAD¹ WITH RAYMOND M. FUOSS¹ AND CHARLES A. KRAUS**I. Introduction**

A variety of electrolytes in non-aqueous systems have been studied, but very few examples of very weak electrolytes have been described. Kraus and Fuoss² measured tri-*i*-amylammonium picrate in benzene, in ethylene chloride and in a mixture of these two solvents. The purpose of this paper is to present some data of much higher precision than the earlier work, on tributylammonium picrate in ethylene chloride.

II. Apparatus, Materials and Method

The electrical equipment was the same as that described by Cox, Kraus and Fuoss.³ Conductance cells were of the Erlenmeyer type described by Kraus and Fuoss,² having unplatinized electrodes. The cell constants were (I) 0.21299 and (II) 0.015357, as determined by comparison with a cell standardized using Jones and Bradshaw's⁴ data on potassium chloride.

Tributylammonium picrate was prepared from tributylamine and picric acid in hot alcoholic solution. The salt was recrystallized from alcohol; m. p. 106.5°.

Ethylene chloride was purified in the usual manner.⁵ Solvent conductances ($1.5\text{--}3.5 \times 10^{-11}$ mho) were negligible compared to solution conductance even for the most dilute solutions (1×10^{-7} mho).

For the more concentrated solutions the following procedure was used. A quantity (about 4 g.) of salt was weighed into the weighed conductance cell. About 20 cc. (sufficient to fill the electrode chamber) of ethylene chloride was placed in the cell. After dissolving and mixing thoroughly, the cap of the cell was lifted momentarily to release excess pressure. The cell and solution were then weighed and placed in an oil-bath held at $25.000 \pm 0.002^\circ$. When temperature equilibrium had been established, the resistance of the solution was measured. To make the next solution about 10 cc. of solvent was added. This procedure was repeated until the volume of solution reached about 100 cc., which was the maximum convenient working volume of the cell. In the more dilute region, dilutions were made using a dilution pipet.⁵

Sorption effects in cell II and high resistance values in cell I prevented measurements on solutions more dilute than $10^{-4} N$.

Polarization, as indicated by change of resistance with frequency, was noticed in the more concentrated solutions. In order to correct for

polarization, all solutions were measured at 600, 1000, 2000 and 4000 cycles. Plotting observed resistance against $1/\sqrt{f}$ and extrapolating the resulting straight line gives the resistance corresponding to infinite frequency.⁶ This extrapolated resistance was used in calculating the specific conductance of the solution. Figure 1, in which we have plotted the slope of the polarization curves, calculated as $(R_{1000} - R_\infty)/R_\infty$, against c , shows that this effect decreases approximately linearly with concentration.

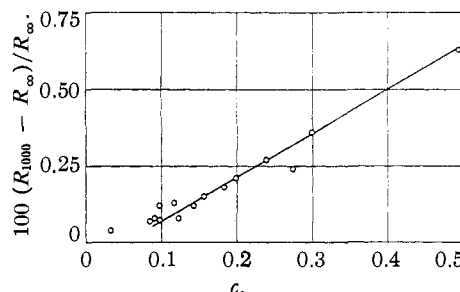


Fig. 1.—Dependence of polarization on concentration.

The solutions used were too concentrated to neglect the difference in density between the solution and the pure solvent in calculating normalities from the experimental weight concentrations. Density measurements were accordingly made at 25° with a Westphal balance. The results are given in Table I. Plotting density against moles of salt per kilogram of solvent gives the following straight line

$$d = 1.2455 - 0.022 M \quad (1)$$

where d is the density and M the molal concentration of the solution.

TABLE I
DENSITY OF SOLUTIONS OF TRIBUTYLAMMONIUM PICRATE
IN ETHYLENE CHLORIDE AT 25°

M	d
0.372	1.2373
.235	1.2404
.136	1.2425
.068	1.2442
.067	1.2443

(1) Present address: General Electric Company, Schenectady, N. Y.

(2) Kraus and Fuoss, *THIS JOURNAL*, **55**, 21 (1933).

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

(4) Jones and Bradshaw, *THIS JOURNAL*, **55**, 1780 (1933).

(5) Mead, Fuoss and Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936).

(6) Jones and Christian, *THIS JOURNAL*, **57**, 272 (1935).

III. Experimental Results and Discussion

The experimental results are summarized in Table II, in which concentration and equivalent conductance are given. Six overlapping runs

TABLE II
CONDUCTANCE OF TRI-BUTYLAMMONIUM PICRATE IN ETHYLENE CHLORIDE AT 25°

c	Λ	c	Λ
0.4945	0.16971	0.031822	0.08582
.4691	.16866	.027174	.08791
.29824	.14140	.024267	.08863
.27426	.13575	.015642	.09752
.23820	.12827	.013818	.09996
.19838	.11875	.012022	.10335
.18214	.11448	.010704	.10805
.15581	.10804	.027921	.11829
.14168	.10441	.027295	.12206
.11582	.09801	.026120	.12985
.11226	.09727	.025354	.13635
.09678	.09352	.024120	.15172
.09508	.09320	.0232326	.16835
.09036	.09236	.0227354	.17964
.06465	.08704	.0215662	.23142
.05251	.08556	.0213743	.24416
.04479	.08519	.036465	.34679
.038162	.08547	.0333864	.4725
.034022	.08603	.0317833	.6425

were made, each with independent initial weighings of salt. The conductance curve is shown in Fig. 2 where $\log \Lambda$ is plotted against $\log c$. In

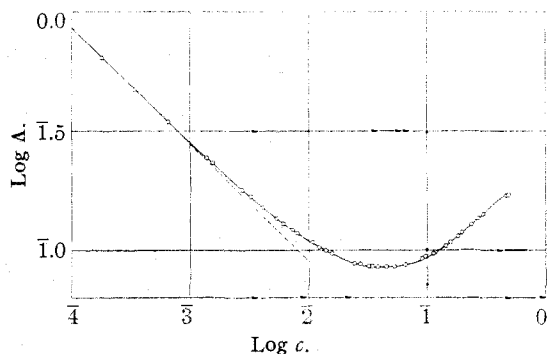


Fig. 2.—Conductance curve for tributylammonium picrate in ethylene dichloride at 25°.

the dilute region we have the usual linear dependence with slope $(-1/2)$, due to mass action.⁷ The minimum, produced by triple ions,⁸ occurs at $c \approx 4.5 \times 10^{-2} N$, with $\Lambda \approx 8.5 \times 10^{-2}$. In the more concentrated region the curve goes through an inflection point which suggests a maximum at still higher concentrations, due to the increased viscosity.

(7) Fuoss and Kraus, *THIS JOURNAL*, **55**, 476 (1933).

(8) Fuoss and Kraus, *ibid.*, **55**, 2387 (1933).

In the analysis of conductance data for strong electrolytes, F/Λ is plotted⁵ against $c\Delta f^2/F$. We have plotted the function for the more dilute points on tributylammonium picrate in Fig. 3.

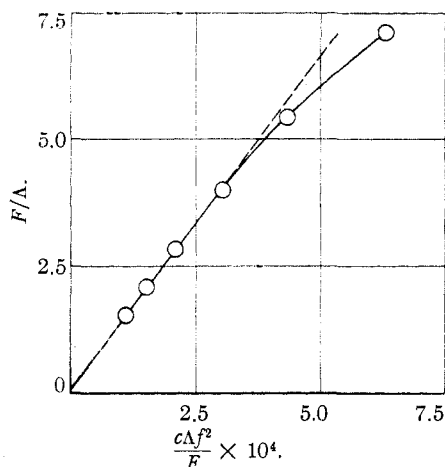


Fig. 3.—Mass action plot.

The intercept is too near zero to allow evaluation of Λ_0 , because the salt is so weak. The slope $(1/K\Lambda_0^2)$ can be calculated from values of K and Λ_0 which follow. This calculated slope is shown as a dotted line in Fig. 3. It is obvious that the points approach a straight line with the proper slope as concentration decreases. The critical concentration⁹ for ethylene chloride at 25° is 3.4×10^{-4} .

The triple ion function⁷ $\Lambda \sqrt{c} g(c)$ is plotted against c in Fig. 4; it is linear up to about $0.06 N$, where it begins to become concave down. The slope gives a value of 0.045 for the triple ion equilibrium constant. The intercept (8.70×10^{-3}) of the straight line is equal to $\Lambda_0 \sqrt{K}$. If we assume $\Lambda_0 = 60$ (tetrabutylammonium picrate

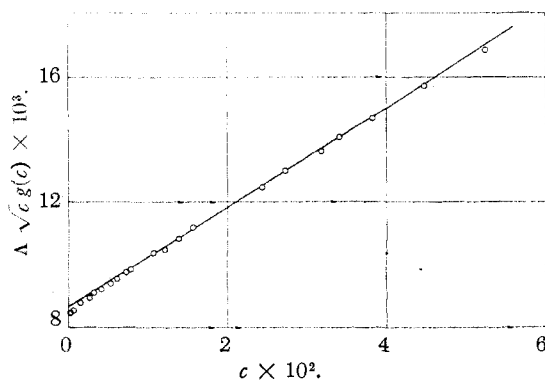


Fig. 4.—Triple ion plot.

(9) Fuoss, *ibid.*, **57**, 488 (1935).

has $\Lambda_0 = 57.40$ in ethylene chloride at 25° ⁴) we find 2.10×10^{-8} for the dissociation constant of tributylammonium picrate. This value of K gives a value of 2.4 \AA. for the parameter a (effective ion size),¹⁰ which seems unexpectedly small.

(10) Fuoss and Kraus, *THIS JOURNAL*, **55**, 1019 (1933).

Summary

The conductance of tributylammonium picrate in ethylene chloride has been measured at 25° . The concentration range covered was $1.8 \times 10^{-4} N$ to $0.5 N$.

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The Equilibrium and Kinetics of the Thermal Isomerization of Dichloroethylene Catalyzed by Iodine

BY REUBEN E. WOOD AND ROSCOE G. DICKINSON

The conversion of *cis*- into *trans*-cinnamic acid, catalyzed by iodine in benzene solution, has been found¹ to proceed at rates which can be interpreted in terms of iodine-atom catalysis just as can the photochemical conversion sensitized by iodine.² We have found that iodine similarly catalyzes the *cis-trans*-isomerization of dichloroethylene, and have measured reaction rates in the pure liquids and in various solutions. Since the isomerization comes to a measurable equilibrium, we have measured equilibrium constants as well as rates of conversion in both directions.

Materials.—The *cis*- and *trans*-dichloroethylenes were prepared by fractional distillation of mixtures of the isomers obtained from the Eastman Kodak Company. It was found desirable to carry out the distillations under carbon dioxide to avoid oxidation by air; pure *trans*-dichloroethylene was noticeably subject to air oxidation. The distillations were carried out with a five-foot (1.5-meter) column; the final products had boiling-point ranges of less than 0.1° and dielectric-constant ranges of 0.003. The boiling point of the *cis*-dichloroethylene was 59.6° at 745 mm.; the dielectric constant was 9.20 at 25° . The boiling point of the *trans*-dichloroethylene was 47.2° at 745 mm.; the dielectric constant was 2.14 at 25° . After purification the liquids were stored in flasks under an atmosphere of carbon dioxide; liquid for use was forced out by carbon dioxide when desired. The same method of storage was applied to stock solutions of the dichloroethylenes in the various solvents. The liquids thus stored were found to retain their original dielectric constants throughout the duration of the experiments (several months).

Thiophene-free benzene was fractionally crystallized, dried, and distilled.

Cyclohexane (Eastman "Practical") was shaken with fuming sulfuric acid, washed with sodium hydroxide solution, then with water, dried, and distilled. Its dielectric constant was found to be 2.013 at 25° .

Decalin (decahydronaphthalene) (Eastman "Practical") was shaken with anhydrous aluminum chloride and then treated similarly to the cyclohexane. It was found that if the treatment with fuming sulfuric acid was not sufficiently prolonged, the decalin added iodine in the subsequent experiments. The dielectric constant of the purified decalin was 2.150 at 25° .

The iodine was sublimed from potassium iodide-iodine mixture, and resublimed.

Dielectric Constant Measurement.—A method of analysis based on dielectric constant measurement was employed to determine the extent of isomerization. This measurement was made by a substitution method in which the capacitance of a cell containing the solution in question was compared with that of a variable precision condenser. The apparatus involved two oscillating circuits coupled to produce an audible heterodyne beat on a telephone receiver. A quartz crystal oscillating at 1.7 megacycles controlled the frequency of one of these circuits. The frequency-controlling part of the other circuit comprised inductance and capacitance, a part of the latter being furnished either by the cell containing the solution, or by the precision condenser. The essence of the measurement was the rapid substitution, by means of a switch, of the measuring cell for the precision condenser in this circuit; the precision condenser was adjusted so that no perceptible change in pitch of the heterodyne beat occurred when this substitution was made.

The precision condenser was a General Radio instrument; the capacitance range used was from 25 to 110 μmf . A calibration was made which gave corrections of the condenser readings to values linear with the capacitance.

The measuring cell was of glass and substantially of the type described by Doborzynski³; it was thermostated at 25° . For analytical purposes only a relation between composition of solution and precision condenser reading was necessary; nevertheless the apparatus was calibrated to give dielectric constants with the aid of a number of liquids of known dielectric constant.

Analytical Method.—The analytical problem was that of determining the fraction of dichloroethylene in the *cis*- or *trans*-form in a solution containing known amounts of solvent, iodine, and total dichloroethylene.

(1) R. G. Dickinson and H. Lotzkar, *THIS JOURNAL*, **59**, 472 (1937).

(2) A. Berthoud and Ch. Urech, *J. chim. phys.*, **27**, 291 (1930).

(3) D. Doborzynski, *Z. Physik*, **66**, 657 (1930).