The Conductance of Some Salts in Chlorobenzene at 25°

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I. Introduction

Specific interaction between solute and solvent is expected when an acid solute such as tributylammonium picrate is dissolved in a basic solvent. For example, in tricresyl phosphate[1] ($D = 6.92$ at 40°) this salt has a dissociation constant of 1.18×10^{-6}, which gives an ion size of 4.66×10^{-8} cm. But in ethylene chloride[2] ($D = 10.23$ at 25°), the dissociation constant is only 2.10×10^{-8}, which leads to an ion size of 2.4×10^{-8} cm. The ion sizes are calculated on the assumption that the interaction between ions can be represented as that between uniformly charged spheres in a homogeneous medium,[3] and if this model were correct, the ion size calculated from the dissociation constant of the solute and the dielectric constant of the solvent would be independent of solvent. Clearly tributylammonium picrate in tricresyl phosphate is electrolytically quite different from tributylammonium picrate in ethylene chloride, even after allowing for the difference in dielectric constant. A possible explanation can be found in an interaction between solute and solvent, which gives an effectively stronger electrolyte in the former solvent, which is equivalent to saying that the non-electrolytic dissociation[1] is suppressed in the basic solvent. Ethylene chloride is aprotonic and does not enter the equilibria.

But for completely substituted quaternary salts, independence of ion size on solvent has in general been found, so that it was possible to predict approximate values of dissociation constant from the dielectric constant of the solvent. In this paper, we shall present data showing that specific interaction between solute and solvent, as indicated by variation of ion size with solvent, is also possible for quaternary salts. The dissociation constants of tetrabutylammonium bromide and picrate in chlorobenzene ($D = 5.63$ at 25° and 60 cycles) are only about one-tenth as large as the values calculated from the ion sizes found for these salts in a number of other solvents.

II. Materials, Apparatus and Procedure

C. p. chlorobenzene was redistilled, and initial and final portions were discarded. It was then dried by two successive treatments with activated aluminum oxide. The solvent conductance was very sensitive to traces of moisture, as was the conductance of dilute solutions of the electrolytes. The best value obtained for the pure solvent was 2×10^{-12} mho. The solvent was stored over aluminum oxide, and filtered just before use directly into the dilutions flasks through a glass cotton plug by dry air pressure.

Tributyl and **tetrabutylammonium picrates** were those used by Elliott and Fuoss.[1] **Tetrabutylammonium bromide** was prepared by neutralizing a solution of tetrabutylammonium hydroxide (from tetrabutylammonium iodide and moist silver oxide in alcohol) with hydrogen bromide. It was recrystallized from ethyl acetate; m. p.[4] 103.1–103.3°. *Anal.* Subs., 0.3034, 0.2965: AgBr, 0.1760, 0.1722. Calcd. for Bu$_4$NBr: Br, 24.80. Found: Br, 24.69, 24.72.

Electrical Equipment and Cells.—Measurements were made at low voltage and 60 cycles, using the Schering or resistance bridge.[5] Solutions were made up by weight, and pumped by dry air pressure from the dilution flask into a platinum conductance cell,[6] which was then placed in an oil-filled thermostat at 25.00°. Several cell fillings were made with each solution in order to eliminate sorption errors.[4]

III. Results

The conductance data are summarized in Table I, and are shown as log Λ–log c plots in Fig. 1. Several dilution runs were made for each salt. In the case of the tributyl salt, three solu-

TABLE I

CONDUCTANCE OF SALTS IN CHLOROBENZENE AT 25° AND 60 CYCLES

Tributyl-ammonium picrate		Tetrabutyl-ammonium bromide		Tetrabutyl-ammonium picrate	
$c \times 10^3$	$\Lambda \times 10^3$	$c \times 10^4$	Λ	$c \times 10^4$	Λ
19.84	1.093	12.38	0.1570	19.62	0.266
18.19	1.015	7.67	.1585	14.24	.284
14.26	0.917	6.01	.1593	11.87	.305
10.08	.834	4.84	.1701	6.94	.370
7.62	.800	2.550	.1966	6.50	.380
5.17	.790	2.436	.1909	2.827	.542
3.165	.824	2.408	.1888	1.310	.770
2.998*	.847	1.284	.2352	0.610	1.103
2.000*	.847	0.534	.333	.407	1.340
1.076	1.043	.512	.328	.172	2.02
1.000*	1.001	.512	.338	.091	2.72
		.1998	.504		
		.1501	.574		
		.0710	.830		

(1) Elliott and Fuoss, This Journal, 61, 294 (1939).

(2) Mead, Kraus and Fuoss, ibid., 61, 3257 (1939).

(3) Fuoss, Chem. Rev., 17, 27 (1935).

(4) Cox, Kraus and Fuoss, Trans. Faraday Soc., 31, 749 (1935), report 113° for the m. p. of the bromide; in view of our analytical results, we conclude that the earlier figure is a misprint.

(5) Fuoss, This Journal, 60, 451 (1938).

(6) Mead and Fuoss, ibid., 61, 2047 (1939).

tions in the dilute range, marked with an asterisk in Table I, were also prepared directly, in order to be certain that solvent of low conductance was used. The point at $1.076 \times 10^{-3} N$ looks high, as would be expected if the solutions absorbed a little moisture during preceding dilutions.

IV. Discussion

As is seen in Fig. 1, the conductance curves approach a straight line of slope $(-\frac{1}{2})$ in the dilute region, indicating a simple binary equilibrium in this range. The curve for the bromide shows a broad minimum, similar to that shown by this salt in other solvents. As expected, the quaternary bromide is a weaker electrolyte than the quaternary picrate, while the tertiary picrate is much weaker than either. Quantitative comparison can be made by determining the constants of the curves.

From the viscosity[7] of chlorobenzene, $\eta_{25} = 0.00752$, and the limiting conductance of salts of this type in ethylene chloride[4,8] we estimate $\Lambda_0 = 60$. The $\Lambda\sqrt{c}g(c)-c$ plots[9] are linear, and give the values found in Table II for the dissocia-

TABLE II
CONSTANTS IN CHLOROBENZENE AT 25°

	Bu₄NPi	Bu₄NBr	Bu₃HNPi
K	1.88×10^{-8}	1.13×10^{-9}	2.10×10^{-13}
k	6.75×10^{-3}	0.42×10^{-3}	4.22×10^{-3}
a	4.75×10^{-8}	3.86×10^{-8}	2.98×10^{-8}

tion constants K and k corresponding to the ion pair and triple ion equilibria. In the last line are the a values calculated from K by the relationship[3]

$$K^{-1} = \frac{4\pi N}{1000} \left(\frac{\epsilon^2}{DkT}\right)^3 Q\left(\frac{\epsilon^2}{aDkT}\right) \quad (1)$$

where $Q(x)$ is the function

$$Q(x) = \int_2^x e^y y^{-4} dy \quad (2)$$

The ratio of the dissociation constants of the quaternary picrate and bromide is 16.6, with an ion size *difference* of 0.89×10^{-8} cm. This is about the same as was found in anisole[4] $(5.60 - 4.61 = 0.99)$ and in diphenyl ether[10] $(5.33 - 4.60 = 0.73)$. In other words, the two salts have about the same *relative* strengths in these three solvents. But both have equivalent ion sizes nearly an ångström unit smaller in chlorobenzene than in the ethers; that is, they are much weaker

(7) Meyer and Mylius, *Z. phys. Chem.*, **95**, 349 (1920).

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

(9) Fuoss and Kraus, THIS JOURNAL, **55**, 2387 (1933).
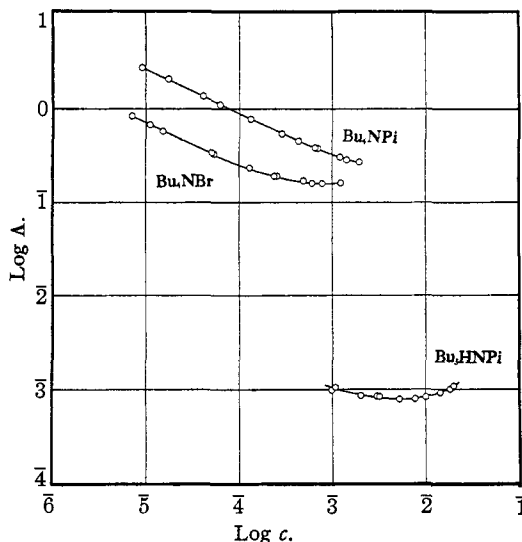
(10) D. J. Mead, unpublished observation.

Fig. 1.—Conductance curves in chlorobenzene at 25°.

electrolytes in chlorobenzene than their behavior in the other solvents would lead one to expect.

The following values for the parameter a for tetrabutylammonium picrate have been found: 5.83 in ethylene chloride[8] $(D_{25} = 10.23)$, 5.80 in tricresyl phosphate[1] $(D_{40} = 6.92)$, 5.60 in anisole[4] $(D_{25} = 4.27)$, 5.33 in diphenyl ether[6] $(D_{50} = 3.53)$ and 5.7 in benzene[11] $(D_{25} = 2.28)$. A salt in chlorobenzene, for which $a = 5.6 \times 10^{-8}$, would have at 25° $K = 21.3 \times 10^{-8}$, which is 11.3 times as large as the dissociation constant found here for tetrabutylammonium picrate.

The tributyl salt is very weak in chlorobenzene, although relatively stronger than in ethylene chloride; the corresponding ion sizes are 2.98 and 2.40×10^{-8} cm.

The only conclusion to be reached at present is that other forces than coulomb interaction between ions must be considered in a general quantitative description of electrolytic behavior. Equation (1) gives the dependence of the ionic equilibrium on dielectric constant of solvent, but the variation of the parameter a from solvent to solvent for a given electrolyte shows that the present model is an over-simplification, and that even for strong electrolytes, specific interactions with solvent may be expected in some cases.

Summary

1. The conductances of tributylammonium picrate, tetrabutylammonium picrate and tetrabutylammonium bromide in chlorobenzene at 25° have been determined.

(11) Fuoss and Kraus, THIS JOURNAL, **55**, 3614 (1933).

2. The effective ion sizes of the quaternary bromide and picrate in chlorobenzene are about one ångström unit smaller than in a number of other solvents; this result indicates

that specific interaction between solvent and solute can appear even in the case of strong electrolytes.

SCHENECTADY, N. Y.   RECEIVED DECEMBER 8, 1939

Relative Efficiency of Active Wave Lengths of Ultraviolet in Activation of 7-Dehydrocholesterol

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The sterols which have received major attention in respect to their photochemical conversion into antirachitics are ergosterol and cholesterol, associated respectively with lower plants and with animal materials. Crystalline ergosterol may be regarded as the precursor of vitamin D_2 (Calciferol), the principal form of antirachitic vitamin now available from commercial activation; crystalline cholesterol, on the other hand, does not itself constitute a significant provitamin, but its derivative, 7-dehydrocholesterol, when irradiated with appropriate ultraviolet energy, is converted into vitamin D_3,[1,2] a form which has been found only in animal tissues.

In the present study the quantum efficiencies of certain wave lengths of ultraviolet in the activation of 7-dehydrocholesterol in ether have been measured and compared.

Irradiation Procedure.—Details of the irradiation procedure already have been published.[3] A cylindrical quartz vessel of 80 cc. capacity was filled with a 0.1% solution of 7-dehydrocholesterol[4] in anhydrous ether, C. P., and placed in the optical axis of the beam emerging from a quartz monochromator.[5] Exposure times were calculated from data on preliminary tests so that an approximation of 33 U. S. P. XI units (10 Steenbock units) would be produced with each batch. Since one batch would give sufficient active material for assay on only ten rats and since the protocol for this series called for groups of forty or fifty rats each, the irradiation procedure was repeated four or five times for each wave length. This was done over a period of five days during which time repetitive irradiations were scattered at random through the whole series, thereby distributing any undetected variations in the conditions of the irradiation. At each wave length each unit batch was subjected to 2475×10^{12} quanta of monochromatic ultraviolet energy.

Feeding of Activated Materials.—All batches of 7-dehydrocholesterol solution irradiated at a given wave length were pooled with three ether washings of the quartz vessel and with olive oil in the proportion of one gram of oil for each rat to be fed. The ether was removed under carbon dioxide in a moderate vacuum and the oil residue thoroughly incorporated into Steenbock #2965 ration in the proportion of 29 g. of diet to each gram of oil solution. The eight milligrams of treated 7-dehydrocholesterol which this oil contained had an expected potency of about 3.3 U. S. P. units of vitamin D.

These mixtures were then fed to groups of rats previously rendered rachitic in twenty-one days on the Steenbock #2965 ration. Group size was selected as follows (based on probability predictions from previous similar experiments involving a total of approximately three hundred rachitic rats): 40 rats each for the testing of materials irradiated with 2483 Å., 2537 Å., 2652 Å., and 3025 Å.; 50 rats each for testing 2804 Å., 2894 Å., and 2967 Å.; and 18 rats for testing 3130 Å., which previous tests had shown to be probably inactive.

During the six-day feeding period each animal consumed its quota of 30 g. of ration. Empty feeding jars were replenished with additional amounts of the #2965 diet, unfortified, until the end of the seventh day.

Observations.—A total of 328 rats entered the test period and all but two survived. At the end of this period these animals were killed, the left leg of each was X-rayed, then line tested, and the right legs were taken for ashing.

A summary of essential data including line test observations is presented in Table I. The whole bone ash values (on a fat-free dry basis) were between 31.7 and 33.6% for all active wave lengths; 28.8% for the inactive 3130 Å. line; and 27.3% for the rachitic controls.

In a previous communication we expressed the opinion that recorded differences between group responses must be greater than the quantities which by purely statistical computation are barely significant, if they are to be accepted as real. This restriction of the use of statistical methods applies to the evaluation of data derived from the usual sized bioassay groups but the restriction is lifted when the number of animals tested concurrently is sufficiently large.

Interpretation of Observations.—In respect to bone ash determinations, the group values for the active wave lengths varied within a small range

(1) Boer, Reerink, van Wijk and van Niekerk, *Proc. Acad. Sci., Amsterdam*, **39**, 622 (1936).

(2) Windaus and Bock, *Z. physiol. Chem.*, **245**, 168 (1936).

(3) Harris, Bunker and Mosher, THIS JOURNAL, **60**, 2579 (1938).

(4) Acknowedgment is made for the contribution of the 7-dehydrocholesterol by Winthrop Chemical Company.

(5) Bunker and Harris, *New Engl. J. Med.*, **216**, 165 (1937).