[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY AND THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Dependence of Conductance on Field Strength. III. Some Amine Picrates in Toluene at 35°

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I. Introduction.—Previous work[3] on quaternary ammonium salts in diphenyl ether showed good agreement with Onsager's theory[4] of the Wien effect, in the lower range of concentration where the solute exists mostly as ion pairs[5] and free ions. These solutions could not be investigated by our procedure at higher concentrations, where triple ions[6] appear, because their conductance here is high enough to give disturbing temperature changes at high voltages. Substituted ammonium salts with at least one proton on the nitrogen are much weaker[7] electrolytes than quaternary salts and seemed to be more promising compounds for investigation above the conductance minimum, especially in solvents of low dielectric constant.

We present herewith some results on the high (a. c.) voltage conductance of tri-*n*-butylammonium picrate, tribenzylammonium picrate and di-*n*-propylammonium picrate in toluene at 35°. For supplementary information, we also measured the absorption near 4750 Å. of solutions of mono-, di- and tri-*n*-propylammonium picrates in water, dioxane and several mixtures of these solvents. Very briefly summarized, we find that these systems also conform to the Onsager theory. A dispersion of the Wien effect, for which no detailed theory is yet available, was observed when the period of the measuring field was of the order of the Langevin time constant of the solutions.

II. Materials, Apparatus and Procedure.—Toluene was purified by shaking with concentrated sulfuric acid, washing with dilute sodium bicarbonate solution followed by water, drying with calcium chloride and distilling. It was stored over sodium or activated alumina.[8] Specific conductance of solvent was $0.2\text{–}0.7 \times 10^{-12}$.

Dioxane was refluxed for ten hours over flake caustic, followed by twenty-four hours over sodium. It was then distilled (b. p. 101–102°) and stored over sodium.

Tributylammonium picrate[9] melted at 106.5°.

Tribenzylammonium picrate[10] was that prepared by Elliott and Fuoss.

Di-*n*-propylammonium picrate was prepared by mixing 34.8 g. of picric acid in 200 ml. of alcohol with 16.1 g. of dipropylamine in 20 ml. of alcohol, evaporating to dryness at *ca.* 40° and recrystallizing. Recrystallization from xylene gave light yellow needles, melting at 75.5–76°; recrystallization from a mixture of ethyl acetate and heptane gave orange crystals which melted at 96–97°. By choice of solvent, the following series of transformations were made on one sample: crude → 75° → 95° → 75° → 95° → 75° material. A sample of the yellow needles was melted and held at the melting point about thirty minutes, cooled and remelted; the melting point then found was 85°. On repeating, the melting point rose to 89°, where it stayed on four successive solidifications and remeltings. The same experiment left the melting point of the orange modification unchanged. Experiments with other solvents lead to the conclusion that the yellow low-melting modification crystallizes out of non-polar solvents, while the orange high-melting product crystallizes out of polar solvents. Salt recrystallized from xylene and salt recrystallized from water were both investigated.

Apparatus and procedure were essentially as described by Mead and Fuoss.[3] The Schering bridge at Yale (used for tributylammonium picrate measurements) differed from the one in Schenectady in a number of minor details, but gave results on solutions of tetrabutylammonium picrate in diphenyl ether at 50° which checked the previous results within the experimental error. One new conductance cell was constructed; it was of the concentric type[11] but was sealed directly to a glass-stoppered erlenmeyer flask, so that solutions could be made up and measured in the same vessel without transfer. The (inner) test electrode is 1.63 cm. outside diameter and 3.03 cm. long; the (outer) high potential electrode is 1.86 cm. inside diameter and 3.76 cm. deep; wall thickness 0.75 mm., capacity empty is 12.66_0 $\mu\mu f$.

III. Experimental Results and Discussion.—In the first experiments with tributylammonium picrate in toluene, precautions to exclude water vapor were inadequate. While the low voltage 60-cycle conductances were approximately correct, fantastic "Wien effects" were found, especially at low concentrations. The conductance–voltage curves usually started concave-up and eventually approached linearity in the range 20–40 kv. cm. with a slope very much larger than theoretical. An example of the spurious effect is given in Table I, where c is concentration in equivalents per liter, κ_0 is low voltage conductance, Λ is equivalent conductance ($1000\ \kappa_0/c$) and S is the chord slope of the linear portion of the curve, $(\Delta\kappa/\kappa_0)/\Delta E$, expressed as relative conductance change. The theoretical value of S in toluene at 35° is 0.0217 for a dielectric constant of 2.352.

After care was taken to keep apparatus and solutions dry, better results were obtained. Several examples are shown in Fig. 1, where

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[3] D. J. Mead and R. M. Fuoss, THIS JOURNAL, **61**, 2047, 3589 (1939); **62**, 1720 (1940).

[4] L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

[5] R. M. Fuoss, *Chem. Revs.*, **17**, 27 (1935).

[6] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 2387 (1933).

[7] R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 3614 (1933).

[8] Activated alumina (Aston, *ibid.*, **68**, 52 (1946) recommends heating twenty-four hours at 225°) is an excellent means for removing traces of electrolytic impurities from organic solvents. It is naturally essential that all suspended alumina be removed from the solvent before making up solutions. We found it convenient to pump the toluene from the storage flask into the conductance cells, weight burets, etc., through a sintered glass filter tube by dry air pressure.

[9] D. J. Mead, R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **61**, 3257 (1939).

[10] M. A. Elliott and R. M. Fuoss, *ibid.*, **61**, 294 (1939).

[11] Ref. 3, Fig. 1.

TABLE 1

CONDUCTANCE OF TRIBUTYLAMMONIUM PICRATE IN TOLUENE AT 35° AND 60 CYCLES

$10^3 c$	$10^{12} \kappa_0$	$10^6 \Lambda$	S
7.56	39.72	5.25	0.039
3.55	5.49	1.547	.082
2.29	2.266	0.988	.122
1.040	0.482	.463	.281
0.610	.243	.398	.438
.423	.212	.500	.454
.259	.140	.538	.725

the curve is drawn to conform to the limiting theoretical equation

$$\kappa/\kappa_0 = 1 + e^3X/4\epsilon k^2T^2$$

where e is the electron change, X is field strength in electrostatic units and ϵ is dielectric constant. In toluene at 35°

$$\kappa/\kappa_0 = 1 + 0.0217\ E$$

where E is field strength in kilovolts per cm., or

$$\kappa/\kappa_0 = 1 + 0.0290\ V$$

where V is field strength in r. m. s. kilovolts/cm. and where conductance is measured by a circuit which filters out harmonics of the fundamental. The open circles are for a solution of 9.64×10^{-3} normal ($\Lambda = 1.04 \times 10^{-5}$) and the solid circles for $c = 2.42 \times 10^{-3}$, ($\Lambda = 2.46 \times 10^{-6}$).

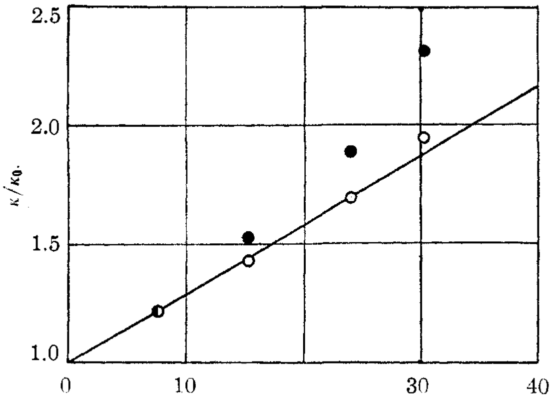

Fig. 1.—Wien effect for tributylammonium picrate in toluene at 35°: solid line, Onsager's theoretical curve; open circles, $c = 9.64 \times 10^{-3}$; solid circles, $c = 2.42 \times 10^{-3}$.

It will be seen that the Wien effect at the higher concentration (which is well above the minimum in conductance for this salt[12]) is normal, and that agreement is still fair for the more dilute range. At 10^{-3} normal and 30 kv./cm., the observed conductance is about 20% greater than that calculated; we believe this high result to be due to residual traces of moisture or other basic impurities.

Tribenzylammonium picrate was weighed out and dissolved in toluene by heating to about 45°, to give a 3.00×10^{-3} normal solution. The specific conductance at 120 cycles and low voltage was 0.212×10^{-10} nine minutes after the cell was filled and placed in the thermostat. It will be recalled that the outer cell wall is platinum, so that temperature equilibrium in the thin layer of solution between the electrodes must be reached very rapidly. Nevertheless, the conductance *decreased* steadily with time, as shown in Fig. 2.

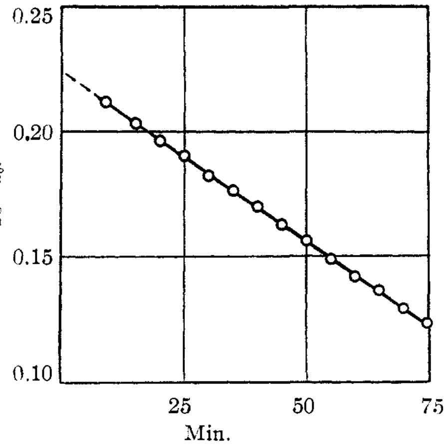

Fig. 2.—Change of conductance of tribenzylammonium picrate ($c = 3.00 \times 10^{-3}$) in toluene at 35° with time.

Other fillings gave similar behavior: the conductance decreased with time, linearly at first, and then in the course of 24–48 hours approached a steady value about one-third of the initial value. The initial change was more rapid if the solution was heated to 100° before being placed in the cell, but the conductance levelled off at the same value. No significant difference was found between the behavior of salt recrystallized from toluene and from ethanol. If the solutions were allowed to stand about a week (in glass) at room temperature and were then placed in the cell in the thermostat at 35°, the conductance started about 10% below the asymptotic value mentioned above, and gradually approached it. The Wien effect, at 120 cycles and up to about 15 kv./cm. at both 0.003 and 0.002 normal agreed closely with the theoretical value after the solutions came to equilibrium.

The above observations on tribenzylammonium picrate lend support to the suggestion[10,13,14,15,16] that amine picrates exist in solution as an equilibrium mixture of two forms, differing by the position of the proton

$$\mathrm{R_3N{\cdot}HPi} \rightleftarrows \mathrm{R_3NH^+{\cdot}Pi'} \qquad (1)$$

The first is a molecular addition compound, in which the proton remains in (non-electrolytic) picric acid, and which can dissociate molecularly

$$\mathrm{R_3N{\cdot}HPi} \rightleftarrows \mathrm{R_3N + HPi} \qquad (2)$$

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(12) C. A. Kraus and R. M. Fuoss, This Journal, **55**, 21 (1933).

(13) K. J. Pedersen, *ibid.*, **56**, 2615 (1934).

(14) C. R. Witschonke and C. A. Kraus, *ibid.*, **69**, 2472 (1947).

(15) C. A. Kraus, *J. Phys. Chem.*, **43**, 231 (1939).

(16) M. M. Davis and E. A. McDonald, *J. Research Nat. Bur. Standards*, **42**, 595 (1949).

The second is an ion pair, held together by coulomb attraction, in which the proton has moved over to the nitrogen atom to produce an ammonium ion, and which can dissociate into free ions

$$R_3NH^+{\cdot}Pi' \rightleftharpoons R_3NH^+ + Pi' \qquad (3)$$

Our experimental observations suggest that at least one of the three equilibria is established at a measurably slow rate. Since the a. c. Wien effect in the stabilized solution is normal, the ionic equilibrium (3) presumably can be established in less than milliseconds. Witschonke and Kraus[14] mention no dependence of conductance on time when base was added to amine picrates; if we assume that the rate for equilibrium (2) is also rapid, then step (1), which involves an intramolecular proton shift, appears to be the slow reaction. This conclusion is compatible with the experimental observation that the dielectric constant, for the system shown in Fig. 2, decreased from 2.382 to 2.379 while the conductance underwent the change shown. This change in dielectric constant, while small, is real because it is nine times the experimental precision (one in 6000). A shift of equilibrium (1) to the left would give a smaller moment per unit volume, and would correspond to a decrease in conductance. We also observed that water extracted picric acid from a toluene solution of tribenzylammonium picrate.

The Wien effect in solvents of low dielectric constant, where the resistance is high, should show a frequency dependence. The Langevin time constant τ for a solution of dielectric constant ϵ and conductance κ is

$$\tau = \epsilon/8\pi \times 9 \times 10^{11}\,\kappa \qquad (4)$$

or $1.04/10^{10}\,\kappa$ in toluene. Figure 3, for 0.003 normal tribenzylammonium picrate in toluene, shows that the Wien effect decreases with increasing frequency. Here τ = 14 millisec. and the periods of the fields used (90, 120 and 240 cycles) are of the same order of magnitude. Our qualitative expectation is thus verified. It will be noted, incidentally, that the linear portions of all three curves of Fig. 3 extrapolate to the same limit at zero field, as they should. Their intercept[3,4] gives 0.968 as the activity coefficient of the solute at 0.003 N in toluene.

Di-n-propylammonium picrate crystallizes from water (4 g./100 cc.) as orange prisms, m. p. 96°, from xylene (250 mg./100 cc.) as yellow needles m. p. 76°. Solutions at 0.002 N in toluene of both forms gave identical conductances at 35°. Here, the conductance was independent of time. But if the solution were heated (thirty minutes at 85°) before being placed in the conductance cells, behavior similar to that of tribenzylammonium picrate was observed; the conductance decreased with time for several hours, and became substantially constant on standing overnight. Normal Wien effects were found at 0.003 and 0.002 N; at lower concentrations, the voltage dependence was apparently higher than theoretical. At 10^{-4} N, runs were made in two different cells, with spacings 2.4 and 4.9 mm.; the values of $\Delta\kappa/\kappa\Delta V$ at 120 cycles were 0.0635 and 0.0573, respectively. The smaller value in the cell with the wider spacing suggests that the field may have driven some adsorbed electrolyte from the electrodes, an effect which would lead to a fictitiously high voltage dependence. At concentrations above 0.001 N, however, the Wien effect was normal, and a frequency dependence similar to that shown in Fig. 3 was observed. Data are omitted here in order to save space.

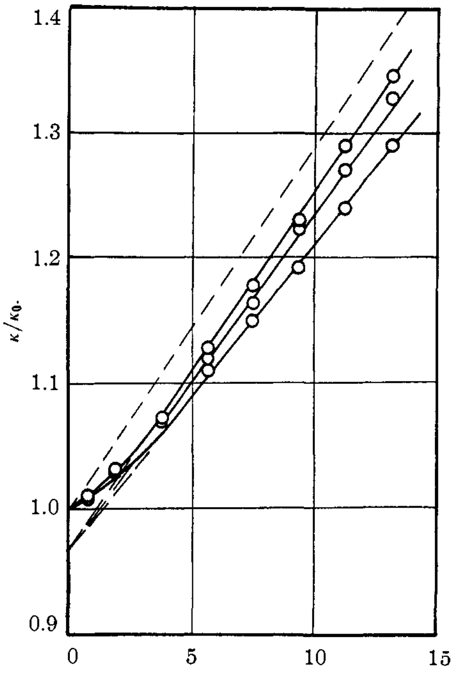

Fig. 3.—Dispersion of Wien effect for tribenzylammonium picrate (c = 3.00 × 10^{-3}) in toluene at 35°: dotted curve, theoretical; points, data at 90 cycles (top solid curve), 120 cycles and 240 cycles (bottom solid curve).

Absorptions were measured by means of a Beckman spectrophotometer for solutions of mono-, di- and tri-n-propylammonium picrates in water, in dioxane and in mixtures of these solvents containing 75, 50 and 25 mole % water, in the approximate concentration range 0.001–0.03 N. Above 5250 Å. all the solutions were transparent, up to the near infrared limit of the instrument (*ca.* 2 μ). Below 4600 Å., the solutions at the above concentrations were opaque. Our measurements were limited to the long wavelength edge of the absorption near 4750 Å. In order to present the rather voluminous data[17] compactly, Figs. 4 and 5 were drawn. In Fig. 4 are plotted values of $\log_{10} I/I_0$ were I is transmitted intensity and I_0 is incident intensity, as a

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(17) David Edelson. Thesis, Yale University, 1949.

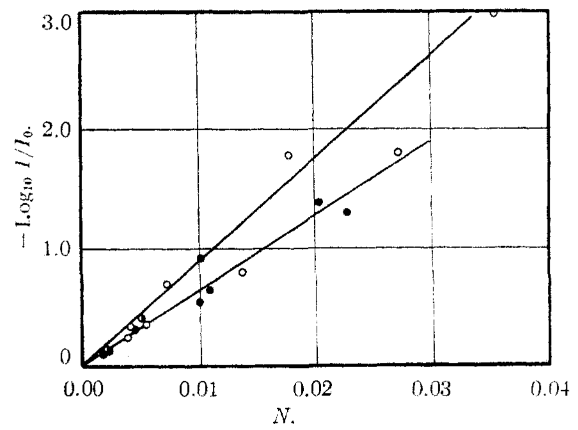

Fig. 4.—Absorption as a function of concentration of *n*-propylammonium picrates (open circles, mono-; solid circles di-; half-black circles, tri-) in water at λ4840 (top curve) and in dioxane at λ4700 (bottom curve).

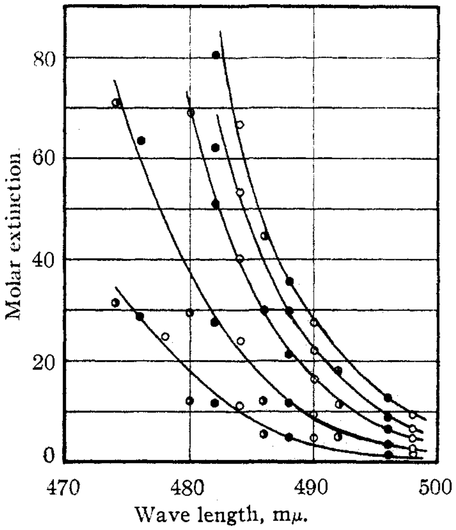

Fig. 5.—Absorption as a function of wave length and solvent for propylammonium picrates (same code as for Fig. 4) in water (top curve), 25:75 dioxane–water, 50:50 dioxane–water, 75:25 dioxane–water and dioxane (bottom curve).

function of concentration N in equivalents per liter for the mono- and dipropylammonium picrates in water at 4840 Å. and for all three propyl picrates in dioxane at 4700 Å. It will be noted that the plots are linear, *i. e.*

$$\log_{10} I/I_0 = -\epsilon N d \tag{5}$$

where ϵ is the molecular extinction coefficient and d = 1.0 cm. is cell thickness. In other words, the three picrates all satisfy Beer's law and have the same *molecular* extinction, regardless of the number of propyl groups attached to the nitrogen atom. This simple result permits the condensation of the data to Fig. 5, where molecular extinction as a function of wave length is shown for water, 0.751:0.249 water–dioxane, 0.501:0.499 water–dioxane, 0.252:0.748 water–dioxane and dioxane. The points shown were selected from the full tables of data; actually, of course, complete curves were determined for each salt in each solvent. At a given wave length, absorption increases with increasing dielectric constant of the solvent, indicating that more of the compound exists as picrate ion in solvents of higher dielectric constant. The ϵ–λ curves have all essentially the same shape; a plot of the ratio of absorption coefficient $\epsilon(x)$ at a given fraction x of dioxane in the mixed solvent to the absorption coefficient $\epsilon(0)$ in water against x is approximately linear, with the empirical equation

$$\epsilon(x)/\epsilon(0) = 1 - 0.87\,x \tag{6}$$

for all wave lengths in the region investigated. If we assume[18] that the absorption is due to picrate ions (free and in ion pairs), then Eq. (6) also gives the picrate content as a function of solvent composition. If we assume further that the compound is all salt in water, then 87% is in the form of molecular addition compound in dioxane.

Summary

1. The deviations from Ohm's law of the conductance of solutions of tri-*n*-butylammonium, tribenzylammonium and di-*n*-propylammonium picrates in toluene at 35° conform to Onsager's theory of the Wien effect.
2. A dispersion of the Wien effect has been observed in the range of frequencies where the period of the field is of the order of the Langevin relaxation time of the solution.
3. Dipropylammonium picrate exists in two enantiomorphic states, a yellow one from non-polar solvents, melting at 76° and an orange one from polar solvents, melting at 97°.
4. Conductance and absorption (near 4800 Å.) data indicate that amine picrates containing at least one proton on the nitrogen exist as an equilibrium mixture of a molecular addition product of amine and picric acid and of an ion pair. The rearrangement from one isomer to the other, involving a proton shift, is a slow reaction. The relative amount of electrolytic modification increases with increasing dielectric constant of the solvent.

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[18] H. von Halban and B. Szigeti, *Helv. Chim. Acta*, **20**, 746 (1937).