The existing data on monammine formation with silver ion are collected in Table VI. The last column indicates a lack of parallelism between k_1 and pK. Even here, however, the comparison has not been made in the most favorable case; it might be that if a series of primary amines was compared, and a series of secondary amines, etc., a parallelism within each series might still be found.

The sixth column in Table VI gives the ratio of the two successive formation constants for the silver ammines; this measures the relative stability of the mono- and di-ammine. The data would indicate that with increasing size and degree of substitution of the amine the stability of the monammine increases with respect to the di-ammine. The number of cases is, however, small, and more data may be necessary before drawing a final conclusion.

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Summary

1. The formation curves for the reactions of cadmium, zinc, nickelous and cupric ions with ethylenediamine and propylenediamine, and of silver ion with ethylamine and diethylamine have been determined; from the data the formation constants for the intermediate steps in the formation of the complex ions, and the complexity constants for the over-all reactions, have been calculated.

2. Under the conditions of the experiments, cadmium, zinc and nickel ions form triammine complexes, while copper and silver ions form only diammines.

3. There is no difference in complex formation with ethylenediamine and with propylenediamine for cadmium, nickel and copper ions.

4. Formation of a chloro complex is appreciable with cadmium ion, but is absent with copper ion.

5. The data available indicate that the formation constants for silver monammines do not change in the same order as the dissociation constants of the amines.

6. Values for the dissociation constants of ethylenediamine, propylenediamine, ethyl- and diethyl-amine in salt solutions at 30° have been determined.

COLUMBUS, OHIO

Electrolytic Polarization of Solutions of Tributylammonium Picrate in Tricresyl Phosphate at 40°

BY RAYMOND M. FUOSS AND MYRON A. ELLIOTT[1]

Introduction

The literature contains many studies of polarization in aqueous solutions of electrolytes,[2] but little attention has been given to non-aqueous systems. The latter offer a number of advantages: a wide range of viscosity and dielectric constant can be investigated and, most important of all, quite low ionic concentrations can be studied with precision. In this paper, we present the results of a preliminary investigation of solutions of tributylammonium picrate in tricresyl phosphate at 40°.

Experimental

Preparation and purification of salt and solvent are described in an earlier paper.[3] Part of the measurements were made in a cell[4] whose electrodes were concentric platinum cylinders 3 mm. apart, with cell constant 0.004423. Other measurements were made in the guarded cell with gold-plated nickel electrodes[3]; here the electrode spacing was 2.1 mm. with cell constant 0.002720. The volume of electrolyte between the test and high potential electrodes was about 15 cc. The cells were immersed in

an oil thermostat held at 40 ± 0.01° for the conductance experiments. Conductances at 60 cycles were measured on the Schering bridge.[5]

The polarization phenomena appeared when the conductance was measured on the d. c. bridge.[6] It was observed that the apparent resistance of a given solution increased with time if the bridge voltage was kept on, until eventually a steady resistance much higher than the a. c. or initial d. c. value was reached. In order to study the changes quantitatively, the pointer type microammeter in the plate circuit of the amplifier was replaced by a recording microammeter. Suitable switches made it possible to short the grid-cathode line[6] of the 6J7 tube through 10^5 ohms and ground the cathode. so that the zero of the meter could be checked without interrupting cell current. Measurements were then made as follows. The variable arm of the bridge, R_4, was set to a value somewhat lower than that calculated to balance for the a. c. resistance. The zero point for bridge balance was set on the center line of the recorder chart. and the recorder started. At time "zero." bridge current was turned on. After the recorder pen showed that the bridge had gone through balance, the zero was checked, R_4 set to another round value in the direction toward which the resistance was heading. and another balance recorded. This procedure was repeated until a steady R_4 was obtained. Then from the recorder chart, the times for balance at the different R_4 values were read off. and the specific conductance of the solution (which is proportional to R_4) was calculated as a function of time. After standing or stirring to restore the initial conductance.

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(2) Jones and Christian. THIS JOURNAL. **57**, 272 (1935): Acree. Bennett. Gray and Goldberg. J. Phys. Chem.. **42**, 871 (1938).

(3) Elliott and Fuoss. THIS JOURNAL. **61**, 294 (1939).

(4) Deits and Fuoss, ibid., **60**, 2394 (1938).

(5) Fuoss. ibid.. **59**, 1703 (1937).

(6) Fuoss, ibid., **60**, 451 (1938).

a run at another voltage was made. The results were independent of the sequence of voltages used.

Results

In general, the drop of conductance was faster, the higher the voltage across the cell and the lower the concentration. The limiting value of conductance was higher for higher voltage. For example, a 6.92 × 10⁻⁷ normal solution had an a. c. cell resistance of 3.11 megohms. At 10.8 seconds after 22.5 volts d. c. were applied, the resistance had increased to 4.76 megohms; at 30 seconds, to 6.26 megohms; at 165 seconds, to 12.5 megohms; and at 10 minutes, to 22.8 megohms, approaching an asymptote of 25.0 megohms. At 90 volts, the resistance was steady at 23.0 megohms after about 5 minutes; and at 180 volts at 19.7 megohms after about 2.5 minutes.

If the cell voltage were interrupted, the resistance gradually decreased on standing as determined by a. c. or low voltage d. c. measurements of short duration. If the platinum cell were tipped, to mix the liquid between the electrodes with the bulk of the solution, after a d. c. steady state had been reached, the a. c. resistance returned immediately to its initial value. Similarly, a rapid return to the initial conductance could be produced in the nickel cell by rotating the inner electrode. If, after a steady state was reached, the cell voltage was reversed in polarity, the cell resistance started at once to decrease, went through a minimum equal to the initial a. c. value, and then started to increase again. These effects all indicate that something happens in the *volume* of electrolyte between the electrodes.

On interrupting the d. c. bridge voltage, a back e. m. f. immediately appears on the chart of the recorder as an apparent shift in the bridge zero. This back e. m. f. decays at a rate which is unaffected by tipping the cell and builds up to its peak value within at least a second of applying bridge voltage. Its magnitude is practically independent of the applied voltage. It therefore appears to be an electrode effect, or else is located in a very thin layer of solution adjacent to the electrodes.

Numerical data for four typical solutions measured in the gold cell are given in Table I, where time is in minutes. The a. c. conductance (or d. c. conductance at $t = 0$) is given as κ_0, and the limiting values κ_∞ at $t = \infty$ are given for each voltage.

Discussion

Tricresyl phosphate[3] has a dielectric constant equal to 6.92 at 60 cycles and 40°, and a viscosity of 0.295 at 40°. In this solvent, tributylammonium picrate has a dissociation constant[3] K of 1.18 × 10⁻⁶.

The calculated ionic concentrations ($c\gamma$, Table II) for the solutions of Table I range from 0.49 to 11.8 $N/10^6$. We thus are dealing with very low ionic concentrations in a solvent of quite high viscosity.

TABLE I
CHANGE OF CONDUCTANCE WITH TIME
$c = 6.92 \times 10^{-7}$, $\kappa_0 = 8.67 \times 10^{-10}$

t	$V = 22.5$ $10^{10}\kappa$	t	$V = 90$ $10^{10}\kappa$	t	$V = 180$ $10^{10}\kappa$
0.18	5.65	0.15	4.04	0.14	3.50
1.13	3.23	.36	2.96	.24	2.69
1.35	2.96	.58	2.43	.55	1.89
2.77	2.16	.75	2.16	.89	1.62
3.60	1.89	1.00	1.89	1.33	1.48
8.75	1.19	1.50	1.62	2.00	1.40
∞	1.08	∞	1.18	∞	1.37

$c = 5.63 \times 10^{-6}$, $\kappa_0 = 3.65 \times 10^{-9}$

t	$V = 22.5$ $10^9\kappa$	t	$V = 90$ $10^9\kappa$	t	$V = 180$ $10^9\kappa$
0.60	2.16	0.62	1.64	0.30	1.64
0.92	1.91	0.93	1.36	.58	1.36
1.20	1.77	1.30	1.23	.90	1.17
1.92	1.50	1.75	1.09	1.40	1.09
2.42	1.36	2.8	0.95	2.47	1.06
3.00	1.25	3.7	.89	∞	1.04
5.3	0.98	∞	.84		
7.9	.82				
12.9	.68				
∞	.56				

$c = 2.40 \times 10^{-5}$, $\kappa_0 = 8.70 \times 10^{-9}$

t	$V = 22.5$ $10^9\kappa$	t	$V = 90$ $10^9\kappa$	t	$V = 180$ $10^9\kappa$
0.48	6.54	0.17	6.26	0.18	5.45
0.92	5.45	.32	5.45	.48	4.09
1.83	4.62	.64	4.62	.78	3 54
2.83	4.09	.93	4.09	1.13	3.26
3.83	3.54	1.17	3.81	1.57	3.10
7.83	2.72	1.45	3.54	∞	2.92
13.4	2.18	1.92	3.26		
19.8	1.91	3.27	2.75		
∞	1.66	∞	2.42		

$c = 1.30 \times 10^{-4}$, $\kappa_0 = 2.25 \times 10^{-8}$

t	$V = 22.5$ $10^8\kappa$	t	$V = 90$ $10^8\kappa$	t	$V = 180$ $10^8\kappa$
0.6	1.850	1.0	1.360	0.4	1.442
0.9	1.798	1.4	1.252	.6	1.280
1.3	1.715	3.8	0.925	.9	1.170
2.3	1.525	11.4	.735	1.4	1.090
2.9	1.415	∞	.708	2.3	0.980
4.4	1.225			2.5	.900
6.0	1.115			4.4	.844
10.8	0.900			∞	.816
18.4	.735				
∞	.545				

TABLE II
SUMMARY OF DERIVED QUANTITIES

$10^6 c$	$10^9 \kappa_0$	$10^6 c\gamma$	μ'	μ''	μ'''	0.434β
0.692	0.867	0.49	0.057	0.010	0.009	0.110
5.63	3.65	2.06	0.24	0.084	.068	.081
24.0	8.70	4.76	0.57	0.240	.192	.060
130.0	22.5	11.80	1.50	1.95	.545	.044

Experimentally, we found two contributing factors in the difference between a. c. and d. c. conductance: an almost instantaneous back

e. m. f. which we shall call the electrode effect, and a time dependent increase in resistance which occurs in the volume of liquid between the electrodes and which we shall call the space charge effect.

It should be pointed out that a back e. m. f. in the cell produces an apparent *decrease*[4] of resistance when the cell resistance is measured on a bridge (voltage measurement) and an apparent *increase* when cell current is used to calculate resistance by Ohm's law.[7] In tricresyl phosphate solutions, the space charge effect completely masked the electrode effect, as is shown by the limiting conductances κ_∞ of Table I: at each concentration, κ_∞ is *larger* for 180 volts than for 22.5 volts. For a constant back e. m. f. E as the cause of polarization, κ_∞ varies as $(1 + E/V)$ where V is the voltage applied to the bridge.[4] A back e. m. f. of the order of 10 volts would cause an apparent increase of about 5% in κ_∞ at 180 volts as compared to κ_0; since the 180 volt values of κ_∞ were from one-third to one-eighth κ_0, there is no point in trying to calculate the small electrode effect from the present data.

The space charge effect might, at first guess, be ascribed to electrolysis. In Table II, μ' gives the number of microequivalents calculated by Faraday's law for the passage of a current corresponding to κ_0 (upper bound) at 180 volts for 100 seconds, μ''' the number corresponding to κ_∞ (lower bound) and μ'' the number of micro-equivalents actually in the space between the electrodes. These numbers are all within one order of magnitude at a given concentration. But ultimate electrolysis cannot possibly be the explanation; the return to initial high conductance on standing or stirring and the immediate reversal of slope of the κ–t curve on reversal of polarity of bridge voltage argue too strongly against the destruction of ions by electrodeposition.

A study of the data showed that all the curves could be represented by the simple empirical equation

$$\kappa(t) = \kappa_\infty + (\kappa_0 - \kappa_\infty) \exp(-\alpha\sqrt{t}) \quad (1)$$

and inspection of the slopes of the $\log \kappa - \sqrt{t}$ curves suggested that the voltage dependence of the rate of approach to a steady state was given by

$$\alpha = \beta\sqrt{V} \quad (2)$$

i. e., doubling the voltage produces a given relative change in κ in half the time. A test of equations (1) and (2) is given in Fig. 1, where $\log \kappa$ is plotted against $\sqrt{Vt}$ for the most dilute solution. (A single straight line is drawn although the intercepts, $\log (\kappa_0 - \kappa_\infty)$ at $\sqrt{Vt} = 0$, differ slightly for the three voltages; see Table I.) Similar plots for the other concentrations also gave straight lines, whose slopes decreased with increasing concentration. The slopes are given in Table II; a plot
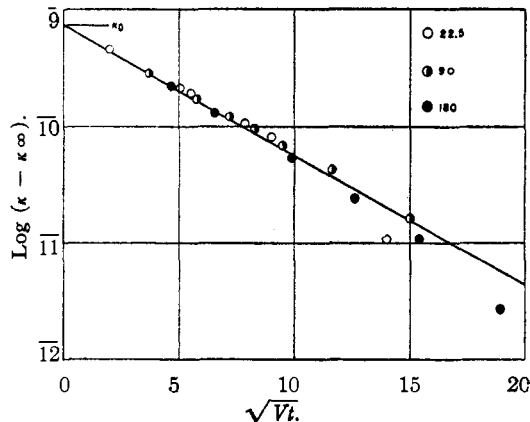
(7) Luder, P. B. Kraus, C. A. Kraus and Fuoss, THIS JOURNAL, 58, 255 (1936).

Fig. 1.—Test of equations (1) and (2).

(Fig. 2) of $\log \beta^2$ against $\log c$ is linear, with slope $(-\frac{1}{3})$, which suggests

$$\beta = C/\sqrt{c^{1/3}} \quad (3)$$

where C is now independent of voltage and concentration. This appearance of $c^{-1/6}$, which is proportional to the average distance between ions, *if the salt were completely dissociated*, is both surprising and puzzling. The empirical relationship (3) holds, however, over a 200-fold variation in concentration and no simple function correlates the slopes with the ionic concentration $c\gamma$ calculated in the usual way from the known value of K, as may be seen by the dotted curve $\log c\gamma - \log\beta^2$ in Fig. 2. The average field strengths involved (less than 1 KV./cm. maximum) are too small to produce any appreciable Wien effect.[8]
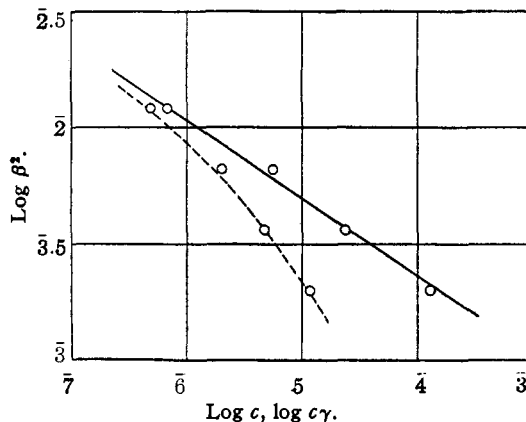

Fig. 2.—Dependence of exponent on concentration.

Combining equations (1), (2) and (3) and rearranging, we have

$$\kappa(t) = \kappa_0\{1 - (1 - \kappa_\infty/\kappa_0)(1 - \exp[-C\sqrt{Vt/c^{1/3}}])\} \quad (4)$$

The limiting conductance κ_∞ depends on voltage and concentration in too complicated a way to be determined empirically from the present data;

(8) Wien, *Ann. Physik.*, 73, 162 (1924); 83, 327 (1927); Onsager, *J. Chem. Phys.*, 2, 599 (1934); Mead and Fuoss, THIS JOURNAL, 61, 2047 (1939); 61, 3589 (1939); 62, 1720 (1940).

both κ_∞ and C probably depend on cell geometry and dimensions.

The appearance of $\sqrt{t}$ in the exponent suggests a diffusion mechanism as the explanation for the apparent increase in resistance. Qualitatively we may argue as follows. Under the influence of the field, ions diffuse toward the electrodes and build up space charges of opposite polarity in the volume of liquid near the electrodes, until equilibrium between external and internal electrostatic forces on the one hand and Brownian motion on the other is established. These space charges alter the gradient in the cell from the initial uniform one of Fig. 3A ($t = 0$) to that indicated in Fig. 3B ($t = \infty$); i. e., the voltage drop across the electrodes remains substantially unchanged, but the gradient across the central layers of the solution between the electrodes is decreased. (The cell resistance is very much larger than that of the bridge arm in series with it.) Under the effect of the lower field strength, the ionic velocities in the bulk of the solution are naturally less, and the cell resistance is increased, because the cell is effectively converted into a series circuit, with one high resistance unit which throttles down the cell current. Further qualitative arguments based on the variation of κ_∞ with voltage and concentration may also be adduced to support the proposed mechanism.
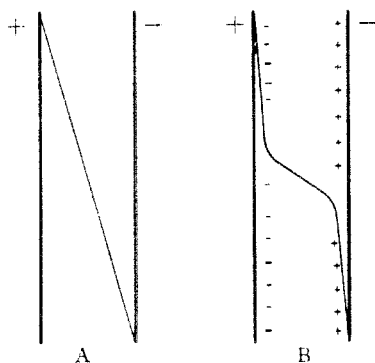

Fig. 3.—Field distribution: A at $t = 0$. B at $t = \infty$.

If diffusion is involved, a correlation should be found between the coefficient C of equation (4) and the diffusion constant D of the solute as solute (ion size) and solvent (viscosity) are varied. Further experimental and theoretical work is

planned, because the method may offer a simple means of determining diffusion coefficients and mobilities in non-aqueous solutions of electrolytes. Experiments with crossed a. c. and d. c. fields and with probe potentiometer electrodes should give considerable information.

Some additional information may be obtained on the basis of dimensional arguments, because the exponent in Eq. (4) must be a pure number. Let d be the distance between electrodes, ϵ the unit charge, k Boltzmann's constant and T the temperature. Then given $\sqrt{t}$ in the numerator, we expect to find it multiplied by $\sqrt{D}/d$, because a distance determined by the boundaries usually appears in diffusion problems as a divisor of $\sqrt{Dt}$. Furthermore, given $\sqrt{V}$ in the numerator, we expect multipliers $1/d$ and $\sqrt{\epsilon/kT}$; the first to convert voltage to field strength and the second to obtain the ratio of ionic potential energy to mean thermal energy. The exponent should therefore be proportional to

$$(V\epsilon Dt/kTd^3)^{1/2} \qquad (5)$$

which is dimensionless. The empirically found $c^{-1/4}$ in the exponent remains a problem. To keep the exponent dimensionless, assuming (5) is correct, other factors are needed to cancel the dimensions of $c^{-1/4}$. Also, its presence implies the existence of a distance of molecular dimensions in the theoretical description of the process. Obviously further work is necessary.

Summary

The apparent resistance of solutions of tributylammonium picrate in tricresyl phosphate at 40° increases with time toward an asymptotic value when the resistance is measured on a d. c. bridge. The increase in resistance is not due to permanent depletion of the solution by electrolysis. The approach to the limiting conductance is exponential; the appearance in the exponent of the square root of applied voltage times elapsed time suggests that the increase is due to the formation of a space charge near the electrodes which reduces the voltage gradient in the volume between the electrodes. Measurement of these polarization rates is suggested as a method of determining diffusion constants in non-aqueous solutions.