the final fusion atmosphere was pure air. The silver chloride of Analysis 3 after being thoroughly washed was tested spectroscopically and found to be free from all but the merest trace of thallium.

## Summary

Samples B and C of thallium chloride, which were undoubtedly the purest, give identical results for the atomic weight of thallium, while the difference between these two samples and Sample A is no larger than the experimental error.

The atomic weight of thallium found in this work, 204.40, confirms very closely the work of Hönigschmid, Birckenbach and Kothe, and Hönigschmid and Striebel, as well as that of Aston.

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# Properties of Electrolytic Solutions. IV. The Conductance Minimum and the Formation of Triple Ions Due to the Action of Coulomb Forces[1]

BY RAYMOND M. FUOSS AND CHARLES A. KRAUS

## I. Introduction

In the first paper[2] of this series, we presented the results of an experimental study of the influence of the dielectric constant of the solvent medium on the conductance of electrolytic solutions. It was shown that the general conductance–concentration curve includes four fairly well-defined regions whose location depends upon the structure of the salt and the properties of the solvent: (1) starting from zero concentration, the conductance initially decreases proportionally to the square root of concentration, in accordance with Onsager's equation; (2) for weaker electrolytes, or for strong electrolytes in solvents of intermediate and low dielectric constant, the conductance begins to fall much more rapidly than corresponds to the coefficient computed on the basis of the interionic attraction theory; (3) an inflection point appears in the conductance curve and, in solvents of sufficiently low dielectric constant, a minimum may eventually appear; (4) and finally, after the minimum, the conductance increases very rapidly as the concentration increases. The stronger the electrolyte or the higher the dielectric constant, the fewer are the number of the above regions which appear in the accessible concentration range. In our second paper[3] we showed that the second region may be accounted for on the basis of an equilibrium between ions and neutral

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[1] Presented at the Symposium on Electrolytes during the Washington Meeting of the American Chemical Society, March 28, 1933.

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

[3] Fuoss and Kraus, *ibid.*, **55**, 476 (1933).

molecules (ion pairs), corrected for the influence of interionic forces, and a method was developed for obtaining the two constants $\Lambda_0$ and $K$ from conductance data. We next investigated[4] the binary equilibrium, and found that the dissociation energies calculated from the experimental $K$ values are in agreement with energies calculated on the hypothesis that the mass action equilibrium is due to the specific action of Coulomb forces between ions pairwise. It is our present purpose to discuss the third region of the conductance curve, the neighborhood of the minimum, and to suggest a possible explanation of the fourth region.

In view of the fact that most of the previously observed minima in conductance have appeared at total concentrations higher than 0.01 $N$,[5] it seemed quite natural to include this effect among the phenomena characteristic of moderately concentrated solutions. We have found, however, that, in solvents of very low dielectric constant (approaching 2.0), the minimum in conductance appears at concentrations which may be considered dilute even in the classical sense of the word. For example, the minimum *equivalent* conductance of tetraisoamylammonium nitrate is $1.07 \times 10^{-4}$ at a salt concentration of $6.65 \times 10^{-5}$ in a dioxane–water mixture of dielectric constant 2.38. Since $\Lambda_0$ is presumably about 30, the ion concentration is of the order of $5 \times 10^{-12}$; it seems hardly necessary to point out that, at this extremely low ion concentration, none of the present theories of electrolytic solutions accounts for the observed course of the conductance curve, and that any corrections due to the usual interionic effects are infinitesimal. We must therefore look for some new process which can occur in extremely dilute solution which, combined with the mass action equilibrium, accounts for the observed appearance of the minimum in conductance.

We have already shown that in solvents of sufficiently low dielectric constant, the forces of electrostatic attraction yield fairly high potential energies for ion pairs. For example, for tetraisoamylammonium nitrate in a dioxane–water mixture of dielectric constant 2.38, the dissociation energy is about 22,000 cal., which is greatly in excess of the mean molar thermal energy, $^1/_2\, RT$, per degree of freedom. On the basis of classical electrostatic theory, the potential energy of a system composed of a negatively charged sphere in contact with two positively charged spheres, the centers lying on a straight line, is 3/2 the energy of two oppositely charged spheres of the same radius at contact. We might therefore expect that a complex ion of the type $(+\ -\ +)$ or $(-\ +\ -)$, formed from a neutral ion pair which is really a dipole and a single ion, might be stable in solvents of sufficiently low dielectric constant, because the excess potential energy due to the third ion is of the order of 10,000 cal. We therefore make the hypothesis that the following equilibria exist

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

(5) Walden, *Z. physik. Chem.*, **100**, 512 (1922).

$$A^+ + B' \rightleftharpoons AB$$
$$AB + B' \rightleftharpoons AB_2'; \quad AB + A^+ \rightleftharpoons A_2B^+$$

The consequences of this assumption are: first, that the conductance function should have the limiting form (valid at low total ion concentrations)

$$\Lambda = Ac^{-1/2} + Bc^{1/2}$$

where $A$ and $B$ are constants; second, that there should be a minimum in the conductance curve; and third, that the minimum in conductance for a given electrolyte should move toward higher concentration with increasing dielectric constant of the solvent and eventually should disappear for values of the dielectric constant greater than a critical value.

In Section II the limiting conductance function is derived and an estimate is made of the correction terms due to interionic effects which must be included when the minimum appears at concentrations greater than 0.001 $N$. In Section III the equilibrium constant describing the formation of triple ions is calculated on the basis of Coulomb forces as the source of potential energy; and in Section IV a comparison between experiment and theory is presented.

## II. The Conductance Function

For simplicity, we shall first consider the case of very low ion concentrations, where the activity coefficients and (square root) mobility corrections may be set equal to unity, and where the fraction of solute present as ions may be neglected in comparison with unity. The mass action equation for the binary equilibrium

$$A^+ + B' \rightleftharpoons AB$$

then reduces to

$$c\gamma^2 = K \qquad \gamma = \sqrt{K/c} \tag{1}$$

where $c$ is total concentration, $K$ is the mass action constant and $\gamma$ is the fraction of solute present as simple ions $A^+$ or $B'$. If, in addition, there exist equilibria between free ions and neutral molecules (ion pairs) of the type

$$AB + A^+ \rightleftharpoons A_2B^+ \text{ and}$$
$$AB + B' \rightleftharpoons AB_2'$$

we have as the mass action equations describing the formation of ion triples the following

$$\frac{[AB]\,[B']}{[AB_2']} = k_1 \qquad \frac{[AB]\,[A^+]}{[A_2B^+]} = k_2$$

Since the energies of the two configurations $(+-+)$ and $(-+-)$ differ only due to specific differences in the size of the separate ions, which we cannot evaluate at present, we may make the approximation that $k_1 = k_2 = k$, or, in other words

$$\frac{[AB_2^-]\,[A^+]}{[A_2B^+]\,[B']} = 1 \tag{2}$$

The approximation will, of course, be absorbed in the average ion size computed from the reaction. Then, if $\gamma_3$ designates the ratio of the actual concentration of one of the species of triple ions to the stoichiometric concentration,[6] the equilibrium equation becomes

$$c\gamma/\gamma_3 = k \qquad \gamma_3 = c\gamma/k = \sqrt{Kc}/k \tag{3}$$

(As pointed out above, we have replaced $(1-\gamma-3\gamma_3)$ by unity in (1) and (3).)

If $\Lambda_0$ represents the sum of the limiting conductances for the simple ions, and $\lambda_0$ the sum of the limiting conductances of the two kinds of triple ions (which, according to (2), are assumed to be formed in the same ratio as the number of simple ions present), the observed conductance $\Lambda$ is given by

$$\Lambda = \gamma\Lambda_0 + \gamma_3\lambda_0$$

provided the effects of interionic forces on mobility are neglected. Substituting from (1) and (3), we obtain as the limiting conductance function, valid at low ion concentrations

$$\Lambda = (\Lambda_0\sqrt{K})/\sqrt{c} + (\lambda_0\sqrt{K}/k)\sqrt{c} \tag{4}$$

which is of the form

$$\Lambda = Ac^{-1/2} + Bc^{1/2} \tag{5}$$

Differentiating (5), we see that the condition for a minimum in $\Lambda$ as a function of $c$ is

$$-\frac{1}{2}Ac^{-3/2} + \frac{1}{2}Bc^{-1/2} = 0, \text{ or}$$

or

$$A = Bc_{min.} \tag{6}$$

This result leads to several important relations

$$k = (\lambda_0/\Lambda_0)c_{min.} \tag{7}$$

$$K = (c\Lambda^2)_{min.}/4\Lambda_0^2 \tag{8}$$

$$\Lambda_{min.} = 2(\gamma\Lambda_0)_{min.} = 2(\gamma_3\lambda_0)_{min.} \tag{9}$$

Equations (7) and (8) make it possible to compute the equilibrium constants $k$ and $K$ from the conductance and concentration at the minimum, provided $\lambda_0$ and $\Lambda_0$ are known, and equation (9) shows that the minimum appears when the conductance due to complex ions just equals that due to the simple ions.

In order to compare (4) with experiment, it is convenient to multiply through by $\sqrt{c}$, giving

$$\Lambda\sqrt{c} = A + Bc \tag{10}$$

which is a linear relationship between $\Lambda\sqrt{c}$ and concentration. The constants $A$ and $B$ are determined by the intercept and slope of the line.

The above equations are, of course, applicable only in the case of solvents of very low dielectric constant. As the dielectric constant of the solvent

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(6) If $c$ represents total concentration in equivalents per liter, and the quantities in brackets represent concentrations of the included species, then $c = [AB] + {}^1/_2([A^+] + [B']) + {}^3/_2([A_2B^+] + [AB_2'])$. Assuming that $[A^+] = [B']$ and $[A_2B^+] = [AB_2']$, $c = [AB] + c\gamma + 3c\gamma_3$.

increases, $K$ increases, and with it, the free ion concentration. At the same time, the minimum moves toward higher total concentrations, so that the over-all effect is a shift of the minimum to relatively high ion concentrations as $D$ increases. It therefore becomes necessary to include the interionic terms in $\sqrt{c}$ in activity and mobility. When these are not too great, an upper estimate can be obtained by substituting $2c\ \Lambda/\Lambda_0$ for the ion concentration $2c\ (\gamma + \gamma_3)$ in the usual formulas and applying the results as appropriate[3] correction terms to (4). This procedure is at best a rough approximation, but serves up to dielectric constants of about 8–10. For higher dielectric constants, the ion concentrations in the neighborhood of the minimum are so high that the first $\sqrt{c}$ term in $\log f$ no longer suffices to represent the activity, and cross product terms in the mobility equation also become significant. Hence, only a qualitative analysis of data *at the minimum* is possible at present for cases where the minimum in conductance appears at concentrations greater than 0.001 $N$. If the minimum occurs at higher concentrations, and data are available at concentrations well below the minimum, it is possible, however, to estimate $k$ from such data unless $k$ is too near unity, because the effect which eventually produces the minimum shows itself first as a deviation from the usual mass action equation. Specific examples of these various cases will be discussed in Section IV.

If the various corrections are made to (1), (3) and (4), we obtain, within the above approximation for ion concentration compared to total concentration

$$c\gamma^2 f^2/(1 - \Lambda/\Lambda_0) = K \quad c\gamma(1 - \Lambda/\Lambda_0)/\gamma_3 = k$$

and

$$\Lambda = (1 - \alpha\Lambda_0^{-3/2}\sqrt{c\Lambda})\,(\gamma\Lambda_0 + \gamma_3\lambda_0)$$

Combining these equations and substituting

$$-\ln f = \beta'\Lambda_0^{-1/2}\sqrt{c\Lambda}$$

for the activity ($\beta = 0.4343\ \beta'$; natural logarithms are used here merely for simplicity in writing the exponential function), we have the approximate equation

$$\begin{aligned}\Lambda\sqrt{c}\,g(c) &= \frac{\Lambda\sqrt{c}\,\exp\,(-\beta'\Lambda_0^{-1/2}\sqrt{c\Lambda})}{(1 - \alpha\Lambda_0^{-3/2}\sqrt{c\Lambda})\,(1 - \Lambda/\Lambda_0)^{1/2}} \\ &= \Lambda_0\sqrt{K} + \frac{\lambda_0\sqrt{K}}{k}\left(1 - \frac{\Lambda}{\Lambda_0}\right)c \end{aligned} \qquad (11)$$

The correction factor $g(c)$ includes the estimate of the activity and mobility terms, as well as of the neglected factor $(1-\gamma-3\gamma_3)$. In the mobility factor, effects due to mixed ionic atmospheres[7] have been neglected; despite the presumably rather large difference in mobility of simple and complex ions, this error is certainly less than that made in replacing ion concentration by $2c\ \Lambda/\Lambda_0$. In order to obtain $k$ from experimental data,

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[7] Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

we plot $\Lambda\sqrt{c}\,g(c)$ against $(1-\Lambda/\Lambda_0)\,c$, and determine the slope and intercept of the resulting curve, which will be a straight line if the ion concentrations at which the values of $g(c)$ are calculated are not too high.

## III. The Triple Ion Equilibrium

The equilibrium constant $k$ may be calculated theoretically if some simplifying assumptions are made regarding the mechanism of the reaction involved. We shall consider only symmetrical ions of the type $R_4N^+$, $Na^+$, $Cl'$, $NO'_3$, etc. If we imagine the ions to be uniformly charged *spheres*,[8] two negative ions and one positive ion forming a complex will be in their most stable configuration if the three centers are on a line with the positive ion in the center, thus $(-+-)$. Among the various mechanisms by which this triplet can form, the simplest is the approach of a negative ion to an ion pair. If the distance between the ions of the pair is $a$, and $\theta$ is the angle between the extended axis of the pair and the line drawn through the center of the approaching negative ion and the center of the positive ion in the pair, the potential energy $\epsilon$ of a negative ion at a distance $r$ from the positive ion is

$$\epsilon = \frac{-e^2}{D}\left(\frac{1}{r} - \frac{1}{\sqrt{r^2+a^2+2ar\cos\theta}}\right)$$

(Here, $e$ is the ionic charge and $D$ is the dielectric constant of the medium, which is assumed to be homogeneous.) As a function of $\theta$, $\epsilon$ has a minimum for $\theta = 0$

$$\epsilon_0 = \frac{-e^2}{D}\left(\frac{1}{r} - \frac{1}{r+a}\right)$$

that is, approach along the axis of the dipole toward the positive ion is most favorable for triple ion formation, and the dissociation energy of a triplet is greatest along this line. If the average concentration of free ions is $n$ per unit volume, and an ion pair is in a volume element $dv_1$ of the total volume $V$ of solution, the probability $P$ of finding a negative ion in a volume element $dv_2$ at a distance $r$ from the positive ion of the ion pair is

$$P = ne^{-\epsilon/kT}\,dv_1dv_2$$

or, in polar coördinates with the origin at the center of the positive ion

$$P = ne^{-\epsilon/kT}\,2r^2\sin\theta\,d\theta\,dr\,dv_1 \tag{12}$$

This may be written as

$$P = ne^{-\epsilon_0/kT}\,e^{(\epsilon_0-\epsilon)/kT}\,2r^2\sin\theta\,d\theta\,drdv_1$$

where

$$\epsilon_0 - \epsilon = \frac{e^2}{D}\left(\frac{1}{r+a} - \frac{1}{\sqrt{r^2+a^2+2ar\cos\theta}}\right)$$

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[8] This assumption is permitted by the restriction to symmetrical ions. The proposed mechanism of triple ion formation would hardly apply to unsymmetrical ions, for, in this case, the two like ions retain their identity in the triple. That is, the symmetrical structure $(-)(+)(-)$ can dissociate equally well by either negative ion leaving, while $(\ldots -)(+\ldots)(-\ldots)$ can dissociate in only one way to give an ion and a normal ion pair.

The function $r^2e^{-\epsilon_0/kT}$ has a minimum for the value $R$ of $r$ which is a root of

$$\frac{1}{r} = \frac{2Dkt}{e^2} + \frac{r}{(r+a)^2} \tag{13}$$

or, if we substitute

$$\begin{aligned} x &= r/a & X &= R/a \\ q &= e^2/2Dkt & b &= 2q/a \end{aligned} \tag{14}$$

and rearrange the cubic equation (13), the minimum corresponds to the root $X$ of

$$\frac{1+2x}{x(x+1)^2} = \frac{a}{q} = \frac{2}{b} \tag{15}$$

Roots of this equation are given in the last column of Table II. We shall make the assumption that an ion which approaches an ion pair to a distance $r \leqslant R$ along the ray $\theta = 0$ will form a triple ion, and that a triplet is to be considered dissociated into an ion pair and a free ion if one of the two like atoms is displaced to a distance $r > R$. This assumption is entirely analogous to that made first by Bjerrum[9] to describe ion pair formation. We may now evaluate the dissociation constant $k$ for the reactions

$$\mathrm{AB} + \mathrm{A}^+ \rightleftharpoons \mathrm{A_2B}^+$$
$$\mathrm{AB} + \mathrm{B}' \rightleftharpoons \mathrm{AB}_2'$$

by integrating (12), as follows

$$k^{-1} = \frac{2\pi N}{1000}\int_a^R e^{-\epsilon_0/kT}\, r^2 \mathrm{d}r \int_0^\pi e^{(\epsilon_0-\epsilon)/kT} \sin\theta\, \mathrm{d}\theta$$

For numerical computation, it is more convenient to use the variable $x$; making the substitution, we obtain

$$\begin{aligned} k^{-1} &= \frac{2\pi Na^3}{1000}\int_1^X x^2 e^{b/(x(x+1))}\, J(b,x)\mathrm{d}x \\ &= \frac{2\pi Na^3}{1000} I(b) \end{aligned} \tag{16}$$

The function $J(b, x)$ includes the integration over $\theta$ and is defined as

$$J(b,x) = \int_{-1}^{+1} \exp\left\{\frac{b}{x+1}\left(1 - \frac{x+1}{\sqrt{x^2+1+2xz}}\right)\right\} \mathrm{d}z$$

where the variable of integration has been replaced by $z = \cos\theta$. A series of values of $J(b, x)$ were determined by planimeter integration and are given in Table I.

TABLE I

VALUES OF $J(b, x)$

| $x$ | $J(35, x)$ | $J(30, x)$ | $J(25, x)$ | $J(20, x)$ | $J(15, x)$ | $J(10, x)$ |
|---|---|---|---|---|---|---|
| 1 | 0.200 | 0.224 | 0.262 | 0.310 | 0.391 | 0.522 |
| 2 | 0.306 | 0.350 | 0.405 | 0.475 | 0.586 | 0.757 |
| 3 | 0.454 | 0.515 | 0.591 | 0.692 | 0.834 | 1.042 |
| 4 | 0.637 | 0.710 | 0.805 | 0.922 | 1.082 | 1.285 |
| 5 | 0.826 | 0.912 | 1.012 | 1.130 | 1.281 | 1.470 |
| 6 | 1.010 | 1.100 | 1.192 | 1.300 | 1.425 | 1.582 |

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(9) Bjerrum, *Kgl. Danske Vidensk-Selskab.*, **7**, No. 9 (1926).

These values, together with the following (mathematically useful but physically absurd) conditions satisfied by $J(b, x)$ suffice to draw interpolation graphs for the function

$$J(b, \infty) = 2 \qquad J(b, o) = 2$$
$$J(o, x) = 2 \qquad J(\infty, x) = 0$$
$$\left(\frac{dJ(b, x)}{dx}\right)_{x=0} = -2b \qquad \left(\frac{dJ(b, x)}{db}\right)_{b=0} = \frac{-2}{x(x-1)}$$

It is obvious that $J(b, x)$ accounts for the orienting influence of the single ion on the ion pair; if it were not for the repulsion between the two like ions, $J(b, x)$ would be replaced simply by $\int_0^\pi \sin\theta \, d\theta = 2$ in the evaluation of the phase integral.

The integral function $I(b)$ is, of course, completely determined by $b$ because $X$ is determined as the root of a cubic equation (16) whose constant term is $2/b$. Table II gives values of this integral and its logarithm for round values of $b$.

TABLE II

VALUES OF $I(b)$ AND $X$

| $b$ | $\log I(b)$ | $I(b)$ | $X$ |
|---|---|---|---|
| 3.5 | 0.096 | 1.25 | 1.225 |
| 5 | 0.668 | 4.66 | 1.56 |
| 10 | 1.534 | 34.2 | 2.46 |
| 15 | 2.183 | 152.4 | 3.17 |
| 20 | 2.894 | 784 | 3.76 |
| 25 | 3.732 | $5.40 \times 10^3$ | 4.28 |
| 30 | 4.634 | $4.30 \times 10^4$ | 4.75 |
| 35 | 5.565 | $3.67 \times 10^5$ | 5.19 |
| 36.6 | 5.878 | $7.55 \times 10^5$ | 5.33 |

It should be noted that $I(b) = 0$ when $X = 1$, so that $\log I(b)$ is asymptotic to the vertical line at $b = 8/3$ on a $\log I(b)$–$b$ plot. The physical significance of this fact is that equilibria of the type here considered are possible only for $b > 8/3$; for $b \leqslant 8/3$, the ion triples become unstable with respect to thermal agitation. According to (14), $b$ is inversely proportional to the dielectric constant of the medium for a given solute ($a$ fixed); therefore ion triples cannot form in solvents having a dielectric constant greater than a definite critical value. This accounts in part for the experimental fact that, with increasing dielectric constant of solvent, the minimum moves to higher concentrations, and eventually disappears altogether. The activity coefficient is also involved in the location of the minimum: the actual minimum appears at a lower concentration than it would if $f$ were equal to unity on account of the factor $f^2$ in the mass action equation describing the equilibrium between simple ions.

## IV. Comparison with Experiment

The conductances of tetraisoamylammonium nitrate in dioxane–water mixtures are the only data available which cover a concentration range where the formulas of Section II are applicable.[2,10] The conductance curves in mixtures containing less than 20% water ($D < 12$) all exhibit minima. As the dielectric constant decreases, the minimum shifts steadily toward lower concentrations, as is shown in the third column of Table III where the approximate logarithms of the concentrations corresponding to the minima are given.

TABLE III

LOCATION OF THE MINIMUM IN CONDUCTANCE FOR TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE–WATER MIXTURES

EXPERIMENTAL AND CALCULATED CONSTANTS FOR TRIPLE IONS

| % Water | $D$ | $-\text{Log}\ c_{\text{min.}}$ | $-\text{Log}\ k$ (expt.) | $-\text{Log}\ k$ (calc.) |
|---|---|---|---|---|
| 0.60 | 2.38 | 4.10 | 4.68 | 4.34 |
| 1.24 | 2.56 | 3.60 | 4.12 | 4.03 |
| 2.35 | 2.90 | 3.15 | 3.50 | 3.56 |
| 4.01 | 3.48 | 2.60 | 3.00 | 3.02 |
| 6.37 | 4.42 | 2.30 | 2.5 | 2.50 |
| 9.50 | 5.84 | 2.05 | 2.0 | 2.06 |
| 14.95 | 8.5 | 1.60 | .. | 1.56 |

In the 14.95% mixture, the minimum appears at too high a concentration to permit application of any of our equations of Section II. For the other mixtures, however, equation (11) or its limiting form (4) may be used. In Fig. 1, we have plotted $\Lambda\sqrt{c}\ g(c)$ against $c(1-\Lambda/\Lambda_0)$ for the mixtures containing 0.60–9.50% water. (The weight percentage of water in each mixture is given above the corresponding line in the figure. The $\Lambda\sqrt{c}\ g(c)$ scales are given to the right or left. Each concentration scale starts at the left at $c = 0$; the number in the lower right corner of each heavy lined rectangle gives the concentration corresponding to the full concentration scale covered, so that each abscissa unit on the figure is one fifth of this number. When the lines are carried through the concentration at which the minimum appears, this concentration is marked by a vertical line.) In the two mixtures of lowest dielectric constant (0.60 and 1.24% water), the interionic correction factor $g(c)$ reduces to unity. The corresponding $\Lambda\sqrt{c} - c$ curves are linear up to and through the region of the minimum, a fact which indicates that the functional form of (4) is correct. In the remaining mixtures, $g(c)$ became of increasing importance as is shown by the following figures: 2.35% water, highest concentration appearing in Fig. 1, $1.05 \times 10^{-3}$ $N$, corresponding $g(c)$, 0.955; 4.01%, $2.35 \times 10^{-3}$ $N$, 0.895; 6.37%, $4.96 \times 10^{-3}$ $N$, 0.722; 9.50%, $3.81 \times 10^{-3}$ $N$, 0.625. At the zero concentration side of the figure, $g(c)$ is, of course, in all cases unity. It will be noted that the plots are all linear, and that the slope decreases as the dielectric constant increases. This clearly corresponds to the increase of $k$ with $D$.

As an example of the limiting case of low ion concentration, let us con-

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(10) Further experimental work is in progress in this Laboratory.

sider the line corresponding to the mixture containing 1.24% water. The intercept at $c = 0$ is $2.85 \times 10^{-6}$ and the slope is $1.19 \times 10^{-2}$. If we assume that $\Lambda_0 = 30$ and $\lambda_0 = 10$, we obtain $\sqrt{K} = 9.5 \times 10^{-8}$ and $k = 8.0 \times 10^{-5}$. In order to see the influence of the two terms of (4), we refer to Fig. 2. Curve I is a graph of $\gamma$ against $\sqrt{c}$ for $\sqrt{K} = 9.5 \times 10^{-8}$, and is simply a rectangular hyperbola. If mass action were the sole factor controlling conductance, the conductance curve would be parallel to the $\gamma$-curve; that is, $\Lambda$ would decrease steadily as concentration increases. Curve II is a graph of $\gamma_3$ against $\sqrt{c}$ for $k = 8.0 \times 10^{-5}$ and in accordance with (3) is, of course, linear. Curve III is a calculated conductance curve obtained by multiplying $\gamma$ by $\Lambda_0 = 30$ and $\gamma_3$ by $\lambda_0 = 10$ and adding, so that $\Lambda = 30\ \gamma + 10\ \gamma_3$. It will be noted that the increasing conductance due to the triple ions produces a minimum in the curve. The circles represent the observed conductance values. Agreement between the experimental values and those calculated by means of

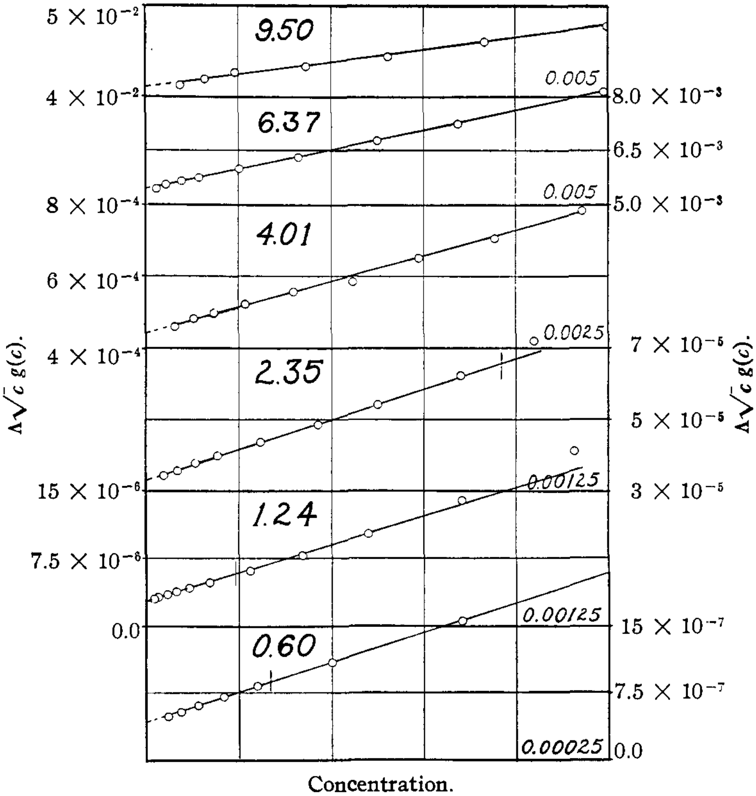

Fig. 1.—Test of equation (11) for tetraisoamylammonium nitrate solutions in dioxane–water mixtures.

(4) is satisfactory through the minimum. Beyond the minimum, the actual conductance curve begins to rise more sharply than proportional to $\sqrt{c}$; this fact indicates that the conductance function includes still higher powers of concentration. Higher powers could be accounted for by an increasing complexity of cluster ions, but very few independent data are available to test this hypothesis. Molecular weight determinations on quaternary ammonium salts in benzene and dioxane[11] yield very high values for the apparent molecular weight at concentrations between 0.01 and 0.001 $N$, and these might be interpreted to mean that in solvents of low dielectric constant the Coulomb forces cause a clustering of ions which increases as concentration increases.

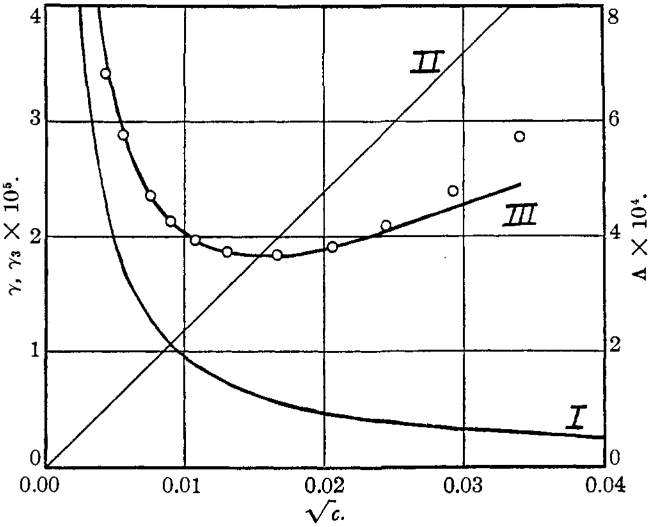

Fig. 2.—Conductance and ionization curves for tetraisoamylammonium nitrate in dioxane–water (1.26% water).

We shall next consider the values of the constant $k$. In order to evaluate $k$ from the constants of the lines of Fig. 1, it is necessary to assume a value for $\lambda_0$, the limiting conductance of the triple ions. From the fluidity of the solvents, we estimate that $\Lambda_0$ is about 30. We shall use $\lambda_0 = 10$, that is, one-third of the estimated value of $\Lambda_0$, which represents the sum of the limiting conductances for the simple ions. In round numbers, $\log (\Lambda_0/\lambda_0) = 0.50$. This value was used to calculate the experimental values of $-\log k$ given in the fourth column of Table III.

If we substitute numerical values of the universal constants in (14) and (16), we obtain

$$\begin{aligned} -\log k &= 3 \log a + 24 + \log I(b) - 2.42 \\ aDb &= 558 \times 10^{-8} \qquad (17) \end{aligned}$$

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[11] R. A. Vingee, Thesis, Brown University, 1931; F. M. Batson, unpublished observations made in this Laboratory.

Using $a = 9.0 \times 10^{-8}$ cm., we have calculated the dissociation constants of the triple ions as a function of dielectric constant by means of (17); the results are given in the last column of Table III. Agreement between calculated and observed values is satisfactory over the available range. The value of $a$ required for the ion–ion pair equilibrium is greater than the value $6.4 \times 10^{-8}$ calculated from the dissociation constant $K$ for the binary equilibrium. This might be expected, because the $a$ corresponding to $K$ represents an average value for the relatively large $(C_5H_{11})_4N^+$ ion and the $NO_3^-$ ion, while the $a$ corresponding to $k$ represents the average for the triple ions, one kind of which contains two of the larger simple ions.

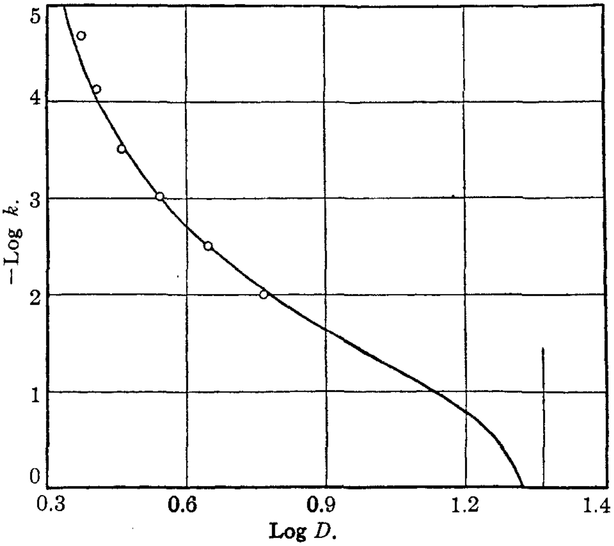

Fig. 3.—Dissociation constant for triple ion equilibrium as a function of dielectric constant of solvent.

The limit $I(b) = 0$ corresponds to $b = 8/3$; for $a = 9.0 \times 10^{-8}$, the limit is reached at $D = 23.2$. On a plot of $-\log k$ against $\log D$, the curve becomes asymptotic to a vertical line at $D = 23.2$, as shown in Fig. 3. Triple ions become unstable for $D > 23.2$, and a minimum in conductance due to this effect cannot appear at any concentration for tetraisoamylammonium nitrate in dioxane–water mixtures of greater dielectric constant. Since $k$ is approximately proportional (*cf.* (7)) to the concentration at which the minimum appears, we thus have a theoretical explanation for the shift of the minimum in conductance with dielectric constant, and its eventual disappearance. For low values of the dielectric constant, the log $c$ (min.) and log $k$ curves run parallel; as the concentration at which the minimum appears increases, the interionic correction terms, particularly the activity, cause deviations. The net effect is that the log $c$ (min.)–log $D$ curve is somewhat less steep than the log $k$–log $D$ curve in the region of the inflection point of the latter. Since we may write (16) as

$$k^{-1} = \frac{A}{D^3}\frac{1}{b^3}I(b)$$

where $A$ represents universal constants, and since $b^{-3}$ $I(b)$ is not very sensitive to the value of $b$ in the inflection region of the log $k$–log $D$ curve, we see that $D^{-3}$ is the controlling factor in this region. This fact is probably the explanation of the empirical rule discovered by Walden, which states that the product $D^3V$ is approximately constant, where $V$ is the volume at which the minimum appears.

## Summary

1. The hypothesis is made that a triple ion, formed from a neutral molecule and a simple ion by the action of electrostatic forces, will exist as a stable structure in solvents of low dielectric constant.

2. The presence of triple ions of the above type accounts in a large measure for the appearance of minima in conductance curves.

3. Dissociation constants for the triple ions computed theoretically agree with values obtained from conductance data.

4. The observed shift of the minimum of conductance toward higher concentrations with increasing dielectric constant of the solvent is given theoretical basis.

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# Polymorphism in the Substituted Thiazole, 3-Phenyl-2,4-thiazolidione

BY R. E. GIBSON AND K. S. MARKLEY[1]

# Optical Crystallography of 3-Phenyl-2,4-thiazolidione

BY H. E. MERWIN

In the course of a study of the reaction between monochloroacetic acid and thiocarbanilide Markley and Reid[2] repeatedly prepared quantities of 3-phenyl-2,4-thiazolidione and recrystallized each preparation from hot glacial acetic acid. Thus obtained, the compound melted at 143–144°, as determined by the capillary tube method, in which a totally immersed thermometer and electrically heated melting apparatus[3] was used. Repeated crystallization from glacial acetic acid failed to effect a change in the melting point of the compound but after recrystallization from hot

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[1] Part III of the Ph.D. dissertation of K. S. Markley, June, 1929.

[2] Markley and Reid, THIS JOURNAL, **52**, 2137 (1930).

[3] Sando, *Ind. Eng. Chem., Anal. Ed.*, **3**, 65 (1931).