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Citation: [The Journal of Chemical Physics](#) **2**, 188 (1934); doi: 10.1063/1.1749449

View online: <http://dx.doi.org/10.1063/1.1749449>

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On Electrolytes in Media of Small Dielectric Constant

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(Received February 15, 1934)

The authors give a general summary of some recent theoretical views concerning the characteristic features of electrolytes in media of small dielectric constant. After a discussion of conductivity observations in water-dioxane mixtures, previous attempts for their theoretical

interpretation are criticized. It is shown that in agreement with previously proposed views of the authors the experimental data can be qualitatively and partly quantitatively understood by considering the activity-coefficient arising from ion-dipole interaction. (See preceding paper.)

I. RECENT CONDUCTIVITY OBSERVATIONS AND THEIR INTERPRETATIONS

THE behavior of electrolytes in solvents of low dielectric constant is known to show a number of anomalies when compared with aqueous solutions. The electrolytes are apparently of high molecular weight when judged by osmotic phenomena. At the same time these seemingly highly associated electrolytes show comparatively high electric conductivity. This conductivity does not depend on concentration in the way to which we are accustomed in the case of water, or media of considerable dielectric constant. Here the equivalent conductance decreases with increasing concentration, in accordance with Ostwald's law of dilution or with the theory of the conductivity coefficient (interionic forces). The authors¹ have some time ago (1925) given a general discussion in which these various contradictory phenomena are brought into harmony. By assuming interaction forces between the ions and between the ions and molecules they provided a suitable explanation for the apparent contradiction between "high association" on the one hand and anomalous conductivity on the other. The most powerful

tool for treating these problems was offered by the conditions for thermodynamic stability.²

Quite recently, several papers have appeared which are of importance for the problem under consideration. An investigation by V. K. La Mer and Harold C. Downes³ has again drawn attention to the appearance of anomalous conductivity of acids in benzene. These authors explain their results by making use of the views which have been given by the writers. Still later in a paper by Kraus and Fuoss⁴ the conductivity of tetraisoamylammonium nitrate (and some other salts) has been studied with a solvent composed of dioxane and water in shifting proportions. Furthermore in several theoretical investigations the activity coefficients which are due to interaction between dipoles and ions have been studied by Fuoss and Kraus.⁵ In this paper we shall mostly be concerned with the theoretical interpretation of the experimental results obtained by Fuoss and Kraus.

¹ Phys. Zeits. **26**, 636 (1925).

The authors wish to make use of this opportunity to correct a point in their previous presentation. In the paper quoted above they made use of an expression for the activity coefficient of the ions as given by Debye's theory of electrolytes. This application is certainly untenable, since the behavior of ions in media of small dielectric constant cannot even approximately be described by Debye's formula.

² Rodebush (Rodebush and Ewart, J.A.C.S. **54**, 419 (1932)) claims that the ideas presented above have been anticipated in a paper by himself and Latimer (J.A.C.S. **42**, 1419 (1920)). We readily admit that Rodebush and Latimer have in a general way mentioned the influence of electric forces the existence of which was in fact obvious. The determining influence of the activity coefficient on anomalous conductivity, the connection between anomalous conductivity and small osmotic pressure, and the general thermodynamic relations were not mentioned.

³ La Mer and Downes, J.A.C.S. **53**, 891 (1931).

⁴ Kraus and Fuoss, J.A.C.S. **55**, 21 (1933).

⁵ Fuoss and Kraus, J.A.C.S. **55**, 476 (1933).

Fuoss and Kraus, J.A.C.S. **55**, 1019 (1933).

Fuoss and Kraus, J.A.C.S. **55**, 2387 (1933).

Fuoss, Zeits. f. Elektrochemie **39**, 513 (1933).

The experimental results obtained by these two authors can perhaps be simply summarized as follows: The conductivity of tetraisoamylammonium nitrate is rather small at most concentrations, if pure dioxane or mixtures with a small percentage of water are used as solvents. If the solvent contains a large percentage of water the conductivity (i.e., the dissociation) increases very rapidly. Keeping the solvent constant the equivalent conductivity shows a minimum with increasing concentration, and increases fairly rapidly after passing this minimum. The location of this minimum shifts markedly to a higher concentration with increasing dielectric constant (i.e., higher water percentage of the solvent). For sufficiently high dielectric constant the equivalent conductivity shows no more minima, and changes only slightly with concentration.

Fuoss and Kraus have attempted to explain these observed facts by making use of the concept of "ionic association" which has been introduced into the theory of electrolytes by Bjerrum.⁶ According to this author ions which are at a distance R from each other smaller than $\epsilon_i \epsilon_k / 2DkT$ (ϵ_i , ϵ_k charge of ion, D , dielectric constant, k , Boltzmann's constant, T , abs. temp) shall be considered as forming a neutral molecule which contributes neither to the interionic forces nor according to Fuoss and Kraus to the electrical conductance. As Bjerrum already mentioned, and as actually worked out by Fuoss and Kraus, in their paper IV, this formation of complexes was not considered to cease with molecular formation, but should proceed to complexes of higher type (triple ions, quadruple ions, and so on). Thus, for example, a dipole carrying molecule and an ion were considered to form a "triple ion," provided the distance R' between them is less than a quantity R' defined by the relation

$$1/R' = 2DkT/\epsilon^2 + R'/(R' + \delta)^2,$$

where δ = dipole moment μ divided by ϵ .

With the help of Bjerrum's formulae Fuoss and Kraus calculated the "dissociation constant" for

the various equilibria

$$c_J^2 f_J^2 / c_M = K_1,$$

$$c_M c_J f_J / c_{J'} f_{J'} = K_2.$$

(c_J , c_M , $c_{J'}$ denote respectively the concentrations of free ions, "molecules" and triple-ions; f_J and $f_{J'}$ are the ionic activity coefficients due to *interionic* forces.) Into these formulae, parameters enter which denote the minimum distance between two ions, between an ion and a molecule, and so on. These were so determined as to give the best fit with their observation. In this way the authors were able to account for the increase of the dissociation with increasing dielectric constant, for the minimum in the conductivity-concentration curve, and for the shift of this minimum to higher values of the concentration with increasing dielectric constant. The authors furthermore made use of the Debye formula for the activity coefficient of the ions arising from the interionic forces; since the ionic concentration is very small it would follow (assuming correctness and applicability of this formula) that the *interionic* effect is of secondary importance only.⁷

The main points which Fuoss and Kraus consider as experimental verifications of Bjerrum's ionic association may be enumerated as follows: (a) With a suitably chosen value a_1 for the minimum distance of approach between the ions it is possible to calculate the variation of the logarithm of the molecular dissociation constant for changes in the dielectric constant of the medium; the following relation is found to hold:

$$\log K_1 \sim 1/D.$$

(b) By introducing *another* molecular diameter

⁷ Into the formula for the activity coefficient there enters the actual ionic concentration to be determined from the analytic concentration with the aid of the law of dilution which itself contains the activity coefficients. The authors Fuoss and Kraus quote, as their sources, papers by Davis, J. Phys. Chem. **29**, 977 (1925).

Sherill and Noyes, J.A.C.S. **48**, 1861 (1926).

MacInnes, J.A.C.S. **48**, 2068 (1926).

It may be mentioned that a discussion of the influence of the activity coefficient and the law of dilution for weak electrolytes has been given in a paper by Gross and Halpern, Phys. Zeits. **25**, 393 (1924).

⁶ Bjerrum, Copenhagen, Akad. fys. Medd. **7**, 9 (1926).

a_2 they calculated a dissociation constant for the equilibrium

$$c_J f_J c_M / c_{J'} f_{J'} = K_2.$$

This dissociation constant K_2 permits the determination of the shift of the minimum in the conductance-concentration curve with changing dielectric constant of the solvent. The authors furthermore claim that there exists a range in which the product D^3/c_{\min} is constant according to their theory of interaction between molecules and ions (triple ion formation). This they consider to be a theoretical explanation of an empirical law previously found by Walden.

For the reasons given in the following discussion we do not consider an explanation given on the basis of Bjerrum's theory of ionic association to be tenable.

II. BJERRUM'S CONCEPT OF IONIC ASSOCIATION AND ITS APPLICATION TO CONDUCTIVITY PHENOMENA

In a previous paper⁸ by one of the writers a discussion of Bjerrum's "ionic association" has been given to which the reader should refer for details. It has there been shown that the Helmholtz-relation between energy and free energy of the ions is not satisfied in Bjerrum's theory. This result is due to the fact that the maximum distance at which two ions are considered as forming a molecule depends on the temperature according to the relation $R = \epsilon_i \epsilon_k / 2DkT$. Notice that R depends on T and D only in the form $R = f(D \cdot T)$; since this is a general consequence of statistical mechanics elimination of the temperature-dependence by some modification of the expressions for R would likewise eliminate the influence of a variation of D and thereby completely invalidate the application of the theory to media of low dielectric constants. The same objections must of course be raised against the calculations of higher complexes (triple-ion equilibria etc.).

A correction which is of slight importance in the case of aqueous solutions (or in the mathematically equivalent case of van der Waals forces in non-ideal gases⁹) becomes of decisive importance for media of small dielectric constant.

Here we are referring to the determination of the volume which is accessible to the free ions. According to the general concept of ionic association an ion is considered to be free if its distance from the closest ion of opposite sign is larger than R . For determining the free energy of the ions one therefore has to consider them as contained in a volume which is equal to the total volume minus the "volume occupied by the molecules." (This corresponds to the correction for the proper-volume in van der Waals theory). The "molecules" in Bjerrum's theory of ionic association have a "radius" R which for media of low dielectric constant (e.g., dioxane $D=2.2$) takes a value 1.3×10^{-6} cm. Since almost all the salt dissolved is forming "molecules" the volume accessible to the "free ions" becomes very much reduced (sometimes even negative); the free energy of the ions therefore is very much increased as compared with the value it would take if the total volume were accessible to the ions.

To illustrate this fact let us consider an actual case of practical interest: a normal solution of tetraisoamylammonium nitrate in dioxane ($D=2.2$). With the value R we obtain for the *volume per liter* occupied by the "molecules" 5000 cc. There is no rational way of correcting for these quite enormous errors. They are fundamentally associated with the unsound basis of the theory which treats long range (Coulomb) forces like short range (van der Waals) forces.

Furthermore Fuoss and Kraus have to assume that these associated ions do not contribute anything to the conductivity of the solution. They have not given any reasons to support this contention, nor is it by any means intuitively obvious why two ions with some forty molecular layers of liquid between them and negative potential energy ($2kT$) only slightly in excess of their average kinetic energy should not participate in electric conduction. On the other hand, they have to assume for example that a molecule and an ion are bound to a triple ion even though the binding energy in some cases is smaller than kT , that is to say to less than two-thirds of the *average* kinetic energy.

The idea in the papers of Fuoss and Kraus of explaining conductivity curves by partial dissociation is not new. What is new is only the

⁸ O. Halpern, J. Chem. Phys. 2, 85 (1934).

⁹ Cf. e.g., R. H. Fowler, *Statistical Mechanics*, § 9.6.

interpretation of partial dissociation as ionic association in Bjerrum's sense. This method of computation we have already criticized from a theoretical point of view. The fact that the logarithm of the dissociation constant varies proportional to $1/D$, and that this variation is implied in Bjerrum's picture cannot be thought to corroborate the latter. *Every model* will show the same dependence, because the work necessary to remove two ions from each other varies as $1/D$. Deviation from this simple relation could only be expected if the ions had a different solvation energy in the various media. Since some traces of water appear to be always present, the ions would be mostly surrounded by water dipoles (salting-out effect), so that the energy of solvation probably varies but slightly. This view is supported by experimental evidence gained through observations of the index of absorption of ions. The index of absorption of the anion of picric acid dissolved in pure ethyl alcohol ($D=26$) shifts to the value which it shows for aqueous solutions if only a small amount of water (0.7 m/lit.) is added to the alcohol.¹⁰

Remembering the difficulties introduced by the contradiction with thermodynamics, by the impossibility of a correct statistics (volume-correction) and by the crude assumptions of widely distant but nevertheless nonconducting ion-pairs, we feel justified in rejecting the quantitative application of the hypothesis of ionic association.

III. THE INFLUENCE OF THE ACTIVITY-COEFFICIENT ARISING FROM THE ION-DIPOLE INTERACTION

As mentioned in the introduction, it has been pointed out by the authors that anomalous conductivity can be explained by the influence of the activity coefficient due to the interaction of the ions with each other and with neutral molecules. The ion-dipole interaction we have treated in the preceding note; the formulae for the dissociation-equilibrium and for the concentration of minimum dissociation apply directly to the present case.

The evaluation of the activity-coefficient due to interionic forces is at present impossible. It

¹⁰ Ph. Gross, *Zeits. f. Elektrochemie* **36**, 789 (1930).

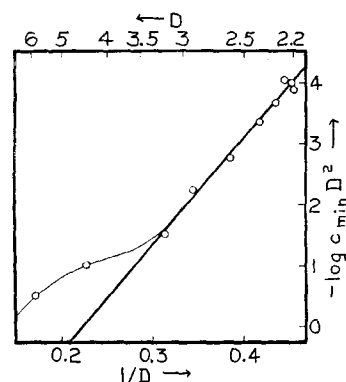


FIG. 1. Test of Eqs. (8, 9, 10) of the preceding paper. The connection between minimum-conductance concentration ($c_{\min.}$) and dielectric constant of the medium. Tetraisoamylammonium nitrate dissolved in various dioxane-water mixtures.

has been shown⁸ that in media of small dielectric constant the Debye-formula for the activity-coefficient *does not give the right order of magnitude even at the lowest concentrations which are accessible to observation*. From the curves given below we learn that it is possible to reproduce quantitatively several features of the conductivity phenomena by tentatively neglecting the interionic effects and merely considering the ion-dipole interaction. This very crude procedure cannot of course claim any accuracy; but it is significant that the agreement is best for very low dielectric constants and near the minimum of dissociation, in which cases the ionic concentration becomes very small.

Fig. 1 has been constructed with the aid of

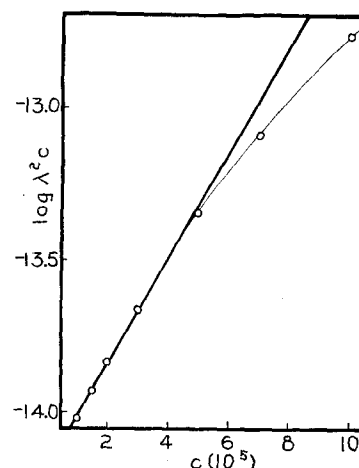


FIG. 2. $\log \lambda^2 c$ as a function of the concentration c of tetraisoamylammonium nitrate dissolved in pure dioxane.

formulae (8), (9) and (10) of the preceding paper. The degree of dissociation is replaced by the equivalent conductivity λ to which it is here assumed to be (nearly) proportional. For values of the constants we have taken $a = 4.2 \times 10^{-8}$ cm and $\mu = 5.8 \times 10^{-18}$ cm e. s. u. In Fig. 2 the observed values of $\log \lambda^2 c$ are compared with the theoretical values given by (8) and (9) of the preceding paper.

This agreement is much less satisfactory than it appears, and is partly misleading, since we are not able to reproduce theoretically by means of (8) of the preceding paper the whole conductivity-concentration curve for all media. Our formula gives satisfactory results principally for the region close to the minimum-conductivity

and for the case of very small dielectric constants. Otherwise the activity coefficient due to interionic forces becomes important. We have furthermore already pointed out in the preceding paper that the meaning of the dielectric constant at the surface of the ion becomes somewhat ambiguous.

The formulae of Kraus and Fuoss can only be considered to be empirical laws. Their claim to have provided a theoretical basis for Walden's

$$D^3/c_{\min.} = \text{const.}$$

does not seem tenable, since this law relates to ionic concentrations which are so high that the interionic forces become dominant.