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Dielectric Properties of Aqueous Ionic Solutions. Parts I and II.

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The dielectric constants and loss angles of a series of concentrated aqueous ionic solutions have been measured at wave-lengths of 10 cm, 3 cm, and 1.25 cm. From these results the values of the static dielectric constant and relaxation time for these solutions have been calculated on the basis of the Debye formula, which appears to hold accurately. All salts show a lowering of the dielectric constant and a shift in the relaxation time of water. It is found that the dielectric constant ϵ can be represented by a formula $\epsilon = \epsilon_\infty + 2\bar{\delta}c$, where ϵ_∞ is the dielectric constant of water, c is the concentration in moles per liter, and $\bar{\delta}$ has values between -7 and -15 for various salts in concentrations of up to $2 M$.

In Part I the measurements are described and the results discussed in relation to the structure of ionic solutions. In Part II the validity of the Debye-Sack saturation theory of the dielectric constant and the effects of the fall of dielectric constant on the electrolytic properties of concentrated solutions are discussed.

PART I

Introduction

A LARGE variety of methods have been used to determine the dielectric properties of salt solutions. The difficulty of the determination lies in the high value of the loss angle δ which is given by the relation, $\tan\delta = 2\sigma/f\epsilon$ where σ is the conductivity, in e.s.u., f the frequency, and, ϵ the dielectric constant.

At the frequencies available when the early measurements were carried out, it was necessary either to work with extremely dilute solutions, the deviations of which from the dielectric properties of water are correspondingly small, or to work with very high values of $\tan\delta$, which greatly limits the accuracy of measurement. It is even difficult from a study of the literature to decide whether the dielectric constant of an ionic solution increases or decreases with in-

creasing concentration.¹ It was shown by Hückel² that a variation of dielectric constant would have a significant, if not dominating, effect on the properties of concentrated salt solutions. Further, Sack made a theoretical estimate of the lowering of dielectric constant that would be expected because of the saturation of the dielectric in the neighborhood of an ion. Both these studies are of great theoretical interest. It is therefore important to study the dielectric properties of ionic solutions in a region where $\tan\delta$ is comparatively low, i.e., at frequencies of the order of 10^{10} cycles a second. We have previously described methods used to determine the dielectric properties of water in the range $\lambda = 1$ to 10 cm. The methods used depended only on the validity of Maxwell's equations, and the use

¹ See for summary C. H. Douglas Clark, *The Fine Structure of Matter* (Chapman and Hall, Ltd., London, 1941), p. 232.

² E. Hückel, *Phys. Zeits.* 26, 93 (1925).

of standard attenuator technique.³ The limits to the accuracy of measurement were entirely technical and did not arise from any uncertainty in the theory. It was found possible to work with reasonable accuracy with values of $\tan\delta$ of the order of 1.5.

In the present paper these methods are applied to ionic solutions. There are two disadvantages of measurements at these frequencies:

(1) Correction must be made for anomalous dispersion so that measurements at a number of frequencies are necessary. It can be shown that the results obtained may be interpreted on the basis of a single time of relaxation, slightly different from that of water. This enables accurate calculation of the static dielectric constant to be made, and further conclusions to be drawn from the behavior of the relaxation time. An apparent disadvantage may thus be turned to good account.

(2) With the 2-4 percent accuracy in ϵ , obtainable in solutions of $\tan\delta=1.5$, deviations from the static dielectric constant of water are only noticeable in solutions of 0.5- to 2-*M* concentration; dilute solutions can therefore not be studied by these methods.

Methods of Measurement

Of the methods developed for the measurement of the dielectric properties of water and heavy

water, which are fully described by the authors,⁴ the three most suitable have been selected for study of ionic solutions. These are: (1) the direct measurement of the absorption coefficient κ in a rectangular wave guide; (2) the measurement of absorption coefficient in two cylindrical wave guides full of solution, the two diameters being selected to be just above and just below cut-off for the wave guide used. By this method both n , the refractive index, and κ , the absorption coefficient, are determined; (3) measurement of the change in Q of an H_{01} resonator on the introduction of an axial capillary containing liquid.

(1) The rectangular wave-guide cell used for measurements of κ at 3 cm and 1.25 cm is shown diagrammatically in Fig. 1A. A pure H_{01} mode is propagated in the liquid-filled guide, and a smaller guide picks up the wave after a known distance. The variation of response as the smaller guide is moved through the liquid is compared with the response variation of a standard piston attenuator. Since the attenuation is exponential, a plot of absolute attenuation, as determined by the distance moved through the liquid against the piston attenuator, should be a straight line, from the slope of which κ may be calculated. The achievement of a straight-line plot confirms that a single pure mode is being propagated in the liquid. With a movement through 30 db of attenuation, with a dead space at the beginning of 15 db, which is possible if a superheterodyne method of response measurement is used, an accuracy of 1 percent in κ is obtained. The method was found to give results at 3 cm in agreement with those obtained by the second method described here.

(2) Absorption coefficients were measured at both 3 cms and 10 cm by similar technique using the H_{11} mode in filled cylindrical wave guides near the cut-off diameter, fed from a rectangular guide as shown in Fig. 1B. A loop on the end of concentric line is used to pick up the response. The propagation constants p_1 and p_2 in the cylindrical guides are given by the relations:

$$\begin{aligned} p_1^2 &= (n_1 - j\kappa_1)^2 = \epsilon' - j\epsilon'' - k_1^2 c^2 / \omega^2, \\ p_2^2 &= (n_2 - j\kappa_2)^2 = \epsilon' - j\epsilon'' - k_2^2 c^2 / \omega^2, \end{aligned}$$

where $k_1 = 1.831/r_1$ and $k_2 = 1.831/r_2$, r_1 and r_2

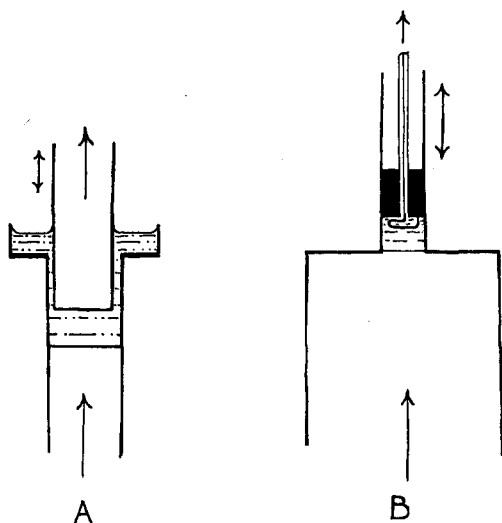


FIG. 1.

³ R. J. Clayton, J. E. Houldin, H. R. L. Lamont, and W. E. Willshaw, *J. Inst. Elec. Eng.* **93**, 97 (1946).

⁴ C. H. Collie, J. B. Hasted and D. M. Ritson, *Proc. Phys. Soc.* **73** (1948).

TABLE I. Dielectric properties of NaCl solutions. Observed values of ϵ' and ϵ'' , the latter corrected for conductivity, are compared with values calculated from the corresponding values of ϵ_s and λ_s .

| Temperature | Normalcy | Equivalent conductivity (I.C.T.) | 10 cm | | | | 3 cm | | | | 1.27 cm | | | | ϵ_s ± 2 | λ_s in cm $\pm .04$ |
|-------------|----------|----------------------------------|---------------------------------|--|----------------------------|-----------------------------|-----------------------------------|--|----------------------------|-----------------------------|---------------------------------|--|----------------------------|-----------------------------|----------------------|-----------------------------|
| | | | $\epsilon'_{\text{obs.}} \pm 3$ | $\epsilon''_{\text{obs. corr.}} \pm 3$ | $\epsilon'_{\text{calc.}}$ | $\epsilon''_{\text{calc.}}$ | $\epsilon'_{\text{obs.}} \pm 1.3$ | $\epsilon''_{\text{obs. corr.}} \pm 1$ | $\epsilon'_{\text{calc.}}$ | $\epsilon''_{\text{calc.}}$ | $\epsilon'_{\text{obs.}} \pm 1$ | $\epsilon''_{\text{obs. corr.}} \pm 1$ | $\epsilon'_{\text{calc.}}$ | $\epsilon''_{\text{calc.}}$ | | |
| 21°C | 0.5 | 85.6 | 72.8 | 12.6 | 71.9 | 11.3 | 58.6 | 28.3 | 58.9 | 28.4 | — | — | — | — | 73.9 | 1.71 |
| | 1.0 | 78.7 | 67.4 | 13.1 | 67.5 | 10.1 | 56.2 | 25.0 | 56.0 | 25.7 | 30.1 | 30.4 | 29.6 | 30.8 | 69.1 | 1.63 |
| | 1.5 | 73.0 | 61.5 | 12.7 | 63.1 | 8.9 | 52.5 | 22.3 | 53.3 | 23.1 | — | — | — | — | 64.3 | 1.55 |
| | 2.0 | 68.6 | 56.2 | 11.8 | 58.0 | 7.9 | 49.6 | 20.7 | 49.4 | 20.6 | 27.8 | 26.0 | 27.6 | 26.3 | 59.0 | 1.51 |
| | 3.0 | 59.7 | — | — | — | — | 45.8 | 18.5 | 45.5 | 18.4 | — | — | — | — | 54.0 | 1.47 |
| | 5.0 | 42.4 | — | — | — | — | 41.8 | 15.7 | 41.9 | 15.8 | — | — | — | — | 48.4 | 1.39 |
| 1.5° | 0.5 | 54.3 | — | — | — | — | 44.7 | 36.1 | 44.5 | 35.9 | — | — | — | — | 77.6 | 2.95 |
| | 1.0 | 49.7 | — | — | — | — | 43.0 | 32.8 | 42.7 | 32.4 | — | — | — | — | 71.0 | 2.80 |
| | 2.0 | 43.3 | — | — | — | — | 39.4 | 26.4 | 39.6 | 26.5 | — | — | — | — | 60.0 | 2.49 |
| | 3.0 | 38.0 | — | — | — | — | 35.9 | 21.4 | 35.9 | 21.3 | — | — | — | — | 51.0 | 2.26 |
| | 5.0 | 32.3 | — | — | — | — | 28.8 | 15.1 | 28.6 | 14.9 | — | — | — | — | 38.3 | 2.07 |
| 0° | .66 | 50.1 | 70.7 | 22.9 | 71.2 | 19.4 | 45.5 | 36.5 | 45.3 | 36.7 | — | — | — | — | 79.1 | 2.96 |
| 10° | .66 | 63.2 | 70.4 | 19.1 | 72.2 | 14.5 | 51.9 | 32.1 | 53.4 | 32.4 | — | — | — | — | 75.5 | 2.17 |
| 20° | .66 | 81.2 | 69.1 | 15.1 | 70.1 | 11.0 | 56.3 | 27.2 | 57.5 | 27.6 | — | — | — | — | 72.0 | 1.70 |
| 30° | .66 | 98.8 | 67.7 | 12.0 | 65.8 | 8.1 | 55.7 | 21.8 | 56.8 | 21.6 | — | — | — | — | 66.6 | 1.35 |
| 40° | .66 | 117.4 | 62.8 | 10.0 | 62.4 | 6.3 | 54.3 | 16.9 | 54.4 | 16.8 | — | — | — | — | 63.0 | 1.10 |

being the radii of the guides. We thus have the equations:

$$\epsilon' = \frac{(c^2/\omega^2)(k_1^2\kappa_1^2 - k_2^2\kappa_2^2)}{\kappa_1^2 - \kappa_2^2} - (\kappa_1^2 + \kappa_2^2),$$

$$\epsilon'' = 2\kappa_1[\epsilon'_1 - (k_1^2c^2/\omega^2) + \kappa_1^2]^{\frac{1}{2}},$$

representing both dielectric constants ϵ' and ϵ'' in terms of the two absorption coefficients κ_1 and κ_2 . The latitude in the choice of r_1 and r_2 is sufficient to allow the two measurements of the attenuation in the guide to be approximately independent measurements of n and κ , the optical constants in free space.

This method is used for the real dielectric constant at 3 cm and for both dielectric constants at 10 cm. It was found to give results for water at 10 cm in agreement with those obtained by a similar method in rectangular guide, and also using an E_{010} resonator with axial capillary.

In both methods constancy of power during the experiments was insured by checking back to the initial position of liquid cell or attenuator movement and noting the (unchanged) value of the response. Detailed descriptions of the experimental methods are given in the earlier papers.

(3) The H_{01} resonator method for the determination of n at 1.25 cm is described in an earlier paper.⁴

In all methods the circulation of water pumped

from a thermostat through jackets on the apparatus provided temperatures constant to $\pm 0.2^\circ\text{C}$.

Conductivity Measurements

It is necessary to make a correction for the conductivity before the correct value of ϵ'' can be found. On solutions of which the low frequency conductivity was not available in the literature, rough measurements were made in a cell with platinum electrodes of area 0.2 sq cm, 8 cm apart, using standard a.c. bridge technique. The accuracy was about 2 percent. The values obtained are given in the same table as the dielectric constant results.

Results

The experimental values of ϵ' and ϵ'' at 10 cm and 3 cm for sodium chloride solutions are given in Table I and those of other solutions in Table II. The measurements in Table II are all at $25^\circ \pm 0.2^\circ\text{C}$, but those on NaCl in Table I were taken at various temperatures in order to study the effects more fully. For the same reason some readings at 1.25 cm were taken on the NaCl solutions. Corrections for conductivity are made according to the equation:

$$\epsilon''_{\text{correct}} = \epsilon'_{\text{observed}} + (2\sigma/f),$$

where σ is the specific conductivity in e.s.u. and

f the frequency. For the purpose of these corrections there is assumed to be no change in this conductivity with frequency, an assumption which is discussed later. It is possible to analyse the corrected results in terms of a static dielectric constant ϵ_s , falling to an atomic dielectric constant ϵ_0 . If there is a single relaxation time the relations below are generally true, and not dependent on the dielectric model.

$$\epsilon' = n^2 - \kappa^2 = (\epsilon_s - \epsilon_0) / (1 + \omega^2 \tau^2) + \epsilon_0$$

$$= (\epsilon_s - \epsilon_0) / (1 + [\lambda_s / \lambda]^2) + \epsilon_0,$$

$$\epsilon'' = 2n\kappa = \frac{(\epsilon_s - \epsilon_0)\omega\tau}{1 + \omega^2 \tau^2} = \frac{(\epsilon_s - \epsilon_0)[\lambda_s / \lambda]}{1 + [\lambda_s / \lambda]^2},$$

$$\lambda_s = 2\pi c \tau,$$

where τ is a single time of relaxation, corresponding to a wave-length λ_s ("Sprungwellenlänge") and λ , ω , and c have their usual sig-

nificance. In the tables the experimental values of ϵ' and ϵ'' at each frequency are compared with the values calculated from the corresponding values of ϵ_s and λ_s . These values of ϵ_s and λ_s are chosen so as to give the best fit to the experimental data when the above equations are used.

It is clear that the accuracy of measurement depends on the value of $\tan\delta$, being greatest where $\tan\delta$ is smallest, that is, for solutions of lowest conductivity. The estimated accuracies given below are those for a typical case, a normal solution of KCl, NaCl, or RbCl.

| | |
|----------------------------------|------------|
| Accuracy in ϵ' at 10 cm | ± 3 |
| ϵ'' 10 cm | ± 3 |
| ϵ' 3 cm | ± 1.3 |
| ϵ'' 3 cm | ± 1 |
| ϵ' 1.25 cm | ± 1 |
| ϵ'' 1.25 cm | ± 1 |
| ϵ_s | ± 2 |
| λ_s | ± 0.04 |

TABLE II. Dielectric properties of solutions at 3 and 10 cm, at 25°C. Observed values of ϵ' and ϵ'' , the latter corrected for conductivity, are compared with values calculated from the corresponding values of ϵ_s and λ_s . Conductivity values are denoted "T" when taken from the International Critical Tables, "E" when found experimentally.

| Salt | Normalcy | Equivalent conductivity | $\epsilon'_{\text{obs.}}$ ± 1.3 | 3 cm | | | | 10 cm | | | | ϵ_s ± 2 | λ_s in cm $\pm .04$ | |
|---------------------------------|----------|-------------------------|--|----------------------------|----------------------------|--|-----------------------------|--|----------------------------|----------------------------|--|-------------------------|--------------------------------|-----------------------------|
| | | | | $\epsilon'_{\text{calc.}}$ | $\epsilon''_{\text{obs.}}$ | $\epsilon''_{\text{obs.}}$ corr. ± 1.0 | $\epsilon''_{\text{calc.}}$ | $\epsilon'_{\text{obs.}}$ ± 3.0 | $\epsilon'_{\text{calc.}}$ | $\epsilon''_{\text{obs.}}$ | $\epsilon''_{\text{obs.}}$ corr. ± 3.0 | | | $\epsilon''_{\text{calc.}}$ |
| LiCl | 0.5 | 81.0T | 58.3 | 58.9 | 33.6 | 26.0 | 25.7 | 69.0 | 70.6 | 34.6 | 10.7 | 10.0 | 71.2 | 1.55 |
| | 1.0 | 72.9T | 53.9 | 53.6 | 37.4 | 23.3 | 22.5 | 60.6 | 63.0 | 51.9 | 8.0 | 8.6 | 64.2 | 1.52 |
| | 1.5 | 67.0T | 49.0 | 48.1 | 39.6 | 20.2 | 19.7 | 52.5 | 55.5 | 64.8 | 5.0 | 7.4 | 57.0 | 1.49 |
| | 2.0 | 62.0T | 44.2 | 44.1 | 41.1 | 17.0 | 17.5 | | | | | | 51.0 | 1.45 |
| RbCl | 0.5 | 125.5E | 59.5 | 60.8 | 37.0 | 25.0 | 26.5 | 72.1 | 72.0 | 46.2 | 8.9 | 10.2 | 73.5 | 1.54 |
| | 1.0 | 114.7E | 56.1 | 57.1 | 45.1 | 23.2 | 24.1 | 71.0 | 67.0 | 77.5 | 9.4 | 9.2 | 68.5 | 1.50 |
| | 1.5 | 107.5E | 52.5 | 53.4 | 52.8 | 22.0 | 21.9 | | | | | | 63.5 | 1.47 |
| | 2.0 | 104.5E | 49.2 | 49.7 | 59.9 | 20.2 | 19.7 | | | | | | 58.5 | 1.43 |
| KCl | 0.5 | 117.2T | 60.0 | 60.8 | 37.2 | 25.9 | 26.5 | 70.3 | 72.0 | 45.7 | 10.5 | 10.2 | 73.5 | 1.54 |
| | 1.0 | 111.9T | 57.4 | 57.1 | 45.2 | 23.6 | 24.1 | 64.3 | 67.0 | 73.9 | 6.8 | 9.8 | 68.5 | 1.50 |
| | 1.5 | 107.6T | 54.4 | 53.4 | 53.0 | 21.8 | 21.9 | | | | | | 63.5 | 1.47 |
| | 2.0 | 104.2T | 49.0 | 49.7 | 58.4 | 18.4 | 19.7 | | | | | | 58.5 | 1.43 |
| BaCl ₂ | 1.0 | 80.5T | 52.3 | 53.4 | 37.7 | 22.2 | 22.4 | 64.1 | 62.8 | 57.1 | 8.8 | 8.6 | 64.0 | 1.50 |
| | 2.0 | 68.5T | 44.1 | 43.6 | 43.3 | 16.9 | 16.8 | | | | | | 51.0 | 1.42 |
| HCl | 0.25 | 377.0T | 58.3 | 59.3 | 44.2 | 26.0 | 26.6 | 75.9 | 71.0 | 64.4 | 7.8 | 10.2 | 72.5 | 1.59 |
| | 0.5 | 360.0T | 55.7 | 56.5 | 63.6 | 26.3 | 25.3 | | | | | | 69.0 | 1.59 |
| NaOH | 0.25 | 206.0T | 58.9 | 60.0 | 36.5 | 26.6 | 26.8 | 75.7 | 71.0 | 42.6 | 11.7 | 10.3 | 73.0 | 1.58 |
| | 0.5 | 196.0T | 57.0 | 55.7 | 43.6 | 24.7 | 24.4 | 66.5 | 67.0 | 56.4 | 4.9 | 9.5 | 68.0 | 1.56 |
| KI | 0.198 | 126.4T | 61.0 | 61.5 | 32.0 | 27.2 | 27.2 | 73.1 | 74.0 | 25.5 | 10.4 | 10.7 | 75.0 | 1.56 |
| | 0.396 | 122.0T | 58.7 | 59.8 | 34.4 | 25.1 | 25.7 | 73.3 | 71.0 | 40.1 | 11.1 | 10.0 | 72.0 | 1.52 |
| NaF | 0.415 | 83.7E | 58.3 | 60.4 | 31.7 | 25.0 | 26.6 | 71.3 | 72.0 | 28.2 | 7.4 | 10.3 | 73.0 | 1.55 |
| | 0.830 | 70.2E | 56.2 | 57.3 | 35.2 | 24.0 | 24.5 | 72.4 | 68.0 | 43.4 | 8.4 | 9.5 | 69.0 | 1.52 |
| LaCl ₃ | 0.52 | 77.5E | 57.3 | 58.4 | 33.0 | 25.2 | 25.6 | 70.9 | 70.0 | 33.1 | 8.9 | 9.9 | 71.0 | 1.54 |
| | 1.04 | 69.2E | 52.6 | 53.3 | 35.9 | 22.0 | 22.4 | 66.1 | 63.0 | 51.0 | 7.8 | 8.8 | 64.0 | 1.50 |
| KF | 0.242 | 108.9E | 61.5 | 61.5 | 32.0 | 27.9 | 27.5 | 73.5 | 73.5 | 24.6 | 8.8 | 10.7 | 75.0 | 1.58 |
| | 0.484 | 98.4E | 58.9 | 59.3 | 34.9 | 25.7 | 26.1 | 72.1 | 70.5 | 35.9 | 7.3 | 10.1 | 72.0 | 1.56 |
| NaI | 0.428 | 100.8T | 59.4 | 59.3 | 33.4 | 25.1 | 25.3 | 71.5 | 70.0 | 34.2 | 8.3 | 9.5 | 71.0 | 1.50 |
| | 0.856 | 94.4E | 54.5 | 54.2 | 36.4 | 20.8 | 21.5 | | | | | | 64.0 | 1.42 |
| MgCl ₂ | 0.468 | 84.9T | 57.4 | 58.5 | 32.9 | 25.2 | 25.7 | 70.0 | 70.0 | 36.9 | 13.0 | 10.1 | 71.0 | 1.56 |
| | 0.935 | 74.3E | 53.8 | 53.5 | 36.3 | 23.0 | 22.9 | 64.9 | 63.5 | 49.8 | 8.1 | 8.6 | 64.5 | 1.53 |
| Na ₂ SO ₄ | 0.5 | 70.0T | 57.3 | 57.9 | 33.2 | 26.4 | 25.0 | | | | | | 73.0 | 1.54 |
| | 1.0 | 59.0T | 55.0 | 55.9 | 36.5 | 25.1 | 23.4 | | | | | | 67.0 | 1.49 |
| | 2.0 | 45.5T | 51.2 | 51.7 | 38.4 | 20.8 | 20.1 | | | | | | 60.5 | 1.40 |

The accuracy of the calculated values of ϵ_s and λ_s depends on the correct choice of ϵ_0 . This has been taken as 5.5, the value which has been found most suitable in the interpretation of our previous results on water. Additional weight is lent to this value for water by the infra-red measurements of Rubens⁵ and Hawley Cartwright.⁶ It is found that n , which is not much greater than 2 at 152μ , rises as the wave-length increases. It is unlikely that a very large depression or elevation of ϵ_0 for water occurs when ions are added, but a variation of ± 1 would only alter the values of ϵ_s by ± 1 percent.

The possibility of fitting the data to the above equations employing a single time of relaxation adds additional weight to the results; but the accuracy of some measurements at 10 cm is unsatisfactory when compared with our similar measurements on water, even when allowing for the higher loss angle. The experimental method was not pushed to its limit of accuracy, there being three principal defects:

- (1) Selection of too large a diameter of smaller wave guide for the absorption measurement of ϵ' .
- (2) Unevenness in the cylindrical wave-guide walls in absorption measurements.
- (3) Mechanical defects of the pick-up probe movement.

The first two defects arose owing to the difficulty of drilling 5-mm diameter holes through distances greater than about 7 cm if commercial drills are used. Therefore the wave guides were made of extruded copper tube, which is only available in certain diameters, and which shows defects when it is strained by the soldering of water jackets. The movement of the pick-up probe was designed for measurements on water, through which greater distances are traveled; it was therefore not so accurate for the small movements required in measurements on ionic solutions.

At 3 cm the cylindrical wave guides of diameters of a few millimeters were machined, and a standard micrometer used for the movement. There is every prospect of being able to increase the accuracy of these methods beyond even that at 3 cm, since the errors are not theoretical but technical in origin.

⁵ H. Rubens, *V. D. Physik. Ges.* **17**, 315 (1915).

⁶ C. Hawley Cartwright, *J. Chem. Phys.* **4**, 413 (1936).

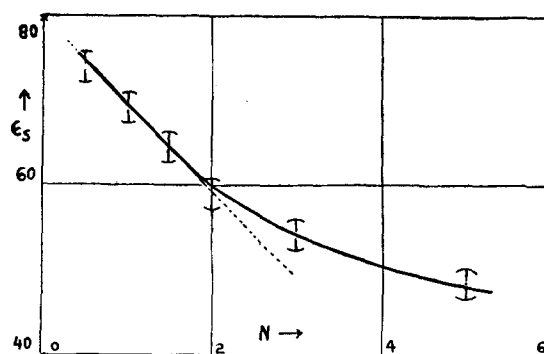


FIG. 2. Static dielectric constant of NaCl solution plotted against normality N . Temperature 21.0°C .

Previous Measurements

Previous measurements on ionic solutions at low frequencies suffer from the drawback of a high loss angle mentioned above.

The small increase in the dielectric constant of dilute solutions observed by Wien is not in conflict with the present results, since the variations in question are not of great magnitude, and might very well take place before the fall in the dielectric constant of concentrated solutions comes into play. This can be seen from Fig. 2 in which the static dielectric constant of NaCl solution is plotted against the concentration. It is clear, however, that the considerable fall of dielectric constant observed by Sack is in disagreement with the present results. Some of the most reliable work, that of Wyman,⁷ and Drake, Pierce and Dow⁸ on dilute solutions at 60 cm and 4 meters, shows that the lowering of dielectric constant is of such small magnitude as would be in keeping with our results on concentrated solutions. The only available results on concentrated solutions at centimetric wave-lengths are those of Elle⁹ at 4 cm using a free-wave method with damped waves from a Herizian oscillator, and those of Cooper¹⁰ on NaCl solutions at wave-lengths down to 7 cm using a transmission-line reflection method. The latter are in rough agreement with the results of the present authors, though not interpreted as such. (In his Fig. 4 much better agreement would be obtained by employing our values of the dielectric constant.)

⁷ J. Wyman, *Phys. Rev.* **35**, 623 (1930).

⁸ F. H. Drake, G. W. Pierce, and M. T. Dow, *Phys. Rev.* **35**, 613 (1930).

⁹ D. Elle, *Ann. d. Physik* **30**, 355 (1937).

¹⁰ R. Cooper, *J. Inst. Elec. Eng.* **93**, 69 (1946).

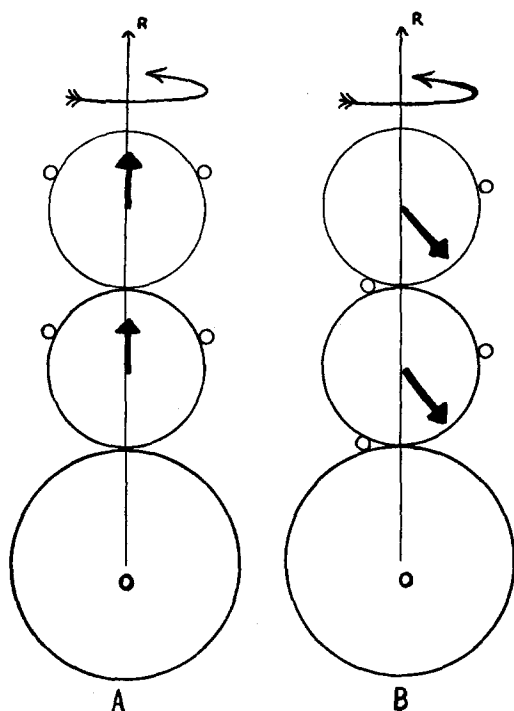


FIG. 3. Methods of hydration round an ion—A, cation; B, anion.

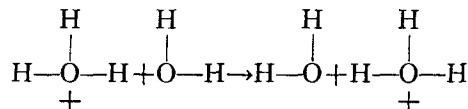
Discussion

(a) Conductivity

The consistency of the results with the above equations, assuming the conductivity to be the same as the d.c. value, is in confirmation not only of the accuracy of the results but also of the correctness of choice of value for the conductivity. It is interesting to note that the increase of conductivity of a dilute solution at a sufficiently high frequency predicted on the Debye-Falkenhagen theory¹¹ cannot be of significant size in these concentrated solutions. It can be seen from the experimental results that an increase in conductivity of more than 3 percent at 10 cm or 10 percent at 3 cm is not likely. The Debye-Falkenhagen theory does not apply quantitatively to solutions of these concentrations, but for a weaker solution, $N/2$ NaCl, the increase would be of the order of 20 percent at 3 cm and 5 percent at 10 cm. It is therefore probable that the effect is smaller, or occurs at a higher frequency,

than would be predicted for these concentrations by use of the theory in its present form.

There is also the possibility of a fall of conductivity in solutions containing ions of abnormal mobilities such as H^+ . The abnormal mobility of the hydrogen is believed to be due to its passage through water by an exchange mechanism which is written as follows:



It was predicted by Hückel¹² that at wave-lengths of the order of 8 cm the conductivity of hydrogen ions should fall to the normal value for monovalent ions. Hückel's treatment, like that of other authors, assumes a Lorentz field

$$E + [(\epsilon + 2)E/3]$$

acting on the ions, but this should perhaps be replaced by an Onsager field $3E/2$. With this modification we should not expect the fall of conductivity to occur until about 5 mm.

TABLE III. Values of δ and $\delta\lambda_s$.

| | $\delta \pm 1$ | $\delta\lambda_s \pm 2$ |
|---|-------------------------------|---|
| HCl | -10 | 0 |
| LiCl | -7 | -3.5 |
| NaCl | -5.5 | -4 |
| KCl | -5 | -4 |
| RbCl | -5 | -4.5 |
| NaF | -6 | -4 |
| KF | -6.5 | -3.5 |
| NaI | -7.5 | -9.5 |
| KI | -8 | -9.5 |
| MgCl ₂ | -15 | -6 |
| BaCl ₂ | -14 | -8.5 |
| LaCl ₃ | -22 | -13.5 |
| NaOH | -10.5 | -3 |
| Na ₂ SO ₄ | -11 | -9.5 |
| Values of δ^+ , δ^- , $\delta\lambda_s^+$, $\delta\lambda_s^-$ | | |
| | δ^+ , $\delta^- \pm 1$ | $\delta\lambda_s^+$, $\delta\lambda_s^- \pm 2$ |
| H ⁺ | -17 | +4 |
| Li ⁺ | -11 | -3 |
| Na ⁺ | -8 | -4 |
| K ⁺ | -8 | -4 |
| Rb ⁺ | -7 | -5 |
| Mg ⁺⁺ | -24 | -4 |
| Ba ⁺⁺ | -22 | -9 |
| La ⁺⁺⁺ | -35 | -15 |
| F ⁻ | -5 | -4 |
| Cl ⁻ | -3 | -4 |
| I ⁻ | -7 | -15 |
| OH ⁻ | -13 | -2 |
| SO ₄ ⁻ | -7 | -11 |

¹¹ H. Falkenhagen, *Electrolytes* (Oxford University Press, London, 1934), p. 73.

¹² E. Hückel, *Zeits. f. Elektrochemie* **34**, 546 (1928).

TABLE IV. Minimum hydration of positive ions.

| | |
|-------------------|----|
| H ⁺ | 10 |
| Li ⁺ | 6 |
| Na ⁺ | 4 |
| K ⁺ | 4 |
| Rb ⁺ | 4 |
| Mg ⁺⁺ | 14 |
| Ba ⁺⁺ | 14 |
| La ⁺⁺⁺ | 22 |

Now the maximum decrease of conductivity is estimated as above from the experimental results on HCl in Table II to be 3 percent at 10 cm and 10 percent at 3 cm. This would indicate either that the replacement of the Lorentz field by the Onsager field in Hückel's treatment is justified, or that the exchange process occurs at a still greater rate. Measurements were also made of the absorption coefficient of 2*N* and 5*N* HCl at 1.25 cm, and the experimental values are sufficiently large (2*N*, $\kappa=4.74$, 5*N*, $\kappa=5.04$) to indicate that at this wave-length there is no considerable decrease in conductivity.

(b) Dielectric Constant

We shall now consider qualitatively the experimentally measured depression of the dielectric constant of water brought about by the addition of ions. The most acceptable model is one of each ion attracting a sheath of several layers of water molecules around it; the dielectric properties of these molecules are naturally different from those of the molecules not in the neighborhood of an ion, and the effects fall off as we go further from the ion itself. The types of hydration believed to exist round a positive and a negative ion are shown in Fig. 3, *A* and *B*.

In solutions of concentrations less than 2*M*, a linear relationship between the dielectric constant and the concentration is found:

$$\epsilon = \epsilon_w + 2\bar{\delta}c,$$

where ϵ_w is the static dielectric constant of water, *c* is the concentration in moles per liter, and $\bar{\delta} = (\delta^+ + \delta^-)/2$, δ^+ and δ^- being the (negative) contributions from the two ions, assumed univalent in this case. Values of $\bar{\delta}$, δ^+ and δ^- are given in Table III, it being necessary to assume the relative contributions of the two ions in a single case. We choose the case of sodium chloride, and $\delta^+_{Na^+}$ is taken as -8 and $\delta^-_{Cl^-}$ as -3

on the following basis; a negative ion, attracting water molecules as in Fig. 3*B*, still leaves them partially free to rotate, and so saturates them less than would a cation which attracts them as in Fig. 3*A*.¹³ Therefore, the depression of dielectric constant is much larger for cations than anions; quantitative treatment in Part II of this paper gives $\delta^+ = -10$, $\delta^- = -1$; on the other hand, the differences between the saturation are probably not so sharply defined as this; we have therefore estimated that

$$\delta^+_{Na^+} = -8 \pm 1 \quad \text{and} \quad \delta^-_{Cl^-} = -3 \pm 1.$$

It is possible to estimate the minimum hydration possible round a cation from the values of δ^+ , on the following basis: the model adopted in Part II of this paper is one in which short-range order dominates the orientation of the inner hydration sheath, effectively removing a fraction of the water molecules from playing any part in the dielectric process; outside this there is a region in which a small amount of saturation takes place, so that these molecules make a small contribution to the fall of dielectric constant; it is reasonable to assume that this accounts for about a quarter of $\delta^+_{Na^+}$, that is, -2 . Subtracting this contribution, we have for the minimum number of water molecules in the inner sheath, *N*,

$$(-\delta^+ - 2)/\epsilon_w = NM/1000,$$

where *M* is the molecular weight of water. Values of this minimum hydration number *N* are given in Table IV.

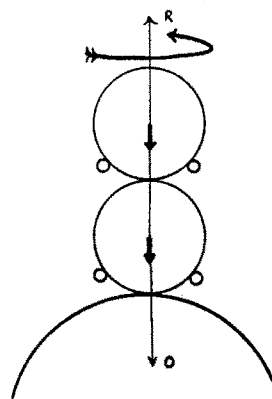


FIG. 4. Possible hydration round a large anion.

¹³ D. H. Everett and C. H. Coulson, Trans. Faraday Soc. 36, 633 (1940).

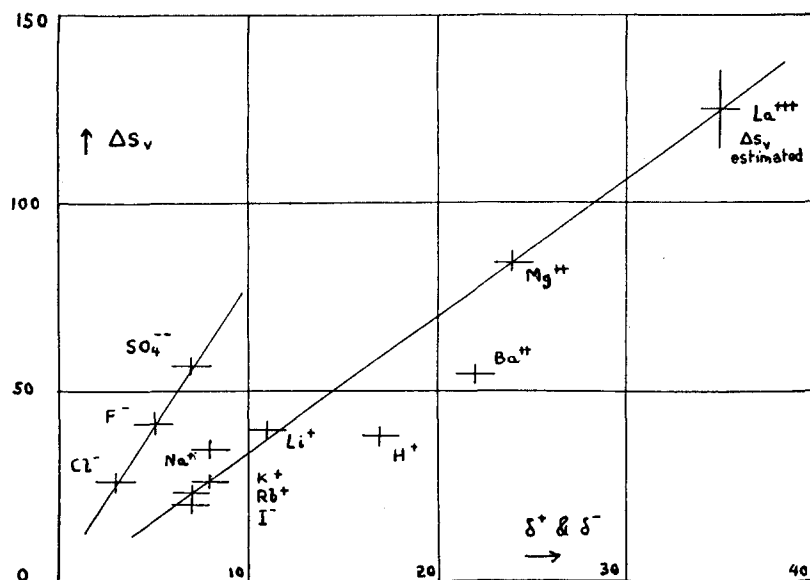


FIG. 5. Plot of ΔS_v against δ^+ and δ^- various ions.

These results, in particular the value of $N=4$ for ions such as Na^+ are of the correct order so far as the inner sheath is concerned, but it should be emphasized that this method can only give a lower limit to the hydration number; molecules in the first sheath are only incompletely prevented from taking part in the dielectric process, and therefore the hydration number will be correspondingly greater. The freedom of rotation of the water molecules in the sheath round an anion makes it impossible to treat these ions in the same way.

A quantitative treatment of the dielectric constant depression is given in Part II of this paper, but the following points may be noted here.

1. The cation contribution is dependent on its charge.

2. Cations of small radius make a larger contribution than those of large radius. Both these facts are in accordance with the present ideas on the hydration of cations.

3. A number of effects operate in determining the anion contribution, which is on the whole smaller than that of the cation. It is possible that large anions such as I^- bind the water molecules by both hydrogen atoms, as in Fig. 4, and so have a greater saturating effect than the small anions, which leave their hydration molecules free to rotate as in Fig. 3b. The large contribution of OH^- is explained on the basis that it can attract and saturate water molecules very easily, in a pattern similar to that of the water itself, without undue disturbance of the water lattice.

4. As will be recalled later, values of δ^+ and

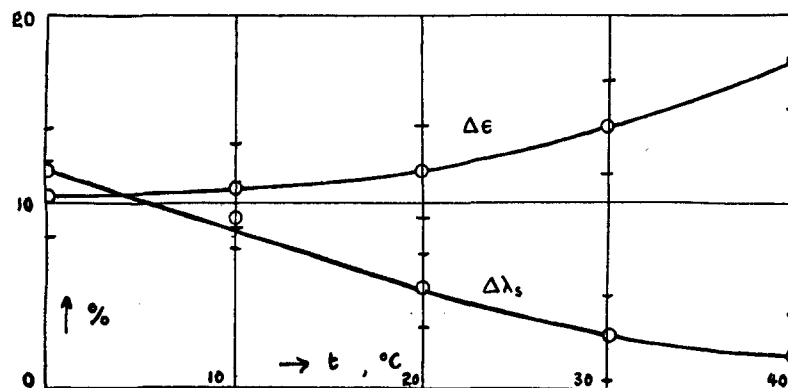


FIG. 6. Plot of percentage depressions of dielectric constant ($\Delta\epsilon$) and relaxation wave-length ($\Delta\lambda_s$) against temperature for $0.66N \text{ NaA}$.

δ^- are of the same order as those assumed by Hückel in his theory of concentrated solutions; but the relative values for different ions are not quantitatively the same.

It is of interest to compare our values of δ^+ and δ^- with ionic entropy data. In a recent paper,¹⁴ Frank and Evans give the molal entropy of vaporization of ions at 25°, on changing from a molar solution to a gas at one-atmosphere pressure. This entropy change ΔS_v is to be regarded as being a measure of the ordering of water molecules in the vicinity of an ion (compare with Latimer¹⁵) comparable to the lining up of the water molecules. According to Frank and Evans part may be due to the restriction of an ion into a free volume box of water molecules. Since the solutions are of molar concentration in each case, there should be a certain correlation between ΔS_v and δ^+ , and probably a different correlation with δ^- . These are shown in Fig. 5. It is significant that δ_{I^-} lies on the cation correlation line, indicating the rigid dipole type of hydration.

The "structure-breaking entropy" of Frank and Evans is considered under the heading of relaxation-time depression.

As can be seen from Fig. 2, the linear dependence of dielectric-constant depression on concentration no longer holds at concentrations above 2M. It is possible to regard solutions in this region as ionic lattices with interspersed

water molecules. At least we may be certain that the saturation effects of adjacent ions overlap. On this type of model the prediction of dielectric constant behavior is much more difficult.

It may be seen from Table I that the dielectric-constant depression is greater at high temperatures than at low. This is more clearly shown in Fig. 6, in which the percentage depression of the dielectric constant of water by 0.66*N* NaCl is plotted against temperature. This effect could be explained on the assumption that the short-range order round an ion increases with the temperature, as the competing order of the water decreases. This would imply that the hydration increases with the temperature, a problem which requires further experimental elucidation.

(c) Relaxation Time

The linear depression of the relaxation wavelengths of water by the addition of ions at concentrations of less than 1.5*M*, which is shown in Fig. 7, may be discussed on the same basis as the dielectric constant depression. The authors⁴ discuss the mechanism of re-orientation in water and heavy water in the light of experimental results. Comparison with the viscosity data of water and heavy water over a temperature range leads us to believe that re-orientation takes place by molecules undergoing the same process as that of viscous flow, or self-diffusion, that is, a

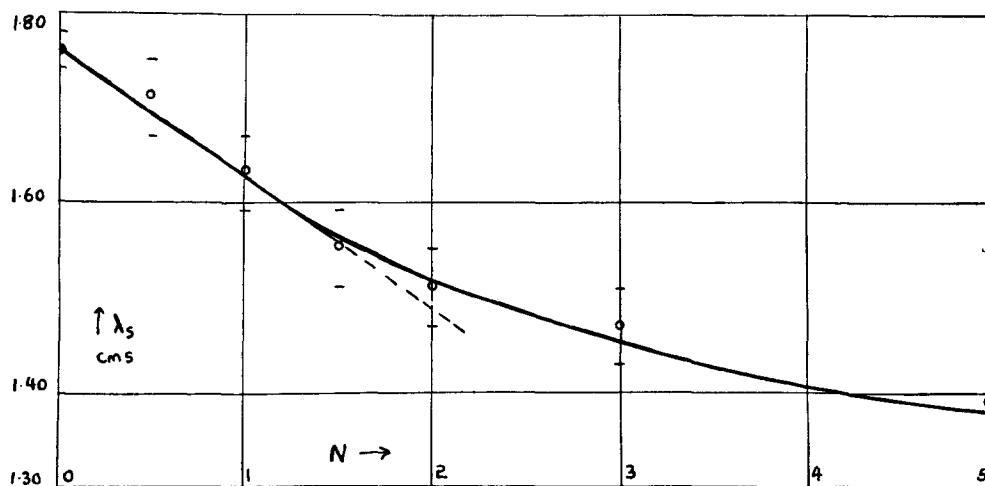


FIG. 7. Plot of relaxation wave-length of NaCl solution against normality *N*.

¹⁴ H. S. Frank and M. Evans, *J. Chem. Phys.* **13**, 479 (1945).

¹⁵ W. M. Latimer, *Chem. Rev.* **18**, 349 (1935).

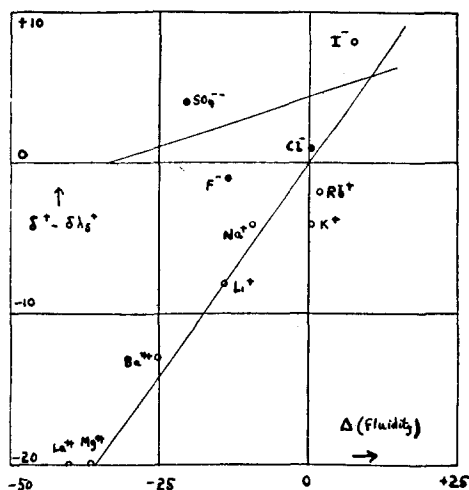


FIG. 8. Speculative correlation of fluidity elevation with sum of short-range and long-range effects. Anions, represented as blackened circles, lie on shorter line. Errors of ± 6 in $\delta^+ - \delta\lambda_s^+$ not marked in.

replacement of empty lattice spaces by molecules which themselves leave further spaces for replacement. Thus re-orientation takes place at the moving boundaries of the broken pieces of "lattice."

Most ions when added to water rupture the lattice, creating more boundaries at which re-orientation can take place; they have a so-called "structure-breaking" effect, of which the depression of relaxation time or wave-length is a reasonable index.

Using a similar notation to that of dielectric-constant depression, we have at concentration lower than $1.5M$; $\lambda_s = \lambda_{s0} + 2\delta\lambda_s c$, where λ_{s0} is the relaxation wave-length of water, and $\delta\lambda_s = (\delta\lambda_s^+ + \delta\lambda_s^-)/2$, $\delta\lambda_s^+$ and $\delta\lambda_s^-$ being the (negative) contributions from the two ions, both taken as univalent in this case. In Table III are given values of $\delta\lambda_s^+$, $\delta\lambda_s^-$, and $\delta\lambda_s$, it being assumed that in a solution of ions of equal radius, such as KF, there are equal contributions from K and F (compare with Bingham¹⁶). The error of ± 2 in $\delta\lambda_s$ is such that these values can only be regarded as semiquantitative.

It is apparent that $\delta\lambda_s^+$ is dependent on the charge of the cation, and is greater for large ions than for small, much-hydrated ions of the type of Li^+ , Mg^{++} , and H^+ . The concept of a large ion breaking the structure more than a small

ion, because it is difficult to fit into the structure without splintering, is reasonable. Moreover these qualitative differences are in agreement with the generally accepted views on the interpretation of x-ray diffraction, Raman and infra-red absorption spectra, and on the depression of the temperature of maximum density.

It is usual to correlate relaxation-time data with macroscopic viscosity data, as was done by the authors in the case of water and heavy water. In dilute solution the increase of viscosity is satisfactorily explained on the theory of Falkenhagen and Dole,¹⁷ which employs the concept of the ionic atmosphere, but at high concentrations there is a negative viscosity effect which requires a different explanation. Finkelstein¹⁸ developed a theory of the re-orientation of solvent molecules, giving a positive viscosity effect varying with the concentration; but we must be able to explain the effects of various ions in concentrated solution in both elevating and depressing the viscosity. In this connection the "ionic elevation of fluidity" of Bingham¹⁶ is of value. Let us first examine the relaxation-time data purely from the point of view of "structure-breaking" effect. Frank and Evans¹⁴ tabulate values of a quantity ΔS_s , which can be regarded as the entropy change due to the disturbing effect of the ion and hydration sheath on the surrounding water; but it contains other factors also. We should expect this to be correlated with $\delta\lambda_s^+$ and with Bingham's elevation of fluidity. The values of $\delta\lambda_s^+$ are not sufficiently accurate to correlate with ΔS_s , but for monovalent ions there is no violent disagreement. For polyvalent ions, however, ΔS_s is not calculated, and large negative values of fluidity elevation appear. Now polyvalent ions are shown on the basis of relaxation time to have a strong structure-breaking effect and they should therefore give large positive elevations of fluidity. There is, therefore, a second factor operating in the cases of viscosity or fluid flow. This is the short-range order effect, by which water molecules in the inner hydration sheath, by reason of their strong orientation, are made more viscous and depress the fluidity. This effect, analogous to the depression of dielectric constant, will be greater for polyvalent ions, and

¹⁶ E. C. Bingham, J. Phys. Chem. **45**, 885 (1941).

¹⁷ See H. Falkenhagen, reference 11, p. 245 for summary.

¹⁸ B. N. Finkelstein, Phys. Zeits. **31**, 130, 165 (1930).

will be correlated to δ^+ . A speculative treatment involving both effects, that is, correlating fluidity elevation, with values of $\delta^+ - \delta\lambda_s^+$, is shown in Fig. 8, but the present level of accuracy is such that further measurements of relaxation wave-length are necessary before this picture of viscosity can be regarded as fully justified by relaxation-time measurements.

The variation of depression of relaxation wave-length with temperature is shown in Fig. 6, in which the percentage depression by 0.66*M* NaCl is plotted against temperature. The effect of the ions is greater at low temperatures than at high, as can be seen from the following picture; the low values of the relaxation wave-length of water at low temperatures indicate that the boundaries at which re-orientation takes place are much more rare; yet the effect of the ions

in introducing new boundaries is of the same order as at higher temperatures, since the size and number of the hydration sheaths is of the same order; therefore, the introduction of the ions into the water will have a proportionately greater effect on the frequency of occurrence of the boundary, and so on the relaxation wave-length.

Conclusion

We therefore find that it is possible to give a reasonable qualitative explanation of our results on depression of dielectric constant and relaxation time on the basis of the model outlined above. In Part II of this paper we shall consider the depression of dielectric constant from the standpoint of dielectric theory, and the bearing of these results on electrolyte theory.

PART II

D. M. RITSON AND J. B. HASTED

In Part II of this paper the theory of dielectric saturation in the neighborhood of an ion is shown to give values for the depression of dielectric constant of concentrated ionic solutions of the same order as those found experimentally in Part I. Modern theories explaining the deviations of concentrated solutions from the Debye-Hückel theory are considered, and semi-quantitative estimations made of the various contributing factors—*viz.*: Dielectric constant variation, Bjerrum-type association, co-volume correction, and structure-breaking effect.

Theoretical Treatment of the Dielectric Constant Depression

It was predicted by Sack¹ that the dielectric constant of an aqueous ionic solution would be considerably lower than that of water. On the basis of the Debye theory of dielectrics he calculated a depression which was about a hundred times greater than the experimental values recorded in Table III, Part I of this paper.

In general we should expect that any theory based on the assumption that an ion is surrounded by a continuous dielectric medium of macroscopic dielectric constant, should give a lower limit to the actual dielectric saturation in the neighborhood of an ion; short-range order round the ion, which is ignored when we treat the surrounding medium as continuous, must further increase the saturation.

The apparent discrepancy between calculation and experiment arises from the use of a Debye model for the dielectric constant, which assumes an improbably small value for the dipole moment in water. We have attempted in this paper to bring Sack's original conception of the electric field of an ion effectively saturating the surrounding dielectric into line with more recent views on the structure of water.

There are two fundamental difficulties encountered in any such treatment. There is still considerable uncertainty as to the correct model for the dielectric constant of water, and there is no method of treating the short-range order round the ion. One is therefore limited to obtaining a qualitative estimate of the effect, and showing that this estimate is in agreement with experiment.

We consider first a point charge placed in a continuous dielectric medium. For this dielectric medium we take two models.

¹ H. Sack, *Phys. Zeits.* 27, 206 (1926); *ibid.* 28, 199 (1927).

Model 1 is a dielectric obeying Onsager's equation exactly. At 25°C we can approximate to water by taking values for the dipole moment μ_0 of 1.88 Debye units and refractive index $n^2=4.13$, leading to a dielectric constant of 78.7. There is one grave drawback to this model, namely, that it gives an effective moment (the dipole moment plus the dipole moment induced by the reaction field) of 3.77 Debye units, which is rather improbable.

We obtain for the dielectric constant ϵ

$$\epsilon E = \frac{4\pi}{V} \frac{(n^2+2)(2\epsilon+1)}{3(2\epsilon+n^2)} L \left[\frac{\epsilon(n^2+2)}{(2\epsilon+n^2)} \frac{\mu_0^2}{kT} E \right] + \frac{3\epsilon(n^2-1)E}{2\epsilon+n^2},$$

where L is the Langevin function, and all the other symbols have their usual significance.

We can make the approximation

$$\epsilon E = \frac{4\pi}{V} \frac{(n^2+2)}{3} L \left(\frac{(n^2+2)}{2} \frac{\mu_0^2}{kT} E \right) + \frac{3}{2} (n^2-1) E,$$

and on substituting the values given above we find at 25°C that

$$\epsilon E = 5.69E + 1.58 \cdot 10^6 L(1.39 \cdot 10^{-4} E).$$

In addition to this treatment, which is open to the criticism given above, we have taken a second model. This is an empirical modification of Kirkwood's² formula for small fields, so that it applies to large fields. Kirkwood's formula gives

$$\epsilon E = (4\pi/V) [\alpha E + (u\bar{u}/3kT) E],$$

where u is the effective dipole moment, and \bar{u} is the moment plus the moment induced in the surroundings.

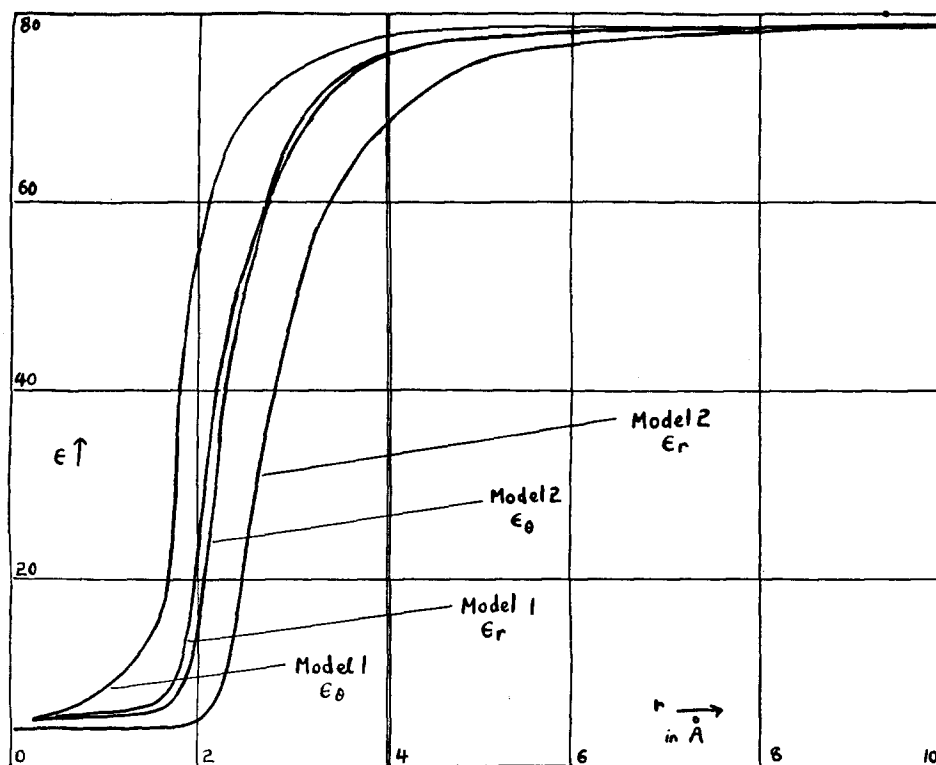


FIG. 1. Plot of dielectric constants ϵ_r , ϵ_θ against distance r in angstroms from an ion.

² J. Kirkwood, J. Chem. Phys. 4, 592 (1936).

We have made the empirical modification

$$\epsilon E = (4\pi/V)\alpha E + uL(u/kT)E.$$

Putting $u = 2.45$ Debye units, which is Verwey's³ estimate of its magnitude, we obtain

$$\epsilon E = 4E + 1.03 \cdot 10^6 L(2.18 \cdot 10^{-4} E).$$

Although this second formula is certainly not entirely correct, our main interest is to show that our value for the saturation effect is not markedly dependent on the model we adopt.

Now consider the point charge as the center of coordinates r_1 and θ . We know that the field E_r round the ion must obey the equation

$$\text{div}(E + 4\pi P) = 0,$$

or

$$E + 4\pi P = e/r^2. \quad (1)$$

We shall write this equation in the form

$$AE_r + BL(CE_r) = e^2/r^2, \quad (1a)$$

where for, model 1,

$$A = 5.69, \quad B = 1.58 \times 10^6, \quad C = 2.18 \times 10^{-4},$$

and for model 2,

$$A = 4, \quad B = 1.03 \times 10^6, \quad C = 2.18 \times 10^{-4}.$$

We now define two dielectric constants

$$\epsilon_r = \partial P / \partial E_r, \quad \epsilon_\theta = \partial P / \partial E_\theta.$$

The significance of these quantities lies in the fact that they represent the effective dielectric constants when a small additional field is applied.

From Eq. 1(a) we see that

$$\epsilon_r = A + BC[dL(CE_r)/d(CE_r)], \quad (3a)$$

and

$$\epsilon_\theta = A + B[L(CE_r)/E_r]. \quad (3b)$$

These are the effective dielectric constants when a small additional field is applied either along or perpendicularly to the radius vector.

We have plotted in Fig. 1 values of ϵ_r and ϵ_θ against those calculated from Eqs. 3(a), 3(b), and (1).

When $r > 4A$, the values of ϵ do not differ appreciably from ϵ_s and can be expressed accurately by the approximations

$$\epsilon_r = \epsilon_s[1 - (3b/r^4)], \quad (4a)$$

$$\epsilon_\theta = \epsilon_s[1 - (b/r^4)], \quad (4b)$$

³ E. J. W. Verwey, Rec. Trav. Chim. 60, 127 (1941).

where in model 1, $b = 57.8 \times 10^{-32}$, and in 2, $b = 163 \times 10^{-32}$. These results are obtained by expanding $L(x)$ as $(x/3) - (x^3/45) + \dots$, and neglecting terms above the second.

Returning now to the original problem of the effect of an ion of finite size on the surrounding dielectric, it is apparent that in the region below $4A$, which is of the order of the radius of the first hydration sheath, the representation of the dielectric as continuous will not be a valid approximation. Therefore, for simplicity, we have made the following assumptions:

(a) That we can represent a positive ion as surrounded by a completely saturated first shell, and beyond that by continuous dielectric of dielectric constant given by (4a) and (4b). We assume that a saturated shell has a radius $r_+ + 2r_\omega$ where r_+ is the radius of the ion, r_ω that of the water.

(b) That the negative ion can be represented by a completely unsaturated first shell of dielectric constant ϵ_s , surrounded outside a radius of $r_- + 2r_\omega$ by continuous dielectric.

We shall now consider the application of a small field to the region round a point charge. We can represent the applied field E by a potential ψ . We shall only briefly indicate the argument which can be found in full in Debye's *Polar Molecules*, Chapter VI. As $r \rightarrow \infty$ we know that ψ must be of the form

$$\psi = -[E_r + (\mu/r^2)] \cos \theta. \quad (5)$$

We assume that

$$\begin{aligned} \psi &= -[Ef(r) + (\mu/r^2)g(r)] \cos \theta \\ &= E \cdot R(r) \cos \theta, \end{aligned}$$

for

$$r > r_\pm + 2r_\omega.$$

Now it is a fundamental equation of electromagnetic theory that

$$\text{div} \epsilon \cdot \text{grad} \psi = 0.$$

This gives, on rearrangement,

$$\frac{d}{dr} \left[\epsilon_r r^2 \frac{dR(r)}{dr} \right] - 2\epsilon_\theta R(r) = 0. \quad (6)$$

The solution of this equation is

$$f(r) = -r[1 - (2b/r^4)], \quad (6a)$$

$$g(r) = (1/r^2)[1 + (b/r^4)], \quad (6b)$$

if

$$r < r_{\pm} + 2r_{\omega}.$$

The solution must be of the form $\psi = Ar \cos \theta$, where A is a constant, as the dielectric constant is now independent of r and θ .

Putting in the boundary condition that ψ is everywhere continuous and that $\epsilon_r(d\psi/dr)$ is also continuous, we obtain

$$\mu = (\epsilon_{\theta} - 1)/(2\epsilon_{\theta} + 1)(r_{\pm} + 2r_{\omega})^3.$$

The total polarization P_r outside $r = r_{\pm} + 2r_{\omega}$ is given by

$$P_r = \frac{1}{4\pi} \int \left(\epsilon_r \frac{d\psi}{dr} + \epsilon_{\theta} \frac{d\psi}{d\theta} \right) dT,$$

where dT is any volume element. Therefore,

$$P_r = \frac{1}{2} \int_{r_{\pm} + 2r_{\omega}}^{\infty} \int_0^{\pi} r^2 \left(\epsilon_r \frac{d\psi}{dr} + \epsilon_{\theta} \frac{d\psi}{d\theta} \right) \sin \theta \cdot dr d\theta. \quad (7)$$

We require to obtain the decrease in polarization ΔP of the medium caused by the presence of the central ion. If we write P_0 for the polarization of the medium if no ion were present, P_s for the polarization in the first sheath round the ion, we obtain

$$\Delta P_+ = P_0 - P_{r+} - P_{s+}. \quad (8)$$

The dielectric constant ϵ_s for a normal solution is, therefore, $\epsilon_s = \epsilon_{\omega} + 2\bar{\delta}c$, where $\bar{\delta} = (\delta^+ + \delta^-/2)$ and

$$\delta^+ = N\Delta P_+ \cdot 4\pi \cdot 10^{-3}. \quad (9)$$

Substituting the values we have obtained for ϵ_r , ϵ_{θ} , and ψ , and ignoring terms of the order of $(b/r^4)^2$, we find

$$\Delta P = [-Db/4(r + 2r_{\omega})^4] - P_s. \quad (10)$$

It also follows from our initial assumptions that for negative ions $P_s = 0$, for positive ions $P_s = r^3 \epsilon_{\omega}/3$. This leads directly to the following values for δ^+ and δ^- for ions of radii $r_+ = r_- = 1\text{\AA}$, and r_{ω} equal to 1.36\AA :

Model 1, $\delta^+ = -11.5$, $\delta^- = -1.5$, and $\bar{\delta} = -6.5$.
Model 2, $\delta^+ = -13$, $\delta^- = -3$, and $\bar{\delta} = -8$.

The calculated values of $\bar{\delta}$ are thus of the right order of magnitude. The main contribution to the dielectric lowering comes almost entirely from the first sheath. The large increases for

Li^+ , H^+ , and OH^- ions are undoubtedly due to the extent of short-range order round the ions. For divalent and trivalent ions the above calculation is unsatisfactory, as the short-range order probably extends further than the first shell.

Theory of Concentrated Solutions of Strong Electrolytes

In 1926 Hückel⁴ suggested that the deviations from the Debye-Hückel theory of strong electrolytes at moderate concentrations could be explained by supposing that the dielectric constant was a function of the concentration. He suggested the law for the dielectric constant D of a solution of molecular concentration c , $D = D_0 - 2\bar{\delta}_c$ where D_0 is the dielectric constant of the solvent; he showed that this led to a formula for the activity of an electrolyte of the following type:

$$\log_{10} f = D + Bc, \quad (11)$$

where D is the usual Debye-Hückel term of the type $[0.4343z_+z_-e^2\kappa/2D_0kT(1+\kappa a)]$, where

$$\kappa = \left[\frac{4\pi ne^2(\nu_+z_+^2 + \nu_-z_-^2)}{D_0kT} \right]^{\frac{1}{2}}, \quad (11a)$$

n is the number of molecules of salt per cc, ν_+ and ν_- the numbers of positive and negative ions of valencies z_+ and z_- , corresponding to one molecule of salt, e the electronic charge in e.s.u., k the Boltzmann constant, and a the ionic radius measured in angstrom units.

Hückel's term Bc , due to the variation of the dielectric constant, is given by the relation:

$$Bc = \frac{0.4343e^2}{nD_0^2kT} \left(\frac{\nu_+\delta^+}{a^+} + \frac{\nu_-\delta^-}{a^-} \right). \quad (11b)$$

Now the type of relation $\log_{10} f = D + Bc$ is a well-known explanation of the variation of activity with concentration, found experimentally. Values of $B_{\text{experimental}}$ for a large number of salts are given by Harned and Owen.⁵ Using $\bar{\delta}$ and a as adjustable parameters, Hückel obtained remarkably good agreement with these values of $B_{\text{experimental}}$. We were interested to find

⁴ E. Hückel, *Phys. Zeits.* 26, 93 (1925).

⁵ Harned and Owen, *The Physical Chemistry of Electrolytic Solutions* (Reinhold Publishing Corporation, New York, 1943).

that our experimental values of δ^+ and δ^- , given in Part I of this paper, were of the same order of magnitude and showed the same qualitative trends as those used by Hückel, although quantitatively the agreement is not good.

Later authors rejected the view that the deviations were due to changing dielectric constant, and attributed them to other causes. It is likely that a number of different factors contribute, each one involving a term Bc ; we shall consider each in turn and attempt to assess semiquantitatively its contribution to B . They are as follows:

1. Van der Waals co-volume correction.
2. Correction due to the breaking up of the water structure by the ions.
3. Correction due to the type of ionic association envisaged by Bjerrum.
4. Varying dielectric constant correction, outlined above.

Co-Volume Effect

Since the distance of closest approach of two ions is fairly large, it would seem likely that a van der Waals co-volume correction must be made to the activity. Van Rysselberghe and Eisenberg⁶ have calculated values of B on this basis, using Ursell's treatment. We have investigated whether it is legitimate to apply such a correction by assuming a highly simplified lattice model.

If we consider the distribution of n molecules on N lattice points, such that around each molecule the neighboring positions must be unoccupied, we find that the number of distinguishable configurations Ω is given by

$$\Omega = \left(\frac{(N-n)! \cdot (N-n)!}{(N-2n)! N!} \right)^x \cdot \frac{N!}{(N-n)! n!}, \quad \text{for } N \gg n. \quad (12)$$

This result is obtained by using a very general method of enumerating lattice configurations, which we shall describe elsewhere. The equation for Ω follows from the fact that we have x axes along which each center must be separated by at least two lattice points. The probability that any random configuration satisfies this condition

along any axis is given by the expression in the brackets. The power x gives the simultaneous probability that we can satisfy the condition along the axes simultaneously. $N!/(N-n)!n!$ represents the total number of random distinguishable configurations.

We now consider a model approximating to a number of solvated molecules B in a solvent A . A two-dimensional model is shown diagrammatically in Fig. 2. The B molecules and their solvation sheath occupy one unit cell of the lattice. This type of model is chosen as being similar to water, where the coordinated sheath of water molecules fits into the general lattice structure. For simplicity we consider a cubic lattice.

Let there be N_A solvent molecules A , and N_B solute molecules B . $8N_B$ of the solvent molecules A are held by the N_B solute molecules. There are 13 axes along which the B 's must be separated by at least one cell. Four axes are shown in the two-dimensional figure. The number of positions that it is possible for B molecules to occupy is N_A . Making the assumption that the solution is "regular," i.e., that the potential and molecular energies are not altered for the different configurations, we can write down the configurational partition function with the aid of Eq. (12) as

$$\Omega = \left(\frac{(N_A - N_B)! (N_A - N_B)!}{(N_A - 2N_B)! N_A!} \right)^{13} \cdot \frac{N_A}{(N_A - N_B)! N_B!} \quad (13)$$

The "partial potentials" are given by

$$\mu_A = \mu_{0A} - kT(\partial \ln \Omega / \partial N_A), \quad (14a)$$

$$\mu_B = \mu_{0B} - kT(\partial \ln \Omega / \partial N_B). \quad (14b)$$

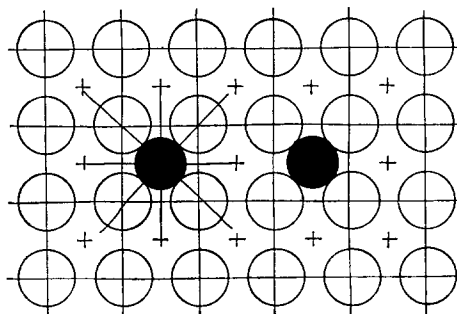


FIG. 2. Two-dimensional cubic lattice of (unfilled) solvent molecules A , showing closest position of approach of two (blackened) solute molecules B .

⁶ P. van Rysselberghe and S. Eisenberg, J. Am. Chem. Soc. 61, 3030 (1939).

If we consider the case for $N_A \gg N_B$ so that we can ignore term in $(N_B/N_A)^2$ we find that

$$\mu_A \approx \mu_{0A} + kT \ln(N_A/N_A + N_B), \quad (15a)$$

$$\mu_B \approx \mu_{0B} + kT \ln(N_B/N_A + N_B) \times [1 + 28(N_B/N_A)]. \quad (15b)$$

If we had assumed van der Waal's law we should have written the equation as

$$\mu_A \approx \mu_{0A} + kT \ln(N_A/N_A + N_B), \quad (16a)$$

$$\mu_B \approx \mu_{0B} + kT \ln(N_B/N_A + N_B) \times [1 + 32(N_B/N_A)]. \quad (16b)$$

We see, therefore, that in the particular case we have considered above, the expressions reduce to a form very near to that of van der Waals law; it follows that the treatment of ions in solution may be made along similar lines to that of molecules in a gas, and it is likely that the application of Ursell's method may be made with success. Harned and Owen's⁵ revision of van Rysselberghe and Eisenberg's⁶ treatment gives a value of $B = 2.2063 \times 10^{-3} \times a^3$ for a single 1:1 electrolyte, or $\frac{3}{2} \times 2.2063 \times 10^{-3} \times a^3$ for a single 2:2 electrolyte, where a represents the distance of closest approach of two ions measured in angstrom units. For consistency we have used the empirical values of a which are obtained by fitting the experimental activity coefficients to Eq. (11). These values are given by Harned and Owen⁵ and are greater than the crystallographic radii.

Structure-Breaking Effect

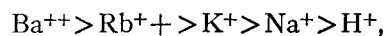
The interactions of the ion with the water lattice is also an important contributing factor; it has been brought out clearly in a recent paper of Frank and Evans.⁷ The authors point out that for "structure-breaking" salts the water lattice becomes increasingly random with increasing concentration. Accordingly, dilution should be accompanied by a decrease of entropy. The change of entropy of dilution with concentration is a measure of the structure-breaking effect of an ion, and values obtained by this method show correlation with those obtained from Raman and infra-red absorption spectra, viscosity data, etc. There is, in addition, some sort of correlation

⁷ H. S. Frank and M. Evans, *J. Chem. Phys.* **13**, 479 (1945).

with the shift of relaxation time of the water by the ion, experimental values of which were given in Part I of the present paper. When the relaxation-time measurements are considered in conjunction with the previous study by the authors of the re-orientation process in water and heavy water, it appears likely that relaxation-time shift can be regarded as a fairly reliable measure of structure-breaking effect. As was demonstrated by Falkenhagen,⁸ it is impossible to obtain the correct heats of dilution from Hückel's theory, and it would seem equally difficult for modern theories to account fully for the activity coefficient deviations without taking lattice effects into account. It is, however, the free energy and not the entropy change with which we are concerned, and this is, of course, smaller. We found in the first part of this paper that the effect was much greater at low temperatures than at high, and this will lead us to predict that activity deviations are likely to be much greater near the freezing point than at high temperatures.

However, it is not yet possible to calculate even approximately the contribution made by this effect to the value of B , and we have, therefore, made an estimate simply by subtracting the other contributions from the experimental value.

It will be seen from Table III where the contributions to B are tabulated, that the structure-breaking contributions so obtained are in accordance with the usual comparisons between various ions, i.e.,



and are, moreover, fairly small.

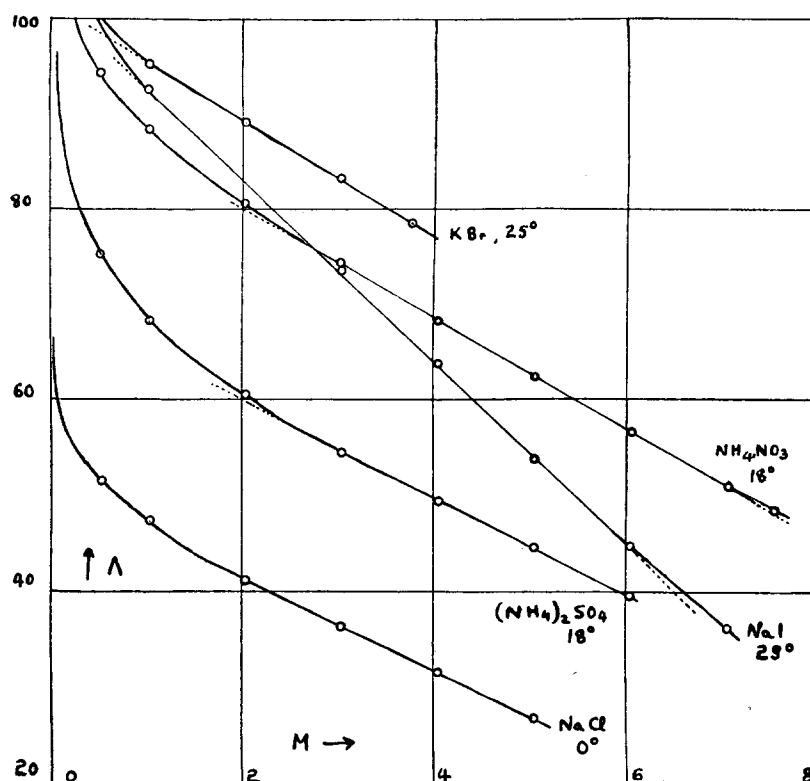
Bjerrum-Type of Ionic Association

Bjerrum⁹ attempted to account for anomalies at high concentrations by assuming that ionic association occurs. He calculates the electrostatic and other forces acting between two ions, and equates the resulting potential energy with mean kinetic energy at various inter-ionic distances. Within a certain distance the ions will "associate." The association constant $(1-\alpha)$ depends on concentration in a complicated, but

⁸ H. Falkenhagen, *Electrolytes* (Clarendon Press, Oxford, England, 1934), p. 282.

⁹ N. Bjerrum, *D. Kgl. Dansk. Vid. Selsk. Medd.* **7**, No. 9 (1926); *Ergeb. der exakt. Naturwiss.* **6**, 125 (1926).

FIG. 3. Typical equivalent conductivities $\Lambda \times 10^{-8}$ mho/ 10^{-3} gmole plotted against concentration M . Data from I.C.T. Values of Λ for KBr at 25° , depressed by 20 divisions for reasons of space.



approximately linear, manner, but may be shown to be of the order of 0.14 in molar solution of 1:1 electrolyte of ionic radii sum equal to 2.82Å. For higher concentrations, smaller ions, ions of higher valency, and solvents of low dielectric constant the association will be higher.

It is unfortunately impossible to accept the calculated values of $(1-\alpha)$ on Bjerrum's theory, or to calculate back from the heats of dilution, since a number of approximations are made which are not permissible in more concentrated solutions; moreover, at distances of less than 4Å from an ion the dielectric constant is a rapidly varying quantity, as is shown above. However, it appears very likely that some sort of association of this type occurs in concentrated solutions because there certainly are strong forces acting between ions at very short distances.

The only method of estimating Bjerrum's association that remains is by treatment of the conductivity data. Let us consider in detail the simplest case, a 1:1 strong electrolyte at 25°C , in which there can be little question of incomplete dissociation in the usual sense of the term, but for which accurate conductivity data over a

wide concentration range exist. Such a case is potassium bromide, for which there are the measurements of Jones and Bickford.¹⁰ Between concentrations of 1.5–6*N* many such salts, including the present case, show a linear dependence of equivalent conductivity on concentration. This is illustrated for a number of cases in Fig. 3, for which the data have been taken from the International Critical Tables. It is true that many salts show a non-linear dependence in such concentrated solution, for instance, salts of lithium. But, nevertheless, the dependence in a large number of the simplest cases is linear, and this fact must be explained. Now it is with solutions of these concentrations that we are concerned when investigating Bjerrum association, because the effect is more significant in this range. It is well known that for the conductivity of dilute solutions, many equations with satisfactory theoretical basis have been proposed (Onsager¹¹), but all explain the dependence on the square root of the concentration which is found

¹⁰ G. Jones and C. F. Bickford, J. Am. Chem. Soc. 56, 602 (1934).

¹¹ L. Onsager, Phys. Zeits. 28, 277 (1927).

TABLE I. Approximate percentage Bjerrum association $100(1-\alpha)$ calculated from conductivities of concentrated solutions.

| Electrolyte | Approximate percentage association estimated for normal solution | Temperature °C | Data |
|-------------------|--|----------------|---------------------|
| HCl | 11 | 18 | I.C.T. |
| NaCl | 10 | 0 | I.C.T. |
| NaCl | 10 | 18 | I.C.T. |
| KCl | 5 | 18 | I.C.T. |
| NaI | 9 | 25 | I.C.T. |
| KBr | 5 | 25 | Jones and Bickford* |
| KI | 5 | 18 | I.C.T. |
| RbCl | 4 | 18 | I.C.T. |
| CsCl | 4 | 18 | I.C.T. |
| BaCl ₂ | 12 | 25 | Jones and Dole** |

* See reference 10.

** See reference 12.

in dilute solution; modifications are made to Onsager's equation to explain deviations from this. It is very unlikely that such modifications will transform the dependence into a linear one in concentrated solution, by the addition of a term which counter-balances the non-linear dependence, nor is it likely that a viscosity correction will transform the relationship into a linear one; in other words, a single equation of the accepted type will not hold over the entire concentration range unless the Onsager term reduces to a constant value and a linear term, $-Kc$, is introduced at high concentrations only. The empirical equation of Jones and Dole¹² is an example of this type of behavior:

$$\Lambda = \Lambda_{\infty} - A\sqrt{c}/(1 + G\sqrt{c}) - Kc, \quad (17)$$

but in order to fit the dilute solution data, the constants of this equation are so chosen that it does not reduce to a linear equation until very high concentrations ($\sim 10N$) are reached. Although this equation is capable of explaining the experimental data over the widest concentration range, and is of a theoretically satisfactory form, the parameters are chosen entirely empirically, and a single equation of this type would not be capable of explaining both the dilute solution data and the linear dependence in concentrated solution. In particular, the values of K are such that it is difficult to find a theoretical explanation of them. It is necessary to find a theoretical

equation which holds in dilute solution and reduces to a constant term by the time a concentration of about $2N$ is reached; at greater concentrations, a new effect comes into play to explain the linear dependence. We shall assume that this effect is the Bjerrum association. Its linear dependence on concentration cannot be predicted theoretically, in fact, as we have seen above, the dependence on concentration is believed to be complicated, but only approximately linear. But in view of the criticisms of the theory given above, the original treatment is not unsatisfactory.

We have thus two equations involving the concentration on which the conductivity depends:

(1) An equation which we will call C , tending to a constant conductivity value at concentrations greater than $1.5M$. The form of this equation will be discussed later.

(2) A simple equation D , holding over the linear range; $\Lambda = \alpha\Lambda'$ where $1-\alpha$ is the degree of association and Λ' is the constant value to which equation C has tended. We can estimate the association approximately from the slope of the conductivity-concentration curve. The accuracy is limited by the following facts:

(1) It is not possible to obtain a good value for Λ' ; we have used what seems the most reasonable value, namely, that obtained by producing the linear section back to zero concentration.

(2) It is doubtful whether a viscosity correction should be applied and if so what form it should take. There seems to be insufficient justification for simply multiplying the conductivity by the macroscopic viscosity, as, for instance, Jones and Dole have done. We have omitted the viscosity correction entirely.

The approximate values of percentage association in normal solution estimated in this way for a number of electrolytes are given in Table I, to the nearest whole number. The qualitative dependence on ionic radius and valency are according to theory.

It remains to discuss the form of equation C . It is possible to explain the data below $0.02N$ on a theoretical basis, and at the same time obtain a relation which is capable of tending to a constant value. The equation

$$\Lambda = \Lambda_{\infty} - A\sqrt{c}/(1 + G\sqrt{c})$$

¹² G. Jones and M. Dole, J. Am. Chem. Soc. **52**, 2245 (1930).

which was first suggested by Lattey¹³ as an empirical relationship, and was used with the addition of a Kc term by Jones and Dole, has actually a theoretical basis provided the constants are chosen correctly. Kaneko¹⁴ suggested that the introduction of a factor of $1+\kappa a$ in the denominator would correct the Onsager theory for the finite size of the ion. Although this suggestion has not been given much consideration, and although the treatment has been criticized, it is apparent that this factor corresponds to the $1+\kappa a$ which appears in the denominator of the Debye-Hückel expression for the logarithm of the activity coefficient of a concentrated solution; it seems perhaps a plausible correction. For dilute solutions we have the equation (C'):

$$\Lambda = \Lambda_{\infty} - O\sqrt{c}/(1+\kappa a), \quad (C')$$

where $O\sqrt{c}$ is the theoretical Onsager term, a modification of the original Debye-Hückel expression.

This type of treatment is supported by our experimental results on Debye-Falkenhagen conductivity increase at high frequency. We found the increase in concentrated solutions to be much smaller than would be expected on the original theory. If the Debye-Hückel conductivity term is diminished by the factor $1+\kappa a$, this becomes intelligible, since it is only this term which is annulled at high frequencies. An independent term reducing the equivalent conductivity of concentrated solutions below its value at infinite dilution, the type of term we introduce as being due to Bjerrum association, would not be affected: so that the high frequency conductivity would not show such a large increase above the d.c. conductivity.

In the above equation for dilute solutions there are no empirical factors, but the equation will not hold except in dilute solutions, although its range is greater than that of the Onsager equation. The exact position for potassium

TABLE II. Experimental data of Jones and Bickford for KBr equivalent conductivity at 25°C compared with various equations.

| C | $\Lambda_{\text{obs.}}$ | $\Lambda_0(\text{Onsager})$ calculated back from obs. | $\Delta\text{Shedlovsky}$ | $\Delta\Delta\text{Shedlovsky}$ | $\Lambda_{\text{Jones and Dole}}$ | $\Delta\Lambda_{\text{Jones and Dole}}$ | $\Lambda_{\text{Present equation}}$ | $\Delta\Lambda_{\text{Present equation}}$ |
|---|-------------------------|---|---------------------------|---------------------------------|-----------------------------------|---|-------------------------------------|---|
| 0.00025 | 150.16 | 151.65 | 150.16 | 0.00 | 150.24 | -0.08 | 150.16 | 0.00 |
| .00036 | 149.87 | 151.66 | 149.88 | -.01 | 149.93 | -.06 | 149.89 | -.02 |
| .0005 | 149.55 | 151.66 | 149.57 | -.02 | 149.61 | -.06 | 149.57 | -.02 |
| .00075 | 149.12 | 151.70 | 149.12 | .00 | 149.13 | -.01 | 149.12 | .00 |
| .001 | 148.78 | 151.76 | 148.75 | .03 | 148.74 | .04 | 148.75 | .03 |
| .0016 | 148.02 | 151.79 | 148.02 | .00 | 147.98 | .04 | 148.02 | .00 |
| .002 | 147.64 | 151.86 | 147.62 | .02 | 147.56 | .08 | 147.61 | .03 |
| .005 | 145.47 | 152.14 | 145.46 | .01 | 145.36 | .11 | 145.44 | .03 |
| .01 | 143.15 | | 143.19 | -.04 | 143.11 | .04 | 143.12 | .03 |
| .02 | 140.26 | | 140.25 | .01 | 140.25 | .01 | 140.07 | .15 |
| .05 | 135.44 | | 135.36 | .08 | 135.51 | -.07 | 134.74 | .70 |
| .1 | 131.19 | | 131.19 | .00 | 131.27 | -.08 | | |
| .2 | 126.59 | | 127.61 | -1.02 | 126.62 | -.03 | | |
| .5 | 120.35 | | 127.33 | -6.98 | 120.23 | .12 | | |
| 1.0 | 115.46 | | | | 115.50 | -.04 | | |
| 2.0 | 109.37 | | | | 110.98 | -1.61 | | |
| 3.0 | 103.55 | | | | 108.39 | -4.84 | | |
| 3.75 | 98.70 | | | | 106.98 | -8.26 | | |
| <hr/> | | | | | | | | |
| Onsager | | $\Lambda_0 = (\Lambda + 59.790\sqrt{c})/(1 - 0.2274\sqrt{c})$ | | | | | | |
| Shedlovsky | | $\Lambda = 151.63 - 94.27\sqrt{c} + 100.96c(1 - 0.2274)\sqrt{c}$ | | | | | | |
| Jones and Dole | | $\Lambda = 151.84 - 103.77\sqrt{c}/(1 + 1.8953\sqrt{c}) - 0.492c$ | | | | | | |
| Present equation | | $\Lambda = 151.63 - 94.27\sqrt{c}/(1 + 1.08\sqrt{c})$ | | | | | | |
| Horizontal lines indicate limits beyond which equations do not fit the observed data. | | | | | | | | |

¹³ R. T. Lattey, *Phil. Mag.* **4**, 831 (1927).

¹⁴ S. Kaneko, *J. Chem. Soc. Japan* **56**, 793, 1320 (1935); *ibid.* **58**, 985 (1937).

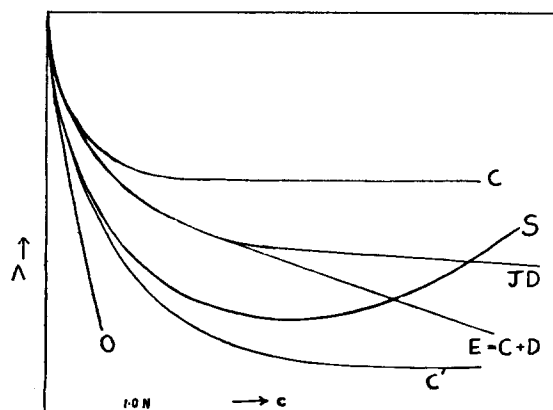


Fig. 4. Qualitative variation of equivalent conductivity with concentration according to various equations. E , experimental; C , C' , D , equations as in text; O , Onsager; S , Shedlovsky; JD , Jones and Dole.

bromide at 25° is given in Table II,* and the type of behavior of the Onsager, Shedlovsky,¹⁵ and present equations is shown qualitatively in Fig. 4. Our values of a are from the ionic radius in the crystal.

There is no doubt that the equation of Jones and Dole fits the data over the widest concentration range, but it fails at high concentration and is moreover entirely empirical. The viscosity correction which the authors apply widens the range, but will not reduce the equation to a linear variation; moreover, it is of doubtful theoretical validity. The Onsager equation deviates steadily at concentrations greater than 0.001*N*, but when modified, as suggested here, will hold to 0.02*N*, whereas the Shedlovsky equation with one empirical factor deviates from 0.1*N*. We have tried our modification of the Onsager equation on Shedlovsky's data for HCl, LiCl, NaCl, KCl,¹⁶ for which the agreement is satisfactory up to about 0.01*N*.

The form of the equation is therefore promising, but it cannot be regarded as even approximately correct in concentrated solution, since the assumptions underlying the Onsager term do not apply. We cannot therefore offer any detailed explanation of how the equation of type C is made up, and must be content simply to offer this as a possible method of treatment of the

linear variation of conductivity with concentration in concentrated solution.

It will be seen that this method of estimating association is somewhat similar to that used by Davies and his collaborators¹⁷ in more dilute solutions of incompletely dissociated salts. The cases considered here, would, however, be regarded as completely dissociated on Davies' treatment.

Our estimated values of $1 - \alpha$, given in Table I, are a direct contribution to the value of B in the activity equation. Although the contributions to B are estimated in other cases at 25°, there are no sufficient experimental data available at this temperature. In these cases, estimations of $(1 - \alpha)$ at 18°C have been used. As will be seen by comparing the values of NaCl at 0° and 18°, there is very small temperature dependence. But it appears that the amount of Bjerrum association is an extremely difficult term to estimate.

Variable Dielectric-Constant Correction

If we accept the fact that this correction is only a contribution to the value of B and need not be equated to the experimentally determined values of this constant, it is no longer necessary to treat a or δ^\pm as adjustable parameters in Hückel's theory. We have, therefore, calculated contributions to B on the basis of Eq. (11b), using Harned and Owen's⁵ experimental values of a and our experimental values of δ^\pm . The justification for using these values of a is that the dielectric constant will only vary outside the distance of closest approach of the ions.

Conclusions

In Table III are given the contributions to B from the various effects considered above; the contribution from the structure-breaking effect

TABLE III. Values of contribution to activity coefficient correction factor B .

| Electrolyte | B Experimental | B Bjerrum | B Hückel | B Co-volume | B Structure |
|-------------------|------------------|-------------|------------|---------------|---------------|
| HCl | +0.13 | -0.11 | +0.09 | +0.18 | -0.03 |
| NaCl | +0.04 | -0.10 | +0.05 | +0.16 | -0.07 |
| KCl | +0.02 | -0.05 | +0.05 | +0.09 | -0.07 |
| RbCl | +0.02 | -0.04 | +0.06 | +0.07 | -0.08 |
| BaCl ₂ | +0.03 | -0.12 | +0.11 | +0.18 | -0.14 |

$B_{\text{experimental}} = B_{\text{Bjerrum}} + B_{\text{Hückel}} + B_{\text{co-volume}} + B_{\text{structure}}$.

* The calculations are taken from the paper of Jones and Bickford.

¹⁵ T. Shedlovsky, J. Am. Chem. Soc. **54**, 1405 (1932).

¹⁶ T. Shedlovsky, J. Am. Chem. Soc. **54**, 1411 (1932).

¹⁷ C. W. Davies, Trans. Faraday Soc. **23**, 351 (1927).

is not calculated theoretically, but estimated by subtracting the other contributions from the experimental value of B . It should be possible eventually to correlate the values estimated in this way with data obtained by other methods, although only entropies, and not free energy data are at present available. As has been mentioned above, the structure-breaking contributions are qualitatively correct for different ions, i.e.,



This order would be more strongly accentuated if the crystallographic radii, with an allowance for the first hydration sheath, had been used instead of Harned and Owen's empirical values in calculating the various contributions.

Unfortunately the Bjerrum association for lithium cannot be easily estimated, as the conductivity curve is not linear with concentration over a wide range. It is clear that considerable progress must be made in study of the various effects before a quantitative verification of the behavior of activity coefficients of concentrated solutions can be made. Our table is extremely tentative and little weight should be attached to the numerical values.

Many of the effects described would be capable of direct experimental verification.

Accurate measurements of the Falkenhagen effect over a concentration range 0–1*N* and over a frequency range would be capable of showing whether the high frequency conductivity is a linear function of concentration, and, hence, whether Bjerrum association can be evaluated

from conductivity data, as has been done in this paper. Further experimental work on this problem is in the course of preparation.

The importance of structure-breaking effects of the ions could be evaluated by measuring activities and heats of dilution at low temperatures where this effect should be very marked, and at high temperatures when it should be of much less importance. Further comparison of the dilution of salts with those of rare gases, to explain the anomalies mentioned by Frank, are also indicated.

Significant data could be obtained by carefully selected experiments and analyses of the existing data on mixtures of electrolytes where the co-volume effect and dielectric effect of the salts present would probably be the determining factors.

It appears that future progress in electrolyte theory of concentrated solutions must be in an experimental evaluation of the various factors involved and by a vigorous theoretical attack on the basic problems of solute-solvent interaction.

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