The Dispersion of Electrical Conductance and Dielectric Constant in Dilute Strong Electrolyte Solutions [1]

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Introduction

The mechanism of electrolytic conduction has been disclosed to us gradually. To make use of a recent survey of the situation by Hartley [2], there have been, since the electrochemical discoveries of Faraday, three main phases in the development of the problem — firstly, the discovery of the general relationships between the conductivity of solutions and the concentration and nature of the dissolved substances; secondly, the recognition of the relation of these facts to the general theories of chemistry; and, lastly, the quantitative explanation of the properties of electrolytes in mathematical theory. We propose to give here a preliminary and much abbreviated account of an extended series of experiments, begun in the fall of 1928, which originated in our desire to contribute toward seeing whether or not the purely physical and mathematical interionic attraction theory does adequately explain and describe the dispersion behaviour of an ideal electrolyte.

Both the reversible and irreversible processes in an electrolytic solution are affected by the interionic forces. Thus, the limiting law for the variation of ordinary molar conductance, Λ, with the molar concentration, c, is of the form,

$$\Lambda = \Lambda_0 - \alpha \sqrt{c}$$

in which the term $-\alpha \sqrt{c}$ represents the influence of the interionic forces [3]. These forces cause deviations from random distribution in

[1] Preliminary contribution. A detailed account of the work is being submitted to the Journal of the American Chemical Society.

[2] Hartley, Presidential Address, Centenary (1931) Meeting of the B. A. A. S. Heffer, Cambridge 1932.

[3] Debye a. Hückel, Physik. Z. **24**, 305 (1923); Onsager, ibid. **27**, 388 (1926); **28**, 277 (1927).

the solution, as atmospheres of ionic charge form about each ion. For this reason, the ions will influence each other's motion. In general there are two different effects to be considered, the direct transfer of electrical forces between the ions, described as the electrical force of relaxation, and a hydrodynamic effect, known in the literature as the electrophoretic force. It is a consequence of the interionic attraction that at high frequencies the effect of this electrical force of relaxation is reduced, thus the theory [4] requires an increased conductance when the frequency used to measure it is sufficiently increased. It also requires that the dielectric constant excess of the solution over that of the solvent will decrease under these conditions, approaching the value zero at infinite frequency.

If a unidirectional or low frequency current is passed through a solution, the atmosphere of ionic charge builds up a dissymmetry in the direction of the current and the mobility of the ions is decreased. This dissymmetry is not formed in zero time, neither will the symmetry be restored in the moment the field is cut off. Rather, a finite period, known as the time of relaxation, is required. Now, if the frequency of the applied field is increased to the extent that the time necessary for one vibration becomes comparable with the time of relaxation, the dissymmetry of the atmosphere will not be able to complete its formation. As the frequency is made higher and higher the degree of dissymmetry is continually decreased and a smaller diminution of ionic mobility results. The theory requires this effect to be of such magnitude at frequencies between 10^6 and 10^8 periods per second that it can be detected and measured by refined observations.

The following qualitative statements will make it apparent why a change of dielectric constant with applied frequency is to be expected in electrolyte solutions. Because of the time required to form the atmosphere of ionic charge there will be, at the higher frequencies, a noticeable phase displacement between the direction of the periodically changing electrical impulse on an ion and the velocity of the ion, giving rise to a complex current. Thus, in addition to the current component in phase with the applied field which determines the conductance, there is a displacement current. The latter is recorded expe-

[4] Debye a. Falkenhagen, Physik. Z. **29**, 121, 401 (1928).

rimentally as an effect, actually an increase, in the dielectric constant. Since this phase displacement is a function of the applied frequency, not only the conductance, but also the dielectric constant excess will be variable with frequency. To present the situation in a more descriptive way, let us suppose a given positive ion to be displaced in zero time to a short distance from its position at the center of an atmosphere. Because of its finite time of relaxation the ionic atmosphere cannot go at once with the ion, but it is centered about the original position of the positive ion. However, the displaced ion and atmosphere are bound by a quasi-elastic force to give an interionic coupling, and the system thus formed (displaced ion—atmosphere) contributes to the dielectric constant of the solution since it has the properties of an electrical dipole.

Until a few years ago, at least, it was rather widely believed that in dilute electrolyte solutions the dielectric constant of the system diminished with increasing ionic concentration, according to an equation of the form,

$$\varepsilon = \varepsilon_0 (1 - Ac),$$

where A is a constant characteristic for the salt and the solvent. The decrease in dielectric constant was attributed to the saturation of the molecules of the liquid by the intense electrical fields arising from the dissolved ions. But, more recently, improvements in technique have been such that more reliance can be placed upon the results, and it appears that the observed dielectric constant change, now found to be an increase, can be accounted for largely on the basis of the couplings due to interionic electrical forces. Thus the electrical saturation effects must be of much smaller magnitude than Sack[5] calculated.

In this work attention is focussed upon the frequency variation of both electrical conductance and dielectric constant for strong electrolytes of several valence types in extremely dilute aqueous solution. The results of the experiments are found to be in satisfactory quantitative agreement with the requirements of the dispersion theory, and they indicate that the electrical saturation effects, mentioned above, must be small indeed.

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[5] Sack, Physik. Z. **28,** 199 (1927).

Resumé of Pertinent Theory

To present and describe the results of the experimental work it will be convenient to write down, without deduction, the final theoretical equations of Debye and Falkenhagen which describe the dispersion effects we have sought to find. We have seen that the ionic atmosphere affects the ordinary mobility of an ion in two ways. First, as the ion travels through the medium this atmosphere must be always forming about the ion and dying away behind it. Since this formation of the atmosphere cannot take place in zero time the ion will be continually moving away from the atmosphere of unlike sign and be retarded in its motion. In addition to this electrical force of relaxation, there exists the hydrodynamic force which also acts to decrease the mobility of the ion. Since positive and negative ions are moving in opposite directions through the medium, and in so doing impart some of their momentum to solvent molecules, the motion of each ion will be opposed by a greater frictional force than if it were moving through the stationary solvent. The magnitudes of these forces, both of which turn out to be proportional to the square root of the concentration, can be expressed in conductance units. Thus, the molar conductance of an electrolyte solution of finite concentration, Λ, may be expressed in terms of the molar conductance at infinite dilution, Λ_0, and the two interionic forces in the following manner,

$$\Lambda = \Lambda_0 - \Lambda_{I_0} - \Lambda_{II}.$$

Here Λ_{I_0} expresses the maximum effect of the electrical force of relaxation, in conductance units, and Λ_{II} measures the electrophoretic force, also in conductance units.

Now, if an alternating field is applied, rather than a static one, each ion will acquire a periodic motion, and if the frequency of the field becomes high enough, that is, with period of oscillation approaching the time required for the formation of the atmosphere of ionic charge, the dissymmetry of the atmosphere necessary for the existence of the electrical force of relaxation will form to a lesser extent, and an increased conductance will result. The mobility of the central ion will increase until such time as the frequency has been made so high that during the time of a single oscillation the atmosphere cannot

be deformed by the field at all. Under these conditions the not electrostatic interaction between an ion and its atmosphere will be zero, and the conductance term, Λ_I becomes vanishingly small. Nothing that has been said leads to the expectation of any change in the magnitude of the electrophoretic force, Λ_{II} and, as a matter of fact, in treating the problem mathematically the assumption is made that this force is independent of the frequency of the applied field. Thus, if one plots the molar conductance as a function of frequency, Λ varies between $\Lambda = \Lambda_0 - \Lambda_{I_0} - \Lambda_{II}$ and $\Delta = \Lambda_0 - \Lambda_{II}$ in the frequency region where the product $\omega\Theta$ is of the order of magnitude one. Here ω is the frequency of the applied field and Θ is the time of relaxation.

The expression for the electrical force of relaxation as a function of frequency, Λ_{I_ω}, is,

$$\Lambda_{I_\omega} = \frac{|e_1 e_2|}{3D\,kT} \cdot k\Lambda_0 \bar{x},$$

where

$$x = \frac{\sqrt{q}\left(\sqrt{1 - i\omega\Theta} - \frac{1}{\sqrt{q}}\right)}{1 + i\omega\Theta - \frac{1}{q}}$$

and

$$\bar{x} = \frac{\sqrt{q}}{\left(1 - \frac{1}{q}\right)^2 + \omega^2\Theta^2}\left[\left(1 - \frac{1}{q}\right)\left(R - \frac{1}{\sqrt{q}}\right) + \omega\Theta\bar{Q}\right] =$$

$$= \text{Real Part of } x.$$

In the expression for $\bar{x}$

$$\bar{R} = \frac{1}{\sqrt{2}}\sqrt{\sqrt{1 + \omega^2\Theta^2} + 1},$$

$$\bar{Q} = \frac{1}{\sqrt{2}}\sqrt{\sqrt{1 + \omega^2\Theta^2} - 1}.$$

When $\omega = 0$, $\bar{x}$ simplifies to

$$\bar{x} = \frac{q}{1 + \sqrt{q}}.$$

In the above formulae,

$$\Theta = \Theta(c,\ D,\ \Lambda_0),$$

and

$$q = q(z_1,\ z_2,\ L_1,\ L_2).$$

The quantities c, D, z and L refer to molar concentration, dielectric constant of solvent, and valence and mobility of the ions, respectively. The subscripts refer to the kinds of ions. Thus, the theory enables one to predict the effect of ion concentration, solvent, temperature, and electrolyte upon the dispersion of conductance. Explicitly,

$$\Theta = \frac{z_1^2 z_2^2}{z_2^2 L_1 + z_1^2 L_2} \cdot \frac{15{,}3 \cdot 10^{-8}}{kTq\varkappa^2},$$

where

$$\varkappa^2 = \frac{4\pi e^2}{DkT} \sum_i n_i z_i^2$$

and

$$q = \frac{(L_1 z_2 + L_2 z_1)\, z_1 z_2}{(z_1 + z_2)(L_1 z_2^2 + L_2 z_1^2)}.$$

In the discussion of the data for the frequency dependence of conductance of the electrolyte solutions it is convenient to express the decrease in the effect of the electrical force of relaxation by the ratio, $\Lambda_{l_\omega}/\Lambda_{l_0}$.

The theoretical equation for the dielectric constant excess is,

$$D_\omega - D = \frac{4\pi}{\omega} \frac{|e_1 e_2|}{3DkT} \cdot \varkappa \cdot \sum \nu_i e_i \omega \overline{\overline{\gamma}},$$

where

$$\overline{\overline{\gamma}} = \frac{\sqrt{q}}{\left[\left(1 - \frac{1}{q}\right)^2 + \omega^2\Theta^2\right]} \left[\overline{Q}\left(1 - \frac{1}{q}\right) - \omega\Theta\left(\overline{R} - \frac{1}{\sqrt{q}}\right)\right] =$$

$$= \text{Imaginary Part of } \gamma,$$

and the terms Θ, ω, q, $\overline{R}$ and $\overline{Q}$ have the significance given above. For use it can be brought into the form,

$$D_\omega - D = \frac{1{,}97 \cdot 10^6 z_1 z_2 \sqrt{\nu_1 z_1^2 + \nu_2 z_2^2}\,\sqrt{q}}{T\sqrt{DT}\cdot\omega\Theta\left[\left(1-\frac{1}{q}\right)^2+\omega^2\Theta^2\right]} \times$$

$$\times\left[\overline{Q}\left(1-\frac{1}{q}\right)-\omega\Theta\left(\overline{R}-\frac{1}{\sqrt{q}}\right)\right]\sqrt{c}.$$

When $\omega = 0$, the dielectric constant of the system reaches its maximum value and the excess becomes,

$$D_{\omega=0} - D = \frac{1{,}97 \cdot 10^6 z_1 z_2 \sqrt{\nu_1 z_1^2 + \nu_2 z_2^2}}{T\sqrt{DT}\cdot 2\left(1+\frac{1}{q}\right)^2}\sqrt{q}\,\sqrt{c}.$$

The effect of frequency variation on the magnitude of the dielectric constant excess may be expressed in several ways; in this report we shall compare the observed excess of solution over solvent with that required by the theory, stated in the form just given.

Statements as to Method, Apparatus and Materials

The apparatus used may be described as being of the comparator resonance type, and is, in principle, not unlike that described by Sack and his associates [6]. It was built with extreme care. It was arranged to permit the simultaneous comparison of the conductance and dielectric constant of a given electrolyte solution with the corresponding properties of standard potassium chloride solutions at a number of wave-lengths. It consisted of three distinct units, a variable high frequency vacuum tube oscillator circuit, an intermediate or tank circuit, and a comparator circuit with a thermocouple-galvanometer measuring system. It is shown diagrammatically in Fig. I.

For the evaluation of electrical conductance changes there were required observations of the comparator circuit galvanometer deflections, at resonance and with the conductance cell connected and disconnected. Dielectric constant change was calculated from a com-

[6] Sack et. al., Physik. Z. **29**, 627 (1928); **30**, 576 (1929); **31**, 345 (1930) **32**, 327 (1931).

parison of the settings of the standard variable precision condenser in the comparator circuit, again at resonance and with the cell connected and disconnected.

Analysis of the comparator circuit shows that the numerical value for the resistance of any solution compared to that of a standard potassium chloride solution (for which an allowance for the frequency variation has been made) may be obtained from the ratio,

$$\frac{I_2^2}{I_1^2} = \frac{d}{d_1}$$

provided the resistances of the two solutions are very nearly alike. In this expression I_2 and I_1 are the currents through the unknown

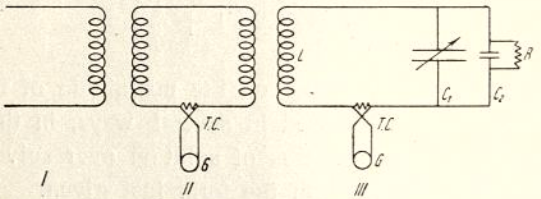

Fig. 1. Schematic Diagram of High Frequency Apparatus. L—Inductance in Measuring Circuit, C_1—Standard Precision Condenser, C_2 - Dielectric Cell Capacity, R—Resistance of Solution in the Cell, T. C.—Thermocouple, G—Galvanometer.

and standard solutions, and d_2 and d_1 are the corresponding galvanometer deflections. The differences in precision condenser settings necessary to bring the comparator circuit to resonance are interpreted in terms of the dielectric constant of the solutions in the cell, reference always being made to the behaviour of a standard potassium chloride solution of the same conductance and assumed dielectric constant. Of course, use must be made of the theory to calculate the dielectric constant of the reference solution, but, since the electrolyte is of the simplest valence type, small changes in dielectric constant with frequency and small excess are to be expected.

Throughout the course of the experimental work the greatest effort was made to obtain results of high precision. Particular attention was paid to the preparation and purification of all materials used, and to the design, construction, and position in the circuit and thermostat of the vessels which served simultaneously as conductance and dielectric cells. These cells were especially disigned to reduce

as much as possible capacitative effects between the electrode leads, and to fit a standard clamp in the thermostat bath in order to have reproducible position from experiment to experiment. They were constructed of either Jena Geräte or Jena 16_{111} glass, with sealed in bright platinum electrodes. The temperature was controlled to $25{,}000 \pm 0{,}002°$ C by means of a light-oil thermostat. The specific conductance of the aged water, when used, was in the neighbourhood of $0{,}40 \cdot 10^{-6}$ mhos.

Experimental Results

It is our intention to present in another place complete theoretical and practical description of the apparatus, an account of the measurements themselves, and a summary of the calculations made from them. In the space available we can give only a partial resumé of the experimentally determined frequency variations of electrical conductance and dielectric constant, and we compare them with the corresponding values required by the Debye-Falkenhagen theory, calculated very carefully by us from the best available static conductance data.

In all, three series of experiments were made. The last of these, which includes experiments 14 to 25, was most successful. In Table 1 are presented some typical experimental values, (E), of the conductances, Λ_{I_ω}, and of the conductance ratios, $\Lambda_{I_\omega}/\Lambda_{I_0}$ for salts of several valence types at wave-lengths 170, 100, 50 and 15 meters. In this table there are also included the corresponding theoretical values, (T), so that direct comparison with the requirements of the theory is readily possible. In Fig. 2 there are plotted as points observed values of the ratio, $\Lambda_{I_\omega}/\Lambda_{I_0}$, as a function of the wave-length, for barium chloride solutions of three concentrations, while the solid lines express the demands of the theory. Certain of the data used to construct this figure have been taken from the first and second series of experiments.

The calculations for the dielectric constants of these solutions are not entirely completed, but we can give provisional data for the wave-lengths 170 and 15 meters. These data are presented in Table 2. Again, there are included the corresponding theoretical values; in addition, similar values for infinite wave-length are computed.

Table 1

Theoretical and Experimental Values of Λ_{I_ω} and $\frac{\Lambda_{I_\omega}}{\Lambda_{I_0}}$

Electrolyte	Wave-Length: Molar Conc.	No. of Expt.	T or E	170 m: Λ_{I_ω}	170 m: $\Lambda_{I_\omega}/\Lambda_{I_0}$	100 m: Λ_{I_ω}	100 m: $\Lambda_{I_\omega}/\Lambda_{I_0}$	50 m: Λ_{I_ω}	50 m: $\Lambda_{I_\omega}/\Lambda_{I_0}$	15 m: Λ_{I_ω}	15 m: Λ_{I_ω}/I_0
KCl	0,000985	14 25	T	1,045	0,977	1,008	0,942	0,909	0,850	0,639	0,597
KCl	0,00100	15 24	T	1,054	0,977	1,017	0,943	0,919	0,852	0,647	0,600
$BaCl_2$	0,000560	16	T E	4,618 4,508	0,981 0,958	4,478 4,528	0,951 0,962	4,087 3,978	0,868 0,845	2,946 3,008	0,626 0,639
$MgSO_4$	0,000644	18	T E	12,121 —	0,982 —	11,784 11,94	0,955 0,968	10,798 10,43	0,875 0,845	7,786 7,46	0,631 0,605
$La(IO_3)_3$ . . .	0,000445	19	T E	10,495 10,55	0,979 0,983	10,146 —	0,946 —	9,214 8,48	0,859 0,790	6,570 5,21	0,613 0,485
$Ce(SO_4)_3$ . . .	0,000366	20	T E	93,02 92,84	0,995 0,994	92,29 2,43	0,988 0,989	89,39 89,97	0,951 0,963	73,58 74,59	0,787 0,798
$Pr_2(SO_4)_3$ . . .	0,000366	21	T E	92,13 —	0,996 —	91,38 90,98	0,988 0,983	88,47 88,64	0,956 0,958	72,67 72,19	0,785 0,780
$Co(NH_3)_6Cl_3$ . .	0,000253	22	T E	11,912 11,77	0,976 0,965	11,481 11,70	0,940 0,958	10,348 —	0,847 —	7,322 5,17	0,600 0,424

Discussion

Since the appearance, in 1928, of the quantitative theory describing the dispersion of electrical conductance and dielectric constant for very dilute strong electrolyte solutions there have been published

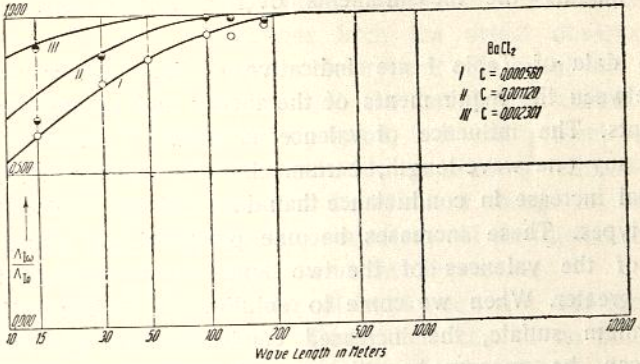

Fig. 2.

the results of a number of experimental researches intended to test the validity of the theory in so far as it applies to conductance measurements. In the majority of cases the results of these studies

Table 2

Theoretical and Provisional Experimental Values of Dielectric Constant Excess (Corrected for Dielectric Constant Change in KCl Solutions)

Electrolyte	Molar Conc.	No. of Expt.	$(D_{\omega=0} - D)$ Theory	$(D_\omega - D)_{\lambda=170\,m}$ Theory	$(D_\omega - D)_{\lambda=170\,m}$ Experiment	$(D_\omega - D)_{\lambda=15\,m}$ Theory	$(D_\omega - D)_{\lambda=15\,m}$ Experiment
$BaCl_2$	0,000560	16	0,260	0,246	0,44	0,068	0,06
$MgSO_4$	0,000774	17	0,824	0,795	0,89	0,268	0,57
$MgSO_4$	0,000664	18	0,752	0,715	0,83	0,206	0,35
$La(IO_3)_3$ . . .	0,000445	19	0,499	0,468	0,67	0,067	0,14
$Ce(SO_4)_3$ . . .	0,000366	20	1,574	1,556	1,85	0,796	0,87
$Pr_2(SO_4)_3$ . . .	0,000366	21	1,571	1,552	1,95	0,789	0,79
$CO(NH_3)_6Cl_3$.	0,000253	22	0,346	0,321	0,67	0,079	0,46

have been consistent with the requirements of the theory, at least in a semi-quantitative way. It has been our object to undertake a more careful and more systematic study of the problem than has been attempted to date, by using electrolytes of many different valence types and ion sizes at several very low concentrations, and by making the measurements over a considerable frequency range.

The data of Table 1 are indicative of the order of agreement found between the requirements of the theory and the results of the experiments. The influence of valence is shown in striking manner. Thus, at any one wave-length, barium chloride solutions show much less actual increase in conductance than do solutions of salts of higher valence types. These increases become progressively larger as the product of the valences of the two kinds of ion forming the salt becomes greater. When we come to solutions of cerium sulfate and praseodymium sulfate, the increased conductance is so pronounced that it can be measured with a very considerable degree of accuracy. The measurements are much less complete as regards the effect of concentration change, but as far as the experiments extend, this influence is correctly predicted by the dispersion theory.

The published results of experimental investigations of the dispersion of dielectric constant are far fewer in number and more limited in extent. We mention here only the pioneer work of Wien [7] who, working at wave-lengths 10, 20, 30 and 40 meters with dilute magnesium sulfate and barium ferricyanide solutions, found the dielectric constant to increase with concentration in such a way that it is nearly proportional to the square root of the concentration. Thus, the effect of the interionic forces far outweighed the influence of the saturation effect due to the presence of the ions. It was our purpose to establish the existence of a dispersion of dielectric constant and to determine whether the dispersion, if observed, is in quantitative agreement with the demands of the theory.

It is apparent from the data presented in Table 2 that there can be no question about the existence of a dispersion of dielectric constant in the sense and magnitude required by the interionic attraction

[7] Wien, Ann. Physik, **11**, 429 (1931).

theory. The data, incomplete to be sure, are admittedly meagre, and the dielectric constant values are generally above the theoretical values.

This is especially true at the longer wave-length, but here a very small dielectric cell had to be used and a lesser accuracy has to be expected. It is believed that when the results of more complete and exact calculations from the actual observations are available the agreement between theory and experiment will be somewhat improved. Thus, in spite of the fact that in certain instances this agreement is not particularly good, it is our present belief that the results of the experimental work do constitute a verification of the theory, especially with regard to the effect of change in valence type of the salt, in modifying the magnitude of the dielectric constant excess and in shifting the region of the dispersion.

In every case studied the dielectric constant was increased by the addition of salt to water. Thus, there can be no doubt that in very dilute salt solutions the interionic attraction effects exert a greater influence on the dielectric constant than do saturation effects. The data of the literature, never very consistent to be sure, have been usually taken to prove that dissolved ions lower the dielectric constant of a solution. A saturation effect is undoubtedly still present, but it must be of such small consequence that it is almost completely masked by the increase of the susceptibility due to the interionic effects.

Summary

With a comparator-resonance apparatus designed for the simultaneous observation of the electrical conductance and dielectric constant of very dilute electrolyte solutions at high frequencies there has been made an experimental study of the Debye-Falkenhagen dispersion theory.

The preliminary results reported here are found to be in satisfactory quantitative agreement with the requirements of the theory in so far as they involve changes in the valence type and concentration of the dissolved salt.

Thus, in the purely physical interionic attraction theory we find an adequate explanation and description of the dispersion behaviour of an ideal electrolyte.

The dielectric constant data are of further value in that, in dilute solution, they prove to be small, and even negligible, any decrease in dielectric constant caused by the saturation of the molecules of the liquid by the intense electrical fields arising from the dissolved ions. The observed increases in susceptibility must be due to inter-ionic couplings.

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