

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Dielectric Constant of Conducting Solutions

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Investigators using the Furth ellipsoid method for measuring the dielectric constant of conducting solutions obtain results somewhat consistent with theoretical requirements.¹ The resonance method at high frequencies yields data containing a minimum at low concentrations. The Debye-Hückel relation should be most valid at low concentrations. Walden, Ulich and Werner,² Sack,³ Hellmann and Zahn,⁴ and Schmidt⁵ have reported minima in dielectric constants and Wien's⁶ data show an initial decrease of the dielectric constant. It is the purpose of this investigation to determine more fully the nature of this effect. Lattey,⁷ using a "Voltage Tuning" method, does not report a minimum in the dielectric constant of solutions.

Experimental

The resonance circuit is shown in Fig. 1. The oscillator frequency remained constant within 1000 cycles per second.

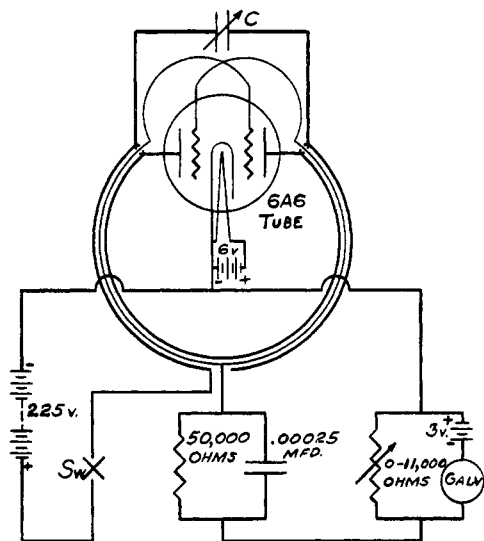


Fig. 1.—Circuit.

The frequency of the oscillator was determined by means of Lecher wire measurements. It was 8.04×10^7 cycles per second for potassium sulfate and 7.83×10^7 for potas-

(1) Falkenhagen, "Electrolytes," translation by R. P. Bell, Oxford University Press, London, 1934.

(2) Walden, Ulich and Werner, *Z. physik. Chem.*, **116**, 261-90 (1925).

(3) Sack, *Physik. Z.*, **28**, 199-210 (1927).

(4) Hellmann and Zahn, *Ann. Physik*, **81**, 711-756 (1926).

(5) Schmidt, *Phys. Rev.*, **30**, 925-930 (1927).

(6) Wien, *Ann. Physik*, **11**, 429-453 (1931).

(7) Lattey and co-workers, *Phil. Mag.*, [7] **12**, 1111 (1931); **13**, 444 (1932).

sium chloride and magnesium sulfate. The tuning condenser, C, was a three-plate Hammarlund isolantite insulated midget condenser. The separation between plates was 4 mm.

The "grid-dip" method of determining resonance was used. The galvanometer used for measuring the current had a sensitivity of 2×10^{-8} amperes per scale division.

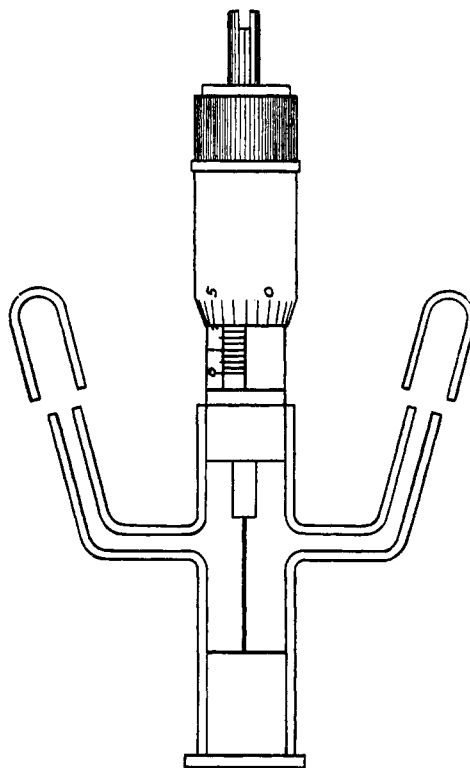


Fig. 2.—Cell.

Figure 2 shows the cell. The platinum electrode at the bottom and the micrometer were permanently fixed to the glass. The upper electrode could be moved by turning the micrometer with a long screw driver which extended outside the thermostat. The air thermostat ($25.00 \pm 0.01^\circ$) contained all of the apparatus and was kept dry with concentrated sulfuric acid.

The tuning coil consisted of three turns of number 16 bare copper wire wound on 38-mm. Pyrex tubing. The turns were spaced 3 mm. from center to center, and were held in place by a thin coat of lacquer. One lead of the coil went to a brass clip which held the body of the micrometer by friction. The other lead went to a mercury switch from the other side of which a lead went to the lower electrode of the cell. The arrangement was such that the cell could be removed quickly. About 3 cm. of air pressure was sufficient to operate the mercury switch, and was controlled by a stopcock located outside the

thermostat. The coil, mercury switch, and clips were rigidly mounted on a base made of bakelite.

Solutions were made from analytical reagent grade potassium chloride, potassium sulfate, and magnesium sulfate by direct weighing of the salts to give an initial normality of 0.125. Calibrated pipets were used to make solutions of lower concentrations. Redistilled water having a specific conductance of 2×10^{-6} mho per centimeter was used in all cases. Great care was taken to prevent contamination of the solutions by carbon dioxide or other substances. The cell was cleaned with concentrated sodium hydroxide, then with sulfuric acid and potassium dichromate cleaning solution. The cell was rinsed until minimum conductivity was reached, then the resonance point for water and increasing concentrations of a salt were determined, the highest concentration measured being 0.005 *N*. At this concentration the resonance became too broad to be determined accurately.

With the filled cell in place, the resonant circuit was coupled loosely to the oscillator, the mercury switch being open. By means of the dial box, the galvanometer was set at -25 . If the mercury switch was then closed by applying air pressure, the galvanometer deflected as the cell was tuned through resonance. This deflection was maintained at approximately 45 divisions maximum, regardless of the concentration of the solution, by varying the coupling of the coil. From seven to twelve determinations of the resonance point were made for each concentration of each salt. This procedure was followed to eliminate small random deflections of the galvanometer. Immediately following the determination of the resonance point, the resistance of the cell was determined by means of a Kohlrausch bridge, the cell being set at the average value obtained from the resonance determinations.

Discussion of Results

Since the grid-dip is due to power absorption, the maximum occurs at zero reactance of the coupled circuit and is given by

$$wL = \frac{1}{wC} \left(1 - \frac{1}{R^2 w^2 C^2 + 1} \right)$$

to within 0.1% for the most concentrated solutions used. Here $w = 2f\pi$, where f is the frequency of the oscillator, L is the total inductance of the circuit, and R is the resistance of the cell. This equation is derived as follows

$$Z_{RC} = \frac{R(-j/wC)}{R - j/wC}$$

where Z_{RC} is the impedance of R and C in parallel.

$$Z_{RC} = -j/wC \left(1 - \frac{1}{R^2 w^2 C^2 + 1} \right) + \frac{R}{R^2 w^2 C^2 + 1}$$

$$Z_s = j(wL - 1/wC) \left\{ 1 - \frac{1}{R^2 w^2 C^2 + 1} \right\} + \frac{R_L + \frac{R}{R^2 w^2 C^2 + 1}}{R^2 w^2 C^2 + 1}$$

where Z_s is the series impedance of L , R_L and Z_{RC} .

$$P = I^2 R_T = \frac{E^2}{Z_s^2} R_T$$

where P is the power dissipated in the circuit, R_T is the effective series resistance, E is the impressed voltage, and I is the current.

$$R_T = R_L + \frac{R}{R^2 w^2 C^2 + 1}$$

$$P = E^2 \frac{R_L + \frac{R}{R^2 w^2 C^2 + 1}}{\left\{ wL - 1/wC \left(1 - \frac{1}{R^2 w^2 C^2 + 1} \right) \right\}^2 + \left(R_L + \frac{R}{R^2 w^2 C^2 + 1} \right)^2}$$

Since for an electrolytic cell, $R \propto 1/C$ (neglecting distributed capacity) and $R^2 w^2 C^2$ is constant.

Let

$$\frac{R}{R^2 w^2 C^2 + 1} = K'/C$$

$$wL = A; \text{ and } K/wC = B$$

$$1 - \frac{1}{R^2 w^2 C^2 + 1} = K$$

$$P = E^2 \left\{ \frac{R_L + K'/C}{(A - B)^2 + (R_L + K'/C)^2} \right\}$$

for $\partial P / \partial C = 0$ we get

$$A^2 - \{ 1 - (K'w/K)^2 \} B^2 - (2R_L K/wK' + 2R_L K'w/K)B + 2R_L K A/wK' - R_L^2 = 0$$

$$A = B \sqrt{1 - (K'w/K)^2 + \frac{2R_L K/wK' + 2R_L K'w/KB + R_L^2/B^2 - 2R_L K A/wK'B^2}{1 - (K'w/K)^2}}$$

This is equal to

$$A = B \sqrt{1 + \frac{2R_L K/wK'B(1 - A/B)}{1 - (K'w/K)^2}}$$

to within 0.08% for 0.005 *N* potassium chloride. $A = B$, or

$$wL = 1/wC \left(1 - \frac{1}{R^2 w^2 C^2 + 1} \right)$$

is a solution of this equation. Strictly, the high-frequency resistance should be used, but since the accuracy is not great for concentrated solutions, it was considered that this correction (0.01%) need not be applied. Since the method is not suitable for measuring absolute values of dielectric constant, the value for pure water was taken as 79 at 25° as a reference. Comparisons of micrometer settings were then made from which the dielectric constants of the solutions were calculated. Since wL is constant

$$\frac{D_s}{D} = \frac{d_s}{d_w} \left(1 - \frac{1}{R^2 w^2 C^2 + 1} \right)$$

where D_s and D are average dielectric constants of solution and water, respectively, each including effects of the glass of the cell. Here d_s and d_w are the total electrode separations for solution and water. Since presumably the full area of the glass is effective, we find that

$$\frac{D_s}{D} = \frac{D_g A_g + D A_1}{D_g A_g + D_s A_1}$$

where D_g , D and D_s are the dielectric constants of

the glass, pure water, and solution, and A_g and A_l are the areas of glass and liquid, respectively. From measurements of these areas and known values of the dielectric constants, it is found that

$$D_g A_g = 0.026 D A_l$$

If we further let

$$D_s = D + k$$

$$d_s = d_w + d$$

we may substitute them in the two expressions for D_s/D . Expanding in power series, and neglecting higher order terms easily below experimental error, we get

$$k = 1.026 D \left(\frac{1}{R^2 w^2 C^2 + 1} - \frac{d}{d_w} \right)$$

From this equation the values of k shown in Table I, Column 2 are calculated, C being calculated from measured areas and known dielectric constants. The value used is $4.06 \mu\mu f$ for potassium sulfate, and for magnesium sulfate and potassium sulfate, $4.28 \mu\mu f$, the difference being due to the slightly different frequencies employed.

Concn.	TABLE I	
	k	D
	KCl	
0.0000		79.00
.0002	-0.807	78.19
.0005	- .932	78.07
.0010	- .715	78.28
.0025	+ .01	79.01
.0040	2.57	81.57
.0050	3.57	82.57
	K_2SO_4	
0.0000		79.00
.0002	-0.516	78.48
.0005	- .531	78.47
.0010	+ .283	79.28
.0025	+1.071	80.07
.0040	+2.107	81.11
.0050	+2.425	81.43
	MgSO ₄	
0.0000		79.00
.0002	-0.885	78.11
.0005	- .712	78.29
.0010	- .82	78.18
.0025	+ .028	79.03
.0040	+1.263	80.26
.0050	+1.665	80.67

Plots of D_s against the square root of normality are given in Figs. 3, 4 and 5 for magnesium sulfate, potassium chloride, and potassium sulfate, respectively. It is seen immediately that the decreases of dielectric constant cannot be reconciled with Debye-Hückel theory, which requires that

$$k = F_1(f\theta, q)F_2(z, D, T, q)N^{1/2}$$

where N is the normality of the solution, and both F_1 and F_2 are positive quantities; θ is the relaxation time of the ionic atmosphere, q is a function of the ionic valences and mobilities, z is the valence, and T is the absolute temperature.

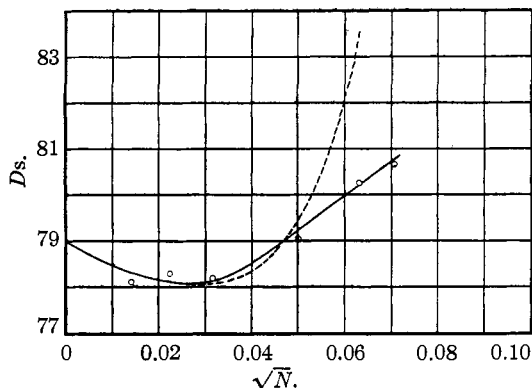


Fig. 3.—MgSO₄.

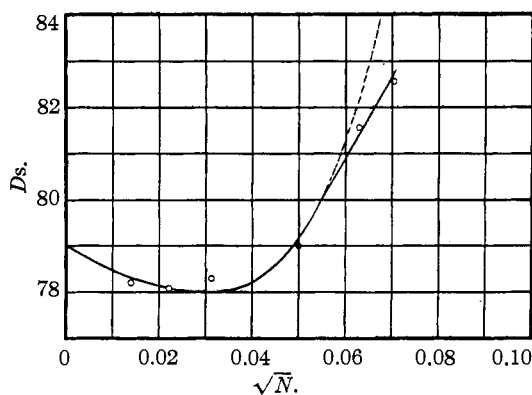


Fig. 4.—KCl.

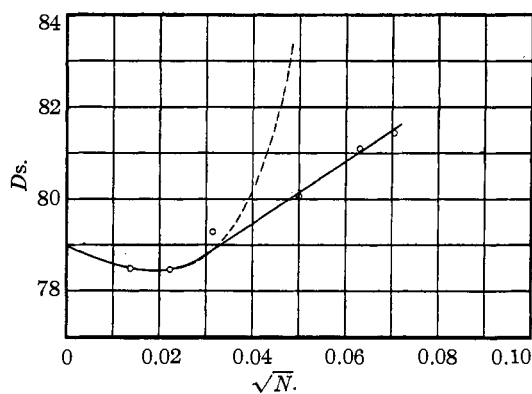


Fig. 5.—K₂SO₄.

Modern theories of liquids strongly indicate that the best concept of a liquid is to regard it as a quasi-crystal. According to Fowler,⁸ a liquid

(8) Fowler, "Statistical Mechanics," The Macmillan Co., New York, N. Y., 1936, pp. 522-560.

may be expected to have a fundamental vibrational frequency or band of frequencies. Eyring⁹ has obtained satisfactory results for the heat capacity of liquid mercury by assuming a characteristic temperature near that of solid mercury, and Fuoss¹⁰ has shown that ions in a solution occupy, in the main, positions consistent with a simple cubic structure. Thus it seems possible to regard ions in a solution as possessing simple cubic symmetry in the immediate neighborhood of a given ion. It also seems possible that a rather definite vibrational frequency might be associated with such an arrangement. It is obvious that if such a vibrational frequency occurred near the frequency of measurement, it would lead to just such effects as have been observed. In other words, the ions in solution would exhibit the usual effects of resonant systems, and would have a corresponding reaction on the measuring circuit. This possibility is not included in the Debye-Hückel theory.

It does not seem possible at present to calculate such ionic vibration frequencies. A simple alternative is to regard this frequency as inversely proportional to the time of relaxation of the ionic atmosphere as given by the Debye-Hückel theory, or

$$f_i = c_1/\theta$$

where

$$\theta = 8.85 \times \frac{10^{-11}D}{NL_\infty}$$

Here L_∞ is the limiting equivalent conductance of the salt. We should also expect the constant c_1 to be of the order of 1. Furthermore, if the ions have relatively little effect on the solvent water in these very dilute solutions, we should expect the dielectric constant of the solution to return to the value for pure water when the frequency used in measurement equals the vibrational frequency of the ions. Another possibility is that the time of relaxation changes with changing concentration and for a certain frequency this dispersion should have a minimum. Table II gives the value of c_1 for each of the salts measured. The values found are of the proper magnitude.

TABLE II

Salt	N	L_∞	θ	f used in measurement	c_1
KCl	0.00240	150	$1.94 \cdot 10^{-6}$	$7.83 \cdot 10^7$	1.52
K_2SO_4	.00109	155	$4.14 \cdot 10^{-6}$	$8.04 \cdot 10^7$	3.33
$MgSO_4$.00221	134	$2.36 \cdot 10^{-6}$	$7.83 \cdot 10^7$	1.85

We may now attempt to calculate the effect of changing the concentration of the solution. If

(9) Kincaid and Eyring, *J. Chem. Phys.*, **5**, 587-96 (1937).

(10) Fuoss, *Trans. Faraday Soc.*, **30**, 967 (1934).

we compare a vibrating ion to a simple series resonant circuit, the reactance is given by

$$X = \frac{j(R^2 + (wL - 1/wC)^2)}{wL - 1/wC}$$

The usual analogies between electrical and mechanical quantities apply here, or L is equivalent to mass, R to the frictional constant, and $1/C$ to the Hooke's law constant. "j" is the complex operator. If the total reactance of the ions in the cell is considered as proportional to the distance between electrodes and the number of ions per centimeter, and inversely proportional to the cross sectional area of the solution and the number of ions per square centimeter, we have

$$X(\text{ions}) = c_2 \frac{Xd_s}{\sqrt[3]{N} A_1}$$

since the number of ions per centimeter is proportional to the cube root of the concentration. The proportionality constant is c_2 . If this total reactance of ions is equated to

$$X_c = \frac{-j}{wC} = \frac{-4j\pi d_s}{wkA_1}$$

where X_c is the reactance of an equivalent condenser, we may solve the equation for k and obtain

$$k = - \frac{\sqrt[3]{N} \left(wL - \frac{1}{wC} \right)}{wc_2 \left[R^2 + \left(wL - \frac{1}{wC} \right)^2 \right]}$$

Since the value of R^2 is probably high compared to $(wL - 1/wC)^2$, and cannot be calculated at present, it may be included in the constant. At the resonant frequency of the ions, we have

$$wL = 1/wC$$

$$f = c_1/\theta$$

Solving for $1/C$, we obtain

$$1/C = 4\pi^2 c_1^2 L / \theta^2$$

Making these substitutions in the relation for k , we have

$$k = -c_3 \sqrt[3]{NL} \left(1 - \frac{c_1^2}{f^2 \theta^2} \right)$$

where c_3 is the new proportionality constant. The mass of the ions presumably remains constant, and hence may be included also in a new proportionality constant, A . Remembering that for a given salt the relaxation time, θ , is inversely proportional to the normality of the solution, we may lump all constant terms together in a new constant B_1 , giving

$$k = -A \sqrt[3]{N} \left(1 - \frac{B_1 N^2}{f^2} \right)$$

Finally, if measurements are made at a constant

frequency, B_1/f^2 may be called a new constant B , giving

$$k = -A\sqrt[3]{N}(1 - BN^2)$$

At present the only procedure possible is to evaluate A and B to fit the data obtained. The curves shown by dotted lines in Figs. 3, 4, and 5 represent the best fits for the salts measured. The correspondence is good in dilute solutions. The structures of potassium chloride and magnesium sulfate solutions may be similar but different from that of potassium sulfate. The constants A and B confirm this hypothesis. Table III gives values of A and B .

TABLE III

Salt	A	B
KCl	12.00	$1.705 \cdot 10^6$
K_2SO_4	8.63	$8.45 \cdot 10^5$
$MgSO_4$	12.08	$2.05 \cdot 10^5$

The deviation which occurs in more concentrated solutions is consistent with increased formation of ion pairs, which presumably would not be effective in changing the dielectric constant of the solution. Little need be said on this score, for

the results of measurements carried out at various frequencies. First, investigators using different frequencies in the range of these effects would not be able to obtain the same results, although the general nature of the curves obtained would be similar. In general, measurements made at low frequencies would not show a minimum, since the lowest concentration measured would be past the region of the minimum. On the whole this describes the results given in the literature.

The theory also predicts that at the frequency at which the dielectric constant of the solution equals that of pure water

$$N/f = \sqrt{1/B_1}$$

Very few data are available on which this equation may be tested. Table IV gives values of $\sqrt{1/B_1}$ for the three salts measured. Predictions from this equation are compared with the available data. The difference between the calculated and observed value for concentrated solutions is to be expected and corresponds with the trend in the salts measured. The agreement in the remaining cases is good.

TABLE IV

Salt	$\sqrt{1/B_1}$	N (calcd.)	N (obsd.)	f	Investigator
KCl	$3.1 \cdot 10^{-11}$	0.0093	0.1	$300 \cdot 10^6$	Hellmann and Zahn ⁴
K_2SO_4	$1.4 \cdot 10^{-11}$				
$MgSO_4$	$2.8 \cdot 10^{-11}$.00085	Between .00065 and .00090	$30 \cdot 10^6$	Wien ⁶
		.00014	.0001	$5 \cdot 10^6$	Jezewski and Komecki ¹¹

even if these suggested relations are valid at high dilutions, relatively large deviations are to be expected even in the range of the present measurements.

Our explanation is in some respects the opposite of Walden's,² who proposes that the decrease in D_s is due to the immobilization of the water dipoles by the strong fields around the ions and that in concentrated solutions we have ion clusters formed with large dipole moments.

The proposed theory offers an explanation for

Summary

1. The dielectric constant of dilute aqueous solutions of potassium chloride, potassium sulfate, and magnesium sulfate has been measured at 25° by the grid-dip method using a frequency of about 80 megacycles.

2. A new theory has been evolved which accounts satisfactorily for the results found and explains the large discrepancies in the work of several investigators. In three cases quantitative comparisons have been made.

(11) Jezewski and Komecki, *Physik. Z.*, **34**, 561-5 (1933).