DECEMBER, 1927 PHYSICAL REVIEW VOLUME 30

THE DIELECTRIC CONSTANTS OF FOUR ELECTROLYTES AS GIVEN BY THE CARMAN ELECTROMETER METHOD

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Abstract

The electrometer method devised by Professor A. P. Carman is used to measure the dielectric constants of aqueous solutions of NaCl, KCl, $BaCl_2$ and $CuSO_4$. Curves showing the relation between dielectric constant and concentration of the solution are obtained for each of these four substances, up to an equivalent normal concentration of 0.018 for NaCl, of 0.01 for KCl, of 0.024 for $BaCl_2$, and of 0.028 for $CuSO_4$. These curves each show first a decrease of the dielectric constant with increasing concentration. After passing through a minimum the dielectric constant increases with the concentration, rising in each case to a value greater than that of water. For solutions of $BaCl_2$ and $CuSO_4$, there is in each case a second minimum in the rising branch of the curve. These experimental results for the dielectric constants of aqueous electrolytes can be explained by an hypothesis in accordance with the general dipole theory of Debeye, as interpreted by Walden, Ulich and Werner.

In 1897, J. F. Smale,[1] working in Nernst's laboratory by a Nernst force method, got values of the dielectric constants of several electrolytes which showed an increase of the dielectric constant with the concentration of the solution, these values being greater than that of water. Lattey[2] and Walden,[3] on the other hand, find that for aqueous electrolytes the dielectric constants of the solution is less than that of water, and further that the dielectric constant decreases as the concentration increases. Lattey and Walden used resonance methods and could get results only for dilute solutions. Recently Fürth[4] has given results on solutions of NaCl, by a force method, in which he gets first a decrease and then an increase of the dielectric constant of the solution as the concentration increases, but his curves do not show a value of the dielectric constant of the solution greater than that of water. His measurements are peculiar in showing higher values in an electric field of 30 volts than in a field of 15 volts. The following investigation of this interesting subject of the dielectric constants of aqueous electrolytes was carried out by an electrometer method devised by Professor A. P. Carman. This method has proved to be especially adapted for obtaining the relative values of the dielectric constant of two liquids, and in the new arrangement described elsewhere[5] has given consistent and satisfactory results for electrolytes as well as for non-electrolytes.

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[1] J. F. Smale, Ann. d. Physik **60**, 625 (1897).

[2] R. T. Lattey, Phil. Mag. **41**, 829 (1921).

[3] P. Walden and Assistants, Zeits. d. Phys. Chem., vols. **110**, **111**, **115**. Otto Blüh, in Physik. Zeits. (April, 1926) discusses the recent results on the dielectric constants and gives an extended bibliography. L. F. Gilbert in Sc. Progress (July, 1926) discusses the dielectric constants of liquids.

[4] R. Fürth, Physik. Zeits. **25**, 676 (1924).

[5] A. P. Carman and C. C. Schmidt, Phys. Rev. **30**, 922 (1927).

Aqueous solutions of NaCl, KCl, $BaCl_2$ and $CuSO_4$ were used. The materials were marked "c.p." and were probably very nearly pure. In preparing the solutions "conductivity" water obtained from the Department of Chemistry of the University of Illinois was used. This was prepared by redistilling the distilled water from the regular supply in the following manner. After filling the still with distilled water, a solution of $KMnO_4$ dissolved in an alkali, was added. The treated water was then heated and left for six hours or more. This was to insure complete oxidation of organic matter. The solution was prepared by adding twelve grams of $KMnO_4$ to a solution of 120 grams of NaOH in one liter of water. While distilling, the flow of cooling water and steam for heating were so regulated that some steam passed out with the water. This was to prevent CO_2 from going into the bottle. Water obtained by this process was found to have a conductivity of 0.6 to 0.92×10^{-6} mhos by Hovorka.[6] The water was used as soon as possible after it was obtained so as to give less chance for absorption of impurities. Before making up solutions, the water was kept in Jena glass bottles reserved for that one use. The water was usually used within a few hours, although measurements made on water two or three days old showed no apparent differences. Solutions of normal concentration were prepared by weighing the salt to within a milligram and the water to within a gram, giving an accuracy within other experimental errors. The plates used on each side of the electrometer were of gold 2.5 cm square and 0.055 cm thick. There was no sign of any chemical action on the plates by any of the liquids used. The distances between the wires themselves and between the wires and the sides of the vessel were great enough to eliminate capillary attractions. The separation of the needle plates from the fixed plates could be varied, and was usually made as small as possible to get sensitivity. The needle plate and its fixed plate on the left side were immersed in pure water, and the plates on the right side in the solution. As the densities of the liquids on the two sides were very nearly the same, there was no disturbing effects from buoyancy.

The electric current between the plates through the electrolyte amounted in some cases to nearly an ampere, and the rise of temperature was often considerable. While measurements could be made upon non-conducting liquids at room temperatures without temperature disturbances, this could not be done for conducting solutions. It was necessary to measure the temperatures of the solution between the plates where the heat was generated. This was done by a small glass-sheathed thermocouple of copper-constantan. The thermocouple was placed between the plates against the fixed plate, and as the thermocouple was very small and fixed in position for all measurements, it was assumed to have no effect on the results. The e.m.f. of the thermocouple was found by means of a potentiometer and a standard Weston cell, and the temperatures determined from a calibration curve. The temperature could be determined to a tenth of a degree Centigrade, which was considered sufficiently accurate. Because of the heating of the conducting

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[6] F. Havorka, Master's thesis in Phys. Chem., University of Illinois Library, 1925.

solutions, it was not practical to get a balance of the electrometer at the exact temperature desired. It is, however, necessary that the values of the dielectric constant should be reduced to the same temperature. By obtaining several electrometer balances and observing the corresponding temperature for each balance reading, it was possible to obtain the ratio of the potential differences for several temperatures; then from a curve with potential ratios as ordinates and temperatures as abscissas, the value of the potential ratio for the derived temperature was obtained. The use of such a curve had also the advantage of averaging the determinations. It is very important in getting a comparison of the dielectric constants of water and of a solution, that the balancing water remain at a constant temperature. It was found possible to maintain the water temperature practically constant for several hours. By making a checking determination with water on both sides in connection with measurements on each sample of the solution, the variations were reduced still further.

The measure of the ratio of the potential differences for the two pairs of evidently all-important for accuracy in the dielectric constants by a force method. These potential differences were measured by two electrostatic voltmeters, using for this purpose two Dolezalek electrometers connected idiostatically. These were used ballistically and calibrated before and after each run of readings. An accuracy within one-half of one percent was reached. An assistant was used in making these potential observations so as to get the readings rapidly and simultaneously with the readings of the electrometer balance. Our first measurements were made on two non-electrolytic aqueous solutions, the solutions chosen being two for which we have measurements made by Fürth,[7] by a resonance method. For these measurements, we used two Kelvin multicellular voltmeters for the potential differences between the plates. Alternating potentials of 60 cycles and about 50 volts on each side were used. The results are shown in the curves on Fig. 1. These

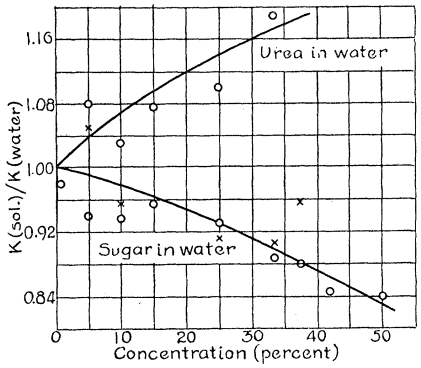

Fig. 1. Variation with concentration of the dielectric constants of solutions of urea and of sugar in water.

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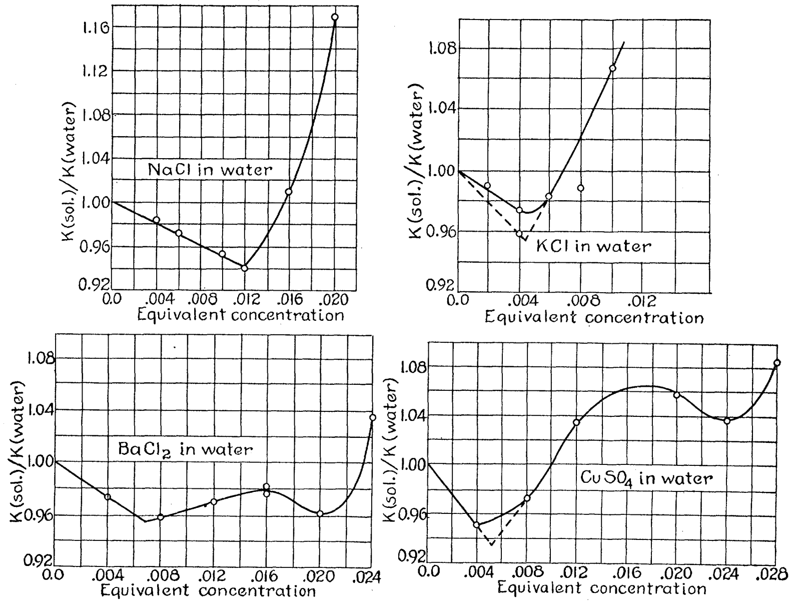
[7] Fürth, Ann. d. Physik **70**, 63 (1923).

show good general agreement with the values obtained by Fürth. The individual observations did not fall as close to the curve as desired, because of the difficulty of estimating fractions of a volt with the pointer instrument. These curves show that the dielectric constants of sugar solutions decrease with the concentration, while for urea the dielectric constants increase with the concentration. Fürth found this also. For the measurements of the dielectric constants of the aqueous solutions, the specially adapted quadrant electrometers were used as voltmeters, and a Crocker-Wheeler motor-generator producing an alternating e.m.f. of 500 cycles was the potential source. Earlier trials with an e.m.f. of 60 cycles had showed irregularities which we believed due to electrolytic polarization. These irregularities disappeared with the 500 cycle potential source. The results of measurements of the dielectric constants of the four electrolytes are given in the curves Figs. 2–5. These curves show the relation between the dielectric constant and the normal concentration of the solution for each of the four substances. All values are given for 20°C. The alternating e.m.f. used on each side was about 25 volts at 500 cycles. The values of the dielectric constants are given in terms of the dielectric constant of water as unity.



Figs. 2-5. Variation with concentration of the dielectric constants of solutions of NaCl, KCl, $BaCl_2$ and $CuSO_4$ in water.

A sample set of observations for a single point is given in Table I for a solution of NaCl of normal concentration 0.006. Curves showing the variation of dielectric constant with concentration in aqueous solutions of NaCl, KCl, $BaCl_2$ and $CuSO_4$ are presented in Figs. 2, 3, 4, and 5. It is seen that the curves for NaCl and KCl are similar. Both show a decrease of the dielectric constant with increase of concentration until a minimum is reached, after which the curve rises rapidly. The change of slope is apparently more abrupt in the case of NaCl than it is for KCl, though the number of observations is as yet insufficient to warrant definite conclusions. In NaCl the minimum is found at a concentration 0.012 normal while in KCl it is between 0.004 and 0.006 normal. The existence of these sharp minima for aqueous solutions is here shown definitely for the first time, as far as we know, though such minima had been predicted by Walden, Ulich and Werner[7] from similar curves which they obtained with chloroform, pyradin, dichlorbenzol, etc., as solvents. Fürth[8] found for aqueous solutions of NaCl a bend in the dielectric constant—concentration curves, but the bend was very gradual and small. Fürth used a nickel ellipsoid suspended in the liquid at an angle with the impressed alternating electric field. The frequency was only 50 cycles per sec. and hence his results are almost certainly complicated by electrolytic polarization. The fact that he obtains different curves for different impressed electromotive forces also suggests that electrolytic polarization is a factor in his results.

TABLE I

Sample set of observations. NaCl solution, concentration 0.006 normal.

Solution on right, water on left				Water on both sides			
Temp.	Potential differences			Temp.	Potential differences		
	E_1'(left)	E_2'(right)	$(E_1/E_2')^2$		E_1(left)	E_2(right)	$(E_1/E_2)^2$
10.7°C	23.1 v	26.6 v	0.755	19.9°C	23.2 v	27.2 v	0.728
12.1	22.8	26.7	.73	19.9	23.2	27.3	.724
14.1	22.8	26.8	.723			(mean)	0.726
16.3	22.6	26.7	.712				
20.1	22.5	26.8	.705	$k_{sol}/k_{water}=0.706/0.726=0.972$			
20.0		(from curve)	0.706				

Walden, Ulich and Werner, with their resonance method, were not able to make measurements on aqueous solutions as far as the minimum points indicated on our curves, but they state that such a minimum point should be found for a solution of NaCl at an equivalent concentration of about 0.25. The beginning of the upward bend in Fürth's curve is in the region of 0.003 to 0.006 concentrations, while our curve for NaCl starts up at 0.012, somewhere between Fürth's values and Walden, Ulich and Werner's estimated value.

Our curves for $BaCl_2$ and $CuSO_4$ both show the existence of a second minimum point. In the case of $BaCl_2$ the value of the dielectric constant at the intervening maximum is less than the value for water while in the case of $CuSO_4$ it is greater. It is reasonable to suppose that the presence of the double minima in the case of these solutions is to be associated with the bivalent nature of the metal ion. Walden, Ulich and Werner found such a second minimum point for tetra-prophylammonium iodide in acetylene tetrachloride, but gave no explanation of it.

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[7] Walden, Ulich and Werner, Zeits. f. Phys. Chem. **115**, 177 (1925); **116**, 261 (1925).

[8] Fürth, Phys. Zeits. **25**, 676 (1924).

Walden, Ulich and Werner's general explanation of the decreasing and increasing branches of the curve for concentration and dielectric constant is as follows. For the pure solvent the dielectric constant is determined by the dipoles present. When the liquid is placed in an electric field the dipoles arrange themselves in the general direction of the external field. If a substance which is ionized is added to the solvent, then for weak solutions, the ions are widely separated, and each ion has its own electric field. The dipoles of the solvent are attracted by these charged ions, and the directive action of the external electric field is consequently decreased. With the addition of more ions, that is, for more concentrated solutions, the number of ions becomes such that complex formations or groups of ions are formed and these groups direct themselves with the external field and thus tend to increase the dielectric constant again. Our present knowledge of the dielectric constants of electrolytes is too meager to give more than this general explanation. There is evidently need of extended data on the dielectric constants of a considerable number of electrolytes through a wide range of concentrations before a more complete explanation of the phenomena described in this paper is assured. Plans are being made to continue in this laboratory this investigation.

The writer thanks Professor A. P. Carman, who suggested the problem and directed the work, for his suggestions and encouragement during this investigation.

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University of Illinois,
June, 1927.

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[9] Walden, Ulich, Werner. Zeits. f. Phys. Chem. **116**, 288 (1925).