

**ON THE DIELECTRIC
CONSTANTS OF PURE
SOLVENTS, PP. 356-389**

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BY

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ON THE DIELECTRIC CONSTANTS OF PURE SOLVENTS.

Introduction.

In 1893 Nernst,¹ from theoretical considerations based upon the theory of electrolytic dissociation, deduced his well known rule, that—other things being equal—the greater the dielectric constant of a medium the greater is its dissociating power. In the same year J. J. Thomson² also pointed out this relation, saying that if we accept the view that the forces between the atoms are electrical in their origin then the effect of surrounding the molecules of a substance by a medium possessing a very high dielectric constant like water, would be to practically dissociate them. According to Nernst, proportionality between the dielectric constant and dissociating power need not necessarily exist, but a close parallelism between the two doubtless prevails. He adds that other factors besides the dielectric constant doubtless exist, which probably influence the dissociating power of the solvent. The experimental facts, Nernst³ says, show beyond a doubt that a marked parallelism exists between the dissociating power and the dielectric constant. Exceptions to the rule he explains by assuming the existence of specific influences, of which the association of the ions with the molecules of the solvent is probably of prime importance.

The existing experimental data at the time the above relation between the dielectric constant and dissociating power was pointed out accorded well with it, and subsequent investigations furnished numerous additional examples in support of it. But

¹ Göttinger Nachrichten No. 12, (1893); Zeit. phys. Chem. 13, 531, (1894).

² Phil. Mag. 36, 229, (1893).

³ Theoretische Chemie p. 365, (Dritte Auflage).

exceptions also appeared which point to a marked specific influence of the solvent. Some of these exceptions are noted and considered in another part of this paper.

The following table taken from Nernst's¹ Theoretical Chemistry illustrates the general parallelism between the dielectric constant and the dissociating power.

TABLE I.

Medium.	Dielectric Constant.	Electrolytic Dissociation.
Gas.....	1.0	Not perceptible at ordinary temperatures.
Benzene	2.3	Exceedingly low; but distinctly perceptible conductivity indicates traces of dissociation.
Ether	4.1	Perceptible conductivity of dissolved electrolytes.
Alcohol	25	Dissociation quite marked.
Formic acid	62	Marked dissociation of dissolved salts.
Water	80	Very marked dissociation.

Since the formulation of the Nernst-Thomson rule excellent new methods for determining dielectric constants have been devised by Thwing,² Nernst,³ and Drude;⁴ and these investigators have measured the dielectric constants of a number of substances. The pupils of Nernst, and of Drude, and others have elaborated, modified and perfected these methods, so that the determination of dielectric constants at ordinary temperatures is now a comparatively simple operation. During this period the electrical conductivity of non-aqueous solutions has also received considerable study, and the dissociating power of various solvents, which yield conducting solutions, has moreover been investigated by means of cryoscopic and boiling-point determinations. The selected examples given in the following table will serve to show that various other solvents besides water possess ionizing power in a very marked degree. Under V, in the third

¹ P. 395, third edition. (1900).

² Phys. Review, 2, 35. (1894). Also Zeit. phys. Chem. 14, 286. (1894).

³ Zeit. phys. Chem. 14, 622. (1894).

⁴ Zeit. phys. Chem. 23, 267. (1897).

column, the volume in liters is given in which one gram molecule of substance is dissolved; and the next column gives the corresponding molecular conductivity, while the fifth column gives the temperature at which the measurements were made.

TABLE II.

Solvent	Solute	V	Cv	t°C	Observer
Water.....	KI	2	99.7	18	Kohlrausch ¹⁾
		100	116.1		
		1000	120.3		
Methyl alcohol.....	LiCl	11.7	40.1	18	Völlmer ²⁾
		117.4	57.5		
		1174.0	65.3		
Formic acid.....	KCl	32	40.7	25	Zanninovich-Tessarin ³⁾
		1024	57.8		
Liquid ammonia.....	K Br	301.9	210.6	-38	Franklin and Kraus ⁴⁾
		1364	272.9		
		65040	240.2		
Liquid sulphur dioxide..	N(C ₂ H ₅) ₄ I	16	43.1	0	Walden ⁵⁾
		128	51.6		
		1024	54.8		
Acetone.....	KI	144.7	109.4	18	St. v. Laszynski ⁶⁾
		1157.6	145.8		
Benzonitrile.....	Ag NO ₃	9.43	5.2	25	Lincoln ⁷⁾
		151.96	16.4		
Acetonitrile.....	Ag NO ₃	8	54.5	25	Dutoit and Friderich ⁸⁾
		128	118.3		
Pyridine.....	NH ₄ I	76	16.7	25	St. v. Laszynski and St. v. Gorski ⁹⁾
		1234.82	36.9		
Phosphorus oxy-chloride	S(CH ₃) ₂ I	204	26.4	25	Walden ¹⁰⁾
		1224	38.2		
Arsenic trichloride.....	S(CH ₃) ₂ I	250	51.4	25	Walden ¹⁰⁾
		1500	66.6		

¹⁾ Wied. Ann. 26, 161. (1855).

²⁾ Wied. Ann. 52, 328. (1894).

³⁾ Zeit. phys. Chem. 19, 251. (1896).

⁴⁾ Am. Chem. Jour. 23, p. 288. (1900).

⁵⁾ Ber. d. Deutsch. Chem. Gesell. 33, 2362. (1899).

⁶⁾ Zeit. Elektrochem. 2, 55. (1896).

⁷⁾ Jour. Phys. Chem. 3, 457. (1899).

⁸⁾ Bull. Soc. Chem. [3] 19, 327. (1896).

⁹⁾ Zeit. Elektrochem. 4, 290. (1897).

¹⁰⁾ Zeit. anorg. Chem. 23, 209. (1900).

The dielectric constants of the last four solvents given in the table have, to my knowledge, not been determined before. That these solvents possess marked dissociating power the results given in the table clearly show. Hence by the Nernst-Thomson rule they should have high values for their dielectric constants. The dielectric constant of benzonitrile was measured by Drude,¹ and found to be 26.0 at 21° C. Drude also measured the dielectric constant of benzyl cyanide, but his extensive investigation does not include any of the nitriles of the aliphatic series. The dielectric constant of liquid ammonia was measured by Goodwin and Thompson² who found the value 22.0 at -34° C., and by Coolidge,³ who gives the value 16.2 at 14° C. The substituted ammonias, Prof. Kahlenberg⁴ finds, also yield good conducting solutions. In view of the great dissociating power of the nitriles and the substituted ammonias it seemed of special interest to determine the dielectric constants of these compounds, and at Prof. Kahlenberg's suggestion this work was undertaken. The investigation also embraces a number of other organic compounds containing nitrogen, and includes most of the inorganic solvents in which Walden⁵ made electrical conductivity measurements.

During the progress of his researches on non-aqueous solutions, Prof. Kahlenberg collected a choice lot of preparations which he kindly placed at my disposal. This greatly facilitated the experimental part of my work, and I desire to express to him my thanks for this favor.

Method and Apparatus.

In measuring the dielectric constants the method devised and elaborated by Drude⁶ was used. It is unnecessary for me to give a complete description of this method and of the details of

¹ *Zeit. phys. Chem.* 23, 309. (1897).

² *Phys. Rev.* 8, 33. (1899).

³ *Wied. Ann.* 69, 140. (1899).

⁴ *Jour. phys. Chem.* June (1901).

⁵ *Ber. d. Deutsch. Chem. Gesel.* 33, 2372, (1899). *Zeit. anorg. Chem.* 25, 239. (1900).

⁶ *Zeit. phys. Chem.* 23: 267. (1897). See also *Wied. Ann.* 55, 633. (1835); 58, 1; 59, 17 (1896); 60, 23, 500. (1897).

the apparatus employed. The reader is referred to Drude's original articles, after reading which the additional remarks on the method contained in the paragraphs that now follow will be much better understood.

The apparatus used for these measurements was a trifle larger than the one described by Drude. The wave-length of the electrical waves in the two parallel wires in air was about 84 cm. as compared with 74 cm. of the apparatus employed by Drude. A vacuum tube containing hydrogen was used to determine the settings for maximum resonance. It served very well indeed for this purpose.

Of the two methods described by Drude the first is the more accurate, but it necessitates the use of comparatively large quantities of substance, at least 200 cc, which, in most cases, were not available. Moreover, the poisonous nature of many of the compounds made it desirable to work with small quantities which could be kept in a closed cell while under investigation. Drude's "second" method, although less accurate, was therefore chosen. This method enables one to operate with less than a cubic centimeter of solvent and gives results accurate to within two per cent. In this method the substance to be measured is introduced into a small condenser which is placed in the secondary circuit. The length of the secondary circuit is then adjusted for maximum resonance. The dielectric constant corresponding to the length noted is found from a calibration curve representing the results obtained in calibrating the apparatus for the particular condenser.

Four cells similar in form but of different capacities served as condensers. The apparatus was calibrated for each cell with the liquids recommended by Drude, namely: benzene, acetone, water, mixtures of benzene and acetone, and mixtures of acetone and water. Seventeen liquids whose dielectric constants range from 2.26 to 80.9 at 19° C. were prepared. The benzene used for these calibrating solutions was Kahlbaum's thiophene free preparation, purified by crystallization. Its boiling point was 79.2° C. under 744.6 mm of pressure. The acetone was like-

wise Kahlbaum's preparation—it was prepared from the bisulphite compound. It boiled at 55.7° C. under 746 mm of pressure. The water used had a specific conductivity of 3.6×10^{-6} .

In calibrating, the "zero" of the apparatus, obtained by placing a straight piece of copper wire in place of the cell, was frequently redetermined, as a change in the position of certain parts of the apparatus may produce a change of the "zero" point. This precaution was also taken whenever solvents of unknown dielectric constants were under examination. As a check on any change in the capacity of the cells, the calibrating liquids whose dielectric constants were nearest in value to that found for the solvent under examination were introduced into the cell and the settings for maximum resonance determined. In this way any change in the position of the condenser plates could be readily detected. This procedure also gives all the necessary data for calculating the dielectric constant according to the formula given by Drude:¹

$$D = D_1 + (D_2 - D_1) \frac{\cot \frac{2\pi l}{\lambda} - \cot \frac{2\pi l_1}{\lambda}}{\cot \frac{2\pi l_2}{\lambda} - \cot \frac{2\pi l_1}{\lambda}}$$

in which λ is the wave-length of the electric waves in air, D is the dielectric constant sought, l is the setting for maximum resonance when the cell contains the solvent whose dielectric constant is sought; D_1 , l_1 and D_2 , l_2 , are the dielectric constants and settings of the calibrating solutions. In working with pyridine the dielectric constant was calculated by this formula using 84 cm for λ . The value found was the same as the value obtained with the aid of the calibration curve.

From 10 to 30 settings for maximum resonance were made for each solvent examined, and the average of these was the value used for obtaining the dielectric constant.

The methods of dehydrating and rectifying the various solvents will be found under the head of each particular solvent in the statement of results given below.

A series of trial experiments was at first made with the appa-

¹ *Zeit. phys. Chem.* 23, 306. (1897).