ON THE DIELECTRIC CONSTANTS OF NITRILES

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INTRODUCTION

Recent investigations on the dissociative power of solvents and the electrical conductivity of non-aqueous solutions by Dutoit and Friderich,¹ Kahlenberg and Lincoln,² and Lincoln,³ show that salts dissolved in acetonitrile, propionitrile and benzonitrile yield solutions that conduct well. For example, Dutoit and Friderich¹ found the molecular conductivity at 25° C of silver nitrate dissolved in acetonitrile to be 54.5 at a dilution of 1 g-mol in 8 liters, and 118.3 at a dilution of 1 g-mol in 128 liters. The molecular conductivity of aqueous solutions of silver nitrate at 18° C, according to Kohlrausch,⁵ is 88.6 at a dilution of 1 g-mol in 10 liters, and 103.3 at a dilution of 1 g-mol in 166.7 liters. It appears then that dilute solutions of silver nitrate in acetonitrile have a greater molecular conductivity than the corresponding aqueous solutions. The molecular conductivity of silver nitrate dissolved in benzonitrile, although lower than the conductivity of aqueous solutions, is still of considerable magnitude. For example, Lincoln⁶ found the molecular conductivity of silver nitrate dissolved in benzonitrile, at 25° C, to be 5.18 and 16.38 at the respective dilutions of 1 g-mol in 9.43 and 151.96 liters.

¹ Bull. Soc. Chim. (Paris) (3) **19**, 321 (1898).

² Jour. Phys. Chem. **3**, 12 (1899).

³ Trans. Wis. Acad. Sciences, Arts and Letters, **12**, 395. Also Jour. Phys. Chem. **3**, 457 (1899).

⁴ l. c.

⁵ Wied. Ann. **26**, 161 (1885).

⁶ l. c.

Assuming the dissociation theory, the conclusion to be drawn from these results is, that acetonitrile and benzonitrile possess dissociating power in a high degree. On the basis of Nernst's¹ and Thomson's² argument that the greater the dielectric constant of solvents the greater is their dissociative power, the nitriles should have high values for their dielectric constants.

The dielectric constant of benzonitrile was measured by Drude³ and found to be 26.0 at 21° C. Drude measured the dielectric constant of another nitrile, namely, benzyl cyanide, but his extensive investigation does not include any of the nitriles of the aliphatic series. In view of the great dissociating power of acetonitrile, it seemed of special interest to determine its dielectric constant and that of some of its homologues, and at the suggestion of Prof. Kahlenberg the investigation was undertaken.

Lincoln's⁴ measurements of the electrical conductivity of salts dissolved in pyridine show that it must be added to the list of solvents that possess marked dissociating power. Its dielectric constant was therefore also measured, and the value will be found appended to the results found for the nitriles investigated. The homologues of pyridine, the substituted ammonias, together with other compounds, are now being investigated.

During the progress of his researches on non-aqueous solutions, Prof. Kahlenberg has 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 Drude⁵ was used. It is unnecessary for me

¹ Zeit. phys. Chem. **13**, 531 (1893).

² Phil. Mag. **36**, 320 (1893).

³ Zeit. phys. Chem. **23**, 267 (1897).

⁴ l. c.

⁵ l. c. See also Wied. Ann. **55**, 633 (1895); **58**, 1; **59**, 17 (1896); **60**, 28, 500 (1897).

to give a complete description of this method and of the details of the apparatus employed, since Drude has already done this. The reader is therefore simply referred to Drude's original article after reading which the additional remarks on the method that are 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 the nitriles 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 2 percent. 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.

Three 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. pressure. The acetone was Kahlbaum's preparation; it was prepared from the bisulphite compound. It boiled at 55.7° 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 constant 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 developed 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.

¹ I. c., p. 290.

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 apparatus in order to test it thoroughly. The dielectric constants of ethyl ether, chloroform, ethyl benzoate, salicylic aldehyde, benzonitrile, and nitrobenzene were measured; and the results obtained agreed very well with those given by Drude. It is therefore, entirely superfluous to again report the numerical results obtained for these substances.

Experimental Results

The dielectric constants of the following aliphatic nitriles were measured: hydrocyanic acid, acetonitrile, propionitrile, butyronitrile, isopropyl cyanide, valeronitrile, isobutyl cyanide, and capronitrile. In the aromatic series benzonitrile, benzyl cyanide, and orthotoluenitrile were measured.

Hydrocyanic Acid

The sample of hydrocyanic acid used was prepared in the usual way by slowly adding a strong aqueous solution of potassium cyanide to sulphuric acid of sp. gr. 1.25 in a retort connected with a reflux condenser kept at 30° C. The gas was then dried at 30° C by passing it through a series of three large U-tubes, kept at 30° C, and containing fused calcium chloride. The gas was condensed in a tube provided with glass stop-cocks suspended in a bath at 0°. A colorless liquid was thus obtained, which left no residue upon evaporation. Some of the liquid was introduced into the cell adapted for the measurement of liquids having a high dielectric constant. The cell was securely stoppered and the measurements were made at 21° C. No appreciable absorption was observed, the position for maximum resonance being about as well defined as in the case of acetone. The dielectric constant found is higher than the dielectric constant of water. This necessitated an extrapolation of the calibration curve in order to get an approximate value. The dielectric constant found in this way is 95.0 ± 3.5 .

After this exceedingly high result had been obtained a second sample of hydrocyanic acid was prepared by redistilling the first sample from a water-bath kept at 30° C. The gas was again passed through the drying tubes and condensed as before. Measurements with this sample gave the same readings for maximum resonance as in the first case. The temperature coefficient is negative; but it was not accurately determined.

The specific conductivity of the sample of hydrocyanic acid was not determined; but an investigation of the conductivity and other properties of salts dissolved in hydrocyanic acid is now in progress in this laboratory. Perhaps the specific conductivity will be low enough to permit the use of Nernst's apparatus for determining the dielectric constant. The improved form of Nernst's apparatus as described by Turner¹ will soon be at hand, when an attempt to measure the dielectric constant of hydrocyanic acid by means of it will be made.

Acetonitrile

The sample of acetonitrile first measured was obtained by distilling a sample of Kahlbaum's make. Its boiling-point was very constant, being 80.9° C under a pressure of 745 mm. The average of four determinations gave the value 36.5 for the dielectric constant at 21° C.

A second sample, prepared by Prof. Kahlenberg from the Kahlbaum preparation by dehydrating it with phosphorus pentoxide and redistilling twice was measured. Its boiling-point was 80.7° under 749 mm pressure. The measurements were made at 22° and gave the same result as was obtained with the first sample.

A third sample, also furnished by Prof. Kahlenberg, was finally measured. This sample was twice dehydrated with larger quantities of phosphorus pentoxide than were used in the previous case, and was distilled from phosphorus pentoxide. It had a boiling-point of 80.2° C under a pressure of 736 mm. The dielectric constant was calculated by the formula given above and found to be 36.1 at 21° .

¹ Zeit. phys. Chem. 35, 385 (1900).

Propionitrile

This sample was Schuchardt's preparation. Its boiling-point was 94.6° . The average of four determinations at different times gave the value 26.5 for the dielectric constant at 22°C . The absorption was slight.

Butyronitrile

The sample tested was Schuchardt's preparation. It was redistilled from calcium chloride. Its boiling-point was 116.5° to 118°C under 742 mm of pressure. The average of three different determinations was 20.3 at 21°C .

Isopropyl Cyanide

The sample was Schuchardt's preparation. It was dehydrated with calcium chloride and redistilled. Its boiling-point was 106° – 107°C under 744 mm pressure. The average of three determinations gave the value 20.4 for its dielectric constant at 24°C .

Valeronitrile (normal)

The sample was obtained from Schuchardt. It was redistilled from calcium chloride, and the portion which distilled between 137° – 139°C , under 743 mm of pressure, was taken for the measurements. Its dielectric constant was found to be 17.4 at 21°C .

Isobutyl Cyanide

The sample was Schuchardt's preparation; it was redistilled from calcium chloride, and the portion distilling between 129° – 130.5°C under a pressure of 742 mm was taken for the measurements. Its dielectric constant was found to be 17.95 at 22°C .

Capronitrile

The sample used was obtained from Schuchardt. It was redistilled from calcium chloride, and the portion distilling between 153° – 154°C , under 743 mm pressure, was taken for the measurements. Its dielectric constant was found to be 15.5 at

22° C. The higher members of the series show a slight amount of absorption; but the maximum resonance is still well enough defined without increasing the intensity of the oscillations in the secondary circuit.

Toluenitrile (ortho)

Schuchardt's preparation was redistilled from calcium chloride. A straw-colored distillate, boiling at 200°–201° C, under a pressure of 733 mm, was thus obtained. Its dielectric constant was found to be 18.5 at 23° C. It showed slight absorption.

Pyridine

The first sample was Schuchardt's preparation. It was redistilled and found to boil from 115.5° to 117° under 745 mm pressure. With this several measurements were made, the average of the results for the dielectric constant being 12.35 at 21° C.

A second sample was furnished by Prof. Kahlenberg. Kahlbaum's best preparation was carefully purified by him according to the method given by Ladenburg.¹ The portion boiling at 114° C under 744.6 mm of pressure, was used for the measurements. The dielectric constant was found to be 12.55 at 20° C, a result which agrees well with the foregoing. The settings for maximum resonance were well defined.

Quinoline

Two samples of quinoline were measured. The first was obtained by redistilling Schuchardt's preparation marked, "Quinoline from Coal Tar." The portion which distilled at 232° C under 746 mm of pressure, was measured. Its dielectric constant was found to be 8.7 at 22° C.

The second sample was a synthetic preparation, made by Messrs. Maxon and Thomas in this laboratory according to the method of Skraup. The boiling-point of the sample measured was 232° C under 746 mm of pressure. Its dielectric constant

¹ Liebig's *Annalen*, 247, 1 (1888).

was found to be 8.9 at 20.5° C. The agreement is close enough to fall within the limit of error. The absorption is slight. These values of the dielectric constant agree well with the result, 8.9, obtained by Turner,¹ who worked with Nernst's apparatus.

The foregoing results are summarized in the following table, the third column giving the temperatures at which the dielectric constants were determined.

TABLE I

Solvent	Formula	<i>t</i> °	Dielectric constant (Air = 1)
Hydrocyanic acid	HCN	21	9.5
Acetonitrile	CH ₃ CN	21	36.4
Propionitrile	C ₂ H ₅ CN	22	26.5
Butyronitrile	C ₃ H ₇ CN	21	20.3
Isopropyl cyanide	(CH ₃) ₂ CHCN	24	20.4
Valeronitrile(<i>n</i>)	C ₄ H ₉ CN	21	17.4
Isobutyl cyanide	(CH ₃) ₂ CHCH ₂ CN	22	17.95
Capronitrile	(CH ₃) ₂ CHCH ₂ CH ₂ CN	22	15.5
Benzonitrile ²	C ₆ H ₅ CN	21	26.0
Benzyl cyanide ³	C ₆ H ₅ CH ₂ CN	21	14.9
Toluenitrile (ortho)	C ₆ H ₄ < $\begin{smallmatrix} \text{CH}_3 \\ \text{CN} \end{smallmatrix}$	23	18.4
Pyridine	C ₅ H ₅ N	21	12.4
Quinoline ⁴	C ₉ H ₇ N	21	8.8

The results obtained with the aliphatic nitriles are also presented graphically in Curve I, in the accompanying figure. The dielectric constants are plotted as ordinates, and the members of the homologous series are noted as abscissæ, a definite distance being chosen for each addition of CH₂.

Curve II, represents Drude's⁵ values for the dielectric constants of the alcohols, while Curve II(*a*), presents approximately

¹ Zeit. phys. Chem. **35**, 385 (1900).

² Measured by Drude, who found 26.0 at 21° C.

³ Drude found 15.0 at 19° C.

⁴ Turner found 8.9 with Nernst's apparatus.

⁵ l. c.

the values obtained by Thwing,¹ Nernst,² and Tereschin³ for the dielectric constants of the alcohols. Curve III. represents the values obtained by Drude for the dielectric constants of the fatty acids. Hence in Curve I., R represents the cyanogen group (CN), in Curves II. and II(a), R represents the hydroxyl group (OH), while in Curve III. it represents the carboxyl group (COOH).

Discussion of Results

The high dielectric constant found for hydrocyanic acid is of special interest from a theoretical point of view, since by the Nernst-Thomson rule, that the greater the dielectric constant of a solvent, the greater is its dissociating power, hydrocyanic acid should show extraordinary dissociating power. The

¹ Zeit. phys. Chem. 14, 286 (1894).

² Ibid., 14, 622 (1894).

³ Wied. Ann. 36, 792 (1889).

publication of the electrical conductivity measurements of salts dissolved in hydrocyanic acid, which are in progress in this laboratory, will therefore be awaited with interest.

The marked differences in the physical properties between the first two members of any homologous series are well exemplified here by the great differences in the dielectric constants between hydrocyanic acid and acetonitrile, water and methyl alcohol, formic acid and acetic acid. The curves show that an increase in the size of the molecule by the addition of carbon and hydrogen lowers the dielectric constant. This also holds for the aromatic nitriles and for pyridine and quinoline.

The isomeric nitriles examined have nearly the same dielectric constant, the iso-compounds showing a slightly higher value.

A comparison of the values of the dielectric constants of the alcohols and nitriles by means of Curves I. and II. shows that for high frequency oscillations the nitriles have higher values for their dielectric constants throughout than the corresponding alcohols. For oscillations of low frequency the values for the dielectric constants of the higher members of the alcohol series are nearly the same as the values found for the corresponding nitriles with high frequency oscillations. Compare Curves II(a) and I. Since the nitriles show but slight absorption, the dielectric constants when determined with Nernst's apparatus will probably agree closely with the values found with Drude's apparatus.

The researches of Dutoit and Friderich¹ on the electrical conductivity of salts dissolved in acetonitrile, propionitrile, and butyronitrile show that the dissociating power decreases in the order in which the solvents are named. Their dielectric constants also decrease in the order named, thus supporting the Nernst-Thomson rule. This relation between the dielectric constant and the electrical conductivity is illustrated by the following table. The molecular conductivity measurements are taken from the work of Dutoit and Friderich. In the table μ stands

¹ l. c.

for the molecular conductivity at 25° C, and z' the number of liters in which one gram-molecule of silver nitrate is contained.

TABLE II

Solvent	z'	μ_{∞}	Dielectric constant at 21° C.
Acetonitrile	64.0	103.7	36.4
Propionitrile	63.7	46.0	26.5
Butyronitrile	75.6	25.4	20.3

Propionitrile and benzonitrile have about the same dielectric constant; but the molecular conductivities of silver nitrate dissolved in these nitriles are quite different, as a comparison of the results in the following table shows. The molecular conductivities for silver nitrate in benzonitrile are taken from Lincoln's¹ work. The molecular conductivities for silver nitrate are taken from the work of Dutoit and Friderich.²

TABLE III

Benzonitrile		Propionitrile	
z'	μ_{∞} at 25° C.	z'	μ_{∞} at 25° C.
24.06	7.66	32.0	34.9
58.98	11.19	63.7	46.0
83.92	13.41		

The molecular conductivities of silver nitrate dissolved in pyridine and in butyronitrile furnish another interesting comparison.

TABLE IV

Solvent	z'	μ_{∞} at 25°	Dielectric constant
Butyronitrile ³	75.6	25.4	20.3
	150.4	32.1	
Pyridine ⁴	60.9	30.17	12.4
	140.7	36.21	

¹ l. c., p. 422.

² l. c., p. 330.

³ Dutoit and Friderich. l. c., p. 331.

⁴ Lincoln. l. c., p. 423.

While Table II. shows that the Nernst-Thomson rule holds for the three members of the same homologous series, Table III. demonstrates that chemically analogous substances having about the same dielectric constants may nevertheless yield solutions (containing the same solute) with very different electrical conductivities. Table IV. shows conclusively that a pyridine solution of silver nitrate conducts better than a corresponding one in butyronitrile, notwithstanding the fact that the dielectric constant of pyridine is only 61 percent of that of butyronitrile. We have here then a striking case in which the Nernst-Thomson rule does not hold. It is well in this connection to bear in mind the fact that Goodwin and Thompson¹ have found that liquid ammonia is also a striking exception to the Nernst-Thomson rule.

It is evident from the above results that the Nernst-Thomson rule holds at best only for the members of the same homologous series. It is also clear that the dielectric constant of a solvent is not the sole factor determining whether solutions in that solvent will conduct electricity or not.

I am indebted to Prof. Kahlenberg for his suggestions and assistance, and I take this means of acknowledging the same.

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¹ Phys. Review, 8, 43 (1899).