ON THE RELATION BETWEEN ELECTROLYTIC CON-
DUCTION, SPECIFIC INDUCTIVE CAPACITY
AND CHEMICAL ACTIVITY OF CER-
TAIN LIQUIDS (WITH A BIBLIOG-
RAPHY OF DIELECTRIC
CONSTANTS)

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Introduction

For a number of years investigations have been carried on in this laboratory on the relations between electrolytic conduction, specific inductive capacity and chemical activity. The present investigation is a natural outgrowth of that work.

In 1901 Schlundt¹ published an interesting set of exceptions to the Nernst²-Thomson³ rule. He showed conclusively that this rule could not be held in the light of the facts presented. In the case of hydrocyanic acid, for example, we have the exceptionally high dielectric constant of 95. One would expect from the rule above-mentioned that substances dissolved in this solvent would yield exceedingly good conducting solutions, but such is not always the case. While some substances which give conducting solutions with water give better conducting solutions with liquid HCN, on the other hand, many substances which yield excellent conducting solutions with water yield very poorly conducting solutions with HCN. Again, in the case of the amines, whose dielectric constants are low, we get solutions that are fairly good conductors of electricity. A pyridine solution of silver nitrate is a better electrolyte than a butyro-nitrile solution of silver nitrate although the dielectric constant of pyridine (12.4) is very much lower than that of butyro-nitrile (20.3). Other marked exceptions noted by Franklin and Kraus⁴ are those of solutions in which liquid ammonia

¹ Jour. Phys. Chem., 5, 157, 503 (1901).

² Götting. Nach., 12 (1893); Zeit. phys. Chem., 13, 53 (1894).

³ Phil. Mag., 36, 320 (1893).

⁴ Am. Chem. Jour., 207, (1900).

plays the part of solvent. Kahlenberg and Lincoln¹ have shown that ferric chloride in chloral does not give a solution having an appreciable conductivity, while ferric chloride in ethyl acetate gives a solution which does conduct. For these solvents, Drude² found the values of the dielectric constants to be 6.67 and 5.85 respectively. From a consideration of the facts presented, it is clear that we must recognize the important rôle which the solvent plays. Whether a solution will conduct or not depends as much upon the solvent as upon the dissolved substance. It has been said that the conductivity of a solution depends not only on the number of ions present, but also on their speed. However, solutions are known, which, by freezing- or boiling-point methods, contain few or no ions and still conduct well, and yet their viscosity does not vary enough from that of good conducting aqueous solutions of the same solute to admit of the explanation that the difference in conductivity is due to the difference in the speed of the ions in the respective solutions.

In 1903, Kahlenberg in his work upon the sulphocyanates and mustard oils³ pointed out that solutions of trichloroacetic acid in the mustard oils are extremely poor conductors, notwithstanding the fairly high dielectric constant of some of these solvents, and that this non-conducting solution of trichloroacetic acid still acts rapidly upon carbonates and metals. I have personally confirmed the results obtained by Prof. Kahlenberg, and some new examples illustrating the same principle will be given in the present paper. It has been the popular thing for years to believe that such action could only take place in conducting solutions. The researches of Patten⁴ upon the action of solutions of hydrochloric acid in various solvents upon the metals show that this belief is untenable. There is also a current belief that the presence of minute quantities of water is sufficient to make a non-conducting solution conduct. When investi-

¹ Jour. Phys. Chem., 3, 12 (1899).

² Zeit. phys. Chem., 23, 309 (1897).

³ Ibid., 46, 64 (1903).

⁴ Trans. Wis. Acad. Sciences Arts and Letters, 14, Part I, 316 (1903); Jour. Phys. Chem., 7, 153 (1903).

gators were at a loss to explain the conductivity of certain non-aqueous solutions they neatly avoided accepting the true explanation by saying that the conductivity could only be due to the presence of minute traces of moisture.¹ This belief, however, has no foundation in fact. A good illustration will be given later.

In the present investigation I have continued the researches begun by Prof. Kahlenberg on the sulphocyanates and mustard oils, and have gone over the work of Eggers² and Walden³ on the dielectric constants of these substances. I have also determined the dielectric constants of a considerable number of liquids which have not been previously measured and have checked others previously determined. The dielectric constants of a number of previously uninvestigated solutions have been determined and their conductivity and chemical activity studied. Two further solvents, methyl and ethyl silicates, have been prepared, their dielectric constants determined, and their specific conductivity and the specific conductivity of solutions of a few substances in them measured. The relation between chemical activity and electrolytic conductivity has been more fully investigated.

In addition it was thought that a complete bibliography of the work done on dielectric constants would be of great benefit to those who have occasion to deal with this interesting subject. I am greatly indebted to the article by L. Graetz,⁴ for a considerable number of references which I should not have otherwise secured. I have not had access to all of the literature there referred to, so the titles of some of the original articles could not be obtained. However, the references are included in the bibliography.

Method and Apparatus

All conductivity measurements were made at 25° C. The Kohlrausch method was employed, a glass-stoppered graduated resistance cell being used.

¹ Trans. Faraday Soc., Vol. 1, Pt. 1, 59 (1905).

² Jour. Phys. Chem., 8, 14 (1904).

³ Zeit. phys. Chem., 46, 103 (1903).

⁴ Winkelmann: Handb. d. Phys., 4, 1 Teil 1 (1903).

The dielectric constant apparatus used was that devised by Drude.¹ A Tesla transformer was used. The coil and transformer were made by Drude's mechanician and personally inspected by Prof. Drude before being shipped. The remainder of the apparatus was built at this University. The use of the transformer enabled me to make measurements of greater accuracy and with considerably more ease and certainty than by the method employed by Schlundt and Eggers. A new Zehnder's vacuum tube was procured, which was very much more satisfactory than the one previously used in this laboratory. The apparatus now stands so perfected that it is but a matter of a few minutes time to make a very accurate measurement. The liquids recommended by Drude, *viz.*,—benzene, acetone, water, and mixtures of benzene and acetone, and acetone and water, seventeen in number, were used to calibrate the condensers employed. The benzene and acetone used were pure, and were carefully dried and redistilled. The water used was specially prepared and had a very low conductivity. As a check several substances of known dielectric constant were run. In determining the "zero" of the apparatus it has been the custom to use a copper wire. I found it very much more satisfactory to select about three liquids of the series and by running these determine any change in the "zero". The advantages of this process are these: If there was any error in the original "zero" it would thus be corrected. Other things being equal, the average of three "zeros" so determined would be more nearly correct than the determination of one "zero". Lastly, when a wire is used, the luminosity is so greatly increased that it is more difficult for the eye to judge the maximum resonance than when a liquid is used. The "zero" was checked very frequently. With such precautions it is possible to secure very satisfactory results.

Two condensers were used. One of the L form² for dielectric constants below twenty and one of the bulb form for dielectric constants above twenty. These gave calibration curves of the desired form and accuracy.

¹ Zeit. phys. Chem., 23, 267 (1897).

² Jour. Phys. Chem., 8, 16 (1904).

The kerosene about the spark gap of the vibrator had to be renewed occasionally, though less frequently than when the transformer is not used. Filtering was not as satisfactory as renewing with fresh material. It is essential to the success of the method that the kerosene be kept clean.

Experimental Part

In the light of the facts presented in Prof. Kahlenberg's work upon the conductivity of solutions in the sulphocyanates and mustard oils it seemed desirable to investigate further solutions in which a mustard oil plays the part of solvent. Accordingly an exhaustive list of substances was tested. The results obtained were in the main merely qualitative in character. Where solution took place the conductivity was measured. The materials used were of standard make (Schuchardt or Kahlbaum) and were marked pure. The hydrochloric acid was dried by passing over phosphorus pentoxide. The solution containing the hydrochloric acid was momentarily exposed to the air while being poured into the resistance cell, which was then stoppered. Therefore, the conductivity of this solution probably is too high, due to the moisture taken up from the air. The solvents used were carefully dried and redistilled. For the sake of convenience I have tabulated the results obtained. When the statement is made that the solution does not conduct, it is meant that it does not conduct better than the solvent used.

TABLE I—CONDUCTIVITY OF VARIOUS SUBSTANCES DISSOLVED IN THE MUSTARD OILS

Solvent	Solute	Sp. cond.	Remarks
Allyl mustard oil			
"	Hydrochloric acid	2.48×10^{-5}	Dried, b.p. 150° . Pure
"	Sulphuric acid (fuming)	1.04×10^{-4}	Saturated with dried gas
"	Nitric acid (conc.)		Decomposed the solvent
"	Telluric acid		Decomposed oil. ¹ Does not conduct
"	Acetic acid	2.8×10^{-5}	Not soluble. No change
"	Trichloroacetic acid	3.5×10^{-5}	1 part acid to 10 parts oil
"	Oxalic acid		Saturated solution
"	Tartaric acid		Slightly sol. Does not conduct
"	Citric acid		" " "
"	Salicylic acid		Insoluble. No change
"	Succinic acid		Slightly sol. Does not conduct
"	Quinine sulphate		Insoluble. No change
"	Quinine (pure)		Slightly soluble. Does not conduct
"	Brucine chloride		Soluble. Does not conduct
"	Atropine		Insoluble. No change
"	Morphine hydrochloride		Very soluble. Does not conduct
"	Saponine		Sparingly soluble. Does not conduct
"	Cinchonidine		Soluble. Does not conduct
"	Monomethyl aniline		Sparingly soluble. Does not conduct
"	Dimethyl aniline		Miscible. Does not conduct
"	Ortho toluidine		" " "
"	Benzylamine		" " "
"	Tripropylamine		" " "

¹ Conductivity not appreciably greater than that of pure solvent.

TABLE I (Continued).—CONDUCTIVITY OF VARIOUS SUBSTANCES DISSOLVED IN THE MUSTARD OILS

Solvent	Solute	Sp. cond.	Remarks
Allyl mustard oil	Phenyl hydrazine	4.2×10^{-5}	Heats up. Miscible
"	Acetyl chloride		Miscible. Very slight increase in conductivity
"	Ethyl chloride		Miscible. Does not conduct
"	Sulphur monochloride	8×10^{-5}	Miscible
"	Tetrachloride of tin		Decomposes solvent
"	Trichloride of antimony	30×10^{-4}	Quite soluble
"	Trichloride of arsenic		Miscible. Heats. Does not conduct
"	Trichloride of iodine		Reacts violently
"	Aluminium chloride		Insoluble. No change.
"	Isobutylene bromide		Miscible. Does not conduct
"	Mercuric bromide	7.8×10^{-5}	Quite soluble. Saturated solution
"	Nickel bromide		Insoluble. No change
"	Cadmium bromide		Insoluble
"	Iodoform	5.3×10^{-5}	Soluble
"	Iodide of lead		Insoluble
"	Mercurous iodide	4.3×10^{-5}	Sparsingly soluble. Saturated solution
"	Mercuric iodide	9.8×10^{-5}	Somewhat soluble. Saturated solution
"	Copper iodide		Slightly soluble. Does not conduct
"	Cadmium iodide		Insoluble
"	Arsenic triiodide (com.)		Very soluble. Conducts
"	Arsenic triiodide (pure)	1.4×10^{-4}	Saturated solution. Purified by extraction with mustard oil
"	Iodide of tin	4.08×10^{-4}	Soluble saturated solution
"	Triiodide of iron	2.2×10^{-4}	Extremely soluble. Dilute solution

TABLE I (*Continued*).—CONDUCTIVITY OF VARIOUS SUBSTANCES DISSOLVED IN THE MUSTARD OILS

Solvent	Solute	Sp. cond.	Remarks
Allyl mustard oil	Manganese iodide	9.7×10^{-5}	Slightly soluble
"	Zinc iodide	3.1×10^{-4}	Slightly soluble. Saturated solution Insoluble. Does not conduct
"	Strontium iodide		Insoluble
"	Lithium iodide		"
"	Sodium iodide		"
"	Ammonium iodide		"
"	Phosphorus triiodide	3.8×10^{-4}	Fairly soluble
"	Strychnine, mercuric iodide	5.8×10^{-5}	Sparsingly soluble. Saturated solution
"	Propyl iodide		Miscible. Does not conduct
"	Bromine (liq.)		Reacts violently
"	Iodine	1.15×10^{-3}	Dissolves readily. Saturated solution
Phenyl mustard oil	"	2.3×10^{-4}	Less soluble than in allyl mustard oil
Phenyl sulphocyanate	"	1.44×10^{-3}	Quite soluble. Saturated solution
Phenyl isocyanate	"		Dissolves. Does not conduct
Allyl mustard oil	Cyanogen iodide	1.36×10^{-3}	41.09 p. c. ICN
"	Pyridine	1.88×10^{-5}	Equal parts by volume
"	Ethyl carbonate		Miscible. Does not conduct
"	Sulphur		Somewhat soluble. Does not conduct

IODINE IN THE MUSTARD OILS.—Iodine dissolves in allyl mustard oil in considerable amount, and gives a conducting solution. During solution heat is evolved, showing that the chemical action is fairly pronounced. An addition product is evidently formed. A series of quantitative measurements upon the specific conductivity of various strengths of solution were undertaken. Small weighed quantities of iodine were added from time to time and the conductivity measured. At first the conductivity did not reach a maximum for nearly half an hour after the addition of iodine, then when once obtained the conductivity gradually diminished again. The maximum was recorded. As the determinations proceeded, this time factor, *i. e.*, the time required for the maximum conductivity to develop became less and less and the tendency for the conductivity to decrease became greater and greater. The readings became approximately constant when a specific conductivity of 6.8×10^{-4} was reached. Further addition of iodine did not materially change the conductivity. The reason for this constancy evidently is that the tendency for the conductivity to decrease became equal to the natural increase in conductivity due to the addition of small quantities of iodine. It will be noted that the maximum conductivity so obtained is considerably less than that obtained when a saturated solution of iodine in the mustard oil is made up directly, *i. e.*, when enough iodine is added *at once* to make a saturated solution. This solution had a specific conductivity of 1.14×10^{-3} . In the case where the saturated solution was made by addition of small quantities of iodine from time to time the addition product was continually forming and thereby reducing the conductivity. In the case where the excess of iodine was added at one dose the proportion of the addition product in the solution was much less and the conductivity higher. Owing to this time factor any attempt to make an accurate measurement of the specific conductivity of a solution of certain strength is futile.

Another fact in favor of the addition product idea is that from a freshly prepared solution of iodine in mustard oil the iodine may be extracted by shaking with an aqueous solution of

sodium thiosulphate. But after standing for some time this extraction becomes more difficult, finally reaching a point where it is apparently impossible to free the entire iodine content. However, this might be possible in time.

A solution of iodine in phenyl mustard oil was made which showed a specific conductivity of 1.90×10^{-4} . The specific conductivity of the solvent was 1.4×10^{-6} . Having observed the effect of time upon the conductivity of the iodine-allyl mustard oil solution and sought for its probable explanation, the same question arose in the case of the iodine-phenyl mustard oil solution. In view of the constitution of the latter mustard oil the same behavior would not be expected. Such was found to be the case. The solution having an initial specific conductivity of 1.90×10^{-4} was allowed to stand for ninety-six hours. At the end of that time the specific conductivity had experienced but a very slight change, it having risen only to 2.00×10^{-4} .

In connection with the behavior of iodine in the mustard oils as regards electrical conductivity, it is interesting to note that iodine also dissolves in pyridine and alcohol to give conducting solutions. The specific conductivity of the pyridine used was 1.6×10^{-5} . This value was raised to 1.14×10^{-3} by the addition of iodine. In like manner the specific conductivity of alcohol was changed from 5.8×10^{-6} to 1.61×10^{-4} for a saturated solution of iodine.

It has been observed that iodine dissolves in the phenyl mustard oil to give a conducting solution. According to Brühl¹ those substances which contain oxygen should have a high dielectric constant and high dissociating power. Now iodine is soluble in phenyl isocyanate. Iodine dissolved in phenyl isocyanate does *not* yield a conducting solution. The dielectric constant of phenyl isocyanate is 8.77. Here we have an instance where it is not the substance containing the oxygen which gives a high "dissociating power" and therefore a conducting solution, but a substance containing sulphur which has displaced the oxygen. Numerous exceptions have been found to Brühl's generalization, and it is difficult to see how it can possibly be held.

¹ Zeit. phys. Chem., 18, 514 (1895).

ARSENIC TRIIODIDE.—Arsenic triiodide as ordinarily obtained contains some free iodine. This can be extracted by repeated decantations of allyl mustard oil. The remaining crystals are red and I found that they analyzed up to the theoretical composition required for the formula AsI_3 . The pure salt so obtained is somewhat soluble in the mustard oil at room temperature, and at 60°C it is extremely soluble. Upon cooling a few degrees below this temperature, beautiful crystals of AsI_3 separated out. The conductivity of a saturated solution of AsI_3 in allyl mustard oil was measured, as indicated in the table. The figure found for the specific conductivity was 1.4×10^{-4} .

A short U tube was filled with AsI_3 and the salt fused. Wires were introduced and a pressure of 154 volts impressed, a D'Arsonval galvanometer being in the circuit to detect any current which might pass. The galvanometer showed no deflection. The fusion was then allowed to solidify. The solid salt did not conduct. Therefore, it is perfectly safe to say that AsI_3 does not conduct the current appreciably.

AsI_3 was dissolved in allyl mustard oil and the solution electrolyzed. A gummy deposit was obtained upon the cathode which showed the presence of a considerable amount of arsenic. The electrolytic cell had to be water-jacketed to prevent boiling. Platinum electrodes were used and the anode was corroded considerably.

SULPHOCYANIC ACID.—Following out the work done in this laboratory upon the sulphocyanates and mustard oils by Prof. Kahlenberg¹ it was desired to prepare sulphocyanic acid and investigate its properties as a solvent. Eggers² found the following results for the dielectric constants of the mustard oils and sulphocyanates measured by him.

¹ Zeit. phys. Chem., 46, 64 (1903).

² l. c.

TABLE II

Material	Dielectric constant	Temp.
Methylsulphocyanate	33.3	15°.5 C.
Ethylsulphocyanate	31.2	11°.5 C.
Amylsulphocyanate	17.1	19°.5 C.
Ethyl mustard oil	22.0	15°.0 C.
Allyl mustard oil	17.3	17°.6 C.

From these results one would naturally expect to find the dielectric constant of sulphocyanic acid to be higher than that of methyl sulphocyanate which has a value of 33.3. It has been pointed out that the dielectric constant decreases with the increase of molecular weight in a homologous series.¹ Walden² even goes so far as to predict the value to be 85.9 or 85.1 for HCNS. He finds that in homologous series in general the first addition of CH_2 produces a decrease in the value of the dielectric constant of approximately 50. Therefore, since the dielectric constant of the methyl compound is 35.9 (the figure obtained by him) the dielectric constant of the sulphocyanic acid should be $35.9 + 50 = 85.9$. Or, comparing methyl alcohol with methyl sulphocyanate whose dielectric constants are 32.5 and 35.9 respectively, the CNS group exceeds the OH group about 3.4. Then since water has a dielectric constant of 81.7 (the value used by him) the dielectric constant of sulphocyanic acid should have a value of $81.7 + 3.4 = 85.1$.

There is considerable question whether Walden's reasoning is justifiable. He quotes³ the cases of water and methyl alcohol, where the difference is 49.2, formic acid and acetic acid where the difference is 50.54, and hydrocyanic acid and acetonitrile where the difference is 59. Thus it will be seen that in the examples that he himself gives there is considerable deviation from the rule he tries to establish. In the case of liquid ammonia, whose dielectric constant is 16.2⁴ and methylamine whose

¹ Schlundt: l. c.

² l. c.

³ Zeit. phys. Chem., 46, 187 (1903).

⁴ Coolidge: Wied. Ann., 69, 130 (1899).

dielectric constant is 10.5,¹ we have no relation such as that suggested by Walden.

After several very unsatisfactory attempts were made to prepare pure HCNS, the method of Klason² was tried with somewhat better results. The reagents employed were HCl and KCNS. The two aqueous solutions, one containing 32 grams KCNS and the other 30 cc. of concentrated hydrochloric acid, were cooled to zero. The apparatus consisted of a distilling flask with separatory funnel; a dryer, consisting of four large glass-stoppered U tubes filled with CaCl_2 immersed in a constant temperature bath kept at 40° C.; the condensing chamber, consisting of a smaller U tube immersed in a freezing-mixture of snow and salt, a manometer, and a suction-pump.

The cold KCNS solution was poured into the distilling flask, connections were made and a vacuum of 40 mm or less secured. The cold HCl solution was then cautiously run in by means of the separatory funnel. After starting the action by means of a little heat, the reaction went on of its own accord. A pressure of less than 40 mm was maintained throughout the process. The condensed solid obtained was straw-yellow in color. Polymerization started in even at the temperature of the freezing-mixture. It was found impossible to prevent this, even with a freezing-mixture of calcium chloride and snow. The melted substance became darker, heated up considerably and then solidified to a pumiceous structure.

Some of the unpolymerized material was quickly transferred to a condenser, sealed, and an attempt made to measure its dielectric constant. It showed *complete absorption*. Polymerization was allowed to set in and as soon as this process began, the absorptive power decreased. Finally, when the process was complete, a good resonance was obtained, and the dielectric constant found to be 4.9.

Owing to the extreme instability of the compound it was not possible to make any conductivity measurements.

It will be noted that the value 4.9 is for the polymerized

¹ Schlundt: l. c.

² Jour. prakt. Chem., 35, (2) p. 401.

material. It is not pretended that it is the true value, for the product obtained was unsatisfactory. It is very doubtful to my mind whether pure anhydrous sulphocyanic acid has ever been made. The properties as given by the different authorities are very unlike. The experimental difficulties encountered in the preparation and handling of the product are so great that satisfactory results are well nigh impossible. Why this material should show complete absorption I am at loss to state, but such is the fact.

METHYL SILICATE.—This material was prepared, according to the method of Friedel and Crafts,¹ from silicon tetrachloride and absolute methyl alcohol. Considerable care has to be exercised to procure *absolute* methyl alcohol. It was distilled from anhydrous copper sulphate and finally from sodium. The alcohol was added little by little to the silicon tetrachloride contained in an *open* distilling flask. When the violent reaction was over distillation was commenced. The portion passing over between 120° and 122° C was collected separately and several times redistilled.

Measurements of the dielectric constant made upon separate samples of methyl silicate gave the values 5.9 and 6.00. Ferric chloride dissolves in methyl silicate and gives a conducting solution. The specific conductivity of the solvent was measured and found to be 1.6×10^{-6} . The specific conductivity of the saturated solution of ferric chloride was 2.28×10^{-4} . Trichloroacetic acid dissolves freely, but does *not* give a conducting solution. The dielectric constant of this solution was found to be 10.3.

ETHYL SILICATE.—A sample of ethyl silicate of Schuchardt's manufacture was redistilled and found to boil at 165°.5 C at 740 mm pressure. The specific conductivity of this solvent was found to be less than 3×10^{-8} . It dissolves iodine in a considerable amount. The dielectric constant of the solvent was found to be 4.10, and the dielectric constant of a saturated solution of iodine was 4.25. Here we have a slight rise in the value of the dielectric constant caused by the dissolved halogen.

¹ Ann. Chim. Phys., (4) 9, 32 (1856).

Trichloroacetic acid dissolves readily in ethyl silicate but does *not* give a conducting solution, its specific conductivity being less than 3×10^{-5} . The dissolved trichloroacetic acid, however, raises the dielectric constant from 4.10 to 5.97 for an approximately saturated solution. This solution, though *non-conducting*, attacks metallic magnesium rapidly with the evolution of hydrogen gas.

DIELECTRIC CONSTANTS OF THE MUSTARD OILS AND SULPHOCYANATES.—In view of the discrepancies existing between the measurements made by Walden¹ and Eggers¹ it was deemed advisable to repeat the determinations.

The materials used were of standard make and were dried with fused CaCl_2 and redistilled. Conductivity measurements were then made as a check on their purity. It will be observed that only in one case was I able to secure a specific conductivity of the order obtained by Walden. With the utmost care and impartiality, this was impossible. The boiling-point determinations showed the materials to be pure.

The dielectric constant was carefully measured in each case. The values obtained appear in Table III below. For reference I have also included the results obtained by Eggers and by Walden.

¹ l. c.

TABLE III.—COMPARISON OF RESULTS OBTAINED ON THE MUSTARD OILS AND SULPHOCYANATES

Substance	D. C. Mathews	D. C. Eggers	D. C. Walden	Sp. C. Mathews	Sp. C. Walden	B. P. Mathews	B. P. Eggers	B. P. Walden	Temp.
Ethylsulphocyanate	31.0	31.2	26.5	$\left\{ \begin{array}{l} 2.16 \\ 10^{-5} \end{array} \right\}$	$\left\{ \begin{array}{l} 0.26 \\ 10^{-5} \end{array} \right\}$	143°	142° .5	143° -4	12°
Methylsulphocyanate	35.5	33.3	35.9	$\left\{ \begin{array}{l} 3.7 \\ 10^{-5} \end{array} \right\}$	$\left\{ \begin{array}{l} 0.146 \\ 10^{-5} \end{array} \right\}$	129°	—	130°	12°
Ethyl mustard oil	18.7	22.0	19.4	$\left\{ \begin{array}{l} 2.25 \\ 10^{-5} \end{array} \right\}$	$\left\{ \begin{array}{l} 0.6 \\ 10^{-6} \end{array} \right\}$	130°	131° .2	131° -2.5	18°
Methyl mustard oil	20.3	17.9	19.7	—	—	116°	—	119° .5	38°
Phenyl mustard oil	10.0	8.5	11.0	$\left\{ \begin{array}{l} 2.55 \\ 10^{-5} \end{array} \right\}$	$\left\{ \begin{array}{l} 0.18 \\ 10^{-6} \end{array} \right\}$	218°	219°	222°	20°
Allyl mustard oil	17.2	17.33	—	$\left\{ \begin{array}{l} 8.10^{-6} \end{array} \right\}$	—	150°	150°	—	18°

¹ Eggers had not redistilled his samples of methyl mustard oil and methyl sulphocyanate, so that the corresponding boiling-points do not appear in the table.

TABLE IV

Eggers took measurements at lower temperatures as follows:

Methyl sulphocyanate,	-	-	-	15°.5 C.
Ethyl sulphocyanate,	-	-	-	11°.5 C.
Ethyl mustard oil,	-	-	-	15°.0 C.
Allyl mustard oil	-	-	-	17°.6 C.
Phenyl mustard oil,	-	-	-	11°.6 C.

Walden's temperatures correspond more closely to mine. Measurements of conductivity were made at 25°C.

A considerable discrepancy was found in the case of phenyl mustard oil. It was thought that the slow decomposition which this substance undergoes might possibly account for this variation. Consequently a sample which had been carefully dried, redistilled and allowed to stand for a month or more was measured. The sample was again dried and redistilled and measurements made on this fresh sample. Precisely the same result was obtained in both instances. The true value has thus been shown to be 10.0 as indicated in the table.

In the case of ethyl sulphocyanate Walden gets the value 26.5 and Eggers 31.2. Working upon a pure sample which had been carefully dried and redistilled the value 31.0 was obtained. This measurement was several times repeated, always with the same result.

In the main the results obtained by Walden were found to be more nearly correct. But this is not at all surprising considering the less perfect apparatus with which Eggers made his measurements.

DIELECTRIC CONSTANTS OF SOME SOLUTIONS.—The dielectric constant of pure, dry, redistilled pyridine was found to be 12.5. A test was made to determine what effect dissolved sugar would have upon the dielectric constant. The pyridine contained 6.47 percent of sugar and the dielectric constant of the solution was found to be 13.5. This result is of interest since Thwing¹ finds the dielectric constant of sugar to be quite low, namely, 4.16.

¹ Phys. Rev., 2, 51 (1894).

A mixture of aniline and cresol was made and its dielectric constant measured. The value obtained was 6.70 which result falls between the values obtained for the two constituents.

Acetonitrile and alcohol were mixed in approximately equal volumes and the dielectric constant of the resulting mixture was found to be 29.4. Here again we have the dielectric constant of the mixture falling between the values for the constituent substances.

Arsenic trichloride was saturated with dry hydrochloric acid gas and the dielectric constant of the mixture quickly determined.¹ The dielectric constant of arsenic trichloride is 12.35. The dielectric constant of the solution measured was 12.80. In this case we have a slight rise due to the dissolved HCl.

Tin tetrachloride was saturated with HCl gas and the dielectric constant measured. The dielectric constant was not appreciably altered, the slight difference could well be considered as falling within the limit of experimental error. The dielectric constant of the SnCl_4 was 3.20 and the dielectric constant of the solution was 3.15.

Carbon tetrachloride was saturated with dry HCl gas and the dielectric constant of the solution thus obtained, measured. The dielectric constant of the solution was found to be the same as that of the carbon tetrachloride.

Nitrobenzene was saturated with dry HCl gas and the dielectric constant of the solution thus obtained was found to be 35.8. The dielectric constant of the pure nitrobenzene is 34.0. Here again we have a rise in dielectric constant due to the dissolved HCl which is known to have a low dielectric constant.

Nitrobenzene dissolves a great amount of trichloroacetic acid with considerable absorption of heat. The dielectric constant of a saturated solution was found to be 14.7. The dielectric constant of the solvent being moderately high (34.0), we ought to find a solution of trichloroacetic acid a fairly good conductor according to the Nernst-Thomson rule. Accordingly the conductivity of this solution was measured. The specific

¹ In those cases where HCl was used as solute, it is probable that no great amount was absorbed.

conductivity was found to be 1.46×10^{-5} . Here again we have an interesting exception to the Nernst-Thomson rule. It is perfectly clear that no such relation as this rule maintains actually exists.

In connection with work previously done in this laboratory¹ it was thought advisable to test the action of this solution on the metals. The results obtained appear in Table V, below.

TABLE V

Metal	Remarks
Aluminum	No action
Zinc (cast)	Rapid production of aniline, no gas
Zinc (dust)	Same as for cast zinc. More rapid
Nickel	Solution showed presence of small amounts of aniline at end of twenty-four hours
Chromium	No action
Magnesium (ribbon)	Very rapid formation of aniline with considerable evolution of gas
Magnesium (dust)	Action extremely rapid. Developed heat enough to boil violently. Aniline formed rapidly
Cobalt	Aniline formed. No gas. Action comparatively slow
Cadmium	Action fairly rapid. Aniline formed. No gas
Antimony	No action
Silver	No action
Gold	No action
Copper	Solution turned green. No gas
Palladium	No action
Platinum	No action
Tin	No aniline formed. Metal blackens
Bismuth	Metal and solution darken, stick notched at surface
Iron	Aniline formed. No gas. Action moderate
Mercury	No action
Sodium	Brisk evolution of gas. Aniline formed. (Sodium was placed in the pure nitrobenzene and no evolution of gas took place. This showed that the solvent was dry. No action upon the sodium was apparent after several hours standing)

¹ Kahlenberg: *Zeit. phys. Chem.*, 46, 64 (1903). Patten: *Trans. Wis. Acad.*, 14, 316 (1903); *Jour. Phys. Chem.*, 7, 153 (1903).

This experiment affords us another interesting indication that chemical action and electrical conductivity do not necessarily go hand in hand. It is clear that in this case cited chemical action is not in any way connected with any electrical phenomena. To further establish this principle, trichloroacetic acid was dissolved in benzene in which it is quite soluble. The resulting solution acts upon the metals vigorously. Its specific conductivity was measured and found to be less than 3.0×10^{-8} . This is even a more drastic case than the previous one.

To still further substantiate this point, trichloroacetic acid was dissolved in dry kerosene and its action tried upon the metals. The same result was experienced as in the case of benzene.

The dielectric constant of a saturated solution of trichloroacetic acid in benzene (containing 74.1 percent of the acid) was measured and found to be 3.65, as against 2.26 for the pure solvent.

The action of various acids in nitrobenzene upon metallic magnesium was tried with the following results:

TABLE VI

Nitrobenzene with	Remarks
Crotonic acid	Gas given off copiously
Trichloro lactic acid	Rapid evolution of gas
Acetic acid (glacial)	Magnesium disappears in time
Dichloroacetic acid	Rapid evolution of gas. Solution shows presence of aniline
Oxalic acid	No action apparent
Fumaric acid	Little if any action (twenty-four hours)
Itaconic acid	No action

In all these cases where action occurred we have chemical action of a decided character where electrical conductivity is practically wanting. I say "practically" because no solvent has yet been shown to be an absolute non-conductor. In the light of the facts presented, it is difficult to see how chemical action can be considered as being electrical in character.

CYANOGEN IODIDE.—The iodide of cyanogen was found to dissolve well in allyl mustard oil. It is possible to secure a so-

lution containing over 40 percent of the salt at room temperatures. The specific conductivity of a 41.09 percent solution was found to be 1.36×10^{-3} . The dielectric constant was also determined and the value 19.9 obtained. Metallic magnesium was treated with this solution and bubbles of gas were formed on the surface of the metal and were liberated rapidly. Metallic magnesium remains unacted upon in the pure solvent. When sodium is added to the solution of cyanogen iodide in allyl mustard oil, gas is liberated rapidly and cyanogen iodide is apparently precipitated from the solution. Sodium also reacts somewhat on the pure solvent, but the gas is liberated very much slower. Metallic zinc produces no liberation of gas, but appears corroded. The solution has the characteristic color of a weak solution of iodine in allyl mustard oil.

The fact that the dielectric constant of allyl mustard oil is raised by the addition of the iodide of cyanogen is interesting. The dielectric constant of cyanogen is known to be low (2.52).¹ Schlundt found iodine to have a value of 10.3. In general the addition of more halogen lowers the dielectric constant of a halogen-containing substance. From this fact we should expect the value for cyanogen iodide to be low, at least below the value for iodine. The dielectric constant of allyl mustard oil has been shown to be 17.2. Yet when the iodide of cyanogen is dissolved in this solvent, the dielectric constant is raised from 17.2 to 19.9¹

A solution of iodine in allyl mustard oil was then made which had the same iodine content as the cyanogen iodide solution just described. The dielectric constant of this solution was found to be 14.8 as compared with the value 19.9 obtained in the case of the cyanogen iodide solution. While cyanogen itself has a low dielectric constant, we find that combined CN has a tendency to raise the dielectric constant, examples of which fact are seen in the following table.

¹ Schlundt l. c.

TABLE VII

Name	Formula	D. C.	Name	Formula	D. C.
Hydrocyanic acid ¹	HCN	95	Water	HOH	80
Acetonitrile	CH ₃ CN	36.4	Methyl alcohol ²	CH ₃ OH	32.5
Propionitrile	C ₂ H ₅ CN	26.5	Ethyl alcohol	C ₂ H ₅ OH	21.7
Butyronitrile	C ₃ H ₇ CN	20.3	Propyl alcohol	C ₃ H ₇ OH	12.3
Benzyl cyanide	C ₆ H ₅ CH ₂ CN	14.9	Benzyl alcohol	C ₆ H ₅ CH ₂ OH	10.6

Similar differences would be observed in the comparison of the dielectric constants of ethers, acetates, ketones, aldehydes and acids with corresponding cyanides.

Carbon tetrachloride, having a dielectric constant of 2.7 was treated with iodine and the dielectric constant of the resulting solution found to be 2.4. An attempt was made to dissolve cyanogen iodide in this solvent to study further the effect of the cyanogen radical, but it would not dissolve to any extent without the application of heat.

Carbon tetrachloride being a compound well loaded with halogen was treated with more halogen in the form of iodine monochloride. The dielectric constant of this solution was, within the limit of error, the same as for the pure solvent. In this case a further addition of chlorine does not seem to affect the dielectric constant though a change would be expected inasmuch as the dielectric constant of iodine monochloride is in the neighborhood of 30. (Made upon a specimen sample not further purified.)

Iodine monochloride was mixed with benzene with which it reacts violently, and the dielectric constant of the solution determined. The dielectric constant was found to be raised by the presence of the iodine monochloride.

In the case of the HCl in nitrobenzene cited above we have an example similar to that of cyanogen iodide in mustard oil. The dielectric constant of mixture is plainly not additive in character.³ The grouping of the atoms must be considered. At

¹ Values taken from work of Schlundt l. c.

² Values taken from work of Drude l. c.

³ See Eggers l. c.

the present state of our knowledge it is impossible to foretell, with any degree of accuracy, the dielectric constant of any unmeasured substance. We know, in a general way, the effect of certain radicals and the effect of the different grouping of the same, but this subject still needs further investigation.

We are continually warned against using solvents that contain the minutest traces of water in our experimental investigations. Some seem to regard it an impossibility to free an organic solvent from water. The conductivity of non-aqueous solutions was by some ascribed to the presence of minute traces of water, which it was impossible to remove. Such an idea has since been shown to be quite erroneous. To make a non-conducting solution conduct by the addition of water it is found that quite an appreciable amount is necessary; an amount, which is greatly in excess of that in a dried sample of the ordinary solvents such as we encounter. In the case of benzene and trichloroacetic acid, which solution I have found to be an excellent insulator, I have made successive additions of small known quantities of water and

Fig. 1

Curve showing the effect upon the specific conductivity of a non-conducting solution produced by the addition of small quantities of water. The values along the abscissa equal the specific conductivity times 10,000.

measured the specific conductivity after each addition. I found that it takes an appreciable amount of water to give a measurable increase in the electrical conductivity and that for a relatively considerable addition of water the conductivity does not increase rapidly. I have plotted a curve showing my results. Upon the

basis of actual experimental work the curve was extended much farther than indicated in the figure, but the general direction was found to be the same. The curve shows that the conductivity does not increase rapidly until we have added 0.1 percent of water. At 0.13 percent it reaches a point where further addition of water causes a steady increase in the conductivity.

DIELECTRIC CONSTANTS.—I have measured a considerable number of dielectric constants which have hitherto not been determined, and have checked up a number that have been determined. Practically all of the substances used were dried and redistilled as indicated. For the sake of convenience in reference I have tabulated them alphabetically. It will be seen that in the main those which have been redetermined agree very well with former results.

Summary

The electrical conductivity of a large number of substances dissolved in the mustard oils has been measured. A few of the acids dissolve to form slightly conducting solutions. None of the alkaloids or alkaloid derivatives yield conducting solutions. The same is true of the amines. Some of the chlorides, iodides, and bromides dissolve to give slightly conducting solutions. Iodine, itself a non-conductor, yields a fairly good conducting solution.

Sulphocyanic acid was prepared, though in all probability not in the pure state, and, have found that the product secured gives complete absorption.

I have prepared methyl silicate, measured its dielectric constant and specific conductivity and have employed it as a solvent. Measurements of like character have also been made on ethyl silicate.

The results of Walden and of Eggers have been gone over and checked up. The dielectric constants of some new solutions have been measured as well as their conductivity, and their chemical activity studied. It has been shown that, in many cases at least, chemical action is wholly independent of any electrolytic phenomena, that we may have various chemical

TABLE VIII

Substance	Maker	D. C.	Reso- nance	Temp.	B. P.	Remarks
Amyl nitrate	Schuchardt	8.95	good	18°	140-45°	Not redistilled
Amylene	"	6.9	"	22		Schlundt 7.20
Aniline	Kahlbaum	7.2		24	180	
Amyl benzoate		4.62		18	238-40	
Anisol	Kahlbaum	3.55	good	18	152	
Benzoic aldehyde	E. de Haen	14.0	"	18	185(?)	
Benzoic chloride	Schuchardt	7.4	"	20		Not redistilled
Cymene	"	2.43	"	18	170-72	Nernst 2.25
Carvol	"	11.0	"	18	224-5	Unopened sample
Benzoylchloride	Kahlbaum	18.6	"	24		
Diamylamine	Schuchardt	2.52	"	18	184	
Diethylamine	"	3.7	"	23		
Dibenzylamine	"	3.6	"	23		
Diphenylmethane	Trommsdorf	2.5	"	18	243-44	Schlundt 3.58
Dipropylamine	"	2.45	"	18	245	Schlundt 3.55
Dimethylaniline	Schuchardt	2.9	"	18	110(?)	New sample
Dipentene	"	5.0	"	18	189.5-90	Schlundt 2.90
Eugenol	"	3.2	"	21	170	Schlundt 5.07
	"	6.0	{ some absor.	18	234	
Ethyl carbonate	"	2.8	good	18	124	
Ethylene diamine	"	15.7	"	18	118-21	
Ethyl benzoate	Kahlbaum	5.6	"	24	207-7.5	
Kresol methyl ether	"	3.47	"	18	165-67	
Kresol (ortho)	Kahlbaum	5.65	"	24	187	

TABLE VIII—(Continued)

Substance	Maker	D. C.	Reso- nance	Temp.	B. P.	Remarks
Kresol (meta)	Kahlbaum	4.95	{some absorb.	24°	197.5-8	
Kresol (para)	"	5.48	"	24	197.5	
Methyl benzoate	Schuchardt	6.25	"	24	195.5	Schlundt 5.8
Monomethylanilin	"	5.3		23		
Menthone	"	8.78	good	18	197-99	
Mercurydiethyl	"	2.45	"	23		Not redistilled
Naphthalenemonobromide	"	4.5	"	18	255-58	Fresh sample
Nitrotoluol	Schuchardt	20.3	"	18	206.5-7	Thuring 26.6
Phenyl acetate	"	6.40	"	24		Drude 5.29. Not redistilled
Phenetidene	"	7.2	"	21	241-2.5	
Phenyl hydrazine	"	5.7	"	18	225.5	Turner 7.15
Pinacone	"	7.38	poor	24	174-75	
Phenetol	"	4.47	good	21	166.5	
Phenylisocyanate	Kahlbaum	8.77		20	160	
Quinoline	Schuchardt	8.7	good	21	231-33	Schlundt 8.8. Turner 8.9
Safrol	"	2.52	"	18	200	
Terpinol	"	3.7	"	21	178-80	Drude 2.75
Terpinene	"	2.7	"	21	171-4	
Tin tetrachloride	"	2.0	"	18		Fresh sample
Titanium tetrachloride	"	2.73	"	24		Hermetically sealed
Xylidine (meta)	E. and A	4.9	"	18	210-12	

Cyanogen iodide—Decomposed when an attempt was made to melt it. Dissolved in benzene it did not affect the dielectric constant of the benzene in any degree (2.26). A 41.09 percent solution of cyanogen iodide in allyl mustard oil gives a dielectric constant of 19.9.

actions of a most decided character in solutions which are not conductors of electricity. It has moreover been further emphasized that the Nernst-Thomson rule has no foundation in fact and that the exceptions are as numerous as the confirmations.

The dielectric constants of a number of liquids hitherto undetermined have been measured and presented in ready form for reference.

An exhaustive bibliography of the literature on dielectric constants has been compiled and arranged in the alphabetical order of the authors' names.

In conclusion, it is a pleasure to express my gratitude to Professor Kahlenberg, under whose direction this research was made, for his many suggestions, for his interest in my work, and for the many opportunities he has placed before me.

PREFACE TO THE BIBLIOGRAPHY ON DIELECTRIC CONSTANTS

This bibliography has been compiled in the hope that it may be useful to those who desire to make a study of the subject of specific inductive capacity. By having such a bibliography of the literature upon the subject at hand for ready reference much of the labor of future investigation may be saved and many of the errors of the earlier experimenters avoided. All classes of articles upon the subject have been included without regard to their merits.

This is probably not an absolutely complete bibliography of the literature upon the subject, but it is as nearly complete as time and opportunity have enabled the author to make it. For convenience in reference, the arrangement has been made alphabetically with respect to the name of the author. The abbreviations are such as are in common use and need no further explanation.

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