

THE DISSOCIATIVE POWER OF SOLVENTS

BY LOUIS KAHLENBERG AND AZARIAH T. LINCOLN

The theory of electrolytic dissociation has greatly stimulated inquiry into the electrical conductivity of solutions. Naturally aqueous solutions, which possess the power of conducting electricity in a high degree, have thus far attracted most attention. Solutions in which the solvents are mixtures of water and other liquids, especially alcohols, have been studied, and lastly attention has been turned to the investigation of the conductivity of solutions that contain no water.¹ The investigation of the electrical conductivity of this latter class of solutions is of great interest in answering the question as to the cause of the dissociative power of solvents. It need scarcely be stated that the use of non-aqueous solutions as electrolytes would prove of considerable industrial value.

Nernst has pointed out that the greater the dielectric constant of a solvent is, the greater is its dissociative power. Proportionality between the two, however, does not exist. Dutoit and Aston² claim that only those solvents that in the liquid state are to be regarded as polymerized possess dissociative power. They show that compounds that contain no oxygen, such as nitriles, when used as solvents, yield solutions that conduct electricity very well. Brühl³ claims that solvents possessing dissociative power contain elements that have unsatisfied valences or, in other words, are unsaturated compounds. He

¹ H. P. Cady, *Jour. Phys. Chem.* **1**, 707 (1897). E. Bouty, *Comptes rendus*, **106**, 595 (1888). Dutoit and Aston, *Comptes rendus*, **125**, 240 (1897). Dutoit and Friedrich, *Bull. Soc. Chim. Paris*, (3) **19**, 321 (1898). St. v. Laszczynski u. St. v. Gorski, *Zeit. Elektrochemie*, **4**, 290 (1897). C. Carrara, *Gazz. chim. Ital.* **27**, 1, 207 (1897). See also *Jahrbuch f. Elektrochemie*, **1897**, 45.

² l. c.

³ *Zeit. phys. Chem.* **18**, 514 (1895); *Ibid* **27**, 317 (1898); *Ber. chem. Ges. Berlin*, **30**, 163 (1897).

ascribes the polymerization of the molecules of the solvent as well as the dissociative power that the latter exerts upon the dissolved substance to these spare valences. His theory of the tetravalency of oxygen is used to explain the dissociative power possessed by so many oxygen compounds. That some compounds containing nitrogen, when used as solvents, yield solutions that conduct electricity, Brühl explains is due to the fact that in these compounds nitrogen is a triad and that the dissociative power of the solvent is due to the extra valences of the element. He predicts that hydrazine will prove to have dissociative power; and that in general, in the case of nitrogen compounds this property will vary with the nitrogen content (without being proportional to it, however) just as he claims it varies with the oxygen content in oxygen compounds. He also predicts that all amines will prove to have dissociative power, which will be found to increase with the activity of the compounds. Finally diazo compounds, anhydrous hydrocyanic acid, and even unsaturated compounds of elements other than nitrogen, viz.: — the trichlorides of phosphorus and arsenic, mercaptans and sulphur ethers will according to Brühl be found to have dissociative power. The theory of Brühl will be considered again after the experimental data have been presented, as will also the theories of Nernst and of Dutoit and Aston.

We have for some time been working on the problem of the electrical conductivity of solutions that are not aqueous. In connection with the conductivity determinations we have in a few cases ascertained the molecular weights of the dissolved substances by either the boiling- or freezing-point methods. Since the promulgation of the theory of electrolytic dissociation by Arrhenius¹ it has been assumed that whenever any solution conducts electricity the dissolved substance in it is dissociated electrolytically and consequently the solvent possesses dissociative power. In using the term dissociative power as we do in this paper this assumption has been retained. In view of the splendid success achieved by the theory of electrolytic dissociation in

¹ *Zeit. phys. Chem.* **1**, 631 (1887).

explaining the various properties of aqueous solutions of salts, acids and bases, one would be disposed to apply the same to non-aqueous solutions without further question. It is pertinent to inquire, however, whether in non-aqueous solutions that conduct electricity the dissolved substances are in the dissociated condition; in other words, whether the osmotic pressure, the lowering of the freezing-point or elevation of the boiling-point of the solutions indicates that the molecular weights of the dissolved substances are less than the theoretical to a degree sufficient to account for the conductivity of the solutions. In view of the opposition that the theory of electrolytic dissociation had to meet at the time of its promulgation, and in view of the fact that even at present a number of scientists are opposed to it, we may well hesitate to apply this theory (which is based primarily upon a study of aqueous solutions) to non-aqueous solutions without a firm experimental basis for doing so. In investigating the dissociation power of solvents then, it is very desirable that in connection with conductivity measurements molecular weight determinations be made also, until sufficient data have been collected to establish the fact that in non-aqueous as in aqueous solutions dissociation and electrical conductivity go together. It will no doubt be difficult in many cases to draw conclusions from molecular weight determinations, for some of the solutions conduct so poorly that the dissociation cannot be detected, much less estimated by boiling-point or cryoscopic methods. When the solutions conduct sufficiently well, however, this difficulty will not be met.

The conductivity determinations that we have to present are in part qualitative and in part quantitative. In our search for solvents that yield conducting solutions several difficulties were met, the solvent and the dissolved substance had to be perfectly anhydrous, and again the latter had to be sufficiently soluble to allow measurements to be made readily. Thus far the determinations of electrical conductivity in non-aqueous solutions made by others have been largely confined to salts of the alkalis, ammonium and substituted ammonium. The solubility of

these salts we found to be very slight in some of the solvents we desired to test.

It was found that several chlorides of the heavy metals are readily soluble in many solvents; and as these chlorides are not very difficult to prepare in pure anhydrous form, and as on account of the strong ionizing tendency of chlorine in aqueous solutions they suggested themselves as promising objects to try, they were employed as the dissolved substances in our work thus far. The chlorides used are those of the following formulae: — FeCl_3 , AlCl_3 , SbCl_3 , BiCl_3 , CuCl_2 , AsCl_3 , and PCl_3 ; the last two were used both as solvents and as dissolved substances.

In the majority of cases ferric chloride was found to be the most soluble of these salts, although antimony trichloride was exceedingly soluble in many of the solvents. Cupric and stannous chlorides were found to be sparingly soluble, speaking generally; aluminum chloride reacted with the solvent in many cases liberating hydrochloric acid. Mercuric chloride was generally found to be more soluble than bismuth chloride, which was not as soluble as antimony trichloride. Stannic chloride and the trichlorides of arsenic and phosphorus were miscible with many of the solvents without causing decomposition; with some solvents reaction did occur. Phosphorus trichloride, it is well known, reacts with many organic solvents forming substitution-products. Whenever chemical action was made apparent by the formation of precipitates or liberation of gases the solutions were not further tested.

Ferric chloride was prepared by passing anhydrous chlorine gas over pure iron wire contained in a heated hard glass tube. Cupric chloride was prepared in an analogous manner. Stannous and aluminum chlorides were obtained by passing dry hydrochloric acid gas over the respective metals contained in heated tubes of glass. The trichloride of antimony was prepared by treating the metal with dry chlorine in a small retort of good glass, with addition of heat, and then distilling the product. Trichloride of bismuth was formed by treating hydroxide of bismuth with concentrated hydrochloric acid,

evaporating to a thick syrup and allowing the mass to cool. The latter was then broken up, the pieces were transferred to a retort of Berlin porcelain, and the product purified by distillation. All of these chlorides were pure and perfectly anhydrous. The mercuric chloride was the C. P. sublimed preparation of Kahlbaum. The stannic chloride was an anhydrous product obtained from Schuchardt. Arsenic trichloride was prepared by treating arsenious acid with dry hydrochloric acid gas in a retort and purifying the product by distillation. It had a very constant boiling-point. The trichloride of phosphorus was a sample obtained from Kahlbaum. It was redistilled and had a very constant boiling-point.

In presenting the results the qualitative determinations will be given first. We found it necessary to make these determinations in order to find out solutions that conduct sufficiently to make quantitative investigations profitable; and as a large number of solvents were tested, it will prove of value to give the results, especially as they cast light upon the question of the cause of the dissociative power of solvents (considering for the present that electrical conductivity of the solution is always caused by electrolytic dissociation).

In this qualitative, or very roughly quantitative, work the plan of experimentation was as follows: In the circuit of a large Leclanché cell were placed a rheostat, a fairly delicate galvanometer and a resistance cell (of the type devised by Arrhenius) into which the solutions tested were introduced. The electrodes of the cell were about four millimeters apart. It was seldom that any of the plugs of the rheostat had to be pulled out, as the resistance in the cell was generally so large that but a small throw of the galvanometer needle resulted in most cases on closing the circuit. The circuit was closed only for a second or two in each case. Of course in operating thus with a direct current polarization could not be avoided; it was the sole purpose of these experiments, however, to find out whether a current could be made to pass through the solution, and if so whether the conduction was sufficient to make it desirable to attempt an exact quantitative determination.

In each case the solvent was first tested as to whether it would conduct. It was found that nearly all the solvents were excellent insulators. In the case of acetic aldehyde and furfural a slight deflection of the galvanometer needle was observed; in the case of most of the other solvents absolutely no motion of the needle was noted, while in a few instances a mere trace of movement was discernible on closing the circuit. The solvents were all of the C. P. varieties of standard makes, — Schuchardt, Kahlbaum, Merck or Trommsdorf. Prof. Kremers, of the pharmacy department of this university, kindly furnished us several compounds from his collection. Prof. Hillyer, too, was kind enough to place at our disposal a number of preparations in his possession. We desire here to express our thanks to both of these gentlemen for thus furthering our experimental work.

The salts used in making these rough, preliminary tests of conductivity were ferric chloride, antimony trichloride, mercuric chloride and bismuth trichloride. In nearly all of the solvents the order of the solubility of these salts proved to be that just given, ferric chloride being the most soluble. Without exception, the ferric chloride solutions conducted better than the others. We soon found it useless to try solutions of the other three salts if the solutions of ferric chloride did not conduct. After the solvent had been tested in the resistance cell, the salt solutions were likewise tested. The latter were frequently prepared by introducing a little of the salt directly into the solvent contained in the cell. This was the method used whenever the salt dissolved readily; when such was not the case, the solution was prepared in a small test-tube, frequently with the aid of heat; it was then rapidly cooled, introduced into the cell and tested. The strength of the solutions was not accurately ascertained; it varied from about one to five percent.

The results of these tests are given in Table I. The first two columns contain the names and formulae of the solvents. In the next four columns is indicated the electrical conductivity of the solutions of the salts whose formulae head the columns.

When the solution conducted so poorly that no throw of the galvanometer needle was observed, this is indicated by the minus sign (—). A plus sign (+) indicates that the solution did conduct. The addition of the interrogation point to the plus sign (—?) indicates that only a very slight movement of the needle was observed, and the addition of the exclamation point to the plus sign (—!) shows that the solution conducted well enough to make a quantitative determination desirable. An idea as to how great a conductivity this is can be obtained by inspecting the results of conductivity determinations of ferric chloride solutions given farther below. In Table I blank spaces indicate that the solutions were not tested, and the letter (i) shows that the salt was found to be insoluble or at least difficultly soluble. The dielectric constants of the solvents, as far as we were able to obtain them from the literature, are given in the seventh column. Finally, the last column contains the coefficients of association of the solvents, as far as we were able to find them in the literature. The coefficients marked R. & S. are taken from the article of Ramsay and Shields, *Jour. Chem. Soc.* **63**, 1089 (1893); R. & A. refers to the work of Ramsay and Aston, *Ibid.* **65**, 168 (1894); D. & F. refers to Dutoit and Friedrich (*l. c.*).

In addition to the results in the following table, it was found that stannic chloride in arsenic trichloride does not conduct, and phosphorus trichloride in arsenic trichloride does not conduct. Mercuric chloride in arsenic trichloride conducted a little, but when phosphorus trichloride was added to the solution the conductivity diminished to such an extent that the galvanometer needle did not stir. The action of the phosphorus trichloride in the latter case in diminishing the conductivity is possibly analogous to that of alcohol when added to an aqueous solution that conducts.

Looking over the results in Table I it appears that ferric chloride dissolved in hydrocarbons or their halogen substitution products does not conduct. This is in perfect harmony with what others have found regarding solutions of other salts in solvents of this nature. The low dielectric constants and coeffi-

TABLE I

Solvent	Formula	FeCl ₃	SbCl ₃	BiCl ₃	HgCl ₂	Dielectric constant (air = 1)	Coefficient of association
Heptane	C ₇ H ₁₆	—	—	—	—	2.301 Landolt & Jahn	0.95 R. & S.
Amylene	C ₈ H ₁₀	—	—	—	—	2.3377 Palaz	(Schiff)
Benzene	C ₆ H ₆	—	—	—	—	2.3648 "	1.01 R. & S.
Toluene	C ₇ H ₈	—	—	—	—	2.2758 Negreano	
Xylene	C ₈ H ₁₀	—	—	—	—	2.4706 "	
Cymene	C ₁₀ H ₁₄	—	—	—	—		
Menhene	C ₁₀ H ₁₄	—	i	—	—		
Chloroform	CHCl ₃	—	—	—	—	3.95 Thwing	0.94 R. & S.
Carbon tetrachloride	CCl ₄	—	—	—	—	2.2 Tereschin	(Eötvös)
Methylene iodide	CH ₂ I ₂	—	—	—	—		1.01 R. & S.
Ethylene chloride	C ₂ H ₄ Cl ₂	—	—	—	—		
Ethylene bromide	C ₂ H ₄ Br ₂	—	—	—	—		0.95 R. & S.
Monobrom-benzene	C ₆ H ₅ Br	—	—	—	—		(Eötvös)
Benzyl chloride	C ₆ H ₅ CH ₂ Cl	—	—	—	—		
Benzal chloride	C ₆ H ₅ CHCl ₂	—	—	—	—		
Benzotrithloride	C ₆ H ₅ CCl ₃	—	—	—	—		
Acetyl chloride	CH ₃ COCl	+	+	i	i	25.30 Thwing	
Benzoyl chloride	C ₆ H ₅ COCl	+	+	i	+	15.40 Drude	1.05 R. & S.
Methyl alcohol	CH ₃ OH	+	+	—	—	32.65 Tereschin	3.45 R. & S.
Ethyl alcohol	C ₂ H ₅ OH	+	+	—	—	25.7 Rosa	2.74 R. & S.
Allyl alcohol	C ₃ H ₅ OH	+	+	—	—	21.6 Thwing	1.55 R. & S.
Benzyl alcohol	C ₆ H ₅ CH ₂ OH	+	+	—	—	10.6 Drude	
Ethylene glycol	C ₂ H ₄ (OH) ₂	+	+	—	—		2.92 R. & S.
Glycerine	C ₃ H ₅ (OH) ₃	+	+	—	—	16.5 Drude	1.50 D. & F.
Epichlorhydrin	C ₂ H ₅ OCl	+	+	—	—		
Phenol	C ₆ H ₅ OH	+	+	—	—	9.65 Drude	1.42 R. & A.
Meta-cresol	C ₆ H ₄ CH ₃ OH	+	+	—	—(?)		
Ethyl ether	(C ₂ H ₅) ₂ O	—	—	i	—	4.373 Donle	0.99 R. & S.
Phenyl methyl ether	C ₆ H ₅ OCH ₃	—	—	i	—		
Acetic anhydride	(CH ₃ CO) ₂ O	+	—	(?)	—		0.99 R. & S.
Acetic aldehyde	CH ₃ COH	+	+	—	+	18.55 Thwing	
Chloral anhydride	CCl ₃ COH	+	+	—	+	5.47 "	1.02 R. & S.
Paraldehyde	C ₃ H ₄ O ₃	+	+	+	+		0.85 R. & S.
Benzaldehyde	C ₆ H ₅ COH	+	+	i	—	14.48 Thwing	0.97 R. & S.
Cinnamic aldehyde	C ₆ H ₅ C ₃ H ₃ COH	+	+	—	—		
Furfural	C ₅ H ₄ O ₂	+	+	—	—	39.4 Drude	
Acetone	(CH ₃) ₂ CO	+	+	—	—	21.85 Thwing	1.26 R. & S.
Methyl-propyl ketone	CH ₃ C ₃ H ₇ CO	+	+	—	+	16.75 "	1.11 R. & S.
Aceto-phenone	CH ₃ COOC ₆ H ₅	+	+	—	+	16.24 "	1.10 D. & F.
Ethyl acetate	CH ₃ COOC ₂ H ₅	+	+	—	+	6.5 Tereschin	0.99 R. & S.
Ethyl monochloracetate	CH ₂ ClCOOC ₂ H ₅	+	+	—	+		
Ethyl cyanacetate	CH ₂ CN.COOC ₂ H ₅	+	+	—	+	26.7 Drude	
Ethyl aceto-acetic ester	CH ₃ CO.CH ₂ COOC ₂ H ₅	+	+	—	+	15.7 "	0.96 R. & S.
Propyl acetate	CH ₃ COOC ₃ H ₇	+	+	—	—	6.3 Tereschin	
Butyl "	CH ₃ COOC ₄ H ₉	+	+	—	—	5.0 Drude	
Propyl propionate	C ₂ H ₅ COOC ₃ H ₇	+	+	—	—		
Amyl butyrate	C ₄ H ₉ COOC ₅ H ₁₁	+	+	—	—		
Amyl valerianate	C ₄ H ₉ COOC ₆ H ₁₁	+	+	—	—		
Ethyl benzoate	C ₆ H ₅ COOC ₂ H ₅	+	+	—	—	6.5 Tereschin	
Ethyl oxalate	(COO C ₂ H ₅) ₂	+	+	—	+		
Ethyl carbonate	CO (OC ₂ H ₅) ₂	+	+	—	+		
Ethyl chlorcarbonate	CO Cl OC ₂ H ₅	+	+	—	+		
Ethyl nitrate	C ₂ H ₅ NO ₃	+	+	—	+	17.72 Thwing	
Amyl nitrite	C ₅ H ₁₁ NO ₂	+	+	—	+		
Nitro-benzene	C ₆ H ₅ NO ₂	+	+	—	+	32.19 Thwing	0.93 R. & S.
o-Nitro-toluene	C ₆ H ₄ CH ₃ NO ₂	+	+	—	+	25.58 "	1.15 R. & S.
Aniline	C ₆ H ₅ NH ₂	—(?)	i	i	—(?)	7.5 Tereschin	1.05 R. & S.
Methyl aniline	C ₆ H ₅ NHCH ₃	—(?)	i	i	—	7.15 Drude	
Dimethyl "	C ₆ H ₅ N(CH ₃) ₂	—(?)	i	i	—		
Benzyl amine	C ₆ H ₅ CH ₂ NH ₂	—	i	i	—		
Toluidine (ortho)	C ₆ H ₄ CH ₃ NH ₂	—(?)	—	—	(?)		
Toluidine (meta)	C ₆ H ₄ CH ₃ NH ₂	—(?)	—	—	(?)		
Xylidene (meta asym.)	C ₆ H ₃ (CH ₃) ₂ NH ₂	i	i	i	i		
Phenylhydrazine	C ₆ H ₅ NH.NH ₂	—	i	i	i		
Benzonitrile	C ₆ H ₅ CN	+	+	—	+	26.0 Drude	0.97 R. & S.
Pyridine	C ₅ H ₅ N	+	i	i	—		1.02 R. & S.
Piperidine	C ₅ H ₁₁ N	i	i	i	—(?)		0.92 R. & S.
Quinoline	C ₉ H ₇ N	—	i	i	—		1.08 R. & S.
Carbon disulphide	CS ₂	+	—	i	—	2.61 Palaz	0.81 R. & S.
Phosphorus trichloride	PCl ₃	i	—	i	—		1.07 R. & S.
Arsenic trichloride	AsCl ₃	+	—	—	(?)		1.02 R. & S.
Tin tetrachloride	SnCl ₄	i	i	i	i		

cients of association (as far as available) will be noted in this connection. The acid chlorides, acetyl and benzoyl chloride, do yield solutions that conduct. The dielectric constant of acetyl chloride is much higher than that of chloroform for example, though the results of Thwing and Drude (see table) do not agree. The coefficient of association of acetyl chloride is nearly unity; this shows that there is practically no polymerization of the molecules in the liquid state.

The alcoholic solutions (including glycol and glycerine) conduct sufficiently to make quantitative determinations desirable. The dielectric constants of these solvents are relatively higher and the coefficients of association indicate that the solvents contain polymerized molecules. The viscosity of the solutions of glycol and glycerine no doubt diminishes their conductivity. Solutions in phenol and cresol did not conduct as well as alcoholic solutions. The dielectric constant of phenol is not as high and the coefficient of association is not as great as in the case of the alcohols.

The ethers and even acetic anhydride proved to have but slight dissociative power. Their molecules are not polymerized and the dielectric constant of ether is low.

Acetic aldehyde yielded solutions that conducted fairly well relatively; one would expect this from the dielectric constant found by Thwing (see Table I). On the other hand solutions in chloral did not conduct, which fact harmonizes with the low dielectric constant of this substance. The molecules of chloral are not polymerized as the table shows; unfortunately the coefficient of association of aldehyde has not been determined. Paraldehyde has considerable dissociative power in spite of the fact that its coefficient of association indicates that its molecules are not polymerized. Benzaldehyde solutions of ferric chloride conducted sufficiently to make quantitative measurements desirable (see results below); the dielectric behavior of this solvent is such as to lead one to expect this. The molecules of this solvent are not polymerized according to the determinations of Ramsay and Shields. Solutions in cinnamic aldehyde did not

conduct very well ; but those in furfural were found to conduct very well relatively. The high dielectric constant of this substance will be noted in this connection.

The three ketones tested yielded solutions that conduct well. This was to be expected from their dielectric constants. It will be observed, however, that their coefficients of associations are such as to indicate but very slight polymerization of their molecules.

Among the esters, ethyl acetate, in spite of its low dielectric constant (compare the same with that of chloral), yielded solutions that conduct (see measurements below). Solutions in monochloracetate of ethyl seemed to conduct about the same and the cyanacetate did not appear to yield better conducting solutions in spite of the fact that it contains the CN group and has a relatively high dielectric constant. Aceto-acetic ester solutions of ferric chloride conducted well relatively (see determinations below), though its dielectric constant is only 15.7,¹ and its coefficient of association shows that its molecules are not polymerized. The solutions in propyl acetate, butyl acetate and ethyl benzoate conducted but slightly ; their dielectric constants are low. However, since the dielectric constant of butyl acetate is rather lower than that of chloral one would expect the ferric chloride solution of the former to show no conductivity. Ferric chloride in propyl propionate conducted slightly, while its solutions in amyl butyrate and amyl valerianate showed but the slightest movement of the galvanometer needle. The dielectric constants of these solvents are probably also low, though they have, to our knowledge, not been determined. The solutions in ethyl oxalate conducted fairly well ; but those in ethyl carbonate, in spite of the high oxygen content of this solvent, did not conduct noticeably at all. Again, ethyl chlorcarbonate yielded solutions that conducted well relatively.

The results obtained by using nitrogen compounds as solvents are of particular interest. Ethyl nitrate, amyl nitrite, nitrobenzene and nitrotoluene it will be noted yielded solutions

¹ That of ethyl cyanacetate is 26.7.

that gave a fair degree of conduction (see determinations for nitrobenzene solutions below). The dielectric behavior of these solvents would lead one to expect this. The molecules of nitrobenzene are, according to Ramsay and Shields, not polymerized. In aniline, methyl- and dimethylaniline, and in benzylamine, ferric chloride is quite soluble but the solutions conduct very poorly indeed. The benzylamine solutions seemed to conduct a little better than the others. In the toluidines ferric chloride was not readily soluble; only a very slight deflection of the galvanometer needle was observable on testing the solutions. Xylylidine did not dissolve the salts tested, as shown in the table. Only the dielectric constant of aniline was found in the literature. This constant is low and one would expect low dissociative power. The molecules of aniline are not polymerized, according to the coefficient of association. Although phenylhydrazine dissolves ferric chloride readily, the solution so obtained does not conduct; not the slightest movement of the galvanometer needle was observable. Benzonitrile yielded solutions that conducted very well. This is in harmony with the results of Dutoit and Friedrich, that solutions in nitriles conduct well. The relatively high dielectric constant of benzonitrile will be noted; on the other hand, its coefficient of association is so low as to show that its molecules are not polymerized. Pyridine yielded solutions that conduct. St. v. Laszczynski u. St. v. Gorski¹ determined the conductivity of solutions of salts of the alkalies in this solvent. It will be noted that its molecules are not polymerized. Piperidine did not dissolve the salts tested appreciably, except in the case of mercuric chloride. The conductivity of this solution was very slight. The coefficient of association of this solvent indicates no polymerization. Quinoline yielded solutions that conducted slightly. Its molecules are not polymerized. The dielectric constants of the last three bases appear not to have been determined thus far.

Carbon disulphide solutions of ferric chloride do not con-

¹ l. c.

duct, which is in harmony with the low dielectric constant of this solvent whose molecules are also not polymerized.

Antimony trichloride dissolves readily in phosphorus trichloride, but the solution does not conduct; neither does the solution of mercuric chloride in phosphorus trichloride conduct. The coefficient of association of phosphorus trichloride shows that its molecules are not polymerized.

Ferric chloride dissolved in arsenic trichloride, conducts fairly well, and the solutions of the other three salts in this solvent conduct, but not as well.

The rule that the greater the dielectric constant of the solvent, the greater is its dissociative power, holds in general. A few apparent deviations were noted above.

Since only the hydroxyl derivatives in Table I have coefficients of association that indicate polymerization of their molecules, and since the solutions they yield are by no means the only ones that conduct electricity, it is clear that the theory¹ that only those solvents whose molecules are polymerized possess dissociative power is untenable.

In summing up the relations between the chemical composition of the solvent and its dissociative power, it appears that solutions in hydrocarbons or their halogen substitution-products do not conduct. Alcoholic solutions conduct well comparatively. The higher the carbon content of the alcohol, the less is its dissociative power. The hydroxyl derivatives of the aromatic series possess less dissociative power than those of the fatty series; this is especially true when the hydroxyl group occurs in the benzene ring. Ethers and acid anhydrides do not possess dissociative power, or possess it only in a slight degree. The behavior of carbon disulphide would indicate that this possibly holds true also for other sulphur compounds.² Aldehydes on

¹ Compare Dutoit and Aston, *l. c.* Also Dutoit and Friedrich, *l. c.* The influence of viscosity on the conductivity, upon which the latter insist, can not be doubted.

² As a matter of fact, Werner, *Zeit. anorg. Chem.* **15**, 39 (1897), found that cuprous chloride, though fairly soluble in methyl sulphide, conducts very poorly in that solvent.

the whole yield solutions that conduct relatively well. This cannot be ascribed solely to the presence of the aldehyde group, for solutions in chloral do not conduct. Here is a case where substitution of chlorine for hydrogen is accompanied by a reduction of dissociative power. On the other hand, when in acetic- or benzaldehyde the hydrogen of the aldehyde group is replaced by chlorine, the acid chlorides result and the compounds do not lose their dissociative power. When the hydrogen of the aldehyde group is replaced by an alkyl radical, the resulting compounds, the ketones, retain dissociative power. Esters have slight dissociative power on the whole, which decreases as their carbon content increases. Substitution of Cl, CN or CH_3CO for one of the hydrogens of the methyl group does not cause the compound to lose its dissociative power. (In the latter instance it has been found to increase it.) Ethyl carbonate does not yield conducting solutions, but when one of its ethoxy groups is replaced by chlorine the solvent becomes endowed with dissociative power. This shows that it would not be correct to make the general statement that substitution by halogen in a compound has a tendency to reduce dissociative power. The nitrogen compounds containing oxygen combined with that element possess dissociative power. The amido compounds of the aromatic series have but very slight dissociative power. Phenylhydrazine yields a non-conducting solution of ferric chloride. Nitriles yield conducting solutions, as do also ring compounds containing nitrogen. The trichloride of phosphorus does not have dissociative power, while the opposite is true of arsenic trichloride.

Finally, how do these results agree with the theory of Brühl? In the case of all the compounds containing oxygen there would be an abundance of spare valences because Brühl regards oxygen as tetravalent. In general it has been found to be true that oxygen compounds do possess dissociative power. But chloral, ethyl carbonate and ethers¹ have no dissociative power, while esters with high carbon content yield solutions

¹ Compare also the remarks of Dutoit and Friedrich, l. c.

that practically do not conduct. Again when chlorine is substituted for an ethoxy group, the number of spare valences is certainly reduced (assuming oxygen to be a tetrad), nevertheless solutions in ethyl chlorcarbonate conduct well. The amido compounds yielded solutions that conducted but very slightly, contrary to Brühl's prediction. Perhaps he would characterize the amido compounds tested as not sufficiently active. Again the phenylhydrazine solution did not conduct. Of course it remains for future experimentation to show what hydrazine will do. Substitution of CN for hydrogen in ethyl acetate did not seem to affect the dissociative power much. Solutions of antimony trichloride, mercuric chloride, stannic chloride and arsenic chloride in phosphorus trichloride did not conduct. This too is contrary to Brühl's prediction. Solutions in arsenic trichloride did conduct as Brühl predicted. Solutions of cuprous chloride in methyl sulphide conduct very poorly according to Werner's¹ determination; this is also contrary to Brühl's expectation. On the whole it is evident that Brühl's theory is in many instances not supported by the facts, and consequently it must be pronounced untenable.

The results of the accurate measurements of the electrical conductivity will now be given together with the molecular weight determinations, when such have been made. The conductivity was measured in each case according to the method of Kohlrausch, the results being given in reciprocal mercury units. A cell patterned after that of Arrhenius was used. It had a tightly fitting cover so as to exclude the moisture of the air as much as possible. The determinations were made at 25° C unless otherwise indicated. In no case has the conductivity of the solvent been deducted. It has in each case been determined, however. The cryoscopic determinations were made with Beckmann's apparatus, all the usual precautions being taken. In the tables of electrical conductivity v indicates the volume in liters in which one gram-molecule is contained, and μ the molecular conductivity.

¹ l. c.

SOLUTIONS IN METHYL ALCOHOL

The solvent was the C. P. commercial article. It was distilled twice from anhydrous copper sulphate after having stood over this substance for several days. Finally it was treated with metallic sodium, distilled and again redistilled. Its boiling-point was then quite constant, and its specific conductivity was 5.7×10^{-6} .

TABLE II

Solvent: methyl alcohol

Ferric Chloride, FeCl_3				Antimony Trichloride, SbCl_3			
ν	μ	ν	μ	ν	μ	ν	μ
3.20	20.81	102.48	60.55	8.15	15.68	260.96	89.47
6.41	25.26	204.96	72.61	16.31	18.94	521.91	118.34
12.81	31.09	409.91	89.11	32.62	28.52	1043.83	156.32
25.62	40.90	819.83	111.08	65.24	43.32		
51.24	49.00	1639.66	147.08	130.48	63.33		

SOLUTIONS IN ETHYL ALCOHOL

This solvent was prepared in the same manner as was methyl alcohol. Its boiling-point was quite constant also. Its specific conductivity was found to be 7.7×10^{-9} .

TABLE III

Solvent: ethyl alcohol

Ferric Chloride, FeCl_3				Antimony Trichloride, SbCl_3			
ν	μ	ν	μ	ν	μ	ν	μ
2.89	9.91	46.28	15.51	8.11	4.18	129.81	18.23
5.79	13.06	92.56	16.69	16.23	5.68	259.62	29.43
11.57	13.70	195.12	19.33	32.45	7.94		
23.14	14.50	390.24	21.20	64.91	12.30		

SOLUTIONS IN ACETONE

The solvent was a C. P. commercial sample. It was allowed to stand over fused calcium chloride for over two weeks. Finally it was redistilled four times from fused calcium chloride. It then had a very constant boiling-point. Its specific conductivity was 5.4×10^{-6} . In this solvent bismuth trichloride was practically insoluble.

TABLE IV

Solvent: acetone

Ferric Chloride, FeCl ₃		Antimony Tri- chloride, SbCl ₃		Cupric Chloride, CuCl ₂		Stannous Chloride, SnCl ₂	
<i>v</i>	μ	<i>v</i>	μ	<i>v</i>	μ	<i>v</i>	μ
14.65	51.70	7.07	1.23	45.87	25.72	37.78	8.77
29.30	59.90	14.14	1.55	91.74	27.10	75.56	8.09
58.60	64.65	28.27	1.83	183.48	28.71	113.33	6.87
117.19	68.68	56.56	2.13	366.96	28.94		
234.39	70.67	113.10	3.34	733.91	29.18		
468.77	72.28						
937.54	83.76						
1875.08	91.22						

SOLUTIONS IN ETHYL ACETATE

The solvent was of the C. P. variety. It was treated repeatedly with anhydrous copper sulphate from which it was distilled each time. Finally it was redistilled, when it showed a constant boiling-point. Its specific conductivity was 4.5×10^{-7} .

TABLE V

Solvent: ethyl acetate

Ferric Chloride, FeCl ₃		Antimony Tri- chloride, SbCl ₃		Stannous Chloride, SnCl ₂		Bismuth Trichloride, BiCl ₃	
<i>v</i>	μ	<i>v</i>	μ	<i>v</i>	μ	<i>v</i>	μ
16.89	0.87	10.92	0.013	68.05	0.042	112.12	0.034
33.78	1.12	21.84	0.019				
67.46	1.25						

SOLUTIONS IN ETHYL ACETOACETATE

This solvent was a product obtained from Schuchardt. It was subjected to fractional distillation. A sample which boiled between 174° and 176° C at 736 mm, was used in the experiments. Its specific conductivity was 4×10^{-8} .

Ferric Chloride, FeCl ₃		Antimony Tri- chloride, SbCl ₃		Bismuth Tri- chloride, BiCl ₃		Arsenic Trichloride, AsCl ₃	
<i>v</i>	<i>μ</i>	<i>v</i>	<i>μ</i>	<i>v</i>	<i>μ</i>	<i>v</i>	<i>μ</i>
5.46	10.82	0.75	0.031	5.65	0.059	0.47	0.087
15.04	14.04	0.94	0.034	11.31	0.053	0.65	0.071
16.31	14.08	1.34	0.041	27.09	0.098	0.84	0.068
22.14	14.62	2.76	0.044	48.20	0.137	1.13	0.067
24.12	14.63	4.34	0.050	83.00	0.164	1.37	0.067
27.59	15.04	8.18	0.059	288.96	0.472	2.49	0.084
31.90	15.25	17.02	0.076	Mercuric Chloride, HgCl ₂		3.50	0.070
44.64	15.94	36.69	0.108			10.20	0.085
157.98	19.79	59.86	0.132	<i>v</i>	<i>μ</i>	31.13	0.114
240.51	20.65	511.50	0.529	0.91	0.012	Stannic Chloride, SnCl ₄	
503.56	23.43	Phosphorus Tri- chloride, PCl ₃		1.35	0.013		
				2.91	0.017	<i>v</i>	<i>μ</i>
		<i>v</i>	<i>μ</i>	36.33	0.072	2.02	1.08
		1.80	0.026			4.13	1.71
		4.48	0.097			8.76	2.37

t	μ	t	μ	t	μ	t	μ
25° C	12.0	60° C	18.2	75° C	20.7	90° C	21.7
50	16.8	65	19.2	81	21.2	95	21.8
56	17.5	70	19.9	86	21.7	100	21.7

SOLUTIONS IN BENZALDEHYDE

Ferric Chloride, FeCl ₃		Antimony Trichloride, SbCl ₃			
<i>v</i>	<i>μ</i>	<i>v</i>	<i>μ</i>	<i>v</i>	<i>μ</i>
25.58	14.32	1.96	0.12	33.10	0.86
51.65	14.58	2.42	0.14	62.52	1.24
117.91	13.05	3.51	0.17	155.22	1.68
157.79	12.14	5.80	0.28	523.39	2.62
237.14	10.50	14.89	0.48		

t	μ	t	μ	t	μ	t	μ
25° C	14.3	65° C	23.1	85° C	26.4	105° C	24.1
52	20.5	70	24.3	90	26.4	111	24.0
55	20.9	75	25.1	95	24.5	125	24.0
60	22.1	80	25.9	102	24.1		

[illegible]

t	μ	t	μ	t	μ	t	μ
25° C	5.2	70° C	9.2	95° C	12.5	130° C	16.4
52	7.2	75	9.8	100	13.3	135	16.7
56	7.6	80	10.3	110	14.6	140	16.8
61	8.1	85	11.0	123	15.7	145	16.9
67	8.8	90	11.6	125	15.9	150	16.9

The following cryoscopic determinations in nitrobenzene solutions are of interest in connection with the results of the measurements of the electrical conductivity. The solvent used in these determinations was that already described. It was, how-

ever, recrystallized several times in this case before being used. The molecular lowering of the freezing-point used in the calculations was 70.70 (Compare Ostwald's *Grundriss der allgemeinen Chemie*).

TABLE XII

Solvent : nitrobenzene

Ferric Chloride, FeCl_3 Mol. Wt. = 161.14			Arsenic Trichloride, AsCl_3 Mol. Wt. = 179.98		
Substance in 100 g sol- vent	Lowering	Mol. wt.	Substance in 100 g sol- vent	Lowering	Mol. wt.
1.4792	0.330°	316.9	0.3997	0.223°	126.7
1.6510	0.433	269.6	0.9756	0.493	139.9
1.9661	0.575	241.7	1.2298	0.568	153.1
2.3582	0.728	229.2	1.7010	0.763	157.6
3.0566	1.065	203.0	2.7756	1.189	156.1
3.4823	1.255	196.2	3.7299	1.554	169.7
4.0097	1.501	188.9	4.5366	1.857	172.7
4.7389	1.756	190.8	5.2582	2.138	174.3
Antimony Trichloride, SbCl_3 Mol. Wt. = 225.06			6.4207	2.613	173.7
2.5811	0.714°	255.6	7.8651	3.179	174.9
3.1528	0.910	245.5	10.4542	4.207	175.7
5.2983	1.585	236.3	Bismuth Trichloride, BiCl_3 Mol. Wt. = 312.08		
6.3113	1.928	231.4	0.6833	0.230°	203.9
7.2706	2.248	228.7	0.9190	0.250	258.1
8.3095	2.625	223.3	1.1268	0.280	282.6
10.6533	3.555	211.9	1.4927	0.340	301.8
Stannic Chloride, SnCl_4 Mol. Wt. = 258.87			1.8563	0.410	317.9
2.1259	0.337°	445.9	3.0829	0.662	326.9
3.4059	0.742	332.1	Phosphorus Trichloride, PCl_3 Mol. Wt. = 136.33		
5.3896	1.242	306.8	0.9339	0.530°	124.6
6.8268	1.662	290.4	1.3482	0.758	125.8

The relatively high values of μ for ferric and antimony chlorides in methyl alcohol (Table II) and also their great increase with the dilution, showing no tendency toward a maximum will be noted. The figures remind one of the behavior of ferric chloride in aqueous solutions, where hydrolytic decomposition occasions great increase of conductivity with increase of dilution. In ethyl alcohol (Table III) the conductivity of these salts is very much less. The values of μ for ferric chloride

show relatively less change with increasing dilution, while those of antimony trichloride increase more rapidly with the dilution than in the corresponding solutions in methyl alcohol.

In acetone (Table IV) the values of μ for ferric chloride are higher than in methyl alcohol, except at the higher dilutions. The low conductivity of antimony trichloride in acetone as compared with its conductivity in methyl or even ethyl alcohol is striking. Cupric chloride dissolved in acetone conducts well. The values of μ change but little with the dilution and appear to tend towards a maximum. Stannous chloride shows a rather low molecular conductivity when dissolved in acetone. The values of μ show a decrease with the increase of dilution.

In ethyl acetate (Table V) the conductivity of the various salts was uniformly low.

In ethyl acetoacetate (Table VI) the values of μ for ferric chloride are, roughly speaking, of the order that they are in ethyl alcohol solution (Table III). The relatively slight change of the conductivity with the dilution will be noted. The change of the conductivity with the temperature too is of interest (Table VII). At first μ increases with the temperature, but the change per degree grows less as the temperature rises, finally (at about 86°) becoming practically nil.¹ The low values of μ for all the other salts in ethyl acetoacetate will be noted. It is especially interesting that antimony trichloride here, as in acetone, gives a very low value for μ as compared with that of ferric chloride.

In benzaldehyde antimony trichloride conducts but slightly (Table VIII). Ferric chloride has a much greater conductivity, which shows a decrease with increase of dilution. The change of μ for the ferric chloride solution with the temperature is interesting (Table IX). At first there is a gradual increase up to about 90° or 95° ; then there is a slight decrease, the values soon becoming constant.

¹ Dutoit and Friedrich (l. c.) found that cadmium iodide dissolved in acetonitrile, or acetone shows no variation of μ with the dilution or with the temperature. They incline to ascribe this behavior to a combination between the solvent and the dissolved substance.

In nitrobenzene (Table X) the conductivity of all the solutions except that of ferric chloride is low. The values of μ for the latter become practically constant at the higher dilutions. The conductivity of a ferric chloride solution (Table XI) increases steadily with the temperature until about 130° C has been reached, when it becomes constant.

The cryoscopic determinations in nitrobenzene solutions (Table XII) indicate that the molecular weight of ferric chloride is uniformly higher than the theoretical, and that it decreases with increase of concentration of the solution. This decrease of molecular weight with increase of concentration is also to be observed in case of the solutions of antimony trichloride, though here the variation is much less relatively and the more concentrated solutions show a molecular weight slightly below the theoretical. Stannic chloride behaves like ferric chloride in that the molecular weight is greater than the theoretical and that it decreases with increase of concentration of the solution. The trichlorides of bismuth, arsenic and phosphorus in dilute solutions give molecular weights that increase with the concentration of the solutions. In the more dilute solutions the values are lower than the theoretical.

As the molecular weights of the chlorides of iron, antimony and tin in nitrobenzene increase with the dilution, it is clear that the number of dissolved molecules must decrease with the dilution. A simple polymerization of the molecules of the respective salts, seems here excluded, as it would naturally decrease rather than increase with the dilution. Some combination with the molecules of the solvent such that the total number of dissolved molecules suffers a reduction, therefore seems to take place. If this assumption be made, it is clear that electrolytic dissociation might still take place to a certain extent in the solution and yet the cryoscopic results be such as they are.

Dutoit and Friedrich¹ state that they have found normal molecular weights by the boiling-point method for the compounds of the formulæ CNS.NH_4 , HgCl_2 , NaI , LiCl , CdI_2 ,

¹ l. c.

when dissolved in acetone. These solutions conduct electricity well. The authors claim that this behavior is not in contradiction to the dissociation theory. Their explanation is to appear later.

A Werner¹ has made molecular weight determinations of inorganic salts in pyridine, benzonitrile, methyl sulphide, ethyl sulphide, and piperidine by the boiling-point method. He finds as a general result that his determinations indicate little or no dissociation of the salts tested. The latter included, among others, silver nitrate, mercuric iodide and mercuric chloride in benzonitrile, and silver nitrate and ferric chloride in pyridine. The calculated² molecular weight of silver nitrate is 170; in benzonitrile it was found to be 176, and in pyridine 165.42³. Again the calculated molecular weights of mercuric iodide and mercuric chloride are 454 and 271 respectively; in benzonitrile they were found to be 474 and 300 (in another series 238) respectively. It must be added that Werner does not claim a very high degree of accuracy for these results. We have not made accurate determinations of the electrical conductivity of the solutions just mentioned, but we have tested them roughly and know that they do conduct very well. It is not easy to explain from the standpoint of the dissociation theory why they should conduct well and still yield molecular weights that are normal or nearly so. Accurate measurements are of course necessary before the extent of the discrepancy, which apparently exists, can be determined. When solutions of silver nitrate and mercuric iodide in benzonitrile are mixed there is formed momentarily a curdy precipitate that has every outward appearance of silver iodide. This fact would indicate that silver and iodine ions are present in the solutions. It remains to be seen whether the degree of ionization is sufficient to account for the conductivity. Unfortunately the amount of benzonitrile we have on hand is not sufficient to investigate this matter at once.

Werner³ has isolated and analyzed addition-products of

¹ Zeit. anorg. Chem. **15**, 1 (1897).

² The averages of several experiments are given here.

³ l. c.

piperidine with inorganic salts. He states that the molecular weight determinations of these salts in piperidine solutions are but slightly influenced by the fact that piperidine can form addition-products with the salts. This appears to be analogous to the fact that a salt, although it is capable of crystallizing with one or more molecules of water, yields the same molecular weight whether dissolved as anhydrous salt or with its crystal water. We desire to quote a sentence from Werner in this connection: "*Da nicht bezweifelt werden kann, dass in bestimmten organischen Lösungen hydratähnliche Additions-producte von Lösungsmittel und Metallsalz als beständige Verbindungen gelöst sind, so muss auch angenommen werden, dass bestimmte Hydrate in den wässrigen Lösungen enthalten sein können; wenn im letzterem Fall eine elektrolytische Dissoziation eintritt, so entstehen nicht Metallionen, sondern an deren Stelle treten ionisierte Metallwasserradikale.*" While we do not think that Werner's argument warrants drawing this conclusion, yet the sentence seems very suggestive.

It would to our minds prove rather premature to try to decide at this time whether the dissociation theory in its present form can account for the conductivity and other properties of solutions of salts in solvents other than water, for the experiments performed by us and by others are as yet too few to warrant broad generalization. This paper, moreover, is only preliminary in character. From the results above detailed, it seems safe to say that different solvents act differently on one and the same salt. The general outlook at present appears to be that in order to harmonize the molecular weight determinations in many non-aqueous solutions with the relatively high electrical conductivity of the latter, the assumption that combination between solvent and dissolved substance takes place, will have to be made. Can it be true that after its glorious success in explaining the properties of aqueous solutions of acids, bases and salts, the dissociation theory will need the help of its old rival, the hydrate theory (perhaps in somewhat modified form), to explain the facts in the case of non-aqueous solutions? Further diligent

experimental investigation only can definitely answer this question. We need not only to know the molecular weights of the dissolved substances and the electrical conductivity of the solutions, but we need to know whether the reactions that take place in them are momentary; in other words, whether they are ionic reactions, as in the case of aqueous solutions. The behavior of non-aqueous solutions upon electrolysis, their optical and other properties must be studied. The potentials of the galvanic chains in which these solutions are used as the electrolytes, must be investigated.

The electrolysis of non-aqueous solutions and the potentials that exist between the metals and non-aqueous conducting solutions of their salts are being studied in this laboratory. Further work on conductivity and molecular weight determinations is also in progress.¹

*Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, Dec. 19, 1898.*

¹ Since the above was written, Prof. Bancroft in a letter to us directed our attention to the theory of Konowalow (Wied. Ann. **49**, 733, 1893) that a solution conducts only when there is a chemical reaction between solvent and dissolved substance. The work was done on salts of the amines. Referring to Konowalow's work Bancroft wrote:—"These experiments are not conclusive because aniline and acetic acid both conduct a little in water and there is always a possibility of dissociation into $C_6H_5NH_3^+$ and CH_3COO^- . In view of this hypothesis, would it not be a good plan to try the conductivity of picric acid in benzene? Benzene picrate exists in solution and it would certainly be a very surprising phenomenon if it should be an electrolyte. As it would take you but a little while to settle the question one way or the other, it would seem worth while to make the determinations." Among many other tests, the results of which have not been published, we had tried the conductivity of picric acid in benzene some weeks before Prof. Bancroft's letter arrived, but we have again repeated the test with the same result that picric acid in benzene does not conduct. Not the slightest movement of the galvanometer needle could be observed (see plan of experimentation above). The result simply shows that chemical action between solvent and dissolved substance may take place and yet the solution formed need not necessarily conduct electricity.