THE ELECTRICAL CONDUCTIVITY OF NON-AQUEOUS SOLUTIONS¹

BY AZARIAH T. LINCOLN

A preliminary report on the electrical conductivity of nonaqueous solutions by Professor Kahlenberg and myself has appeared in an article entitled "The Dissociation Power of Solvents."² I have since been engaged in investigating the subject further, and desire in this present article to present the experimental results that I have obtained and also to inquire what the bearing of these facts is upon the theory of electrolytic dissociation as promulgated by Arrhenius, and to determine to what extent this theory can be applied to non-aqueous solutions. I 11 view of the fact that Arrhenius' theory is not accepted by a large number of chemists to-day, and in the face of the data that have been collected, one may well hesitate to apply this theory to nonaqueous solutions until there is a sufficiently firm experimental basis to justify it. Auxiliary theories have been promulgated to explain the facts presented by numerous investigators, and an attempt will be made to show to what extent these theories are compatible with the experimental results herein presented.

In an investigation of the electrical conductivity of nonaqueous solutions, the chief requirement is that both the solvents and the dissolved substances be absolutely free from water. To accomplish this is not an easy task. Then, too, the question arises as to what anhydrous salts are soluble in the various solvents. In many cases this could only be answered by experi-

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² Jour. Phys. Chem. 3, 12 (1899).

ment. The qualitative results previously published were confined to ferric chloride, antimony trichloride, bismuth trichloride and mercuric chloride. In addition to these, salts of other heavy metals have been employed in this investigation. Even when these salts were readily soluble, conducting solutions were not always obtained. In order to determine what solutions conduct and to estimate roughly at least the relative magnitude of the conductivity, it was necessary to perform an elaborate series of qualitative experiments to ascertain what solvents yield solutions having a conductivity sufficient to justify quantitative measurements.

The method employed in making these tests has been previously described. The solvents were all of the C. P. variety of standard makes. The salts employed were absolutely anhydrous and the method employed in their preparation and dehydration will now be given. The preparation of cupric chloride, mercuric chloride, stannous and aluminium chlorides, stannic chloride, arsenic trichloride, and the trichloride of phosphorus has been previously described. A C. P. sample of lithium chloride from Merck was dehydrated for several days at a temperature not to exceed 120° . It was then removed to a mortar, thoroughly pulverized and then replaced in the air-bath for about a day longer. The following salts were recrystallized several times and then dehydrated in the manner just described : manganous chloride from Merck, chlorides of nickel and cadmium from Schuchardt, and cobaltic chloride from Trommsdorff. The C. P. samples of lead nitrate and mercuric iodide from Merck, mercuric evanide from Trommsdorff, and zine chloride from Kahlbaum, were dehvdrated in the manner similar to that just described. The silver evanide was prepared from potassium evanide and silver nitrate by Professor Kahlenberg, who dehydrated it and upon subsequent analysis found it to be pure.

Since the qualitative determinations throw some light upon the dissociative power of the solvents, the following additional results are given in Table I. In the first two columns are given

the names and formulæ of the solvents. In the next eighteen columns is indicated whether the solutions of the salts whose formulæ head the respective columns, conduct electricity. When the solution conducted so poorly that no deflection of the galvanometer needle was observed, the fact is indicated by the minus sign (-). The plus sign (-) indicates that the solution did conduct. The addition of the interrogative sign to the plus sign (-?) indicates that a very slight movement of the needle was detected; and when the plus sign is followed by the exclamation mark (--!), this indicates that the solution conducts sufficiently well to make a qualitative determination desirable. Blank spaces indicate that determinations were not made, and the letter i indicates that the salt was insoluble in the solvent or very difficultly soluble. In the last two columns respectively are given the dielectric constants and the coefficients of association of the solvents. The data in these two columns are as complete as could be obtained from the literature.⁴ The letters R and S refer to the article by Ramsav and Shields² as authority, R and A to the work of Ramsav and Aston,3 and D and F to that of Dutoit and Friderich.⁴ The letter V designates determinations by Vollmer, C by Carrara, and S by Schlamp.

As many quantitative determinations of the conductivity of alcoholic⁵ solutions have been made, it was unnecessary to make

¹ Thwing. Zeit. phys. Chem. 14, 286 (1894). Drude. Zeit. phys. Chem. 23, 308 (1897).

² Jour. Chem. Soc. **63**, 1089 (1893).

³ Ibid. 65, 168 (1894).

⁴ Bull. Chim. Soc. Paris, (3) 19, 321 (1898).

³(1) Carrara. Gazz. Chim. Ital. 24, II, 504. (Ref.) Jour. Chem. Soc. 68, ii, 302 (1895); Ibid. 26, I, 119. (Ref.) Jour. Chem. Soc. 70, ii, 511 (1896); Ibid. 27, I, 422. (Ref.) Jour. Chem. Soc. 72, ii, 473 (1897). (2) Cattaneo. Rend. Accad. Line. (5) 4, II. 63, 73 (1895). (Ref.) Jour. Chem. Soc. 72, ii, 537 (1897). (3) Cohen. Zeit. phys. Chem. 25, 1 (1898). (4) Fitzpatrick. Phil. Mag. (5, 24, 322 (1887). (5) Holland. Wied. Ann. 50, 261 (1893). (6) Kablukoff. J. Russ. Chem. Soc. 23, 391. (Ref.) Jour. Chem. Soc. 64, ii, 151 (1893). (7) Pfeiffer. Wied. Ann. 26, 31 (1885). (8) Schall. Zeit. phys. Chem. 14, 701 (1894). (9) Schlamp. Zeit. phys. Chem. 14, 273 (1894). (10) Vollmer. Wied. Ann. 52, 328 (1894). (11) Zelinsky and Krapiwin. Zeit. phys. Chem. 21, 35 (1896).

TABLE I

Solvent	Formula	AIC1 _a	crc1,	MnCl ₂	ZnCl ₂	CoClz	NIC12
Methyl alcohol Ethyl alcohol Propyl alcohol Allyl alcohol Benzyl alcohol Benzyl alcohol Benzaldehyde Salicylic aldehyde Furfurol Acetone Methyl-propyl ketone Acetophenone Ethyl acetate Ethyl acetate Ethyl nonochloracetate Ethyl cyanacetate Ethyl acetoacetate Ethyl benzoate Ethyl benzoate Ethyl nitrate Amyl nitrite Nitrobenzene <i>o</i> -Nitrotoluene	CH ₃ OH C ₁ H ₈ OH C ₁ H ₈ OH CH ₅ (CH ₂) ₂ OH C ₈ H ₈ OH C ₈ H ₈ OH C ₈ H ₈ CH C ₈ H ₄ CH C ₈ H ₄ CH CH ₄ CO CH ₈ C ₂ CO CH ₈ C ₈ H ₄ CO CH ₈ COC ₈ H ₅ CH ₂ COOC ₉ H ₅ C ₈ H ₈ COOC ₉ H ₅ C ₉ H ₈ NO ₉ C ₈ H ₈ NO ₂ C ₈ H ₄ CH ₃ NO ₂	i	i i i	i i i i i i i i i i i i i	i 	i i i	i i i i i i i i i i
Aniline Xylidine (meta asym.) Benzonitrile Pyridine Piperidine Quinoline Phosphorus trichloride Tin tetrachloride	$C_{e}H_{s}NH_{y}$ $C_{a}H_{s}(CH_{y})_{y}NH_{y}$ $C_{b}H_{t}CN$ $C_{b}H_{b}N$ $C_{b}H_{t}N$ $C_{a}H_{t}N$ $PC1_{s}$ $SnC1_{t}$			i i			i

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CuSO ₄	CuCl ₂	cacı,	$AsCl_3$	SuC1 ₂	$Pb(NO_3)_2$	$Hg(CN)_2$	$\Pi_{g}I_{z}$	AgNO ₃	AgCN	KCI	I,iCI	Dielectric Coefficient constant of (Air = 1) association
				i								
											V T	32.65 Teres n 3.43 R and S
	!	1						\ 1		İ	N a	25.7 Rosa 2.74 R and S
											S	20.8 Thwing 2.25 R and S
				; !						1		21.6 1.88 R and S
								•••••			!	10.6 Drude
				l				1				14.48 Thwing 0.97 R and S
					i	i		i			1	19.21
i		i		į –			/	`	•		! <u></u> !	39.4 Drude
	···!			; <u></u>							C	21.85 Thwing 1.26 R and S
	- ;	i.		ļ.				i			i	16.75 '' 1.11 R and S
i	i	i			i			.)			(?)	16.4 " 1.10 R and S
								İ				6.5 Teresh'no.99 R and S
• • = • •	- 1 ⁴⁴ · · ·	, i			i	i				i	$\dot{-}(?)$	
i		i			i	_		¦ !		i	i	26.7 Drude
					i			i			!	15.7 '' 0.96 R and S
	i							i			i	6.5 Teresh'n
i		i			i			i			(?)	
	i	i			i	i	i				i	17.72 Thwing
i	i	i			i	i	. — .	i		i		
	i							i		i		32.19 [0.93] RandS
i	(?) i			i			i			i	26.58 [1.13]
		÷							!			(7.5 Teres'n
												7.15 Drude 1.05 R and S
									!			
									1			26.0 Drude 10.97 R and S
;		:						. —	• •		1	(1.00 Tranbe
1		1			;				•		·	0.93 K and S
		1			1		_					
		. 1			1	:	_	-		•		0.81 K and S
						1				1		1.02 K and S
			1				-			1		

TABLE I-(Continued)

qualitative tests in this connection. Solutions of lithium chloride in salicylic aldehyde conducts very well. The specific inductive capacity of furfurol would indicate that this solvent would yield solutions that conduct; and such is the case. The dissociative power of the solvents has been previously considered and consequently there are but few additions to be made to what has already been given. Silver nitrate is quite soluble in aniline and xylidine and both yield solutions that conduct very well. A large number of other tests were made which were too detailed to be included in these tabulated results. Suffice it to say, however, that of the very large number of tests made both of organic and inorganic substances in these numerous solvents, there was not one instance when the solution conducted electricity, in which the dissolved substance was not an acid, a base, or a salt.

The additional results of the quantitative measurements of the electrical conductivity will now be given. A resistance cell of the Arrhenius pattern with the electrodes about three millimeters apart was used in making these determinations. The usual method of making the dilutions could not be employed owing to the small quantity of the solvents available. Into the resistance cell was introduced ten cc of the solvent by means of a carefully calibrated burette. The conductivity was measured and then a weighed portion of the salt was introduced, and when this was all in solution the conductivity was measured. Portions of the salt were successively introduced and the conductivity measurements made, until the requisite number of dilutions were made.

In the following tables v represents the volume in liters in which one gram-molecule was contained and μ the molecular conductivity expressed in reciprocal mercury units. The measurements were made at 25° unless otherwise specified. The higher temperatures were obtained by heating the cell with its contents in a paraffin bath and the conductivity was measured as the temperature increased.

ALLYL ALCOHOL

A C. P. sample of allyl alcohol from Merck was treated with

poatssium carbonate, over which it stood for several days. From this it was distilled and the distillate treated with fused potassium hydroxide. The distillate from this was treated with caustic potash in contact with which it stood several days and it was then distilled. This distillate was redistilled twice and the conductivity determinations made as soon as possible. The specific conductivity was 6.5×10^{-6} .

TABLE II

Ferric Chloride, FeCl₃ Ferric Chloride, $(v = 20.02 \text{ at } 25^\circ)$ μ t 21 μ 17.42 25° 20.02 17.42 23.03 50 53.7134.62 115.60 32.15 73 43.63 80 45.65

Solvent: allyl alcohol

BENZYL ALCOHOL

The sample of benzyl alcohol employed was from Merck and was rectified by distillation. The portion used had a very constant boiling-point. Owing to the difficult solubility of the salts and the slight conductivity of solutions of this solvent, very few determinations were made. The specific conductivity was 1.76×10^{-6} .

TABLE III

Solvent	:	benzvl	alcohol

Ferric Chlo	ride, FeCl _s	Ferric Chloride,	(t' = 88.06 at 25°)
τ'	μ	t	μ
88.06	2.62	25°	2.62
895.22	6.31	54	5.08
		85	6.46
		100	7.19

PARALDEHYDE

The sample of paraldehyde from Kahlbaum was distilled and the portion coming over at a very constant temperature was employed. The specific conductivity was less than 3.4×10^{-7} .

TABLE IV

Ferric C Fe	hloride, Cl _a	Antimony Sb(Trichloride,	Antimony Trichlorid $(v = 5.57 \text{ at } 25^\circ)$			
۲	μ	7،	°μ	t	μ		
4.37	9.81	5.57	0.202	25.2°	0.295		
21.32	16.91	20.76	0.356	26.6	0.299		
42.52	18.76	61.16	0.532	29.0	0.298		
81.88	19.16			32.0	0.295		
183.11	16.51						
575.50	16.91						

SALICYLIC ALDEHYDE

The sample of salicylic aldehyde from Schuchardt was rectified by distillation. The portion taken had a constant boilingpoint and the specific conductivity was 5.98×10^{-6} .

TABLE V

Solvent : salicylic aldehyde

Ferric Ch	iloride	, ¹ FeCl ₃ u	Fei	rric Chloride	e, (z' :::	20.39 at 25°)
20.39 81.38 220.74	:	3.76 4.71 5.60	, ,	25° 45 50 109	 :	3.76 6.30 6.73 6.46

FURFUROL

The sample of furfurol from Merck was treated with fused calcium chloride, over which it stood for several weeks. It was then distilled and the distillate again distilled. The portion coming over between 156° and 158° at 744 mm pressure was collected and its specific conductivity was 2.4×10^{-5} .

TABLE	e VI
Solvent :	furfurol

Ferric (Fe	Chloride, eCl ₃	Ferric $(\tau) = 45$	Chloride, .60 at 25°)	Ferric Chloride, $(z'=45.60 \text{ at } 25^\circ)$		
7'	΄΄ μ	t	μ	t	u	
45.60 80.98 149.21	20.78 22.20 26.42	25° 45 55 65	20.78 37.83 40.98 44.06	75° 85 95 105	47.96 51.41 56.07 60.02	

¹ Apparently this did not quite all dissolve. After cooling it became a viscous mass.

METHYL-PROPYL KETONE

The sample of methyl-propyl ketone employed was from Schuchardt and gave a specific conductivity of 9.5×10^{-7} .

TABLE VII

Solvent : methyl-propyl ketone

Ferric C Fe	hloride, Cl _s	Ferric Cl Fe	hloride, Cl ₃	Ferric $(v = 13.$	Chloride, 64 at 25°)	Ferric (<i>t'</i> = 13.	Chloride, 64 at 25°)
v	μ	ζ'	μ	t	μ	t	μ
13.64	28.25	111.13	41.59	25°	28.25	60°	34.07
22.83	31.07	164.43	46.15	49	33.47	70	35.60
53.36	36.98	358.09	50.28	50	33.66	75	35.89
100.71	42.76	1074.27	59.52	55	33.79	80	36.17

CuCl₂ in less than 460.28 liters gave $\lambda = 5.22 \times 10^{-6}$. A resistance of 6000 ohms was introduced in the measuring.

ACETOPHENONE

A sample of acetophenone from Schuchardt was treated with barium oxide, over which it stood for several days, and then distilled. The distillate was redistilled and the portion coming over between 194° and 195° at 745 mm pressure was taken. The specific conductivity of this portion was 1.8×10^{-7} .

TABLE VIII

So:	lvent	:	acetophenone
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Ferric	Ferric Chloride, FeCl ₃			Ferric Chloride, $(t' = 23.46 \text{ at } 25^\circ)$				Ferric Chloride, (1 = 23.46 at 25°			
2'		μ	t		μ		t		μ		
23.46		10.28	25°		10.28		114°		27.49		
46.71		11.03	50		15.17	1	125		28.74		
65.77	i	11.59	" 65		17.52	i.	135		28.85		
124.91		12.03	80		20.52	1	150		28.16		
292.98		13.08	100		23.90	;					

ETHYL MONOCHLORACETATE

This solvent was a C. P. sample from Schuchardt, the boiling-point of which was 143.5°. The specific conductivity was less than 1.7×10^{-6} .

TABLE IX

Ferric C Fe	hloride, :Cl _a	Ferric (2' == 7.2	Chloride, 76 at 25°)	Antimony Trichloride, SbCl ₃
v	μ	t	μ	v μ
7.76	12.45	25°	12.45	4.25 0.174
14.96	13.14	50	15.21	11.49 0.201
19.18	13.49	55	15.77	44.73 0.337
22.09	13.75	67	16.28	Cupric Chloride.
45.63	14.78	80	16.28	
92.05	16.38	92	15.61	$v \mu$
152.55	17.88	100	14.73	13.32 1.24
		IIO	13.11	

Solvent	:	ethvl	monochloracetate
		_	

The CuCl₂ did not quite all dissolve; so $\lambda = 1.33 \times 10^{-5}$.

ETHYL CYANACETATE

This solvent was a C. P. sample from Schuchardt and was rectified by redistillation. The boiling-point was very constant, and the portion collected came over between 203° and 203.5° at 744 mm pressure. The specific conductivity was 3.7×10^{-7} .

TABLE X

Solvent	: ethvl	cvanacetate
20110110		

Silver N Ag2	vitrate,		Ferric Chloride, FeCl ₃		Ferric Chloride,Ferric Chloride,FeCl. $(\tau' = 15.30 \text{ at } 25^{\circ})$		Cupric Chloride CuCl ₂	
t, c,	Ϊμ		2'	μ	t	- μ	ζ'	μ
10.62	4.19		15.30	8.88	25°	8.88	 29.85	7.00
19.00	4.78		19.72	8.99	49	13.40	41.67	7.50
28.30	5.29	· ·	27.08	9.29	60	15.85	59.40	8.08
58.57	6.46		44.64	9.80	75	20.14	97.77	12.80
110.97	7.66	1	185.22	11.57	87	22.44		
		•			100	24.83		
		1			125	29.49		
					1 50	38.70		

ETHYL OXALATE

This solvent was a C. P. sample from Merck, and its specific conductivity was 7.12 \times 10^{-7}.

TABLE XI

Ferric C	hloride,	Ferric Cl	iloride,	Fe	erric C	hloride,	Ferric C	hloride,
ге 7	΄, μ	۲e ۲'	μ^{α}	(2)	t = 13.1	$\mu^{(5 \text{ at } 25^{\circ})}$	t^{-13}	$\mu^{15 \text{ at } 25^{-}}$
13.15	5.88	94.79	6.25	1	25°	5.88	75°.	10.15
22.07	5.89	342.85	7.70		50	8.11	100	11.14
42.29	5.92				62	9.2I	125	9.58
				(At	148°	solution	began	to boil.)

Solvent : ethyl oxalate

ETHYL BENZOATE

This sample was a C. P. sample from Trommsdorff, and its specific conductivity was about 1.8×10^{-7} .

TABLE XII

Solvent : ethyl benzoate

Ferric (Fe	hloride, 21 ₈	Ferric Chloride, $(\tau = 29.54 \text{ at } 25^\circ)$		
ζ'	μ	t	μ	
29.54	1.55	 25°	1.55	
174.28	1,61	56	1.16	
517.21	1.91	75	0.82	
		IOO	0.48	

AMYL NITRITE

This solvent was a C. P. sample from Schuchardt, and its specific conductivity was 1.8×10^{-7} .

TABLE XIII

Solvent : amvl nitrite

Ferric Chloride, FeCl ₃		Ferric Chloride, FeCl ₃		Ferri (7 = 21	c Chloride, .34 at 25°)	
ť		μ	2'	μ	t	μ
 21.34	-	1.54	104.64	2.29	25°	1.54
29.03	,	1.63	264.16	3.00	50	1.13
38.74		1.74	644.56	3.73	55	1.08
69.46		2.02			6.1	I, 2I
			(At about	TOC the	solution	horan to boil

(At about 70° the solution began to boil.)

NITROBENZENE

The sample of nitrobenzene employed was from Kahlbaum and was prepared from crystallizable benzene. The specific conductivity was less than 3.5×10^{-7} .

TABLE XIV

Solver	1t :	nitro	benzene

Bismuth Trichloride, BiCl ₃		Bismuth Trichloride, BiCl ₃		Aluminium Chloride, Al Cl_3^{x}	
τ'	μ	71	μ	τ'	μ
8.50	0.80	68.04	1.03	4.69	3.67
17.01	0.91	136.07	1.07	9.38	4.51
34.02	0.96	272.14	Ι.ΙΙ	1	

ORTHO NITROTOLUENE

The C. P. sample of this solvent employed was from Kahlbaum, and the specific conductivity was less than 1.8×10^{-7} .

TABLE X	. V
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Solvent : ortho nitrotoluene

Ferric Cl	iloride,	Ferric (Chloride, ²	Antimony I	richloride,
Fe	Cl _a	($v = 10.$	91 at 25°)	Sb	Cl _a
v	μ	t	μ	7'	μ
10.94	8.37	25°	9.39	3.40	0.056
16.38	9.44	46	11.98	6.55	0.088
25.99	10.74	60	12.77	19.82	0.244
74.28 201.43	13.32 15.24	70 80 90 100	12.92 12.67 12.12 11.46	34.10 Mercuric Cl v 105.43	0.389 1loride, HgCl ₂ µ 0.628

META NITROTOLUENE

The C. P. sample of this solvent was from Kahlbaum, and the specific conductivity was less than 1.8×10^{-7} .

TABLE XVI

Solvent:	meta	nitrotoluene

 Ferric Cl	hloride,	Ferric (Chloride, 6 at 25°)	Ferric Cl $(7' = 10.86)$	iloride,	
22	μ	t	μ	t	μ	
10.86	6.86	2.5°	6.86	80	15.66	
46.93	11.10	50	12.28	90	17.35	
84.77	12.55	60	13.05	100	18.20	
448.14	19.00	70	13.82	125	16.80	
814.81	18,20			1		

¹ Aluminium chloride dissolved with evolution of heat. When the solution was diluted the evolution of hydrochloric acid gas was very perceptible, and for this reason no further determinations were made.

 $^{\circ}$ This solution remained in the resistance cell for two hours before the determinations were made.

BENZONITRILE

The C. P. sample of this solvent employed was from Trounnsdorff, and the specific conductivity was $1.9 < 10^{-6}$.

TABLE XVII

Solvent : benzonitrile

Silver Nitrate, AgNO $_3$		 Siiver N Ag	Vitrate, NO _a		Silver Nitrate, $(v = 2.09 \text{ at } 25^\circ)$		Silver	Nitrate, 9 at 25° 1
τ'	μ	ī '	μ		t	μ	t	μ
2.09	3.37	58.98	11.19		25°	5.55(?)	95°	9.26
9.43	5.18	83.92	13.41		50	6.75	105	9.65
16.33	6.37	151.96	16.38		56	7.05	114	10.09
24.06	7.66	301.21	18.20		65	7.59	125	10.69
44.62	10.12	803.24	21.64	1	77	8.11	135	11.20
					87	8.75	150	11.70

PYRIDINE

The sample of pyridine from König was fractionated, and the portion distilling over between 106° and 117° was treated with fused caustic potash from which it was distilled. The distillate was again treated with caustic potash, over which it stood for several days and was then distilled. The distillate was redistilled and the portion coming over between 113° and 114° at 742 mm pressure was employed in some of the following determinations. The specific conductivity was 7.6×10^{-7} . For other determinations a C. P. sample of the solvent from Kahlbaum was employed, and its specific conductivity was about 7.5×10^{-7} .

TABLE XVIII

Solvent : pyridine

				· · · · · · · · · · · · · · · · · · ·		-	
Ferric C	hloride	Ferric Cl λ of solvent	hloride,	Ferric	Chloride,	Ferric (hloride.
יז ז'	μ	7' T	μ	t	μ	t = 0.0	μ
First	Series	(Second	$\mathbf{Series})$	2,5 0	7.96	80°	21.16
6.06	7.96	45.5^{2}	6.32	54	16.50	85	22.71
15.02	7.5^{2}	93.69	5.91	59	17.24	90	23.36
24.56	6.85	159.55	5.57	65	18.23	95	24.12
42.18	6.82			70	19.59	100	24.80
95.35	6.41			75	20.40	105	25.61
						110	25.61

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Silver Nitrate, AgNO $_3$		Silver 1 Ag2	Nitrate, NO ₃	Lead Pb(1	Nitrate, NO ₃) ₂	Mercuri He	e Iodide, gI ₂
υ	̈μ	υ	μ	۲,	μ	۲	μ
First	Series	Second	Series	21.10	0.81	21.78	0.35
7.55	24.07	392.28	40.16	55.96	1.57	93.61	1.39
10.71	24.87	588.42 :	43.13	168.47	3.25	200,12	2.70
17.70	25.79 26.01	784.56	45.21	Cupric C	hloride,	Silver T C _s H ₄ (artrate, D _e Ag _o
27.13	27.29	AgC	N	7' Cuc	μ	7′ ۲	μ
37.32	27.96	2'	μ	45.10	0.98	340.74	14.64
51.43	29.49	14.64	4.78	57.04	1.16	1305.91	35.29
60.90 93.71	30.17 30.83	24.52 38.40	5.04 5.4^{2}	Mercuric Hg(Cyanide, CN)	Cobaltic (Co	Chloride, Cl ₂
140.57	36.21	100.47	6.16	2،	μ	2،	μ
1.07	0	393.01	6.47	5.35 13.09	0.01 <i>2</i> 0.014	74.06 805.31	0.20 1.45
	:	1		357.42	0.153		

A solution of cobaltic chloride becomes deep blue at a temperature between 40° and 50° . The following specific conductivity determinations were made in order to ascertain whether the two differently colored solutions had the same conductivity.

	λ at 25°	λ at 55°
Solvent Saturated solution of CoCl ₂ at 25°	$\begin{array}{c c} 7.5 \times 10^{-7} \\ 2.9 \times 10^{-6} \end{array}$	1.4×10^{-6} 5.5 × 10^{-6}

PIPERIDINE

A C. P. sample of this solvent from Kahlbaum was employed, and its specific conductivity was less than 1.8×10^{-7} .

TABLE XIX

Solvent : piperidine

Sil ver Nitrate, AgNO $_3$			Silver N AgN	Vitrate, NO ₃	Silver (v = 4.2)	Silver Nitrate, $z' = 4.24 \text{ at } 25^\circ$) Silver Nitrate, $t = \mu$ $z_5^\circ \mid 0.368 = 40^\circ 0.453$			
v	μ		7'	μ	t	μ		t	μ
4.24	0.368	. 1	10.50	0.091	250	0.368		40°	0.453
5.25	0.277	1	15.62	0.043	30.5	0.391		45	0.478
7.88	0.154	.1			35	0.432	i	50	0.508

QUINOLINE

The sample of this solvent employed was from Merck, and its specific conductivity was 3.7×10^{-7} .

		Solvent	: quinoim	e		
Silver N AgN	itrate, O ₃	Silve $(t' = 4)$	r Nitrate, 80 at 25°)	$\operatorname{Silve}_{(z')}$	er Nitrate, 4.80 at 25°)	
τ'	μ	t	μ	t	μ	
 4.80	2.45	25°	2.45	85°	5.89	
9.60	2.79	50	4.67	104	5.75	
34.92	2.80	62	5.20	I 24	5.77	
129.83	3.62	70	5.52	136	5.52	

TABLE XX

Limiting values for the molecular conductivity can be obtained in aqueous solutions, but this is, however, generally not the case in non-aqueous solutions. A few examples of those solvents that yield solutions that conduct the best will be given to illustrate this.



In Fig. 1 is plotted the molecular conductivity of various salts in methyl alcohol from the determinations of Vollmer at 18°. The molecular conductivity is represented by the ordinates and the cube root of the volume in which one grammolecule of the substance was dissolved by the abscissas. The cube root of the volume was employed in order to represent the values for the more dilute solutions in the figure. In Fig. 2 are plotted the results of Zelinsky and Krapiwin determined at 25°. In most cases, it will be observed that limiting values are

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reached, CdI_2 being, however, an exception, Zelinsky's and Krapiwin's determinations for KI indicate that the curve would probably not become asymptotic and, therefore, no limiting value for μ would be reached. Nevertheless, Carrara assigns 97 as the value for μ_x . Cohen has pointed out that the difference in the determinations of Zelinsky and Krapiwin and of Carrara may be attributed to the effects of the alcohol on the platinum black electrodes which they employ. In Fig. 3 is plotted the molecular conductivity of various salts in ethyl alcoholic solutions from the determinations of Vollmer at 18°. It will be noticed that the salts of the alkalies yield limiting values for μ , while in the case of CaCl₂ there seems to be no tendency for the curve to become asymptotic. The same is true for Ca(NO₃)₂, and according to my determinations for FeCl₂ and SbCl₂.

Carrara has calculated the values of μ_{∞} for a number of halogen salts from Campetti's' determinations of the transfer-

¹Nuovo Cimento [3] 35, 225. (Ref.) Jahr. der Elektrochemie, 1, 22 (1894).



ence figures of the halogens in methylic alcohol solutions. He finds these values to agree very closely with his own experimental results. In the following table are given these results and also the value of μ_{∞} in water.

TABLE AA.	TA	BLE	Х	Х	I
-----------	----	-----	---	---	---

	Valı	tes of μ_x		
	In Met	hyl Alcohol		
	CI	Br	I	OH
Н	133.80	• • • •	134.50	
Li	77.30		• • • •	• • • •
Na	86.80	87.58	89.77	71.83
K	95-57	96,52	97.63	75.75
$\rm NH_{+}$	96.24	99.93	105.25	82.00
$N(CH_p)_q$	• • • •		115.30	
$N(C_2H_k)_4$	95.76	96.6 <i>2</i>	113.76	91.13
$S(C\dot{H}_{s})_{s}$	100.09	102.50	116.38	97-34
	I	n Water		
	CI	Br	I	OH
Η	395.20	398.0	397.0	• • • •
Li	110,00	• • • •		• • • •
Na	119.40	122.2	121.4	216.2
K	140.80	143.6	142.6	237.6
NH_{4}	140.6	143.4	142.6	230.0
$N(CH_s)_4$	• • • •		115.6	
$\mathbf{N}(\mathbf{C}_{2}\mathbf{H}_{p})_{4}$	102.4	105.2	104.2	199.2
$\mathbf{S}(\mathbf{CH}_{s})_{s}$	117.8	120.3	119.3	214.0

From Campetti's results Carrara calculated the rate of migration of the ions in methyl alcoholic solutions and the results are given in the following table, which is taken from the *Jahrbuch der Elektrochemic*, **3**, **1**3 (1896).

TABLE XXII

	Speed c	of Migratic	n			
	Cl In	In Methyl Alcohol Cl Br I				
Li	27.83			39.8		
Na	37.33	37.33	37.33	49.2		
K	46.10	46.26	45.19	70.6		
NH_{*}	46.77	49.49	53.81	70.4		
$N(\dot{C}H_{s})_{s}$			63.08	43.6		
$N(C_{o}H_{o})$	46.29	46.36	61.34	32.2		
$S(CH_{3})$	51.43	49.85	63.94	47.6		
H	85.53	••••	82.50	325.0		
OH	· · · · · · · · · · · · · · · · · · ·	32.00		170.0		
C1		49.47		70.2		
Br		50.24		73.0		
I		52.44		72.0		
CH,COO	1	32.99		38.4		
CCI COO		35.95		32.8		

Kawalki¹ found that the diffusion coefficient of a number of substances in ethyl alcohol is 0.34 times as great as in water. Vollmer from his work observed that the conductivity in ethyl alcoholic solutions at 18° is approximately 0.34 times as great as in aqueous solutions, while his empirical factor for methyl alcohol is 0.73. In general limiting values can be obtained for μ in methyl and ethyl alcoholic solutions except in the case of some salts of the heavy metals.

In other alcoholic solutions no such uniformity seems to exist. This is perhaps best illustrated in the case of solutions in propyl alcohol. The molecular conductivity of solutions in this solvent is represented in Fig. 4. The determinations are from Schlamp's² work. It will be noted that lithium salicylate is the only salt the conductivity of which appears to approach a

^{&#}x27; Wied. Ann. 52, 300 (1894).

² Zeit. phys. Chem. 14, 272 (1894).

limiting value. Schlamp does not hesitate, however, to assign values for μ_x in all cases, and from the plotted results this seems hardly justifiable. In the case of other alcoholic solutions, the



experimental evidence is so meagre that no generalization can be made (See Tables II, III).

The ketones were found to yield solutions that conduct electricity and this is in keeping with what the other investigators¹ have found.

Acetone yields solutions the conductivity of which is, in general, better than in the case of many of the other ketones. In Fig. 5 is represented the conductivity of a number of salts in this solvent. The results plotted are from the determinations of Carrara principally, while those designated L are from Laszczynski, and those with D from Dutoit and Aston.

It will be noted that very few salts yield solutions in acetone that have limiting values for μ . The values for two curves, for NaI and for $N(C_2H_5)_4I$, appear to indicate a decrease in the conductivity after certain dilutions are reached. The two curves

 $^{^{\}rm t}$ (1)Laszczynski. Zeit. Elektrochemie, 2, 55 (1895). (2) Carrara. Gazz. Chim. Ital. 27, I, 207. (Ref.) Jahr. der Elektrochemie, 4, 48 (1897). (3) Du-toit and Aston. Comptes rendus, 125, 240 (1897).

plotted for KI apparently intersect at about $\mu = 153$. Laszczynski thinks the value of μ_x lies between 160 and 170. Assuming the former value he calculates the factor k in the formula $\mu_x = k(\mu \pm \tau)$ where $(\mu \pm \tau)$ is the conductivity at infinite dilution in water and k is a constant. The value of k he finds to be 1.3. If this method be applied to salts other than the one he



employed, KI, — to CdI_2 for instance, — it will be found that different values for k will be obtained. There is no such agreement between the limiting values for μ in acctone and in water as Vollmer found to hold in the case of ethyl alcohol and water.

In the other ketones the conductivity is not as great as in acetone, and while limiting values are obtained in some cases, they are of the same order as CdI_{z} in acetone, that is, the value

of μ remains virtually constant with the dilution. So in general limiting values in the ketones cannot be obtained.

Laszczynski and Gorskiⁱ have measured the molecular conductivity of a number of salts in pyridine and their results are plotted in Fig. 6. They assign limiting values to μ in the case



of NH₄CNS, NH₄I, KI, and NaI. It appears that the curves representing the conductivity of the solutions of these salts might become asymptotic. The values for AgNO₃ are my own determinations and these do not appear to approximate to a limiting value for μ , at least not in the dilutions at which the measurements were made. The conductivity of the other salts in pyridine is rather low and limiting values cannot, in general, be obtained.

Silver nitrate in benzonitrile does not yield limiting values for μ . The solutions in the other nitriles conduct well, but they do not generally yield limiting values for μ . Ferric chloride in nitrobenzene yields solutions in which the value of μ approaches a limit.

From the preceding it appears that there is no general uni-

¹ Zeit. Elektrochemie, 4, 290 (1897).

formity of limiting values in non-aqueous solutions as is found in the case of aqueous solutions.

The degree of dissociation in aqueous solutions is calculated from either the boiling-point or cryoscopic determinations or from the electrical conductivity of the solution. These methods yield concordant results, but in non-aqueous solutions this is not the case.

In order to calculate the degree of dissociation from the electrical conductivity measurements it is necessary to know the value of μ_{∞} . It has been pointed out in the preceding that limiting values for μ are not always obtainable in non-aqueous solutions. In alcoholic solutions values for μ_{∞} can generally be found. In the following table from Woelfer are given the values of the degree of dissociation, a, in methylic alcohol solutions as calculated from the boiling-point determinations of Woelfer, and from the conductivity measurements of Vollmer:

TABLE XXIII Values of α

Salt		Percent	From boiling-point		From conductivity
 LiCl		0.45	0.63	T	0.57
KI		0.36	0.61		0.79
NaI	i	0.44	0.87	1	0.74
CH _s COOK		0.48	0.48		0.63
CH COONa		0.40	0.49		0.63

The degrees of dissociation in methyl alcoholic solutions as calculated from the boiling-point determinations, show closer agreement with those obtained from the conductivity determinations than in the case of the other alcoholic solutions.

Salvadori¹ found HgCl₂ to be more highly dissociated in the methyl alcohol according to the boiling-point determinations than in aqueous solutions. Beckmann² found the reverse to be true in ethyl alcoholic solutions. Jones and King³ calculated

¹ Gazz. Chim. Ital. **26**, I, 237 (1896). (Ref.) Jour. Chem. Soc. **70**, ii, 712 (1896).

² Zeit. phys. Chem. **6**, 437 (1890). ³ Am. Chem. Jour. **19**, 753 (1897).

the dissociation of KI in ethyl alcohol, from their boiling-point determinations, to be 25.4 percent in a 2 percent solution, and 27.2 percent in a 3 percent solution, i. e. the dissociation increases with the concentration. Cohen,¹ from the conductivity determinations at 18°, found the degree of dissociation of KI to increase with the dilution, being about 80 percent dissociated at a dilution of about 1000 liters. This disagreement of the dissociation values obtained by these two methods will be made more apparent perhaps by Table XXIV, which is copied from Woelfer's paper. The results by the boiling-point method were obtained by himself, those by the conductivity method by Vollmer.

TABLE XXIV

Values of a

Salt	Percent in ethyl alcohol	From boiling-point	From conductivity
LiCl	0.9	0.35	0.32
CH ₃ COOK	1.07	0.18	0.27
KI	0.78	0.29	0.49
AgNO_{s}	0.53	0.65	0.38
NaI	2.I.	0.27	0.45
NaI	0.68	0.51	0.56
CH _s COONa	0.97	0.01	0.24

It is to be remembered that these two sets of values are calculated from results obtained at different temperatures; in the case of the conductivity measurements at 18° , when the viscosity factor is about 0.01211, and in the other case at 78° when that factor had decreased (at 70° to 0.00521). Yet it will be seen that there is no regularity of the results and that the degree of dissociation according to the boiling-point determinations is not invariably higher than that obtained by the conductivity method. It is no doubt but natural to ask, which of these methods gives the correct measure of the amount of dissociation of the dissolved substances.

There have been too few molecules weight determinations of salts in the ketones made by the boiling-point method. This

¹ loc. cit.

method, according to Dutoit and Friderich¹, yields normal molecular weights for a number of salts when dissolved in acetone. These substances, with the exception of LiCl and CdI₂, yield solutions that conduct fairly well. This would tend to indicate that they are quite highly dissociated while the boiling-point determinations indicate that they are not dissociated.

Attention has already been called to the fact of the conductivity of ferric chloride in nitrobenzene while the cryoscopic determinations indicate higher molecular weights than the theoretical.

In benzonitrile Werner² found normal molecular weights for AgNO₃ while from Table XVII it will be seen that this solvent yields solutions of AgNO₃ that conduct well. It still remains to be seen what the molecular condition of substances in other nitriles is according to the boiling-point determinations.

Werner's boiling-point determinations show normal molecular weights for the salts of the heavy metals in pyridine. The average of his determinations for AgNO₃ is 165.4, theory 169.55; for Hg(CN)₂, 216.68, theory 251.76; for HgI₂, 308.0, theory 452.88; and for Pb(NO₃)₂, 352.07, theory requires 330.35. In most cases he obtained values a little under the theoretical. The greatest discrepancy occurs in the case of HgCl₂, and it will be observed that the solution of this salt yields small values for μ . From Table XVIII it will be observed that this solvent yields conducting solutions and since μ_{z} is not known the degree of dissociation cannot be calculated.

From the preceding consideration it is apparent that there is not that agreement between the degrees of dissociation as calculated from the boiling-point or cryoscopic determinations and from the conductivity measurements in non-aqueous solutions as has been found to hold in aqueous solutions.

In aqueous solutions the molecular conductivity always increases with the dilution. From the analogy of the electrolytic dissociation of substances in aqueous solutions to the dissociation

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

^a Zeit. anorg. Chem. 15, 1 (1897).

of gases, Ostwald formulated a law of dilution for binary electrolytes which is as follows: $K = \frac{a^2}{(1-a)V}$; where $a = \frac{\mu_v}{\mu_x}$ and V is the volume in which one gram-molecule of the dissolved substance is contained. In aqueous solutions of weak electrolytes this law generally holds fairly well; and attempts have been made to apply it to non-aqueous solutions. Most investigators, Vollmer, Woelfer, Cattaneo, and others have found that Ostwald's dilution law does not hold for methyl and ethyl alcoholic solutions. Cohen has considered this subject at considerable length and comes to the same conclusion.

Rudolphi's formula, which differs from Ostwald's in having 1 V for V, has been shown to hold no better than Ostwald's. The values of the constant as calculated by these two formulae from the conductivity determinations of potassium acetate are given in the following table which is taken from Cohen's article. K_R indicates that those values were obtained by using Rudolphi's formula while K_{\circ} indicates that Ostwald's was employed.

TABLE XXV.

V.	μ	100 K_R	100 K ₀
II.4	8.28	0.82	0.242
113.0	17.18	0.59	0.055
II20.0	27.00	0.49	0.014
3520.0	29.20	0.36	0,006

From the preceding it therefore appears that neither the dilution law of Ostwald nor that of Rudolphi holds for alcoholic solutions. It has been shown in the case of propyl alcoholic solutions that we are not justified in extrapolating values for μ_{ex} , hence the validity of the law of Ostwald and that of Rudolphi cannot be tested in regard to this solvent nor are the data sufficient to warrant conclusions being drawn concerning the applicability of these laws to other alcoholic solutions.

From Fig. IV it will be observed that the molecular conductivity increases with the dilution except in the case of CdI_{ϕ} in acetone. The value of μ remains virtually constant and Dutoit and Friderich found the same to be true for solutions of this salt in acetophenone. In the case of solutions of CdI_2 in methyl-propyl ketone and methyl-ethyl ketone the conductivity decreases with the dilution and the same was found by us to be the case for stannous chloride in acetone. Euler¹ found the molecular conductivity of both NaI and NaBr in benzonitrile to decrease with the dilution. The conductivity of ferric chloride solutions in benzaldehyde decreases with the dilution and the same is true of solutions in pyridine. Silver nitrate in piperidine yields solutions the conductivity of which decreases with the dilution.

In face of these experimental results and in view of the fact that in non-aqueous solutions there are but few cases where values for μ_{∞} can be obtained, it appears that neither the dilution law of Ostwald nor that of Rudolphi can hold in non-aqueous solutions.

In general the conductivity of non-aqueous solutions increases with the increase of the temperature. There are no exceptions to this in aqueous solutions, but in non-aqueous solutions there are a few. The molecular conductivity of solutions of CdI₂ in acetone remains the same at 50° as at 25°; but it must also be remembered that the conductivity of this salt does not change with the dilution. Solutions of CdI₂ in acetonitrile yield virtually the same values of μ at 0.2° as at 37.2°. The values of μ for SbCl₃ in paraldehyde are practically the same at 25.2° as at 32°. In ethyl benzoate the conductivity of solutions of FeCl₃ decreases from 1.55 at 25° to 0.48 at 100°, and the conductivity of solutions of FeCl₃ in amyl nitrite is practically constant at all temperatures tested.

There are not sufficient data to determine accurately the temperature coefficient of most of the non-aqueous solutions and particularly of the alcoholic solutions with which the most work has been done. But it can be stated that, in general, the conductivity does not increase proportionately with the temperature. It has been pointed out by Zelinsky and Krapiwin and later it has been confirmed by Cohen, as well as by Walker and Ham-

¹ Zeit. phys. Chem. **28,** 619 (1899).

bly, that the temperature coefficient seems to be but slightly influenced by the addition of a non-electrolyte or even of a small quantity of water.

Although this investigation has been confined to the study of the conductivity of anhydrous salts and solvents it may be of interest to call attention to the work of some investigators on mixtures of water and alcohol. The following table of comparative conductivities is taken from the work of Zelinsky and Krapiwin. In the column headed A is given the conductivity in aqueous solutions, under B in methyl alcoholic solutions and under C is given the conductivity in a 50 percent solution of methyl alcohol and water.

			KBr			NH₄Br	
τ		А	В	С	А	В	С
16		123.1	• • • •	59.82	I 27.2	65.43	61.16
32	l	127.5	69.02	62.46	131.8	72.73	63.81
64	1	130.5	76.70	65.36	135.3	79.56	66.04
128	- i	132.9	83.60	67.11	138.6	85.80	67.45
256		136.4	88.96	69.26	141.2	90.88	68.32
512		140.2	93.26	70.53	143.5	94.99	69.10
1024		143.4	97.25	• • • •	145.6	98.24	70.11
			KI			NHI	
τ'		А	В	С	A	В	С
16		124.5	69.20	62.13	125.4	72.24	62.63
32		128.2	76.35	64.37	129.6	78.74	65.04
64	Ì	130.5	82.52	66.01	133.4	85.0	67.48
128		133.0	88.69	67.45	135.9	91.14	69.28
256		135.8	93.85	. 68.28	138.7	96.20	70.34
512		137.9	98.19	69.65	141.3	100.6	71.12
1024		140.9	102.2	70.55	143.7	104.7	71.57

TABLE XXVI

It will be noticed that the conductivity of the halogen salts of the alkalies in methyl alcohol (B) is considerably less than in aqueous solutions (A). When water is added to the extent of 50 percent even (C), the molecular conductivity is somewhat less than it is in methyl alcohol. Cohen and others have pointed out the same fact : that is, at 18° the conductivity of a mixture of water and alcohol, containing more than 60 percent of alcohol,

¹ Jour. Chem. Soc. 71, i, 66 (1897).

is less in dilute solution than in absolute alcohol. This fact seems to be rather difficult to reconcile with the electrolytic dissociation theory, for here we have two solvents that possess dissociative power in a high degree, and yet a salt dissolved in a mixture of equal parts of these yields a solution the conductivity of which is less than that of the solutions formed when dissolved in either.

Carrara¹ has shown that the electrolytic dissociation of water in methyl alcohol is greater than in aqueous solutions, while the reverse is the case in ethyl alcohol. It is also of interest to note that KOH and NaOH in methyl alcohol show the same conductivity as CH₂OK and CH₂ONa.

As has been previously noted,² Nerust calls attention to the fact that solvents which have a high specific inductive capacity, vield solutions that conduct; and he argues that the greater the dielectric constant of a solvent, the greater is the power of dissociation. In general, those solvents that have a high dielectric constant do yield solutions that conduct, but the molecular conductivity is not commensurate with the dielectric constant. Lithium chloride in an aqueous solution (dielectric constant of H₂O is 78), gives a value of 95 for μ_{∞} at 18°; while in propyl alcohol (dielectric constant is 20.45) in a volume of about 3000 liters, the value of μ at 15° is given as 128.9. In fact, most of the values of μ in dilute solutions of propyl alcohol are, according to Schlamp, greater than the values of μ_{z} in water. In methyl alcohol (dielectric constant is 32.65) the value for μ_{∞} for $N(C_2H_2)$, I is 113.8, while in water it is 107.6; for $N(CH_2)$, I the values of μ_{∞} in both solvents are virtually the same (115.3). In other alcoholic solutions the values of μ do not even approximate to those in aqueous solutions, however.

Esters, the dielectric constants of which are very low, yield solutions that conduct, — for example — ethyl oxalate, ethyl benzoate, and ethyl acetate. Attention has previously been called³

¹ Gazz. Chim. Ital. 27, I, 422 (1897). (Ref.) Jour. Chem. Soc. 72, ii, 473 (1897).

² Jour. Phys. Chem. **3**, 12 (1899).

³ Ibid. 3, 21 (1899).

to the fact that ethyl acetoacetate yields solutions of ferric chloride that conduct better than those in ethyl cyanacetate, the dielectric constant of the latter being 26.7, while that of the former is only 15.7. The values of μ in acetone approximate to and in some cases exceed the values in methyl alcoholic solutions. Benzonitrile was the only nitrile the dielectric constant of which could be found in the literature, but it is probable that the value of the other constants is relatively high. The value of μ for acetonitrile solutions approximate closely to those obtained for aqueous solutions, while for CNS.NH₄ and NaI, μ is of about the same magnitude as for AgNO₃ in benzonitrile. The dielectric constants of pyridine, piperidine and of quinoline could not be found in the literature.

From these considerations it therefore appears that while those solvents which have a high specific inductive capacity are the ones which, in general, yield solutions that conduct the best, the magnitude of μ is not proportional to the value of the dielectric constants.

Dutoit and Friderich,' from the results of other investigators and from their own researches on the ketones and nitriles, conclude that "la conductibilité des electrolytes dissous dans un dissolvant non polymérisé est null." The degree of accuracy of this statement will become manifest when the following table is examined. In Table XXVII are arranged the names of a number of solvents in the order of increasing coefficients of association. The names appear in the first column, the coefficients of association in the second. These values were mostly determined by Ramsav and Shields (See Table I). The third column contains the viscosity factors, η , as far as they could be obtained from the tables of Dutoit and Friderich and of Landolt and Börnstein. The last three columns contain the formulæ of the salts, the volume in liters in which one gram-molecule was dissolved, and the molecular conductivity at that particular concentration. That salt was usually chosen which gave the largest value for μ .

⁴ Bull Soc. Chim. Paris, (3) **19**, 321, (1898).

	Coefficient of	Dielectric constant				
Solvent	association	(Air I)	h.	Salt	12	μ
Quinoline	0.81		•	AgNO	120.8	3.62
Paraldehyde	0.85		•	l'eCl	575.5	17.00
Pyridine	0.93	•	••••	I'HN	2528.6	41.00
Nitrobenzene	0.93	32.19	:	FeCi	1451.0	20.80
Ethyl acetoacetate	0.96	15.70	•••••	FeCL	503.5	23.40
Benzonitrile	0.97	26.00		AgNO,	803.0	21.64
Benzaldehyde	0.97	14.48	· · · ·	FeCI	25.6	14.30
Phosphorus trichloride	1.02	: : :	•	•	:	
Auiline	1.05	7.50	••••	•	:	••••
Acetophenone	1.05	16.40	•	FeCI	293.0	13.00
Carbon disulphide	1.07	2.61	0.00357	•	•	
Piperidine	1.08	• • •	•	AgNO	4.24	0.37
Methyl-propyl ketone	1.1.1	16.75	0.0044	AgNO.	1074.0	50.50
Methyl-ethyl ketone	1.15	18.44	0.0041	CNS.NH	94.8	19.70
Butyronitrile	1.22	•	0.0056	AgNO ₃	150.4	32.10
Acetone	1.26	21.85	0.0031	KI	2315.2	153.20
Propionitrile	1.40	••••	0.0040	AgNO ₃	256.0	38.86
Acetonitrile	1.60	•	0.0033	Ag NO ₃	1141.4	159.30
Allyl alcohol	1.88	21.60	0.0130	FeCI	115.6	32.20
Propy1 alcohol	2.25	20.45	0.0200	NaI	4495.5	174.70
Ethyl alcohol	2.74	25.70	0.0109	KI	8	46.00
Methyl alcohol	3.43	32.65	0.0055	KI	8	89.60
Water	3.60	78.00	0.0080	KI	8	142.60

Тлві, ХХVІІ

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Azariah T. Lincoln

It will be observed that those solvents down to and including benzaldehvde, are not polymerized liquids according to the values of their coefficients of association, and they all produce solutions that conduct electricity. Among these are benzaldehyde and paraldehyde, both of which vield solutions that conduct well. Benzonitrile, the coefficient of association of which. even according to Traube, shows virtually no polymerization, vields solutions that conduct very well; and according to Werner gives normal molecular weights by the boiling-point method. Further, ethyl acetoacetate yields solutions that conduct very well; vet its molecules are not polymerized. It will also be noted that all of these solvents have relatively high dielectric constants. Solutions in nitrobenzene conduct; but according to Ramsev and Shields its molecules are not polymerized. Traube, however, gives a value of 1.47 for the coefficient of association of this substance. Of the organic bases quinoline vields solutions that conduct and shows the lowest degree of association of any of the solvents. Pyridine dissolves a large number of salts, and vields solutions that conduct; vet its molecules are not polymerized. It will be seen that the group of solvents whose coefficients of association are between 1 and 1.08 inclusive, thus indicating a very slight degree of polymerization, vield solutions that conduct slightly, and Ramsey and Shields regard most of these as non-polymerized liquids. Aniline yields solutions that conduct, particularly solutions of silver nitrate; acetophenone solutions do not conduct very well; and those in piperidine conduct poorly; while phosphorus trichloride and carbon disulphide, whose molecules are slightly polymerized, do not vield solutions that conduct electricity.

The molecular conductivity of solutions of different solvents is not commensurate with the degree of polymerization of their molecules. The examples given to illustrate that the molecular conductivity is not proportional to the dielectric constants of the solvents are applicable here as well. The value of μ depends, however, to a great extent upon the salts chosen; for example, the molecular conductivity of CdI_a is virtually constant (11.7) in acetone and in propionitrile it is 19.2 at dilution 512 liters; while the molecular conductivity of silver nitrate is 35 in ethyl alcohol at dilution 41,000 liters and 159 in acetonitrile at 1,141 liters. The coefficient of association of ethyl alcohol is 2.74 and that of acetonitrile is 1.60.

The coefficients of association as determined by Ramsey and Shields have been employed in preference to those by Traube' because the method of the former has a better theoretical basis, and their results are more in accord with those of other investigators. Traube gives for the value of the coefficient of association for benzene 1.18, for toluene 1.08, for ethylene chloride 1.46; and not any of these solvents yield solutions that conduct electricity. Then he gives values for the esters that are very much in excess of the determinations of other investigators, whereas the values for the alcohols are very much less. For example, for methyl alcohol he gives as the coefficient of association 1.79, for ethyl alcohol 1.67, for propyl alcohol 1.55, and for water 3.06. (Compare with the values given in Table I.)

Many solvents, whose molecules are polymerized, yield solutions that conduct electricity, and there are some whose molecules are supposed to be polymerized that do not yield solutions that conduct; and if Traube's results be taken, a large addition to those cited above could be given. It has also been pointed out that there are a considerable number of solvents, whose molecules are apparently not polymerized, yet whose solutions conduct electricity well,—for example, benzonitrile, ethyl acetoacetate, etc.

From the considerations presented in the preceding it appears that the theory as promulgated by Dutoit and Friderich, that only polymerized solvents yield solutions that conduct, is untenable.

Sometime before Dutoit and Friderich published their conclusions, Crompton² assigned a wider rôle to the associative property of liquids. He presents the view, that by means of this

¹ Ber. chem. Ges. Berlin, **30**, 273-4 (1897).

² Jour. Chem. Soc. 71, ii, 925(1897).

theory of association the anomalous results obtained in the case of certain dissolved substances, electrolytes, by the boiling-point, freezing-point and osmotic pressure determinations, can be easily explained; and aims to show that the electrolytic dissociation theory is not only unnecessary but in many respects inadequate. As has been previously pointed out no proportionality exists between the values of the dielectric constants of the solvents and the molecular conductivity of their solutions. Crompton calls attention to the connection between the specific inductive capacity and the degree of association of the solvents. This parallelism has also been pointed out by Abegg¹ who further observes that nitrobenzene, ethyl nitrite and benzonitrile all have high dielectric constants; vet their association factor is unity. This, he thinks, fulfills the primary conditions of a self-dissociating substance. Crompton further states: "It is almost impossible to doubt that association plays an all-important part in determining the value of the specific inductive capacity of a liquid, and that if there is any connection between the specific inductive capacity and the power of forming electrolytes, it may be looked for rather in the fact that electrolytes are solutions of approximately monomolecular salts in an associated solvent, than in there being any peculiar 'dissociative power' attached to the solvent." From the experimental results herein presented it appears that it is a *fact*, that *all* solvents that vield solutions which conduct are not associated liquids.

Crompton further aims to explain the conductivity of fused salts upon the dissociation of the associated molecules of the fused salts, wherein a small proportion of the salt is in the monomolecular condition. Abegg, however, shows that in many cases the melted salt has a higher dielectric constant than its "ice,"—for example, the dielectric constant of water is 78 while that of ice is 2.85 according to Thwing; and that in these fused salts the self-ionization or self-dissociation is very slight. He states that in about 100 liters of fused AgCl there is about one gram-molecule of AgCl completely dissociated. Kohlrausch^{*}

¹ Zeit. Electrochemie, 5, 48 (1899).

² Wied, Ann. 53, 209 (1894).

has shown that in about eleven million liters of water there is one gram of hydrogen ions; while in methyl alcohol Carrara⁴ found one gram-molecule of methyl alcohol dissociated in about five and a half million liters. If water and methyl alcohol manifest such great dissociative power upon salts dissolved in them, why is it that they do not dissociate their own molecules to a greater extent?

It is quite noticeable, that a large number of the investigators of the properties of non-aqueous solutions, express the thought that there is manifested considerable influence between the dissolved substance and the solvent. This factor of the influence of the solvent upon the dissolved substance, is one that is no doubt of very great importance; and in the development of the electrolytic dissociation theory(which is based upon the behavior of aqueous solutions) the action of the solvent upon the dissolved substance has been entirely neglected. The opponents of the dissociation theory present this fact in rather forcible manner.²

Fitzpatrick³ concludes from his investigation on the conductivity of alcoholic solutions that the action of the solvent upon the dissolved substance is a chemical one. He conceives the dissolved salt as decomposing and forming molecular groups in the solvent. Owing to the large excess of the solvent there will be a continual decomposition and recombination of these molecular groups. He cautions one against regarding the solvent as a medium in which the salt particles are suspended or as a dissociating agent. Wildermann,4 on the other hand, recognizes two kinds of dissociation-one, the electrolytic dissociation of the dissolved substance, and the other, the dissociation of the larger molecular aggregates into smaller ones. For example, in a solution of KCl in water the following aggregates are assumed to exist: K Cl., KCl, K Cl, K Cl., K and Cl. He

¹ Gazz. Chim. Ital. 27, I, 422 (1897). (Ref.) Jour. Chem. Soc. 72, ii, 473 (1897).

² Fitzgerald's "Helmholtz' Memorial Lecture "Jour. Chem. Soc. **69**, i, 885 (1896).

³ loc. cit.

⁴ Ber. chem. Ges. Berlin, **26**, 1773, 2881 (1893).

further maintains that solutions of all substances, whatever the solvent or the concentration, undergo electrolytic dissociation.

Cattaneo¹ was impressed with the fact that the molecular conductivity is greatly influenced by the nature of the solvent employed. He was not able, however, to point out any direct relation existing between the various properties of the solvents which vield solutions that conduct electricity. Konovaloff² from his work on the amines, concludes that only those solvents that react chemically with the dissolved substances yield solutions that conduct. It is true that there are many solvents of this nature which do react with the dissolved substance, and vet which do not vield solutions that conduct electricity. Pieric acid reacts with benzene but the resulting solution does not conduct. Hence chemical combination of the dissolved substance with the solvent may take place and yet the solutions need not necessarily conduct. Werner³ has isolated and analyzed a large number of products of pyridine and piperidine among other organic solvents, with salts of the heavy metals. From the boiling-point determinations, the molecular weights of these salts seem to be very slightly influenced by their union with the solvent. This is analogous to the fact, that salts which crystallize from an aqueous solution with water of crystallization, yield the same molecular weight whether dissolved in the anhydrous form or with their water of crystallization. Carrara thinks that the union of solvent and dissolved substance accounts for the slight conductivity in certain cases. The low values of μ in the case of acetone solutions of hydrochloric acid and lithium chloride he attributes to this fact.

It has been pointed out by Ciamician⁴ that the dissociative power of a solvent depends principally upon its chemical structure. That is, compounds of the same chemical type, for example, of the HOH type, yield solutions that conduct electricity

¹ Rend, Accad. Line, (5) **4**, II, 63, 73 (1895). (Ref.) Jour. Chem. Soc. **72**, ii, 537 (1897).

² Wied, Ann. **49**, 733 (1893).

³ loc. cit.

⁴ Zeit. phys. Chem. 6, 403 (1890).

well. This is true in the case of alcoholic solutions, which are not the only class of compounds, however, that possess dissociative power, as has already been pointed out. In general, however, if one member of a particular type of compounds (e. g. nitriles) yield solutions that conduct, it has been found that other members also possess this property; and if a member of some other type (e. g. hydrocarbons) is found not to yield solutions that conduct, other members do not possess dissociative power.

The data collected are as yet insufficient to show what the relation between solvent and dissolved substance must be in order to yield solutions that conduct electricity. Enough facts have been presented, however, to make it apparent that any theory that aims to explain the electrical conductivity of solutions in general, must take into consideration the influence of the solvent upon the dissolved substance. This subject is replete with interest, for closely connected with it is the true cause of the solubility of substances.

From the foregoing the following general statements may be made :

I. In methyl and ethyl alcoholic solutions limiting values for μ can usually be obtained. The salts of the heavy metals are apparently exceptions. In other solvents a limiting value is very seldom obtained.

2. The degrees of dissociation of the dissolved substances in non-aqueous solutions, as calculated from the boiling-point or cryoscopic determinations and from the conductivity measurements, show very great disagreement. No such agreement is manifest as is observed in the case of aqueous solutions.

3. Neither the dilution law of Ostwald nor that of Rudolphi holds in the case of alcoholic solutions. In other solvents (since the conductivity remains virtually constant in some cases with the increased dilution, while in others it decreases) it is very apparent that the above-named laws do not hold. Then, too, since the value of μ_{∞} cannot be obtained in the case of so many solvents, the validity of the dilution laws could not be tested.

4. The molecular conductivity, in general, increases with the dilution; but in several cases the conductivity decreases with the successive dilutions.

5. The molecular conductivity usually increases with the temperature, but not proportionally. In some cases it remains virtually constant with increase of temperature, while in others it decreases. The changes in the viscosity accompanying a varying temperature have not been determined.

6. Solvents that have a high dielectric constant yield solutions that conduct the best. Some solvents, the dielectric constants of which are very low, give poorly conducting solutions. The molecular conductivity is not, however, proportional to the dielectric constant of the solvent.

7. Some associated solvents yield solutions that conduct electricity, whereas others do not. Some solvents whose molecules are not polymerized yield conducting solutions. The value of μ , in those solutions that conduct, is not commensurate with the degree of association of the solvent.

8. The conductivity of electrolytes depends very much upon the nature of the solvent employed. No rigid classification can be made, but, in general, solutions in the hydrocarbons and their halogen substitution-products do not conduct. Alcoholic solutions conduct well, and the conductivity, in general, decreases with the increase of the carbon content. Solutions in esters conduct, but those of high carbon content usually yield solutions that conduct very poorly. The ketones and the aldehydes yield solutions that conduct well. Of the nitrogen compounds, liquid ammonia and ammonia substitution-products, or amines, conduct. The nitriles of both the aliphatic and aromatic series yield conducting solutions; and of the organic bases pyridine and quinoline come under this same category.

9. The dissociation theory as promulgated for the explanation of the electrical conductivity of aqueous solutions, apparently cannot be applied in its present form to explain the conductivity in non-aqueous solutions. It further appears that the auxiliary theories which are based upon the specific inductive capacity,

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the polymerization of the molecules, and the self-ionization of the solvent, are not sufficient to explain satisfactorily the facts that have been accumulated. Notwithstanding the work that has been done, the data at hand are as yet insufficient for the formulation of a theory by means of which a satisfactory explanation can be given of the phenomenon of electrical conductivity of solutions in general.

This investigation was carried on under the supervision of Professor Kahlenberg, to whom I am under many obligations for his valuable suggestions, and I take this means of acknowledging the same.

Laboratory of Physical Chemistry, University of Wisconsin, Madison, July 15, 1899.