XXVIII.—*The Conductivity of Electrolytes in Nitromethane.*

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MEASUREMENTS of the conductivity of electrolytes in methyl and ethyl alcohols have shown that differences of behaviour in the two solvents are primarily to be accounted for by the difference in dielectric constant. The greater tendency for ionic association to take place in ethyl alcohol is shown for strong electrolytes by the greater deviation of the experimental results from the theoretical equation of Debye and Hückel as modified by Onsager, and for weak electrolytes by their smaller dissociation constant. Nitromethane has a larger dielectric constant (*viz.*, 37) than the alcohols, so that, if the ionic association were controlled by the interionic forces alone, electrolytes would be expected to approach more closely to ideal behaviour in this solvent. The results of the present investigation show that this is not the case for the majority of electrolytes and that the chemical properties of nitromethane, which are very different from those of the alcohols, have a large influence in determining the behaviour of electrolytes dissolved in it. For instance, a number of salts which behave as strong electrolytes in methyl and ethyl alcohols are found to be weak electrolytes in nitromethane; and the hydrion no longer possesses the abnormal mobility which it has in hydroxylic solvents.

Philip (J., 1910, **97**, 1271; 1924, **125**, 1189) and Walden (*Z. physikal. Chem.*, 1905, **54**, 202; 1907, **58**, 509) have both measured the conductivity of solutions of tetraethylammonium iodide but their results do not agree, nor is there satisfactory concordance between Walden's various series of measurements, which give values of Λ_0 differing by more than 6%. Philip also investigated potassium iodide; the results obtained in his later work are in quite good agreement with ours in the range in which they overlap, but most of his measurements were made in more concentrated solution. It has now been found that iodides tend to react with the solvent, which may account for the discrepancies; a solution of ammonium iodide became yellow too rapidly for measurements to be made and lithium iodide also reacted on standing for some time. The measurements described for the latter were made within two hours of preparing the solution.

EXPERIMENTAL.

Purification of Nitromethane.—The nitromethane obtained from Poulenc Frères was pale yellow and smelt strongly of cyanide; it was therefore carefully purified. After a preliminary distillation, the relative efficiency of various drying agents was tested and compared with that of fractional distillation by measuring the viscosity of the dehydrated products; the sample which had the longest time of flow in an Ostwald viscometer was assumed to be the driest, since addition of water to nitromethane lowers the viscosity. Phosphoric oxide was found to be unsuitable as it forms a sol in nitromethane, and a white solid was deposited in the condenser when it was distilled. None of the other drying agents tried was so efficient as fractionation, and the final procedure adopted was as follows. Most of the water was removed with calcium chloride, and the final traces were eliminated by two distillations through a 3-foot Hempel column, the course of the distillation being followed by the boiling point measured by a thermometer near the top of the column. Volatile impurities were removed by refluxing for several hours in a current of dry air, followed by distillation through a siphon conductivity cell, so that the resistance of each portion of the distillate could be measured. The slight smell of cyanide, which generally remained after the second fractionation, was always removed by this treatment.

When it was necessary to recover the nitromethane from solutions, several modifications had to be introduced. It was found impossible to obtain nitromethane of low conductivity if it had been distilled off residues containing thiocyanates, which apparently reacted with the solvent. Solutions of thiocyanates were therefore always treated with aqueous silver nitrate immediately after use, and the silver thiocyanate was removed before distilling the nitromethane. Solutions of other salts were distilled directly, as this did not affect the conductivity. Solutions of acids were extracted with water, hydrogen chloride being removed easily but perchloric acid much more slowly. Even with this treatment it was sometimes impossible to obtain nitromethane of low conductivity, but it was finally discovered that the conducting impurities were removed by refluxing with animal charcoal for some hours before fractionation.

The lowest conductivity obtained, as measured in the cell on the final still, was $0{\cdot}15 \times 10^{-7}$ mho, and the best specimen used in a series of measurements was $0{\cdot}4 \times 10^{-7}$ mho; in general, the conductivity of nitromethane was 1—3×10^{-7} mho. The values quoted by Walden (*Z. physikal. Chem.*, 1905, **54**, 202) and by Philip and Oakley (J., 1924, **125**, 1189) are 16×10^{-7} and 4×10^{-7} mho, respectively.

Density of Nitromethane.—This was measured at 25° in a glass pyknometer, which was filled with nitromethane in such a way that the liquid never came into contact with moist air. The values of $D_{4^\circ}^{25^\circ}$ for three different specimens were 1·1311, 1·1312, and $1{\cdot}1312_5$. The mean, *viz.*, 1·1312, was used in calculating the conductivity results.

Dielectric Constant of Nitromethane.—This was measured over a range of temperature, and the results have already been published by Lattey and Gatty (*Phil. Mag.*, 1929, **7**, 985). The value at 25° is 37.

Viscosity of Nitromethane.—This was measured at 25° in an Ostwald viscometer which had a time of flow for water of 200·0 secs. The time of flow for a number of specimens of pure nitromethane was 123·6 ± 0·1 secs., which leads to a value for the viscosity of nitromethane of 0·00627, if the above value for its density is used together with a value of 0·00895 for the viscosity of water at 25°.

Measurements were also made to determine the change of viscosity of nitromethane caused by adding small amounts of water, and the following times of flow were obtained :

Water, %	0·000	0·245	0·437
Time of flow (secs.)	123·6	122·7	122·2

The addition of 0·1% of water therefore lowers the viscosity of nitromethane by about 0·3%. Similar measurements were made of the change of viscosity of water due to addition of nitromethane, with the following results :

Nitromethane, %	0·00	0·506	1·903	4·130
Time of flow (secs.)	200·0	200·8	202·5	204·5

These show that the viscosity of water is raised by the addition of nitromethane. It is remarkable that the addition of small quantities of a more viscous liquid, such as water, should lower the viscosity of nitromethane; while exactly the reverse takes place on the addition of nitromethane to water. No other pair of liquids is known to behave in this manner. If the curve for the whole range of concentrations could be realised, it would have both a maximum and a minimum, but this is not possible owing to the limited miscibility of the two liquids even at 100°.

Mutual Solubilities of Nitromethane and Water.—The viscosity results were used to find the mutual solubilities of nitromethane and water. Layers of each liquid were allowed to reach mutual saturation at 25° and the time of flow for each layer was measured. The upper layer, a saturated solution of nitromethane in water, was diluted with water so that solutions containing known amounts of the saturated solution were obtained. The times of flow for these solutions were measured and compared with those for water containing weighed quantities of nitromethane. Similar measurements were made with the lower layer after dilution with nitromethane. By this means the following values of the mutual solubilities at 25° were obtained :

Solubility of water in nitromethane = 2%.
Solubility of nitromethane in water = 10%.

Preparation of Solutions.—Salts. Approximate values of the relative solubilities of salts in nitromethane were obtained by measuring the conductivity of saturated solutions in an Ostwald cell; the peculiar solubility relations greatly restricted the choice of salts that could be measured in nitromethane, as many of them were only sparingly soluble. Apart from the tetraethylammonium salts, all of which are very soluble, no soluble chlorides, bromides, or nitrates were found, so the work was restricted to the iodides, thiocyanates, and perchlorates. Solutions were made by dissolving a known weight of dry salt in a weighed quantity of nitromethane. The methods for drying most of the salts have been described elsewhere (for the thiocyanates, see Unmack, *Proc. Roy. Soc.*, 1930, **127**, 228; and for the perchlorates, Copley and Hartley, J., 1930, 2488). A full account of the methods we investigated for drying the tetraethylammonium salts will be published later, but in the present research they were dried in an air-bath at 110° except the nitrate, which was dried in a current of nitrogen at 120°. Lithium iodide was dried in a vacuum over phosphoric oxide at about 90°.

Acids. Perchloric acid, the only acid with which accurate measurements were attempted, was made by mixing solutions of hydrogen chloride and silver perchlorate. A solution of hydrogen chloride can be made by bubbling the gas into nitromethane, but its analysis presents considerable difficulties. Titration with alkali is impossible because nitromethane is itself a pseudo-acid; attempts were made to determine the concentration by means of Volhard's method after adding excess of water, but no accurate end-point was obtained since the colour of the ferric thiocyanate faded continuously, probably owing to its reacting with the nitromethane. Finally, solutions of perchloric acid were made by adding a slight excess of hydrogen chloride solution to the silver perchlorate; most of the hydrogen chloride could be removed by exhausting the solution, for it has a high vapour pressure even at room temperature, and any small quantity remaining in solution would not affect the conductivity results as it is not appreciably ionised.

Determination of Conductivity.—The method has already been described in detail (Frazer and Hartley, *Proc. Roy. Soc.*, 1925, **109**, 351). The cell used was of the type described by Hartley and Barrett (J., 1913, **103**, 786), but of only 100 c.c. capacity. Weighed amounts of solution were added from a weight burette to the cell, which contained a known weight of nitromethane, and the resistance was measured after each addition.

Results.

Values of the equivalent conductivity at various concentrations are given in Table I. An empirical equation, representing the variation of conductivity of each electrolyte with concentration, and also the value of Λ_0 obtained therefrom are given at the head of the corresponding sections, except in the case of weak electrolytes; these equations are discussed later. Col. 1 gives the specific conductivity of the solvent in reciprocal megohms; the solvent correction was applied by subtracting this value from the conductivity of the solution at each concentration. Col. 2 gives the values of $c \times 10^4$, where c is the concentration in g.-equivs. per litre; col. 3, the values of $c^{\frac{1}{3}} \times 1000$, or, in the case of the tetraethylammonium salts, of $100\sqrt{c}$; col. 4, the equivalent conductivity, Λ_c, and col. 5 the values of the difference between the observed value of Λ_c and that calculated from the equation at the head of the section.

TABLE I.

Lithium thiocyanate.

κ.	$c \times 10^4$.	$c^{\frac{1}{2}} \times 1000$.	Λ_c.
0·33	1·418	2·72	32·45
	3·080	4·56	21·08
	5·810	6·96	16·36
	12·44	11·56	13·10
	18·86	15·26	11·51

Ammonium thiocyanate.

κ.	$c \times 10^4$.	$c^{\frac{1}{2}} \times 1000$.	Λ_c.
0·04	1·221	2·46	118·5
	2·519	4·00	107·8
	4·766	6·10	95·7
	8·513	8·98	83·1
	13·22	12·05	73·3
	19·60	15·62	64·7

Sodium thiocyanate.

κ.	$c \times 10^4$.	$c^{\frac{1}{2}} \times 1000$.	Λ_c.
0·47	1·157	2·37	107·2
	2·255	3·70	97·9
	4·130	5·55	87·1
	5·902	7·04	79·9
	7·591	8·32	74·7
	9·129	9·41	71·2
0·33	0·857	1·94	110·8
	1·717	3·09	101·7
	3·539	5·00	89·5
	5·126	6·42	82·4
	6·837	7·79	76·4
	9·082	9·38	70·3

Lithium perchlorate.

κ.	$c \times 10^4$.	$c^{\frac{1}{2}} \times 1000$.	Λ_c.
0·32	1·253	2·50	117·8
	2·443	3·91	112·3
	4·737	6·07	104·9
	8·639	9·06	95·9
	14·341	12·71	86·7
	20·89	16·34	79·1
	26·77	19·27	74·0
0·29	1·153	2·37	118·0
	2·240	3·69	113·1
	3·741	5·20	108·1
	6·031	7·14	102·2
	8·223	8·78	97·6
	13·03	11·93	89·9

Potassium thiocyanate.

$\Lambda_c = \Lambda_0 - 1560c^{\frac{1}{2}}$; $\Lambda_0 = 130·0$.

κ.	$c \times 10^4$.	$c^{\frac{1}{2}} \times 1000$.	Λ_c.	Diff.
0·11	3·254	4·72	123·6	+1·0
	6·449	7·46	118·6	+0·2
	11·717	11·11	113·0	+0·3
	20·488	16·13	105·9	+1·1
0·13	1·271	2·52	126·2	+0·1
	3·205	4·69	123·1	+0·4
	7·138	7·99	117·9	+0·3
	12·639	11·68	112·2	+0·4
0·10	1·477	2·80	125·3	−0·3
	2·649	4·12	123·4	−0·2
	4·686	6·02	120·4	0·0
	8·220	8·76	116·0	−0·3
	12·729	11·73	111·4	−0·3

Sodium perchlorate.

$\Lambda_c = \Lambda_0 - 1640c^{\frac{1}{2}}$; $\Lambda_0 = 122·5$.

κ.	$c \times 10^4$.	$c^{\frac{1}{2}} \times 1000$.	Λ_c.	Diff.
0·10	1·310	2·58	117·8	+0·5
	2·458	3·91	115·7	+0·4
	3·864	5·30	113·2	+0·6
	5·954	7·07	110·4	+0·5
	7·613	8·34	108·2	+0·6
	10·519	10·34	105·1	+0·5
0·24	0·770	1·81	118·7	−0·8
	1·507	2·83	117·2	−0·7
	3·061	4·52	114·7	−0·4
	5·522	6·72	111·2	−0·3
	8·131	8·70	108·2	0·0
	11·75	11·13	104·5	+0·3
0·26	0·863	1·95	119·2	−0·1
	1·710	3·08	117·7	+0·2
	3·172	4·65	115·3	+0·4
	5·648	6·82	111·6	+0·3
	7·369	8·15	109·5	+0·3
	10·56	10·36	105·9	+0·3

Ammonium perchlorate.

$\Lambda_c = \Lambda_0 - 1330c^{\frac{1}{2}}$; $\Lambda_0 = 128·3$.

κ.	$c \times 10^4$.	$c^{\frac{1}{2}} \times 1000$.	Λ_c.	Diff.
0·08	1·065	2·25	125·3	0·0
	2·025	3·45	123·7	0·0
	3·415	4·89	121·8	0·0
	5·435	6·66	119·5	+0·1
	7·719	8·42	117·0	−0·1
	10·54	10·36	114·6	+0·1

Thallium perchlorate.

$\Lambda_c = \Lambda_0 - 1400c^{\frac{1}{2}}$; $\Lambda_0 = 124·4$.

κ.	$c \times 10^4$.	$c^{\frac{1}{2}} \times 1000$.	Λ_c.	Diff.
0·14	0·964	2·12	121·3	−0·2
	1·835	3·23	119·9	0·0
	3·000	4·48	118·2	+0·1
	4·612	5·96	116·1	0·0
	6·291	7·34	114·2	+0·2
	8·455	8·93	111·9	0·0

Silver perchlorate.

$\Lambda_c = \Lambda_0 - 705c^{\frac{2}{3}}$; $\Lambda_0 = 116{\cdot}5$.

κ.	$c \times 10^4$.	$c^{\frac{2}{3}} \times 1000$.	Λ_c.	Diff.
0·25	1·463	2·78	114·4	−0·1
	2·997	4·48	113·9	+0·6
	6·055	7·16	112·3	+0·8
	10·51	10·34	110·1	+0·9
	14·82	13·00	108·2	+0·8
	19·96	15·86	106·1	+0·8
0·10	2·573	4·05	113·0	−0·7
	4·993	6·29	111·6	−0·5
	7·452	8·22	110·4	−0·3
	10·90	10·59	108·8	−0·2
	16·19	13·79	106·6	−0·2
0·12	1·336	2·61	114·5	−0·2
	2·652	4·13	113·7	+0·1
	4·756	6·09	112·4	+0·2
	7·660	8·37	110·7	+0·1
	10·90	10·59	109·2	+0·2
	15·40	13·33	107·2	+0·1

Lithium iodide.

$\Lambda_c = \Lambda_0 - 2100c^{\frac{2}{3}}$; $\Lambda_0 = 117{\cdot}5$.

κ.	$c \times 10^4$.	$c^{\frac{2}{3}} \times 1000$.	Λ_c.	Diff.
0·12	1·507	2·84	109·9	−0·6
	3·212	4·69	106·5	−1·0
	6·327	7·37	100·8	−0·2
	9·697	9·80	95·7	−0·2
	14·18	12·62	90·3	+0·2
0·18	0·987	2·14	111·8	−0·2
	2·842	4·32	108·1	+0·7
	6·061	7·16	101·8	+0·3
	12·72	11·74	92·2	+0·3

Tetraethylammonium perchlorate.

$\Lambda_c = \Lambda_0 - 227\sqrt{c}$; $\Lambda_0 = 113{\cdot}4$.

κ.	$c \times 10^4$.	$100 \times \sqrt{c}$.	Λ_c.	Diff.
0·43	2·002	1·42	110·0	−0·2
	3·432	1·85	109·1	−0·1
	5·411	2·33	108·0	−0·1
	8·015	2·83	106·9	−0·1
	13·21	3·63	105·2	−0·1
0·85	1·623	1·27	110·5	0·0
	2·953	1·72	109·5	0·0
	5·271	2·30	108·2	0·0
	8·539	2·92	106·7	−0·1
	13·23	3·64	105·1	−0·1
0·13	1·293	1·09	110·8	−0·1
	2·826	1·68	109·6	+0·1
	5·993	2·43	107·9	+0·1
	9·981	3·16	106·1	−0·1
	14·62	3·82	104·7	0·0

Perchloric acid.

$\Lambda_c = \Lambda_0 - 2340c^{\frac{2}{3}}$; $\Lambda_0 = 127$ (approx.).

κ.	$c \times 10^4$.	$c^{\frac{2}{3}} \times 1000$.	Λ_c.	Diff.
0·12	1·045	2·22	115·0	−7·0
	2·042	3·47	113·6	−6·0
	3·921	5·36	111·1	−4·2
	7·087	7·94	106·8	−1·6
	9·552	9·70	102·9	−1·4
	11·13	10·73	100·5	−1·3
0·27	1·361	2·64	118·0	−2·8
	2·705	4·17	115·5	−1·8
	4·717	6·05	112·3	−0·7
	7·328	8·12	108·6	+0·6
	12·08	11·34	101·6	+1·2
	16·72	14·06	95·7	+1·7
	22·72	17·26	89·6	+3·0
0·44	1·319	2·59	116·9	−4·0
	2·684	4·16	114·9	−2·4
	5·340	6·58	110·8	−0·8
	9·218	9·47	104·5	−0·1
	12·78	11·77	98·5	−0·6
	17·04	14·16	91·5	−2·5
	21·27	16·54	85·3	−2·1

Potassium iodide.

$\Lambda_c = \Lambda_0 - 936c^{\frac{2}{3}}$; $\Lambda_0 = 121{\cdot}9$.

κ.	$c \times 10^4$.	$c^{\frac{2}{3}} \times 1000$.	Λ_c.	Diff.
0·12	0·985	2·13	118·8	−1·1
	1·818	3·22	118·5	−0·4
	3·455	4·91	117·1	−0·2
	5·517	6·72	115·5	−0·1
	6·676	7·64	114·6	−0·2
	9·432	9·60	112·7	−0·2
0·12	0·974	2·11	119·1	−0·8
	1·821	3·21	118·7	−0·1
	3·610	5·07	117·3	+0·2
	5·790	6·94	115·6	+0·2
	8·056	8·65	114·0	+0·3
	10·26	10·18	112·6	+0·2

Tetraethylammonium nitrate.

$\Lambda_c = \Lambda_0 - 220\sqrt{c}$; $\Lambda_0 = 114{\cdot}3$.

κ.	$c \times 10^4$.	$100 \times \sqrt{c}$.	Λ_c.	Diff.
0·25	1·484	1·22	111·6	−0·1
	3·021	1·74	110·5	0·0
	5·496	2·34	109·2	0·0
	8·828	2·97	107·8	0·0
	13·55	3·68	106·3	+0·1
	17·22	4·15	105·2	0·0
0·23	1·193	1·09	111·4	−0·3
	2·255	1·50	110·6	−0·2
	4·023	2·01	109·7	−0·1
	6·374	2·53	108·6	0·0
	9·672	3·11	107·3	+0·1
	14·81	3·85	105·7	+0·1
0·05	1·416	1·19	112·0	+0·3
	2·866	1·69	110·9	+0·3
	6·093	2·46	109·1	+0·2
	10·39	3·22	107·5	+0·3
	16·85	4·11	105·6	+0·3

Tetraethylammonium iodide.

$\Lambda_c = \Lambda_0 - 210\sqrt{c}$; $\Lambda_0 = 111{\cdot}2$.

κ.	$c \times 10^4$.	$100 \times \sqrt{c}$.	Λ_c.	Diff.
0·28	1·204	1·10	107·5	−1·4
	2·367	1·54	107·6	−0·4
	4·035	2·01	107·0	0·0
	7·915	2·81	105·5	+0·1
	12·05	3·47	104·0	+0·1
	16·88	4·11	102·6	0·0
0·24	1·416	1·19	107·9	−0·8
	2·715	1·65	107·5	−0·1
	5·104	2·26	106·5	−0·1
	7·638	2·76	105·5	−0·1
	11·96	3·46	104·0	−0·1

Tetraethylammonium thiocyanate.

$\Lambda_c = \Lambda_0 - 218\sqrt{c}$; $\Lambda_0 = 119{\cdot}7$.

κ.	$c \times 10^4$.	$100 \times \sqrt{c}$.	Λ_c.	Diff.
0·15	1·137	1·07	117·4	0·0
	2·095	1·45	116·6	0·0
	4·219	2·05	115·3	+0·1
	7·067	2·66	113·9	0·0
	9·955	3·15	112·8	0·0
0·19	1·236	1·11	117·0	−0·3
	2·875	1·69	116·0	0·0
	5·256	2·29	114·7	0·0
	9·122	3·02	113·0	+0·1
	12·40	3·52	111·8	−0·2

Tetraethylammonium picrate.

$\Lambda_c = \Lambda_0 - 191\sqrt{c}$; $\Lambda_0 = 93{\cdot}5$.

κ.	$c \times 10^4$.	$100\sqrt{c}$.	Λ_c.	Diff.
0·05	0·879	0·93	91·74	+0·02
	1·810	1·34	90·80	−0·13
	3·267	1·81	89·95	+0·10
	5·454	2·84	88·98	−0·06
	9·123	3·02	87·62	−0·11
0·06	1·013	1·01	91·68	+0·10
	2·024	1·42	90·89	+0·11
	3·824	1·96	89·84	+0·08
	6·101	2·47	88·87	+0·09
	10·59	3·25	87·37	+0·08

Graphical Representation of Results.—The usual graphical method of representation is to plot the equivalent conductivity against the square root of the concentration, as there is generally a linear relation between these two quantities for strong electrolytes in dilute solution, and this is used for extrapolation to infinite dilution in order to obtain values of Λ_0 in water, the alcohols, and other solvents. In nitromethane, however, it is found that none of the highly dissociated salts, with the exception of the tetraethylammonium salts, gives this linear relation; the experimental points lie on a curve which is generally concave to the concentration axis but in some cases approximates to a straight line between the concentrations $N/2500$ and $N/500$. These curves are useless for extrapolation to infinite dilution, especially as the points in the most dilute region are the least trustworthy, and it is very possible that some of the curvature is due to reaction with the solvent or with impurities, as this would be most noticeable in dilute solutions. It has been found, however, that most of the salts giving curves of this type give approximately straight lines when the conductivity is plotted against the two-thirds power of the concentration. The use of this function is entirely arbitrary, but it makes an extrapolation to infinite dilution possible. On the other hand, the results for the tetraethylammonium salts are represented graphically in the normal manner, for, excepting the iodide, which reacts with the solvent, they give straight lines for the square-root relation. The differences in behaviour are illustrated in Fig. 1, in which the equivalent conductivity is plotted against the square root of the concentration for a number of electrolytes of different types.

Values of Λ_0.—Table II gives the values of Λ_0 obtained by the methods of extrapolation just described; more confidence is to be placed on the results for the tetraethylammonium salts, which obey the square-root relation, than for the other salts, as the extrapolation for these is probably not correct to nearer than 1—2%.

FIG. 1.

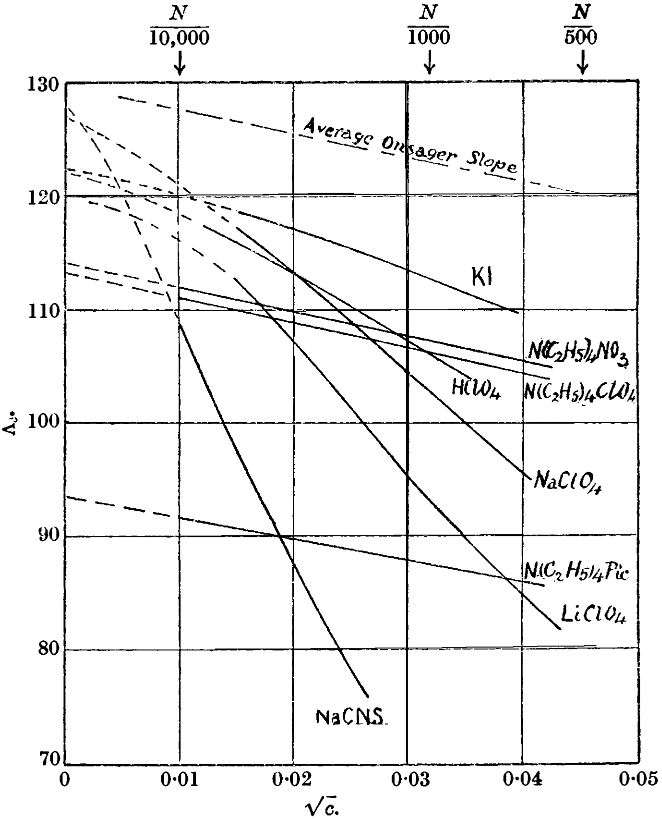


TABLE II.

Salt.	Λ_0.	Salt.	Λ_0.	Salt.	Λ_0.
KI	122	$AgClO_4$	116·$_5$	$N(C_2H_5)_4CNS$ ...	119·7
LiI	117·$_5$	$TlClO_4$	124·$_5$	$N(C_2H_5)_4ClO_4$ ...	113·4
KCNS	130	NH_4ClO_4	128·$_5$	$N(C_2H_5)_4NO_3$ ...	114·3
$NaClO_4$	122·$_5$			$N(C_2H_5)_4I$	111·2
		($HClO_4$)	127	$N(C_2H_5)_4$Pic	93·5

It is unfortunate that there are not sufficient data for a satisfactory test of the applicability of the law of independent mobilities to solutions in nitromethane; the fact that many salts are insoluble and that others behave as weak electrolytes has made it impossible to obtain two independent values of the mobility of any single ion. The difference between the mobilities of the thiocyanate and those of the iodide ions can be determined from the results for the tetraethylammonium and the potassium salts and the values are concordant :

$$\Lambda_{0\mathrm{KCNS}} - \Lambda_{0\mathrm{KI}} = 8,$$
$$\Lambda_{0\mathrm{NEt_4CNS}} - \Lambda_{0\mathrm{NEt_4I}} = 8{\cdot}5;$$

but this concordance does not provide a test of the accuracy of the values of Λ_0 for the potassium salts as they were both determined by the same method of extrapolation.

Ionic Mobilities.—No measurements of the transport number of any ion in nitromethane are available, so it is not possible to obtain direct values of the individual ionic mobilities. The only other course is to use Walden's relation that the product $l_0\eta$ is constant for all solvents, where l_0 is the mobility of a large ion and η is the viscosity of the solvent. Walden has measured the conductivity of tetraethylammonium picrate in a number of solvents, and found that the product $\Lambda_0\eta$ has the value of 0·560 (approx.) in each case. The value for this product in nitromethane is 0·586, and the results of measurements in other solvents, which have been carried out in this laboratory and will shortly be published, have shown that there may be larger variations than Walden's results suggest. Nevertheless, this product is more nearly constant for tetraethylammonium picrate than for any other salt, presumably owing to the fact that neither of the ions is heavily solvated. The values of the mobility of the picrate ion in water and in methyl and ethyl alcohols give a more constant value for the product $l_0\eta$ than those of the tetraethylammonium ion, and Table III has been compiled showing approximate ionic mobilities on the assumption that for the picrate ion $l_0\eta = 0{\cdot}275$, giving a value of l_0 for this ion of 44.

TABLE III.

Ionic mobilities in nitromethane.

Ion.	l_0.	Ion.	l_0.	Ion.	l_0.
$H^{\cdot}$	63	$NH_4^{\cdot}$	64	Picrate	44 *
$Li^{\cdot}$	55	$NEt_4^{\cdot}$	49·5	ClO_4'	64
$Na^{\cdot}$	58	$Ag^{\cdot}$	52	NO_3'	64·5
$K^{\cdot}$	60	$Tl^{\cdot}$	60	I'	62
				CNS'	70

* Calculated from the product $l_0\eta = 0{\cdot}275$.

Discussion of Results.

Comparison with Onsager's Equation.—The variations in behaviour of the different salts can best be seen from a comparison of the experimental results with the theoretical behaviour of an ideal electrolyte as expressed by Onsager's modification of Debye's equation. The value of x in the equation $\Lambda_c = \Lambda_0 - x\sqrt{c}$, as calculated from the Debye–Hückel–Onsager equation, reduces for uni-univalent electrolytes to the expression

$$x = \left\{\frac{5{\cdot}85 \times 10^5}{(DT)^{\frac{3}{2}}}\Lambda_0 + \frac{58{\cdot}0}{(DT)^{\frac{1}{2}}\eta}\right\}\sqrt{2}$$

and for nitromethane at 25° ($\eta = 0{\cdot}00627$; $D = 37$) this gives

$$x = 0{\cdot}727\Lambda_0 + 125{\cdot}8.$$

In order to compare the experimental values of x with those given by this equation, values of the percentage deviation, $100(x_{\text{obs.}} - x_{\text{calc.}})/x_{\text{calc.}}$, have been calculated and are given in Table IV. In the cases when a straight line is not given for the Λ_c–$\sqrt{c}$ relation, the observed value of x is taken as the slope of the curve at about $N/1000$, where usually it approximates to a straight line. Although the values of Λ_0 are not known accurately for these electrolytes, the values of x are not seriously affected, as an error of 2% in Λ_0 would only change x by about 1%, and this is negligible when differences of the order of 100% are being considered.

TABLE IV.

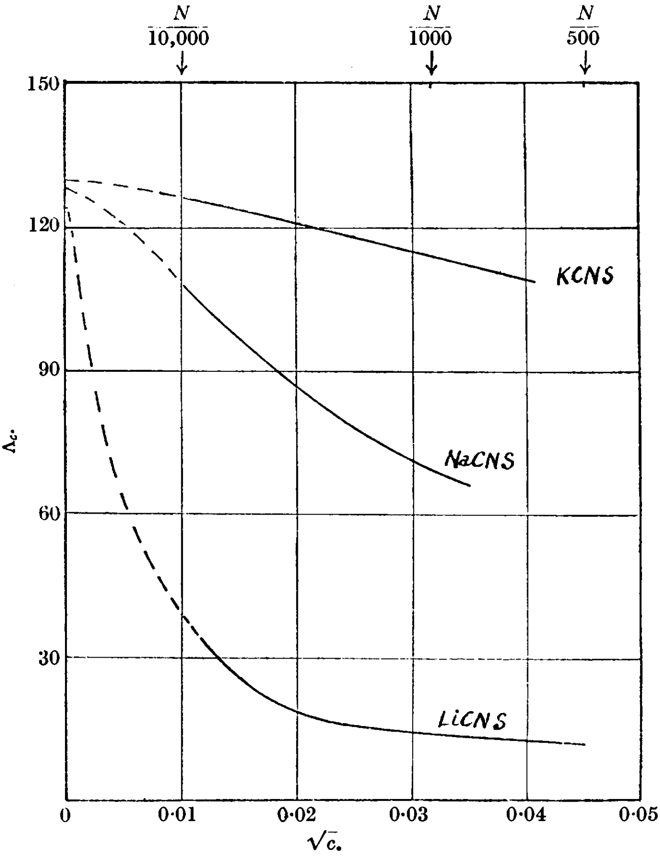
Values of $100(x_{\text{obs.}} - x_{\text{calc.}})/x_{\text{calc.}}$.

	I.	ClO_4.	CNS.	NO_3.	Picrate.
Li	300	430	weak	—	—
Na	—	175	weak	—	—
K	73	—	188	—	—
Ag	—	26	—	—	—
NH_4	—	135	weak	—	—
NEt_4	2	9	2	5·3	−1·5

This table shows that there is excellent agreement for the tetraethylammonium salts between the observed values of x and those calculated from Onsager's equation, and it is significant that these are the only electrolytes in nitromethane which have been found to give a linear relation between Λ_c and $\sqrt{c}$ over the whole range of concentration studied. The iodide gives a line which is curved in the dilute region, but it is nearly linear at concentrations greater than $N/2000$, and in this region the slope is very close to the theoretical value, so it is probable that the deviation from the straight line is due to reaction with the solvent. The tetraethylammonium salts also differ from those of the metals in their ease of solubility, and it is possible that this is connected with the fact that they show little tendency to ionic association in solution, as seen from the agreement of their behaviour with that of an ideal electrolyte.

On the other hand, all the salts which fail to obey the square-root relation give large deviations from the theoretical slope and so are presumably considerably associated in solution, and it is probable that the curvature of the Λ_c–$\sqrt{c}$ curves is partially due to the ionic association being less in the dilute region. The amount of association varies considerably, but the figures in the table indicate that there are certain regularities depending on the nature of the ion. The results for the thiocyanates of the alkali metals are plotted in Fig. 2, and show that the tendency for ionic association

FIG. 2.



to take place is greater for the elements of lower atomic number: the sodium salt is intermediate in strength between the potassium and the lithium salt, the latter being quite a weak electrolyte. The perchlorates show less tendency to associate than the thiocyanates, but the influence of the kation is similar, lithium perchlorate showing greater deviation from the ideal slope than either the sodium or the ammonium salt; potassium perchlorate is too insoluble to be measured, but the difference between lithium and potassium is again shown by the results for the iodides. This influence of the nature of the kation upon the degree of association is exactly the opposite to that found in methyl and ethyl alcohols, for in these solvents the lithium salts show the least deviation from the Onsager equation and the tendency to associate increases with atomic number. The results in alcohol agree with Bjerrum's view that there is a greater tendency for association in the case of ions of smaller diameter; for if it is assumed that the relative mobilities of the alkali ions are a measure of the relative sizes of the solvated ions in solution, then lithium is the largest ion and there is a continuous decrease of size from lithium to cæsium. In nitromethane, however, the departure from ideal behaviour shows that there is much greater tendency for the kation to associate with the anion than in the alcohols, and in this solvent the influence of the nature of the kation on the degree of association is in accordance with Fajans's rule that there is more tendency to form covalent links when the kation is small. It is clear that in this respect it is the size of the unsolvated ion which is to be considered, lithium having the smallest ionic radius of the ions of the alkali metals, although the relative mobilities of the alkali metals in nitromethane indicate that the size of the solvated ions varies in the same order as in the alcohols.

Apart from these differences the outstanding fact is that, although all the alkali-metal salts in the above table behave as strong electrolytes in methyl and ethyl alcohols with a maximum deviation from Onsager's equation of 50% for sodium perchlorate in ethyl alcohol, yet in nitromethane they show a wide divergence from ideal behaviour, proving conclusively that the association of ions to form molecules or neutral doublets is not governed entirely by the electrical forces between them. The molecules of the alcohols possess both donor and acceptor properties and can thus form co-ordinate links with both kation and anion, whereas nitromethane, being a pure donor, can only attach itself by such links to the kation, any solvent molecules round the anion being held electrostatically merely as a result of their dipole character. This suggests that the prevention of ionic association in hydroxylic solvents may be due to the protective sheath formed round them by the solvent molecules, and that the absence of co-ordinate linkages between the anions and nitromethane facilitates their association with the kation. This view of the influence of the solvent on ionic dissociation is practically the same as Brönsted's theory that the dissociation of acids is conditioned by the relative affinity of the proton for the anion and for the solvent molecule respectively :

$$\mathrm{HA} + \text{solvent} = \mathrm{H(solvent)}^{\cdot} + \mathrm{A}'.$$

In this case the action should be represented

$$\mathrm{M}^{\cdot}\mathrm{X}' + \text{solvent} = \mathrm{M}^{\cdot}\text{(solvated)} + \mathrm{X}'\text{(solvated)}.$$

Confirmation of this suggestion of the protective action of the hydroxylic solvent molecules is afforded by the effect of small quantities of water on the conductivity of solutions in nitromethane, since the changes in conductivity for weak salts are far greater than could be due to any change in the dielectric constant.

Change in Conductivity due to Addition of Water.—A small amount of water was added in a few cases at the end of a series of measurements, when the concentration of the solution was between *N*/1000 and *N*/500. Table V shows the effect on the conductivity. The increase of fluidity of pure nitromethane caused by 0·1% addition of water was 0·3%. The third column shows the percentage deviation from Onsager's equation, and comparison of this with col. 2 shows that there is a large increase in conductivity when the electrolyte deviates widely from ideal behaviour. It is interesting to note that in the case of the tetraethylammonium salts, which are normal in their behaviour, the increase in conductivity is very close to that expected from the increase of fluidity.

TABLE V.

Salt.	Increase in conductivity on addition of 0·1% of water.	Deviation from ideal slope.
$LiClO_4$	12%	430%
$NaClO_4$	1·4	175
LiCNS	60	(weak)
NaCNS	10	(weak)
NEt_4I	0·22	2
NEt_4ClO_4	0·28	9
NEt_4NO_3	0·07	5·3

Acids.—Perchloric acid is the only acid with which accurate measurements were attempted, but several other acids have been investigated by measuring their conductivity in an Ostwald cell and comparing it with that of *N*/100-perchloric acid in the same cell, which gave an equivalent conductivity of about 70. Sulphuric, thiocyanic, benzenesulphonic, and nitric acids were measured at concentrations between $N/20$ and $N/50$ and gave values of Λ_c varying from 1 to 5 units. Thiocyanic acid was made by mixing solutions of potassium thiocyanate and hydrogen chloride, the latter being in excess, and the conductivity rose quickly during the measurement owing to reaction with the solvent. The solutions of sulphuric and nitric acids were made by adding a few drops of the concentrated acids to the nitromethane, and that of benzenesulphonic acid by adding a few crystals of the solid, so that the values for the conductivity represent a maximum as a certain amount of water was present in each case. Picric and trinitrobenzoic acids gave even lower conductivities, whilst hydrogen chloride scarcely altered the resistance of the pure nitromethane. Although these results are only approximate, they show that perchloric acid is the only acid which is strongly ionised. In methyl and ethyl alcohols it has been found that there is a number of acids that are strong electrolytes, so the difference must be due to the relative affinities of the anion and of the solvent molecule for the proton; and it appears that the tendency for the perchlorate ion to associate with the proton is sufficiently small to enable the acid to remain dissociated in solution. It is also noteworthy that the hydrogen ion has no longer the abnormal mobility which it possesses in the hydroxylic solvents. If the abnormal mobility in water and the alcohols is to be explained, as Hückel has suggested (*Z. Elektrochem.*, 1928, **34**, 546), by a chain mechanism involving the transference of a proton from one molecule to another, then the normal mobility of the hydrogen ion in nitromethane is to be expected, since the absence of a hydroxyl group in the nitromethane molecule makes the proton exchange much less probable. On this view, the movement of the hydrion in nitromethane would be similar to that of any other solvated kation, the relative mobilities being primarily governed by the size of the solvated ions.

A striking difference between solutions of perchloric acid in nitromethane and in the alcohols is shown by the effect on the conductivity of adding small amounts of water. Murray-Rust and Hartley (*Proc. Roy. Soc.*, 1929, **126**, 84) have shown that the addition of 0·1% of water to a solution of perchloric acid either in methyl or in ethyl alcohol causes a decrease in the conductivity of about 5%; this is probably due to the affinity of water for the proton which hinders its transference from one alcohol molecule to another, thereby reducing its abnormal mobility. In nitromethane, however, a corresponding addition causes an increase of about 6%, which presumably is mainly due to an increase of ionisation, since perchloric acid shows a large deviation from the ideal slope.

Summary.

1. A method of preparing nitromethane suitable for conductivity work is described.

2. The density and viscosity of nitromethane at 25° are respectively 1·1312 and 0·00627. The addition of water to this liquid lowers its viscosity, and the addition of nitromethane to water has the opposite effect, in spite of the fact that water is the more viscous liquid. The mutual solubilities of water and nitromethane at 25° are approximately: water in nitromethane, 2%; nitromethane in water, 10%.

3. The electrical conductivity of nitromethane solutions of certain uni-univalent salts and of perchloric acid ranging from 0·0001*N* to 0·002*N* has been measured at 25°.

4. Only the tetraethylammonium salts give a linear relation between Λ_c and $\sqrt{c}$, whilst other salts conform to the empirical relation $\Lambda_c = \Lambda_0 - xc^{\frac{1}{3}}$.

5. Approximate ionic mobilities have been calculated on the basis of Walden's rule, assuming for the picrate ion $l_0\eta = 0{\cdot}275$.

6. The results for the tetraethylammonium salts show good agreement with the Debye–Hückel–Onsager equation. All other salts show large divergences from ideal behaviour; some of them are weak electrolytes in nitromethane though they all behave as strong electrolytes in methyl and ethyl alcohols. As the dielectric constant of nitromethane is greater than that of the alcohols, the results show that ionic association is not entirely controlled by the electrical forces between the ions.

7. The addition of small quantities of water increases the conductivity of electrolytes in nitromethane, the increase being greater for salts with large divergences from ideal behaviour. For the tetraethylammonium salts, the increase in conductivity is of the same order as the increase in fluidity.

8. Perchloric acid is a fairly strong electrolyte in nitromethane and the mobility of the hydrogen ion is 63; it thus has not the abnormal mobility in this solvent that it possesses in hydroxylic solvents. Approximate measurements with other acids showed that they are all very weak electrolytes in nitromethane.

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