283. *The Conductivity of Tetramethylammonium Salts in Methyl and Ethyl Alcohol.*

By T. H. Mead, O. L. Hughes, and (Sir) Harold Hartley.

The systematic study by Walden and his co-workers (Walden and Ulich, "Uber die Beweglichkeit der elektrolytischen Ionen," *Fortschritte der Chemie*, 1926) of the tetrasubstituted ammonium salts, and particularly of tetraethylammonium salts, in various organic liquids has yielded much interesting information as to the state of electrolytes in different solvents. The ready solubility of these salts in solvents both of high and of low dielectric constant and of different chemical types has made it possible to study the effect of the properties of the solvent on the behaviour of dissolved electrolytes over a much wider range than would be possible with inorganic salts. In addition, the tetraethylammonium and similar ions have a special interest in view of their comparatively large size and their symmetrical character. Walden has shown that in organic solvents the ionic mobility of the tetraethylammonium ion is approximately proportional to the fluidity of the solvent, indicating that it must be mainly unsolvated in solution. In hydroxylic solvents, in which the mobility of the tetraethylammonium ion is exceptionally high as compared with other ions, its salts show the largest deviations from the Debye–Hückel–Onsager theory, whilst in nonhydroxylic solvents, on the other hand, where this ion has a relatively slow velocity, the behaviour of its salts agrees closely with theory. The salts of tetramethylammonium have not hitherto been studied in the same detail, and the experiments now described were made with the object of comparing the behaviour of corresponding salts of the two ions in methyl and ethyl alcohol.

Previous Work.—Walden (*Bull. Acad. Imp., St. Petersburg*, **1913**, **427**, 559) measured the conductivities of three tetramethylammonium salts in methyl alcohol.

Salt	Iodide	Nitrate	Thiocyanate
Λ_0	133	128	131

Later measurements (Walden, Ulich, and Laun, *Z. physikal. Chem.*, 1925, **114**, 275) with the chloride gave the following results:

	Λ_0.	Mobility of cation.
In methyl alcohol	117·0	65·5
,, ethyl alcohol	50·6	29·4

EXPERIMENTAL.

Preparation of Materials.—Solvents. Methyl alcohol was prepared by the method of Hartley and Raikes (J., 1925, **127**, 524), and ethyl alcohol by that of Copley, Murray-Rust, and Hartley (J., **1930**, **2492**).

Salts.—All the salts were prepared from a sample of tetramethylammonium bromide supplied by Messrs. Harrington. This was first recrystallised from methyl alcohol. Difficulty was anticipated in separating the salt from compounds of related bases, such as ammonium and tetraethylammonium, on account of the possible existence of mixed crystals. Specimens of tetramethylammonium bromide to which the salts of the other two bases had been added were recrystallised twice from methyl alcohol and then analysed by weight titration with silver nitrate. The results are the mean values of three concordant analyses :

	Br, % (±0·1%) (Calc.: 51·90%).
Original salt	51·78
,, + 5% ammonium bromide	51·60
,, + 10% tetraethylammonium bromide	51·73

Recrystallisation from methyl alcohol thus appears to free tetramethylammonium bromide from the salts of similar bases but it retained a small amount of impurity. It was thought that this would have a smaller effect on the mobility of the tetramethylammonium ion than the probable error in extrapolating to infinite dilution. Except in the case of the thiocyanate, the second series of conductivity determinations in methyl alcohol was carried out with samples of salt which had been crystallised once more than those used for the first series; the two series are concordant. A platinum centrifuge was used to free crystals from mother-liquor as completely as possible, and filtration was carried out in Jena all-glass filters.

Hydroxide. A solution of this base was prepared by the interaction of recrystallised bromide and excess of carefully washed silver oxide. The reaction was complete after 3 hours' stirring at 40—50°. The filtered solution was kept in a stoppered flask of hard Jena glass, and from it the chloride, iodide, picrate, and thiocyanate were prepared.

Chloride. The pure synthetic hydrochloric acid of commerce was diluted to *d* 1·1 and distilled in an all-glass still. The middle fraction was neutralised with a portion of the hydroxide solution, and the mixture concentrated and cooled. Three crops of crystals thus obtained were united and dried at 100°. Some of the crude chloride was crystallised from hot methyl alcohol by adding acetone and cooling. A second specimen was obtained by precipitation of the salt from methyl alcohol solution by adding acetone, followed by crystallisation from methyl alcohol and acetone. The salt was dried at 70° in a vacuum over phosphoric oxide.

Iodide. Iodine, purified by the method of Baxter (*J. Amer. Chem. Soc.*, 1904, **26**, 1577), was reduced by hydrogen sulphide, the solution boiled to expel excess of gas, and then filtered from sulphur. The final solution of hydriodic acid was distilled in a current of hydrogen in an all-glass still. The middle fraction was collected separately. Immediately before neutralisation with the hydroxide solution, the acid was warmed with finely divided electrolytic silver and filtered through glass to remove a trace of free iodine. The neutral solution of iodide was concentrated, and the resulting crystals recrystallised from water. A second specimen was obtained bv a further crystallisation from methyl alcohol. The salt always remained pure white. It was dried as for the chloride.

Perchlorate. Berk's pure perchloric acid was diluted and neutralised with the hydroxide solution, an excess of acid being avoided. The salt was crystallised from water, and a second specimen obtained by another recrystallisation from water; they were dried at 100° in the electric oven.

Picrate. Poulenc's picric acid was crystallised twice from benzene. After removal of solvent of crystallisation, the acid was crystallised from ethyl alcohol, and then had a very pale yellow colour. It was neutralised with hot hydroxide solution, and the salt crystallised from water. A second specimen was obtained by crystallisation of this from methyl alcohol. The salt darkens when dried at 100°, but the pale yellow colour is restored on cooling. One specimen was dried at 70° in the vacuum oven, and the other at 100°.

Thiocyanate. This salt is apt to decompose while drying unless the thiocyanic acid is pure. The latter was prepared by distilling a solution of A.R. potassium thiocyanate with phosphoric acid in an atmosphere of hydrogen at 12 mm. The condenser was cooled with ice-water, and water was added slowly to the contents of the still during the distillation to prevent the concentration rising above 5%. Rubber was avoided, as it produces a red coloration in the thiocyanic acid. The first runnings contained about 1% of acid and were rejected. No hydrogen sulphide or hydrogen cyanide could be detected in the first runnings or in the major portion of the distillate. The latter was redistilled into the hydroxide solution, after the rejection of first runnings. When the base had been neutralised, the distillation was stopped and the solution of the thiocyanate evaporated. The salt was recrystallised from ethyl alcohol, and dried either in a vacuum oven at 70° or in an electric oven at 100°.

Nitrate. Silver nitrate was recrystallised from dilute nitric acid and then from methyl alcohol after being dried at 150°. A solution of the purified salt was precipitated with a solution containing a slight excess of tetramethylammonium bromide. After filtration, the solution was evaporated. The salt was recrystallised from ethyl alcohol, and another specimen was submitted to a second crystallisation. The salt was dried at 100°.

Procedure.—All solutions were made up by weight, and the weights were corrected to vacuum standard. Concentrations are expressed in g.-mols. per 1000 c.c. of solution. The measurements of conductivity were made by Murray-Rust and Hartley's method (*Proc. Roy. Soc.*, 1929, *A*, **126**, 84) in a thermostat at 25·00° ± 0·01°; in the case of those with the picrate in ethyl alcohol, which only gives an approximately 0·0025*N*-solution, it was necessary to make withdrawals from the cell in order that sufficient solution could be added. Two cells were employed, the constants, *viz.*, $0{\cdot}03408_3$ and $0{\cdot}03826_0$, being verified several times during the investigation. In every case the conductivity of the pure solvent was subtracted from that of the solution. The values of Λ_c were plotted against $\sqrt{c}$, and the lines were extrapolated on that basis to give values of Λ_0. In the most dilute solutions, *i.e.*, in the neighbourhood of 0·0001*N*, there was a marked falling-off in the conductivity from the value demanded by the square-root relation, so that it seemed probable that the values of Λ_0 given by the straight-line extrapolation were too high. In addition to these extrapolations, curved extrapolations were also made, the curve being tangential to the slope calculated from the Debye–Hückel–Onsager equation where it cut the $c = 0$ axis.

Results.—The results are set out in tabular form. At the head of each table are given Λ_0, the conductivity at infinite solution, and x, the slope of the conductivity curve. Col. 1 shows the values of $c \times 10^4$, where c is the concentration; col. 2 the values of Λ_c; and col. 3 the differences between the observed values of Λ_c and those calculated from the equation $\Lambda_c = \Lambda_0 - x\sqrt{c}$. The values of κ, the specific conductivity of the solvent in reciprocal megohms, are given with each series.

In Methyl Alcohol.

Tetramethylammonium chloride. $\Lambda_0 = 121{\cdot}7$; $x = 337$.

	$c \times 10^4$.	Λ_c.	Diff.		$c \times 10^4$.	Λ_c.	Diff.
$\kappa = 0{\cdot}036$	1·1553	117·93	−0·17	$\kappa = 0{\cdot}030$	1·2863	117·94	+0·04
	2·2680	116·57	−0·08		2·3945	116·54	+0·03
	4·2528	114·78	±0·00		4·4896	114·67	+0·03
	7·6268	112·35	−0·07		7·5753	112·43	−0·05
	9·5535	111·34	+0·02		10·353	110·98	+0·10
	12·5035	109·77	−0·04		14·155	109·03	−0·02
				* MeOH + 0·143% H_2O	14·142	108·78	

* See p. 1214.

Tetramethylammonium bromide. $\Lambda_0 = 126{\cdot}3$; $x = 363$.

$\kappa = 0{\cdot}065$.			$\kappa = 0{\cdot}081$.			$\kappa = 0{\cdot}056$.		
$c \times 10^4$.	Λ_c.	Diff.	$c \times 10^4$.	Λ_c.	Diff.	$c \times 10^4$.	Λ_c.	Diff.
1·0080	122·38	−0·29	0·9479	122·52	−0·31	0·9575	122·38	−0·47
1·8837	121·22	−0·11	1·8736	121·17	−0·16	1·8683	121·14	−0·20
3·7790	119·27	+0·01	3·6299	119·41	±0·00	3·5657	119·49	+0·04
7·7541	116·16	−0·05	6·6763	116·89	+0·05	6·1756	117·29	+0·01
10·290	114·70	+0·05	9·6491	115·10	−0·09	8·2516	115·83	−0·04
13·122	113·25	+0·09	12·666	113·39	−0·24	10·773	114·36	−0·03

Tetramethylammonium iodide. $\Lambda_0 = 133{\cdot}0$; $x = 393$.

	$c \times 10^4$.	Λ_c.	Diff.		$c \times 10^4$.	Λ_c.	Diff.
$\kappa = 0{\cdot}022$	1·1771	128·48	−0·30	$\kappa = 0{\cdot}033$	0·7205	129·19	−0·50
	2·0670	127·24	−0·15		1·6616	127·76	−0·21
	3·8047	125·38	+0·01		2·9029	126·29	−0·07
	5·2416	124·09	+0·05		4·0302	125·17	−0·01
	7·2845	122·40	+0·02		5·6422	123·72	−0·01
	10·006	120·70	+0·09		8·1093	121·77	−0·07
				MeOH + 0·151% H_2O	8·1014	121·40	

Tetramethylammonium perchlorate. $\Lambda_0 = 141{\cdot}2$; $x = 460$.

$\kappa = 0{\cdot}040$	0·6015	137·56	−0·07	$\kappa = 0{\cdot}033$	0·49120	137·75	−0·23
	1·0369	136·54	+0·02		0·9720	136·63	−0·04
	1·6745	135·36	+0·11		1·7294	135·13	−0·02
	2·3155	134·28	+0·08		2·3113	134·18	−0·03
	3·2065	133·04	+0·08		3·3185	132·83	+0·01
	4·6435	131·03	−0·26		4·7490	130·85	−0·33
MeOH + 0·148% H_2O	4·6392	130·52					

Tetramethylammonium picrate. $\Lambda_0 = 116{\cdot}7$; $x = 323$.

$\kappa = 0{\cdot}033$	1·1486	113·24	±0·00	$\kappa = 0{\cdot}048$	0·80096	113·71	−0·10
	2·1182	112·07	+0·07		1·5011	112·70	−0·04
	3·8611	110·46	+0·10		2·4100	111·68	−0·01
	6·4349	108·47	−0·04		3·6691	110·52	±0·00
	8·8933	107·16	+0·09		4·9970	109·50	+0·02
	12·435	105·31	±0·00		7·0448	107·99	−0·14
				MeOH + 0·165% H_2O	7·0369	107·49	

Tetramethylammonium thiocyanate. $\Lambda_0 = 131{\cdot}8$; $x = 384$.

$\kappa = 0{\cdot}038$	1·0697	127·71	−0·09	$\kappa = 0{\cdot}042$	2·6593	125·42	+0·01
	2·0628	126·25	−0·01		4·9535	123·17	−0·06
	3·6056	124·57	+0·10		7·0953	121·45	−0·09
	5·9020	122·40	−0·04		9·4716	119·83	−0·12
	7·9264	121·00	+0·03		12·119	118·29	−0·11
	11·515	118·75	±0·00	MeOH + 0·210% H_2O	12·103	117·67	

Tetramethylammonium nitrate. $\Lambda_0 = 130{\cdot}2$; $x = 370$.

$\kappa = 0{\cdot}015$	1·1677	126·06	−0·04	$\kappa = 0{\cdot}038$	1·2101	126·00	−0·10
	2·3202	124·54	−0·11		2·3537	124·48	−0·01
	4·4561	122·45	+0·18		4·4073	122·45	+0·06
	6·2882	121·13	+0·25		6·6254	120·41	−0·18
	8·4544	119·40	+0·08		8·9270	119·03	−0·07
	12·114	117·32	+0·13		12·2895	117·07	−0·11
MeOH + 0·197% H_2O	12·096	116·87					

In Ethyl Alcohol.

Tetramethylammonium chloride. $\Lambda_0 = 52{\cdot}68$; $x = 307$.

	$c \times 10^4$.	Λ_c.	Diff.		$c \times 10^4$.	Λ_c.	Diff.
$\kappa = 0{\cdot}010$	1·8297	48·47	−0·06	$\kappa = 0{\cdot}023$	1·1467	49·42	+0·02
	3·2286	47·14	−0·03		2·5185	47·91	+0·10
	6·1383	45·00	−0·08		4·7697	46·05	+0·10
	9·9488	42·97	−0·03		7·1717	44·52	+0·06
	12·738	41·76	+0·04		10·447	42·82	+0·06

Tetramethylammonium bromide. $\Lambda_0 = 55{\cdot}10$; $x = 338$.

$\kappa = 0{\cdot}011$.			$\kappa = 0{\cdot}009$.			$\kappa = 0{\cdot}010$.		
$c \times 10^4$.	Λ_c.	Diff.	$c \times 10^4$.	Λ_c.	Diff.	$c \times 10^4$.	Λ_c.	Diff.
0·9856	51·59	−0·13	1·1160	51·41	−0·09	1·2394	51·24	−0·07
1·9966	50·28	−0·01	2·2955	49·97	+0·02	2·3364	49·92	+0·02
3·6034	48·65	−0·01	4·3052	48·08	+0·02	4·4568	47·93	−0·01
5·4701	47·15	−0·02	6·4199	46·47	−0·04	6·5820	46·37	−0·03
7·7015	45·66	−0·03	8·6005	45·15	−0·01	9·2309	44·81	+0·01
10·626	44·07	+0·02	11·776	43·54	+0·07			

Tetramethylammonium picrate. $\Lambda_0 = 55{\cdot}63$; $x = 282$.

	$c \times 10^4$.	Λ_c.	Diff.		$c \times 10^4$.	Λ_c.	Diff.
$\kappa = 0{\cdot}009$	0·3061	53·90	−0·17	$\kappa = 0{\cdot}010$	0·1010	54·80	+0·06
	1·1515	52·65	+0·04		0·1905	53·96	−0·42
	1·6143	52·10	+0·04		0·3545	53·58	−0·36
	2·1669	51·55	+0·06		0·6430	53·30	−0·06
	3·0917	50·74	+0·07		1·0866	52·71	+0·02
	3·9476	50·07	+0·04		1·5252	52·14	−0·01
					2·1167	51·52	−0·01
					3·0912	50·63	−0·04
					4·1461	49·82	−0·07
					5·0687	49·16	−0·11
					7·2270	47·95	−0·09

Tetramethylammonium thiocyanate. $\Lambda_0 = 58{\cdot}45$; $x = 340$.

$\kappa = 0{\cdot}008$	0·7322	55·46	−0·08	$\kappa = 0{\cdot}008$	0·7588	55·37	−0·12
	1·4835	54·38	+0·07		1·4478	54·35	−0·01
	3·0706	52·57	+0·08		2·9956	52·61	+0·05
	5·5732	50·43	±0·00		4·8289	50·98	±0·00
	8·1671	48·73	±0·00		6·9327	49·48	−0·02
	10·8173	47·32	+0·05		9·3814	48·00	−0·04

Tetramethylammonium nitrate. $\Lambda_0 = 56{\cdot}85$; $x = 325$.

$\kappa = 0{\cdot}010$	0·6995	53·84	−0·21	$\kappa = 0{\cdot}008$	0·6916	53·94	−0·30
	1·3987	52·93	+0·11		1·4178	53·09	−0·08
	3·0710	51·13	+0·11		2·8603	51·46	−0·04
	5·1380	49·43	+0·03		5·0293	49·60	−0·06
	7·1706	48·07	±0·00		7·6967	47·83	−0·07
	9·8599	46·57	+0·02		10·7960	46·20	−0·07

DISCUSSION OF RESULTS.

Values of Λ_0 *and Mobility of the Tetramethylammonium Ion in Methyl Alcohol.*—It will be seen (Fig. 1) that if the values of Λ_c are plotted against $\sqrt{c}$, in three cases the experimental points do not lie on a straight line in the dilute range, and in the case of the perchlorate, which has the largest deviation from the theoretical slope, the points lie on a curve over the whole range of concentration examined. The cause of the curvature of the lines, which increases with the deviation from theoretical behaviour, is presumably ionic association, which decreases with the dilution. Hence it is reasonable to assume that the conductivity curves become tangential to the line of theoretical slope at infinite dilution. Values for Λ_0 are given in Table I, obtained by linear extrapolation neglecting the most dilute points, and also by a curved extrapolation taking these points into account. It will be seen that agreement is rather better between the values obtained by the latter method. The average value for the mobility is 70·6 from a linear extrapolation, and 70·1 if the values for the curved extrapolation for the bromide, iodide, and perchlorate are taken into account. The latter value has been taken as the most probable. The tetraethylammonium and ammonium ions have mobilities of 62·0 and 57·9 respectively (Unmack, Bullock, Murray-Rust, and Hartley, *Proc. Roy. Soc.*, 1931, *A*, **132**, 427), and with the exception of the hydrion the tetramethylammonium ion is the fastest cation in methyl alcohol.

TABLE I.

	Linear extrapolation.		Curved extrapolation.			Linear extrapolation.	
Salt.	Λ_0.	$l_{0\mathrm{NMe}_4}$.	Λ_0.	$l_{0\mathrm{NMe}_4}$.	Salt.	Λ_0.	$l_{0\mathrm{NMe}_4}$.
Chloride	121·7	70·4	—	—	Picrate	116·7	70·0
Bromide	126·3	70·8	125·4	69·9	Thiocyanate ...	131·7	70·7
Iodide	133·0	72·0	131·6	70·6	Nitrate	130·2	69·8
Perchlorate	141·2	70·3	140·3	69·4			

Values of Λ_0 *and Mobility of the Tetramethylammonium Ion in Ethyl Alcohol.*—In this case (Fig. 2) the chloride is the only salt that does not show appreciable curvature of the conductivity curve in the dilute range. Table II gives values for Λ_0 and for the mobility of the tetramethylammonium ion obtained by linear and curved extrapolation as in methyl alcohol. Here again the agreement between the values of $l_{0\mathrm{NMe}_4}$ is better for those obtained by the latter method. The average value for the mobility is 28·9 by linear extrapolation and 28·3 by a curved extrapolation. The value of the mobility of the tetraethylammonium ion by a linear extrapolation is 28·4, and of the ammonium ion 19·2 (Barak and Hartley, *Z. physikal. Chem.*, in the press) so that in ethyl alcohol the tetramethylammonium ion is only slightly faster than the tetraethylammonium ion.

FIG. 1.

Methyl-alcoholic solution.

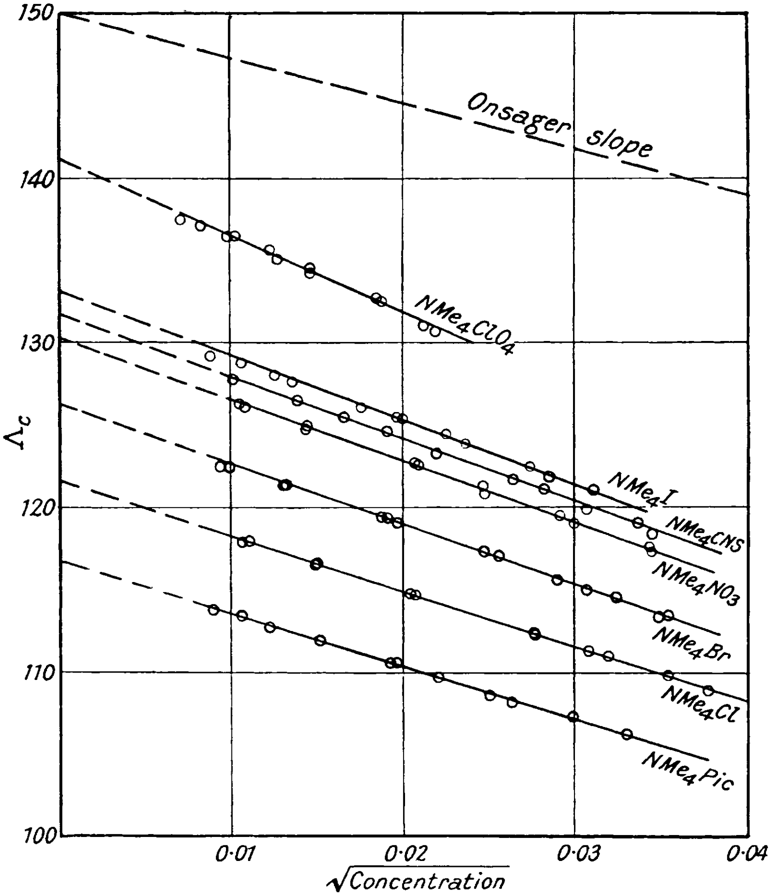

TABLE II.

Salt.	Linear extrapolation.		Curved extrapolation.	
	Λ_0.	$l_{0_{NMe_4}}$.	Λ_0.	$l_{0_{NMe_4}}$.
Chloride	52·7	28·4	—	—
Bromide	55·1	29·3	54·4	28·6
Picrate	55·6	28·8	55·0	28·2
Thiocyanate	58·4	29·2	57·6	28·4
Nitrate	56·9	28·8	56·2	28·1

Deviations from the Debye–Hückel–Onsager Theory.—The Onsager equation for methyl and ethyl alcohols is respectively :

$$\Lambda_c = \Lambda_0 - (0{\cdot}957\Lambda_0 + 158{\cdot}1)\sqrt{c}$$

and $$\Lambda_c = \Lambda_0 - (1{\cdot}44\Lambda_0 + 91{\cdot}9)\sqrt{c}$$

Table III contains the value of Λ_0 for the salts investigated in both solvents, and the corresponding values for Δ, the percentage deviation from the above equation, defined as $\Delta = 100\ (x_{\text{obs.}} - x_{\text{calc.}})/x_{\text{calc.}}$, where x is the constant in the equation $\Lambda_c = \Lambda_0 - x\sqrt{c}$. These values of x are obtained from the straight line drawn through the points in the more concentrated range. This is an arbitrary choice, but it is justifiable to compare the values of x which are all obtained in the same way. Positive values of Δ imply the presence of association between the ions.

FIG. 2.

Ethyl-alcoholic solution.

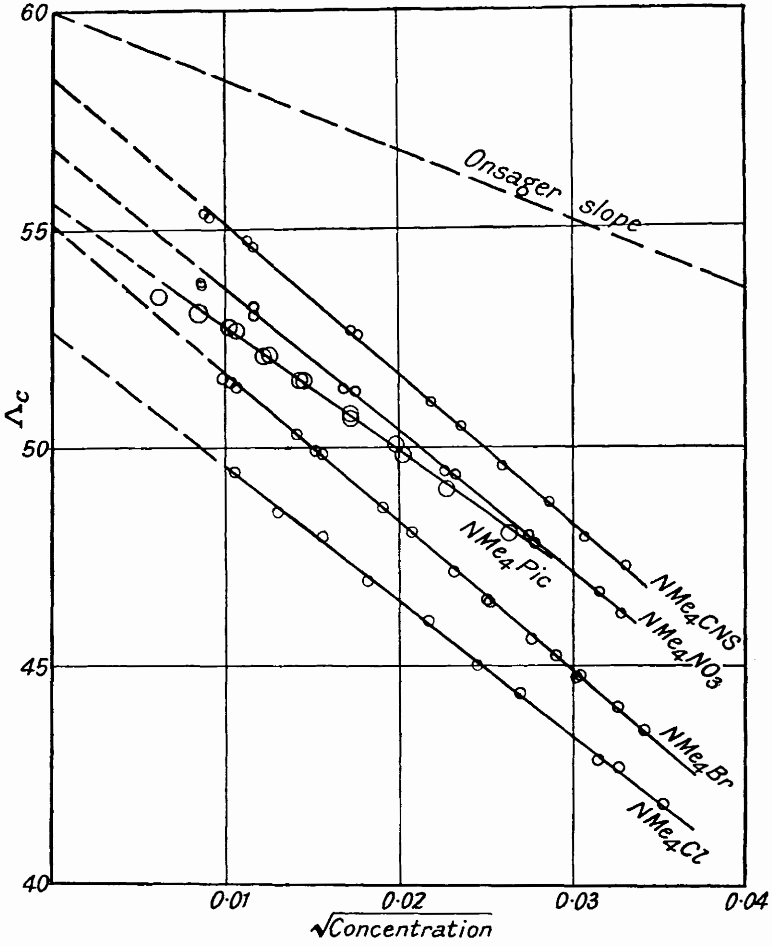

TABLE III.

	Methyl alcohol.		Ethyl alcohol.			Methyl alcohol.		Ethyl alcohol.	
Salt.	Λ_0.	Δ.	Λ_0.	Δ.	Salt.	Λ_0.	Δ.	Λ_0.	Δ.
Chloride	121·7	23	52·7	85	Picrate	116·7	18	55·0	65
Bromide	125·4	30	54·4	100	Thiocyanate	131·7	35	57·6	95
Iodide	131·6	38	—	—	Nitrate	130·2	31	56·2	90
Perchlorate ...	140·3	57	—	—					

In methyl alcohol the deviations are larger in each case than those for the corresponding tetraethylammonium salts, which have a lower conductivity, and it will be seen that the deviation is greatest in the case of salts with the largest values of Λ_0. This qualitative relation between the values of Λ_0 and Δ is in agreement with Bjerrum's [*Kgl. Danske Videnskabs. Selsk. Math.-fys. Medd.*, 1926, **7**, (9), 1] theory that ionic association is more likely to take place with ions of small radius, *i.e.*, of high mobility. In ethyl alcohol also the values of Δ are larger than those for the corresponding tetraethylammonium salts, but apart from this, the qualitative relation between the values of Λ_0 and Δ which exists for a number of series of salts in both alcohols is absent.

Walden's Rule.—Walden (*Fortschritte der Chemie*, 1926) found that the product $l_0\eta$, where η is the viscosity, is approximately constant for large organic ions in a variety of solvents, and this is generally assumed to be evidence that these ions are not solvated. However, as he has since pointed out (Walden and Birr, *Z. physikal. Chem.*, 1932, **140,** 327), the tetramethylammonium ion appears to be an exception to the rule in water and methyl alcohol, the product $l_0\eta$ being higher than in other solvents. He suggests that this is due to the action of the small unsolvated ions of tetramethylammonium in bringing about a local decrease in the macroscopic viscosity of the solvent in liquids like water and methyl alcohol, which contain a large proportion of associated molecules. Walden's mean value for the product $l_0\eta$ for the tetramethylammonium ion in other solvents is 0·317, in contrast to methyl and ethyl alcohol in which it has the values 0·382 and 0·305 respectively, the deviations from the mean value being greater in the former than the latter alcohol.

Addition of Water.—Ulich (*Z. angew. Chem.*, 1928, **41**, 1141) pointed out that the effect of a small addition of water upon the conductivity of a salt in a non-aqueous solvent should give valuable information as to the state of that salt in solution. The only property which is greatly affected by such addition is the viscosity, and one would expect that, for a completely dissociated salt, the fall in conductivity would be proportional to the rise in viscosity. The effects observed when 0·15% of water is added to the following solutions in methyl alcohol are :

Salt	Chloride	Iodide	Perchlorate	Picrate	Thiocyanate	Nitrate
Change produced, %	−0·24	−0·30	−0·39	−0·42	−0·37	−0·29

The change in viscosity is + 0·60%. The fact that the diminutions observed are smaller than expected is probably due to the size of the ion being smaller in water than in methyl alcohol, as Hughes and Hartley (*Phil. Mag.*, 1933, **15**, 610) have suggested.

SUMMARY.

1. The electrical conductivities of seven tetramethylammonium salts have been determined in methyl alcohol at 25° over the range 0·0001N—0·0015N. Similar measurements have been made for five of these salts in ethyl alcohol.

2. The mobility of the tetramethylammonium ion is 70·1 in methyl and 28·3 in ethyl alcohol.

3. The deviations of the tetramethylammonium salts from the Debye–Hückel–Onsager equation are considerable in both alcohols, indicating appreciable ionic association, and in both they are greater than those of the corresponding tetraethylammonium salts.

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