327. *Studies on Hydrogen Cyanide. Part IX. The Conductivity of Electrolytes in Anhydrous Hydrogen Cyanide: Some Ammonium and Tetra-alkylammonium Salts at* 18°.

By J. E. Coates and E. G. Taylor.

The study of conductivity in hydrogen cyanide reported in Part VIII (this vol., p. 1245) has been extended to the ammonium and tetra-alkylammonium salts, which have been investigated in many solvents. The latter salts are extremely soluble in hydrogen cyanide. These large organic cations appear to be relatively unsolvated in other solvents, and their tendency to associate with anions is determined mainly by the dielectric constant of the solvent and not by specific chemical affinities. In solvents of moderately high dielectric constant the tetra-alkylammonium salts are almost completely dissociated. It may be expected that in hydrogen cyanide, with its very high dielectric constant, these salts will be completely dissociated and their behaviour in dilute solution will be in agreement with the physical theory.

Experimental.

Conductivity Measurements.—The bridge assembly, conductivity cells, purification of the solvent, and method of carrying out the conductivity measurements were as described in Part VIII (*loc. cit.*).

Purification of Salts.—*Ammonium salts.* The chloride, bromide, iodide, nitrate, and perchlorate were recrystallised several times from conductivity water. The iodide was then washed with acetone to remove a slight yellow tinge remaining. Another specimen of ammonium bromide was sublimed in an atmosphere of pure dry nitrogen. Ammonium thiocyanate was recrystallised from ethyl alcohol. All the ammonium salts were dried by standing for at least a week in a vacuum over phosphoric oxide and solid caustic potash. Another specimen of the perchlorate was dried in an air-oven at 110°.

Tetramethylammonium salts. The chloride was dried in a vacuum over phosphoric oxide and then recrystallised from acetone. The bromide and iodide were recrystallised from methyl alcohol and water respectively. The three halides were dried at 80° in a vacuum over phosphoric oxide. Tetramethylammonium nitrate, prepared by the interaction of equivalent quantities of the purified iodide with recrystallised silver nitrate, was recrystallised from ethyl alcohol and dried at 110° in an air-oven; it was extremely soluble in hydrogen cyanide and deliquesced immediately in its vapour. Tetramethylammonium perchlorate and picrate were prepared from an aqueous solution of the hydroxide, obtained by 3 hours' interaction at 40—50° (occasional shaking) of the purified iodide with freshly prepared silver oxide. For the perchlorate, the filtrate was neutralised with a solution of perchloric acid, the base being a little in excess; the salt was recrystallised from water and dried in an air-oven at 110°. The picrate, obtained by neutralising the hydroxide solution with recrystallised picric acid, was recrystallised from water and again from methyl alcohol; one specimen was dried in air at 110°, and another in a vacuum over phosphoric oxide at 80°; m. p. 319—320° (decomp.) to a dark brown liquid. Walden (*Z. physikal. Chem.*, 1929, **144**, *A*, 269) gives m. p. 313°. This salt was extremely soluble in hydrogen cyanide.

Fig. 1.

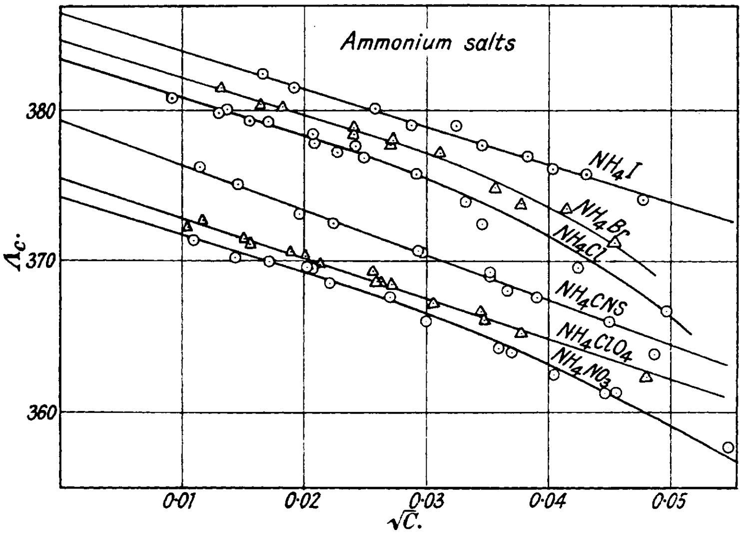
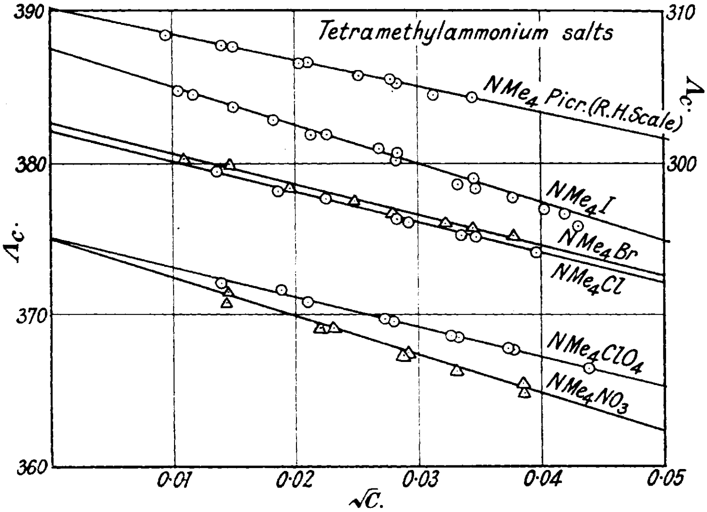
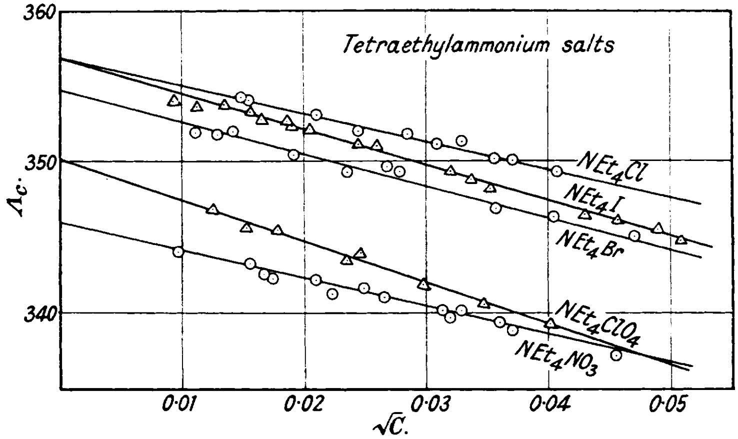


Fig. 2.



Tetraethylammonium salts. Tetraethylammonium iodide was purified by several recrystallisations from methyl alcohol–acetone and also from ethyl alcohol. An aqueous solution of tetraethylammonium hydroxide was prepared from the purified iodide as in the case of the tetramethylammonium compound. A portion of the hydroxide solution was neutralised with hydrochloric acid, the solution evaporated to dryness, and the chloride dried in an air-oven. The salt was then recrystallised from acetone. The bromide was recrystallised from ethyl

FIG. 3.



Ammonium chloride.

$\Lambda_c = 383{\cdot}3 - 245\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D.*
1·36	0·03457	372·4	−1·0
	0·04241	369·5	−3·3
	0·04957	366·8	−4·0
2·64	0·009072	380·8	−0·2
	0·01366	380·1	+0·2
	0·01712	379·2	+0·2
	0·02071	378·5	+0·3
	0·02422	377·7	+0·4
2·64	0·01546	379·3	−0·1
	0·02265	377·2	−0·5
	0·03324	374·0	−1·0
1·54	0·01282	379·9	−0·2
	0·02087	377·9	−0·2
	0·02487	376·9	−0·2
	0·02903	375·8	−0·3

Ammonium nitrate.

$\Lambda_c = 374{\cdot}3 - 245\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D.*
3·36	0·02013	369·7	+0·4
	0·02987	366·1	−1·0
	0·03580	364·4	−1·1
	0·04044	362·6	−1·8
	0·04554	361·3	−1·8
4·75	0·01427	370·3	−0·5
	0·02055	369·6	+0·4
	0·02739	367·9	+0·4
3·43	0·03706	364·1	−1·1
	0·04458	361·4	−2·0
	0·05464	357·8	−2·9
1·71	0·01081	371·4	−0·2
	0·01699	370·0	−0·1
	0·02198	368·6	−0·3
	0·02698	367·6	±0·0

Ammonium perchlorate.

$\Lambda_c = 375{\cdot}8 - 275\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D.*
2·11	0·02619	368·7	+0·1
	0·03773	365·3	−0·1
	0·04793	362·4	−0·3
5·07	0·01169	372·8	+0·2
	0·01882	370·7	+0·1
	0·02710	368·6	+0·2
	0·03440	366·7	+0·4
3·95	0·01503	371·5	−0·2
	0·02115	369·8	−0·2
	0·02578	368·7	±0·0
	0·03065	367·3	±0·0
	0·03473	366·2	±0·0
1·74	0·01042	372·3	−0·7
	0·01544	371·2	−0·4
	0·01995	370·4	+0·1
	0·02551	369·4	+0·6

Ammonium bromide.

$\Lambda_c = 384{\cdot}7 - 250\sqrt{C}$.

2·95	0·01321	381·5	+0·1
	0·01822	380·3	+0·2
	0·02401	378·9	−0·3
	0·02718	378·1	+0·2
	0·03111	377·3	+0·5
3·37	0·02410	378·4	+0·2
	0·03773	373·9	−1·3
	0·04558	371·2	−2·0
2·42	0·01645	380·5	±0·0
	0·02701	377·9	±0·0
	0·03557	374·9	−0·9
	0·04132	373·5	−0·8

Ammonium iodide.

$\Lambda_c = 386{\cdot}5 - 250\sqrt{C}$.

3·43	0·01905	381·5	−0·2
	0·02872	379·0	−0·3
	0·03452	377·8	±0·0
	0·04026	376·2	−0·1
	0·04757	374·2	−0·4
4·15	0·01652	382·3	−0·2
	0·02573	380·2	+0·2
	0·03234	379·0	+0·6
	0·03825	377·0	+0·1
	0·04308	375·8	+0·1

Ammonium thiocyanate.

$\Lambda_c = 379{\cdot}5 - 300\sqrt{C}$.

1·25	0·03664	368·1	−0·3
	0·04856	363·9	−1·1
4·38	0·01135	376·3	+0·2
1·97	0·01955	373·1	−0·5
	0·02961	370·6	±0·0
	0·03510	369·1	+0·2
	0·03908	367·6	−0·1
	0·04496	366·0	±0·0
1·17	0·01446	375·0	−0·1
	0·02240	372·5	−0·2
	0·02937	370·7	±0·0
	0·03515	369·2	+0·3

Tetramethylammonium chloride.

$\Lambda_c = 382{\cdot}3 - 205\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D*.
4·61	0·01874	378·2	−0·3
	0·02819	376·4	−0·1
	0·03348	375·4	±0·0
	0·04000	374·6	+0·5
2·08	0·01362	379·6	+0·1
	0·02247	377·7	±0·0
	0·02908	376·1	−0·2
	0·03473	375·2	±0·0
	0·03950	374·1	−0·1

Tetramethylammonium nitrate.

$\Lambda_c = 375{\cdot}0 - 255\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D*.
1·37	0·01432	371·6	+0·3
	0·02315	369·2	+0·1
	0·02914	367·6	±0·0
	0·03369	366·5	+0·1
	0·03860	364·9	+0·4
2·82	0·01437	370·8	−0·5
	0·02196	369·2	−0·2
	0·02890	367·5	−0·2
	0·03316	366·4	−0·2
	0·03853	365·6	−0·2

Tetramethylammonium perchlorate.

$\Lambda_c = 375{\cdot}3 - 200\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D*.
1·78	0·01405	372·1	−0·4
	0·02087	370·9	−0·2
	0·02800	369·6	−0·1
	0·03270	368·7	±0·0
	0·03742	367·9	±0·0
1·13	0·01876	371·7	+0·2
	0·02726	369·9	±0·0
	0·03321	368·6	±0·0
	0·03781	367·8	±0·0
	0·04390	366·6	+0·1

Tetramethylammonium bromide.

$\Lambda_c = 382{\cdot}4 - 193\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D*.
0·92	0·01091	380·3	±0·0
	0·01938	378·4	−0·2
	0·02777	376·7	−0·3
	0·03437	375·8	±0·0
1·88	0·01453	380·0	+0·4
	0·02479	377·6	±0·0
	0·03203	376·1	−0·1
	0·03770	375·3	+0·2

Tetramethylammonium iodide.

$\Lambda_c = 387{\cdot}6 - 260\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D*.
2·49	0·01047	384·8	−0·1
	0·01810	382·9	±0·0
	0·02678	381·0	+0·4
	0·03313	378·7	−0·3
	0·03756	377·8	±0·0
	0·04177	376·7	±0·0
2·79	0·01165	384·6	±0·0
	0·02125	381·9	−0·2
	0·02819	380·2	±0·0
	0·03468	378·4	−0·2
	0·04017	377·0	−0·1
	0·04300	375·9	−0·5
1·67	0·01486	383·8	±0·0
	0·02255	381·9	+0·2
	0·02829	380·7	+0·5
	0·03460	379·0	+0·4

Tetramethylammonium picrate.

$\Lambda_c = 309{\cdot}9 - 205\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D*.
3·36	0·01501	307·0	+0·2
	0·02104	305·6	±0·0
	0·02784	304·3	±0·0
	0·03464	302·8	±0·0
3·43	0·009436	307·9	−0·1
	0·01395	307·1	±0·0
	0·02042	305·6	−0·1
	0·02512	304·7	±0·0
	0·02841	304·0	±0·0
	0·03130	303·5	±0·0

Tetraethylammonium chloride.

$\Lambda_c = 356{\cdot}9 - 185\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D*.
3·29	0·01483	354·2	±0·0
	0·02095	353·1	+0·1
	0·02828	351·8	+0·1
	0·03281	351·3	+0·5
	0·03696	350·1	±0·0
1·33	0·01550	354·0	±0·0
	0·02440	352·1	−0·3
	0·03077	351·1	−0·1
	0·03538	350·2	−0·1
	0·04062	349·3	±0·0

Tetraethylammonium bromide.

$\Lambda_c = 354{\cdot}6 - 205\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D*.
4·9	0·01109	351·9	−0·4
	0·01926	350·4	−0·2
	0·02790	349·3	+0·4
2·3	0·01279	351·8	−0·1
	0·02359	349·3	−0·4
	0·03574	346·9	−0·3
	0·04703	345·0	+0·2
3·9	0·01416	352·0	+0·3
	0·02686	349·7	+0·6
	0·04041	346·3	+0·1

Tetraethylammonium iodide.

$\Lambda_c = 357{\cdot}0 - 240\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D*.
8·1	0·01892	352·4	±0·0
	0·03511	348·2	−0·3
	0·04560	346·1	+0·1
	0·05069	344·9	±0·0
8·45	0·01104	353·7	−0·6
	0·01646	352·8	−0·2
	0·02045	352·1	+0·1
	0·02584	351·1	+0·3
7·84	0·02444	351·1	±0·0
	0·03364	348·8	−0·3
	0·04278	346·5	−0·2
	0·04892	345·5	+0·2
3·87	0·01335	353·7	±0·0
	0·02035	352·2	+0·1
	0·03194	349·4	+0·1
5·2	0·009177	354·0	−0·8
	0·01552	353·4	+0·1
6·8	0·01860	352·7	+0·2

Tetraethylammonium nitrate.

$\Lambda_c = 346{\cdot}0 - 193\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D*.
2·64	0·01654	342·6	−0·3
	0·02218	341·3	−0·5
	0·03183	339·7	−0·3
	0·03701	338·9	−0·1
	0·04533	337·2	−0·2
2·70	0·01547	343·3	+0·2
	0·02088	342·2	+0·2
	0·02628	341·1	+0·1
	0·03118	340·3	+0·2
	0·03596	339·4	+0·2
1·91	0·009636	344·1	−0·1
	0·01734	342·4	−0·3
	0·02477	341·7	+0·4
	0·03268	340·2	+0·4

Tetraethylammonium perchlorate.

$\Lambda_c = 350{\cdot}2 - 270\sqrt{C}$.

$\kappa \times 10^7$.	$\sqrt{C}$.	Λ_c.	*D*.
2·10	0·01505	345·7	−0·4
	0·02352	343·5	−0·2
	0·02973	341·9	−0·1
	0·03465	340·6	−0·1
	0·04009	339·3	±0·0
1·74	0·01239	346·9	±0·0
	0·01782	345·5	+0·1
	0·02467	344·0	+0·5

alcohol. All three halides were dried at 80° in a vacuum over phosphoric oxide. The nitrate was prepared by the interaction of equivalent quantities of the purified iodide and silver nitrate, as well as from the hydroxide solution by neutralisation with nitric acid. This salt was recrystallised from acetone containing just enough water to dissolve it at the b. p. Another sample was precipitated from acetone solution with benzene. It was dried in an air-oven at 110°. As in the case of the tetramethylammonium salt, this compound dissolved with extreme ease and immediately deliquesced in the vapour of hydrogen cyanide. Tetraethylammonium perchlorate was obtained from the hydroxide solution by neutralising with a solution of perchloric acid, the base being added in slight excess; the salt was recrystallised from water and precipitated from acetone solution with benzene. It was dried at 110° in air and also in a vacuum at 80° over phosphoric oxide.

Analysis of the Salts.—The halides were analysed gravimetrically or volumetrically for halogen content, which was always within 0·1% of the theoretical value.

Results.—The preceding tables give the equivalent conductivities (Λ_c) and the square root of the concentrations ($\sqrt{C}$) expressed as g.-equivs. per 1000 cm.^{3} of solution in a vacuum at 18°. The value of the conductivity of the pure solvent (κ) for each run is given; this was subtracted from the observed conductivity to obtain that of the electrolyte. The equations relating Λ_c and $\sqrt{C}$ for each salt have been obtained from the best straight line drawn through the experimental points (see Figs. 1, 2, 3). Deviations (D) of the actual values from these straight lines are given in the last column.

DISCUSSION.

Λ_0 *Values.*—The Λ_0 values given in Table I have been obtained by extrapolation of the Λ_c–$\sqrt{C}$ plots to zero concentration. The values for the potassium salts (Part VIII, *loc. cit.*) have been included, and it is seen that the law of the independent mobility of ions is obeyed in the case of the ammonium salts but the agreement is only fair for some of the tetra-alkylammonium salts.

TABLE I.

	Cl.	Br.	I.	NO_3.	ClO_4.	CNS.	Picr.
K	363·4	363·2	363·9	353·9	355·3	358·0	—
Diff.	*19·9*	*21·5*	*22·6*	*20·4*	*20·5*	*19·5*	
NH_4	383·3	384·7	386·5	374·3	375·8	379·5	—
Diff.	*1·0*	*2·3*	*−1·1*	*−0·7*	*0·5*		
NMe_4	382·3	382·4	387·6	375·0	375·3	—	309·9
Diff.	*25·4*	*27·8*	*30·6*	*29·0*	*25·1*		*27·6*
NEt_4	356·9	354·6	357·0	346·0	350·2	—	282·3

Walden's Rule and Ionic Mobilities.—In Part VIII (*loc. cit.*) it was shown that for tetraethylammonium picrate in hydrogen cyanide the product $\Lambda_0\eta$ had almost the same value as in a great variety of solvents at different temperatures. For the tetramethylammonium salt in hydrogen cyanide, $\Lambda_0\eta = 0{\cdot}616$. A mean value of 0·586 has been obtained for this salt in a large number of solvents, excluding water and methyl alcohol, in which the values are 0·686 and 0·626 (at 25°) respectively. These high values of $\Lambda_0\eta$ found in associated solvents of high dielectric constant have been ascribed to a depolymerising effect of the more intense electric field of the relatively small (compared with the tetraethylammonium ions) unsolvated tetramethylammonium ion on the neighbouring associated solvent molecules. The viscosity which determines the mobility is thus presumed to be smaller than the measured viscosity of the associated liquid. As hydrogen cyanide is such a liquid, this explanation of the high values of $\Lambda_0\eta$ may be offered.

The following values of the kation mobilities have been calculated, it being assumed (Part VIII, *loc. cit.*) that the mobility of the picrate ion is 134·5 (values in water at 18° are given in parentheses for comparison) : NH_4, 174 (64) ; NMe_4, 175 (40) ; NEt_4, 145 (28).

In the majority of solvents the mobility of the ammonium ion is much smaller than that of the tetramethylammonium ion. The solvation of the former is presumably large enough to build up an ion having a greater effective radius than that of the tetramethylammonium ion. The mobilities of these two ions in hydrogen cyanide are almost identical, and this may be taken as further evidence that the solvating power of this solvent is relatively small.

The Debye–Hückel–Onsager Equation.—Excepting the chloride, bromide, and nitrate of ammonium, the salts investigated obey the Kohlrausch equation $\Lambda_c = \Lambda_0 - x\sqrt{C}$ over the whole concentration range studied. According to the Debye–Hückel–Onsager theory, for salts in hydrogen cyanide, $x = 0{\cdot}127\Lambda_0 + 222$, and $\Lambda_c = \Lambda_0 - (0{\cdot}127\Lambda_0 + 222)\sqrt{C}$.

The percentage deviation from the theoretical slope $[\Delta x = 100(x_{\text{expt.}} - x_{\text{theor.}})/x_{\text{theor.}}]$ for each salt is given in Table II. There is good agreement between theory and experiment in the case of the ammonium salts, although negative deviations appear predominantly. The positive deviations in the more concentrated regions of the curves for the chloride, bromide, and nitrate may be attributed to ionic association, as was found for the chloride, thiocyanate, and nitrate of lithium. It is perhaps remarkable that the thiocyanate does not show a similar behaviour to that of the lithium salt, the latter being relatively highly associated compared with the other salts (Part VIII, *loc. cit.*).

TABLE II.

	NH_4.	NMe_4.	NEt_4.		NH_4.	NMe_4.	NEt_4.
Chloride	−10	−24	−31	Perchlorate	+ 2	−26	+ 2
Bromide	− 8	−29	−23	Thiocyanate	+11	—	—
Iodide	− 8	− 4	−10	Picrate	—	−21	−17
Nitrate	− 9	− 5	−27				

Most of the tetramethyl- and tetraethyl-ammonium salts exhibit large negative deviations from theory, their magnitude being generally within the range 20—30. There are, however, striking exceptions in which the deviation is small. These cannot be ascribed to experimental error, for in every case the data obtained in wholly independent experiments were quite concordant. Negative deviations from the theoretical slopes, of the same magnitude, have been encountered in other solvents : for lithium perchlorate and picrate in water at 18°, $\Delta x = -12$ and -32 respectively; for tetrapropylammonium picrate in water at 0°, $\Delta x = -23$; for the last salt in acetonitrile at 25°, $\Delta x = -16$ (see *Ann. Reports*, 1930; Ekwall, *Z. physikal. Chem.*, 1933, **163**, *A*, 442; Walden and Birr, *ibid.*, 1929, **144**, *A*, 269). For several rubidium and cæsium salts in hydrogen cyanide, similar large negative deviations have been detected. In nearly all such instances at least one of the ions of the salt is relatively large and unsolvated.

SUMMARY.

(1) The investigation of the conductivity of electrolytes in hydrogen cyanide has been extended to some ammonium and tetra-alkylammonium salts at 18° in the concentration range 0·0001—0·002*N*.

(2) Large negative deviations from the Debye–Hückel–Onsager equation have been found in the case of the tetra-alkylammonium salts, but the ammonium salts show good agreement with the theory.

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