XXIX.—*The Conductivity of Electrolytes in Nitrobenzene.*

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THIS work is a continuation of that recorded in the preceding paper, and was undertaken in order to compare the influence of nitromethane and nitrobenzene on the behaviour of electrolytes in solution. These solvents have approximately equal dielectric constants (37 and 35, respectively) and their chemical constitution is similar, so that no large differences in ionising power are to be expected. Previous measurements have been restricted to a few salts with organic kations (Walden, *Z. physikal. Chem.*, 1905, **54**, 203; 1911, **78**, 275), and an attempt was made to extend this investigation to salts with metallic kations, as the results obtained with these electrolytes in nitromethane are particularly interesting; none of these salts except silver perchlorate, however, was sufficiently soluble in nitrobenzene for the purpose.

EXPERIMENTAL.

Preparation of Nitrobenzene.—Harrington's A.R. benzene was further purified by freezing out about half the original quantity; this was nitrated in the cold so slowly that the temperature did not rise above 10°. The nitrobenzene was separated, dried with phosphoric oxide, and distilled under 10 mm. or less. The temperature of the vapour was about 90—95°.

Preparation of Solutions.—Pure specimens of tetraethylammonium picrate and perchlorate and also of silver perchlorate were available, and solutions were made by drying the salt to constant weight and dissolving it in a known weight of nitrobenzene. Silver perchlorate is only sparingly soluble in nitrobenzene, and solutions stronger than $N/100$ could not be obtained.

Perchloric acid was prepared by mixing solutions of silver perchlorate and hydrogen chloride, the latter being made by passing the dry gas into nitrobenzene. It was impossible to make an accurate analysis of solutions of hydrogen chloride because they fumed strongly in air, but the concentration was determined approximately by titration with alkali, and a small excess was always added to the silver perchlorate solution. Any excess of hydrogen chloride was removed by evacuating the solution.

Conductivity Measurements.—The method of measuring the conductivity has been described in detail by Frazer and Hartley (*Proc. Roy. Soc.*, 1925, **109**, 351), and the conductivity cell was the same as that used in the preceding paper.

Results.—The equivalent conductivity at various concentrations is given in the following table. The tetraethylammonium salts obey a linear relation, $\Lambda_c = \Lambda_0 - x\sqrt{c}$, and the best values of Λ_0 and x are given at the head of the appropriate section. Col. 1 gives the values of κ, the specific conductivity of the solvent in reciprocal megohms; col. 2, the values of $c \times 10^4$, where c is the concentration in g.-equivs. per litre; col. 3, the values of $100\sqrt{c}$; col. 4, the equivalent conductivity Λ_c, and col. 5, for the tetraethylammonium salts, the difference between the observed value of Λ_c and that calculated from the values of Λ_0 and x given at the head of the tables.

Tetraethylammonium picrate.

$\Lambda_c = \Lambda_0 - 75\sqrt{c}$; $\Lambda_0 = 32·7$.

κ.	$c \times 10^4$.	$100 \times \sqrt{c}$.	Λ_c.	Diff.
0·03	0·633	0·795	31·97	−0·13
	1·618	1·272	31·74	−0·01
	2·749	1·658	31·48	+0·02
	4·805	2·191	31·07	+0·01
	7·658	2·768	30·63	0·00
	13·05	3·612	29·81	−0·03
0·03	1·469	1·212	31·75	+0·02
	2·626	1·621	31·49	+0·02
	3·573	1·890	31·29	+0·01
	5·293	2·301	30·99	+0·01
	7·405	2·721	30·64	−0·02
	10·92	3·305	30·18	−0·05

Tetraethylammonium perchlorate.

$\Lambda_c = \Lambda_0 - 93\sqrt{c}$; $\Lambda_0 = 37·6$.

κ.	$c \times 10^4$.	$100 \times \sqrt{c}$.	Λ_c.	Diff.
0·04	1·658	1·291	36·40	0·00
	3·510	1·873	35·89	+0·03
	6·014	2·453	35·35	+0·03
	9·703	3·114	34·71	0·00
	14·37	3·791	34·06	−0·03
	21·84	4·672	33·20	−0·06
0·04	1·462	1·209	36·45	−0·04
	3·000	1·732	35·97	−0·02
	5·358	2·319	35·45	+0·04
	7·403	2·721	35·03	−0·04
	11·82	3·438	34·37	+0·04
	17·43	4·200	33·65	+0·04

Silver perchlorate.

$\Lambda_0 = 38·4$ (approx.).

κ.	$c \times 10^4$.	$100\sqrt{c}$.	Λ_c.
0·03	0·851	0·922	37·19
	1·627	1·278	36·34
	3·016	1·738	34·90
	7·109	2·666	31·62
	9·777	3·126	30·12
0·03	0·596	0·721	37·58
	1·292	1·136	36·75
	2·390	1·552	35·38
	3·152	1·775	34·58
0·02	0·986	0·993	37·04
	1·184	1·345	36·19
	3·108	1·763	34·70
	5·593	2·364	32·71
	7·683	2·771	31·32
	10·27	3·203	29·91

Perchloric acid.

$\Lambda_0 = 43$ (approx.).

κ.	$c \times 10^4$.	$100\sqrt{c}$.	Λ_c.
0·03	0·926	0·962	35·9
	1·777	1·334	32·8
	2·922	1·709	30·0
	4·453	2·109	27·6
	6·639	2·577	24·0
	8·812	2·968	22·1
0·04	0·706	0·840	37·1
	1·242	1·135	35·2
	2·016	1·421	32·8
	3·180	1·783	30·2
	4·548	2·133	27·9

Discussion of Results.

The results are shown graphically in the figure, in which the equivalent conductivity is plotted against the square root of the concentration.

Tetraethylammonium picrate and perchlorate. The two series for each salt are in good agreement, and the points lie on a straight line when Λ_c is plotted against $\sqrt{c}$. The slopes of these lines have been compared with those calculated from the Debye–Hückel–Onsager equation $\Lambda_c = \Lambda_0 - x\sqrt{c}$, in which, for uni-univalent electrolytes,

$$x = \left\{\frac{5{\cdot}78 \times 10^5}{(DT)^{\frac{3}{2}}}\Lambda_0 + \frac{58{\cdot}0}{(DT)^{\frac{1}{2}}\eta}\right\}\sqrt{2}.$$

For nitrobenzene at 25°, $D = 34{\cdot}5$ (Lattey and Gatty, *Phil. Mag.*, 1929, **7**, 985) and $\eta = 0{\cdot}0183$, whence $x = 0{\cdot}784\Lambda_0 + 44{\cdot}2$.

A comparison of the observed values of x with those calculated from this equation is given below, together with the values of the percentage deviation $100(x_{\text{obs.}} - x_{\text{calc.}})/x_{\text{calc.}}$.

	$x_{\text{obs.}}$	$x_{\text{calc.}}$	$100(x_{\text{obs.}} - x_{\text{calc.}})/x_{\text{calc.}}$
$N(C_2H_5)_4Pic$	75	70	7
$N(C_2H_5)_4ClO_4$	93	74	26

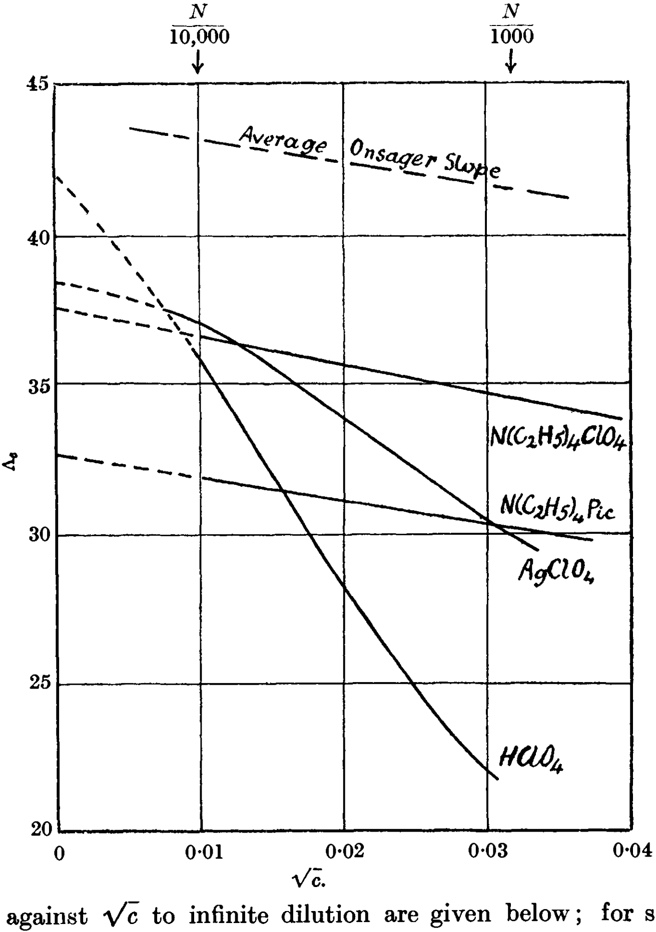
These figures show that neither salt is widely divergent from ideal behaviour and that, as in the case of nitromethane, the deviation is less for the picrate than for the perchlorate. The broken line in the diagram shows the average theoretical slope in nitrobenzene, calculated by putting $\Lambda_0 = 35$ in the above equation.

Silver perchlorate. The three series are in good agreement, but the results do not conform to the relation $\Lambda_c = \Lambda_0 - x\sqrt{c}$. The curve obtained when Λ_c is plotted against $\sqrt{c}$ suggests that silver perchlorate is not completely ionised; there is an approximately linear portion between the concentrations 0·0008*N* and 0·0002*N*, with a slope about five times as large as that calculated from Onsager's equation, but at lower concentrations the curve becomes concave to the concentration axis and at 0·00005*N* its slope is not much greater than the theoretical. The value $\Lambda_0 = 38{\cdot}4$ has been obtained by an approximate extrapolation of the curve in dilute solution.

Perchloric acid. The two series are not in good agreement owing to the errors introduced in preparing the solutions by mixing. The curve is that of an electrolyte of intermediate strength, approximately linear in dilute solutions but convex to the concentration axis at higher concentrations. The slope of the linear portion is approximately ten times the theoretical. Perchloric acid is thus appreciably associated in nitrobenzene solution, the degree of dissociation at *N*/1000 being about 55%, but it is a much stronger electrolyte than any other acid. Approximate measurements of the conductivity of hydrogen chloride, benzenesulphonic acid, and trinitrobenzoic acid showed that these acids are only very slightly ionised in nitrobenzene; at about $N/100$, benzenesulphonic acid has an equivalent conductivity of the order of 1, while the other two acids give considerably lower values.

Ionic Mobilities.—Values of Λ_0 obtained by extrapolating the plot of Λ_c against $\sqrt{c}$ to infinite dilution are given below; for silver perchlorate and perchloric acid the values are only approximate, as there is not a linear relation between Λ_c and $\sqrt{c}$.

FIG. 1.



	Λ_0.		Λ_0.
$N(C_2H_5)_4$Pic	32·7	$AgClO_4$	38·4
$N(C_2H_5)_4ClO_4$	37·6	$HClO_4$	43

There are no data for transport numbers in nitrobenzene, so individual ionic mobilities cannot be calculated directly. The only other method available is that explained in the preceding paper (p. 208). For tetraethylammonium picrate in nitrobenzene, $\Lambda_0\eta = 0{\cdot}598$, and in nitromethane (preceding paper) $\Lambda_0\eta = 0{\cdot}586$, so the product may not be as constant as Walden's results suggest. It is more nearly constant, however, for tetraethylammonium picrate than for any other salt, and the following mobilities have been calculated on the assumption that, for the picrate ion, $l_0\eta = 0{\cdot}275$.

Ion	$NEt_4^{\cdot}$	$Ag^{\cdot}$	$H^{\cdot}$	Picrate	ClO_4'
l_0.	17·7	$18{\cdot}_5$	23	15·0	19·9

It is interesting that in nitrobenzene, as well as in nitromethane, the hydrion has not the abnormal mobility that it possesses in hydroxylic solvents. In the two nitro-compounds its mobility is only 20—30% greater than that of the silver ion, whereas in methyl and ethyl alcohols it is three times as great.

Conclusion.—The results for nitrobenzene show that its behaviour as an ionising agent is similar to that of nitromethane and very different from that of hydroxylic solvents. Each of the four electrolytes investigated in nitrobenzene deviates more from ideal behaviour than in nitromethane, which suggests that there is rather more tendency for ionic association to take place in the former. This cannot be entirely accounted for by the slightly lower dielectric constant of nitrobenzene, but shows that the tendency of this solvent to solvate the ions is less than that of nitromethane; this may also be connected with the lower solubility of electrolytes in nitrobenzene.

Summary.

1. The electrical conductivity of four uni-univalent electrolytes has been measured in nitrobenzene between the concentrations $0{\cdot}0001N$ and $0{\cdot}002N$ at 25°.
2. Tetraethylammonium picrate and perchlorate are strong electrolytes, and the results are in agreement with those calculated from the Debye–Hückel–Onsager equation; but silver perchlorate is appreciably associated.
3. Perchloric acid is an electrolyte of intermediate strength, and gives a value of 43 for the mobility of the hydrogen ion, which shows that it is not abnormally fast in nitrobenzene as it is in hydroxylic solvents. Hydrogen chloride, benzenesulphonic acid, and trinitrobenzoic acid are very weak electrolytes.
4. Nitrobenzene is similar to nitromethane as an ionising solvent, but the tendency towards ionic association is rather greater in the former.

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