LXXV.—*The Electrical Conductivities of Solutions of Tetraethylammonium Iodide in Benzonitrile.*

By Austin Raymond Martin.

Walden has shown that the mobility of the tetraethylammonium ion is inversely proportional to the viscosity of the solvent. On the basis of this relationship and a knowledge of the equivalent conductivity at infinite dilution (Λ_0) of tetraethylammonium iodide in benzonitrile, certain ionic mobilities in this solvent may be determined from the conductivity measurements previously recorded (Martin, J., 1928, 3270). Walden's early measurements of the conductivities of solutions of tetraethylammonium iodide in benzonitrile (*Z. physikal. Chem.*, 1906, **54**, 189; **55**, 710; see also "Elektrochemie nichtwässeriger Lösungen," 1924, p. 135) are too erratic to give an unequivocal value of Λ_0. Hence the present investigation was undertaken. The degree of dissociation of tetraethylammonium iodide in benzonitrile is also of interest.

EXPERIMENTAL.

The apparatus and method used were the same as those described previously (Martin, *loc. cit.*).

Tetraethylammonium Iodide.—Kahlbaum's product was recrystallised three times from redistilled absolute alcohol, powdered in an agate mortar, and dried by being heated electrically in a vacuum at 100° over phosphoric oxide, the drying agent remaining at room temperature (Found: I, 49·30. Calc.: I, 49·36%). The molecular weight of tetraethylammonium iodide has been taken as 257·13.

Solvent Correction.—In series *a* the specific conductivity of the pure solvent at 25° was $0{\cdot}99 \times 10^{-7}$ mho, and in series *b* $0{\cdot}38 \times 10^{-7}$ mho. The conductivity of the solvent was in all cases subtracted from the observed conductivity in order to obtain the conductivity due to the dissolved salt. In series *a* the largest correction was 1·8% and in series *b* 0·5%.

Results.

The results of the conductivity measurements are given in Table I. The dilution, in litres, is denoted by v, and Δ is the difference between the observed value of the equivalent conductivity (Λ) and the straight line obtained by plotting Λ against the square root of the concentration ($\sqrt{c}$), a positive sign before Δ indicating that the observed point is above the straight line.

TABLE I.

Temp. 0°.				Temp. 25°.			
Series.	v.	Λ.	Δ.	Series.	v.	Λ.	Δ.
b	98·95	21·74	—	*b*	101·10	34·00	—
a	100·20	21·85	—	*a*	102·38	34·08	—
c	115·50	22·47	—	*c*	118·02	35·01	—
a	506·9	27·67	−0·10	*a*	517·9	43·53	±0·00
b	758·5	28·83	±0·00	*b*	775·0	45·27	±0·00
a	2030	30·82	+0·09	*a*	2074	48·32	+0·01
b	3754	31·42	−0·07	*b*	3836	49·53	−0·04
b	7579	32·15	±0·00	*b*	7744	50·62	±0·00
a	9558	32·32	+0·03	*a*	9766	50·94	+0·05
Temp. 50°.				Temp. 70°.			
b	103·45	47·15	—	*b*	105·36	58·15	—
a	104·75	47·29	—	*a*	106·69	58·37	—
a	529·9	60·99	±0·00	*a*	539·7	75·83	±0·00
b	793·0	63·60	±0·00	*b*	807·6	79·06	−0·09
a	2122	68·33	+0·12	*a*	2,161	85·38	+0·42 ?
b	3925	70·01	−0·12	*b*	3,997	87·38	±0·00
b	7924	71·70	±0·00	*b*	8,070	89·39	±0·00
a	9992	71·98	−0·14	*a*	10,178	90·04	+0·14

The values of Λ at even dilutions are given in Table II. Interpolation was carried out on a Λ–log c graph.

TABLE II.

	Λ.					Λ.			
v.	0°.	25°.	50°.	70°.	v.	0°.	25°.	50°.	70°.
100	21·79	33·93	46·88	57·50	2,000	30·73	48·22	67·97	84·73
200	24·73	38·29	52·95	65·57	5,000	31·78	50·00	70·68	88·08
500	27·67	43·34	60·55	75·15	10,000	32·36	50·92	72·14	89·88
1000	29·47	46·22	64·88	80·65					

Extrapolation to Λ_0. The square-root law was used to extrapolate to Λ_0. Ferguson and Vogel's method (*Phil. Mag.*, 1925, **1**, 971) gave values of the index n in the formula, $\Lambda_0 = \Lambda + \alpha c^n$, which were so close to 0·5 (namely, 0·507, 0·502, 0·491, 0·500) that this equation led to practically the same values of Λ_0 as the square-root law. The values of Λ_0 are :

Temp.	0°	25°	50°	70°
Λ_0	33·71	53·13	75·47	94·12

Discussion.

Values of Λ_0.—The values of the product of Λ_0 and the viscosity of the solvent (η) at the same temperature are given below. The constancy of this product shows the exactness to which Λ_0 is proportional to the fluidity of the solvent as the temperature is varied. The values of the viscosity of benzonitrile used were those determined previously (Martin, *loc. cit.*).

Temp.	0°	25°	50°	70°
$\Lambda_0\eta$	0·65	0·66	0·66	0·63

In Table III are the ratios of the values of Λ_0 of tetraethylammonium iodide in benzonitrile to the values at the same temperatures in acetone, acetonitrile, and ethylene chloride, the only solvents for which modern data are available. The ratios of the fluidities of the solvents are also given. The data for acetone are those of Walden, Ulich, and Busch (*Z. physikal. Chem.*, 1926, **123**, 429), for acetonitrile those of Walden and Birr (*ibid.*, 1929, **A**, **144**, 269), and for ethylene chloride those of Walden and Busch (*ibid.*, **140**, 89). Extrapolation to Λ_0 was in all cases carried out by the square-root law.

TABLE III.

Temp.	$\frac{\Lambda_0\ PhCN}{\Lambda_0\ Me_2CO}$.	$\frac{\eta\ Me_2CO}{\eta\ PhCN}$.	$\frac{\Lambda_0\ PhCN}{\Lambda_0\ MeCN}$.	$\frac{\eta\ MeCN}{\eta\ PhCN}$.	$\frac{\Lambda_0\ PhCN}{\Lambda_0\ C_2H_4Cl_2}$.	$\frac{\eta\ C_2H_4Cl_2}{\eta\ PhCN}$.
0°	0·203	0·204				
25	0·254	0·255	0·284	0·277	0·695	0·633
50	0·295	0·292				

Ionic Mobilities in Benzonitrile.—On the assumption that the mobility of the tetraethylammonium ion is given by the relation (Walden and Birr, *Z. physikal. Chem.*, 1929, **A**, **144**, 308),

$$\text{Mobility} \times \text{Viscosity of solvent} = 0{\cdot}296,$$

its mobility in benzonitrile has been calculated, and from Kohlrausch's law of the independent migration of ions and the data recorded previously, the ionic mobilities given in Table IV were obtained. In calculating the mobilities of the silver and nitrate ions, Koch's value, 0·475 (determined from *E.M.F.* measurements; J., 1928, 524), was used for the transport number of the silver ion in silver nitrate. In the rows designated l are the ionic mobilities, and in those designated r' are the apparent values of the ionic radii calculated from these mobilities on the assumptions (i) that the only resistance to the motion of the ions at infinite dilution is the viscous drag of the solvent, and (ii) that the magnitude of this drag is given by Stokes's law. In the rows r are the ionic radii obtained from crystal data by Goldschmidt (*Trans. Faraday Soc.*, 1929, **25**, 253); both r and r' are expressed in Ångström units.

TABLE IV.

Ion.		Temperature. 0°.	25°.	50°.	70°.
$NEt_4^{\cdot}$	l	15·26	23·87	33·79	44·45
	r'	2·75	2·75	2·75	2·75
$K^{\cdot}$	l	13·70	21·85	—	40·31
	r'	3·06	3·01	—	3·03
	r	1·33			
$Na^{\cdot}$	l	12·06	18·31	25·11	32·67
	r'	3·48	3·59	3·70	3·74
	r	0·98			
$Li^{\cdot}$	l	10·84	16·73	22·70	—
	r'	3·87	3·93	4·10	—
	r	0·78			

Ion.		Temperature. 0°.	25°.	50°.	70°.
$Ag^{\cdot}$	l	15·82	24·78	—	—
	r'	2·65	2·65	—	—
	r	1·13			
I'	l	18·45	29·26	41·68	49·67
	r'	2·28	2·24	2·23	2·46
	r	2·20			
Br'	l	12·36	19·44	27·39	—
	r'	3·40	3·38	3·39	—
	r	1·96			
NO_3'	l	17·48	27·40	—	—
	r'	2·40	2·40	—	—

The differences between r and r' cannot be used to calculate the degree of chemical solvation of the ions, since Born has shown (*Z. Physik*, 1920, **1**, 220) that on physical grounds a difference is to be expected, owing to the fact that the dipolar solvent molecules take a finite time to orient themselves in the ionic field as the ion moves through the solvent. However, the physical theory is not sufficiently developed to be used for the quantitative interpretation of the present results.

Dissociation of Tetraethylammonium Iodide in Benzonitrile.—The observed slopes of the Λ–$\sqrt{c}$ straight lines are given below, together with those calculated from the Debye–Hückel–Onsager equation

$$\Lambda = \Lambda_0 - \left[\frac{5{\cdot}78 \times 10^5}{(DT)^{3/2}}\Lambda_0 + \frac{58{\cdot}0}{(DT)^{1/2}\eta}\right]\sqrt{2c}$$

where D = the dielectric constant of the solvent, η = the viscosity of the solvent, and T = the absolute temperature.

The author is indebted to Dr. A. O. Ball for the values of D.

Temp.	0°	25°	50°	70°
D	27·58	25·22	23·31	21·98
Slope, obs.	133·6	217·6	332·1	423·3
Slope, calc.	90·9	147·3	202·4	259·4

The values of the degrees of dissociation, α, and of the corresponding dissociation constants, K (corrected for activity), calculated by the method given previously (Martin, *loc. cit.*), are set out in Table V. The Debye–Hückel equations used for calculating the ionic activity coefficients (γ) were (after insertion of numerical values): $-\log_{10}\gamma = 2{\cdot}78\sqrt{c'} - 9{\cdot}66c'$ at 0°; $= 2{\cdot}78\sqrt{c'} - 9{\cdot}69c'$ at 25°; $= 2{\cdot}78\sqrt{c'} - 9{\cdot}66c'$ at 50°; $= 2{\cdot}77\sqrt{c'} - 9{\cdot}63c'$ at 70°; c' being the ionic concentration.

TABLE V.

Temp.		Dilution (litres). 2000.	1000.	500.	200.	100.	Mean.
0°	α	0·9688	0·9516	0·9288	0·8947	0·8619	—
	$K \cdot 10^3$	12	13	15	20	24	17
25	α	0·9667	0·9524	0·9249	0·8833	0·8594	—
	$K \cdot 10^3$	11	14	14	17	23	16
50	α	0·9568	0·9366	0·9056	0·8502	0·8210	—
	$K \cdot 10^3$	8	10	11	12	17	12
70	α	0·9580	0·9385	0·9044	0·8493	0·8132	—
	$K \cdot 10^3$	9	10	11	12	16	12

It is not unlikely that at a dilution of 100 litres the Debye–Hückel–Onsager equation gives too large a value for the diminution in conductivity resulting from the interionic Coulomb forces, perhaps owing to the neglect of higher terms. For K increases at this dilution; and completely dissociated salts such as potassium and sodium chlorides in aqueous and methyl-alcoholic solutions at dilutions less than 100 and 300 litres, respectively, have values of Λ greater than those calculated from this equation (Onsager, *Trans. Faraday Soc.*, 1927, **23**, 341). These deviations from the predicted values are, however, much smaller than those in the opposite direction in the cases of thallium chloride and silver nitrate resulting from incomplete dissociation.

If the foregoing mean values of the dissociation constants be compared with those of the iodides of lithium, sodium, and potassium, lithium bromide, and silver nitrate (Martin, *Phil. Mag.*, 1929, **8**, 547), it is seen that in benzonitrile tetraethylammonium iodide is a stronger electrolyte than any of these salts, although it is apparently only slightly stronger than sodium iodide.

Calculation by means of the van 't Hoff isochore from the variation

of the dissociation constant with temperature indicates that the heat change in the dissociation of tetraethylammonium iodide in benzonitrile is an evolution of approximately 1 kg.-cal. per mol.

Summary.

1. The electrical conductivities of solutions of tetraethylammonium iodide in benzonitrile have been measured at 0°, 25°, 50°, and 70° over the range of dilution 100 to 10,000 litres.

2. By utilising the fact that the mobility of the tetraethylammonium ion is inversely proportional to the viscosity of the solvent, together with data previously recorded, certain ionic mobilities in benzonitrile have been determined.

3. The electrolytic dissociation of tetraethylammonium iodide in benzonitrile has been investigated.

The author wishes to thank Professor J. C. Philip, F.R.S., for very kindly placing at his disposal facilities for carrying out this work.

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LONDON, S.W. 7. [*Received, February 1st*, 1930.]