203. *The Conductivity of Electrolytes in Ethyl Cyanoacetate and in* o-*Toluonitrile.*

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THE present investigation is a continuation of the work of Martin on benzonitrile as a solvent for electrolytes (J., 1928, 3270; 1930, 530). The results recorded below, taken in conjunction with those for benzonitrile, and those of Walden and Birr for acetonitrile (*Z. physikal. Chem.*, 1929, **144**, 269), provide material for the comparative study of a series of solvents with a common characteristic group. The accurate conductivity data accumulated by various workers in recent years indicate that the behaviour of a liquid as a solvent for electrolytes—even at very low concentrations—is not determined solely by its dielectric constant and its viscosity. Specific chemical influences also are operative, and on this ground the investigation of a series of chemically related solvents is important. With this consideration in view, the systematic study of various liquids containing the CN group has been undertaken.

EXPERIMENTAL.

Conductivity Measurements.—The set-up of the bridge was similar to that used by Martin (*loc. cit.*), but the detector consisted of a two-valve amplifier and high-resistance telephones. The advantages of this modification, and the screening and earthing arrangements which it involves, have already been described in a communication from these laboratories (Ives and Riley, J., 1931, 1998).

All the conductivity measurements were carried out at $25° \pm 0{\cdot}01°$, the cell being immersed in an electrically heated water-bath, controlled by a mercury–toluene regulator. The cell used throughout was the one referred to as P I by Martin, and its constant, redetermined on the lines suggested by Frazer and Hartley (*Proc. Roy. Soc.*, *A*, 1925, **109**, 351), was 0·03401.

The solutions employed in the conductivity measurements were in all cases made up by weight, and the procedure and precautions adopted by Martin were followed. Volume concentrations were obtained from the weight of solvent present in a solution, and the density of the pure solvent.

In one or two cases special care had to be taken in order to obtain satisfactory conductivity measurements. Solutions of silver nitrate in ethyl cyanoacetate undergo a slow change (compare Koch, J., 1928, 273), and were therefore examined only when freshly prepared, whilst consistent results for solutions of silver nitrate in *o*-toluonitrile could be obtained only with solvent of the highest degree of purity. Again, solutions of potassium iodide in ethyl cyanoacetate, owing to their sensitiveness, had to be prepared and examined in diffuse artificial light.

Purification of Materials.—*Ethyl cyanoacetate.* The large middle fraction obtained in a fractionation of the commercial product was washed with sodium carbonate solution and extracted with ether. The ethereal extract was washed with water and dried with calcium chloride. The residue then obtained after removal of the ether was distilled in a vacuum, and the middle fraction was shaken or allowed to stand with calcium chloride. Redistillation under reduced pressure gave a product the specific conductivity of which in different cases lay between $1{\cdot}2$ and $3{\cdot}5 \times 10^{-7}$ mho. The density of this pure ethyl cyanoacetate was 1·0607 at 25°, referred to water at 4°. Its viscosity at 25°, measured on 10 c.c. in an Ostwald viscometer with a water period of 258 seconds, was found to be 0·0251 (the value for water being 0·00895).

o-*Toluonitrile.* This was purified in a similar way. The specific

Solvent: Ethyl cyanoacetate.

Silver Nitrate.

$\Lambda = 25{\cdot}46 - 277{\cdot}8\sqrt{c}$.

Series.	$c \times 10^4$.	Λ.	Diff.
a	16·79	14·25	+0·18
c	9·175	17·04	−0·01
a	7·971	17·67	+0·05
b	7·085	18·17	+0·10
c	4·266	19·71	−0·01
b	3·889	19·96	−0·02
b	2·486	21·03	−0·05
c	2·352	21·20	+0·06
b	1·665	21·86	−0·01
c	0·902	22·75	−0·08
c	0·311	23·37	−0·54

Potassium Iodide.

$\Lambda = 25{\cdot}01 - 115{\cdot}2\sqrt{c}$.

Series.	$c \times 10^4$.	Λ.	Diff.
b	17·01	20·26	±0·00
a	11·97	20·96	−0·07
a	7·936	21·77	±0·00
b	5·814	22·23	+0·01
a	4·445	22·59	+0·01
b	3·634	22·78	−0·04
a	2·716	23·05	−0·06
b	2·208	23·25	−0·04
b	1·143	23·79	±0·00

Lithium Bromide.

$\Lambda = 19{\cdot}10 - 196{\cdot}7\sqrt{c}$.

a	15·74	11·68	+0·39
b	9·866	13·04	+0·11
a	6·190	14·30	+0·09
b	3·763	15·39	+0·11
a	2·365	16·14	−0·07
b	1·368	16·80	±0·00
a	0·795	17·34	±0·00
b	0·395	17·88	−0·02
b	0·2052	18·15	−0·06

Tetramethylammonium Iodide.

$\Lambda = 26{\cdot}68 - 72{\cdot}67\sqrt{c}$.

a	10·48	24·35	+0·02
b	8·026	24·64	+0·02
a	6·311	24·86	±0·00
b	5·274	25·02	+0·02
a	4·051	25·25	−0·03
b	1·682	25·72	−0·02
a	1·224	25·87	±0·00
b	0·8044	26·01	−0·02

Sodium Iodide.

$\Lambda = 23{\cdot}40 - 85{\cdot}6\sqrt{c}$.

a	16·16	19·95	±0·00
b	11·42	20·47	−0·03
a	8·590	20·86	−0·03
c	7·420	21·05	+0·02
b	6·183	21·25	−0·01
a	4·335	21·63	+0·01
c	2·927	21·93	±0·00
a	2·342	22·12	+0·03
b	1·143	22·54	+0·06
c	1·001	22·61	+0·06
b	0·5526	22·75	−0·01
c	0·4432	22·82	−0·01
b	0·3340	22·89	−0·01
c	0·2423	22·91	−0·07

Tetraethylammonium Iodide.

$\Lambda = 25{\cdot}75 - 70{\cdot}53\sqrt{c}$.

b	11·325	23·45	+0·07
c	10·470	23·45	−0·02
a	7·665	23·81	+0·01
c	5·712	24·07	+0·01
a	4·701	24·22	±0·00
b	2·590	24·61	±0·00
c	2·312	24·67	+0·02
a	1·576	24·88	+0·02
b	1·015	25·05	+0·01
c	0·958	25·06	±0·00
a	0·687	25·16	−0·01
b	0·371	25·26	−0·06

Tetraethylammonium Bromide.

$\Lambda = 24{\cdot}80 - 86{\cdot}76\sqrt{c}$.

a	20·76	20·92	+0·08
b	12·18	21·83	+0·06
a	11·51	22·01	+0·08
b	7·760	22·44	+0·05
a	4·797	22·93	+0·03
b	2·672	23·36	−0·03
b	1·446	23·75	−0·01
a	1·062	23·90	−0·01
b	0·7995	24·00	−0·03
b	0·6208	24·10	−0·02

Tetrapropylammonium Iodide.

$\Lambda = 23{\cdot}60 - 62{\cdot}74\sqrt{c}$.

a	11·28	21·47	+0·02
b	8·989	21·71	+0·01
a	6·977	21·94	±0·00
b	6·172	22·02	+0·02
b	4·474	22·25	−0·02
a	3·362	22·45	±0·00
b	2·564	22·58	−0·01
b	1·010	23·00	±0·00
b	0·7976	23·02	−0·02

Solvent : o-*Toluonitrile.*

Silver Nitrate.

$\Lambda = 41{\cdot}10 - 1027\sqrt{c}.$

Series.	$c \times 10^4$.	Λ.	Diff.
a	9·481	10·11	+0·61
b	6·436	15·04	−0·01
b	4·571	19·11	−0·03
a	3·497	22·01	+0·09
b	2·769	24·03	+0·03
a	2·161	26·06	+0·06
b	1·631	28·00	±0·00
a	1·119	30·21	−0·03
a	0·5642	33·39	−0·07
a	0·3576	34·79	−0·17

Sodium Iodide.

$\Lambda = 38{\cdot}05 - 249{\cdot}2\sqrt{c}.$

Series.	$c \times 10^4$.	Λ.	Diff.
a	17·62	27·69	+0·10
b	16·42	28·01	+0·05
a	11·57	29·60	+0·03
b	7·997	31·06	+0·05
c	6·155	31·89	+0·02
a	4·666	32·67	±0·00
b	3·614	33·31	±0·00
c	2·726	33·92	−0·01
c	1·395	35·13	−0·02
c	0·479	36·23	−0·09

Tetraethylammonium Iodide.

$\Lambda = 41{\cdot}40 - 236{\cdot}5\sqrt{c}.$

Series.	$c \times 10^4$.	Λ.	Diff.
b	16·89	31·81	+0·13
b	13·84	32·69	+0·08
a	12·14	33·18	+0·02
b	10·50	33·70	−0·02
a	7·997	34·74	+0·02
b	5·712	35·69	−0·04
a	4·326	36·50	+0·01
b	2·292	37·81	−0·01
a	1·156	38·82	−0·04
a	0·4317	39·76	−0·09

Potassium Iodide.

$\Lambda = 41{\cdot}08 - 253{\cdot}3\sqrt{c}.$

Series.	$c \times 10^4$.	Λ.	Diff.
b	6·621	34·59	+0·03
b	4·033	36·02	+0·03
a	3·863	36·12	+0·02
b	2·433	37·13	±0·00
a	2·195	37·37	+0·03
a	1·278	38·21	−0·01
a	0·824	38·73	−0·05

Lithium Bromide.

$\Lambda = 27{\cdot}80 - 780\sqrt{c}.$

Series.	$c \times 10^4$.	Λ.	Diff.
a	5·895	11·03	+2·16
b	2·611	15·31	+0·11
a	1·820	17·29	+0·01
b	1·113	19·59	+0·02
a	0·549	21·99	−0·03
a	0·1832	24·31	−0·05

Tetraethylammonium Bromide.

$\Lambda = 39{\cdot}30 - 248{\cdot}9\sqrt{c}.$

Series.	$c \times 10^4$.	Λ.	Diff.
b	15·59	29·52	+0·05
a	13·61	30·18	+0·06
b	10·90	31·12	+0·04
b	7·733	32·36	+0·04
a	5·756	33·34	+0·01
b	3·972	34·36	±0·00
a	1·806	35·91	−0·04
b	1·208	36·51	−0·05
a	0·755	37·06	−0·08

Tetrapropylammonium Iodide.

$\Lambda = 37{\cdot}00 - 223{\cdot}5\sqrt{c}.$

Series.	$c \times 10^4$.	Λ.	Diff.
b	13·33	28·92	+0·08
a	12·26	29·28	+0·10
b	9·910	30·01	+0·02
a	8·484	30·52	+0·02
b	6·467	31·36	+0·03
a	4·832	32·05	−0·04
b	3·663	32·68	−0·04
b	1·974	33·84	−0·04
a	0·945	34·79	−0·04
a	0·489	35·42	−0·12

conductivity of different pure specimens lay between 0·6 and 1·2 × 10^{-7} mho. The density and viscosity of the purified material were respectively 0·9941 and 0·0157, both at 25°.

Salts. The best products obtainable commercially were recrystallised from conductivity water or redistilled absolute alcohol, according to circumstances, and were thoroughly dried by heating or in a vacuum over phosphoric oxide.

Results.

The results of the measurements are set out in the tables on pp. 1514–1515, where c is the concentration of the electrolyte in g.-equivs. per litre, and Λ is the equivalent conductivity at the given concentration. As is customary, the specific conductivity of the solvent has been deducted from the measured value of that of the solution. In all cases two independent series of measurements (in some cases three) have been carried out, and it is found for each salt examined that Λ is a linear function of the square root of the concentration—in harmony with the results of many recent similar investigations. The linear relation in question may be written in the customary form $\Lambda = \Lambda_0 - x\sqrt{c}$, and the special form of this general equation appropriate for each salt is set out at the top of the corresponding table. The values of Λ_0 and x inserted in the separate equations were obtained by drawing a straight line as nearly as possible through the experimental points, extrapolating to zero concentration for Λ_0, and determining also the slope x of the line. The degree of conformity with the linear relationship may be judged from the figures under "Diff." in the tables. These represent the difference between the experimental value of Λ, and the value calculated by the equation at the head of the table. A + sign indicates that the experimental value is the greater.

Discussion.

The values of Λ_0 for the various salts in ethyl cyanoacetate and *o*-toluonitrile at 25°, obtained by extrapolation as already described, are collected in the following table :—

	Ethyl cyanoacetate.	*o*-Toluonitrile.		Ethyl cyanoacetate.	*o*-Toluonitrile.
KI	25·01	41·08	$N(CH_3)_4I$	26·68	—
NaI	23·40	38·05	$N(C_2H_5)_4I$ ...	25·75	41·40
LiBr	19·10	27·80	$N(C_2H_5)_4Br$ ...	24·80	39·30
$AgNO_3$ ...	25·46	41·10	$N(C_3H_7)_4I$ ...	23·60	37·00

The foregoing figures, combined with the values of the viscosity η of the pure solvents, and the corresponding data for acetonitrile (Walden and Birr, *loc. cit.*) and benzonitrile (Martin, *loc. cit.*), serve to test the validity of the Walden rule $\Lambda_0\eta$ = a constant for a given salt. The results of this test are set out below.

Values of $\Lambda_0\eta$.

	KI.	NaI.	LiBr.	$AgNO_3$.	$N(C_2H_5)_4I$.	$N(C_2H_5)_4Br$.	$N(C_3H_7)_4I$.
$CH_3{\cdot}CN$	0·643	—	—	0·650	0·644	0·625	0·582
$C_6H_5{\cdot}CN$	0·646	0·597	0·448	0·647	0·659	—	—
$CH_2(CN){\cdot}CO_2Et$...	0·628	0·587	0·479	0·639	0·646	0·623	0·592
$C_6H_4Me{\cdot}CN$	0·645	0·597	0·436	0·645	0·650	0·617	0·581

It appears that the value of $\Lambda_0\eta$ is reasonably constant for each salt, except in the case of lithium bromide, where the conductivity measurements also were less satisfactory (see tables on p. 1514). In the present work, determinations were carried out at 25° only, but earlier investigations in nitromethane (Philip and Oakley, J., 1924, **125**, 1189), benzonitrile (Martin, *loc. cit.*, p. 3284), and acetonitrile (Walden and Birr, *loc. cit.*, p. 305) have adequately shown that the value of $\Lambda_0\eta$ for a given salt is independent also of the temperature.

As already stated (p. 1516), the $\Lambda-\sqrt{c}$ plots were found to be straight lines. For the tetra-alkyl iodides in ethyl cyanoacetate, the slopes x of these lines are only slightly greater than those required by the Onsager equation: this is shown by the figures for $100(x_{obs.} - x_{calc.})/x_{calc.}$ set out in the following table. It will be observed that the deviations for the other salts examined in ethyl cyanoacetate and for all the salts in *o*-toluonitrile are much greater, and are in some cases very large indeed.

Percentage deviations from Onsager's equation.

	Ethyl cyanoacetate.	*o*-Toluonitrile.		Ethyl cyanoacetate.	*o*-Toluonitrile.
KI	81	73	$N(CH_3)_4I$	12	—
NaI	39	73	$N(C_2H_5)_4I$ ...	10	57
LiBr	247	529	$N(C_2H_5)_4Br$ ...	41	70
$AgNO_3$ ...	340	585	$N(C_3H_7)_4I$ ...	1·5	57

Except for potassium iodide, the abnormality in *o*-toluonitrile is distinctly greater than in ethyl cyanoacetate. This is perhaps not surprising, since the deviations found by Martin for salts in benzonitrile were much greater than those recorded by Walden and Birr for salts in acetonitrile. There appear to be factors characteristic of the aromatic solvents which lead to more definite departure from the behaviour postulated in the Onsager formula.

The difference between the aromatic and the non-aromatic solvents suggested in the previous paragraph may be emphasised in another way.* The Onsager equation for uni-univalent salts, if divided throughout by Λ_0, gives

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

As already shown, the value of $\Lambda_0\eta$ for tetraethylammonium iodide in the four nitriles considered is 0·65 at 25°: if this value is inserted in the foregoing equation, and c is taken as 0·0005, then the values of Λ/Λ_0 for tetraethylammonium iodide at $N/2000$ concentration in the different nitriles should be given by the formula

$$\frac{\Lambda}{\Lambda_0} = 1 - \left[\frac{1{\cdot}83 \times 10^4}{(DT)^{\frac{3}{2}}} + \frac{2{\cdot}82}{(DT)^{\frac{1}{2}}}\right].$$

* See also "Chemistry at the British Association, 1931," p. 55.

The values of the conductivity ratio calculated by this formula are compared with the observed values in the following table :—

Tetraethylammonium iodide in different nitriles at 25° (c = 0·0005).

	D.	Λ/Λ_0 (calc.).	Λ/Λ_0 (found).
Acetonitrile	36	0·956	0·953
Ethyl cyanoacetate	27·7	0·945	0·930
Benzonitrile	25·2	0·939	0·908
o-Toluonitrile	18·8	0·919	0·872

It is clear that in the two aliphatic solvents the observed value of the conductivity ratio is very close to that calculated by the Onsager equation, whereas in the aromatic solvents—although one of them has a dielectric constant not very different from that of ethyl cyanoacetate—there is a notable discrepancy. It will be interesting to see whether the influence of the chemical nature of the solvent here suggested is confirmed by the results in other nitrilic solvents which are under investigation.

Summary.

(1) The conductivities of a number of salts in ethyl cyanoacetate and in *o*-toluonitrile have been determined at 25°.

(2) In all cases the equivalent conductivity is a linear function of the square root of the concentration. For the tetra-alkyl-ammonium iodides in ethyl cyanoacetate the slope of this line is only slightly greater than that required by the Onsager equation, but for other salts in ethyl cyanoacetate and for all the salts in *o*-toluonitrile the observed slope is definitely greater, sometimes very much greater, than the calculated slope.

(3) An inspection of the data now available for four nitrilic solvents suggests that departure from the behaviour postulated by the Onsager equation is more definitely exhibited in aromatic than in aliphatic solvents.

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