21. *Physicochemical Studies of Some Cyclic Carbonates. Part III.*[1] *Electrical Conductivities in Ethylene Carbonate.*

By R. F. KEMPA and W. H. LEE.

Conductometric measurements in ethylene carbonate of a number of 1 : 1-electrolytes indicate that complete ionisation occurs in this solvent. Positive departures of some of the Kohlrausch plots from the theoretical Onsager lines are explained in terms of extensive solvation of the smaller cations; negative deviations from the Onsager slopes are attributed to a small degree of ion-pair formation. A method is suggested for the estimation of apparent ionic radii and hence of approximate solvation numbers from conductance data. The values of the solvation numbers obtained by this method for the alkali-metal ions in ethylene carbonate support the increase of ionic conductance along the series: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$.

It was reported in Part I of this series that ethylene carbonate is a highly polar solvent, having a dipole moment $\mu = 4{\cdot}87$ D, and dielectric constant $\varepsilon = 89{\cdot}6$, at 40°. Subsequently, the Harris–Alder correlation parameter[2] g was calculated from these data. The value $g = 1{\cdot}25$ for ethylene carbonate at 40° suggests that the liquid is only slightly associated, in contrast to substances of similar and higher dielectric constant, *e.g.*, water and the *N*-monomethyl-amides, all of which are strongly hydrogen-bonded in the condensed phase. It was felt, therefore, that conductometric measurements of electrolyte solutions in ethylene carbonate would provide useful information about the electrochemical behaviour of electrolytes in solvents of high dielectric constant, which, however, in contrast to water and similar hydrogen-bonded solvents, are not appreciably associated.

The alkali-metal halides are, in general, too insoluble in ethylene carbonate for conductivity studies to be made; however, we found the alkali-metal perchlorates and the tetra-alkylammonium halides to be sufficiently soluble for this purpose. The electrical conductances of such 1 : 1-electrolytes in ethylene carbonate have accordingly been measured at 40°.

EXPERIMENTAL

Electrical conductances were measured in borosilicate-glass conductivity cells having rigid bright platinum electrodes; the cell constants were approximately 0·1 cm.$^{-1}$, as determined from conductance measurements of potassium chloride solutions of known concentration, using the equation:[3]

$$\Lambda_c(\text{KCl}) = 149{\cdot}92 - 93{\cdot}85\sqrt{c} + 50c \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Although the values of the constants in this equation refer to conductivities at 25°, the cell constants were assumed to be applicable at 40°; no reference solutions are available for determining cell constants at this temperature.

Measurements were made by means of a conventional Wheatstone bridge circuit, energised by an oscillator of 1500 c./sec. frequency, the off-balance voltage being amplified, detected, and observed on a microammeter.

Solvent.—Ethylene carbonate was purified as described in Part I, and had the following physical properties at the temperature of the experiments: Density $d_4^{40} = 1{\cdot}3208$ g. cm.$^{-3}$, viscosity $\eta = 1{\cdot}850 \times 10^{-2}$ ps., specific conductivity $\kappa = 0{\cdot}04 - 0{\cdot}09 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$; a solvent correction was determined and applied for each solution measured.

Solutes.—Lithium perchlorate was prepared by heating "AnalaR" lithium nitrate with perchloric acid, and recrystallising the salt twice from water. It was dried to constant weight by heating it to 300° in a current of dried air.

Sodium perchlorate was prepared by dissolving sodium carbonate in perchloric acid,

---

[1] Part II, Kempa and Lee, *J.*, 1959, 1576.

[2] Harris and Alder, *J. Chem. Phys.*, 1953, **21**, 1031.

[3] Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1411.

recrystallising the anhydrous salt from water at a temperature above 50°, and drying it to constant weight in an air-bath at about 250°.

Potassium perchlorate was obtained by twice recrystallising a commercial sample from water and drying it in an evacuated desiccator (P_2O_5).

Rubidium and cæsium perchlorates were prepared by dissolving the carbonates in perchloric acid, recrystallising the precipitates from water, and drying.

Tetramethylammonium iodide was prepared from a commercial sample by partial crystallisation from ethyl acetate.

Tetraethylammonium iodide was purified by twice recrystallising a commercial sample of the salt from ethyl acetate containing about 5% of ethanol.

Tetraethylammonium bromide was prepared by treating triethylamine with ethyl bromide in alcoholic solution at 70°. The salt was recrystallised from ethyl acetate.

Tetraethylammonium perchlorate was obtained from the iodide by precipitation with dilute perchloric acid in aqueous alcohol. The salt was washed with cold water and dried *in vacuo* (P_2O_5).

Tetra-n-butylammonium iodide was purified by twice recrystallising a commercial sample from ethyl acetate.

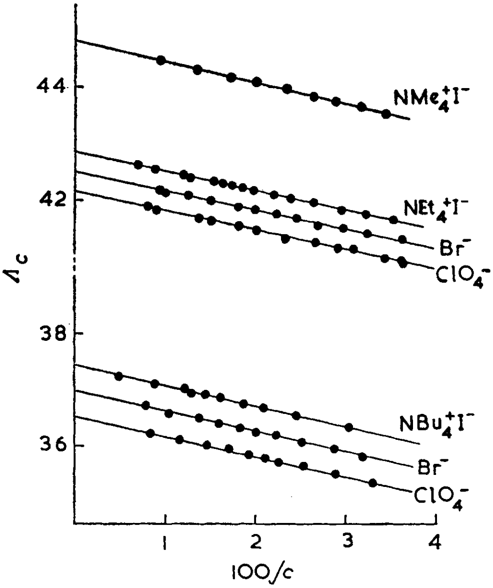

FIG. 1. *Equivalent conductances Λ_c (cm.^{2} ohm^{-1} g.-equiv.$^{-1}$) of some tetra-alkylammonium salts in ethylene carbonate at 40°.*

Tetra-n-butylammonium bromide was prepared by heating n-butyl bromide with tri-n-butylamine in a sealed tube at 100° for 48 hr. The salt was recrystallised several times from ether–ethyl acetate.

Tetra-n-butylammonium perchlorate was prepared from the iodide by metathesis with silver perchlorate. The crude material was recrystallised from ethyl acetate.

Solutions for conductivity measurement were prepared by addition of weighed amounts of stock solution to a known weight of solvent in the cell; a current of dry nitrogen was passed over the solution during the addition.

(1) *Conductivity of some tetra-alkylammonium salts in ethylene carbonate.*

Results.—The Λ_c–$\sqrt{c}$ plots for the tetramethyl-, tetraethyl- and tetra-n-butyl-ammonium iodides, and for the tetraethyl- and tetra-n-butyl-ammonium bromides and perchlorates are shown in Fig. 1. The results for one of these electrolytes, typical of all, are given in Table 1.

The extrapolated Λ_0 values were substituted in the Debye–Huckel-Onsager equation:

$$\Lambda_c = \Lambda_0 - \left[\frac{82 \cdot 5}{(\varepsilon T)^{\frac{1}{2}}\eta} + \frac{8 \cdot 20 \times 10^5}{(\varepsilon T)^{\frac{3}{2}}}\Lambda_0\right]\sqrt{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

TABLE 1. *Conductivity of tetraethylammonium perchlorate in ethylene carbonate at* 40°.

10^4c (mole l.$^{-1}$)	$10^2\sqrt{c}$	Λ_c (cm.^{2} ohm^{-1} g.-equiv.$^{-1}$)	10^4c (mole l.$^{-1}$)	$10^2\sqrt{c}$	Λ_c (cm.^{2} ohm^{-1} g.equiv.$^{-1}$)	10^4c (mole l.$^{-1}$)	$10^2\sqrt{c}$	Λ_c (cm.^{2} ohm^{-1} g.-equiv.$^{-1}$)
0·6296	0·7934	41·85	3·8141	1·9530	41·45	9·6879	3·1117	41·07
0·7779	0·8820	41·83	5·5254	2·3506	41·32	12·0112	3·4657	40·94
1·8959	1·3769	41·65	7·5975	2·6945	41·21	13·5040	3·6749	40·86
2·3054	1·5184	41·60	8·6332	2·9382	41·12	13·6641	3·6965	40·85
3·2954	1·8152	41·50						

and the theoretical limiting slopes determined. In this equation, Λ_c is the equivalent conductance at concentration c (g.-equiv. l.$^{-1}$), Λ_0 the extrapolated equivalent conductance at infinite dilution, ε the dielectric constant, and η the viscosity, of the solvent at T° K.

The Λ_0 values and the theoretical limiting slopes are recorded in Table 2, together with the experimental Λ_c–$\sqrt{c}$ slopes and their deviations from the theoretical, and the values of the Walden product $\Lambda_0\eta$ for each solute.

TABLE 2.

Electrolyte	Λ_0	Slope (exptl.)	Slope (theor.)	$\frac{100\Delta \text{ Slope}}{\text{Theor. slope}}$	$\Lambda_0\eta$
Me_4NI	44·81	37·0	34·44	+7·5	0·828
Et_4NI	42·83	35·0	34·09	+2·6	0·792
Et_4NBr	42·48	34·8	34·03	+2·4	0·785
Et_4NClO_4	42·13	34·4	33·91	+1·2	0·779
n-Bu_4NI	37·41	35·2	33·15	+6·0	0·692
n-Bu_4NBr	36·97	36·3	33·07	+9·7	0·683
n-Bu_4NClO_4	36·52	35·9	32·99	+8·8	0·975

Discussion.—The Λ_c–$\sqrt{c}$ plots are linear within the concentration range studied. The slopes deviate positively from equation (2) in the appropriate form for this solvent and temperature:

$$\Lambda_c = \Lambda_0 - (26{\cdot}61 + 0{\cdot}175\Lambda_0)\sqrt{c} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$= \Lambda_0 - S\sqrt{c}, \text{ where } S = 26{\cdot}61 + 0{\cdot}175\Lambda_0$$

The deviations depend mainly upon the cation, and are large and positive for the tetramethyl- and tetrabutyl-ammonium salts; such deviations are usually regarded as due to incomplete dissociation, or to ion-pair formation. The linearity of the experimental slopes indicates complete dissociation of the electrolytes at these concentrations, and seems to be best described by the second of six characteristic patterns listed by Fuoss and Accascina.[4] This behaviour is ascribed to ion-pair formation with the point of inflection of the curve lying below the minimum concentration studied.

In a medium of dielectric constant 89·6, at very low concentration, association of the solute ions is unlikely to extend beyond pair-formation. We can calculate a dissociation constant for the ion-pairs as follows. If their degree of dissociation at molarity c is α, we may write from equation (3)

$$\Lambda_c = \alpha[\Lambda_0 - S.\sqrt{(c\alpha)}] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

The iteration process of solving equation (4) for α by successive approximations, starting from $\alpha_0 = \Lambda_c/\Lambda_0$, has been considered by Fuoss;[5] he tabulates a function F of the derived variable $Z = (S/\Lambda_0^{\frac{3}{2}})\sqrt{(c\Lambda_c)}$, such that the final value of α in equation (4) is given by Λ_c/Λ_0F. It will be observed that F is a function of the molarity of the solution. From the law of mass action, if K is the thermodynamic dissociation constant for the ion-pairs,

---

[4] Fuoss and Accascina, " Electrolytic Conductance," Interscience, New York, 1959, p. 266.

[5] Fuoss, *J. Amer. Chem. Soc.*, 1935, **57**, 488.

$K = c\alpha^2 f_\pm^2/(1 - \alpha)$. To solve this equation for K, $f_\pm$ the mean-ion activity coefficient of the solute at each concentration is required. This can be calculated from the equation [6]

$$-\log f_\pm^2 = \frac{3{\cdot}6494 \times 10^6}{(\varepsilon T)^{\frac{3}{2}}} \cdot \frac{\sqrt{c}}{1 + \beta a}$$

where

$$\beta = 5{\cdot}0293 \times 10^9 \sqrt{c}/(\varepsilon T)^{\frac{1}{2}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

and a is the distance of closest approach of the ions. However, as equation (3) is the limiting form of the law, it seems more consistent to calculate $f_\pm$, for the evaluation of K, by the limiting form of equation (5), *i.e.*, by the omission of the term $(1 + \beta a)$. We thus obtain, for the ion-pair dissociation constant of tetrabutylammonium bromide in ethylene carbonate, the mean value $K_{40^\circ} = 0{\cdot}26 \pm 0{\cdot}04$, and for tetramethylammonium iodide, $K_{40^\circ} = 0{\cdot}33 \pm 0{\cdot}08$. These solutes appear to be associated, in the form of ion-pairs, to about the same extent as thallous chloride in aqueous solution,[7] for which the dissociation constant has the value $K_{25^\circ} = 0{\cdot}32 \pm 0{\cdot}03$.

Kohlrausch's law of independent ionic mobilities applies to these solutes in ethylene carbonate solution, as the following results show:

	Br^-	I^-	ClO_4^-
$\lambda^\circ_{Et_4N^+} - \lambda^\circ_{n\text{-}Bu_4N^+}$	5·51	5·42	5·61

The cation conductances decrease along the series $Me_4N^+ > Et_4N^+ > n\text{-}Bu_4N^+$; the anion conductances decrease slightly along the series $I^- > Br^- > ClO_4^-$, from which it would appear that the tetralkylammonium cations are practically unsolvated in ethylene carbonate, at least as regards the effective distance of closest approach of the ions.

The Walden's rule products, in Table 2, resemble similar products in other organic solvents, rather than the corresponding values in highly associated solvents such as water.

(2) *Conductivity of alkali-metal perchlorates in ethylene carbonate.*

Results.—The Λ_c–$\sqrt{c}$ plots for the alkali-metal perchlorates are shown in Fig. 2, and the results for one typical member of the series are given in Table 3; Λ_0 values obtained by Shedlovsky's extrapolation formula,[8] the theoretical and experimental Λ_c–$\sqrt{c}$ slopes, and the Walden product $\Lambda_0\eta$ are listed in Table 4.

TABLE 3. *Conductivity of potassium perchlorate in ethylene carbonate at* 40°.

10^4c (mole l.$^{-1}$)	$10^2\sqrt{c}$	Λ_c (cm.^{2} ohm^{-1} g.-equiv.$^{-1}$)	10^4c (mole l.$^{-1}$)	$10^2\sqrt{c}$	Λ_c (cm.^{2} ohm^{-1} g.-equiv.$^{-1}$)	10^4c (mole l.$^{-1}$)	$10^2\sqrt{c}$	Λ_c (cm.^{2} ohm^{-1} g.-equiv.$^{-1}$)
0·7517	0·8670	41·69	4·0172	2·0043	41·32	8·0260	2·8330	41·05
1·1773	1·0850	41·64	4·3530	2·0865	41·31	8·2212	2·8673	41·04
1·6169	1·2715	41·56	4·8003	2·1910	41·25	8·9124	2·9854	41·00
2·4472	1·5644	41·47	5·3418	2·3112	41·21	11·0176	3·3193	40·88
2·5200	1·5874	41·47	6·0189	2·4534	41·18	12·4520	3·5288	40·80
3·4471	1·8569	41·37	6·1980	2·4891	41·17	13·7504	3·7082	40·75

TABLE 4.

Electrolyte	Λ_0	Slope (exptl.)	Slope (theor.)	$\frac{100\Delta \text{ Slope}}{\text{Theor. slope}}$	$\Lambda_0\eta$
$LiClO_4$	32·85	27·5	32·36	−15·1	0·607
$NaClO_4$	38·84	29·5	33·41	−11·7	0·719
$KClO_4$	41·99	33·2	33·96	−2·1	0·776
$RbClO_4$	42·59	34·5	34·06	+1·5	0·788
$CsClO_4$	43·59	35·9	34·24	+5·0	0·807

---

[6] Fuoss and Accascina, *op. cit.*, ref. 4, pp. 107 *et seq.*

[7] Robinson and Stokes, " Electrolyte Solutions," 2nd edn., Butterworths, London, 1959, p. 408.

[8] Sears, Wilford, and Dawson, *J. Electrochem. Soc.*, 1956, **103**, 634.

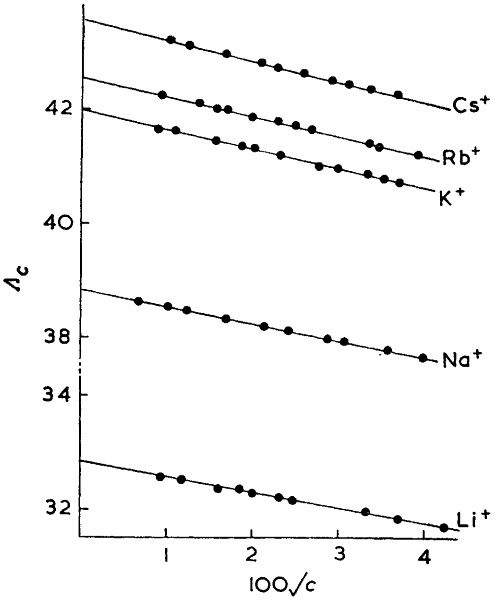

FIG. 2. *Equivalent conductances Λ_c (cm.^{2} ohm^{-1} g.-equiv.$^{-1}$) of some alkali-metal perchlorates in ethylene carbonate at* 40°.

Discussion.—It is seen that the alkali-metal perchlorates are completely ionised in ethylene carbonate solution at 40°. The deviations of the Λ_c–$\sqrt{c}$ plots from the theoretical slopes change from $-15{\cdot}1\%$ (for lithium perchlorate) to $+5{\cdot}0\%$ (for cæsium perchlorate); we may compare these values with the corresponding percentage deviations of slope of the alkali-metal perchlorates in hydrogen cyanide [9] at 18°, and in *N*-methylacetamide [10] at 40°:

	Ethylene carbonate	Hydrogen cyanide	*N*-Methyl-acetamide
$LiClO_4$	−15·1	−16·6	—
$NaClO_4$	−11·7	−14·6	+4·0
$KClO_4$	−2·1	−0·94	+8·0

The alkali-metal halides show positive deviations of slope in hydrogen cyanide solution, the deviations decreasing from lithium to cæsium.

Negative deviations appear to be associated with large ions in a medium of high dielectric constant. Inclusion of the ion-size parameter *a* in equation (2) leads to the extended form:

$$\Lambda_c = \Lambda_0 - (26{\cdot}61 + 0{\cdot}175\Lambda_0)\sqrt{c}/(1 + \beta a) \quad . \quad . \quad . \quad . \quad (6)$$

where β was defined in equation (5); the following *a* parameters would account for the observed slopes in ethylene carbonate solution, the values in parentheses being the corresponding *a*-parameters for these salts in hydrogen cyanide solution:

	$LiClO_4$	$NaClO_4$	$KClO_4$
a (Å)	16·8 (18·6)	13·6 (15·0)	3·15 (1·17)

Whilst the results are not considered to be a very reliable estimate of the sum of the radii of the (solvated) ions, yet they indicate that the Li$^+$ and Na$^+$ ions are extensively

---

[9] Coates and Taylor, *J.*, 1936, 1245.
[10] Dawson, Wilhoit, Holmes, and Sears, *J. Amer. Chem. Soc.*, 1957, **79**, 3004.

solvated in ethylene carbonate and hydrogen cyanide solutions, in agreement with the decrease in equivalent conductance along the series:

$$(Cs^+ > Rb^+)^* > K^+ > Na^+ > Li^+.$$

Unfortunately, the limited solubility of alkali-metal salts in ethylene carbonate does not permit an extended concentration range to be studied. A more reliable series of ionic radii for the alkali-metal ions in ethylene carbonate is evaluated below.

On the other hand, the positive deviation in slope, observed for cæsium perchlorate, might be accounted for by ion-association; on this basis, the value of the ion-pair dissociation constant $K_{40^\circ} = 0{\cdot}67 \pm 0{\cdot}05$ has been obtained for this electrolyte.

The Walden's rule products are similar to those of the tetra-alkylammonium halides and perchlorates in this solvent.

If we assume the tetra-alkylammonium ions to be unsolvated, and that the conductance of the perchlorate ion is independent of the cation present in ethylene carbonate solution, we can estimate the effective radii of the alkali-metal ions in this solvent. Taking the following radii (r in Å) for the tetra-alkylammonium cations:[11] NMe_4^+ 3·47; NEt_4^+ 4·00, NBu_4^+ 4·94, and interpolating the equivalent conductances Λ_0 of the alkali-metal perchlorates on the graph of Λ_0 against ionic radii for the tetra-alkylammonium perchlorates, we estimated the effective ionic radii of the alkali-metal cations, and the solvent molar volume at 40° being taken as 110 Å^3, the solvation number n was obtained:

	Li^+	Na^+	K^+	Rb^+	Cs^+
$r^+ =$	5·31	4·61	4·03	3·90	3·63
$n =$	6	4	2·5	2·2	1·7

The Walden product $\Lambda_0\eta$ has the value 0·294 for the tetraethylammonium cation in a number of different organic solvents;[12] assuming this value in ethylene carbonate, we may derive the following approximate ionic conductances in this solvent:

	Li^+	Na^+	K^+	Rb^+	Cs^+	NMe_4^+	NEt_4^+	NBu_4^+	ClO_4^-	Br^-	I^-
λ°	7	13	15	16	17	18	(15·8)	10	26	26·5	27

These values are consistently higher than the conductances in *N*-methylacetamide[10] at 40°, *viz.*,

	Na^+	K^+	NMe_4^+	NEt_4^+	NBu_4^+	ClO_4^-	I^-
λ°	8·2	8·4	12·0	11·6	7·8	16·8	14·6

This is to be expected from the higher viscosity of the solvent: $\eta_{40^\circ} = 0{\cdot}302$ poise.

We conclude that ethylene carbonate is a good ionising solvent for the alkali-metal perchlorates, and for the tetra-alkylammonium halides.

BATTERSEA COLLEGE OF TECHNOLOGY,
LONDON, S.W.11.

[*Received, April* 13*th*, 1960.]

---

* These perchlorates have not been investigated in hydrogen cyanide solution.

[11] Robinson and Stokes, ref. 7, p. 125.

[12] Uhlich and Burr, *Z. angew. Chem.*, 1928, **41**, 443.