

TABLE 1 — IONIZATION CONSTANTS AND THERMODYNAMIC FUNCTIONS OF SOME HYDROXYCOUMARIN DERIVATIVES

Compound	Temp. °K	Ionization constant	(Ionic strength = 0.1)		ΔH^* kcal/mol	ΔS e.u.
			pK	ΔG kcal/mc		
50% DIOXANE						
HMCCH ₂	288.16	pK_1	4.60	6.07	5.040 ± 0.010	-3.548 ± 0.015
	288.16		4.47	6.10		
	308.16		4.35	6.13		
	318.16		4.23	6.16		
HMCCH ₂	288.16	pK_2	10.35	13.65	8.400 ± 0.010	-18.250 ± 0.012
	298.16		10.15	13.85		
	308.16		9.95	14.03		
	318.16		9.75	14.19		
AHMCH	288.16	pK_1	8.49	11.20	8.400 ± 0.015	-9.766 ± 0.10
	298.16		8.30	11.32		
	308.16		8.10	11.42		
	318.16		7.90	11.50		
NHMCH	288.16	pK_1	5.97	7.87	6.300 ± 0.015	-5.480 ± 0.02
	298.16		5.82	7.94		
	308.16		5.67	8.00		
	318.16		5.52	8.03		
50% ETHANOL						
HMCCH ₂	288.16	pK_1	4.25	5.61	5.050 ± 0.20	-1.947 ± 0.015
	298.16		4.12	5.62		
	308.16		4.00	5.64		
	318.16		3.88	5.65		
HMCCH ₂	288.16	pK_2	10.10	13.32	6.088 ± 0.10	-25.095 ± 0.015
	298.16		9.95	13.57		
	308.16		9.81	13.83		
	318.16		9.66	14.06		
AHMCH	288.16	pK_1	8.15	10.75	6.505 ± 0.015	-14.760 ± 0.020
	298.16		8.02	10.91		
	308.16		7.85	11.07		
	318.16		7.70	11.20		

NHMCH is not soluble in ethanol.
*Average values.

ΔH was assumed constant over the range of temperatures studied and was evaluated from the slope of the plot of pK_a vs $1/T$. From this average value of ΔH , ΔS was calculated using the standard relationship

$$\Delta G = \Delta H - T\Delta S$$

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Ion-Solvent Interaction in Propylene Carbonate from Conductivity Data

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Ion-solvent interaction of some tetraalkylammonium and common ions in propylene carbonate has been studied using electrolytic conductivity data and the derived Walden product. The R_4N^+ and halide ions do not appear to interact appreciably with the solvent but Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ ions are solvated.

THE ion-solvent interaction of tetraalkylammonium and Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ ions has

been studied earlier¹ using electrolytic conductivity data in dimethylsulphoxide. Similar study has now been undertaken in propylene carbonate which has a fairly high dielectric constant² ($\epsilon_{25^\circ} = 64.92$) and like DMSO, little hydrogen bonding interaction. Literature³⁻⁵ records electrolytic conductivity in propylene carbonate only at 25°. The data at 25° are not very useful to give information regarding ion-solvent interaction. This situation calls for a more detailed investigation of conductivities of electrolytes in this solvent.

Propylene carbonate (Fluka, purum) was distilled under reduced pressure and the middle fraction collected and redistilled, the middle cut being retained again and the process was continued till the sample had a conductance of $<10^{-6}$ mho. The salts were purified by the recommended procedures⁶. The experimental procedure for measuring conductance was the same as described in our earlier publication¹. The accuracy of measurements was around $\pm 0.03\%$.

The linear plots of Λ_v versus \sqrt{C} at 40° indicate that in dilute solution, the salts investigated are completely ionized in propylene carbonate. The limiting equivalent conductivities (Λ_0) for different salts at various temperatures, obtained from the usual extrapolation procedure, are given in Table 1. From the Λ_0 values (Table 1), ionic conductivities for different ions were obtained using those for the iodide ion, reported earlier by us⁷.

From the Λ_0 values, the theoretical slope of the Λ_v versus \sqrt{C} curves at 40°, for different electrolytes,

has been obtained and compared with the corresponding experimental slope (Table 2). Dielectric constant² used for calculating theoretical slope was 64.42 and viscosity (η) 1.187 centipoise determined experimentally. There is a good agreement between the experimental and the theoretical slopes, indicating that the Debye-Hückel-Onsager theory of electrolytic conductivity is applicable to these solutions.

The Walden product, $\Lambda_0\eta^\circ$, has been usually employed to study ion-solvent interaction in solution

TABLE 2 — ONSAGER SLOPE IN PROPYLENE CARBONATE

Salt	(Temp. 40°)		Deviation (%)
	Slope		
	Theoretical	Experimental	
LiCl	43.59	41.51	-5.04
LiI	42.75	42.24	-1.02
NaI	43.14	44.50	+3.06
KI	40.37	45.51	+11.27
RbI	44.08	39.80	-1.07
CsI	44.44	42.70	-4.70
Me ₄ NI	45.03	54.10	+16.6
Et ₄ NI	44.65	46.41	+5.91
Pr ₄ NI	43.53	44.20	+1.54
Bu ₄ NBr	43.66	43.81	+0.51
Bu ₄ NI	42.90	42.00	-2.18
Pen ₄ NI	42.96	42.80	+0.37
Hex ₄ NI	40.70	42.03	+3.10
Hep ₄ NI	40.43	41.19	+1.91

TABLE 1 — LIMITING EQUIVALENT CONDUCTIVITIES OF SOME SALTS AND IONS AT DIFFERENT TEMPERATURES

Salt/Ion	Λ_0 at						
	*25°	30°	35°	40°	45°	50°	55°
LiCl	(27.50)	31.85	35.05	38.35	42.10	45.50	48.89
Li ⁺	8.89	9.68	10.55	11.52	12.89	—	—
Cl ⁻	(20.20)	22.17	24.50	26.83	29.31	—	—
LiI	—	29.95	32.55	35.64	39.15	42.12	45.46
I ⁻	18.35	20.28	22.00	24.12	26.26	—	—
Pr ₄ NBr	—	32.15	35.24	38.60	42.38	45.82	49.25
Br ⁻	18.91	20.74	22.39	24.57	26.73	—	—
NaI	27.81	30.75	33.62	36.89	40.45	43.65	47.05
Na ⁺	9.45	10.47	11.62	12.77	14.19	—	—
RbI	—	33.95	37.05	40.55	44.42	48.05	51.62
Rb ⁺	11.90	13.67	15.05	16.43	18.26	—	—
KI	29.56	33.64	36.78	40.37	44.14	47.81	51.43
K ⁺	11.17	13.36	14.78	16.25	17.88	—	—
CsI	—	34.20	37.58	41.12	45.05	48.80	52.35
Cs ⁺	12.66	13.92	15.58	17.00	18.79	—	—
Me ₄ NI	—	35.86	39.35	43.01	47.31	51.12	54.94
Me ₄ N ⁺	14.16	15.58	17.35	18.89	21.05	—	—
Et ₄ NI	—	34.78	38.13	41.79	45.84	49.56	53.29
Et ₄ N ⁺	13.18	14.50	16.13	17.67	19.58	—	—
Pr ₄ NI	—	31.69	34.85	38.15	41.91	45.28	48.67
Pr ₄ N ⁺	10.46	11.41	12.85	14.03	15.65	—	—
Bu ₄ NI	27.32	30.10	33.12	36.21	39.68	42.85	46.12
Bu ₄ N ⁺	8.98	9.82	11.13	12.09	13.42	—	—
Pen ₄ NI	—	29.68	32.55	35.70	39.25	42.40	45.50
Pen ₄ N ⁺	—	9.40	10.55	11.58	12.49	—	—
Hex ₄ NI	—	24.00	26.42	29.12	31.79	34.30	36.91
Hex ₄ N ⁺	—	3.72	4.42	4.88	5.53	—	—
Hep ₄ NI	—	23.30	25.51	28.12	30.67	33.25	35.67
Hep ₄ N ⁺	—	3.02	3.51	4.00	4.41	—	—

*From ref. 5 except those in parentheses which are from ref. 3.

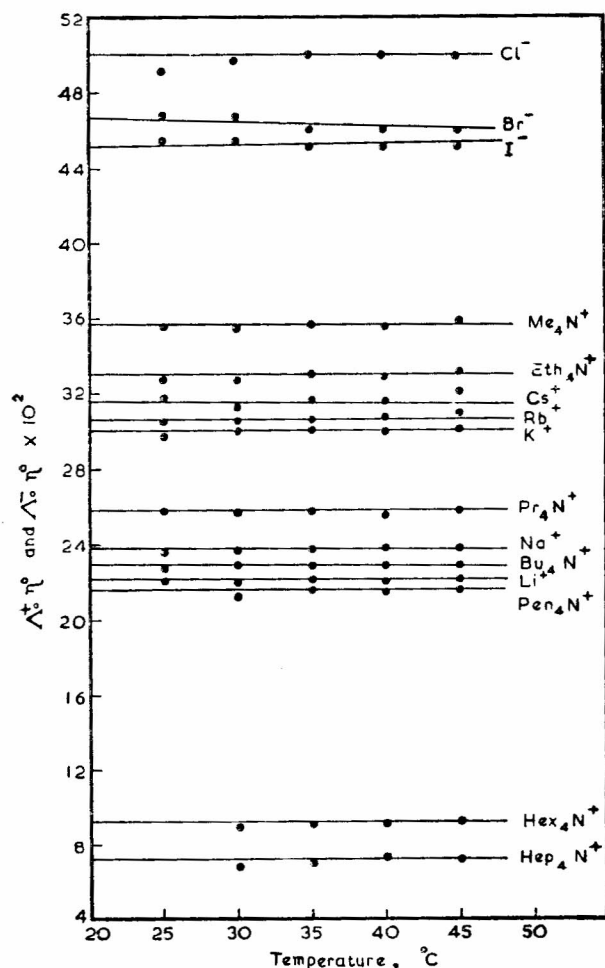


Fig. 1 — Plots of $\Lambda_0^+\eta_0^\circ$ and $\Lambda_0^+\eta_0^\circ$ versus temperature in propylene carbonate

from the conductance data. So the $\Lambda_0^+\eta_0^\circ$ values of the R_4N^+ and Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Cl^- , Br^- and I^- , at different temperatures, were obtained from the limiting ionic conductivity values given in Table 1. The values of viscosity, η_0° , of the solvent were 2.480 (ref. 3), 2.248, 2.050, 1.871 and 1.705 centipoise ($\pm 0.2\%$) at 25°, 30°, 35°, 40° and 45° respectively and were obtained, except that at 25°, in the laboratory. The plots of $\eta_0^\circ\Lambda_0^+$ and $\Lambda_0^+\eta_0^\circ$ against temperatures are given in Fig. 1 from which it may be noted that the Walden product for different ions is almost independent of temperature. This indicates that these ions neither break nor promote the structure of the solvent within the temperature range studied presently, apparently because no hydrogen bond structure is present originally in the pure solvent¹. It appears that the temperature dependence of the Walden product is not very useful in the study of ion-solvent interaction in non-hydrogen bonded solvents.

A better insight about the ion-solvent interaction can be obtained if the relative positions of the $\Lambda_0^+\eta_0^\circ$ versus temperature curves for different ions, given in Fig. 1, are compared. It may be noted that for R_4N^+ ions, the Walden product is larger, the smaller the size of the ion. This indicates that the electrostatic ion-solvent interaction, if at all, is very

weak in these cases so that the smaller the ion, the faster its movement and the larger the Walden product. The same appears to be true for Cl^- , Br^- and I^- ions as well. However, reverse is the case with the common cations which are comparatively much smaller as compared to the R_4N^+ ions. In these cases, Walden product decreases with the decrease in the crystal radius of the cation. This clearly indicates the role of electrostatic charge density on the ion in inducing strong ion-solvent interaction and solvation. The smaller the ion, the greater the electrostatic charge density on the ion, and stronger the ion-solvent dipole interaction, resulting in a larger size of the solvodynamic unit so that the size of the solvated common cations in propylene carbonate solution is in the order: $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$, in spite of the radii of these ions being in the reverse order. These common cations exhibit a similar behaviour in N-methylacetamide and N-methylformamide.

It thus appears that during migration the common cations which are fairly small are covered with a sheath of the solvent molecules. However R_4N^+ and halide ions move more or less as single and bare ions in propylene carbonate. Further, the solvation of ions is not appreciably affected by temperature within the range studied here.

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Conductance of Hydrogen Halides in Diethylene Glycol at Different Temperatures

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Conductance data on hydrogen chloride and hydrogen bromide in diethylene glycol in the temperature range 25–45°C are reported. Further, the temperature coefficient of conductance and the Walden product in this temperature range are presented and it was shown by the application of 1965 Fuoss-Onsager three-parameter equation, that no significant association of the halides occurs in this solvent.

CONDUCTANCE studies on hydrogen halides in non-aqueous solvents, especially the amphiprotic solvents, have received considerable attention¹.

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