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Ionic Conductivity in Binary Solvent Mixtures. 5. Behavior of Selected 1:1 Electrolytes in Ethylene Carbonate + Water at 25 °C

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Electrolytic conductivity measurements for a number of 1:1 electrolytes, including potassium chloride, potassium nitrate, tetramethylammonium chloride, tetraethylammonium bromide, tetraethylammonium perchlorate, hydrochloric acid, perchloric acid, methanesulfonic acid, *p*-toluenesulfonic acid, and the potassium salts of methanesulfonic acid and *p*-toluenesulfonic acid, are reported in binary aqueous mixtures containing 20, 40, 60, and 80 mass % ethylene carbonate at 25 °C. The conductivity data were analyzed by the Fuoss conductance−concentration equation to calculate the limiting molar conductivity Λ_o, association constant K_A, and cosphere diameter R. The limiting ionic conductivities of eight ions were calculated using the known values of potassium and perchlorate ions. Walden products of ions in different compositions of ethylene carbonate + water mixtures were examined with respect to solvent structural effects and ion−solvent interactions.

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1. Introduction

Among solvents classified as dipolar aprotic, ethylene carbonate[1] (1,3-dioxolan-2-one) has several advantages as a medium for proton-transfer reactions ($t_m = 36.4$ °C and $t_b = 238$ °C). Despite its inertness to chemical attack and almost complete lack of acid−base properties, it is an excellent solvent for studying the influence of solvent structure on the behavior of ions. Solute−solvent interactions of the ion−dipole type are favored by the high dipole moment ($\mu = 4.87$ D at 40 °C) of the ethylene carbonate molecule. Ethylene carbonate has a higher relative permittivity than water ($\epsilon = 89.78$ at 40 °C) and is slightly structured.[2,3] Ethylene carbonate is slightly associated[3,4] (Kirkwood g factor of 1.6 at 40 °C, Trouton's constant of 23), with a three-dimensional structure as a result of hydrogen bonding. Thus, in many ways, ethylene carbonate has similarities with water. Although the freezing point of ethylene carbonate is high, it is miscible with water up to a composition of about 90 mass % at 25 °C.

In a continuation of our earlier work,[5] this paper reports the behavior of certain univalent electrolytes, viz., potassium chloride, potassium nitrate, tetramethylammonium chloride, tetraethylammonium bromide, tetraethylammonium perchlorate, hydrochloric acid, perchloric acid, methanesulfonic acid, *p*-toluenesulfonic acid, and the potassium salts of methanesulfonic acid and *p*-toluenesulfonic acid, in 20, 40, 60, and 80 mass % ethylene carbonate + water mixtures conductometrically, including their ionic conductivities, association constants, and cosphere diameters. The variations of ionic conductivities and Walden products are discussed with respect to solvent structural effects and ion−solvent interactions.

2. Experimental Section

2.1. Chemicals. The purification and storage of ethylene carbonate and water have been described elsewhere.[5]

Table 1. Relative Permittivity ϵ, Density ρ, and Viscosity η for Ethylene Carbonate (1) + Water (2) at 25 °C

$100W_1$	ϵ^a	ρ^a (g cm^{-3})	η^b (mPa s)
0^c	78.35	0.9971	0.89
20	80.00	1.0551	1.05
40	81.53	1.1178	1.18
60	83.24	1.1842	1.36
80	86.52	1.2595	1.60
100^d	91.60	1.3360	1.85

[a] Reference 1. [b] Reference 5. [c] Reference 9. [d] At 40 °C.

Known masses of ethylene carbonate and water were mixed to obtain the desired compositions just prior to use. All solutions were prepared using a digital single-pan balance (Mettler Toledo AB204).

Perchloric acid (70% Loba) and methanesulfonic acid (S. D. Fine), being highly pure, were used without further purification.

Potassium chloride (S. D. Fine) and potassium nitrate (S. D. Fine) were recrystallized three times from water and dried at 100−110 °C before use.

Tetramethylammonium chloride (Sisco) and tetraethylammonium bromide (Fluka) were dried under vacuum before use.

Tetraethylammonium perchlorate was prepared by dissolving tetraethylammonium bromide (Fluka) in a slight excess of perchloric acid (70% Loba). The solution was carefully evaporated; the obtained solid was recrystallized twice from water and allowed to dry in a vacuum at ∼60 °C.

Hydrochloric acid stock solutions in the desired compositions of ethylene carbonate + water were prepared by bubbling through the solvent gaseous anhydrous HCl that was generated from concentrated sulfuric acid (S. D. Fine) and sodium chloride (Merck) using an all-glass apparatus.

p-Toluenesulfonic acid (S. D. Fine) was recrystallized from ether and dried under vacuum before use.

Potassium salts of methanesulfonic acid and *p*-toluenesulfonic acid were prepared by neutralizing the methane-

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Table 2. Molar Conductivity Λ at Concentration c of Various Salts in Ethylene Carbonate (1) + Water (2) at 25 °C

$(100W_1 = 20)$				$(100W_1 = 40)$			
10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})
potassium chloride							
110.07	118.87	32.00	122.94	109.52	98.24	31.84	101.03
92.64	120.10	21.11	123.98	92.18	98.82	21.00	101.58
74.52	120.98	9.96	125.13	74.15	99.30	9.91	102.43
55.66	121.70	4.29	125.76	55.39	99.90	4.27	102.81
43.98	122.46	1.44	126.54	43.76	100.48	1.43	103.08
potassium nitrate							
109.01	107.21	31.66	110.57	109.31	88.29	31.98	91.33
91.73	108.00	20.88	111.46	92.00	88.82	20.96	92.12
73.77	108.54	9.85	112.44	74.00	89.26	9.89	92.68
55.09	109.37	4.24	113.26	55.28	90.14	4.26	93.29
43.52	110.00			43.67	90.54		
tetramethylammonium chloride							
110.84	100.20	32.23	104.13	109.85	81.31	31.94	83.04
93.29	100.72	21.25	105.19	92.46	81.68	21.06	83.52
75.04	101.62	10.03	106.44	74.37	82.05	9.94	84.02
56.05	102.69	4.32	107.32	55.55	82.48	4.28	84.38
44.28	103.55			43.89	82.76		
tetraethylammonium bromide							
109.42	93.19	31.81	97.32	110.17	75.07	32.00	77.91
92.09	94.00	20.98	98.48	92.64	75.60	21.11	78.38
74.07	94.99	9.98	99.48	74.52	76.13	9.96	79.24
55.33	95.90	4.27	100.07	55.66	76.69	4.29	79.78
43.72	96.44			43.98	77.38		
$(100W_1 = 20)$				$(100W_1 = 40)$			
10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})
tetraethylammonium perchlorate							
109.63	71.46	31.88	75.44	110.84	62.91	32.23	66.08
92.27	72.18	21.02	75.59	93.29	63.18	21.25	66.99
74.22	72.95	9.92	76.89	75.04	64.01	10.03	68.24
55.44	73.86	4.28	77.86	56.05	65.00	4.32	69.05
43.80	74.31			44.28	65.57		
potassium salt of methanesulfonic acid							
110.40	92.51	32.10	95.41	109.42	73.84	31.81	77.25
92.92	93.23	21.17	95.55	92.09	74.30	20.98	78.20
74.74	93.69	9.99	96.56	74.07	74.96	9.90	79.33
55.83	94.62	4.31	97.21	55.33	76.13	4.27	80.48
44.11	94.82			43.72	76.62		
potassium salt of *p*-toluenesulfonic acid							
110.07	86.33	32.00	90.06	110.40	70.04	32.10	74.85
92.64	87.13	21.11	90.37	92.92	70.95	21.17	75.61
74.52	87.26	9.96	91.39	74.74	72.29	9.99	77.14
55.66	88.25	4.29	92.29	55.83	73.39	4.31	78.40
43.98	89.19			44.11	73.97		
$(100W_1 = 60)$				$(100W_1 = 80)$			
10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})
potassium chloride							
108.87	74.16	31.65	76.89	108.87	51.21	31.65	54.52
91.63	74.69	20.87	77.51	91.63	51.78	20.87	55.03
73.70	75.49	9.85	78.76	73.70	52.43	9.85	55.89
55.05	76.00	4.24	78.87	55.05	53.12	4.24	56.67
43.50	76.19	1.42	79.51	43.50	53.44	1.42	57.20
potassium nitrate							
112.15	70.75	32.61	72.98	109.52	52.63	31.84	54.85
94.39	71.24	21.50	73.67	92.18	52.98	21.00	55.51
75.93	71.68	10.15	74.02	74.15	53.59	9.91	55.98
56.71	72.21	4.37	74.58	55.39	54.05	4.27	56.37
44.81	72.58			43.76	54.43		
tetramethylammonium chloride							
109.63	69.53	31.88	71.31	109.20	57.16	31.75	59.00
92.27	69.94	21.02	71.60	91.90	57.47	20.94	59.33
74.22	70.24	9.92	72.19	73.93	57.92	9.88	59.82
55.44	70.56	4.28	72.54	55.22	58.17	4.26	60.27
43.80	70.86			43.63	58.50		
tetraethylammonium bromide							
110.40	61.99	32.10	64.61	110.29	50.34	32.07	53.80
92.92	62.25	21.17	65.28	92.83	50.98	21.15	54.39
74.74	63.07	9.99	65.76	74.67	51.73	9.98	55.53
55.83	63.66	4.31	66.40	55.77	52.57	4.30	56.53
44.11	64.02			44.07	53.15		

Table 2. (Continued)

(100W_1 = 60)				(100W_1 = 80)			
10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})
tetraethylammonium perchlorate							
109.42	58.80	31.81	62.97	115.24	55.61	40.46	58.36
92.09	59.31	20.98	63.51	100.64	56.06	26.76	58.99
74.07	60.25	9.90	64.95	85.54	56.48	12.67	60.27
55.33	61.32	4.27	65.64	69.93	56.94	5.47	61.17
43.72	62.06			55.42	57.76		
potassium salt of methanesulfonic acid							
110.73	58.46	32.19	60.99	109.74	42.31	31.91	45.50
93.19	58.95	21.23	61.02	92.36	43.24	21.04	46.84
74.96	59.54	10.02	62.13	74.30	43.52	9.93	47.40
56.00	60.43	4.32	62.40	55.50	44.39	4.28	48.29
44.24	60.66			43.85	45.24		
potassium salt of *p*-toluenesulfonic acid							
110.29	56.80	32.07	59.41	110.18	45.14	32.03	46.42
92.83	57.25	21.15	59.82	92.73	45.33	21.13	46.62
74.67	57.74	9.98	60.42	74.59	45.56	9.97	47.13
55.77	58.34	4.30	61.13	55.72	45.84	4.30	47.22
44.07	59.09			44.05	46.20		

Table 3. Molar Conductivity Λ at Concentration *c* of Various Acids in Ethylene Carbonate (1) +Water (2) at 25 °C

(100W_1 = 20)				(100W_1 = 40)			
10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})
hydrochloric acid							
113.24	316.07	32.93	318.75	112.37	248.59	32.67	252.93
95.31	316.35	21.71	319.38	94.57	249.89	21.54	253.59
76.67	317.28	10.25	320.53	76.07	250.33	10.17	255.06
57.27	317.54	4.42	320.99	56.82	251.36	4.38	256.10
45.25	318.15	1.48	321.40	44.90	251.99	1.47	256.31
perchloric acid							
107.23	294.01	31.18	296.89	105.15	242.84	30.57	245.79
90.24	294.74	20.56	297.96	88.50	243.33	20.16	246.22
72.59	295.15	9.70	298.44	71.19	244.07	9.52	247.41
54.22	295.92	4.18	299.33	53.17	244.75	4.10	248.01
42.84	296.34			42.01	245.27		
methanesulfonic acid							
127.23	285.53	32.10	288.72	110.18	225.39	32.03	232.69
110.40	286.48	21.17	289.46	92.73	226.82	21.13	234.97
92.92	286.57	9.99	290.01	74.59	228.76	9.97	237.11
74.74	287.52	7.16	290.27	55.72	229.98	7.14	237.47
55.83	287.76	2.88	290.85	44.02	231.57	2.87	239.11
44.11	288.31						
p-toluenesulfonic acid							
139.46	229.20	32.21	237.23	139.71	189.55	35.25	192.02
121.01	229.88	23.20	238.68	121.23	189.92	23.24	192.48
101.85	231.89	17.11	239.50	102.03	190.27	17.14	192.76
81.93	232.62	10.95	240.91	82.07	190.73	7.86	193.31
61.20	234.62	4.72	242.16	61.31	191.24	4.73	193.51
41.13	236.48	1.58	243.23	48.44	191.68		

(100W_1 = 60)				(100W_1 = 80)			
10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})	10^4c (mol dm^{-3})	Λ (S cm^2 mol^{-1})
hydrochloric acid							
108.76	176.21	31.62	181.02	109.31	74.12	31.78	77.78
91.54	177.35	20.85	181.94	92.00	75.02	20.96	78.72
73.63	177.97	9.84	183.29	74.00	75.84	9.89	79.45
55.00	178.98	4.24	184.32	55.28	76.74	4.26	80.41
43.45	180.28	1.42	184.70	43.67	77.44	1.43	80.56
perchloric acid							
119.48	176.76	34.74	180.01	104.60	82.14	30.41	84.14
100.56	177.34	22.91	180.86	88.04	82.51	20.06	84.59
80.89	177.79	10.81	181.59	70.82	83.02	9.47	85.10
60.42	178.79	4.66	182.68	52.90	83.44	4.08	85.66
47.74	179.38			41.79	83.83		
methanesulfonic acid							
110.18	148.89	32.03	152.48	111.38	71.04	32.38	72.34
92.73	149.30	21.13	153.58	93.74	71.18	21.36	72.65
74.59	149.67	9.97	154.92	75.41	71.51	10.08	72.98
55.72	151.38	7.14	155.36	56.33	71.77	7.22	73.07
44.02	152.07	2.87	156.01	44.50	72.19	2.90	73.66
p-toluenesulfonic acid							
139.96	128.08	23.29	130.31	139.21	52.89	23.16	57.89
121.45	128.36	17.17	130.64	120.79	53.56	17.08	58.29
102.22	128.67	10.99	130.76	101.67	54.39	10.93	58.88
82.22	129.01	7.87	130.98	81.78	54.90	7.83	59.32
61.42	129.48	4.74	131.12	61.09	55.82	4.71	59.58
48.52	129.67	1.58	131.46	41.00	56.79	1.58	60.27
35.31	129.91			32.16	57.31		

sulfonic and *p*-toluenesulfonic acids, respectively, with potassium hydroxide solutions. The respective products were recrystallized twice from water and then from aqueous ethanol and dried at 100−120 °C.

2.2. Standardization of Acids. A Mettler Toledo DL53 Autotitrator with automatic temperature compensation (ATC) was used for the potentiometric titration of hydrochloric and perchloric acids against standardized sodium hydroxide to obtain the exact concentrations of the respective stock solutions prepared in various compositions (viz., 20, 40, 60, and 80 mass %) of ethylene carbonate + water. The probe used was a glass electrode with an inbuilt calomel reference electrode (DG 111-SC).

2.3. Conductivity Measurements. All conductivity values were measured at (25 ± 0.05) °C using a dip-type cell (cell constant 1.068 cm^{-1}) with lightly platinized electrodes. A Chemito 130 autoranging conductivity meter with automatic temperature compensation (ATC) was used for the measurements. The conductivity meter was standardized regularly using standard potassium chloride solutions. Experiments were repeated at least twice for concordant results. All molar conductivities reported have been calculated after the correction for the solvent conductivity.

3. Results and Discussion

The results of conductivity measurements were analyzed by the Fuoss conductance−concentration equation,[6] which is based on the model of coupled equilibria.

$$A^+ + B^- \rightleftharpoons (A^+ \cdots B^-) \rightleftharpoons A^+B^- \rightleftharpoons (AB)$$

where the symbol $(A^+ \cdots B^-)$ represents a solvent-separated pair, A^+B^- a contact pair, and AB a neutral molecule. The equations and notations used are the same as those used by Fuoss and described elsewhere.[7] The program "SCAN ON RHO"[6,8] was used to compute the conductivity parameters, viz., limiting molar conductivity Λ_o, association constant K_A, and cosphere diameter R. To accomplish the required calculations, input is the data set (C_j, Λ_j), the relative permittivity ϵ, the viscosity η, the total number of readings n, the temperature T, the estimated values for Λ_o, the fraction of paired ions present as contact pairs α, and instructions to cover a preselected range of R values. On the basis of the relative permeability of the solvent, the initial α value is set at 0.75, and the initial value of Λ_o is obtained from a freehand extrapolation of the Kohlrausch plot. To cover the R range, three numbers are given, viz., RST, RIN, and RND, where RST is the first value minus the increment RIN in R and RND is the terminal value. Computations are carried out over a range of R values with the help of instructions for all of the sets of data. The values of Λ_o and α are found by minimizing the standard deviation for a sequence of R values and then plotting $\sigma\% = 100\sigma/\Lambda_o$ against R; the best-fit value of R corresponds to the minimum in the $\sigma\%-R$ curve. First, a coarse scan over a fairly wide range of R is made to locate the minimum approximately; then, a fine scan around the minimum is made. Finally, at the minimum value of R, the corresponding values of Λ_o, K_A, and the remaining parameters are calculated. The physical properties of ethylene carbonate + water mixtures are given in Table 1. The molar conductivity values Λ as a function of concentration c in the four compositions of ethylene carbonate + water mixtures at 25 °C are given in Tables 2 and 3. The best-fit conductivity parameters and the other constants derived from analysis of the conductivity data corresponding to the minimum in the $\sigma\%-R$ curve, where $\sigma\%$ is the standard deviation, are presented in Table 4.

Table 4. Derived Conductivity Parameters for Various Salts and Acids in Ethylene Carbonate (1) + Water (2) at 25 °C

$100W_1$	$\Lambda_o \pm \Delta\Lambda_o$ ($S\ cm^2\ mol^{-1}$)	K_A	K_R	K_S	R (Å)	σ (%)	$\Lambda_o\eta$ ($S\ cm^2\ mol^{-1}\ Pa\ s$)
potassium chloride							
20	126.54 ± 0.14	53.33	44.93	0.23	25.2	0.19	1.329
40	103.39 ± 0.03	38.30	31.09	0.23	21.2	0.05	1.220
60	79.71 ± 0.11	77.39	63.08	0.22	27.4	0.23	1.084
80	57.29 ± 0.09	89.84	65.13	0.38	29.0	0.24	0.917
potassium nitrate							
20	113.80 ± 0.07	73.38	61.57	0.19	28.2	0.09	1.194
40	93.74 ± 0.07	50.53	40.34	0.25	24.4	0.11	1.106
60	74.84 ± 0.06	43.89	35.22	1.24	23.2	0.11	1.018
80	56.71 ± 0.04	42.06	30.50	0.38	21.8	0.11	0.907
tetramethylammonium chloride							
20	108.08 ± 0.07	64.34	50.25	0.12	25.6	0.09	1.135
40	84.73 ± 0.03	49.11	42.72	0.15	24.2	0.06	1.000
60	72.89 ± 0.04	71.09	62.19	0.14	27.8	0.08	0.991
80	60.70 ± 0.04	59.07	48.88	0.21	24.4	0.11	0.971
tetraethylammonium bromide							
20	100.87 ± 0.08	39.87	28.13	0.42	20.4	0.11	1.059
40	80.15 ± 0.05	56.80	45.18	0.26	25.6	0.10	0.946
60	66.68 ± 0.07	43.53	31.90	0.37	22.6	0.16	0.907
80	56.94 ± 0.12	77.83	53.08	0.47	27.0	0.27	0.911
tetraethylammonium perchlorate							
20	78.28 ± 0.16	59.71	43.53	0.37	24.6	0.28	0.822
40	69.71 ± 0.10	94.44	70.81	0.33	29.6	0.19	0.823
60	66.21 ± 0.09	54.09	33.50	0.62	22.8	0.19	0.900
80	61.84 ± 0.09	90.25	67.23	1.34	29.2	0.17	0.990
potassium salt of methanesulfonic acid							
0	117.86 ± 0.24	59.29	41.41	0.43	24.8	0.28	1.061
20	97.43 ± 0.14	32.48	25.59	0.27	20.4	0.21	1.023
40	81.11 ± 0.11	104.88	81.96	0.28	31.2	0.18	0.957
60	62.84 ± 0.14	49.76	38.37	0.30	24.0	0.25	0.854
80	48.76 ± 0.16	68.61	42.07	1.63	24.8	0.44	0.780
potassium salt of *p*-toluenesulfonic acid							
0	113.05 ± 0.17	89.20	67.19	0.33	28.6	0.20	1.017
20	92.76 ± 0.16	62.46	49.18	0.27	26.0	0.24	0.974
40	78.81 ± 0.20	55.20	35.30	1.56	23.2	0.34	0.930
60	61.51 ± 0.09	28.22	17.90	0.58	16.6	0.21	0.837
80	47.47 ± 0.04	55.38	47.47	0.19	25.8	0.19	0.759
hydrochloric acid							
20	322.14 ± 0.08	43.17	41.00	0.05	23.4	0.04	3.383
40	256.73 ± 0.12	67.92	62.13	0.09	28.2	0.08	3.029
60	185.07 ± 0.10	53.56	45.32	0.18	25.0	0.09	2.517
80	80.69 ± 0.23	62.76	47.73	0.32	25.8	0.47	1.291
perchloric acid							
20	299.92 ± 0.11	65.77	62.25	0.06	28.2	0.05	3.149
40	248.72 ± 0.09	49.32	45.78	0.08	24.8	0.05	2.935
60	183.44 ± 0.09	55.62	49.91	0.11	25.2	0.07	2.495
80	85.88 ± 0.06	57.38	49.37	0.16	26.2	0.10	1.374
methanesulfonic acid							
20	290.99 ± 0.11	38.58	36.20	0.07	23.7	0.07	3.055
40	240.24 ± 0.16	56.74	46.01	0.23	24.2	0.11	2.834
60	156.54 ± 0.14	81.02	70.14	0.16	29.6	0.15	2.129
80	73.66 ± 0.07	88.43	80.41	0.10	31.1	0.16	1.179
p-toluenesulfonic acid							
20	244.11 ± 0.13	45.28	37.00	0.22	21.8	0.10	2.563
40	193.94 ± 0.03	39.91	37.09	0.08	23.6	0.03	2.289
60	131.45 ± 0.04	52.50	48.73	0.08	26.2	0.06	1.974
80	60.29 ± 0.07	57.33	37.54	0.53	23.2	0.23	0.964

As is evident from Table 4, the limiting molar conductivity Λ_o for each of the systems shows a decrease from the water-rich region to the ethylene carbonate-rich region (Figures 1 and 2). This could be attributed to the preferential solvation of ions by ethylene carbonate and the increasing viscosity of the corresponding solvent systems.

Table 5 contains the estimates of the limiting ionic conductivities (λ_o) for 20, 40, 60, and 80 mass % ethylene carbonate + water solvent systems. The limiting ionic conductivities were calculated by considering the λ_o values of potassium and perchlorate ions reported earlier.[5] The

Table 5. Limiting Ionic Conductivity of Cations and Anions in Ethylene Carbonate (1) + Water (2) at 25 °C

λ_o (S cm^2 mol^{-1})	100W_1					
	0[a]	20	40	60	80	100[b]
K^{+c}	73.48	54.78	51.53	35.15	22.43	15[d]/17.18[e]
H^+	349.65	249.73	204.19	140.91	45.31	
Me_4N^+	44.90	36.32	32.86	28.33	25.84	18[d]/19.11[e]
Et_4N^+	32.60	28.09	25.18	23.68	21.28	15.8[d]/17.13[e]
$ClO_4^{-\,c}$	67.30	50.19	44.53	42.53	40.57	26[d]/24.81[e]
Cl^-	76.31	71.77	51.86	44.56	34.86	22.49[e]
Br^-	78.10	72.78	54.98	43.00	35.66	26.5[d]/25.26[e]
NO_3^-	71.42	59.02	42.21	39.70	34.28	
methanesulfonate$^{-\,f}$	44.38	42.65	29.58	27.70	26.33	
p-toluenesulfonate$^{-\,f}$	39.57	37.98	27.28	26.36	25.04	

[a] Reference 9. [b] At 40 °C. [c] Reference 5. [d] Reference 2. [e] Reference 10. [f] Data obtained from the present work.

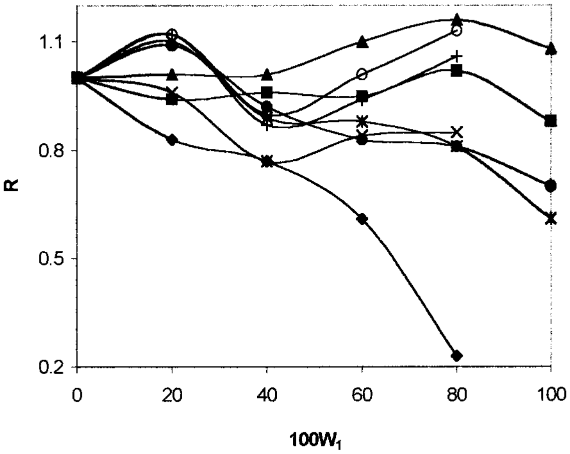

Figure 1. Variation in limiting molar conductivity of various salts with mass % ethylene carbonate: ◆, KCl; ■, KNO_3; *, Me_4NCl; ×, Et_4NBr; ▲, Et_4NClO_4; +, potassium salt of methanesulfonic acid; ●, potassium salt of *p*-toluenesulfonic acid.

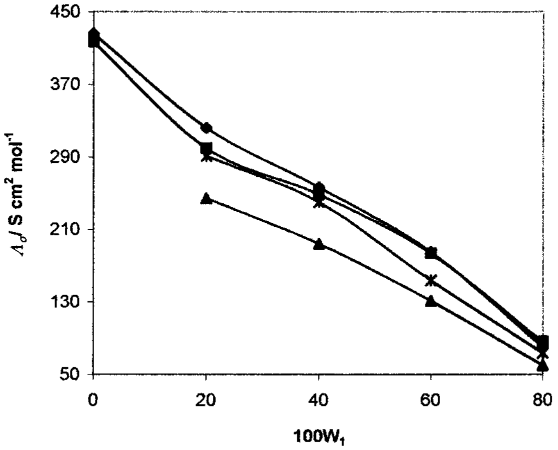

Figure 2. Variation in limiting molar conductivity of various acids with mass % ethylene carbonate: ◆, HCl; ■, $HClO_4$; *, methanesulfonic acid; ▲, *p*-toluenesulfonic acid.

ionic conductivity decreases with increasing amount of ethylene carbonate in the mixture, as expected because of the gradual increase in viscosity of the solvent in the ethylene carbonate-rich region.

The variations in the salt, acid, and ionic Walden products for each system are presented in Figures 3, 4 and 5, respectively. An increase in viscosity leads to a decrease in conductivity. This effect was formulated quantitatively by the Walden rule,[11] which states that the product $\Lambda_o\eta$ should be approximately constant for a given electrolyte/ion, irrespective of the nature of the solvent, provided that the radius of the ion remains unchanged. The Walden

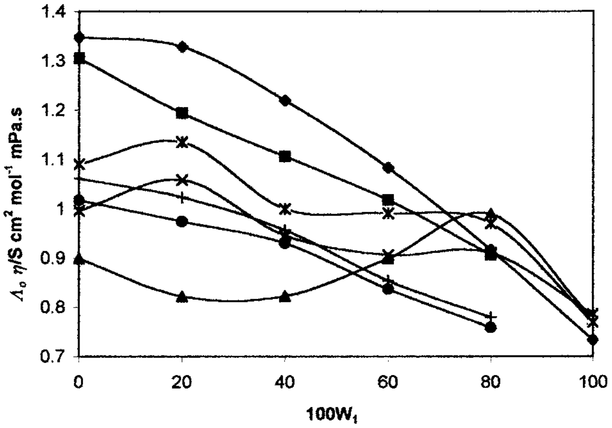

Figure 3. Variation in Walden product of various salts with mass % ethylene carbonate: ◆, KCl; ■, KNO_3; *, Me_4NCl; ×, Et_4NBr; ▲, Et_4NClO_4; +, potassium salt of methanesulfonic acid; ●, potassium salt of *p*-toluenesulfonic acid.

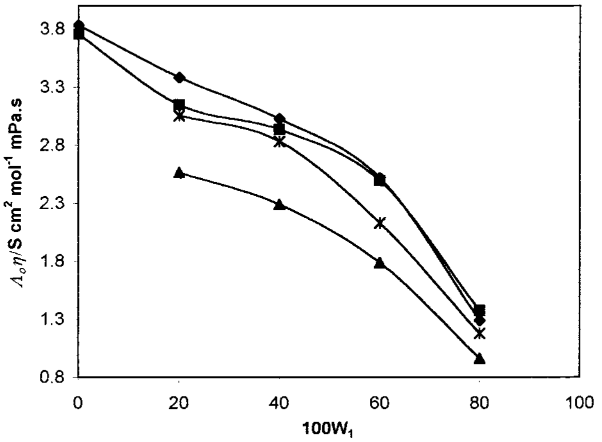

Figure 4. Variation in Walden product of various acids with mass % ethylene carbonate: ◆, HCl; ■, $HClO_4$; *, methanesulfonic acid; ▲, *p*-toluenesulfonic acid.

product is observed to be high for 0 mass % ethylene carbonate as the viscosity of the solvent system is lower. This is found to be the case in all of the systems except in the case of tetraethylammonium bromide and tetramethylammonium chloride. However, to understand ion−solvent interactions in a better way, the ionic, rather than salt or acid, Walden products should be calculated. Different workers[12−15] have explained the variation of the ionic Walden product in different solvent compositions. From Figure 5a, it is observed that the bulkier ions, tetramethylammonium and tetraethylammonium, nearly obey the Walden rule, whereas the other ions show deviations from it. This suggests that these ions do not have the same

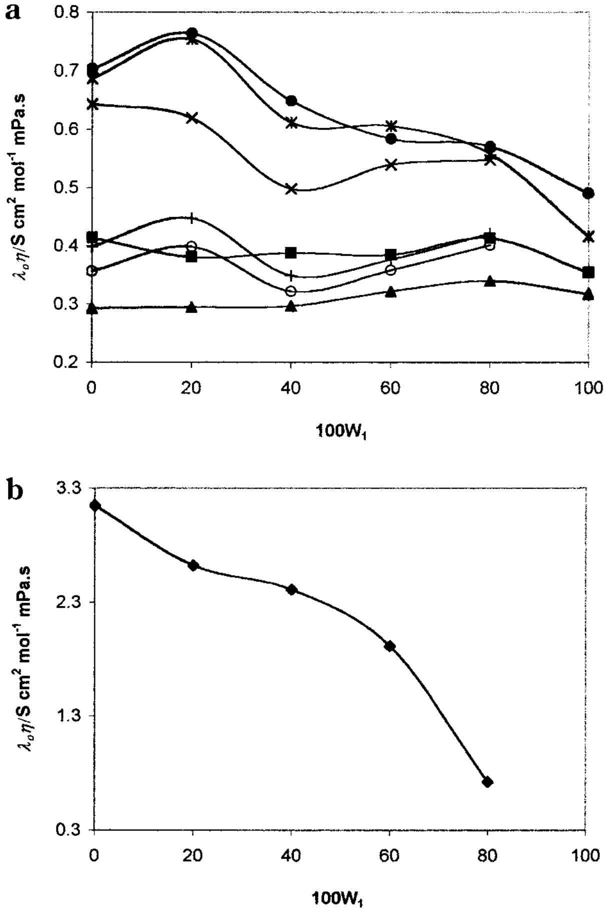

Figure 5. (a) Variation in ionic Walden product of various ions with mass % ethylene carbonate: ■, Me_4N^+; ▲, Et_4N^+; *, Cl^-; ●, Br^-; × NO_3^-; +, methanesulfonate$^-$; ○, *p*-toluenesulfonate$^-$. (b) Variation in ionic Walden product of H^+ ion (◆) with mass % ethylene carbonate.

effective radius in different solvent compositions and provides evidence for the solvation of ions in solution. As can be seen from Figure 5b, the ionic Walden product for the hydrogen ion smoothly decreases with ethylene carbonate enrichment of the solvent. This obviously suggests that the bulk viscosity does not predominantly control hydrogen ion mobility. As is known, the high mobility of hydrogen ion in water depends on the abnormal proton-transfer mechanism among associated solvent molecules. Ethylene carbonate addition to water produces a rapid decrease of proton conductivity, because of the breakup of hydrogen-bonded water molecule chains and, hence, the breakdown of the abnormal transfer mechanism.

The association constants or conductometric pairing constants K_A for all of the systems given in Table 4 are found to be generally appreciable for $K_A > 25$, which reflects a strong association in these solvent mixtures. The association constant is the product of two terms,[6] K_R and K_S. The relationship is expressed as

$$K_A = K_R(1 + K_S)$$

The first term, K_R, describes the formation and separation of solvent-separated pairs by diffusion in and out of spheres of diameter *R* around cations and can be calculated by continuum theory. The second, K_S, is the constant describing the short-range process by which contact pairs form and dissociate. Figures 6 and 7 record the plot of log K_A as a function of the reciprocal of the dielectric constant. No

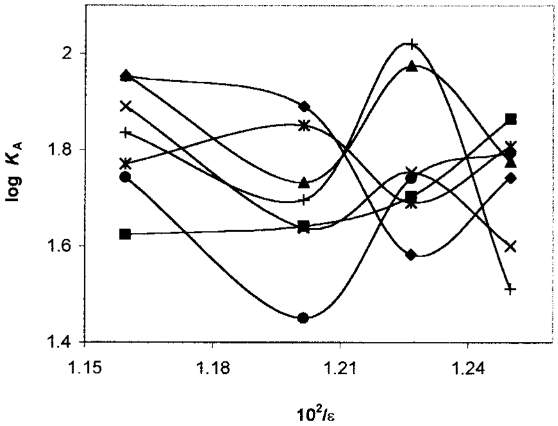

Figure 6. Plots of log K_A vs 1/ϵ for various salts: ◆, KCl; ■, KNO_3; *, Me_4NCl; ×, Et_4NBr; ▲, Et_4NClO_4; +, potassium salt of methanesulfonic acid; ●, potassium salt of *p*-toluenesulfonic acid.

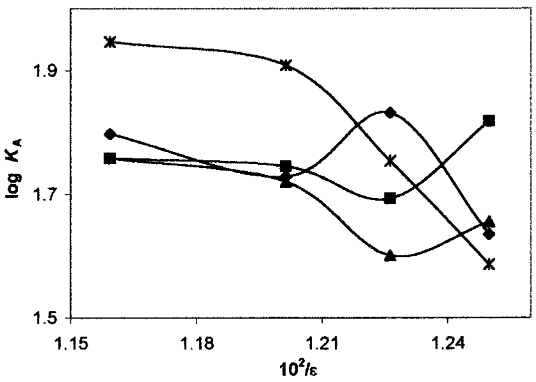

Figure 7. Plots of log K_A vs 1/ϵ for various acids: ◆, HCl; ■, $HClO_4$; *, methanesulfonic acid; ▲, *p*-toluenesulfonic acid.

linear trend could be seen for the electrolytes studied. This observation forces K_A to absorb the multiplicity of short-range system-specific parameters other than the relative permittivity of the medium such as ionic size, shape, charge distribution, dipole moment, and polarizability; possibly other details of solvent–solute interactions could also be taken into account for the rationalization of the K_A values obtained in the present work.

The cosphere diameter (*R*) values for all of the electrolytes studied in ethylene carbonate + water mixtures are given in Table 4. As *R* is the measure of the extent of influence of the ionic charge in the solvent, and consequently the ionic association, *R* values are expected to decrease with increasing relative permittivity of the solvents, as seen in the case of potassium nitrate. Except for the case of methanesulfonic acid, which shows exactly the reverse behavior to that of potassium nitrate, no such significant trend has been observed for all of the other systems. As *R* is increased, more ions are counted as paired; therefore, γ, the fraction of solute unpaired decreases. Because the best-fit conductivity parameters are reproduced equally well over a wide range of arbitrarily chosen *R* values, a comprehensive correlation of the cosphere diameters of the respective systems could not be made in the present instance; the same has been noticed by Fuoss and several other workers.[6,16]

The ratio of the ionic Walden product (R) in each ethylene carbonate + water mixture to its value in water can be represented by

$$R = (\lambda_o\eta)_S/(\lambda_o\eta)_W$$

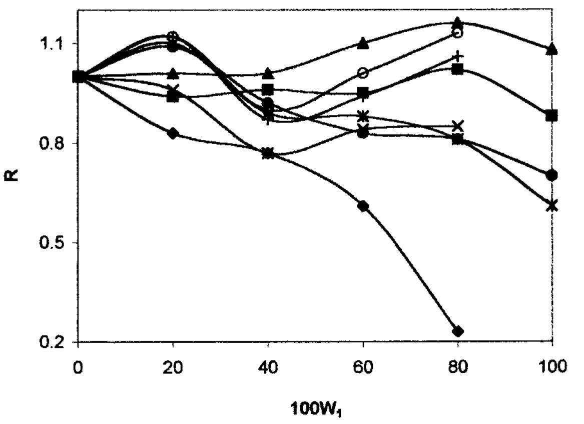

Figure 8. Ionic Walden products $\lambda_o\eta$ normalized to their values in water as a function of mass % ethylene carbonate: ◆, H^+; ■, Me_4N^+; ▲, Et_4N^+; *, Cl^-; ●, Br^-; × NO_3^-; +, methanesulfonate$^-$; ○ *p*-toluenesulfonate$^-$.

This ratio is found to be strongly dependent on the solvent composition. It is observed from Figure 8 that the R values for tetraethylammonium ion are greater than unity in all of the ethylene carbonate + water mixtures, with a maximum at 80 mass % ethylene carbonate. This behavior can be compared with that observed for several ions by Kay and Broadwater[17−19] in other aqueous mixtures. The authors have suggested that maxima in R curves can be explained by assuming that the interactions between the ions and the two solvents in these mixtures are mainly of the acid−base type such that the ionic cosphere is richer in water than the bulk mixture, known as the sorting effect. Because in the low-water-concentration region in the mixtures the viscosity decreases with increasing water content, the viscosity should be lower near the ions than in the bulk mixture. According to this hypothesis, ion−water interactions will be stronger than the ion−ethylene carbonate interactions in ethylene carbonate + water mixtures, because of the inert nature of ethylene carbonate with respect to its acid−base properties. Sorting of water in the ionic cosphere should give a local viscosity lower than the bulk viscosity, as in ethylene carbonate + water mixtures, the viscosity steadily decreases from ethylene carbonate to water. Therefore, ionic Walden products, which involve bulk viscosity, should be greater in the mixtures than in water, as observed for the tetraethylammonium ion.

Methanesulfonate ion showed a maximum and minimum at 20 and 40 mass %, respectively, whereas *p*-toluenesulfonate ion interestingly showed a maximum and a minimum at 80 and 40 mass % ethylene carbonate, respectively. R values for tetramethylammonium ion were observed to be close to unity. The R values for hydrogen, chloride, bromide, and nitrate ions were found to be less than unity in all of the solvent mixtures, except in the case of chloride and bromide, where the 20 mass % ethylene carbonate mixture gave R values greater than unity. These four ions were all found to have minimum values at 80 mass % ethylene carbonate, except for nitrate ion, which exhibits a minimum at 40 mass % ethylene carbonate. This behavior, especially for chloride and bromide ions, which is different from that observed by Kay and Broadwater for the same ions in other aqueous mixtures, is the opposite to that expected on the basis of the sorting of water near the ions.

An attempt to explain this behavior could be made by assuming that structural effects are predominant in this case. In fact, the decrease of the water structure caused by the addition of ethylene carbonate should decrease the excess mobility of structure-breaker ions. For hydrogen, chloride, and bromide ions beyond the maximum (seen at 20 mass % ethylene carbonate), further additions of cosolvent cause a reduction in R, namely, in the ionic Walden products. As the range of water-rich mixtures gets further away, R values steadily decrease from the high values typical of water solutions, approaching the lower values in the pure organic solvent. The decrease in water structure caused by the addition of the cosolvent should reduce the excess mobility shown in pure water by structure-breaker ions such as hydrogen and nitrate ions, and thus, in the mixtures, its ionic Walden product should be less than in water. Consequently, R should be less than 1, as seen experimentally.

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