Ionic Conductivity in Binary Solvent Mixtures. 1. Propylene Carbonate (20 mass %) + Ethylene Carbonate at 25 °C

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The conductance behavior of potassium iodide, potassium perchlorate, potassium methanesulfonate, potassium 2,5-dichlorobenzenesulfonate, silver perchlorate, silver picrate, tetrabutylammonium tetraphenylboride, tetrabutylammonium iodide, ferricinium picrate, and perchloric acid has been studied in a 20 mass % propylene carbonate + ethylene carbonate mixture. The conductance results have been fitted to the Fuoss (1978) conductance–concentration equation using the Fuoss computer program. Values of the limiting molar conductance (Λ_0), association constant (K_A), and cosphere diameter (R) have been obtained. The limiting ionic mobilities of the systems studied have been reported based on tetrabutylammonium tetraphenylboride as the reference electrolyte.

Introduction

Propylene carbonate (4-methyl-1,3-dioxolan-2-one or PC) is recognized as an outstanding dipolar aprotic solvent. It has a convenient liquid range (fp −49.2 °C; bp 241.7 °C) (*1*), and it dissolves a variety of organic and inorganic substances. The inertness of PC toward alkali metals drew early attention for its possible use as a solvent for high-energy electrochemical reactions (*2*). Ethylene carbonate (1,3-dioxolan-2-one or EC) is also a dipolar aprotic solvent with a high dielectric constant (89.78 at 40 °C), but relatively less attention has been directed toward it as a solvent, probably because of its high freezing point (37 °C) (*1*).

Although a considerable amount of information has been accumulated concerning the general behavior of electrolytes in PC at 25 °C (*3–5*), only a few fundamental studies have been reported in EC at other temperatures (*6*) and in the binary mixtures of these solvents (*7*). The dipole moments of PC (4.94 D) and EC (4.93 D) are similar, and a 20 mass % PC + EC mixture has a dielectric constant of 87.2 at 25 °C (*1*) which is higher than that of PC (64.4 at 25 °C). This offers a special advantage over the low dielectric media where ionic association often creates undersirable complications (*3–5, 8*).

Experimental Section

Solvents. The commercially available (99% pure, Fluka) PC and EC were distilled three times under reduced pressure. In the distillation only the 80% middle distilled product was collected. The specific conductivity of the purified solvents varied between 2×10^{-8} and 3×10^{-8} S·cm^{-1} at 25 °C for PC and 1×10^{-7} and 3×10^{-7} S·cm^{-1} at 40 °C for EC.

Both the solvents were stored in sealed containers to prevent contamination from CO_2 and water. Known masses of each solvent were mixed to form the PC + EC mixture, having 20 mass % PC.

Chemicals. Perchloric acid (Sisco), tetrabutylammonium iodide (Sisco), and ferrocene (Sisco) were of analytical reagent grade and were used without further purification.

Potassium perchlorate was prepared by dissolving potassium hydroxide in a slight excess of perchloric acid. On evaporation of this solution, crystals of hydrated potassium perchlorate were separated out, which were recrystallized twice from water and finally from aqueous ethanol and dried in a vacuum oven at 150 °C.

Potassium methanesulfonate and potassium dichlorobenzenesulfonate were prepared by neutralizing the methanesulfonic and 2,5-dichlorobenzenesulfonic acids, respectively, with potassium hydroxide solutions. The products were recrystallized twice from water and finally from aqueous ethanol and dried at 100 °C.

Potassium iodide (Loba) was recrystallized twice from aqueous ethanol and dried at 100–110 °C before use.

Silver perchlorate was prepared by dissolving freshly prepared silver oxide in a slight excess of perchloric acid; the solution was carefully evaporated, and the obtained solid was allowed to dry in vacuum at ~60 °C. The required silver oxide was freshly prepared by adding an excess of sodium hydroxide solution to a solution of silver nitrate and washing the precipitated oxide with water until the filtrate gave only a very faint pink coloration to phenolphthalein indicator.

Silver picrate was prepared by the reaction of picric acid and an excess of silver nitrate; the product obtained was recrystallized twice from ethanol and air dried.

Dicyclopentadienyliron(III) picrate (ferricinium picrate) was prepared according to the method described by Kolthoff and Thomas (*9*).

Bu_4NBPh_4 was prepared by the addition of equimolar quantities of Bu_4NI in aqueous solution to an aqueous solution of sodium tetraphenylboride. The precipitate which formed was filtered and recrystallized from a 3:1 (v/v) mixture of acetone and water. After drying under vacuum, the product had a melting point 235 °C.

Conductivity Measurements. All conductivity measurements were made at 25 ± 0.05 °C using a dip-type cell (cell constant 1.010 cm^{-1}) with a lightly platinized electrode as described earlier (*10*). All molar conductivities reported here have been calculated after correcting for the solvent conductivity.

The perchloric acid used for the preparation of the experimental solutions was standardized in the usual manner. To correct for the effect of the present water, the literature procedure (*4*) was adopted. The conductivity of a particular concentration of acid was measured at different water concentrations. The linear increase in specific conductivity was observed with the increase in water concentration. The plot of specific conductivity vs water concentration was then extrapolated to zero water concentration; the obtained value was taken as the value of the specific conductivity of that

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0021-9568/94/1739-0358$04.50/0

Table 1. Molar Conductance Λ at Concentration *c* of Various Electrolytes in the 20 mass % PC + EC Mixture at 25 °C

$10^4c/(\text{mol·dm}^{-3})$	$\Lambda/(\text{S·cm}^2\text{·mol}^{-1})$	$10^4c/(\text{mol·dm}^{-3})$	$\Lambda/(\text{S·cm}^2\text{·mol}^{-1})$
Bu_4NBPh_4		Bu_4NI	
296.0	17.17	204.0	26.16
249.8	17.70	183.3	26.50
209.9	18.26	154.0	27.26
153.7	19.27	120.1	28.37
101.6	20.00	88.8	29.60
60.6	20.80	55.9	30.84
37.7	21.51	32.9	31.80
25.6	22.01	22.4	32.51
15.6	22.42	14.7	33.19
9.2	22.84	9.2	33.45
5.3	23.08	4.6	34.32
KI		$KClO_4$	
252.0	36.95	402.8	39.27
201.9	37.15	370.3	39.83
105.9	38.17	291.7	40.65
103.8	39.23	211.3	41.82
66.7	39.74	44.8	44.18
46.1	40.46	29.1	44.83
35.2	40.96	18.4	45.07
25.1	41.40	11.1	45.38
15.8	41.83	7.5	45.51
8.6	42.69		
K-MS		K-DCBS	
112.7	28.87	88.5	24.77
99.2	29.59	82.3	25.56
85.0	30.66	70.5	26.72
69.8	31.76	56.1	27.09
54.4	33.15	43.0	28.31
40.3	34.41	30.0	29.45
26.3	36.05	17.9	30.95
16.6	37.42	11.1	32.36
9.6	39.52	7.6	33.20
5.9	40.57	5.7	33.88
Ag-Pic		$AgClO_4$	
54.7	19.66	306.5	41.56
52.5	19.89	215.2	42.11
44.2	20.98	148.8	42.80
33.6	22.36	113.7	43.48
25.8	23.63	77.3	43.88
19.9	24.81	54.7	44.10
11.3	26.41	35.5	44.49
7.4	27.89	19.9	44.60
5.4	28.77	12.0	44.66
4.3	29.21	8.0	44.73
2.5	30.45		
1.0	31.42		
Fc-Pic		Perchloric Acid	
135.6	16.46	147.1	31.13
113.7	17.08	117.2	33.19
86.5	18.19	95.4	33.59
61.5	19.20	73.9	34.36
36.5	20.22	53.1	37.55
19.3	21.70	37.5	38.30
13.1	22.24	25.1	39.98
8.0	22.87	19.3	40.52
4.7	23.36	12.1	42.41
2.0	23.89	2.3	45.00

Table 2. Derived Conductivity Parameters for Salts and Perchloric Acid in the 20 mass % PC + EC Mixture at 25 °C

compound	$\Lambda_0 \pm \Delta\Lambda_0/(\text{S·cm}^2\text{·mol}^{-1})$	K_A	K_R	K_S	R/Å	$100\sigma/\Lambda_0$
Bu_4NBPh_4	23.32 ± 0.13	28.78	6.71	3.29	11.5	0.54
Bu_4NI	34.56 ± 0.17	32.88	6.29	4.23	11.2	0.48
KI	43.35 ± 0.18	66.08	45.07	0.47	23.9	0.42
$KClO_4$	45.58 ± 0.17	7.38	2.19	2.37	8.8	0.36
KhMS	42.41 ± 0.23	115.12	27.83	3.14	20.0	0.55
K-DCBS	35.54 ± 0.19	139.43	39.17	2.56	22.7	0.52
Ag-Pic	31.88 ± 0.22	242.37	25.30	8.58	19.3	0.68
$AgClO_4$	44.95 ± 0.11	6.33	2.92	1.17	9.9	0.26
Fc-Pic	24.11 ± 0.14	84.69	17.27	3.90	16.7	0.58
perchloric acid	45.76 ± 0.45	109.60	33.81	2.24	25.5	0.97

particular acid concentration with the water correction. The values of the molar conductivity (Λ) reported in Table 1 are calculated after the water correction for each acid concentration.

Viscosity Measurements. The viscosity of the 20 mass % PC + EC mixture was determined to be 0.023 12 P using a Brookfield LVT DVII viscometer with UL adapter.

Results and Discussion

The molar conductivity Λ as a function of concentration *c* in the 20 mass % PC + EC mixture at 25 °C is given in Table 1. The conductivity results for tetrabutylammonium tetraphenylboride (Bu_4NBPh_4), tetrabutylammonium iodide (Bu_4NI), potassium iodide, potassium perchlorate, potassium dichlorobenzenesulfonate (K-DCBS), potassium methanesulfonate (K-MS), silver perchlorate, silver picrate (Ag-Pic), ferricinium picrate (Fc-Pic), and perchloric acid are analyzed by the Fuoss (1978) conductance–concentration equation (*11*). For a given set of conductivity values (c_j, Λ_j, $j = 1, ..., n$), preferably spanning a concentration range of at least a decade, the three adjustable parameters, the limiting molar conductivity (Λ_0), association constant (K_A), and cosphere diameter (R) are derived from the following three equations:

$$\Lambda = P(\Lambda_0(1 + \Delta X/X) + \Delta\Lambda_e) \qquad (1)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \qquad (2)$$

$$\ln f = -\beta\kappa/2(1 + \kappa R) \qquad (3)$$

where $\Delta X/X$ and $\Delta\Lambda_e$ are the relaxation and electrophoretic terms, respectively, and expressions used for these terms are the same as those used by Fuoss (*11*).

The program "SCAN ON RHO" was used to compute the conductance parameters as suggested by Fuoss for conductivity results in solvents of high and moderate dielectric constants. Input for the program is the set (c_j, Λ_j, $j = 1, ..., n$), n, dielectric constant (ϵ), viscosity (η), temperature (T), estimated values of α and Λ_0, and instruction to cover a preselected range of R values. The initial value of Λ_0 is obtained from the free-hand extrapolation of the Kohlrausch plot. The best fit conductivity parameters derived from the conductivity data treatment are presented in Table 2.

Bu_4NBPh_4 was used as a reference electrolyte (*12, 13*) for the determination of limiting ionic conductivities. According to the assumption of Fuoss et al. (*14*), the limiting transference number of Bu_4N^+ ion in Bu_4NBPh_4 is 0.519 and independent of the kind of solvent used, so the limiting ionic conductivity was calculated on the basis of the following relation:

$$\lambda_0(Bu_4N^+) = 0.519\Lambda_0(Bu_4NBPh_4) \qquad (4)$$

The values of the limiting ionic conductivity ($\lambda_0^{\pm}$) in 20 mass % PC + EC calculated using the above equation are given in Table 3 along with the values in PC and sulfolane obtained from the literature. From Table 3, the mobility of ions is more in the 20 mass % PC + EC mixture than in PC and sulfolane as expected, because of the increase in the dielectric constant of the medium.

The association constant (K_A) is the combination of two terms, K_R and K_S, and is expressed as

$$K_A = K_R(1 + K_S) \qquad (5)$$

K_R depends explicitly on the dielectric constant of the solvent and K_S is system specific depending on short-range ion–ion

Table 3. Limiting Ionic Conductances, λ_0, in the 20 mass % PC + EC Mixture, in PC at 25 °C, and in Sulfolane at 30 °C

	λ_0		
ion	20 mass % PC + EC mixture[a]	PC	sulfolane
Bu_4N^+	12.10	9.39[b]	2.95,[c] 2.80[b]
K^+	20.90	11.97[b]	4.26,[c] 4.05[b]
Ag^+	20.27	11.30[b]	
H^+	21.10	12.90[d]	
Fc^+	12.52		
Ph_4B^-	11.22	8.60[b]	2.73[c]
ClO_4^-	24.69	18.78[b]	6.68[b]
I^-	22.46	18.78[b]	7.22[b,c]
MS^-	21.52	15.30[d]	
$DCBS^-$	14.64	11.70[d]	
picrate$^-$	11.62	13.00[d]	5.04,[c] 5.28[b]

[a] Present work. [b] Reference 3. [c] Reference 10. [d] Reference 4.

and ion–solvent interactions. The value of K_A along with K_R and K_S obtained in the present work is reported in Table 2. The association constant values for potassium salts in the 20 mass % PC + EC mixture are observed to be in the order

$$KClO_4 < KI < K\text{-}MS < K\text{-}DCBS$$

indicating that ion–solvent electrostatic interaction is greater in the case of perchlorate ion than in the case of other organic anions (cation being common).

The values of the association constants for potassium and silver perchlorates are found to be 7.38 and 6.33, respectively, suggesting that both salts are practically completely dissociated in the 20 mass % PC + EC mixture.

The cosphere diameter (R) values for all the salts under study in the 20 mass % PC + EC mixture are also reported in Table 2. No systematic trend in R values for the salts studied has been observed. Since the best fit conductivity parameters are reproduced equally well over a wide range of arbitrarily chosen R values, a comprehensive correlation of the cosphere diameter of the studied systems could not be made in the present situation.

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Received for review August 30, 1993. Accepted January 24, 1994.®

® Abstract published in *Advance ACS Abstracts,* March 1, 1994.