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Ionic Conductivity in Binary Solvent Mixtures. 7. Behavior of Certain Univalent Acids and Alkaline Earth Metal Perchlorates in 80 Mass % Propylene Carbonate + *p*-Xylene at 25 °C

Damaraju Parvatalu and Ashwini K. Srivastava*

Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz (E), Mumbai - 400 098, Maharashtra, India

The conductance behavior of certain univalent inorganic and organic acids, viz., hydrochloric, hydrobromic, hydroiodic, perchloric, 2,5-dichlorobenzenesulfonic, *p*-toluene sulfonic, and methanesulfonic acids, and certain alkaline earth perchlorates, viz., magnesium, calcium, barium, and strontium perchlorates, has been studied in 80 mass % propylene carbonate + *p*-xylene medium. While the conductivity data of perchloric acid have been processed using the Fuoss conductance−concentration equation, the data of the remaining acids have been interpreted based on assumed equilibria involving simple dissociation, homoconjugation, and dimerization. The derived parameters such as limiting ionic conductivities, equilibrium constants, etc. are reported. The conductance behavior of alkaline earth perchlorates has been studied using the Fuoss−Edelson method; the resulting limiting ionic conductivities of metal ions and first step association constants of these divalent perchlorates are reported. The conductance behavior of salts and acids is interpreted in terms of specific interactions of ions in this medium.

Introduction

Propylene carbonate (PC) is a popular dipolar aprotic solvent extensively used in high-energy density reactions and has been a well-established nonaqueous solvent[1–4] as such or in the form of some binary mixtures containing a wide range of dielectric solvents. Although the recently reported physicochemical and thermochemical properties of the nonconventional binary solvent systems, viz., PC + toluene,[5] *p*-xylene (PX),[6] etc., indicate good promise for possible applications in electrochemical studies, some fundamental electrochemical studies are still necessary to establish these media. Our recent publication[7] on the conductance behavior of certain univalent ions in 80 mass % PC + PX medium and those reported in PC−toluene[8,9] by Ritzoulis et al. might be considered as a beginning in this direction.

The trend of the conductance behavior of a large number of organic and inorganic acids studied earlier by Kolthoff[10] and some other workers[11–17] indicated homoconjugation and dimerization in certain cases in PC, despite the fact that the relative permittivity of the solvent is reasonably high (65.5). Ideally, the presence of an inert hydrocarbon like *p*-xylene (PX) should be thought of as aggravating the situation. However, should the encouraging trend of the observed conductance behavior of several univalent electrolytes in 80 mass % PC + PX[7] and in PC + toluene[8,9] be considered as promising indicators for assessing the behavior of this medium, the behavior of certain monobasic acids and divalent ions will be expected to follow suit. Based on this observation, several monobasic acids and divalent salts were studied by conductometry in this connection. The observed conductance behavior of several acids, viz., acetic, chloroacetic, dichloroacetic, trichloroacetic, phenyl acetic, phosphonoacetic, palmetic, hippuric, oleic, 2,5-dichlorobenzoic, benzoic, *o*-toluic, nitric, picric, 1-amino naphthyl acetic, methyl butyric, acrylic, methacrylic, methyl butyric acids, and glycine, studied in this medium indicated that they are practically nonconductive, with very low values of specific conductance of about 2 $\mu S \cdot cm^{-1}$ and thus were not processed further. However, as reported in the present paper, the conductance behavior of certain univalent acids, viz., perchloric, hydrochloric, hydrobromic, hydroiodic, 2,5-dichlorobenzenesulfonic (DCBSA), *p*-toluene sulfonic (PTSA), and methanesulfonic (MSA) acids, certain alkaline earth perchlorates, viz., Mg, Ca, Ba, and Sr perchlorates, in 80 mass % propylene carbonate + *p*-xylene medium indicates that they are reasonably conductive in this medium. While the conductivity data of $HClO_4$ have been analyzed using the Fuoss (1978) equation,[18,19] those of the remaining acids have been interpreted in terms of assumed equilibria invoking dissociation, homoconjugation, and dimerization. The data with respect to the alkaline earth metal perchlorates, viz., Mg, Ca, Ba, and Sr perchlorates, have been analyzed using the Fuoss−Edelson method.[20] The resulting equilibrium constants and limiting ionic conductivities are reported. The behavior of salts and acids is explained in terms of the relative stabilities and specific interactions of ions in this medium.

Experimental

Solvents and Reagents. Propylene carbonate[2,16] and *p*-xylene[7] were purified and stored as described earlier. The middle fraction boiling in the range (80 to 81) °C (under reduced pressure) in the case of PC and (138 to 139) °C in the case of *p*-xylene, comprising about 80 %, was collected, stored in amber bottles, and sealed for subsequent use in the present investigation. Calculated masses of propylene carbonate and *p*-xylene were mixed to give 80 (± 0.05) mass % composition just prior to use. The conductivity of the freshly prepared 80 mass % propylene carbonate + *p*-xylene ranged from (1.0 to 1.2) $\mu S \cdot cm^{-1}$ at 25 (± 0.05) °C.

2,5-Dichlorobenzenesulfonic acid was prepared according to a published procedure.[21] The product was separated, recrystallized from water twice, and finally recrystallized from toluene

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* Corresponding author. Fax: +91-22-26528547. E-mail: aksrivastava@chem.mu.ac.in; akschbu@yahoo.com.

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Table 1. Molar Conductivity−Concentration of Acids in 80 Mass % PC + PX

10^4c / $mol \cdot dm^{-3}$	Λ / $S \cdot cm^2 \cdot mol^{-1}$	10^4c / $mol \cdot dm^{-3}$	Λ / $S \cdot cm^2 \cdot mol^{-1}$	10^4c / $mol \cdot dm^{-3}$	Λ / $S \cdot cm^2 \cdot mol^{-1}$
$HClO_4$		HCl		MSA	
12.18	35.80	3.28	6.08	8.69	0.71
23.91	34..80	4.63	4.98	19.98	0.70
45.97	33.78	6.00	4.83	33.17	0.70
66.59	33.24	7.78	4.00	46.25	0.70
85.75	32.59	9.55	3.52	72.11	0.69
100.36	31.88	11.70	3.12	97.56	0.68
120.34	31.28	15.92	2.81	128.85	0.68
135.97	30.98	23.81	2.41	159.52	0.68
164.62	29.91	31.25	2.30	189.62	0.67
201.64	28.82	41.35	2.23	249.15	0.67
242.74	27.75	50.55	2.08		
HBr		66.59	2.10		
1.60	18.44	80.10	2.07		
3.19	16.16	98.41	2.08		
4.76	15.27	113.00	2.05		
6.32	14.12	124.55	2.00		
7.87	13.48	DCBSA			
15.44	11.16	3.79	18.92		
29.74	9.54	5.67	17.31		
43.02	8.55	7.52	16.65		
55.38	8.05	9.36	15.50		
72.40	7.47	14.48	13.82		
87.83	7.17	23.60	11.60		
147.10	6.72	40.23	10.01		
150.59	6.14	55.69	8.90		
178.41	5.90	76.93	7.95		
HI		102.10	6.89		
28.27	24.82	113.56	6.39		
41.60	23.41	PTSA			
54.44	22.72	3.40	3.97		
66.82	21.43	4.85	3.42		
90.26	20.02	6.78	2.64		
112.12	19.11	16.58	1.80		
132.54	18.08	19.60	1.38		
151.67	17.42	48.57	1.10		
178.18	16.54	85.05	1.03		
210.00	15.53	132.42	1.02		
275.63	13.79	191.27	1.00		
326.66	13.15				

and then dried under vacuum. The melting point of the anhydrous product was found to be (105 to 106) °C. Methanesulfonic (Fluka), perchloric (70 %), hydroiodic (55 %), hydrochloric (35 %), and hydrobromic (49 %) (Merck, GR) acids were of high purity and thus were used as received. *p*-Toluenesulfonic acid (S. D. Fine) was recrystallized from ether and dried in a vacuum before use.

Calcium(II), barium(II), and strontium(II) perchlorates were prepared by dissolving their respective carbonates (Merck, GR) in a slight excess of 70 % $HClO_4$ (Merck, GR) by carefully evaporating to get the solid products, which were subsequently recrystallized thrice from conductivity grade water and dried in a vacuum at ~60 °C.[22] Magnesium(II) perchlorate (BDH), a microanalytical reagent, was used as such. All metal perchlorates were standardized as per the procedure described earlier.[23] The uncertainty in the determinations of purities of salts was 0.02 % by weight.

A Mettler Toledo AB204 digital single-pan balance (Switzerland), with 0.1 mg sensitivity, was used to weigh all the chemicals.

Procedures

Conductivity Measurements. The details of the procedure and the apparatus used for the conductivity measurements are as described previously.[24] All conductivity values were measured at 25 (± 0.05) °C using a dip-type cell (cell constant 1.063 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 solution. Experiments with freshly prepared solutions were repeated at least twice for concordant results to yield reproducibility within ± 0.1 $S \cdot cm^2 \cdot mol^{-1}$. All molar conductivities reported have been calculated after correction for the solvent conductivity.

Standardization of Acids. A Mettler Toledo DL 53 Autotitrator with automatic temperature compensation (ATC) was used for the potentiometric titration of hydrochloric, hydrobromic, hydroiodic, and perchloric acids against standard sodium hydroxide to get the exact concentration for the respective stock solutions prepared in the present medium. The probe used was a glass electrode with an inbuilt calomel reference electrode (DG111-SC).

Results and Discussion

Conductance Behavior of Acids. The observed molar conductivity−concentration data of all the acids studied are summarized in Table 1.

While all the organic acids, viz., DCBSA, PTSA, and MSA, are free from water, the inorganic acids, viz., $HClO_4$, HCl, HBr, and HI, are aqueous based. Therefore, a separate procedure using conductivity measurements as reported by Kolthoff et al.[10] has

Table 2. Derived Conductivity Parameters of Perchloric Acid in 80 Mass % PC + PX

Λ_0/S·cm^2·mol^{-1}	R	σ %	K_A	K_R	K_S
36.80 ± 0.20	2.8	0.70	19.03	0.55	33.85

been adopted to correct the effect of water on the observed conductance behavior of these acids in this medium.

Conductivity measurements on the effect of water additions, up to a concentration of 0.02 mol·dm^{-3}, were made in the case of each aqueous acid separately at three concentrations of the acid viz., ($4 \cdot 10^{-4}$, $8 \cdot 10^{-3}$, and $2 \cdot 10^{-2}$) mol·dm^{-3}. It was found that there was practically no change in the observed values. Therefore, the observed conductivity data of these aqueous acids have been reported as such without any corrections.

Among these acids, there is a linear variation of conductivity−concentration in the case of $HClO_4$, but a deviation has been observed in the case of the remaining acids and thus the approach is different for analyzing the data.

Perchloric Acid. The experimental data were processed by using the Fuoss[18,19] conductance−concentration equation, which is based on coupled equilibria

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

where the symbol ($A^+ + B^-$) represents a solvent-separated pair, A^+ B^- a contact pair, and AB a neutral molecule. The first equilibrium is diffusion controlled and denoted by K_R, which describes the formation and separation of solvent-separated pairs of diffusion in and out of spheres of diameter R around cations and can be calculated by the continuum theory. The second equilibrium denoted by K_S is the constant describing the short-range process by which contact pairs form and dissociate. The association constant (K_A) is the combination of K_R and K_S and is expressed as

$$K_A = K_R(1 + K_S) \tag{1}$$

The method of calculation and the symbols used are as suggested by Fuoss. The computer program SCAN ON RHO, as described in the previous paper,[24] was used to calculate the conductivity parameters, the molar conductivity Λ_0, the association constants K_A, and the cosphere diameter R.

The treatment of conductivity data of perchloric acid has yielded the values of Λ_0 and K_A, which are 36.80 and 19.03, respectively (Table 2). Subsequently, the value of $\lambda°_{H}{}^{+} = 15.40$ has been calculated by using the value of $\lambda°_{ClO_4}{}^{-}$ (21.40) reported earlier.[7]

Hydrochloric, Hydrobromic, Hydroiodic, 2,5-Dichlorobenzenesulfonic, p-Toluenesulfonic, and Methanesulfonic Acids. The molar conductivities Λ as a function of concentration c of all these acids are summarized in Table 1.

The observed nonlinear variation of molar conductivity vs concentration of these acids, denoted by HA for simplification, is explained on the basis of the following equilibria[16]

$$HA \rightleftharpoons H^+ + A^-; K_{HA} = (a_{H+} \cdot a_A)/a_{HA} \tag{2}$$

$$HA + A^- \rightleftharpoons HA_2{}^-; K_{HA_2{}^-} = a_{HA_2{}^-}/a_{HA}a_A{}^- \tag{3}$$

$$2HA \rightleftharpoons (HA)_2; K_d = a_{(HA)_2}/(a_{HA})^2 \tag{4}$$

where K_{HA}, $K_{HA2}{}^-$, and K_d denote the thermodynamic dissociation, the homoconjugation, and dimerization constants, respectively. If it is assumed that the activity coefficients of all the uncharged species are unity and those of ions H^+, A^-, and $HA_2{}^-$ are equal, denoted by f_i, eqs 3 and 4 can be expressed as

$$K_{HA} = [H^+][A^-]f_i^2/[HA] \tag{5}$$

$$K_{HA_2}{}^- = [HA_2{}^-]/[HA][A^-] \tag{6}$$

Applying the charge neutrality principle and rearranging the equations, the following quadratic equation can be obtained.

$$K_{HA_2}{}^-[H^+]f_i^2[A^-]^2 + K_{HA}[A^-] - K_{HA}[H^+] = 0 \tag{7}$$

If values of K_{HA} and $K_{HA_2}{}^-$ are available, eq 7 can be conveniently solved for $[A^-]$ for a particular value of $[H^+]$ which, in the present situation, can also be used to obtain f_i from the Debye−Huckel limiting law

$$-\log f_i = AZi^2\sqrt{I} \tag{8}$$

where A = 1.1332 for 80 mass % PC + PX at 25 °C which was calculated by using the relative permittivity and viscosity values of 80 mass % PC + PX, (46.1 and 1.822) mPa·s (cP) at 25 °C, respectively.[6,7]

The total acid concentration c_{HA} can be expressed using the principle of mass balance

$$c_{HA} = [A^-] + [HA] + 2[HA_2{}^-] + 2[(HA)_2] \tag{9}$$

Combining eq 9 with eqs 5 and 6, one obtains the total acid concentration in terms of $[H^+]$, $[A^-]$, and the constants K_{HA}, $K_{\ HA_2}{}^-$, and K_d

$$c_{HA} = [A^-] + [H^+][A^-]f_i^2/K_{HA} + 2K_{HA_2}{}^-[H^+][A^-]^2f_i^2/K_{HA} + 2K_d[H^+]^2[A^-]^2f_i^4/K^2{}_{HA} \tag{10}$$

For a particular set of values of K_{HA}, $K_{HA_2}{}^-$, and K_d, eq 10 can now be used to calculate the total acid concentration (c_{HA}) for a series of hypothetical values of $[H^+]$. Also, one is able to calculate the molar conductance, Λ_{HA}, for any given acid concentration, c_{HA}, by making use of the approximation

$$\Lambda_{HA} = \{\lambda^0{}_H{}^+[H^+] + \lambda^0{}_A{}^-[A^-] + \lambda^0{}_{HA_2}{}^-[HA_2{}^-]\}/c_{HA} \tag{11}$$

where $\lambda°_H{}^+$, $\lambda°_A{}^-$, and $\lambda°_{HA_2}{}^-$ are the limiting ionic conductivities.

For any particular acid, a trial and error procedure was repeated with different sets of values for K_{HA}, $K_{HA_2}{}^-$, and K_d, then a plot of log Λ_{HA} vs log c_{HA} was generated for each set of these constants over a range of assumed values of $[H^+]$ using the values for $\lambda°_H{}^+$, $\lambda°_A{}^-$, and $\lambda°_{HA_2}{}^-$, respectively. The $\lambda°_{HA_2}{}^-$ value was taken as half of the $\lambda°_A{}^-$ value as the mobility of the $HA_2{}^-$ species is reduced to half[25] on association of A^- and HA species. The simulated plots were then compared with the experimental ones, using the criterion of best fit. The specific set of values of K_{HA} solvent, $K_{HA_2}{}^-$, and K_d that yielded the most satisfactory agreement was considered to be representative of any particular acid system.

The treatment of conductivity data of the acids, viz., hydrochloric, hydrobromic, hydroiodic, 2,5-dichlorobenzenesulfonic, methanesulfonic, and p-toluene sulfonic acids, has yielded the values of equilibrium constants K_{HA}, $K_{HA_2}{}^-$, and K_d as summarized in Table 3. The observed conductivities of all the acids are plotted in the form of log Λ_c vs −log c_{HA} as shown in Figure 1 (A to F) along with the calculated values of the corresponding acids. A reasonably good agreement of the experimental and calculated plots of the results is imperative so that the proposed equilibria in the present study hold good for the treatment of the observed conductance behavior of these acids in this medium. In general, the dissociation constants of the majority of the acids studied in this medium are higher than

Table 3. Derived Conductivity Data of Various Acids in 80 Mass % PC + PX

acid	K_{HX}	$K_{HX_2^-}$	K_d	$\lambda^0_{A^-}$[15]
HCl	$8.0\cdot10^{-6}$	$5.5\cdot10^{2}$	40	21.90
HBr	$1.9\cdot10^{-4}$	$4.5\cdot10^{3}$	340	22.78
HI	$4.1\cdot10^{-3}$	30	4.4	21.99
DCBSA	$5.7\cdot10^{-4}$	$5.2\cdot10^{3}$	1390	21.22
PTSA	$2.9\cdot10^{-7}$	$7.5\cdot10^{3}$	885	20.88
MSA	$6.8\cdot10^{-8}$	$5.0\cdot10^{4}$	0.01	31.38
[a]$HClO_4$	$5.3\cdot10^{-2}$	-	-	21.40

[a] As calculated from K_A (19.03) which is reported in Table 2.

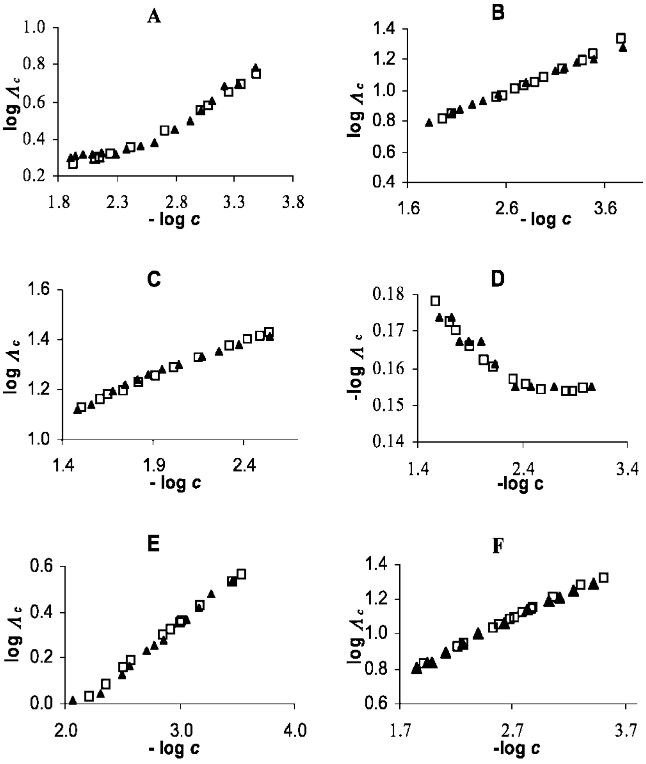

Figure 1. Plots of acids as log Λ_c vs −log *c* plots: ▲, exptl; □, calcd values. (A) HCl. (B) HBr. (C) HI. (D) Methanesulfonic acid. (E) *p*-Toluenesulfonic acid. (F) 2,5-Dichlorobenzenesulfonic acid.

those obtained in PC, which might be attributed to the relative stabilities of the conjugate anions of the acids studied in this medium. For instance, the values of K_{HA} for DCBSA and MSA are found to be $5.7\cdot10^{-4}$ and $6.8\cdot10^{-8}$, respectively, in 80 mass % PC + PX, which are higher than those in PC {DCBSA ($1.5\cdot10^{-5}$) and MSA ($5.4\cdot10^{-9}$)}[10] reported in the literature. The K_{HA} value of HCl in this medium, $8.0\cdot10^{-6}$, is quite higher than that reported in PC ($1.3\cdot10^{-11}$),[11] suggesting that the relative stability of the chloride ion in this medium is much higher, leading to a greater degree of dissociation.

The observed trend of the dissociation constants of the acids studied in this medium (Table 3) can be arranged as shown below:

$$\mathrm{MSA} < \mathrm{PTSA} < \mathrm{HCl} < \mathrm{HBr} < \mathrm{DCBSA} < \mathrm{HI} < \mathrm{HClO_4}$$

It can be inferred from the above trend that $HClO_4$ behaves as a strong electrolyte in 80 mass % PC + PX ($5.3\cdot10^{-2}$) and is almost comparable with PC ($1\cdot10^{-1.3}$).[10] Among the halo acids, the dissociation increases with a corresponding increase in the size of the conjugate anion, and hydroiodic acid appeared to be the strongest acid with a K_A of $4.1\cdot10^{-3}$. However, it is 10 times less strong than perchloric acid ($K_A = 5.3\cdot10^{-2}$) in this medium.

The trend of dissociation constants of the organic acids in 80 mass % PC + PX indicates that DCBSA is stronger ($5.7\cdot10^{-4}$) than MSA ($6.8\cdot10^{-8}$) and PTSA ($5.9\cdot10^{-7}$) which may be attributed to the relative stability of the aromatic sulfonate ions rather than the simple aliphatic sulfonate ion (MSA^-) in this medium. The very high dissociation constant observed in the case of DCBSA may be attributed to the increased inductive and resonance effects as compared to MSA and PTSA.

The observed high values of homoconjugation constants of most of the organic and inorganic acids studied in this medium (> 4500) indicate a strong tendency of ion association in 80 mass % PC + PX. Precisely, this is the reason for the observed nonlinear variation of the conductivity−concentration data of these acids. The dimerization constants do not follow any specific pattern as also observed earlier in PC by Srivastava and Mukherjee.[16] Among various acids studied, an abnormal behavior of methane sulfonic acid is clearly seen in this medium. Exactly similar behavior has been observed for this acid in PC[16] and acetonitrile[26] by Kolthoff et al. Further, this behavior might be attributed to the molecular complex formation of this acid with the solvent medium as reported in the literarature.[27]

The dimerization of DCBSA was not noticed at all in PC[10,16] and also in 20 mass % PC + EC[28] where as in 80 mass % PC + PX the value of K_d is found to be 1390. The high value of the dimerization constant may be due to the presence of PX in the medium that is known to favor ion pair formation.[29]

There is a significant rise in $\lambda^0_{H^+}$ (15.40) in the present medium as compared to that in PC (12.9)[10] indicating a substantial improvement in the mobility of the proton in 80 mass % PC + PX that can be attributed to the lowered viscosity of the medium as explained earlier.[7–9]

Conductance Behavior of Magnesium, Calcium, Barium, and Strontium Perchlorates. The best method for evaluating the conductivity data of weakly associating nonsymmetrical electrolytes is that proposed by Fuoss and Edelson,[20] as used for the treatment of conductivity data of alkaline earth metal perchlorates in PC[30] and PC + EC.[31] The same method has been used in the present work.

The method consists of evaluating limiting molar conductivity, Λ_o, and the first step association constant, k_A, of an electrolyte MX_2

$$M^{2+} + X^- \rightleftharpoons MX^+ \tag{12}$$

$$MX^+ + X^- \rightleftharpoons MX_2 \tag{13}$$

where M = Mg, Ca, Ba, and Sr and X = ClO_4.

The equilibrium leading to a neutral species MX_2 was neglected because of the presence of conducting species, MX^+. The results of the conductivity measurements of magnesium, calcium, barium, and strontium perchlorates in 80 mass % PC + PX are presented in Table 4. The corresponding Λ_c vs. $\sqrt{c}$ plots are given in Figure 2 (A to D). Fuoss−Edelson plots are given in Figure 3 (A to D). It is observed from the Fuoss−Edelson plots that the plots are nonlinear as the concentration increases, which is due to the failure of the approximation used in the treatment. The value reported for K_A of the corresponding salt is obtained from a tangent in the region of the χ value before divergence from a straight line.

The derived values of limiting molar and limiting equivalent conductivities of salts, Λ_o, and $0.5\lambda°_{M}{}^{2+}$ ions and first step association constants for Mg, Ca, Ba, and Sr perchlorates, respectively, in 80 mass % PC + PX are placed in Table 5.

The trend in the values of the $0.5\lambda°_{M}{}^{2+}$ ions for all the four divalent ions studied

Table 4. Molar Conductivity−Concentration Data of Alkaline Earth Metal Perchlorates in 80 Mass % PC + PX

10^3c / $\mathrm{mol \cdot dm^{-3}}$	Λ / $\mathrm{S \cdot cm^2 \cdot mol^{-1}}$	10^3c / $\mathrm{mol \cdot dm^{-3}}$	Λ / $\mathrm{S \cdot cm^2 \cdot mol^{-1}}$
$Mg(ClO_4)_2$		$Ca(ClO_4)_2$	
0.189	55.80	0.171	68.70
0.376	55.13	0.341	66.39
0.654	54.54	0.509	67.19
0.838	53.50	0.676	64.76
1.020	52.96	0.842	64.54
1.998	48.93	1.088	61.86
4.073	44.13	1.331	61.75
6.326	41.50	2.044	57.93
8.356	39.08	3.903	55.97
10.769	35.89	5.272	53.99
12.393	35.87	7.155	51.22
14.346	34.68	9.391	50.34
16.898	32.58	12.266	48.48
		15.411	46.56
$Ba(ClO_4)_2$		$Sr(ClO_4)_2$	
0.190	66.45	0.182	74.90
0.378	65.66	0.362	72.79
0.564	63.90	0.541	69.63
0.750	62.84	0.895	66.82
0.933	62.04	1.070	65.35
1.296	62.25	2.091	62.89
2.006	59.28	4.150	58.92
4.089	56.17	6.297	56.54
5.624	54.89	8.233	55.63
7.733	52.08	9.987	54.84
9.640	49.97	12.085	53.82
11.916	47.72	13.950	51.87
14.404	45.80	16.389	50.74
16.568	44.59	19.714	48.37

$$\mathrm{Mg}\,(7.41) < \mathrm{Ca}\,(13.67) < \mathrm{Sr}\,(16.00) < \mathrm{Ba}\,(16.27)$$

follows the sequence of their respective ionic radii. Also, it is observed that the mobilities of all the alkaline earth metal ions studied in this medium are on the higher side as compared to the values reported in PC.[30] The low value of the Mg^{2+} ion as also observed in PC[30] indicates extensive solvation of this ion in this medium. Further, it may be pertinent to correlate this observed anomaly of the limiting ionic conductivity of this ion with the conclusion drawn by Libus et al.[32] that the MX_6^{2+} type solvo-complex formation of the divalent cation is responsible for the charge transport in donor solvents.

The first step association constants of various perchlorates follow the trend

$$\mathrm{Mg} < \mathrm{Sr} < \mathrm{Ca} < \mathrm{Ba}$$

These values are found to be greater than those reported in PC[30] suggesting significant ion association in this medium. The association behavior of alkaline earth metal ions is also similar to that reported earlier in binary solvent mixtures containing PC.[31,33,34] This could be due to a strong possibility for ion pairing[35] in the present medium that contains PX, a low dielectric cosolvent.

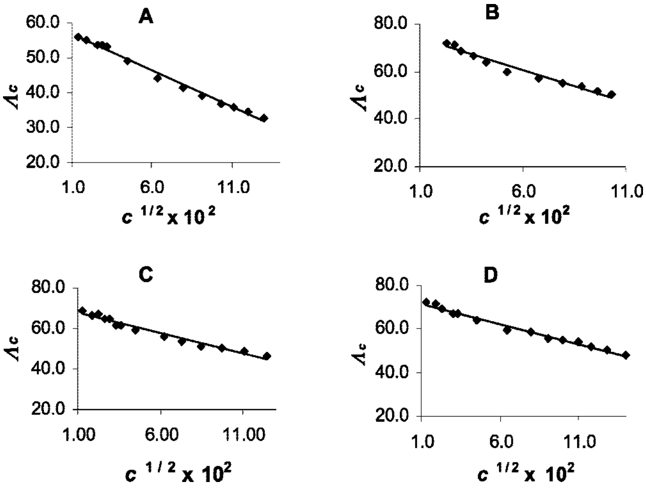

Figure 2. Plots of alkaline earth perchlorates in terms of Λ_c vs $c^{1/2} \cdot 10^2$. (A) Magnesium perchlorate. (B) Calcium perchlorate. (C) Barium perchlorate. (D) Strontium perchlorate.

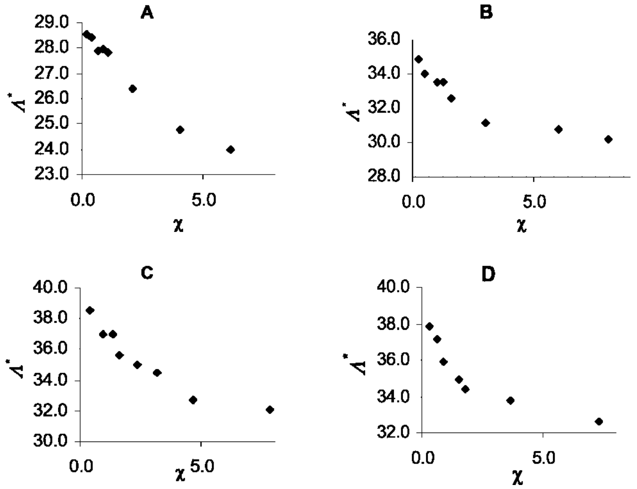

Figure 3. Fuoss−Edelson plots of alkaline earth perchlorates. (A) Magnesium perchlorate. (B) Calcium perchlorate. (C) Barium perchlorate. (D) Strontium perchlorate.

Table 5. Summary of Conductivity Results of Divalent Ions in 80 Mass % PC + PX

ion	Λ_0 ($MClO_4$) ($\mathrm{S \cdot cm^2 \cdot mol^{-1}}$)	k_A	$0.5\lambda^0{}_{M}{}^{2+}$ ($\mathrm{S \cdot cm^2 \cdot mol^{-1}}$)
Mg^{2+}	28.81	31.63	7.41
Ca^{2+}	35.07	45.57	13.67
Ba^{2+}	37.67	58.83	16.27
Sr^{2+}	37.40	44.20	16.00

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