Regular Article

PHYSICAL CHEMISTRY RESEARCH
Published by the
Iranian Chemical Society
www.physchemres.org
info@physchemres.org

Phys. Chem. Res., Vol. 8, No. 3, 429-455, September 2020
DOI: 10.22036/pcr.2020.222456.1740

Conductometric and Refractometric Studies of 1-Propyl-3-methylimidazolium Bromide Ionic Liquid in Water + Ethylene Carbonate Mixtures at T = (298.2, 308.2 and 318.2) K

B. Ghalami-Choobar* and T. Nosrati Fallahkar
Department of Chemistry, Faculty of Science, University of Guilan, P. O. Box: 19141, Rasht, Iran
(Received 5 March 2020, Accepted 15 April 2020)

In this work, we determined thermophysical properties, such as electrical conductivity and refractive index, for 1-propyl-3-methylimidazolium bromide, [PrMIm]Br, in ternary mixtures of [PrMIm]Br + ethylene carbonate + water at T = (298.2, 308.2 and 318.2) K and 0.1 MPa. Conductometric measurements were carried out for [PrMIm]Br ionic liquid in a solvent mixture of ethylene carbonate + water in various compositions: 10, 20 and 30 mass% of ethylene carbonate (EC) with the ionic strength ranging from 0.0029 to 0.2500 mol kg^{-1}. These data were treated by Fuoss-Onsager conductivity equation, and the values of limiting molar conductivity (Λ_0) and ion association constant (K_A) were obtained. These results were used to calculate the Walden product ($\Lambda_0\eta_0$) and the corresponding standard thermodynamic functions of ion association process including Gibbs free energy ($\Delta G°_A$), enthalpy ($\Delta H°_A$) and entropy ($\Delta S°_A$) for the system under study. In addition, refractive indices were measured for the binary and ternary mixtures of [PrMIm]Br + water + EC at T = (298.2, 308.2 and 318.2) K. The refractive index deviations (Δn_D) were calculated and the binary and ternary data of Δn_D were correlated using the Redlich-Kister and Cibulka equations, respectively. Also, the experimentally obtained refractive indices were compared to the calculated values using Lorentz-Lorenz (L-L), Dale-Gladstone (D-G), Eykman (Ek), Newton (N), Heller (H) and Edwards (Ed) mixing rules.

Keywords: Conductivity, Refractive index, 1-Propyl-3-methylimidazolium bromide, Ethylene carbonate, Fuoss Onsager equation, Walden product

INTTRODUCTION

Ionic liquids (ILs) are organic salts having melting points less than 100 °C, comprised of a large organic cation and small organic or inorganic anions [1,2]. They exhibit many unique physical and chemical properties such as nonvolatility, nonflammability, wide liquid range [3], designable physicochemical properties, excellent chemical and thermal stability [4,5], strong solubility power and good heat transfer properties [6]. Because of these characteristics, they have been widely applied in a number of fields; as suitable solvents for lithium-ion batteries [7-10], spectroscopic measurements, chromatographic stationary phases, electrophoresis [11], catalysis, synthesis and extraction processes [12]. Alkylene carbonates for example ethylene carbonate (EC), and propylene carbonate (PC) have attracted a great deal of attention in a variety of syntheses and industrial applications such as cleaning/ degreasing, paint stripping, textile dyeing, *etc.* [13]. Also, they are used as a safe solvent substitute in agriculture, and as a carrier solvent in therapeutic and cosmetic preparations [14]. In addition, the electrochemical stability and the high dielectric constant of organic carbonates made them efficient co-solvent in energy storage applications and lithium-ion batteries [14,15-17]. Nevertheless, organic solvents are flammable, and most of the ILs exhibit high

*Corresponding author. E-mail: B-Ghalami@guilan.ac.ir

viscosity limiting their applications in electrochemical industry. It has been reported that the use of ionic liquids in combination with a small amount of carbonate solvents; *e. g.*, PC, EC and DMC, has the ability to overcome these limiting factors [9,18-22]. Since electrolyte mixtures of ionic liquids with molecular solvents can combine low flammability with high conductivity [23], there is an immense need for determination and generation of thermodynamic and transport data of such solutions.

Recently, mixtures of ionic liquids and different carbonate solvents have been studied based on viscosity, density and conductivity. Zhang *et al.* [24] studied the temperature and concentration dependence on electrical conductivity of N-alkylpyridinium bis (trifluoromethyl-sulfonyl) imide ([BuPy][Tf_2N] and [HePy][Tf_2N]) in acetonitrile (AN)/propylene carbonate (PC). Experimental data were correlated using empirical Casteel-Amis (CA) and Vogel-Tamman-Fulcher (VTF) equations. The results showed that the electrical conductivity was decreased with the extension of the alkyl side chain of the cation. Density, viscosity, conductivity and excess properties of pyrrolidinium nitrate based protic ionic liquid, [Pyrr][NO_3], in a mixture with PC were measured by Pires and coworkers [25] at a temperature range of 283.15-353.15 K. The results demonstrated that this system exhibited a non-Arrhenius behavior, but the experimental viscosity and conductivity data as a function of temperature adjusted by VTF equation. Additionally, the excess molar volume and viscosity deviation from ideality, apparent molar volumes and thermal expansion coefficients were estimated from the experimental results. Vraneš *et al.* [26] reported density, electrical conductivity and viscosity of 1-butyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl) imide + propylene carbonate binary mixtures at a temperature range of 293.15-328.15 K. The results confirmed that PC reduces the viscosity of the binary mixtures and increases its electrical conductivity. The excess molar volumes V^E, apparent and partial molar volumes, excess molar volumes at infinite dilution and the coefficient of thermal expansion were calculated from the density data measured. Redlich-Kister equation was also utilized to fit the V^E and the viscosity deviation values as a function of IL mole fraction at different temperatures. Xu *et al.* [27] performed the electrical conductivity measurements of ionic liquid 1-ethyl-3-methylimidazolium dicyanamide [EMIm][DCA] in propylene carbonate and γ-butyrolactone in a broad range of temperature from 293.15-353.15 K. The results were correlated by VTF model and Arrhenius equation. They also presented an improved equation (quasi-Arrhenius equation) to describe the temperature and IL concentration dependence of electrical conductivity. Lam *et al.* [28] investigated the binary mixture of PC with three types of ILs namely: 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF4), 1-butyl-3-methylimidazolium bis(trifluoro-methylsulfonyl)imide (BMIMTFSI) and 1-butyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Py14TFSI) using several experimental methods including conductivity and viscosity measurements, calorimetry, gas chromatography and FTIR spectroscopy. Results demonstrated that the existence of PC can reduce viscosity and increase the conductivity of pure ILs, while the thermodynamic properties of these solutions depend on the molecular structures of ILs. Fu *et al.* [29] measured the electrical conductivities of 1-butyl-3-methylimidazolium bis(trifluoromethysulfonyl)imide [BMIm][TFSI] in mixed organic solvents of PC + γ-butyrolactone (GBL) and EC + dimethyl carbonate (DMC) at various mixture ratios. The results showed a notable enhancement in ionic liquid conductivity by the organic solvents. The concentration and temperature dependence of the electrical conductivity of the solutions was described by the Casteel-Amis, VTF and the Arrhenius equations. They also investigated the IL concentration dependence of the activation energy, E_a, and the pre-exponential factor, A, in the Arrhenius equation using empirical equations.

EC (1,3-dioxolan-2-one) is a dipolar aprotic co-solvent with a large dipole moment, large dielectric constant, low volatility and also excellent solubility properties. For these reasons, it received more attention as electrolyte of lithium batteries and supercapacitors [16,30]. Among the large variety of ILs known, the imidazolium based ILs are of special interest for many research fields of chemistry, technology and electrochemical supercapacitors due to their low viscosity, high ionic conductivity, electrochemical and chemical stability [31,32].

Under the present background, in this investigation, we determined the physicochemical properties of [PrMIm]Br in aqueous solutions of ethylene carbonate by performing conductometric and refractive index measurements at T = (298.2, 308.2 and 318.2) K. The Fuoss-Onsager model was applied for correlation of conductance data to calculate the limiting molar conductivity (Λ_0) and ion association constant (K_A). These results were used to obtain the Walden product ($\Lambda_\circ\eta_\circ$) and the thermodynamic functions such as Gibbs free energy ($\Delta G°_A$), enthalpy ($\Delta H°_A$) and entropy ($\Delta S°_A$) for the process of ion pair formation. The refractive index deviations (Δn_D) were calculated and fitted to Redlich-Kister equation for binary mixtures, and to Cibulka equation for ternary mixtures. In addition, refractive indices of the investigated mixtures were predicted using Lorentz-Lorenz, Dale-Gladstone, Eykman, Newton, Heller and Edwards mixing rules and compared to the experimental data by means of the average percentage deviations (APD).

EXPERIMENTAL

Materials

The provenance, CAS number and purity in mass fraction of the used materials are given in Table 1. All of them were of analytical reagent grade and were employed without further purification.

Synthesis of the Ionic Liquid

The ionic liquid [PrMIm]Br was prepared using direct combination of N-methylimidazole and excess amount of 1-bromopropane under nitrogen in an analogous way described previously in the literature [33-38]. Briefly, N-methylimidazole was placed into a round-bottom flask equipped with a magnetic stirrer, and an excess amount of 1-bromopropane diluted with ethyl acetate was very slowly added whilst the reaction mass was vigorously stirred and cooled in an ice bath. Afterwards, the reaction mixture was allowed to warm up very slowly to room temperature. The resulting mixture was refluxed under a nitrogen atmosphere condition and an oil bath. Meanwhile the temperature was stepwise risen to 353.2 K and kept constant until the end of reaction for 72 h. After the reaction completion, the primitive product was separated from reagents and then washed several times with ethyl acetate to eliminate any unreacted starting material. The drying of the prepared ionic liquid was performed by heating to 345.2 K under high vacuum with vigorous stirring. Due to the removal of the last vestiges of moisture from the ionic liquid, the vacuum desiccation was done for at least 24 h to yield [PrMIm]Br as a clear viscose oil. The water content of ionic liquid was determined *via* Karl Fischer coulometer which was less than mass fraction 0.2%. At the end, ^{1}H NMR (Bruker Av-300) was used in combination with FT-IR (perkinElmer, Spectrum RXI) to probe the absence of any remarkable impurities (see Figs. S1 and S2 in Supporting Information). ^{1}H NMR was comparable with literature [35].

Apparatus and Procedure

Measurements of solution conductivity were made by means of a digital multimeter (Martini instrument Mi180) with fluctuations of 0.01%. The system of multimeter was equipped with a personal computer to collect data. The Mi 5200 software and Microsoft Excel software were utilized to collect and calculate data. Before and after the conductometric measurements, the calibration of conductivity meter with a cell constant of 1.361 cm^{-1} was done by an aqueous KCl (0.01 M) solution. Also, all data were always corrected with the contribution of the solvent. The samples were stirred before measurements to minimize the concentration gradients. All measurements were made in a double-walled glass vessel, and the test solutions were equilibrated at T = (298.2, 308.2 and 318.2) using a model GFL circulation water bath with an uncertainty ± 0.1 K. The preparation of the stock electrolyte solutions was performed by weighting the ionic liquid and EC using an analytical balance (A & D HR 200) with precision 0.1 mg. We also applied double-distilled water with a conductivity of less than 2.0 μs cm^{-1} to prepare the test solutions.

Refractive indices of the studied solutions were measured with a refractometer (2WAJABBE) having a measuring accuracy of ±0.0002. Calibration of the apparatus was performed with doubly distilled water before each series of measurements as described in the manual instruction. Temperature of the work solution was kept constant at T = (298.2, 308.2 and 318.2) K by employing a Model GFL circulation water bath with a temperature control accuracy of ± 0.1 K.

Table 1. Company and Purity Value of Compounds Used

Chemical used	Company	CAS registry number	Mass fraction purity
Ethylene carbonate (EC)	Merck	96-49-1	>0.99
N-methylimidazole	Merck	616-47-7	>0.99
1-Bromopropane	Merck	74-96-4	>0.99
1-Propyl-3-methylimidazolium bromide	Synthesized	-	0.98 Water content (Karl-Fisher) <0.2%
Ethyl acetate	Merck	141-78-6	>0.998

RESULTS AND DISCUSSION

Conductometric Study

Determination of limiting molar conductivity and ion association constant. The specific conductivities, κ, for the ternary system [PrMIm]Br + EC + water were measured and the molar conductivities, Λ, were calculated by the relation $\Lambda = 1000\kappa/C$, where C is the molar concentration of solutions. Before performing each series of experiments, calibration of the apparatus was controlled by binary solvent mixtures (EC + water) with known conductivity [39]. Table 2 lists the obtained values of molar conductivities Λ as a function of [PrMIm]Br molality in 10, 20 and 30% EC mass fractions in water + EC mixtures at T = (298.2, 308.2 and 318.2) K.

The plot of molar conductivity values, Λ, for [PrMIm]Br against the molal concentration, m_{IL}, monotonically decreases as shown in Figs. 1-3. The similar trends have been reported for ionic liquids in the literature [40]. This indicates that an increase in the ionic liquid concentration causes the ion association, relaxation effect between anion and cation and more aggregation of the ionic liquid in the co-solvent, and consequently the mobility of the charge carriers reduces with increasing the microscopic viscosity of the mixture [41,42]. Figures 1-3 also provide an inspection of the dependence of molar conductivity, Λ, of [PrMIm]Br on the various mass fractions of EC in the solvent mixture at a constant temperature. The molar conductivity of pure [PrMIm]Br in water was taken from the literature [43]. It can be observed that at a specified molality of [PrMIm]Br, with increasing the mass fraction% of EC in the solvent mixture, the molar conductivity, Λ, decreases. This observation can be interpreted on the basis of the preponderant solvation for ions by EC and increase in viscosity of the solvent. Subsequently, increasing viscosity leads to decrease in conductivity [44].

On the other hand, Fig. 4 shows the temperature comparison of electrical conductivity data from 298.2 to 318.2 K at wt_{EC} = 30%. A similar trend was observed for 10 and 20% EC mass fractions (see Figs. S3 and S4 in Supporting Information). As can be observed, the molar conductivities increase as the temperature increases since the mobility of free ions is higher at higher temperatures.

The values of limiting molar conductivity and association constant were obtained by an iterative solution of Fuoss-onsager equation, in the form [45]

$$\Lambda = \Lambda_{\circ} - SC^{1/2}\gamma^{1/2} + E^{'}C\gamma\ln(6E_1^{'}C\gamma) + LC\gamma - K_A C\gamma f^2 \Lambda \quad (1)$$

$$S = \alpha\Lambda_{\circ} + \beta_{\circ} \quad (2)$$

$$\alpha = 0.8204 + \frac{10^6}{(\varepsilon_r T)^{3/2}} \quad (3)$$

Table 2. Molar Conductivities (Λ) of [PrMIm]Br in Ternary Mixtures as a Function of Ionic Liquid Molality (m_{IL}) in Various Mass Fractions (EC/Mixture) at Different Temperatures and P = 0.1 MPa

m_{IL} ($mol\ kg^{-1}$)[a] T (K) = 298.2	Λ ($s\ cm^2\ mol^{-1}$)[b]	m_{IL} ($mol\ kg^{-1}$)[a] T (K) = 308.2	Λ ($s\ cm^2\ mol^{-1}$)[b]	m_{IL} ($mol\ kg^{-1}$)[a] T (K) = 318.2	Λ ($s\ cm^2\ mol^{-1}$)[b]
w/w = 10%					
0.0029	134.24	0.0029	141.85	0.0029	143.92
0.0051	132.44	0.0051	137.36	0.0051	140.29
0.0071	131.20	0.0071	135.86	0.0071	140.10
0.0093	128.68	0.0093	134.46	0.0093	139.34
0.0104	128.56	0.0104	134.18	0.0104	138.97
0.0389	122.10	0.0389	123.13	0.0389	127.61
0.0661	114.91	0.0661	120.25	0.0661	122.72
0.1092	109.65	0.1092	114.46	0.1092	115.55
0.1672	104.22	0.1672	106.97	0.1672	109.64
0.2496	97.21	0.2496	100.21	0.2496	103.33
w/w = 20%					
0.0029	121.49	0.0029	126.58	0.0029	133.27
0.0051	118.95	0.0051	124.70	0.0051	128.81
0.0071	118.74	0.0071	123.67	0.0071	127.34
0.0093	117.42	0.0093	122.59	0.0093	126.74
0.0104	117.27	0.0104	121.70	0.0104	126.90
0.0389	109.34	0.0389	113.38	0.0389	116.35
0.0661	105.93	0.0661	108.45	0.0661	112.72
0.1092	101.65	0.1092	102.96	0.1092	106.69
0.1672	96.13	0.1672	97.69	0.1672	100.63
0.2496	89.86	0.2496	92.81	0.2496	95.53
w/w = 30%					
0.0029	109.65	0.0029	116.59	0.0029	120.73
0.0051	108.84	0.0051	114.06	0.0051	118.58
0.0071	106.68	0.0071	113.73	0.0071	116.98
0.0093	106.34	0.0093	112.16	0.0093	116.74
0.0104	106.11	0.0104	111.93	0.0104	116.66
0.0389	103.20	0.0389	104.94	0.0389	107.89
0.0661	97.37	0.0661	100.89	0.0661	104.69
0.1092	93.89	0.1092	97.47	0.1092	99.19
0.1672	88.51	0.1672	91.53	0.1672	94.53
0.2496	85.53	0.2496	87.14	0.2496	89.47

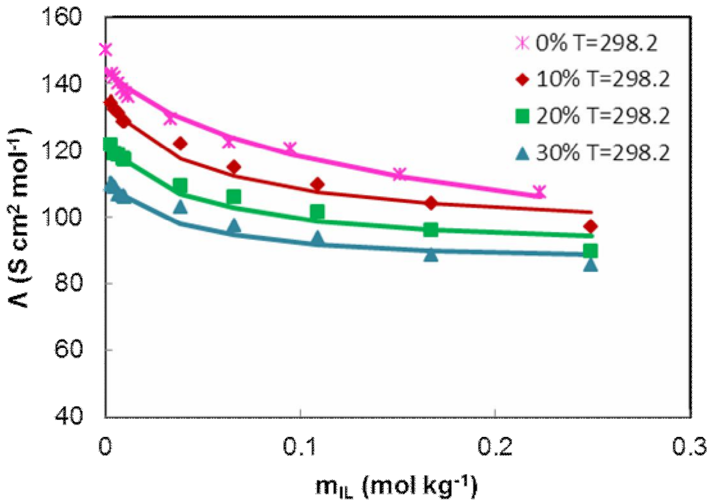

Fig. 1. Molar conductivity of [PrMIm]Br versus the molal concentration (m_{IL}) of ionic liquid in various EC + water mixed solvents containing 0, 10, 20 and 30% mass fraction of EC at T = 298.2 K and P = 0.1 MPa. Solid lines represent Fuoss-Onsager equation.

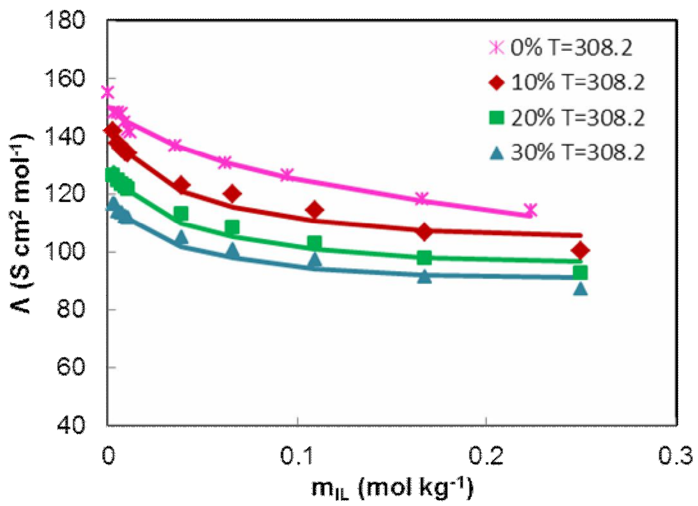

Fig. 2. Molar conductivity of [PrMIm]Br versus the molal concentration (m_{IL}) of ionic liquid in various EC + water mixed solvents containing 0, 10, 20 and 30% mass fraction of EC at T = 308.2 K and P = 0.1 MPa. Solid lines represent Fuoss-Onsager equation.

$$\beta_{\circ} = 82.50/\eta(\varepsilon_r T)^{1/2} \tag{4}$$

$$E' = E_1' \Lambda_{\circ} - E_2' \tag{5}$$

$$E_1' = 2.942 \times \frac{10^{12}}{(\varepsilon_r T)^3} \tag{6}$$

$$E_2' = 0.4333 \times \frac{10^8}{\eta(\varepsilon_r T)^2} \tag{7}$$

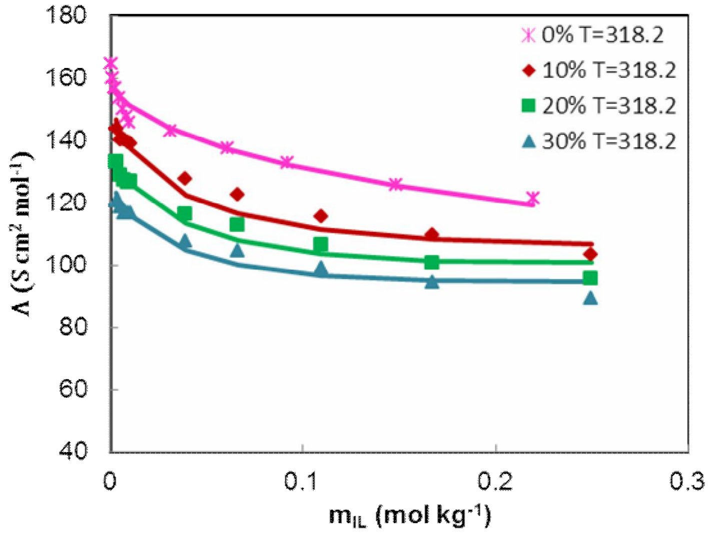

Fig. 3. Molar conductivity of [PrMIm]Br *versus* the molal concentration (m_{IL}) of ionic liquid in various EC + water mixed solvent containing 0, 10, 20 and 30% mass fraction of EC at T = 318.2 K and P = 0.1 MPa. Solid lines represent Fuoss-Onsager equation.

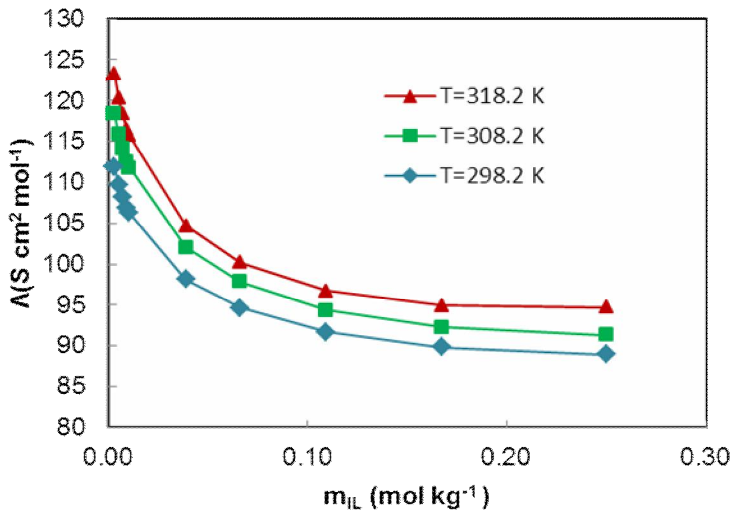

Fig. 4. Molar conductivity of [PrMIm]Br *versus* the molal concentration (m_{IL}) of ionic liquid in mass fraction 30% ($w_{EC}/w_{mixture}$).

$$L = L_1 + L_2(R) \tag{8}$$

$$L_1 = 3.202\,E_1'\Lambda_\circ - 3.420\,E_2' + \alpha\beta_\circ \tag{9}$$

$$L_2(R) = 2E_1'\Lambda_\circ h(R) + 44\frac{E_2'}{3R} - 2E'\ln R \tag{10}$$

$$h(R) = \frac{(2R^2 + 2R - 1)}{R^3} \tag{11}$$

$$f^2 = \exp[-8.405\times10^6 \frac{C^{1/2}\gamma^{1/2}}{(\varepsilon_r T)^{3/2}}] \tag{12}$$

$$1 - \gamma = K_A C\gamma^2 f^2 \tag{13}$$

In these equations C, Λ, $\Lambda_\circ$, R and K_A are molar concentration, molar conductivity, the limiting molar conductivity, distance parameter of ions and the ionic association constant, respectively. $\gamma_\pm$ indicates the mean activity coefficient of the free ions and its value was obtained using extended Debye-Hückel equation and other symbols having their usual meaning. The values of density, d_s, dielectric constant, ε_r, and viscosity, η, for EC + water mixtures were obtained or interpolated from the literature [39,46-49] and are presented in Table 3.

The calculations were performed to find the limiting molar conductivities, $\Lambda_\circ$, and ion association constants, K_A, of [PrMIm]Br in water + EC mixtures through minimizing the following objective function using the Microsoft Excel(solver) program:

$$\sigma(\Lambda) = \sqrt{\frac{\Sigma[\Lambda_{exp}-\Lambda_{cal}]^2}{N}} \tag{14}$$

where Λ_{exp} and Λ_{cal} are the experimental and calculated molar conductivities, respectively, and N is the number of data points. The values of K_A and $\Lambda_\circ$ obtained through this procedure are recorded in Table 4. It is obvious from Table 4 that the $\Lambda_\circ$ values of IL increase as the temperature is elevated from 298.2 to 318.2 K since the solvent viscosity decreases and the movement of free ions is higher with the elevation of temperature. Furthermore, the Λ_0 values show a decrease with increasing the amount of EC in the mixture at a constant temperature. This is due to the fact that the ion-solvent interaction increases at higher mass %EC, causing a reduction in the number of free ions in solution. It can be seen from Table 4 that K_A values increase with rising temperature and reducing mass fraction (%) of EC in EC + water mixed solvent at the same temperature. The increase in the K_A values with temperature suggests that the ion pair formation is an endothermic process. An increase in temperature causes ion desolvation. Desolvation promotes the extent of ion association, resulting in higher association constant. On the other hand, at a fixed temperature, the K_A values are reduced as the mass fraction (%) of EC increases because increasing the EC content of the mixed solvent causes strong ion-solvent interactions in solutions of studied system and as a result reduces the ion-pair formation.

The Walden products ($\Lambda_0\eta_0$) were also derived for the system studied from the limiting molar conductance and the viscosity of the solvent mixtures. These values are recorded in Table 4 and the dependence of Λ_0 on η^{-1} is illustrated in Fig. 5 from 298.2 to 318.2 K.

The decreasing trend of this parameter with EC concentration in the solvent composition is in accordance with the preferential solvation of electrolyte by EC. This leads to an increase in the effective radius of the ions, reduction in their mobility and Λ_0 values [50]. In addition, on increasing the temperature, a decrease of Walden product values was observed. This confirms that with increasing temperature, the decrease in solvent viscosity occurs much faster than the increase in conductivity [51]. Also, the negative temperature coefficient ($d(\Lambda_0\eta_0)/dT$) for [PrMIm]Br in EC + water solutions at T = (298.2, 308.2 and 318.2) K recommends structure breaker behavior of ionic liquid in the solvent system [52].

Thermodynamics of ion association. Using the values of association constant obtained from conductivity data, we calculated the values of thermodynamic properties of the ionic association process by the following relations [53,54]:

$$\Delta G^\circ_A(T) = -\mathrm{RTln}\, \mathrm{K_A}(T) \tag{15}$$

$\Delta G^\circ{}_A(T)$ Can be expressed with the polynomial term:

$$\Delta G^\circ_A(T) = A_0 + A_1(298.2 - \mathrm{T}) + \mathrm{A_2}(298.2\text{-}\mathrm{T})^2 \tag{16}$$

Entropy and enthalpy of ion association are defined as:

$$\Delta S^\circ_A(T) = -\left(\frac{\delta\Delta G^\circ_\mathrm{A}(T)}{\delta T}\right)_\mathrm{p} = A_1 + 2\,A_2(298.2 - \mathrm{T}) \tag{17}$$

$$\Delta H^\circ_A(T) = \Delta G^\circ_A(T) + T\Delta S^\circ_A(T) = A_0 + 298.2\mathrm{A_1} + (298.2^2 - T^2)A_2 \tag{18}$$

The values obtained for coefficients A_0, A_1 and A_2 are listed in Table S1 of the Supporting Information and the thermodynamic functions of the ion pair formation are also collected in Table 4. The data presented in Table 4 reveals that the negative values of $\Delta G°_A$ are observed at all the studied temperatures. This indicates the spontaneous and feasible nature of ion pair formation for the system. The

Table 3. Values of Average Molecular Mass, M_s, Density, d_s, Dielectric Constant, ε_r, Viscosity, η and Debye-Hückel Constants, A_Φ for EC + Water Mixtures

w (%)	M_s (g mol^{-1})	d_s (g cm^{-3})^a	ε_r^b	η (mPa s)^c	A_Φ (kg$^{1/2}$ mol$^{-1/2}$)
			T = 298.2 K		
0	18.02	0.9971	78.38	0.8900	0.3915
10	19.58	1.0263	79.22	0.9601	0.3908
20	21.43	1.0560	79.97	1.0500	0.3908
30	23.67	1.0866	80.70	1.1020	0.3911
			T = 308.2 K		
0	18.02	0.9940	74.90	0.7200	0.3985
10	19.58	1.0178	76.39	0.7710	0.3911
20	21.43	1.0516	77.97	0.8150	0.3856
30	23.67	1.0832	79.56	0.8940	0.3796
			T = 318.2 K		
0	18.02	0.9902	71.59	0.5960	0.4054
10	19.58	1.0117	73.01	0.6350	0.3979
20	21.43	1.0437	74.52	0.6630	0.3919
30	23.67	1.0757	76.04	0.7090	0.3859

Values were taken and interpolated from Refs. [46] and [47]. Values were taken from Ref. [46] and were determined using reported data in the literature [48,49]. Values were taken and interpolated from Refs. [39] and [47].

values of $\Delta G°_A$ become more negative with increasing temperature thus it can be inferred that the ion-solvent interaction is reduced with temperature rising. The values of enthalpy for association are positive over the whole temperature range studied, implying that the ion pair-forming process is endothermic. Table 4 demonstrates that the negative values of $\Delta G°_A$ are mainly due to the positive $\Delta S°_A$. $\Delta H°_A$ is much smaller than the value of $T\Delta S°_A$; therefore, for the investigated system, water + EC + [PrMIm]Br, the association process for [PrMIm]Br is governed by entropy and the driving force for the process is the tendency in the system to destruction of solvation shells, and smaller arranging during the formation of ion pair [55, 56].

Refractometric Study

The knowledge of refractive index property is useful to check purity of substances and to determine the concentration of a mixture [57]. Also, the refractive index deviation is strongly affected by the dispersion interaction upon mixing and depends on the size and shape of the molecules in a liquid mixture [58]. In this work refractive indices of ternary mixtures of EC + water + [PrMIm]Br and

Table 4. Ion Association Constant (K_A), Limiting Molar Conductivity ($\Lambda_\circ$), Thermodynamic Functions ($\Delta G°_A$, $\Delta H°_A$ and $T\Delta S°_A$) and Walden Product ($\Lambda_\circ\eta_\circ$) at Different Temperatures and P = 0.1 MPa

T (K)[a]	K_A (dm^3 mol^{-1})	$\Lambda_\circ$ (s cm^2 mol^{-1})	$\Delta G°_A$ (kJ mol^{-1})	$\Delta H°_A$ (kJ mol^{-1})	$T\Delta S°_A$ (kJ mol^{-1})	$\Lambda_\circ\eta_\circ$ (s cm^2 mPa s mol^{-1})
$w_{EC}/w_{mixture}$ = 10%						
298.2	2.02 ± 0.02	146.08 ± 1.46	-1.74	50.61	52.35	140.25
308.2	3.73 ± 0.04	153.26 ± 1.53	-3.37	42.89	46.26	118.16
318.2	6.01 ± 0.06	158.59 ± 1.58	-4.74	34.91	39.66	100.70
w_{EC}/w_{mixtur} = 20%						
298.2	1.61 ± 0.02	132.14 ± 1.32	-1.18	76.36	77.53	138.74
308.2	3.65 ± 0.04	138.90 ± 1.38	-3.32	48.61	51.93	113.20
318.2	5.58 ± 0.06	145.36 ± 1.45	-4.55	19.94	24.49	96.37
$w_{EC}/w_{mixture}$ = 30%						
298.2	1.29 ± 0.01	119.78 ± 1.20	-0.63	70.56	71.20	132.00
308.2	2.90 ± 0.03	127.18 ± 1.27	-2.73	52.99	55.72	113.70
318.2	4.98 ± 0.05	133.03 ± 1.33	-4.25	34.84	39.09	94.32

Standard uncertainties *u* are u(T) = 0.1 K, $u(p)$ = 2 kPa and $u(wt)$ = 0.0001.

their binary mixtures were measured at T = (298.2, 308.2 and 318.2) K. At first, in order to assess accuracy of the refracetometric results, we compared the measured experimental refractive indices ($n_{D,exp}$) with obtained data from literature ($n_{D,ref}$). Figure 6 presents the comparison of experimental refractive indices $n_{D,exp}$ for EC + water binary mixtures with literature values $n_{D,ref}$ as a function of the molar fraction of EC at T = 298.2 K. It is obvious that the experimental data obtained are in good agreement with the literature [59] and so are suitable for our measurements.

Tables 5 and 6 summarized the experimental values of refractive index n_D and the refractive index deviations Δn_D for binary studied mixtures at T = (298.2, 308.2 and 318.2). The Δn_D values in terms of mole fraction, x_i, for the binary systems can be produced from the following equation as:

$$\Delta n_D = n_D - \sum_{i=1}^{N} x_i n_{D,i} \tag{19}$$

where n_D and $n_{D,i}$ are the refractive indices of the mixture and component i, respectively. The refractive index deviation of the binary mixtures at each temperature was fitted to the Redlich-Kister polynomial type of degree 4 [60].

$$\Delta n_D = x_1 x_2 \sum_{s=0}^{N} A_s (x_1 - x_2)^s \tag{20}$$

In the above equation, x_1 and x_2 represent the mole fraction of components 1 and 2, A_s values are the adjustable coefficients and N = 4 is the degree of the polynomial

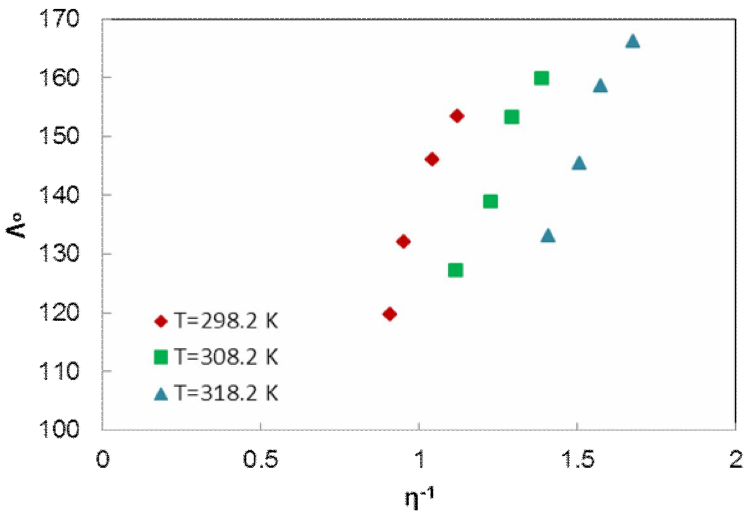

Fig. 5. The Walden plot for ([PrMIm]Br + EC + water) ternary system with different solvent compositions ($w_{Ec}/w_{mixture}$% = 0, 10, 20 and 30) at T = (298.2, 308.2 and 318.2) K and P = 0.1MPa.

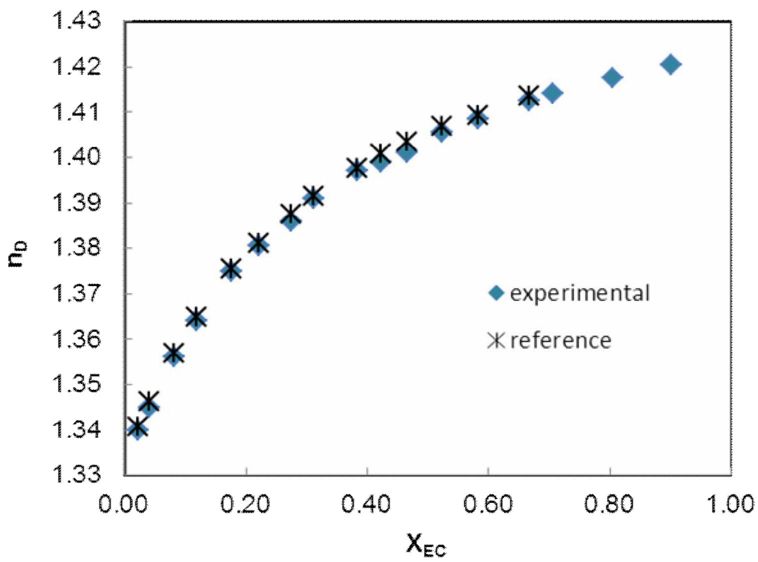

Fig. 6. Comparison of experimental and available literature refractive index values for EC + water mixture as a function of the molar fraction of EC at T = 298.2 K and P = 0.1 MPa.

expansion. Coefficients of the Redlich-Kister polynomial, A_i values were estimated using standard least-squares fit method and are listed in Table S2 of the Supporting Information. Moreover, Table 7 presents the experimental refractive indices and refractive index deviations (Δn_D) for the ternary mixtures of water + EC + [PrMIm]Br at T = (298.2, 308.2 and 318.2) K.

The Δn_D values of the ternary mixtures were correlated by the following expression:

Table 5. Experimental Refractive Indices, n_D, Refractive Index Deviations, $\Delta n_{D(exp)}$, and Refractive Index Deviations Calculated from Redlich-Kister Equation, $\Delta n_{D\,(RK)}$, for the Investigated Mixtures of Water + EC and Water + Ionic Liquid at 298.2, 308.2, 318.2 K and P = 0.1 MPa

T (K) = 298.2				T (K) = 308.2				T (K) = 318.2			
X_{H2o}	n_D[a]	Δn_D (exp)	Δn_D (RK)	X_{H2o}	n_D[a]	Δn_D (exp)	Δn_D (RK)	X_{H2o}	n_D[a]	Δn_D (exp)	Δn_D (RK)
Water + EC											
0.9778	1.3400	0.0070	0.0058	0.9777	1.3385	0.0075	0.0058	0.9777	1.3370	0.0085	0.0059
0.9593	1.3450	0.0103	0.0100	0.9591	1.3435	0.0108	0.0099	0.9590	1.3425	0.0123	0.0101
0.9186	1.3560	0.0175	0.0175	0.9183	1.3540	0.0176	0.0170	0.9181	1.3505	0.0167	0.0172
0.8810	1.3640	0.0221	0.0225	0.8807	1.3610	0.0212	0.0217	0.8803	1.3585	0.0213	0.0219
0.8239	1.3750	0.0278	0.0274	0.8234	1.3705	0.0255	0.0261	0.8228	1.3680	0.0256	0.0262
0.7789	1.3805	0.0292	0.0295	0.7785	1.3765	0.0275	0.0279	0.7779	1.3740	0.0276	0.0279
0.7258	1.3860	0.0298	0.0306	0.7250	1.3810	0.0271	0.0288	0.7243	1.3785	0.0273	0.0287
0.6887	1.3910	0.0314	0.0307	0.6880	1.3875	0.0303	0.0289	0.6871	1.3840	0.0295	0.0287
0.6159	1.3970	0.0307	0.0299	0.6159	1.3925	0.0287	0.0283	0.6147	1.3895	0.0285	0.0279
0.5766	1.3990	0.0290	0.0290	0.5753	1.3955	0.0281	0.0276	0.5744	1.3925	0.0279	0.0272
0.5337	1.4010	0.0271	0.0278	0.5337	1.3985	0.0273	0.0268	0.5315	1.3950	0.0266	0.0263
0.4758	1.4055	0.0263	0.0260	0.4739	1.4015	0.0249	0.0253	0.4730	1.3985	0.0248	0.0248
0.4172	1.4085	0.0239	0.0238	0.4172	1.4055	0.0238	0.0236	0.4172	1.4015	0.0228	0.0232
0.3321	1.4125	0.0201	0.0201	0.3321	1.4090	0.0196	0.0202	0.3321	1.4060	0.0197	0.0199
0.2943	1.4140	0.0181	0.0182	0.2943	1.4110	0.0181	0.0184	0.2943	1.4075	0.0178	0.0181
0.1962	1.4175	0.0126	0.0127	0.1962	1.4145	0.0128	0.0126	0.1962	1.4105	0.0121	0.0125
0.0993	1.4205	0.0066	0.0064	0.0993	1.4170	0.0065	0.0060	0.0993	1.4140	0.0069	0.0059
Water + [PrMIm]Br											
0.8885	1.4261	0.0712	0.0673	0.8886	1.4226	0.0696	0.0660	0.8875	1.4206	0.0697	0.0660
0.7863	1.4607	0.0839	0.0897	0.7850	1.4577	0.0825	0.0874	0.7846	1.4552	0.0820	0.0867
0.6885	1.4911	0.0932	0.0928	0.6870	1.4861	0.0898	0.0893	0.6860	1.4831	0.0884	0.0884
0.5969	1.5045	0.0871	0.0877	0.5983	1.5017	0.0863	0.0839	0.5975	1.4992	0.0853	0.0827
0.4712	1.5186	0.0742	0.0755	0.4715	1.5138	0.0712	0.0715	0.4706	1.5113	0.0699	0.0698
0.3854	1.5275	0.0647	0.0653	0.3829	1.5231	0.0614	0.0611	0.3821	1.5196	0.0590	0.0591
0.2981	1.5303	0.0487	0.0533	0.2949	1.5282	0.0476	0.0493	0.2940	1.5247	0.0450	0.0469
0.1885	1.5396	0.0345	0.0354	0.1801	1.5366	0.0313	0.0309	0.1798	1.5341	0.0296	0.0287
0.0971	1.5438	0.0191	0.0182	0.0930	1.5402	0.0162	0.0154	0.0923	1.5377	0.0142	0.0138

Standard uncertainties, u, are $u(n_D) = 0.0002$, $u(T) = 0.1$ K, $u(x) = 0.0001$ and $u(p) = 2$ kPa.

Table 6. Experimental Refractive Indices, n_D, Refractive Index Deviations, $\Delta n_{D(exp)}$, and Refractive Index Deviations Calculated from Redlich-Kister Equation, $\Delta n_{D\,(RK)}$, for the Investigated Mixtures of EC + Ionic Liquid at 298.2, 308.2, 318.2 K and P = 0.1 MPa

T (K) = 298.2				T (K) = 308.2				T (K) = 318.2			
X_{EC}	n_D [a]	Δn_D (exp)	Δn_D (RK)	X_{EC}	n_D [a]	Δn_D (exp)	Δn_D (RK)	X_{EC}	n_D [a]	Δn_D (exp)	Δn_D (RK)
EC + [PrMIm]Br											
0.8976	1.4500	0.0145	0.0140	0.8976	1.4465	0.0143	0.0141	0.8976	1.4435	0.0144	0.0140
0.8045	1.4675	0.0206	0.0209	0.8045	1.4645	0.0207	0.0211	0.8045	1.4620	0.0211	0.0212
0.7001	1.4840	0.0243	0.0244	0.7001	1.4820	0.0252	0.0248	0.7001	1.4790	0.0248	0.0252
0.6017	1.4970	0.0252	0.0252	0.6017	1.4950	0.0259	0.0257	0.6017	1.4925	0.0257	0.0261
0.4939	1.5090	0.0240	0.0240	0.4939	1.5070	0.0245	0.0247	0.4939	1.5040	0.0235	0.0249
0.4025	1.5190	0.0228	0.0218	0.4025	1.5160	0.0221	0.0224	0.4025	1.5130	0.0208	0.0222
0.3126	1.5250	0.0178	0.0187	0.3126	1.5240	0.0189	0.0189	0.3126	1.5215	0.0179	0.0182
0.2288	1.5320	0.0145	0.0147	0.2288	1.5305	0.0150	0.0146	0.2288	1.5285	0.0142	0.0136
0.1046	1.5405	0.0078	0.0074	0.1046	1.5375	0.0065	0.0068	0.1046	1.5360	0.0058	0.0058

Standard uncertainties, u, are $u(n_D) = 0.0002$, $u(T) = 0.1$ K, $u(x) = 0.0001$ and $u(p) = 2$ kPa.

Table 7. Experimental Refractive Indices (n_D), Refractive Index Deviations ($\Delta n_{D\,(exp)}$) And Refractive Index Deviations Calculated from Redlich-Kister Equation ($\Delta n_{D\,(RK)}$) for the Investigated Water + EC + Ionic Liquid Mixtures at T = (298.2, 308.2, 318.2) K and P = 0.1 MPa

Water + EC + [PrMIm]Br				
X_{H2o}	X_{IL}	n_D [a]	$\Delta n_{D\,(exp)}$	$\Delta n_{D\,(Cibulka)}$
T (K) = 298.2				
0.4513	0.0994	1.4440	0.0503	0.0487
0.2978	0.0991	1.4445	0.0368	0.0373
0.6028	0.1023	1.4410	0.0609	0.0601
0.4192	0.1494	1.4565	0.0538	0.0547
0.6222	0.1497	1.4555	0.0714	0.0720
0.2130	0.1523	1.4600	0.0379	0.0372
0.3897	0.1952	1.4695	0.0584	0.0582
0.5397	0.2036	1.4700	0.0717	0.0739
0.2578	0.2013	1.4690	0.0451	0.0462

Table 7. Continued

0.3716	0.2459	1.4820	0.0631	0.0615
0.5538	0.2537	1.4855	0.0824	0.0816
0.1867	0.2461	1.4785	0.0425	0.0423
0.3458	0.2993	1.4900	0.0621	0.0627
0.4571	0.2962	1.4930	0.0758	0.0751
0.2286	0.3058	1.4890	0.0496	0.0499
T (K) = 308.2				
0.4505	0.0995	1.4400	0.0489	0.0474
0.2971	0.0991	1.4410	0.0360	0.0363
0.6021	0.1025	1.4380	0.0602	0.0587
0.4185	0.1495	1.4530	0.0528	0.0535
0.6214	0.1499	1.4520	0.0701	0.0709
0.2124	0.1524	1.4560	0.0367	0.0362
0.3889	0.1955	1.4655	0.0569	0.0570
0.5389	0.2040	1.4665	0.0704	0.0727
0.2572	0.2015	1.4660	0.0447	0.0453
0.3709	0.2462	1.4775	0.0609	0.0606
0.5531	0.2541	1.4825	0.0814	0.0804
0.1863	0.2463	1.4750	0.0417	0.0417
0.3451	0.2997	1.4875	0.0619	0.0620
0.4563	0.2967	1.4900	0.0749	0.0740
0.2281	0.3061	1.4865	0.0495	0.0496
T (K) = 318.2				
0.4495	0.0997	1.4360	0.0475	0.0464
0.2963	0.0993	1.4375	0.0354	0.0352
0.6011	0.1028	1.4340	0.0587	0.0582
0.4175	0.1498	1.4500	0.0523	0.0523
0.6205	0.1503	1.4490	0.0694	0.0705
0.2118	0.1526	1.4525	0.0360	0.0350
0.3880	0.1958	1.4630	0.0568	0.0557
0.5380	0.2044	1.4635	0.0696	0.0720
0.2565	0.2017	1.4630	0.0442	0.0438
0.3700	0.2466	1.4745	0.0602	0.0592
0.5521	0.2547	1.4790	0.0799	0.0799
0.1857	0.2464	1.4715	0.0407	0.0404
0.3442	0.3000	1.4845	0.0610	0.0607
0.4554	0.2972	1.4865	0.0734	0.0731
0.2274	0.3063	1.4835	0.0488	0.0482

. Standard uncertainties, u, are $u(n_D)$ = 0.0002, u(T) = 0.1 K, u(x) = 0.0001 and $u(p)$ = 2 kPa.

$$\Delta n_D = \sum_{i<j} x_i x_j \sum_{s=0}^{N} A_s^{(ij)} (x_i - x_j)^s + x_1 x_2 x_3 \Delta_{123} \tag{21}$$

The expression suggested by Cibulka is used to correlate the ternary contribution term Δ_{123} [61],

$$\Delta_{123} = B_0 + B_1 x_1 + B_2 x_2 \tag{22}$$

where the B_i values are ternary solution parameters of the Cibulka equation and were calculated using a standard least-squares analysis of the data; the B_i values are recorded in Table S3 of the Supporting Information file. The standard deviation σ is defined by applying the expression

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N} (n_{exp} - n_{cal})^2}{N}} \tag{23}$$

where n_{cal}, n_{exp} and N refer to the calculated value, the measured value and the number of experimental data points, respectively. The results indicate that the n_D values have shown a decreasing tendency with increasing temperature in binary and ternary mixtures. The plots of refractive index deviations (Δn_D) as a function of x_i are displayed for EC + water and IL + water binary mixtures in Figs. 7 and 8, respectively.

These figures and the values of Δn_D in Tables 5, 6 and 7 indicated that the refractive index deviations are positive for all the solutions of this study over the entire composition range for all temperatures tested and they decrease when the temperature increases. This behavior is similar to that reported previously for [EMIm]Br + water + EC/ethanol/1-propanol [62,63]. The positive values of Δn_D arise from the strength of specific interactions such as hydrogen bonding, molecular size, shape and the polar characteristics of the mixture components [64-66]. Figure 9 represents the refractive indices for EC + water + [PrMIm]Br ternary mixtures while mole fractions of water were more than EC at the experimental temperatures.

Furthermore, we tested the validity of several predicting mixing rules to calculate the refractive indices of the binary and ternary mixtures under study. The mixing rules applied here are the equations of Lorentz-Lorenz (L-L), Gladstone-Dale (G-D), Eykman (EK), Newton (N), Heller (H) and Edwards (Ed) corresponding with Eqs. (16)-(21) [67-72]:

Lorentz-Lorenz:

$$\frac{n_D^2 - 1}{n_D^2 + 2} = \sum_{i=1}^{k} \left(\frac{n_{Di}^2 - 1}{n_{Di}^2 + 2}\right) \varphi_i \tag{24}$$

Gladstone-Dale:

$$n_D - 1 = \sum_{i=1}^{k} (n_{Di} - 1)\, \varphi_i \tag{25}$$

Eykman:

$$\frac{n_D^2 - 1}{n_D^2 + 0.4} = \sum_{i=1}^{k} \left(\frac{n_{Di}^2 - 1}{n_{Di}^2 + 0.4}\right) \varphi_i \tag{26}$$

Newton:

$$n_D^2 - 1 = \sum_{i=1}^{k} (n_{Di}^2 - 1)\, \varphi_i \tag{27}$$

Heller:

$$\frac{n_D - n_{D1}}{n_{D1}} = \frac{3}{2} \sum_{i=1}^{k} \left[\frac{\left(\frac{n_{Di}}{n_{D1}}\right)^2 - 1}{\left(\frac{n_{Di}}{n_{D1}}\right)^2 + 2}\right] \varphi_i \tag{28}$$

Edwards:

$$\frac{n_D - 1}{n_D} = \sum_{i=1}^{k} \frac{n_{Di} - 1}{n_{Di}} \varphi_i \tag{29}$$

In these equations, n_D is called refractive index of the mixtures, n_{Di} is the refractive index of the pure components I, and φ_i is the volume fraction of the ith component of the mixture.

$$\varphi_i = \frac{x_i V_i}{\sum_i^k x_i V_i} \tag{30}$$

Here x_i and V_i are the mole fraction and the molar volume of the component i, respectively. Comparison of the predictive ability of these mixing rules was made in terms of the

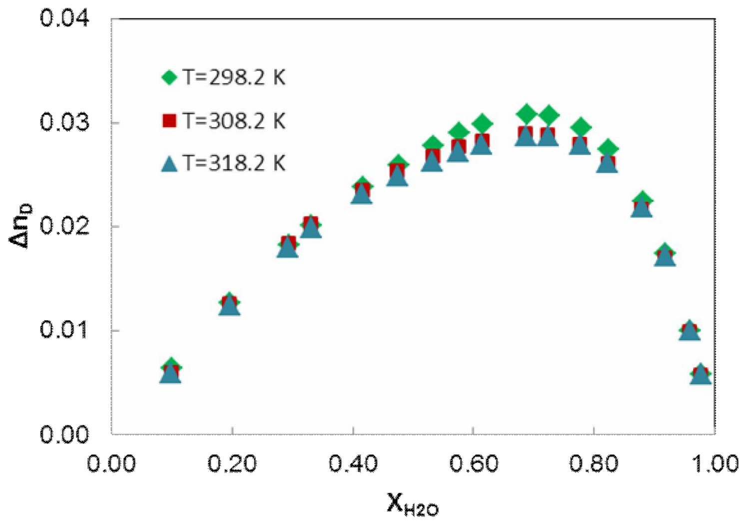

Fig. 7. Refractive index deviations for EC + water as a function of mole fraction (x_{H2O}) of water.

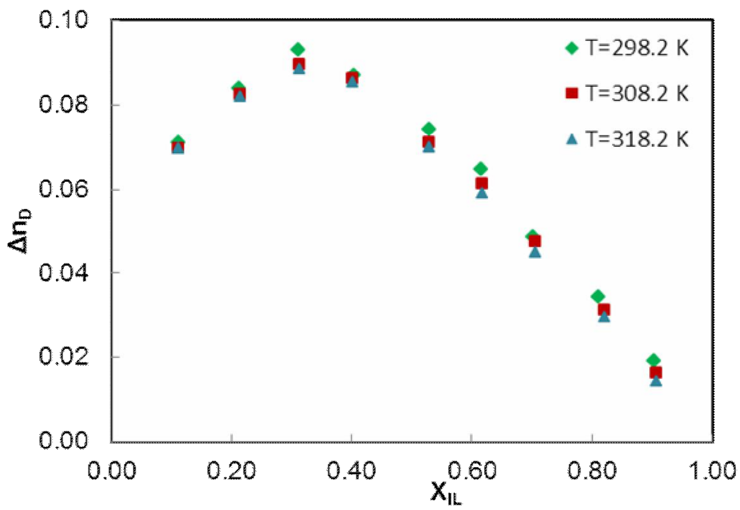

Fig. 8. Refractive index deviations for IL + water as a function of mole fraction (x_{IL}) of ionic liquid.

average percentage deviation (APD) values by applying the following relation:

$$APD = \frac{1}{N}\sum_{i=1} 100 \frac{\left|n_i^{exp} - n_i^{pre}\right|}{n_i^{exp}} \qquad (31)$$

here n^{pre}, n^{exp} are the predicted and measured values of the refractive index, and N is the number of experimental data. The results of the predictions are given in Tables 8-10 and the values of APD for all the mixtures studied are shown in Table S4 in Supporting Information.

A detailed look at this table shows that the Lorentz-Lorenz equation performs in a better agreement with the experimental values of the refractive indices in the case of

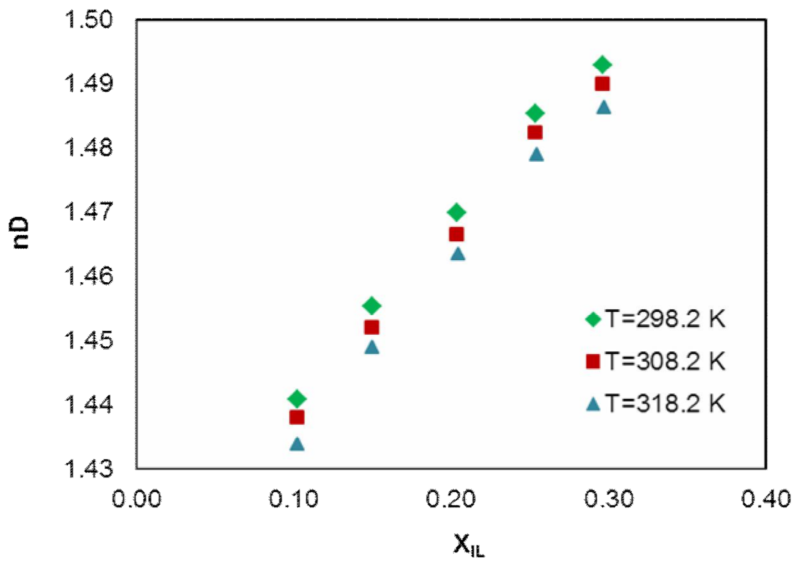

Fig. 9. Refractive indices for EC + water + [PrMIm]Br mixtures while mole fractions of water were more than EC as a function of mole fraction (x_{IL}) of ionic liquid.

water + EC + [PrMIm]Br and EC + [PrMIm]Br mixture, whereas for the water + EC, and water + [PrMIm]Br binary systems under study the Newton and Eykman relations give the best results, respectively.

CONCLUSIONS

In this article, molar conductivities and refractive indices for mixtures of [PrMIm]Br + EC + water were reported at T = (298.2, 308.2 and 318.2) K. Limiting molar conductivities, $\Lambda_\circ$, as well as ion association constants, K_A, were estimated using Fuoss-Onsager equation. The $\Lambda\circ$ and K_A values show a decrease with increasing the EC content in the mixed solvent. These are related to the strong ion-solvent interactions, decrease in mobility of ions solvated, more viscose medium and reduction of ion pairing process in the rich-EC region. Values of Gibbs free energy, $\Delta G°_A$, enthalpy, $\Delta H°_A$, and entropy, $\Delta S°_A$, of association process were obtained at different temperatures using the temperature dependence of the association constants. The results of these thermodynamic functions suggest that the nature of ion-pairing process is spontaneous, endothermic and entropy-driven.

Refractive index deviatins (Δn_D) were calculated from the experimental data for binary and ternary mixtures and correlated with Redlich-Kister and Cibulka equations, respectively. The refractive index data were used to test the prediction capability of several refractive index mixing rules including Lorentz-Lorenz, Gladston-Dale, Eykman, Newton, Heller and Edwards. According to the obtained results from the analysis of <APD> values of the experimental refractive indices, Lorentz-Lorenz mixing rule is the best for [PrMIm]Br + EC + water ternary system with 0.10 <APD> value.

ACKNOWLEDGEMENTS

We thank University of Guilan for supporting this work.

List of Symbols

w	Mass fraction
m	Molal concentration
C	Molar concentration
I	Ionic strength on molality scale
x	Mole fraction
T	Absolute temperature
K_A	Ionic association constant

Table 8. Estimated Refractive Indices Using the Lorentz-Lorenz (L-L), Gladstone-Dale (G-D), Eykman (Ek), Newton (N), Heller (H) and Edwards (Ed) Equations as Volume Fractions (φ) for the Binary Mixtures of Water + EC and Water + Ionic Liquid at 298.2, 308.2 and 318.2 K

φ_{H2O}	$n_{D(L-L)}$	$n_{D(G-D)}$	$n_{D(EK)}$	$n_{D(N)}$	$n_{D(H)}$	$n_{D(Ed)}$
			Water + EC			
			T = 298.2 K			
0.9236	1.3378	1.3380	1.3375	1.3382	1.3379	1.3376
0.8661	1.3430	1.3433	1.3425	1.3437	1.3432	1.3426
0.7560	1.3529	1.3534	1.3522	1.3540	1.3532	1.3523
0.6703	1.3607	1.3613	1.3598	1.3620	1.3610	1.3600
0.5624	1.3706	1.3713	1.3695	1.3720	1.3708	1.3698
0.4916	1.3770	1.3778	1.3760	1.3785	1.3772	1.3762
0.4209	1.3836	1.3843	1.3825	1.3850	1.3836	1.3828
0.3779	1.3875	1.3882	1.3865	1.3889	1.3875	1.3868
0.3057	1.3943	1.3949	1.3934	1.3955	1.3941	1.3936
0.2721	1.3974	1.3980	1.3965	1.3986	1.3971	1.3967
0.2391	1.4005	1.4010	1.3997	1.4016	1.4001	1.3999
0.1995	1.4042	1.4046	1.4035	1.4051	1.4037	1.4036
0.1643	1.4075	1.4079	1.4069	1.4083	1.4069	1.4070
0.1201	1.4116	1.4119	1.4112	1.4123	1.4109	1.4113
0.1028	1.4133	1.4135	1.4129	1.4138	1.4125	1.4130
0.0628	1.4170	1.4172	1.4168	1.4174	1.4161	1.4168
0.0294	1.4202	1.4203	1.4201	1.4204	1.4192	1.4201
			T = 308.2 K			
0.9222	1.3358	1.3360	1.3356	1.3363	1.3360	1.3356
0.8637	1.3410	1.3413	1.3406	1.3417	1.3412	1.3407
0.7521	1.3509	1.3514	1.3502	1.3520	1.3512	1.3503
0.6658	1.3586	1.3592	1.3577	1.3599	1.3589	1.3579
0.5571	1.3684	1.3691	1.3674	1.3698	1.3686	1.3676
0.4868	1.3747	1.3754	1.3737	1.3762	1.3749	1.3740
0.4157	1.3812	1.3819	1.3802	1.3826	1.3812	1.3804
0.3730	1.3851	1.3857	1.3841	1.3864	1.3850	1.3843
0.3020	1.3916	1.3922	1.3907	1.3928	1.3914	1.3909
0.2677	1.3947	1.3953	1.3939	1.3958	1.3945	1.3941
0.2359	1.3976	1.3981	1.3969	1.3987	1.3973	1.3971
0.1955	1.4014	1.4018	1.4007	1.4023	1.4009	1.4008
0.1619	1.4045	1.4048	1.4039	1.4052	1.4039	1.4040
0.1183	1.4085	1.4088	1.4081	1.4091	1.4078	1.4082
0.1012	1.4101	1.4103	1.4097	1.4106	1.4093	1.4098
0.0618	1.4137	1.4139	1.4135	1.4141	1.4129	1.4136
0.0289	1.4168	1.4169	1.4167	1.4170	1.4158	1.4167
			T = 318.2 K			
0.9222	1.3333	1.3335	1.3330	1.3337	1.3334	1.3331
0.8636	1.3384	1.3387	1.3379	1.3391	1.3386	1.3380
0.7521	1.3482	1.3487	1.3475	1.3492	1.3484	1.3476

Table 8. Continued

0.6658	1.3558	1.3564	1.3549	1.3571	1.3560	1.3551
0.5571	1.3655	1.3661	1.3645	1.3669	1.3657	1.3647
0.4868	1.3717	1.3724	1.3708	1.3732	1.3719	1.3710
0.4157	1.3781	1.3788	1.3772	1.3795	1.3782	1.3774
0.3730	1.3820	1.3826	1.3810	1.3833	1.3819	1.3812
0.3018	1.3884	1.3890	1.3876	1.3896	1.3882	1.3877
0.2677	1.3915	1.3920	1.3907	1.3926	1.3912	1.3909
0.2351	1.3945	1.3950	1.3937	1.3955	1.3941	1.3939
0.1955	1.3981	1.3985	1.3974	1.3990	1.3976	1.3976
0.1624	1.4011	1.4015	1.4005	1.4019	1.4005	1.4007
0.1187	1.4051	1.4054	1.4047	1.4057	1.4044	1.4048
0.1015	1.4067	1.4069	1.4063	1.4072	1.4059	1.4064
0.0620	1.4103	1.4104	1.4100	1.4106	1.4094	1.4101
0.0290	1.4133	1.4134	1.4132	1.4135	1.4123	1.4132
			Water + [PrMIm]Br			
			T = 298.2 K			
0.4778	1.4389	1.4430	1.4336	1.4470	1.4394	1.4350
0.2970	1.4782	1.4818	1.4736	1.4850	1.4770	1.4749
0.2024	1.4993	1.5021	1.4956	1.5046	1.4966	1.4967
0.1453	1.5122	1.5143	1.5093	1.5162	1.5085	1.5101
0.0928	1.5241	1.5256	1.5221	1.5269	1.5194	1.5227
0.0672	1.5300	1.5311	1.5285	1.5320	1.5247	1.5290
0.0465	1.5347	1.5355	1.5337	1.5362	1.5290	1.5340
0.0260	1.5395	1.5399	1.5389	1.5403	1.5333	1.5391
0.0122	1.5427	1.5429	1.5424	1.5431	1.5361	1.5425
			T = 308.2 K			
0.4774	1.4372	1.4413	1.4319	1.4453	1.4378	1.4333
0.2949	1.4771	1.4806	1.4724	1.4838	1.4758	1.4737
0.2009	1.4980	1.5008	1.4944	1.5033	1.4953	1.4954
0.1457	1.5105	1.5127	1.5076	1.5146	1.5068	1.5084
0.0927	1.5226	1.5241	1.5206	1.5253	1.5178	1.5212
0.0664	1.5286	1.5297	1.5272	1.5307	1.5233	1.5276
0.0457	1.5334	1.5342	1.5324	1.5348	1.5276	1.5327
0.0245	1.5383	1.5387	1.5377	1.5391	1.5320	1.5379
0.0116	1.5413	1.5415	1.5410	1.5417	1.5347	1.5411
			T = 318.2 K			
0.4743	1.4364	1.4406	1.4310	1.4447	1.4369	1.4324
0.2940	1.4761	1.4797	1.4714	1.4830	1.4747	1.4727
0.1999	1.4973	1.5001	1.4936	1.5026	1.4945	1.4946
0.1451	1.5098	1.5120	1.5069	1.5139	1.5060	1.5077
0.0923	1.5220	1.5235	1.5200	1.5248	1.5171	1.5205
0.0660	1.5281	1.5292	1.5266	1.5301	1.5226	1.5270
0.0455	1.5329	1.5336	1.5318	1.5343	1.5269	1.5321
0.0245	1.5378	1.5382	1.5372	1.5386	1.5313	1.5374
0.0115	1.5408	1.5410	1.5405	1.5412	1.5341	1.5406

Table 9. Estimated Refractive Indices Using the Lorentz-Lorenz (L-L), Gladstone-Dale (G-D), Eykman (Ek), Newton (N), Heller (H) and Edwards (Ed) Equations as Volume Fractions (φ) for the Binary Mixture of EC + Ionic Liquid at 298.2, 308.2 and 318.2 K

φ_{EC}	$n_{D(L-L)}$	$n_{D(G-D)}$	$n_{D(EK)}$	$n_{D(N)}$	$n_{D(H)}$	$n_{D(Ed)}$
			EC + [PrMIm]Br			
			T = 298.2 K			
0.7857	1.4483	1.4493	1.4473	1.4501	1.4488	1.4476
0.6325	1.4667	1.4680	1.4653	1.4692	1.4673	1.4657
0.4940	1.4836	1.4850	1.4820	1.4863	1.4840	1.4825
0.3871	1.4968	1.4981	1.4952	1.4993	1.4969	1.4957
0.2898	1.5088	1.5100	1.5075	1.5110	1.5086	1.5079
0.2198	1.5176	1.5186	1.5164	1.5194	1.5171	1.5168
0.1598	1.5252	1.5259	1.5242	1.5266	1.5243	1.5245
0.1104	1.5314	1.5320	1.5307	1.5325	1.5303	1.5310
0.0466	1.5395	1.5398	1.5392	1.5400	1.5379	1.5393
			T = 308.2 K			
0.7882	1.4449	1.4459	1.4439	1.4468	1.4454	1.4442
0.6360	1.4635	1.4648	1.4620	1.4660	1.4641	1.4624
0.4977	1.4806	1.4820	1.4789	1.4833	1.4810	1.4794
0.3907	1.4940	1.4954	1.4924	1.4966	1.4941	1.4928
0.2929	1.5063	1.5075	1.5049	1.5086	1.5061	1.5053
0.2224	1.5153	1.5163	1.5141	1.5172	1.5147	1.5145
0.1618	1.5231	1.5239	1.5221	1.5245	1.5222	1.5224
0.1119	1.5295	1.5301	1.5288	1.5306	1.5283	1.5290
0.0472	1.5379	1.5381	1.5375	1.5383	1.5362	1.5376
			T = 318.2 K			
0.7873	1.4421	1.4431	1.4410	1.4441	1.4427	1.4413
0.6347	1.4612	1.4626	1.4596	1.4639	1.4618	1.4601
0.4964	1.4787	1.4802	1.4769	1.4816	1.4791	1.4775
0.3894	1.4924	1.4939	1.4907	1.4951	1.4926	1.4912
0.2918	1.5050	1.5063	1.5035	1.5074	1.5048	1.5040
0.2214	1.5142	1.5153	1.5129	1.5162	1.5136	1.5133
0.1611	1.5221	1.5230	1.5211	1.5237	1.5212	1.5214
0.1113	1.5287	1.5293	1.5280	1.5298	1.5274	1.5282
0.0470	1.5372	1.5375	1.5369	1.5377	1.5355	1.5370

Table 10. Estimated Refractive Indices Using the Lorentz-Lorenz (L-L), Gladstone-Dale (G-D), Eykman (Ek), Newton (N), Heller (H) and Edwards (Ed) Equations as Volume Fractions (φ) for the Ternary Mixture of Water + EC + Ionic Liquid at 298.2, 308.2 and 318.2 K

φ_{H2O}	φ_{IL}	$n_{D(L-L)}$	$n_{D(G-D)}$	$n_{D(EK)}$	$n_{D(N)}$	$n_{D(H)}$	$n_{D(Ed)}$
			Water + EC + [PrMIm]Br				
			T = 298.2 K				
0.1528	0.2931	1.4430	1.4448	1.4406	1.4467	1.4422	1.4413
0.0887	0.2570	1.4449	1.4463	1.4431	1.4477	1.4438	1.4436
0.2347	0.3471	1.4415	1.4439	1.4384	1.4463	1.4411	1.4392
0.1274	0.3952	1.4576	1.4597	1.4551	1.4616	1.4564	1.4558
0.2257	0.4728	1.4574	1.4602	1.4539	1.4628	1.4566	1.4548
0.0553	0.3445	1.4586	1.4601	1.4567	1.4616	1.4571	1.4572
0.1082	0.4721	1.4688	1.4709	1.4662	1.4728	1.4672	1.4669
0.1662	0.5460	1.4721	1.4746	1.4688	1.4770	1.4705	1.4697
0.0648	0.4404	1.4692	1.4710	1.4670	1.4726	1.4674	1.4677
0.0951	0.5483	1.4793	1.4814	1.4768	1.4833	1.4773	1.4775
0.1599	0.6378	1.4839	1.4864	1.4806	1.4887	1.4818	1.4815
0.0425	0.4876	1.4771	1.4788	1.4751	1.4804	1.4750	1.4757
0.0814	0.6141	1.4888	1.4907	1.4863	1.4925	1.4862	1.4870
0.1161	0.6556	1.4904	1.4926	1.4876	1.4946	1.4879	1.4884
0.0498	0.5806	1.4878	1.4895	1.4857	1.4911	1.4851	1.4863
			T = 308.2 K				
0.1508	0.2909	1.4402	1.4421	1.4378	1.4439	1.4394	1.4385
0.0874	0.2546	1.4418	1.4433	1.4400	1.4447	1.4408	1.4405
0.2323	0.3453	1.4390	1.4415	1.4360	1.4438	1.4386	1.4368
0.1259	0.3927	1.4549	1.4570	1.4523	1.4590	1.4538	1.4531
0.2237	0.4713	1.4551	1.4579	1.4516	1.4606	1.4543	1.4526
0.0545	0.3415	1.4555	1.4571	1.4536	1.4586	1.4541	1.4541
0.1070	0.4694	1.4661	1.4683	1.4635	1.4702	1.4646	1.4643
0.1647	0.5441	1.4698	1.4723	1.4665	1.4747	1.4683	1.4674
0.0640	0.4373	1.4663	1.4682	1.4641	1.4698	1.4646	1.4648
0.0942	0.5456	1.4768	1.4789	1.4742	1.4808	1.4748	1.4749
0.1586	0.6364	1.4818	1.4844	1.4785	1.4867	1.4798	1.4794
0.0420	0.4843	1.4743	1.4760	1.4722	1.4776	1.4721	1.4728
0.0807	0.6115	1.4863	1.4883	1.4838	1.4901	1.4838	1.4845

Table 10. Continued

0.1152	0.6537	1.4882	1.4905	1.4854	1.4925	1.4857	1.4862
0.0493	0.5775	1.4852	1.4869	1.4830	1.4886	1.4826	1.4836
			T = 318.2 K				
0.1506	0.2920	1.4378	1.4398	1.4354	1.4416	1.4371	1.4361
0.0873	0.2556	1.4393	1.4408	1.4374	1.4422	1.4383	1.4379
0.2318	0.3466	1.4369	1.4394	1.4338	1.4418	1.4365	1.4346
0.1256	0.3940	1.4529	1.4550	1.4502	1.4570	1.4517	1.4509
0.2231	0.4726	1.4534	1.4563	1.4498	1.4590	1.4526	1.4508
0.0544	0.3427	1.4532	1.4548	1.4512	1.4564	1.4518	1.4518
0.1067	0.4707	1.4643	1.4665	1.4616	1.4685	1.4627	1.4623
0.1642	0.5455	1.4682	1.4709	1.4649	1.4733	1.4667	1.4658
0.0638	0.4386	1.4643	1.4662	1.4621	1.4680	1.4626	1.4627
0.0939	0.5470	1.4752	1.4773	1.4725	1.4793	1.4731	1.4732
0.1581	0.6376	1.4805	1.4832	1.4771	1.4855	1.4784	1.4781
0.0418	0.4857	1.4724	1.4742	1.4702	1.4758	1.4702	1.4709
0.0804	0.6128	1.4849	1.4869	1.4823	1.4888	1.4823	1.4830
0.1148	0.6550	1.4869	1.4892	1.4840	1.4913	1.4844	1.4848
0.0491	0.5788	1.4836	1.4854	1.4813	1.4871	1.4809	1.4819

d_s Density
ΔG°_A Gibbs free energy of ion pair formation
ΔS°_A Entropy of ion association
ΔH°_A Enthalpy of ion association
n_D Refractive index
Δn_D Refractive index deviation

Greek Letters

ε_r Relative dielectric constant
η Viscosity
σ Standard deviation
Λ Molar conductivity
$\Lambda_\circ$ Limiting molar conductivity
φ Volume fraction

Abbreviations

EC Ethylene carbonate
[PrMIm]Br 1-Propyl-3-methylimidazolium bromide
ILs Ionic liquids
APD Average percentage deviation
L-L Lorentz-Lorenz
G-D Gladstone-Dale
EK Eykman
N Newton
H Heller
Ed Edwards

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