Advanced Materials Research *Online: 2014-05-07*
ISSN: 1662-8985, Vol. 937, pp 99-104
doi:10.4028/www.scientific.net/AMR.937.99

Influence of Ethanol on the Interactions and Physical properties of Binary Mixtures of 1-ethyl-3-methylimidazolium Based ILs at 298.15 K.

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Keywords: Ionic liquid mixtures, Density, Refractive index, Conductivity, Viscosity, Ethanol.

Abstract. Density (ρ), refractive index (n), conductivity (κ) and viscosity (η) measurements have been carried out for binary mixtures of imidazolium based ionic liquids with ethanol at 298.15 K. Excess molar volumes have been calculated from experimental data and was fitted by Redlich-Kister equation. The density and refractive index increase with increasing ionic liquid (IL) concentration. Addition of IL leads to increased conductivity initially within these mixtures, which is subsequently followed by gradual decrease in IL-rich region showing the restricted ion mobility and enhanced interactions within these mixtures. Viscosity was found to be increase gradually with increasing IL concentration. It has been observed that solubility parameters, dielectric constant and nature of anions of ILs being used play a vital role in determining the fate of resultant properties.

Introduction

Ionic liquids (ILs) are a class of solvents that have shown great potential in different technological processes due to their unique properties such as extremely low vapor pressure [1, 2]. Immidazolium based ionic liquids have found great applicability especially in the processing of polymers, mainly focusing on the dissolution and further processing of lignocellulosic biomass. As it is known that ILs are quite expensive and also exhibit high viscosity in certain cases which could hinder their applicability in certain fields. In order to fully exploit the potential of ionic liquids as solvent and recovery medium in various applications, it would be crucial to investigate certain binary systems of ILs with organic solvents. As the competence of such ILs systems is strongly dependent on the molecular interactions between ILs and organic solvents [3], the studies of various physical properties could definitely provide an insight into the extent of interactions monitoring the resultant properties of the mixtures. Previously, various studies focusing on the mixtures of ILs with organic solvent have been reported [4-8]. The ILs being used in our studies comprise of 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc), 1-ethyl-3-methylimidazolium formate ([EMIM]COOH) and 1-ethyl-3-methylimidazolium methyl phosphate ([EMIM][$PO_2(CH_3)H$]). Immidazolium based ILs have received much more attention due to their applicability in polymer processing most importantly, cellulose [9]. Ethanol is one of the versatile solvents used in various chemical and technological processes and is relatively cheap [10]. Conductivity, density, viscosity and refractive index measurements have been carried out in order to discuss the effect of the underlying interactions on the mass and transport properties of these mixtures.

Experimental

Materials and Instrumentation

[EMIM]OAcand [EMIM]COOH were purchased from Chengjie chemical. Ethanol has been bought from Shanghai chemicals.[EMIM][$PO_2(CH_3)H$] has been prepared in laboratory following the procedure mentioned by Fukaya et al. [9]. The details of the chemicals being used with their

percentage purity and water fraction have been illustrated in Table 1. The purity of ILs was verified in terms of NMR analysis. The water mass fraction of ILs was determined by the Karl Fisher titration (ZSD-2 KF Cany Precision Instruments Co, Ltd.). A 2WAJ Abbe refractometer has been used for the measurements of the refractive index. Calibration of the instrument has been done by means of deionized water.

Table 1. Purity grades with experimental and theoretical values for properties of the pure ILs and ethanol along with Hildebrand, Hansen solubility parameters and dielectric constants at 298.15 K

Purity Grades and physical data for pure components								
Component	Purity [%]	Water Mass Fraction	n		ρ [g.mL^{-1}]		η [mPa.s]	
			Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
[EMIM][$PO_2(CH_3)H$]	>98	0.19	1.489	-	1.191	-	43.14	-
[EMIM]OAc	99.3	0.12	1.49	-	1.135	-	32.13	-
[EMIM]COOH	99.1	0.15	1.466	-	1.229	-	6.734	-
Ethanol	>99.5	-	1.359	1.35[20]	0.786	0.785[20]	1.094	1.09[20]
Solubility Parameters and Dielectric constants								
Solvent	Hildebrand Solubility parameters [MPa$^{1/2}$]		Hansen solubility parameters [MPa$^{1/2}$][19]				Dielectric constants	
	Δ		δ_d		δ_p	δ_h	ε	
Ethanol	12.92		15.8		8.8	19.4	24.20[19]	

The conductivity measurements were made with a DDSJ-308A conductometer (Shanghai Optical Instrument Factory, cell constant=1.0 cm^{-1}); uncertainty was found to be 0.5 %. The viscosity was determined by an Ubbelohde viscometer (inner diameter=1.5 mm). The temperature of the sample was maintained at 298.15±0.01K with an external temperature controller (SYP Electro-thermostatic water cabinet). The uncertainty was found to be 2.0+10^{-3} mPa.s. Before measuring the densities, DA-130N Density Specific Gravity Meter was calibrated with pure water at298.15±0.01 K. The uncertainty in density was estimated to be 5×10^{-4} g.cm^{-3}. Repetition of all the data was carried out three times.

Results and Discussions

Various models have been used for describing the underlying interactions between ILs and ethanol. In order to elucidate the extent of interaction within solute-solvent molecules, the excess molar volumes (V^E) were calculated for all the systems by Eq. 1 [11]:

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right) \quad (1)$$

Where ρ depicts density of mixtures; x and M represents mole fractions and molar masses. Subscripts 1 and 2 correspond to pure ionic liquid and ethanol, respectively. All values of excess molar volume have been fitted by using Redlich-Kister polynomial equation:

$$V^E = x_1(1 - x_1)\sum_{i=0}^{k} A_i\,(2x_1 - 1)^i \quad (2)$$

Where (A_i) is adjustable parameter. The standard deviations (σ) have been calculated by using Eq. 3:

$$\sigma = \left[\sum \frac{(V^E_{exp} - V^E_{calc})^2}{n - p}\right]^{1/2} \quad (3)$$

For viscosity measurements, data has been fitted by empirical equations suggested by Seddon *et al.* [4] as shown below:

$$\eta = \eta_{IL} \exp(A x_s) \quad (4)$$

Here, η and η_{IL} denote the viscosities of mixtures and pure ILs, respectively. x_s is the mole fraction of ethanol in the mixtures; and A is a constant.

Density and refractive index of ILs+ethanol binary mixtures

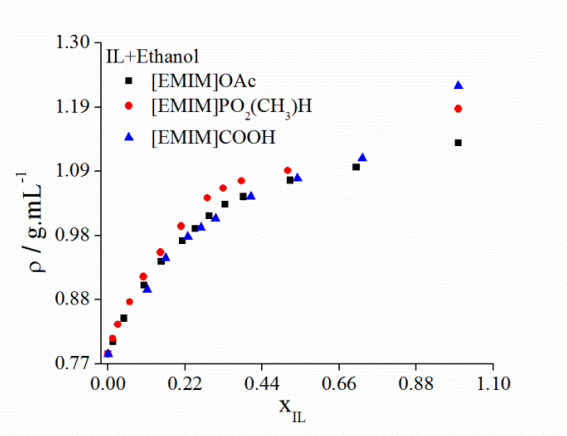

Fig. 1. Relationship between density and mole fraction of IL (x_{IL}) of ethanol with ILs at 298.15 K

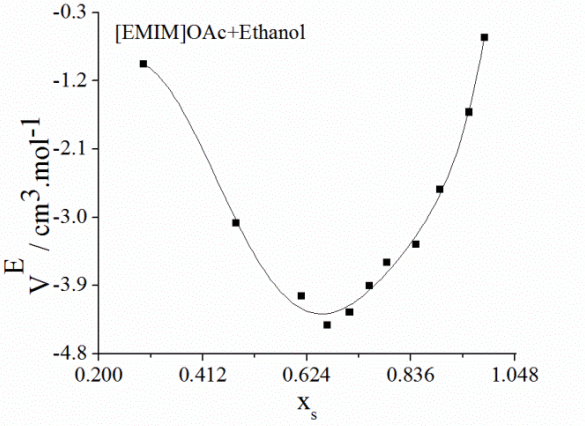

Fig. 2. Plot of excess molar volumes against mole fractions of ethanol (x_s) for the mixture of [EMIM]OAc with ethanol at 298.15 K. Solid line represents the Redlich-Kister fit.

The relationship of densities and mole fractions (x) of different ILs with ethanol has been shown in Fig. 1. It is clearly indicated that density of the mixtures increase with increasing concentration of IL [12, 13]. In order to elucidate further interactions, excess molar volumes (V^E) have been calculated by means of Eq. 1. The data has been fitted by Redlich-Kister equation and has been shown in Fig.2.

Table 2. Coefficients of Redlich Kister Equation for V^E of Different ILs/organic solvents at 298.15 K.

Systems	A_0	A_1	A_2	A_3	A_4	σ
[EMIM]OAc +ethanol	-12.97	-24.23	13.58	33.10	-53.65	0.045
[EMIM]$PO_2(CH_3)$H +ethanol	-3.798	-16.39	-243.7	603.403	-407.6	0.139
[EMIM]COOH +ethanol	7.805	-24.94	-3.765	-52.310	74.11	0.515

The negative values of V_E are due to the chemical intermolecular interactions which lead to volume decrease, and include charge transfer type forces and complex forming interactions among the molecules of ILs and ethanol. For [EMIM]COOH system, certain positive values could be observed for excess molar volumes especially at higher concentrations of IL. It could be suggested that as $COOH^-$-anion is known to make dimmers within solvent system; it's quite obvious that the ethanol moieties failed to disrupt this strong network of dimmers of IL molecules with eachother. This dominant behavior of the IL molecules leads to weak interactions in the IL-rich region. The relationship of refractive index with mole fraction has shown a gradual increase with increasing mole fraction (Fig.3) for all the ILs+ethanol systems as being suggested by many studies reported in literature [14]. Generally, polar and dipolar solvents of high dielectric constants show better miscibility with ILs indicating polar solvents have stronger molecular interactions with ILs [4]. Deetlefs et al. [15] and Brocos et al. [16] reported that the larger the reduced molar free volume of the substance, the smaller would be its refractive index. So it could be suggested that in case of ILs with

anions, $[PO_2(CH_3)H]^-$ and OAc^-; increasing concentration within solution would lead to more interactions and hence more aggregate formation. But in case of [EMIM]COOH+ethanol, the mixture still show aggregates formation or more interactions. Hereby, it is necessary to suggest that absence of free volume in this case is more due to interactions in ILs molecules itself rather than IL-ethanol molecule's interactions.

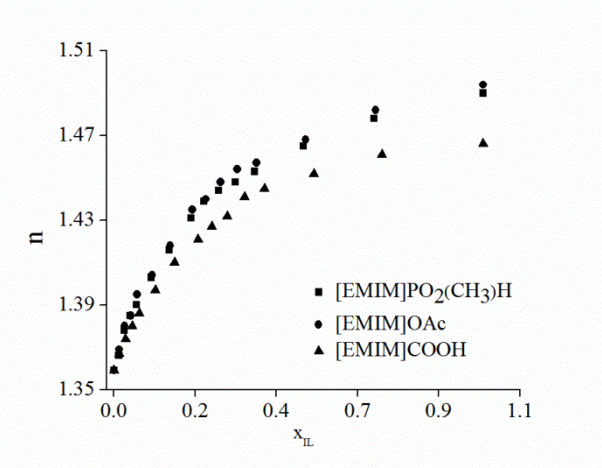

Fig.3. Relationship between refractive index and mole fraction of IL (x_{IL}) of ethanol with ILs at 298.15 K

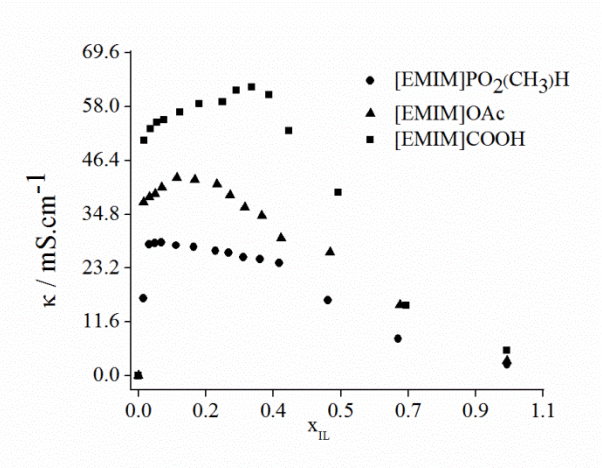

Fig. 4. Relationship between conductivity and mole fraction of IL (x_{IL}) of ethanol with ILs at 298.15 K.

Conductivity and viscosity on ILs+ethanol binary mixtures

Conductivity measurements are quite crucial in liquid systems as it depends on the extent of associations and dissociations within solvent molecules in mixtures. For ethanol+ILs mixtures, it follows the general trend (Fig. 4) i.e. the conductivity increase rapidly in the organic solvent-rich region and then gradually decreases IL-rich region. Related data has been shown in Table 2.
The increase of conductivity in high organic rich-region could be attributed to the rapid and free movement of ions more easily as compared to IL-rich region which can obstruct the motion of ions due to aggregates formation/association [17].

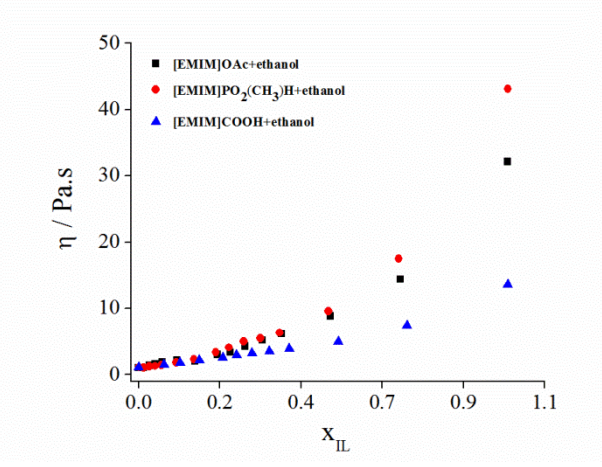

Fig. 5. Relationship between viscosity and mole fraction of ILs (x_{IL}) with different organic solvents at 298.15 K.

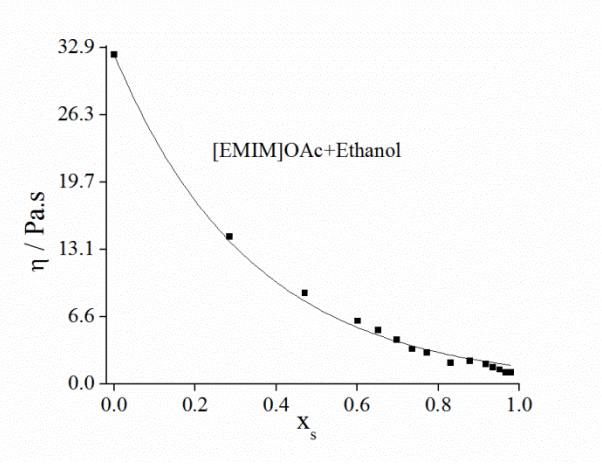

Fig. 6. Relationship between viscosity and mole fraction of ethanol (x_s) with ILs at 298.15 K.

Viscosities of binary mixtures, ILs+ethanol; has been measured as shown in Fig.5. For each IL, ethanol was found to interact in same manner. The data was fitted with Seddon equation (Eq. 4) as shown in Fig. 6. It has been observed that the viscosity of mixtures is decreased with increasing

concentration of organic solvent and vice versa. Due to occurrence of diverse interactions and aggregation within pure ILs, their addition in certain mixture will lead to enhanced viscosities and therefore hindered mobilities of ions. Similar behavior has been observed previously for different mixtures of ILs with organic solvents [18]. The A values along with their standard deviations have been listed in Table 3. It is quite evident that parameter A varies for all the systems. The values show variation depending on the nature of the ILs. The experimental data fit accurately by using Eq. 6.

Table 3. The A values and the standard deviations of the fit for the viscosities of ILs+ethanol.

Systems	A	σ
[EMIM]OAc+Ethanol	-2.877+0.052	0.347
[EMIM]COOH+Ethanol	-2.172+0.031	0.137
[EMIM][PO2(CH3)H] +Ethanol	-3.185+0.051	0.402

Conclusions

The density, refractive index, viscosity and conductivity measurements for the mixtures of [EMIM]-based ILs with ethanol have been reported. All mixtures have shown ideal behavior for the density, and refractive index measurements i.e. increase with increasing IL concentration. Excess molar volumes studies showed the existence of considerable interactions and aggregates formation within these mixtures. This behavior was further confirmed by refractive index measurements by the unavailability of free volume within these mixtures as the concentration of IL is increased. Conductivity measurements have shown enhanced electrical conductivity and ion mobility in organic-rich region. Viscosity was found to be increased by the addition of ILs. It was evaluated that the molar mass and hydrogen bonding ability of anion, solubility parameters and dielectric constants of ethanol play an important role in determining the extent of solute-solvent interactions within these mixtures.

Acknowledgements

This work is supported by a grant from National Natural Science Foundation of China (51273041).

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