Journal of Molecular Liquids 212 (2015) 444–450

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Apparent molar properties of hydroxyethyl ammonium based ionic liquids with water and ethanol at various temperatures

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ARTICLE INFO

Article history:
Received 30 April 2015
Received in revised form 14 September 2015
Accepted 30 September 2015
Available online xxxx

Keywords:
Ionic liquid
Binary mixture
Solute–solvent interaction
Redlich–Mayer equation

ABSTRACT

The density, ρ and speed of sound, u data for binary solutions of protic ionic liquids (PILs) namely N-butyl-2-hydroxyethyl ammonium formate (BHEAF) and N-butyl-2-hydroxyethyl ammonium acetate (BHEAAc) with water and ethanol, as a function of molality, m ranging from (0.1 to 0.8) mol.kg^{-1} were measured from (293.15 to 318.15) K under 0.1 MPa pressure. The apparent molar volume, V_ϕ apparent molar isentropic compressibility, $K_{s,\phi}$ and limiting apparent molar expansion, E_ϕ^∞ have been determined from experimental density and speed of sound data. The apparent molar volume, V_ϕ^∞ and apparent molar isentropic compressibility, K_ϕ^∞ at infinite dilution and corresponding empirical parameters (S_v, B_v, S_k and B_k) were calculated by using the Redlich–Mayer equation. The calculated V_ϕ^∞ and K_ϕ^∞ values indicate that ILs–ethanol interactions are stronger than ILs–water interactions. Further, thermodynamic properties of binary mixtures were explained on the basis of the influence of the anion structural contribution of protic ionic liquids.

1. Introduction

Ionic liquids (ILs) are special classes of substances that possess a melting point below 373.15 K. Generally, ILs are constituted almost entirely with ions i.e., organic cations such as imidazolium, pyrrolidinium, pyridinium, ammonium etc., and organic or inorganic anion such as halogens, sulfates, acetates, phosphates etc. These are broadly classified into protic ionic liquids (PILs) those containing an acidic proton and aprotic ionic liquids (APILs) and those excluding acidic protons in their molecular framework. PILs were synthesized by stoichiometric (equimolar) addition of Bronsted acid to Bronsted base. ILs are environmental "friendly" solvents because they can be recycled and has negligible vapor pressure [1] and they have interesting physical and chemical properties like low melting point, high thermal stability, large liquid range, high conductivity, non-flammability, high solubility for polar, nonpolar, organic and inorganic substances and wide electrochemical window [2–5]. The commercial applicability of ILs makes it essential to establish physico-chemical properties of pure ILs and their combination with organic solvents. In recent years, ILs have been an increasing interest in exploiting the potential as a reaction media aimed to develop green chemistry, avoiding the use of volatile organic solvents. Moreover, ILs find extensive applications in chemical reaction, bio-catalysis, self-assembly media, internal separation, electrochemistry, flue gases absorption and many more areas of varying interests and utility [6–8].

Thermophysical properties of density (ρ) and speed of sound (u) data of binary mixture of pure PILs and molecular solvents are required not only to determine intermolecular interactions and structural effects of PILs upon molecular solvents but also essential for the efficient design of equipment and also the engineering applications concerning fluid flow, mass transfer and heat transfer etc. Volumetric properties of binary mixtures provide extensive information about nature and extent of various interactions namely, ion–ion, ion–solvent and solvent–solvent interactions [9–12]. Thermodynamic properties of ILs like heat capacity, phase equilibrium data (vapor + liquid) (VLE), [13] (liquid + liquid) (LLE) [14–16] and (solid + liquid) (SLE) [17,18], apparent molar volume V_ϕ and apparent molar isentropic compressibility K_ϕ provided a valuable information about structural/chemical bonding information about the behavior of pure as well as mixed states. Various reports are available in literature on thermophysical properties such as density, speed of sound and viscosity of pure ILs and binary solutions of various ILs with solvents [19–23]. Buwalda et al. [19] reported volumetric properties and compressibilities of alkyl tri methyl ammonium bromide in aqueous solutions. These results have been interpreted in terms of mutual interactions occurring in binary solutions. Thermodynamic studies of PILs and their mixtures with other compounds are essential to understand their interactions in a better way and furthermore, to widen their applications in design and control of chemical processes [24–29]. Understanding the solvation behavior of PILs in polar and nonpolar solvents can provide the employing of the nature and extent of various interactions among solute and solvent molecules and make the industrial applications of mixed PILs solutions significant.

In the present study, in order to investigate the nature of molecular interactions, density (ρ) and speed of sound (u) data of binary

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http://dx.doi.org/10.1016/j.molliq.2015.09.050
0167-7322/

system containing N-butyl-2-hydroxyethyl ammonium formate/acetate [BHEAF/BHEAAc] with polar solvents like water and ethanol were measured from (293.15 to 318.15) K. Furthermore, the volumetric and acoustic properties have been used as potential tools to understand and analyze the solvation behavior of solutes in water and ethanol.

2. Experimental methods

2.1. Materials

The mass fraction purity and CAS number of the chemicals used in the present work are given in Table 1. All chemicals were used without further purification. Purity of water and ethanol was further assessed by comparison of the experimental density and speed of sound data with literature values [30–42] are presented in Table 2.

2.2. Synthesis and characterization of hydroxyethyl ammonium based PILs

Hydroxyethyl ammonium based PILs are synthesized by the neutralization reaction of equimolar quantities of Bronsted base and Bronsted acid. N-butyl hydroxyethyl amine was taken in a double necked round bottom flask equipped with a reflux condenser. Under vigorous stirring, acid was added drop-wise through a dropping funnel to amine. Since acid–base reaction is exothermic, the temperature was maintained at about 0–5 °C by using ice bath during the addition of acid. Reaction mixture was stirred continuously for 24 h at room temperature and a colored viscous liquid was obtained, then high vacuum was applied at 323.15 K for 48 h, in order to remove the remaining volatile liquids. The dried neat PILs were stored under nitrogen atmosphere. Dried PILs were characterized by ^{1}H NMR and ^{13}C NMR (Bruker Avance 500 MHz) spectroscopic techniques using $CDCl_3$ as solvent and TMS (Tertramethylsilane) as the internal standard. FTIR spectrums were recorded at room temperature by JASCO FTIR-4100 spectrometer with a resolution of 0.9 cm^{-1} and a signal to noise ratio of 22,000:1.

2.3. Characterization of PILs

2.3.1. N-Butyl-2- hydroxyethyl ammonium formate (BHEAF)

^{1}H and ^{13}C NMR spectrum were obtained by using a Bruker 500 MHz spectrometer, $CDCl_3$ as solvent and TMS (Tetramethylsilane) as internal standard.

[BHEAF] ^{1}H NMR ($CDCl_3$): 0.925 (t, 3 H), 1.337–1.412 (m, 2 H), 1.665–1.727 (m, 2 H), 2.913 (t, 2 H), 3.043 (t, 2 H), 3.852 (t, 2 H), 7.60 (br, 2 H), 8.523 (s, 1 H). ^{13}C NMR: 13.56, 19.95, 27.93, 47.66, 49.91, 57.21 and 169.52.

Table 2
The comparison of experimentally measured density, ρ and speed of sound, u data of pure water and ethanol at $T = (293.15$ to $318.15)$ K with the corresponding literature values.[a, j, n]

Component	T/K	$\rho \times 10^{-3}$ kg·m^{-3}		u/m·s^{-1}	
		Expt.	Lit.	Expt.	Lit.
Water	293.15	0.99823	0.99821[a]	1482.8	1482.8[a]
			0.99820[b]		1482.9[h]
			0.99820[c]		1483.1[i]
			0.99820[d]		
	298.15	0.99706	0.99704[c]	1496.9	1497.0[d]
			0.99704[e]		1496.7[f]
			0.99704[f]		1496.7[g]
	303.15	0.99576	0.99566[a]	1509.2	1509.1[a]
			0.99565[c]		1509.4[d]
			0.99565[d]		1509.0[f]
	308.15	0.99416	0.99404[a]	1519.9	1520.1[d]
			0.99403[e]		1519.8[f,g]
			0.99403[g]		
	313.15	0.99224	0.99220[b]	1528.8	1529.2[d]
			0.99221[d]		1528.8[f]
			0.99216[g]		
	318.15	0.99023	0.99023[a]	1536.5	1536.7[d]
			0.99021[d]		1536.4[f]
			0.99020[e]		1536.4[g]
			0.99021[g]		
Ethanol	293.15	0.78992	0.78975[c]	1162.4	1161.9[a]
			0.78935[f]		1162.0[k]
			0.78840[i]		
	298.15	0.78579	0.78565[a]	1145.6	1145.4[a]
			0.78546[c]		1144.9[k]
			0.78570[j]		1144.2[l]
			0.78521[l]		
	303.15	0.78166	0.78200[j]	1128.7	1128.8[a]
			0.78076[k] 0.78160[n]		1128.0[j]
	308.15	0.77683	0.77699[a]	1111.9	1098.0[j]
			0.77600[k]		1111.1[k]
			0.77650[j]		1110.5[l]
			0.77726[n]		
	313.15	0.77292	0.77360[j]	1095.1	1086.0[j]
			0.77203[k]		1094.3[k]
			0.77230[m]		
	318.15	0.76849	0.76817[a]	1078.4	1076.9[k]
			0.76830[m]		1076.3[l]

[a] Ref [27].
[b] Ref [30].
[c] Ref [31].
[d] Ref [32].
[e] Ref [33].
[f] Ref [34].
[g] Ref [35].
[h] Ref [36].
[i] Ref [37].
[j] Ref [38].
[k] Ref [39].
[l] Ref [40].
[m] Ref [41].
[n] Ref [42].

Table 1
Provenance and purity of chemicals used for the synthesis of protic ionic liquids.

Chemical name	Source	CAS number	Purity (mass fraction)	Water content (mass fraction)
N-butyl-2-hydroxy ethylamine	Sigma Aldrich	111-75-1	>0.98[b]	0.05%
Formic Acid	Sigma Aldrich	64-18-6	>0.99[b]	0.02%
Acetic acid	Sigma Aldrich	64-19-7	>0.99[b]	0.02%
Ethanol	Pharmaco APPER	64-17-5	>0.99[b]	0.02%
N-butyl-2-hydroxy ethyl ammonium formate [BHEAF]	[a]This work	–	>0.97[c]	0.251%
N-butyl-2-hydroxy ethyl ammonium acetate [BHEAAc]	[a]This work	–	>0.97[c]	0.222%

[a] Synthesized in our research laboratory.
[b] Used as received from source without further purification.
[c] Dried under high vacuum at 323.15 K for 48 h and stored under nitrogen atmosphere. The characterization of samples by ^{1}H NMR and ^{13}C NMR spectroscopic techniques.