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Experimental and theoretical excess molar properties of imidazolium based ionic liquids with isomers of butanol

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ABSTRACT

The experimental densities (ρ), speeds of sound (u), and refractive indices (n_D) of binary mixtures of 1-octyl-3-methylimidazolium tetrafluoroborate ([C_8mim][BF_4]) with isomers of butanol (1-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol) were measured at 0.1 MPa and at 298.15, 308.15 and 318.15 K. Excess molar volumes $\left(V_m^E\right)$, excess molar isentropic compressibilities $\left(K_{s,m}^E\right)$, and deviations in refractive index ($\Delta_\phi n_D$) were calculated from the experimental data and were fitted to the Redlich–Kister polynomial equation. The results have been interpreted in terms of interstitial accommodation, ion–dipole interactions, formation of the hydrogen bonds, and structural factors involved in the mixture of ionic liquid and molecular organic solvents. Various mixing rules were used to predict the refractive indices and the data have been compared with the experimental results. In addition, analysis of the present V_m^E data were done through the Prigogine–Flory–Patterson (PFP) theory and the extended real associated solution (ERAS) model.

1. Introduction

Among the various classes of the ILs [1,2], imidazolium based ILs are the most extensively studied and used. The ILs are used in various fields, including in catalysis, in electrochemistry, in preparation of highly efficient fuel and solar cells, in the column as the stationary phase in chromatography, in the synthesis of nano-materials and also in various industrial applications [1–5]. Several technological process used in the industries are designed and implemented successfully from the knowledge of the thermophysical properties of ILs solutions in organic solvents. Reliable and accessible reference data on the physical (density, speeds of sound and viscosity) and chemical properties of pure components (ILs) and their mixtures are very crucial for: several industrial process engineering, transportation and storage of fluids, equipment designing, to develop the models for process design and energy efficient processes, to qualify and quantify the energy efficiency. In the literature, the data pertaining to ILs (pure and mixture with organic solvents) are very limited as well as scattered, which makes them inaccessible to the industry. Furthermore, along with the physical properties, several derived properties are also important to characterize the compounds in their pure form as well as in the mixtures and provide the end user the best information about the behavioral changes occurred when the pure ILs is mixed with the organic solvents through the knowledge of molecular interaction.

Our laboratory is engaged in the systematic experimental and theoretical investigations of the thermodynamic, transport, acoustic, and optical properties of the binary mixtures involving ILs and molecular organic solvents as the functions of composition and temperature [6–12]. In the previous papers [12,13], the thermophysical properties of the binary mixtures of imidazolium based ILs: [C_6mim][BF_4] and [C_8mim][BF_4] with the cyclic ethers and alkyl amines were reported. Alaknol as being highly polar H-bonding molecular solvents and used in many organic synthesis has been selected in the present work. Here we report the volumetric, acoustic and optical properties of binary mixtures; [C_8mim][BF_4] + isomers of butanol (1-butanol, 2-methyl-1-propanol and 2-methyl-2-propanol) at (298.15, 308.15 & 318.15) K and at 0.1 MPa pressure. The isomers of butanol were selected as one of the components in order to see the effect of different position of —OH and —CH_3 groups in butanol molecule on the investigated thermophysical properties. Only the excess molar volumes $\left(V_m^E\right)$ of [C_8mim][BF_4] + 1-butanol at 298.15 K have been reported in literature [14]. The results have been interpreted in terms of interstitial accommodation, ion–dipole interactions, H-bond for-

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Table 1
CAS number, supplier and purity of components.

Component	CAS Number	Supplier	Initial Purity on mass fraction	Final	Purification Method	Purity Analysis
1-butanol	71-36-3	Merck	0.995	0.996	F.D.[b]	GC[a]
2-methyl-1-propanol	78-83-1	Merck	0.990	0.993	F.D.[b]	GC[a]
2-methyl-2-propanol	75-65-0	Merck	0.990	0.993	F.D.[b]	GC[a]
[C_8mim][BF_4][c]	244193-52-0	Synthesized		>0.98	None#	^{1}H NMR$

None# = Synthesized ILs were kept in bottles under an inert gas. To reduce the water content to negligible values, ILs were kept at 0.2 Pa pressure in vacuum and at 343.15 K temperature for several days, prior to their use.
^{1}H NMR$ = Purity was determined through the corresponding NMR spectra with cation and anion specific peak integrals.
[a] GC = Gas Chromatography.
[b] F.D.= Fractional Distillation.
[c] water content was 89 ppm.

Table 2
Comparison of experimental values of densities (ρ), speeds of sound (u), and refractive indices (n_D) of pure liquids with literature at different temperatures literature.

Liquid	T/K	ρ/kg m^{-3}		u/m s^{-1}		n_D	
		Expt.	Lit	Expt.	Lit.	Expt.	Lit.
[C_8mim][BF_4]							
	298.15	1105.02	1105.30 [23] 1104.31 [24] 1114.4 [27] 1091.2 [28] 1103.68 [29] 1114.4 [30]	1485.11	1491 [23] 1482.2 [25]	1.43253	1.43422 [23] 1.4330 [26]
	308.15	1098.32	1085.5 [31] 1107.5 [27]	1458.54	1454.4 [25]	1.42984	
	318.15	1091.54	1090.78 [24]	1433.21	1428.3 [25]	1.42715	
1-butanol							
	298.15	805.758	805.74 [14] 805.76 [33] 805.62 [34,35] 805.75 [36,37] 805.752 [38] 805.64 [39] 805.60 [40] 806.07 [41] 806.282 [36] 806.0 [42]	1242.41	1242.6 [32] 1238.99 [34,35]	1.39728	1.3973 [33]
	308.15	798.046	798.04 [43] 798.053 [33] 797.93 [34,35]	1207.54	1207.6 [44] 1205.79 [34,35]	1.39324	1.39318 [33]
	318.15	790.212	790.18 [45] 790.231 [33]	1171.51		1.38911	1.38901 [33]
2-methyl-1-propanol							
	298.15	797.824	797.84 [46] 798.52 [48] 797.77 [34,35] 798.03 [49] 797.8 [50] 797.72 [43]	1189.02	1189.6 [47] 1186.72 [34,35] 1188.0 [50]	1.39408	1.3939 [46]
	308.15	790.629	790.04 [44] 790.63 [48] 798.90 [34,35]	1155.94	1156.2 [48] 1153.86 [34,35]	1.38925	
	318.15	781.982	781.98 [43]	1118.62		1.38444	
2-methyl-2-propanol							
	298.15	780.720	797.90 [47] 780.80 [51] 780.99 [52] 781.2 [36] 780.68 [42]	1121.41	1121.2 [51] 1188.0 [49]	1.38488	1.3938 [47]
	308.15	770.212	770.19 [33] 770.10 [51]	1081.97	1082.8 [51]	1.37985	1.37947 [33]
	318.15	759.502	759.49 [51] 759.87 [53] 759.45 [54]	1038.22		1.37402	1.37384 [33]

Standard uncertainties u are: $u(\rho)$ = 0.08 kg m^{-3}, $u(u)$ = 0.5 m s^{-1}, $u(n_D)$ = 0.0008, $u(T)$ = 0.01 K and $u(P)$ = 0.005 MPa. All the experiments were carried out at 0.1 MPa.

mation and structural factors involved in the liquid components. Further, the refractive indices of the binary mixtures were correlated with Lorentz–Lorenz, Dale–Gladstone, Eykman, Arago–Boit, Newton, Oster, Heller, and Wiener mixing rules [15]. The PFP theory [16–18] and the ERAS model [17,19,20] were also used to analyse the V_m^E data.