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RESEARCH ARTICLE

STUDIES ACOUSTIC AND REFRACTIVE BEHAVIOUR OF THE BINARY MIXTURE OF 1-BUTYL-3-METHYLIMIDAZOLIUM HEXAFLUOROPHOSPHATE WITH 1- BUTANOL AT 303.15 K

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ABSTRACT

Densities and speeds of sound and their excess properties for 1-butyl-3- methylimidazolium Hexafluorophosphate (Bmim) (PF_6) with 1-Butanol over the entire range of mole fraction are reported at temperature 303.15 K and atmospheric pressure. Isentropic and excess isentropic compressibility for ionic liquid with 1-Butaanol were calculated from the experimental results. The excess values are fitted to the Redlich–Kister polynomial equation to estimate the binary coefficients and standard error between the experimental and calculated values. The measured speeds of sound were compared to the values obtained from Schaaffs' collision factor theory, Jacobson's intermolecular free length theory of solutions and Nomoto's relation. In addition, the experimentally obtained refractive indices were compared to the calculated values using Lorentz-Lorenz, Dale-Gladstone and Eykman mixing rules. The theoretical results obtained from these relations fairly agrees within the experimental precision. Further, the molecular interactions involved in IL binary mixture system were studied.

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INTRODUCTION

Generally, The technological processes use binary mixtures of Ionic liquids with organic and inorganic solvents. The physicochemical and acoustical properties are interesting both from practical and theoretical point of view[1]. Moreover, the knowledge of excess properties helps us to understand the structure- property relation, making it easier to search for an optimal ionic liquid for a specific application[2]. Ionic liquids (ILs) have recently emerged as environment friendly solvents for their use in the industrial manufacture of chemicals. In the past decade, ILs have been increasingly used for diverse applications such as organic synthesis, catalysis, electrochemical devices, and solvent extraction of a variety of compounds[3–6]. The interest in ILs was initiated because of their advantageous physico–chemical properties. ILs are composed of cations and anions having a low melting point. The physico–chemical properties of the ILs can be tuned by changing the cation or the anion. Thus, novel solvents can be formed and can be used for a specific application which cannot be done with the use of conventional organic solvents.

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The information regarding the thermo- physical properties of pure ILs as well as their mixtures with other compounds is essential for the design and development of equipment for commercial applications. (Bmim)(PF_6) is most efficient in the removal of di- benzothiophene (DBT) containing liquid fuels[7]. 1-Butanol is used as a solvent for a wide variety of chemical and textile processes, in organic synthesis and as a chemical intermediate. It is also used as a paint thinner and a solvent in other coating applications where a relatively slow evaporating and ambient cured enamels. Similar study has been carried out by us [8-10] and many other workers for non ionic liquids, particularly hydro carbons, cyclic compound, to validate these theoretical models and also the solvent - solvent interactions present in liquid mixture. The present work is aimed at studying the molecular interactions in the binary mixture of the IL 1-Butyl-3-methylimidazolium Hexafluorophosphate (Bmim)(PF_6) with 1-Butanol. Isentropic and excess isentropic compressibility's for ionic liquids with 1–Butanol were calculated from the experimental results. Excess and deviation properties were further correlated using the Redlich-Kister polynomial eqation [11]. The measured speeds of sound were compared to the values obtained from Schaaffs' collision factor theory (CFT)[12], Jacobson's intermolecular free length theory(FLT)[13-14] of solutions and Nomoto's relation (NR)[15]. In addition, the experimentally obtained refractive indices were compared to the calculated values using Lorentz-Lorenz[16],

Dale-Gladstone [17] and Eykman mixing rules [18]. Experimental values and excess thermodynamic properties of IL systems allow researchers to draw information on the corresponding excess molar volume and excess isentropic compressibility and coefficients of thermal expansion were calculated. Furthermore, the Redlich and Kister (R–K) polynomial was used to obtain the coefficients and to estimate the standard deviations for the calculated excess and deviation properties. Moreover, the effect of the alkyl chain in ILs, chain length of 1–Butanol and the temperature on the excess and deviation properties are investigated.

EXPERIMENTAL

Materials

(Bmim) (PF_6) (mass fraction, 0.99) is procured from Merck, Germany, and is used without further purification. 1-Butanol (mass fraction 0.97) is procured from Sigma-Aldrich, USA, and is purified by the fractional distillation method under reduced pressure. The water content is checked by conductometric titration with platinum electrode. The purity of the chemicals was ascertained by comparing the experimental values of density, Refractive index and speed of sound at temperatures T = 303.15 K with the literature value [19-21] .

Apparatus and Procedure: The binary mixture is prepared by weighing appropriate amounts of pure liquids on a digital electronic balance model Shimadzuax-200 with an uncertainty of ± $1 \cdot 10^{-4}$kg. Before each series of experiments, I calibrated the instrument at atmospheric pressure with doubly distilled water.

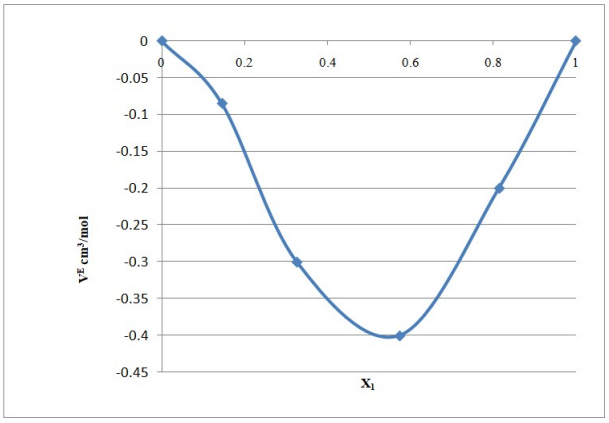

Fig.1: Excess molar volumes V^E, as a function of x_1 for {x (Bmim) (PF_6) + (1 − x) 1-Butanol} binary mixture at 303.15 K

The average uncertainty in the composition of the mixtures was estimated to be less than ±0.0001. A crystal controlled variable path ultrasonic interferometer supplied by M/s Mittal enterprises (model-05F), New Delhi (India), operating at a frequency of 2 MHz was used in the ultrasonic measurements. The reported uncertainty is less than ± 3% which is the highest uncertainty found from all the data points. Refractive index was measured by Abbe refractometer (Agato 3T, Japan). Refractive index data were accurate to ±0.0001units. The purity of chemicals used was confirmed by comparing the densities and ultrasonic speeds with those reported in the literature as shown in Table 1. The uncertainty in the density measurement was within ± 0.7 kg.m^{-3} (about 0.06%).

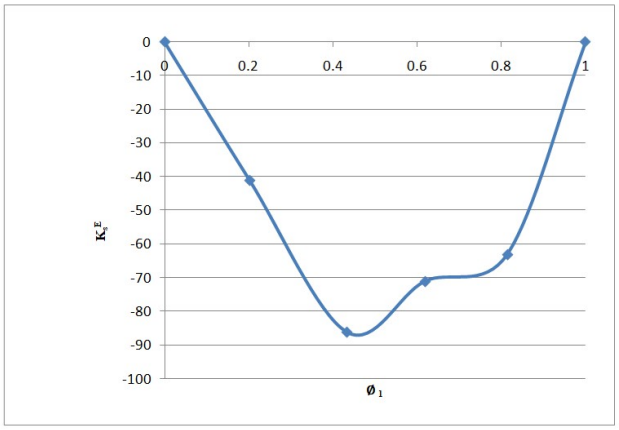

Fig. 2 Excess isentropic compressibility k_s^E, as a function of $\emptyset_1$for {x (Bmim)(PF_6) + (1 − x) 1-Butanol }binary mixture, at 303.15K

The densities of the pure components and their mixture were measured with the bi-capillary pyknometer. The liquid mixture was prepared by mass in an air tight stopped bottle using an electronic balance model Shimadzuax-200 accurate to within ±0.1 mg. Isentropic compressibility, k_s, were calculated from the relation,

$$k_s = u^{-2}\rho^{-1} \quad (1)$$

Where ρ is the density and u is the ultrasonic velocity.

RESULTS AND CALCULATIONS

The experimental density and speed of sound for binary systems of 1 Butyl-3-methylimidazolium Hexafluorophosphate with 1- Butanol are reported at 303.15 K and atmospheric pressure are listed in Table 2. The excess volume, V^E and excess isentropic compressibility values

$$V^E = \sum_{i=1}^{n} \frac{XiMi}{\rho} - \sum_{i=1}^{n} \frac{XiMi}{\rho i} \quad (2)$$

and

$$K_s^E = K_s - K_s^{idl} \quad (3)$$

Where

$$K_s^{idl} = K_s x_1 + K_s x_2 \quad (4)$$

and volume fractions, $\emptyset$ were calculated from the relation;

$$\emptyset = \frac{Xi\,V1}{\sum_{i=1}^{n} Xi\,Vi} \quad (5)$$

The dependency of V^E on composition is shown in figure 1 where all V^E values are negative for the systems under study and this is due to the interstitial accommodation of ILs into 1 - Butanol structure[7]. The negativeV^E trend reflects the formation of hydrogen bonded hetero associations and the association of 1- Butanol structure as the chain length increases. This is conformed from the previously reported studies [4,5,7]. In addition as expected, V^E becomes less negative as the temperature increases for ILs with 1-Butanol. The excess isentropic compressibility values k^E were calculated from relations by Benson et al.[22] where K_s^{idl} is the isentropic compressibility of the ideal solution, K_s is the isentropic compressibility and it is calculated using the Laplace–Newton $V = 1/u^2\rho$ where the relation is judged to be valid and

Table 1. Comparison of Experimental Density (ρ_{exp}), Refractive Index (n_{exp}) and Speed of Sound (u_{exp}) of Pure Components with Literature (lit) Values at Temperature 303.15 K

Components	ρ/kg·m^{-3}		n		u/m·sec^{-1}	
	ρexp	ρlit	n exp	n lit	u exp	u lit
1-Butyl-3-methylimidazolium Hexafluorophosphate	1364.20	1362.98	1.4070	1.4073	1430.94	1430.60
1- Butanol	802.7	802.0	1.3946	1.3947	1223.7	1228.8

Table 2. Experimental Density (ρ_{exp}), Refractive Index (n_{exp}), and Speed of Sound (u_{exp}) and values obtained from theoretical models (u_{Sch}, u_{Nom}, u_{Jacob} and $n_{L\text{-}L}$, $n_{D\text{-}G}$, n_{Eykman}) and Isentropic Compressibility (k_s) of BinaryLiquid Mixtures of 1-Butyl-3- methylimidazolium Tetrafluoroborate + 1-Butanol at 303.15 K

x_1	ρ_{exp}/kg·m^{-3}	n_{exp}	u_{exp}/m·sec^{-1}	u_{Sch}/m·sec^{-}	u_{Nom}/m·sec^{-}	u_{Jacob}/m·sec^{-}	$n_{L\text{-}L}$	$n_{D\text{-}G}$	n_{Eykman}	k_s TPa^{-1}
0.1028	816.30	1.4082	1243.25	1257.41	1259.24	1294.25	1.4086	1.4091	1.4090	398.25
0.2054	864.49	1.4092	1277.62	1283.56	1297.56	1324.51	1.4094	1.4095	1.4093	387.24
0.3027	917.20	1.4107	1304.74	1309.74	1315.24	1372.32	1.4112	1.4114	1.4115	376.41
0.4051	974.45	1.4115	1341.21	1346.08	1355.64	1387.75	1.4024	1.4126	1.4128	364.33
0.5002	1006.21	1.4128	1388.41	1393.21	1401.20	1421.54	1.4141	1.4147	1.4149	353.14
0.6064	1042.63	1.4139	1412.52	1423.45	1432.01	1458.98	1.4158	1.4162	1.4169	349.87
0.7142	1089.47	1.4152	1447.28	1459.58	1464.05	1487.29	1.4167	1.4171	1.4174	338.01
0.8201	1103.01	1.4165	1486.30	1493.45	1499.27	1524.31	1.4179	1.4183	1.4186	327.74
0.9086	1152.85	1.4178	1519.75	1528.65	1537.89	1563.18	1.4193	1.4196	1.4198	315.08

therefore the speed of sound may be regarded as a thermodynamic quantity. The excess isentropic compressibility are negative for the system under study and exhibited a similar trend as the excess volume (see fig.2) while K^E becomes more negative as the temperature increases as shown in Table 2. Which suggest the dominance of interstitial of accommodation of the components effect over the dissociation effect. The calculated excess properties were fitted to the Redlich-Kister (R–K) polynomial equation, Schaaff's Collision Factor Theory (CFT), Jacobson's Free Length Theory (FLT) and Nomoto's relation (NR) [11-15] were used to predict the speed of sound (u_m) for 1-Butyl- 3- methylimidazolium Hexafluorophosphate + 1- Butanol binary systems. The critical temperature for the pure ILs were predicted using available data since they are needed for CFT.

$$u = u_{\infty}^{\sum_{i=1}^{n} \frac{(XiSi)(\sum_{i=1} Xi\,Bi)}{V}} \quad (6)$$

Where u_∞ = 1600 m·s^{-1}, S_i and B_i are the space filling factor and the actual volume of the molecule per mole of pure component i in the mixture. Jacobson's Free Length Theory (FLT) can be expressed as; Where K is the Jacobson's constant and L_f is the intermolecular free length of the binary mixture and Nomoto's relation as;

$$u = \frac{K}{L_f \rho_{1/2}} \quad (7)$$

Where K is the Jacobson's constant and L f is the intermolecular free length of the binary mixture and Nomoto's relation as;

$$u = \left(\frac{\sum_{i=1}^{n} Xi\,ui}{\sum_{i=1}^{n} Xi\,Vi}\right) 3 \quad (8)$$

In addition, Lorentz-Lorenz (L–L), Dale-Gladstone (D–G) and Eykman (Eyk) mixing rules [16- 18] were used to predict refractive indices for studied system. They are given as;

The comparison shows that Nomoto's relation for predicting speed of sound is the best among the relations used in the case of + 1-Butanol while both Nomoto's and Schaaff's Collision Factor Theory are also comparable.

$$\frac{n2-1}{n2+2} = \sum_{i=1}^{n} \emptyset i \left(\frac{n2-1}{n2+2}\right) \quad (9)$$

$$n - 1 = \sum_{i=1}^{n} (\emptyset i\,(n-1)) \quad (10)$$

$$\frac{n2-1}{n2+2} = \sum_{i=1}^{n} \emptyset i \left(\frac{n2-1}{n2+0.4}\right) \quad (11)$$

As for the refractive index mixing rules, all rules used showed good agreement with the experimental data for the system under study.

CONCLUSION

Density, speed of sound and their excess or deviation properties of IL with 1– Butanol binary mixture have been reported at 303.15 K temperature and atmospheric pressure. Although IL show stronger hydrogen bonding 1-Butyl-3-ethylimidazolium Hexafluorophosphate with 1–Butanol than conventional solvents. Prediction of the speed of sound can be obtained using Nomoto's relation and Schaaff's Collision Factor Theory while refractive index can be predicted using Lorentz-Lorenz, Dale-Gladstone and Eykman mixing rules for systems containing ionic liquids. In addition, the calculations showed a systematic dependence of excess and deviation properties on the chain length for investigated mixture.

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