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Measurement and modeling the excess properties of binary and ternary mixtures containing [Hmim][BF_4], 2-methyl-2-propanol, and propylamin compounds at 298.15 K using PFP theory

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ABSTRACT

Density and viscosity of pure components 1-hexyl-3-methylimidazoliumtetrafluoroborate ([Hmim][BF_4]), 2-methyl-2-propanol, and propylamin, along with binary mixtures of {x_1[Hmim][BF_4] + $x_2$2-methyl-2-propanol}, {x_1[Hmim][BF_4] + $x_2$propylamin}, and {$x_1$2-methyl-2-propanol + $x_2$propylamin}, and ternary mixture of {x_1[Hmim][BF_4] + $x_2$2-methyl-2-propanol + $x_3$propylamin} were measured over the entire composition range at atmospheric pressure and 298.15 K. The results of measuring the density and viscosity were used to calculate the excess molar volumes, partial molar volumes, and viscosity deviations. For all of the binary mixtures, the computed excess molar volumes were correlated by applying Redlich–Kister equation and Prigogine–Flory–Patterson (PFP) theory, while the obtained viscosities were correlated using McAllister, Hind, and Nissan equations. The obtained excess molar volumes, V_m^E, and viscosity deviations, $\Delta\eta$, of all of the binary mixtures and ternary mixture are negative over the entire composition range. The Cibulka equation was used to correlate the ternary excess molar volumes and viscosity deviations using the Redlich–Kister parameters of the binary mixtures.

1. Introduction

Ionic liquids (ILs) are a new type of chemical substances which can be considered as "green solvents" since they have specific physicochemical properties like negligible vapor pressure at room temperature and high solvating capacity for polar and non-polar compounds [1,2]. These compounds are of great interest due to their successful applications in chemical industries. Therefore, densities and viscosities of these substances are necessary data for the design of many technological processes. These data can also be used to calculate the excess functions which are helpful for understanding of intermolecular interactions in the binary mixtures containing a nonvolatile ionic liquid [3,4].

The physiochemical properties of binary mixtures containing imidazolium based ILs with organic polar solvents were studied by several researchers [5–8]. The molecular rearrangement in these solutions depends on the possibility of hydrogen bond formation between the imidazole rings themselves and between the imidazole ring and the polar solvent like alcohol [9] on the other hand, and a systematic decrease in the solubility was observed with an increase of the alkyl chain length of an alcohol.

Ionic liquids based on the 1-hexil-3-methylimidazolium cation, $[Hmim]^+$, are also among commonly studied ILs. There are some publications concerning the suitability of these ionic liquids in separating aliphatics from aromatics [10–12]. There are also several publications about the physicochemical properties of binary systems of $[Hmim]^+$ based ionic liquids with alkanols [13–17]. However, there is a lack of data on ternary excess molar volumes for IL $[Hmim]^+$ multi component systems [18–23].

This paper is a part of research on measurement and characterization of the excess properties of mixtures containing [Hmim][BF_4] as IL [24–26] with polar solvents. In this work, the density, ρ, and viscosity, η, for ternary mixture of {x_1[Hmim][BF_4] + $x_2$2-methyl-2-propanol + $x_3$propylamin} and its binary mixtures were measured at 298.15 K and atmospheric pressure. The obtained excess molar volumes were correlated by using Redlich–Kister equation [27] and Prigogine–Flory–Patterson (PFP) theory [28–32]. The measured viscosities were also correlated by using some known correlations like McAllister [33], Hind [34], and Nissan [35] for comparing the applicability of them in correlating the experimental viscosities of the binary mixtures. The Cibulka equation [36] was applied to calculate the values of V_{123}^E and $\Delta\eta_{123}$ using the binary parameters of given binary mixtures that were obtained from Redlich–Kister equation.

2. Experimental

2.1. Materials

The chemicals were supplied by Merck Company with purities in mass fraction more than 99.8% for [Hmim][BF_4], and 99% for 2-methyl-2-propanol and propylamin. Doubly distilled and degassed water was used in density measurements. The water content of the IL was

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determined by Karl Fisher titration, and it was found to be less than 0.76 in mass fraction. The chloride content was found to be lower than 0.007 in mass fraction, using IC method. The purities of the components were verified by comparing the densities and viscosities with literature data [37–41], as are shown in Table 1.

2.2. Density measurements

The densities of all pure chemicals and their mixtures were measured using an Anton Paar DMA 4500 vibrating tube densimeter at temperature of 298.15 K. The accuracy in determining density was estimated to be $\pm 1 \times 10^{-5}$ g·cm^{-3}. The temperature in the cell was controlled with solid state thermostat. The apparatus was calibrated once a day with dry air and double distilled freshly degassed water. Each mixture was prepared by weighing, and was immediately used after it was mixed by shaking. All of the weightings were performed on an electronic digital balance model AB 204-N Mettler with accuracy of $\pm 1 \times 10^{-5}$ g. The error in mole fraction is estimated to be less than $\pm 1 \times 10^{-4}$. Conversion to molar quantities was based on the relative atomic mass table of 2006 issued by IUPAC [42]. The uncertainty in the excess molar volumes estimated to be $\pm 1 \times 10^{-4}$ cm^3·mol^{-1}.

2.3. Viscosity measurements

Viscosity measurements were carried out using an Ubbelohde viscometer which was fixed in a water bath and the temperature was controlled by a thermostat with a precision of ±0.01 K. The flow times were taken by using a digital chronometer model of KENKO KK-5898 with a precision of ±0.01 s. The viscosities were calculated via the following equation,

$$\eta = \rho(ct - k/t) \tag{1}$$

where c and k are viscometer constants, and t is the flow time in second. The k and c parameters were obtained by measurements on pure components at 298.15 K.

ILs usually have high viscosities, so the viscosity influence on the density of Eq. (1) should be evaluated. To determine the viscosity effect on the measured density values of pure IL and its mixture, a viscosity dependent correction term $\Delta\rho$ has been applied as [43],

$$\Delta\rho = \rho(-0.5 + 0.45\sqrt{\eta}) \times 10^{-4} \tag{2}$$

where ρ is the raw density and $\Delta\rho$ is the difference between the raw and corrected density, while the viscosity value, η, is in (mPa·s). The estimated error of the measured viscosities was $\pm 1 \times 10^{-2}$ mPa·s. Measurements of density and viscosity were repeated at least three times to get the best averaged values.

Table 1
Density, ρ, and viscosity, η, of pure components at 298.15 K compared with literature data.

Purity	ρ/g·cm^{-3}		η/mPa·s	
	Exp.	Lit.	Exp.	Lit.
[Hmim][BF$_4$]				
99.8%	1.14522	1.1454 [a]	171.8307	174.1 [b]
2-Methyl-2-propanol				
99%	0.78130	0.7812 [c]	4.4437	4.438 [d]
Propylamin				
99%	0.71102	0.7122 [e]	0.3585	0.356 [e]

[a] Ref. [37].
[b] Ref. [38].
[c] Ref. [39].
[d] Ref. [40].
[e] Ref. [41].

3. Results and discussion

3.1. Binary mixture

Table 2 shows the values of densities, excess molar volumes, viscosities and viscosity deviations for binary mixtures of {x_1[Hmim][BF$_4$] + $x_2$2-methyl-2-propanol}, {x_1[Hmim][BF$_4$] + $x_2$propylamin}, and {$x_1$2-methyl-2-propanol + $x_2$propylamin} calculated via the following equations,

$$V_m^E = \sum_{i=1}^{2}(x_i M_i)\left(\rho^{-1} - \rho_i^{-1}\right) \tag{3}$$

$$\Delta\eta = \eta - x_1\eta_1 - x_2\eta_2 \tag{4}$$

which are valid for ternary mixtures, as well. In Eqs. (3) and (4), x_i, M_i, ρ_i, and η_i refer to mole fraction, molecular weight, density, and viscosity of pure components respectively and quantities without subindex refer to the property of the mixture.

Table 2
Density, ρ, excess molar volume, V_m^E, viscosity, η, and viscosity deviation, $\Delta\eta$, for the given binary mixtures at 298.15 K.

x_1	ρ	V_m^E	η	$\Delta\eta$
	g·cm^{-3}	cm^3·mol^{-1}	mPa·s	mPa·s
{x_1IL + $x_2$2-methyl-2-propanol}				
0.0000	0.1017	0.0000	4.444	0.000
0.1993	0.2993	−0.1335	11.002	−10.465
0.3991	0.5008	−0.2288	13.923	−23.887
0.5992	0.6926	−0.2931	17.996	−36.541
0.8551	0.9000	−0.3281	23.303	−47.945
1.0000	0.78114	−0.3372	34.096	−54.173
0.85854	0.91696	−0.3191	49.753	−54.992
0.96527	1.00495	−0.2799	69.192	−51.177
1.03866	1.06627	−0.1596	115.563	−31.006
1.08883	1.12150	−0.1144	131.432	−23.662
1.12933	1.14522	0.0000	171.831	0.000
{x_1IL + $x_2$propylamin}				
0.0000	0.0988	0.0000	0.358	0.000
0.1934	0.2995	−1.1381	1.672	−15.624
0.4009	0.4948	−1.7161	4.466	−29.051
0.6197	0.7041	−2.0612	10.104	−41.609
0.8051	0.8475	−2.1650	17.700	−51.399
1.0000	0.71100	−2.0735	29.076	−56.132
0.81891	0.89439	−1.7548	50.283	−56.334
0.95825	1.00503	−1.4333	69.172	−51.922
1.03928	1.07519	−0.9605	97.253	−41.158
1.09483	1.11460	−0.7501	109.963	−35.711
1.12198	1.14522	0.000	171.831	0.000
{$x_1$2-methyl-2-propanol + $x_2$propylamin}				
0.0000	0.71102	0.0000	0.358	0.000
0.0967	0.72080	−0.2486	0.512	−0.242
0.2039	0.73035	−0.4019	0.727	−0.464
0.3012	0.73860	−0.5172	0.969	−0.620
0.4000	0.74648	−0.5993	1.263	−0.729
0.4992	0.75374	−0.6282	1.614	−0.784
0.5874	0.75963	−0.6053	1.975	−0.783
0.6813	0.76540	−0.5397	2.415	−0.726
0.7999	0.77204	−0.4049	3.090	−0.567
0.9183	0.77785	−0.1972	3.806	−0.303
1.0000	0.78130	0.0000	4.444	0.000
0.0000	0.71102	0.0000	0.358	0.000
0.0967	0.72080	−0.2486	0.512	−0.242
0.2039	0.73035	−0.4019	0.727	−0.464
0.3012	0.73860	−0.5172	0.969	−0.620
0.4000	0.74648	−0.5993	1.263	−0.729
0.4992	0.75374	−0.6282	1.614	−0.784
0.5874	0.75963	−0.6053	1.975	−0.783
0.6813	0.76540	−0.5397	2.415	−0.726
0.7999	0.77204	−0.4049	3.090	−0.567
0.9183	0.77785	−0.1972	3.806	−0.303
1.0000	0.78130	0.0000	4.444	0.000