

Volumetric and Viscosity Properties for the Binary Mixtures of 1-Hexyle-3-Methylimidazolium Tetrafluoroborate with Propyl Acetates

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Abstract

In the research work carried on, densities and viscosities for the binary mixtures of 1-hexyle-3-methylimidazolium tetrafluoroborate, $[C_6mim][BF_4]$, with propyl acetate, have been calculated at 298 K. These data were used to calculate the excess molar volumes (V_m^E) for the mixtures. It is shown that values of V_m^E are negative, in the whole concentration range. The V_m^E values show their minimum at the composition of $\chi_{IL} \approx 0.3$, exhibit a maximum at the same mole fraction. For the binary systems, the absolute values of V_m^E decrease in the propyl acetate. The results are discussed in terms of the ion-dipole interactions between cations of the ionic liquid and the organic molecules and hydrogen bonding interactions between anions of the ionic liquid and the organic compounds.

Keywords: 1-hexyle-3-methylimidazolium tetrafluoroborate, Density, Viscosity, Excess molar volume, Viscosity deviation, propyl acetate.

1. Introduction

Ionic liquids (ILs) have been used as intriguing solvents in many fields [1-6] of chemistry due to their strong solvating ability, very low volatility, wide liquid temperature range, wide electrochemical [7-9] window and so forth. Although ILs have shown excellent performance in organic catalysis and synthesis, separation and extraction [10], material preparation and electrochemical and energy fields, the fundamental physicochemical properties for both pure ILs and their mixtures with molecular solvents are still necessary. Among these properties, densities and viscosities are essential for the design of many technological processes, and information abstracted from these properties is also very useful for understanding solute-solvent and solute-solute interactions in the mixtures. In this work, densities and viscosities for the binary mixtures of 1-hexyle-3-methylimidazolium tetrafluoroborate, $[C_6mim][BF_4]$, with propyl acetate, are calculated at the temperature 298.15 K. From these data, the excess molar volumes V_m^E for the mixtures have been calculated and correlated using Redlich-Kister polynomials. The negative V_m^E values, their changing tendency with composition of the mixtures are discussed in terms of the ion-dipole interactions between cation of the IL and the organic compounds, the hydrogen bond interaction between anion of the IL and the organic molecules, as well as the packing efficiency.

2 Experimental methods

2.1 Materials preparation

The ILs, $[C_6mim][BF_4]$, was prepared and purified [11-12] according to the procedures. The IL was dried under vacuum at 343 K, to remove trace amounts of water and to minimize its effect on the density and viscosity measurements. The water content was found to be 0.02 mass % as measured by using Karl-Fisher titration. Other impurities that can affect the physical properties [13-14] can be determined. Propyl acetate was purchased from Beijing Xudong Chemical Factory mass purity greater than 99.5 %.

2.2 Methods

Mixtures were prepared by mass on the mole fraction scale[15-16]. The densities were measured using an Anton Paar DMA 60/602 vibrating-tube digital densimeter with an uncertainty of $\pm(5.9 \times 10^{-5}) \text{ g cm}^{-3}$ [17-18]. The temperature around the densimeter cell was controlled by circulating water from a constant temperature bath (Schott, Germany). A CT-1450 temperature controller and a CK-100 ultracryostat were employed to maintain the bath temperature to $(298.15 \pm 0.01) \text{ K}$. The densimeter was calibrated with deionized, doubly distilled water and dry air from time to time at the temperature 298 K. Mixtures viscosities were measured with a suspended level Ubbelohde viscometer, which was placed in a water thermostat (Schott, Germany) and had a flow time of about 200 s for water at the temperature 298 K. The temperature of the water thermostat was controlled to be as precise as in the density measurements. The viscometer was calibrated using the efflux time of water at the temperatures 298 K.

The viscosity of solution is given by the following equation:

$$\eta/q = ct - k/t \quad (1)$$

where c and k are the cell constants, t is the flow time (in seconds). Two Ubbelohde viscometers were used in the experiments because the difference in viscosity is large between the IL and organic solutes. The cell constants are $c_1 = (0.3129 \times 10^3) \text{ cm}^2 \text{ s}^{-2}$, $k_1 = 0.1529 \text{ cm}^2$ and $c_2 = (0.03083 \times 10^3) \text{ cm}^2 \text{ s}^{-2}$, $k_2 = 2.0954 \text{ cm}^2$, respectively. For every sample, the measurement was repeated at least three times, and the results were averaged.

3 Results and Discussion

The experimental densities and viscosities for the pure components determined in this work and those reported in the Tables. The results show that the values are in good agreement with the theoretical values for $[\text{C}_6\text{mim}][\text{BF}_4]$. Collected the experimental data of the densities and viscosities for the binary mixtures of $[\text{C}_6\text{mim}][\text{BF}_4]$ with propyl acetate, the whole concentration range at 298 K. The excess molar volume, V_m^E , and the viscosity deviation, for the systems are calculated, respectively, by the following equations:

$$V_m^E = [\chi M_1 + (1-\chi)M_2]/q - [\chi M_1/q_1 + (1-\chi)M_2/q_2] \quad (2)$$

where q_1 , q_2 , and q in Eq. 2 are the densities of the ILs, molecular compounds and their mixtures respectively. M_1 and M_2 are the molar masses of the IL and organic compounds, and χ is the mole fraction of IL in the mixtures. The values for these properties are also numerically included in Tables. The excess molar volumes and viscosity deviations were fitted to the Redlich–Kister polynomials.

$$Y^E = \chi(1-\chi)\sum B_j(1-2\chi)^j \quad (3)$$

where Y^E refers to V_m^E the coefficients B_j were obtained by fitting equation (3) to the experimental data using a least-squares regression method. The calculated values of B_j are presented in Table 3 along with the standard deviations of the fit. The V_m^E values for the binary systems of $[\text{C}_6\text{mim}][\text{BF}_4]$ with propyle acetate are found to be negative in the whole concentration range and have their minimum at the ionic liquid mole fraction of about 0.3 ($\chi = 0.3$). This change tendency is similar to the results reported by us for the systems of $[\text{C}_6\text{mim}][\text{BF}_4]$ and with some organic compounds $[\text{BF}_4]$. In those investigations, we suggested that the negative V_m^E values are contributions from both the accommodation of organic molecules in the interstice of the ionic liquid networks and the ion–dipole interactions between the organic molecules and cation of the ionic liquid. Therefore, the absolute value of V_m^E ($|V_m^E|$) is an indicative to the difference in the packing efficiency and the interaction intensity.

Table 1 The comparison of experimental densities (ρ) and viscosities (η) with literature values for [C₆mim][BF₄] and propyl acetate at T = 298.15 K

IL/organic compound	$\rho/\text{g.cm}^{-3}$		$\eta/\text{mPa} \cdot \text{s}$	
	Expt.	Lit.	Expt.	Lit.
[C ₆ mim][BF ₄]	1.10502	1.0912 ± 0.0065	336.3	–
Propyl acetate	0.88120	0.88210	0.56	--

Table 2 Experimental densities, absolute viscosities for the $\{\chi [\text{C}_6\text{mim}][\text{BF}_4] + (1-\chi)\}$ molecular solvents at T = 298.15 K.

X	$\rho/\text{g. Cm}^{-3}$	$V_m^E/(\text{cm}^3 \text{mol}^{-1})$	$\eta/(\text{mPa} \cdot \text{s})$	$(\ln \eta)^E$
[C ₆ mim][BF ₄] + propyl acetate				
0	0.80987	0	0.398	0
0.0492	0.84571	-0.143	0.712	0.323
0.0988	0.87912	-0.341	0.994	0.447
0.2011	0.93615	-0.796	2.059	0.638
0.2989	0.99157	-1.014	4.063	0.689
0.3482	1.02053	-1.044	5.978	0.688
0.3972	1.03728	-1.068	7.507	0.696
0.4605	1.04618	-1.049	15.08	0.687
0.4981	1.05705	-0.987	18.673	0.663
0.5512	1.07013	-0.909	28.517	0.637
0.6057	1.08275	-0.814	34.459	0.595
0.7054	1.10284	-0.571	43.382	0.514
0.7955	1.12938	-0.347	79.399	0.421
0.8931	1.13237	-0.155	130.337	0.289
1	1.16617	0	216.367	0

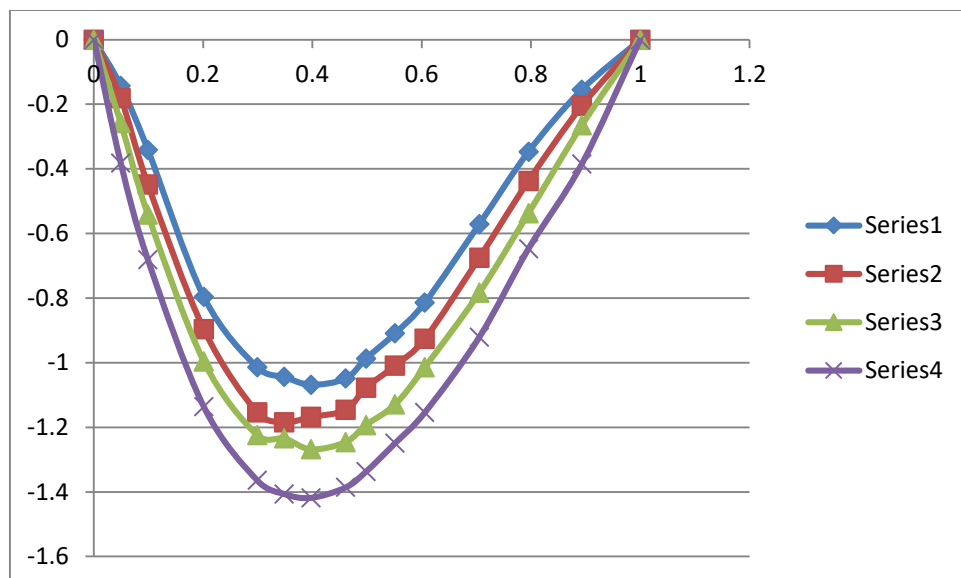


Fig 1: excess molar volumes values

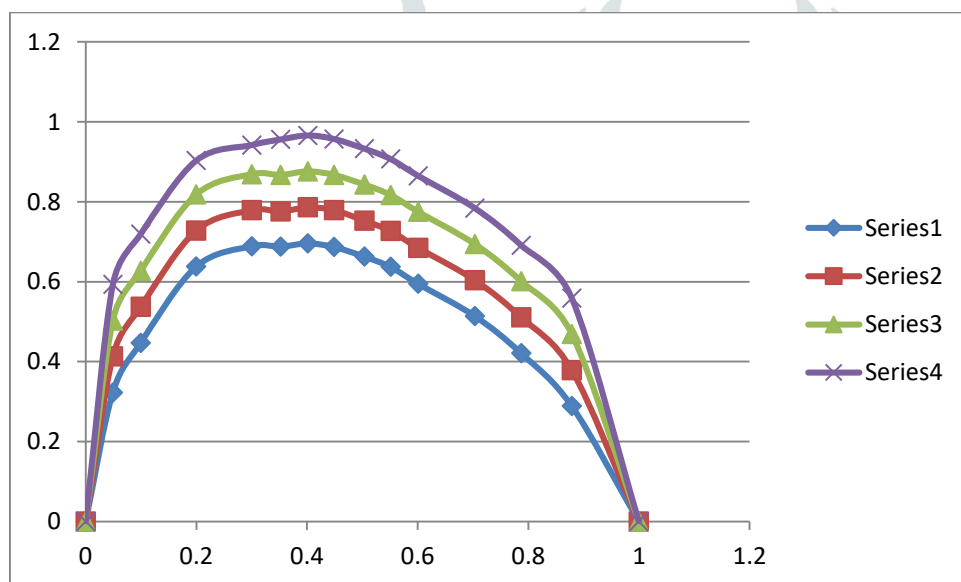


Fig 2: excess logarithmic viscosity values
viscosity

4 Conclusion

In this work, the excess molar volumes and viscosity deviations for the binary systems of [C₆mim][BF₄] with propyl acetate have been determined the values of excess molar volume are negative and those of excess molar volumes are positive and those of excess logarithmic viscosity are positive in the over the whole concentration range from experimental density and viscosity measurements. It was shown that: (i) the effect of the organic molecules investigated on the excess molar volumes follows in the order of [C₆mim][BF₄] > propyl acetate and this order is in agreement with the order of dielectric constants of the organic compounds; (ii) the effect of the cation of the ILs on the excess molar volumes of the mixtures follows in the order of [C₆mim][BF₄] > propyl acetate.

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