## Research Article

# VOLUMETRIC AND VISCOSITY PROPERTIES FOR THE BINARY MIXTURES OF 1-HEXYLE-3-METHYLIMIDAZOLIUM TETRAFLUOROBORATE WITH BUTYL ACETATE

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**ABSTRACT**

In this work, densities and viscosities for the binary mixtures of 1-hexyle - 3-methylimidazolium tetrafluoroborate, $[C_6mim][BF_4]$, with butyl acetate, have been determined at 298.15 K. These data were used to calculate the excess molar volumes $V^E_m$ for the mixtures. It is shown that values of $V^E_m$ are negative, in the whole concentration range. The $V^E_m$ 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 $V^E_m$ decrease in the butyl 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.

## INTRODUCTION

Ionic liquids (ILs) have been used as intriguing solvents in many fields of chemistry due to their strong solvating ability, very low volatility, wide liquid temperature range, wide electrochemical window and so forth[1-2]. Although ILs have shown excellent performance in organic catalysis and synthesis[3-5], separation and extraction[6-8], material preparation[9-11] and electrochemical and energy fields[12-14], 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[15-19].In this work, densities and viscosities for the binary mixtures of 1- hexyle - 3-methylimidazolium tetrafluoroborate, $[C_6mim][BF_4]$, with butyl acetate, at the temperature 298.15 K. From these data, the excess molar volumes $V^E_m$ for the mixtures have been calculated and correlated using Redlich– Kister polynomials. The negative $V^E_m$ values, their changing tendency with composition of the mixtures are discussed in terms of the ion–dipole interactions between cation of the ILs and the organic compounds, the

hydrogen bond interaction between anion of the ILs and the organic molecules, as well as the packing efficiency.

*Experimental methods*

*Materials*

The ILs, $[C_6mim][BF_4]$, was prepared and purified according to the procedures[20-21]. The ILs was dried under vacuum at 343 K, to remove trace amounts of water and to minimize its effect on the density and viscosity measurements[15]. 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 can be determined. Butyl acetatewas purchased by Beijing Xudong Chemical Factory mass purity greater than 99.5 %.

*Methods*

Mixtures were prepared by mass on the mole fraction scale. The densities were measured using an Anton Paar DMA 60/602 vibrating-tube digital densimeter with an uncertainty of $\pm(5.9 \times 10^{-5})$ gcm$^{-3}$ . 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

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maintain the bath temperature to (298.15 ± 0.01) K. The densimeter was calibrated with deionized, doubly distilled water and dry air from time to time at the temperature 298.15 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 temperature298.15 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 298.15 K.The solution viscosity[25] is given by the following equation:

$$\eta/\rho = ct - k/t \qquad (1)$$

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 ILs and organic solutes. The cell constants are $c_1 = (0.3129 \times 10^3)$ cm$^2$ s$^{-2}$, $k_1 = 0.1529$ cm$^2$ and $c_2 = (0.03083 \times 10^3)$ cm$^2$ s$^{-2}$, $k_2 = 2.0954$ cm$^2$, respectively. For every sample, the measurement was repeated at least three times, and the results were averaged.

## RESULTS AND DISCUSSION

The experimental densities and viscosities for the pure components determined in this work and those reported in literatures are collected and compared in Table 1. The results show that the values are in good agreement with the literature data except the viscosity value for [C$_6$mim][BF$_4$]. Collected in Table 2 are the experimental data of the densities and viscosities for the binary mixtures of [C$_6$mim][BF$_4$] with butyl acetate, the whole concentration range at 298.15 K. The excess molar volume, $V^E_m$, and the viscosity deviation, for the systems are calculated, respectively, by the following equations:

$$V^E_m = [\chi M_1 + (1-\chi)M_2]/\rho - [\chi M_1/\rho_1 + (1-\chi)M_2/\rho_2)] \qquad (2)$$

where$\rho_1$, $\rho_2$, and $\rho$ in Eq. 2 is the densities and viscosities of the ILs, molecular compounds and their mixtures respectively. $M_1$ and $M_2$ are the molar masses of the ILs and organic compounds, and $\chi$ is the mole fraction of ILs in the mixtures. The values for these properties are also numerically included in Table 2. The excess molar volumes and viscosity deviations were fitted to the Redlich–Kister polynomials.

**Table 1** The comparison of experimental densities ($\rho$ ) and viscosities (ɳ) with literature values for [C6mim][BF4] and butyl acetate at T = 298.15 K

| IL/organic compound | $\rho$ /g.cm$^{-3}$ | | ɳ /mPaXs | |
|---|---|---|---|---|
| | Expt. | Lit. | Expt. | Lit. |
| [C$_6$mim][BF$_4$] | 1.10502 | 1.0912 ± 0.0065 [22] | 336.3 | – |
| Butyl acetate | 0.87619 | 0.87616[23] | 0.70 | -- |

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

| χ | $\rho$ /(g. Cm$^{-3}$) | $V^E_m$/(cm$^3$ mol$^{-1}$ ) | ɳ /(mPaXs) |
|---|---|---|---|
| | | [C$_6$mim][BF$_4$] + butyl acetate | |
| 0.00 | 0.87619 | 0.00 | 0.70 |
| 0.0501 | 0.89922 | -0.315 | 1.14 |
| 0.0935 | 0.91726 | -0.465 | 1.76 |
| 0.1993 | 0.95571 | -0.628 | 4.31 |
| 0.2925 | 0.98417 | -0.863 | 8.27 |
| 0.3460 | 0.99851 | -1.378 | 11.56 |
| 0.3976 | 1.01086 | -1.575 | 15.79 |
| 0.4452 | 1.02175 | -1.620 | 20.31 |
| 0.4980 | 1.03281 | -1.639 | 27.13 |
| 0.5488 | 1.04225 | -1.477 | 34.10 |
| 0.6009 | 1.05175 | -1.295 | 45.91 |
| 0.6998 | 1.06745 | -1.103 | 74.34 |
| 0.8011 | 1.08198 | -0.913 | 124.44 |
| 0.8860 | 1.09257 | -0.771 | 187.41 |
| 1.00 | 1.10502 | 0.00 | 336.3 |



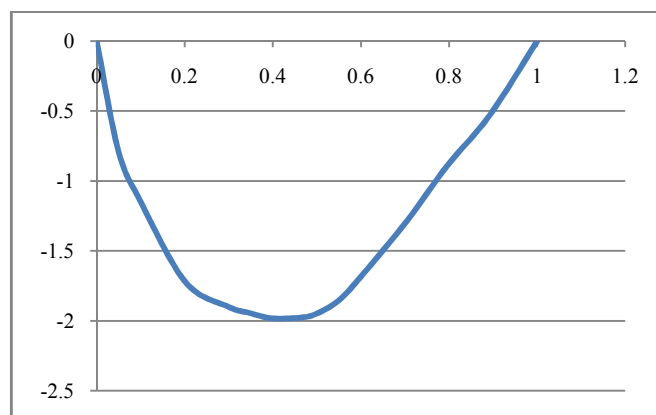**Table 3** Derived parameters and standard deviations (SD) of the fit for the excess molar volume of the [C$_6$mim][BF$_4$] + butyl acetate mixtures at T = 298.15 K.

| | $B_0$ | $B_1$ | $B_2$ | $B_3$ | SD |
|---|---|---|---|---|---|
| | | [C$_6$mim][BF$_4$] + butyl acetate | | | |
| $V^E_m$ | -4.765 | -1.474 | -0.356 | 0.628 | 0.011 |

## CONCLUSION

In this work, the excess molar volumes and viscosity deviations for the binary systems of [C$_6$mim][BF$_4$] with propyl acetate have been determined 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 [C$_6$mim][BF$_4$] >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 [C$_6$mim][BF$_4$] >propyl acetate.

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