Volumetric and Viscosity Properties for the Binary Mixtures of 1-hexyle-3-methylimidazolium Tetrafluoroborate with methyl Acetates

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Abstract: *In this work, densities and viscosities for the binary mixtures of 1- **hexyle** - 3-methylimidazolium tetrafluoroborate, [C6mim][BF4], with methyl acetate, have been determined at 298.15 K. These data were used to calculate the excess molar volumes V^E_m and the viscosity deviations (lng) E for the mixtures. It is shown that values of VE m are negative, while those of (lng) E are positive in the whole concentration range. The VE m values show their minimum at the composition of xIL & 0.3, and the (lng) E values exhibit a maximum at the same mole fraction. For the binary systems, the absolute values of VE m decrease in the order: butanone[methyl acetate [ethyl acetate [propyl acetate[butyl acetate, whereas those of (lng) E decrease in the order: methyl acetate [ethyl acetate [propyl acetate [butyl acetate [butanone. 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 Ionic liquid 1-Octyl-3-methylimidazolium tetrafluoroborate Density Viscosity Excess molar volume Viscosity deviation 1 I1 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 solventsare 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].*

I. INTRODUCTION

In this work, densities and viscosities for the binary mixtures of---------- methyl acetate, at the temperature 298.15 K. From these data, the excess molar volumes VE for the mixtures have been calculated and correlated using Redlich– Kister polynomials. The negative VE m 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.

II. EXPERIMENTAL

2.1 Materials

The IL, [C6mim][BF4], was prepared and purified according to the procedures described in the literature [20, 21]. The IL was dried under vacuum at, 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 are the residual sodium and bromide ions [17, 22]. Methyl acetate (Beijing Xudong Chemical Factory, mass purity greater than 99.5 %),

2.2 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 ±(5 9 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 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 298.15Flow-time measurements were performed by a Schott AVS310 photoelectric time unit with a resolution of 0.01 s. The uncertainty in the experimental viscosity is lower than ±0.5 mPas for the viscosity values larger than 200 mPas, and ±0.01 mPas for the viscosity values less than 200 mPas. The solution viscosity is given by the following equation: g=q ¼ ct k=t ð1Þ 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 c1 = (0.3129 9 10-3) cm2 s -2 , k1 = 0.1529 cm2 ; c2 = (0.03083 9 10-3) cm2 s -2 , k2 = 2.0954 cm2 , respectively. The details of the experimental procedure are given elsewhere [24]. For every sample, the measurement was repeated at least three times, and the results were averaged.

III. 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 [C6mim][BF4] which is not available in literature [25–29].

Collected in Table 2 are the experimental data of the densities and viscosities for the binary mixtures of [C6mim][BF4] with methyl acetate, the whole concentration range at 298.15 K. The excess molar volume, VE m, and the viscosity deviation, for the systems are calculated, respectively, by the following equations:

VE m ¼ ½xM1 þ ð1 xÞM2=q ½xM1=q1 þ ð1 xÞM2=q2   ð2Þ

ðlngÞ E = lng ½xlng1þð1 xÞ lng2   ð3Þ

where q1, q2 and q in Eq. 2 and g1, g2 and g in Eq. 3 are the densities and viscosities of the

Table 1 The comparison of experimental densities (q) and viscosities (g) with literature values for [C6mim][BF4] and the organic compounds at T = 298.15 K

IL/organic compound	q/gcm-3		g/mPas	
	Expt.	Lit.	Expt.	Lit.
[C6mim][BF4]	1.10502	1.0912 ± 0.0065 [25]	336.3	–
Methyl acetate	0.92690	0.92705 [27] a	0.38	0.368 [27] a

a The purity reported is greater than 99.5 %, and used without further purification.
b The purity reported is great than 99.9 % and used without further purification

Table 2 Experimental densities and absolute viscosities for the mixtures of x[C8mim][BF4] ? (1 - x) organic compound at T = 298.15 K

x	q/gcm-3	g/mPas
[C6mim][BF4] ? methyl acetate		
0.00	0.92690	0.39
0.0485	0.95808	0.63
0.1011	0.98388	1.03
0.1990	1.01799	2.29
0.2973	1.04118	5.04
0.3481	1.05037	7.54
0.3944	1.05759	10.26
0.4488	1.06491	13.82
0.5036	1.07144	18.40
0.5489	1.07606	24.78
0.5937	1.08008	34.24
0.7036	1.08894	69.93
0.8010	1.09480	100.30
0.8827	1.09975	187.80
1.00	1.10502	336.3

IL, molecular compounds and their mixtures, respectively. M1 and M2 are the molar masses of the IL and organic compounds, and x is the mole fraction of IL in the mixtures. The values for these properties are also numerically included in Table 2 and are graphically presented in Figs. 1 and 4. The excess molar volumes and viscosity deviations were fitted to the Redlich–Kister polynomials [30]: YE ¼ xð1 xÞ X j 0 Bjð1 2xÞj ð4Þ where YE refers to VEthe Bj are the polynomial coefficients, and j is the polynomial degree, respectively. The

coefficients Bj obtained by fitting Eq. 4 to the experimental results using a least-squares regression method are presented in Table 3 along with the standard deviations of the fit.

It was found that the VE m values for the binary mixtures of [C6mim][BF4] with butanone or alkyl acetates are all negative in the whole concentration range. Similar results have been reported for systems involving imidazolium-based ILs with different organic compounds [16, 18, 19, 31]. The negative VE m values are suggested to result mainly from ion– dipole interactions between the organic molecules and cation of the ILs as well as the accommodation of organic molecules in the interstices of the IL networks. Therefore, the absolute values of VE m is an indicator to the intensity of ion–dipole interactions between the organic molecules and the IL and the packing efficiency of the systems.

ganic molecules and the IL and the packing efficiency of the systems. For the [C8mim][BF4] ? butanone or alkyl acetates binaries investigated in this work, it was found that the absolute values of the excess molar volumes (VE m) in the organic compound-rich region decrease . Therefore, the strength of ion– dipole interactions between cation of the IL and the organic molecules decreases, which then leads to the decrease of the absolute values of the excess molar volumes in the binarysystems. However, in the IL-rich region, the order for the absolute values of the excess molar volumes is complicated, suggesting that the packing effect is more efficient in the IL-rich region, while the contribution of ion–dipole interactions to the volume properties are more prominent in the organic molecule-rich region.

Table 3 Derived parameters and the standard deviations (SD) of the fit for the excess molar volumes and viscosity deviations of the binary mixtures involving [C8mim][BF4] at T = 298.15 K

	B0	B1	B2	B3	SD
[C8mim][BF4] ? methyl acetate					
VE m	-5.231	-3.601	-2.745	-1.722	0.026

IV. CONCLUSION

In this work, the excess molar volumes and viscosity deviations for the binary systems of [C8mim][BF4] with methyl 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 the order: [C8mim][BF4] >methyl 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 the order: : [C6mim][BF4] >methyl acetate

Based on these observations, we suggested that: (i) the ion–dipole interactions between the cation of [C8mim][BF4] and the organic compounds are the main factors controlling the excess molar volumes, but in the IL-rich region, the packing efficiency coming from structure effect of organic compounds are also important.