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Physics

A VOLUMETRIC AND VISCOSITY STUDY FOR BINARY MIXTURES OF 1-HEXYLE-3 METHYLIMIDAZOLIUM TETRAFLUOROBORATE WITH ETHYL ACETATE.

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ABSTRACT Information on the interactions between ionic liquids and molecular solvents are essential properties for the understanding of the function of ionic liquids in related procedures, and excess properties are sensitive probe for these interactions. In this work carried on, excess molar volume (VEm) for the binary mixtures of 1-hexyl-3-methylimidazolium tetrafluoroborate ([C6mim][BF4]) with, ethyl acetate at the temperature of 298.15 K is calculated. It is found that for the studied systems, the values of VEm are negative. The results have been analyzed through the ion–dipole interaction.

KEYWORDS : 1-hexyl-3-methylimidazolium tetrafluoroborate, ionic liquids, ethyl acetate, excess molar volume.

Introduction

Ionic liquids (ILs) have attracted great attention in green chemistry due to their unique properties[1-2] and some successful applications in chemical industry[3-5]. However, fundamental physicochemical properties for the systems involving ionic liquids are still in a great necessary[6-12]. Densities and viscosities for these systems are essential data for the design of many technological processes. At the same time, these data can be used to calculate the excess molar volumes, which are useful for the understanding of intermolecular interactions in the systems[13-15]. A frequently studied ionic liquid, 1-hexyl-3-methylimidazolium tetrafluoroborate [C6mim][BF4] has been used in separation/extraction[16], polymerization[17] . Therefore, in this work, densities and viscosities for the binary mixtures of [C6mim][BF4] with ethyl acetate have been determined over the whole composition range at the temperature of 298.15 K is calculated. From these data, excess molar volumes, VEm for the mixtures have been calculated and then correlated by using Redlich–Kister polynomials. The results have been discussed from the ion–dipole interaction. The information obtained allows us to show how physical properties of molecular solvents affect their interaction with the ionic liquid.

Experimental Techniques

Materials preparation

[C6mim][BF4] was prepared and purified by the procedures described in the literature[18-20]. Because trace amounts of water in ILs can have a dramatic effect on their thermodynamic and transport properties, [C6mim][BF4] was dried under vacuum at 343 K for 2 to 3 days before use. The water content was found at 0.002 mass fraction in the IL, as measured by using Karl–Fisher titration. The other impurities that can affect the physical properties include the residual sodium and bromide [21]. The mass purity of [C6mim][BF4] was estimated to be greater than 0.999(Shanghai Chemical Factory, mass purity greater than 0.995).

Methods

Mixtures were prepared by mass on the molality concentration scale. Every precaution was taken to minimize the contamination by water in the atmosphere. An Anton Paar DMA60/602 vibrating-tube digital densimeter was used to measure the solution densities with an uncertainty of $\pm(5.0 \times 10^{-5})$ g cm-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 of 298.15 K. Solution 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 200s for water at the temperature of 298.15 K. The temperature of the water thermostat was controlled to be as precise as the density measurements. The viscometer was calibrated using the efflux time of water at the temperatures of (298.15 K). Flow-time measurements were performed by a Schott AVS310 photoelectric time unit with a resolution of 0.01s. The estimated error for the experimental viscosity was $\pm 1\%$ mPa X s. The solution viscosity is given by the following equation:

$$\eta/\rho = ct-k/t$$

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 great between the ionic liquid and the organic compounds. The cell constants are c1 = (0.3129X103) cm2 s-2 , k1 = 0.1529 cm2 and c2 = (0.03083X103) cm2 s-2 , k2 = 2.0954 cm2 , respectively[22]. Measurements of densities and viscosities were repeated at least four times for all the mixtures, and the results were averaged.

Results and discussion

Table 1 lists the density and viscosity data for the pure components determined in this work. For the comparison purpose, those reported in literature have also been included in this table. It can be seen that the values for [C6mim][BF4] and the organic compounds are in good agreement with the literature values [23-24]. The experimental density and viscosity data at the temperature of 298.15 K for the binary mixtures of [C6mim][BF4] with ethyl acetate have been calculated by the following equations:

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

where ρ_1, ρ_2, and ρ in equation (2) are the densities of the IL, organic compounds, and their mixtures, respectively. M1 and M2 are the molar mass of the IL and organic compounds, and χ is the mole fraction of ionic liquid in the mixtures. These data have been fitted to the Redlich–Kister polynomial:

$$Y^E = \chi(1-\chi)\Sigma B_j(1-2\chi)^j$$

where YE refers to VE m the coefficients Bj were obtained by fitting equation (3) to the experimental data using a least-squares regression method. The calculated values of Bj are presented in Table 3 along with the standard deviations of the fit. The VEm values for the binary systems of [C6mim][BF4] with ethyle 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 [C6mim][BF4] and with some organic compounds. In those investigations, we suggested that the negative VEm 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.
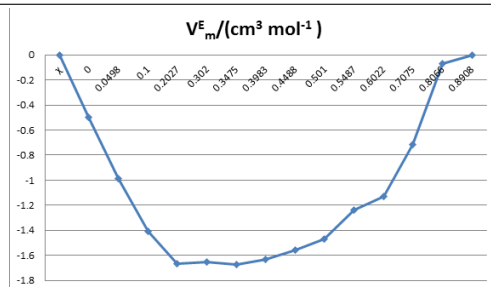
TABLE 1

Comparison of the experimental densities (ρ) and viscosities ( ) with literature values for the ionic liquid and molecular solvents at T = 298.15 K.

IL/organic compound	ρ /(g cm^{-3})		η/(mPaXs)	
	Expt.	Lit.	Expt.	Lit.
[C$_6$mim][BF$_4$]	1.14670	1.15[23]	195.367	---
Ethyl acetate	0.89448	0.8946[24]	0.439	0.430

TABLE 2

Experimental densities, absolute viscosities, excess molar volumes for the {χ [C6mim][BF4] + (1-χ) } molecular solvents at T = 298.15 K.

χ	ρ /(g. Cm^{-3})	V^E_m/(cm^3 mol^{-1})	η /(mPaXs)
	[C$_6$mim][BF$_4$] + ethyl acetate		
0.00	0.89448	0.00	0.437
0.0498	0.92556	-0.505	0.738
0.1000	0.95269	-0.905	1.188
0.2027	0.99778	-1.428	2.674
0.3020	1.03152	-1.663	5.221
0.3475	1.04435	-1.678	6.846
0.3983	1.05737	-1.675	9.328
0.4488	1.06889	-1.620	12.307
0.5010	1.07980	-1.559	16.471
0.5487	1.08862	-1.467	21.492
0.6022	1.09780	-1.345	28.479
0.7075	1.11373	-1.033	48.111
0.8066	1.12646	-0.713	80.426
0.8908	1.13569	-0.371	119.875
1.00	1.14670	-0.00	195.367

V^E_m/(cm^3 mol^{-1})

TABLE 3

Derived parameters and standard deviations (SD) of the fit for the excess molar volume and excess logarithmic viscosity of the [C6mim][BF4] + molecular solvents mixtures at T = 298.15 K.

	B$_0$	B$_1$	B$_2$	B$_3$	SD
	[C$_6$mim][BF$_4$] + ethyl acetate				
V^E_m	6.246	3.371	1.203	0.750	0.010

Conclusions

In this work, the volume and viscosity properties for the binary systems of ionic liquid [C6mim][BF4] with ethyle acetate It is found that the values of excess molar volume are negative the extremum at the composition of   0.3. The absolute values of the excess molar volumes VEm for the mixtures of [C6mim][BF4] > ethyl acetate. In the results suggest that the ion–dipole interactions and the hydrogen bond formation between the ionic liquid.

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