Densities and Viscosities of 1-Butyl-3-methylimidazolium Tetrafluoroborate + Molecular Solvent Binary Mixtures

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The densities and viscosities of 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF_4] ionic liquid with methyl formate, methyl acetate, ethyl formate, and acetone have been measured at 298.15 K. The excess molar volume V_m^E and the viscosity deviations $\Delta\eta$ for the binary mixture have been calculated and were fitted to the Redlich−Kister polynomials. The values of V_m^E and $\Delta\eta$ are negative over the whole composition range. The minima in V_m^E and $\Delta\eta$ are observed at about mole fraction of the ionic liquid, $x \approx$ 0.3 and 0.7, respectively.

Introduction

Ionic liquids (ILs) are a family of substances entirely constituted by ions with melting points below 373 K.[1] Ionic liquids are now being explored in virtually all areas of chemistry, as solvents for organic and inorganic synthesis, as electrolytes in batteries and solar cells, as new types of energetic materials, as stationary phases in chromatography, and in a variety of other analytical applications, as well as being the subject of fundamental study in physical chemistry.[2]

In spite of their importance and interest, accurate values for many of the fundamental physical−chemical properties of this ionic liquid are either scarce or absent.[3] To design any process involving ionic liquids on an industrial scale, it is necessary to know a range of physical properties including viscosity and density.[4] Moreover, knowledge of excess properties helps us develop an understanding of the interactions that determine the physical properties, making it easier to search for an optimal ionic liquid for a specific application. Nonetheless, ionic liquids research is still a relatively new field with insufficient available physical property data or work about correlation and prediction equations.[5]

In this work, we present data on the density and viscosity of mixtures consisting of methyl formate, methyl acetate, ethyl formate, and acetone with 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) ionic liquid over the entire composition range at 298.15 K. Moreover, the excess molar volumes V_m^E and the viscosity deviations $\Delta\eta$ were calculated and correlated with composition data using Redlich−Kister polynomials.

Experimental

Materials. [Bmim][BF_4] was prepared using the procedures described by Seddon and Holbrey.[6] Because trace amounts of water in ILs can have a dramatic effect on physical properties and phase behavior, the ILs were dried under vacuum at 343 K for (2 to 3) days before use. Karl−Fisher analysis of the samples subjected to this treatment indicated that the water mole fraction was reduced to 0.0016. Another impurity that can affect the physical properties is the residual sodium and chloride ions. A chloride content of 0.018 $mol \cdot kg^{-1}$ was determined in the ionic liquid by a chloride-selective electrode. A sodium content of 0.034 $mol \cdot kg^{-1}$ was detected with a Z-5000 polarized Zeeman atomic absorption spectrophotometer. Methyl formate (Shanghai Chemical Factory, A.R.), methyl acetate, and ethyl formate (Beijing Xudong Chemical Factory, A.R.) and acetone (Tianjin Chemical Factory, A.R.) were dried over $NaCO_3$ for several days and then twice distilled. All the purified solvents were stored over P_2O_5 in a desiccator before use. Water mass fraction for the four solvents analyzed by Karl−Fisher titration was less than 10^{-4}.

Methods. Mixtures were prepared by mass, and mole fraction was calculated. Every precaution was taken to minimize contamination by water. Solution densities were determined with an Anton Paar DMA 60/602 vibrating-tube digital densimeter. The uncertainty in the measurement is $\pm\ 1.5 \cdot 10^{-5}\ g \cdot cm^{-3}$. The temperature around the density meter cell was controlled to (298.15 ± 0.01) K using a CT-1450 temperature controller and a CK-100 ultracryostat. The densimeter was calibrated with known densities of pure water and dry air every day. 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 200 s for water at 298.15 K. The temperature of the water thermostat was controlled to ± 0.01 K. The two viscometers were calibrated individually using the efflux time of water and 1,4-butanediol at (298.15 and 308.15) K. Flow time measurements were performed by a Schott AVS 310 photoelectric time unit with a resolution of 0.01 s. Solution viscosity, η, was given by the following equation

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

where c and k are the viscometer constants. Since the viscosity values were greatly different for the ionic liquid and the organic solutes, two Ubbelohde viscometers were used in the experiments according to the varied viscosity values for the mixtures. The viscometer constants were $c_1 = 0.03104 \cdot 10^{-3}\ cm^2 \cdot s^{-2}$, $k_1 = 2.5637\ cm^2$ and $c_2 = 0.3129 \cdot 10^{-3}\ cm^2 \cdot s^{-2}$, $k_2 = 0.1529\ cm^2$ individually. The uncertainty of viscosity measurement was approximately ± 0.3 % for high viscosity samples (between

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Table 1. Comparison of Experimental Density (ρ) and Viscosity (η) with Literature Values for [Bmim][BF_4] and the Organic Compounds Investigated at 298.15 K

	$\rho/\mathrm{g\cdot cm^{-3}}$		$\eta/\mathrm{mPa\cdot s}$	
IL/solute	exptl	lit.	exptl	lit.
[Bmim][BF_4]	1.2111	1.208[7]	110.3	114;[2] 103.9[8]
methyl formate	0.96478	0.9663[9]	0.328	0.328[9]
methyl acetate	0.91597	0.91598[10]	0.379	0.379[10]
ethyl formate	0.92848	0.9285[11]	0.364	0.368[11]
acetone	0.78536	0.785[12]	0.312	0.316[12]

Table 2. Experimental Density (ρ), Viscosity (η), Excess Molar Volume (V_m^E), and Viscosity Deviations ($\Delta\eta$) for [Bmim][BF_4] + Organic Solute Mixtures at 298.15 K[a]

		ρ	η	V_m^E	$\Delta\eta$
x	w	$\mathrm{g\cdot cm^{-3}}$	$\mathrm{mPa\cdot s}$	$\mathrm{cm^3\cdot mol^{-1}}$	$\mathrm{mPa\cdot s}$
[Bmim][BF_4] + Methyl Formate					
0	0	0.96478	0.3	0	0
0.0500	0.1653	1.01172	0.5	−0.905	−5.3
0.1011	0.2974	1.04555	0.9	−1.335	−10.5
0.2030	0.4895	1.09140	1.9	−1.602	−20.7
0.2993	0.6165	1.12147	3.5	−1.632	−29.7
0.3395	0.6592	1.13120	4.4	−1.576	−33.2
0.3994	0.7145	1.14364	6.3	−1.453	−38.0
0.4498	0.7547	1.15273	8.2	−1.337	−41.6
0.4997	0.7899	1.16043	10.6	−1.183	−44.7
0.5482	0.8204	1.16719	13.7	−1.032	−46.9
0.5994	0.8492	1.17337	17.12	−0.841	−49.0
0.6999	0.8977	1.18234	28.3	−0.265	−49.0
0.7996	0.9376	1.19278	44.2	−0.099	−44.1
0.8993	0.9711	1.20231	68.4	−0.019	−30.8
1	1	1.21105	110.3	0	0
[Bmim][BF_4] + Methyl Acetate					
0	0	0.91597	0.4	0	0
0.0501	0.1386	0.96450	0.6	−1.477	−5.3
0.1004	0.2540	0.99604	0.9	−1.804	−10.5
0.1999	0.4326	1.04598	2.0	−2.155	−20.4
0.3031	0.5703	1.08458	3.6	−2.166	−30.1
0.3504	0.6220	1.09890	4.7	−2.072	−34.2
0.3995	0.6699	1.11224	6.2	−1.947	−38.1
0.4511	0.7149	1.12480	8.2	−1.786	−41.8
0.4993	0.7526	1.13601	10.2	−1.689	−45.1
0.5484	0.7875	1.14494	13.1	−1.394	−47.6
0.5995	0.8204	1.15395	16.3	−1.144	−50.0
0.6996	0.8766	1.16955	25.8	−0.635	−51.5
0.8000	0.9243	1.18288	40.8	−0.094	−47.5
0.8999	0.9648	1.19770	63.7	−0.033	−35.6
1	1	1.21105	110.3	0	0
[Bmim][BF_4] + Ethyl Formate					
0	0	0.92848	0.4	0	0
0.0500	0.1384	0.96120	0.6	−0.156	−5.3
0.1004	0.2540	0.98920	1.0	−0.203	−10.4
0.1986	0.4306	1.04081	2.0	−0.839	−20.2
0.3047	0.5721	1.08216	3.8	−1.106	−30.1
0.3560	0.6278	1.09826	5.1	−1.120	−34.4
0.4027	0.6729	1.11127	6.5	−1.091	−38.1
0.4523	0.7159	1.12369	8.5	−1.029	−41.6
0.4971	0.7510	1.13373	10.6	−0.937	−44.4
0.5443	0.7847	1.14334	13.3	−0.817	−46.9
0.5987	0.8199	1.15332	16.9	−0.649	−49.3
0.6976	0.8756	1.16916	26.6	−0.303	−50.5
0.7973	0.9231	1.18378	43.7	−0.057	−44.3
0.8996	0.9647	1.19830	69.0	−0.018	−30.3
1	1	1.21105	110.3	0	0
[Bmim][BF_4] + Acetone					
0	0	0.78536	0.3	0	0
0.0508	0.1724	0.84615	0.5	−0.958	−5.3
0.1006	0.3033	0.89439	0.7	−1.461	−10.6
0.2012	0.4950	0.97029	1.5	−1.942	−20.6
0.3022	0.6276	1.02698	3.0	−2.033	−30.8
0.3501	0.6770	1.04891	4.0	−1.976	−35.5
0.3975	0.7197	1.06829	5.2	−1.887	−39.4
0.4491	0.7603	1.08616	6.9	−1.616	−43.1
0.4965	0.7933	1.10246	9.0	−1.584	−46.0
0.5507	0.8267	1.11843	12.0	−1.384	−48.1
0.5998	0.8536	1.13138	15.1	−1.169	−51.1
0.7037	0.9024	1.15529	25.5	−0.679	−51.5
0.7982	0.9390	1.17432	40.1	−0.284	−47.9
0.8949	0.9707	1.19301	64.7	−0.131	−34.6
1	1	1.21105	110.3	0	0

[a] x is mole fraction of [Bmim][BF_4]; w is mass fraction of [Bmim][BF_4].

(25 and 110) mPa·s) and as much as ± 0.3 mPa·s and ± 0.1 mPa·s for low viscosity samples (below 25 mPa·s). Measurements of density and viscosity were repeated at least four times for all mixtures, and the results were averaged.

Results and Disscussion

A comparison is made for the pure components in Table 1 between the experimental density and viscosity determined in this work and those reported in the literature. It can be seen that the values for [Bmim][BF_4] and organic solutes agree well with those reported in the literature.

Experimental values of density and absolute viscosity at 298.15 K are collected in Table 2 for [Bmim][BF_4], methyl formate, methyl acetate, ethyl formate, acetone, and their mixtures over the whole composition range.

The excess molar volumes V_m^E and the viscosity deviations $\Delta\eta$ have been calculated using the following equations

$$V_m^E = [xM_I + (1-x)M_s]/\rho - [xM_I/\rho_I + (1-x)M_s/\rho_s] \tag{2}$$

$$\Delta\eta = \eta - x\eta_I - (1-x)\eta_s \tag{3}$$

where ρ_I, ρ_s, and ρ in eq 2 and η_I, η_s, and η in eq 3 are the densities and viscosities of [Bmim][BF_4], the organic solutes, and their mixtures at 298.15 K, respectively. M_I and M_s are the molar mass of [Bmim][BF_4] and the organic solutes, and x is the mole fraction of [Bmim][BF_4] in the mixtures. Values of V_m^E and $\Delta\eta$ for the binary mixtures at 298.15 K are also listed in Table 2.

These properties were mathematically represented by the Redlich−Kister polynomials

$$Y^E = x(1-x)\sum_{j\geq 0} B_j(1-2x)^j \tag{4}$$

where Y^E refers to V_m^E or $\Delta\eta$ and B_j are adjustable parameters and can be obtained by least-squares analysis. Values of the fitted parameters are presented in Table 3 along with the standard deviations of the fit.

Figure 1 shows the variation V_m^E as a function of mole fraction of the ionic liquid. It can be seen that the values of V_m^E are negative in all the ranges of composition, indicating negative deviations from ideal behavior. Similar results have been reported for the mixtures of [Bmim][BF_4] + acetonitrile, dichloromethane, 2-butanone, and *N*,*N*-dimethylformamide,[13] for 4-methyl-*N*-butylpyridinium tetrafluoroborate + methanol[14] and for 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6] + organic compounds.[12] It is more interesting that all the V_m^E in every [Bmim][BF_4] + organic solute system have minimum values at about $x \approx 0.3$. The molecular dynamics simulations of the mixture of [Bmim][BF_4] + acetonitrile also showed that the excess molar volumes are negative over the whole concentration range and present a minimum at [Bmim][BF_4] mole fraction of 0.3.[15] In interpreting V_m^E in terms of molecular interactions, positive values are explained by the breaking of chemical or nonchemical interactions among

Table 3. Derived Parameters and the Standard Deviations (SD) of the Fit for the Excess Molar Volumes and Viscosity Deviations at 298.15 K

	B_0	B_1	B_2	B_3	SD
		[Bmim][BF$_4$] + Methyl Formate			
V_m^E/cm^3·mol^{-1}	−4.5306	6.5885	−3.1818	4.6313	0.088
$\Delta\eta$/mPa·s	−177.843	108.685	−71.277	43.984	0.307
		[Bmim][BF$_4$] + Methyl Acetate			
V_m^E/cm^3·mol^{-1}	−6.2382	7.3134	4.7893	10.1898	0.041
$\Delta\eta$/mPa·s	−177.711	116.460	−105.941	80.774	0.550
		[Bmim][BF$_4$] + Ethyl Formate			
V_m^E/cm^3·mol^{-1}	3.7473	5.5509	3.0990	5.4692	0.046
$\Delta\eta$/mPa·s	−178.723	116.802	−68.826	27.680	0.241
		[Bmim][BF$_4$] + Acetone			
V_m^E/cm^3·mol^{-1}	−6.1158	7.1108	−3.2982	4.1960	0.053
$\Delta\eta$/mPa·s	−184.035	123.426	−86.786	48.197	0.161

molecules in the pure components during the mixing process, whereas a more efficient packing and attractive interaction in the mixtures than in the pure liquids is considered to be the major contribution to the negative V_m^E. [16] Methyl formate, methyl acetate, ethyl formate, and acetone as normal polar molecules are with dipole−dipole interaction. Ionic liquids [Bmim][BF$_4$] are with electrostatic attractions between the [BF$_4$]$^-$ anion and [Bmim]$^+$ cation.[17] The positive contribution to V_m^E would be due to the breaking of two kinds of interactions: electrostatic attractions between the [BF$_4$]$^-$ anion and [Bmim]$^+$ cation and dipole−dipole interaction in the organic polar molecules in the mixing process. Wang and co-worker's studies[12,13] of the ionic liquids [Bmim][BF$_4$] and [Bmim][PF$_6$] with organic polar compounds revealed that the filling effect of organic compounds in the interstices of ionic liquids and the ion−dipole interactions between organic polar compound and the imidazolium ring of the ionic liquids are the main contributors to the negative values of the molar excess volumes. The actual value of V_m^E would depend on the balance of the two opposite contributions.[18] According to these investigations, it seems possible to suggest that the filling effect and the ion−dipole interactions predominate for the experimental V_m^E values when methyl formate, methyl acetate, ethyl formate, or acetone is mixed with [Bmim][BF$_4$].

The viscosity deviations $\Delta\eta$ for the mixtures in Figure 2 show a clear trend: all values are negative and very large values due to the big differences between the ionic liquid's and the other compound's viscosity in the studied ranges of composition for every binary mixture. The minium values are observed at about $x \approx 0.7$.

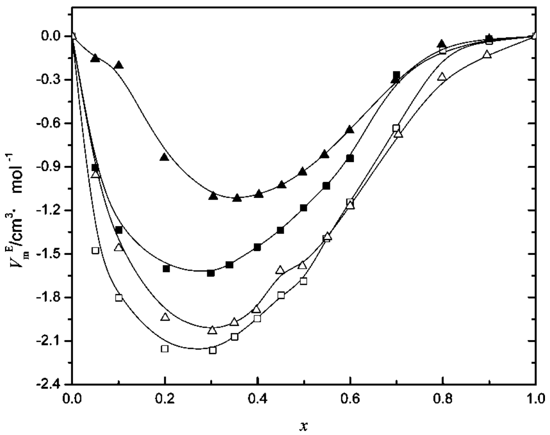

Figure 1. Excess molar volumes V_m^E for the mixtures of x[Bmim][BF$_4$] + (1 − x) organic solutes at 298.15 K. The solid lines were calculated from eq 4 and coefficients given in Table 3. ■, methyl formate; □, methyl acetate; ▲, ethyl formate; Δ, acetone.

As far as the viscosity of the mixtures is plotted against mole fraction of the organic solutes, it is found that the organic solutes appear to have a surprisingly similar effect on the viscosity of the ionic liquids, as shown in Figure 3. In fact, a single exponential equation

$$\eta = \eta_I \exp(-x_s/a) \qquad (5)$$

can be fitted to these data with a correlation coefficient of 0.999 and the standard deviation of 1.020. In this equation, η_I is the viscosity of the pure ionic liquid; x_s is the mole

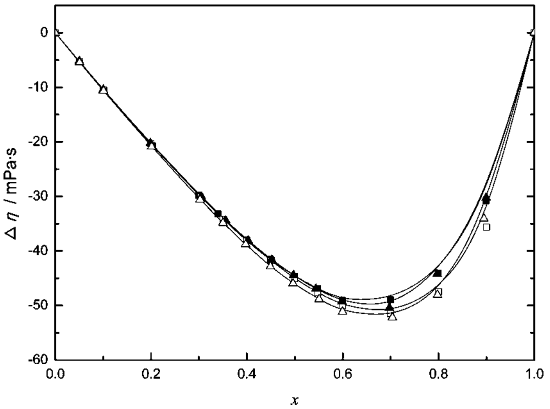

Figure 2. Viscosity deviations $\Delta\eta$ for the mixtures of x[Bmim][BF$_4$] + (1 − x) organic solutes at 298.15 K. The solid lines were calculated from eq 4 and coefficients given in Table 3. ■, methyl formate; □, methyl acetate; ▲, ethyl formate; Δ, acetone.

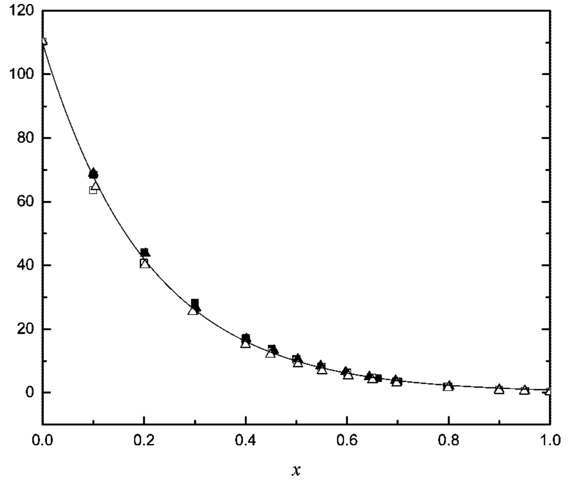

Figure 3. Viscosities for the binaries vs mole fraction of organic solutes. The solid line represents the fit of these data to eq 5: ■, methyl formate; □, methyl acetate; ▲, ethyl formate; Δ, acetone.

fraction of organic solutes; and a is a constant with a value of 0.208 ± 0.001. Similar results have been reported by Seddon[17] and Wang.[13] Therefore, the viscosity of the mixture of a binary system can be predicted as a function of the composition of the organic solutes or the ionic liquid, at given temperature.

As shown in Figure 3, it is clear that the viscosities of the mixtures decrease rapidly when organic compounds are added to the ionic liquid. This decrease is particularly strong in dilute solutions of organic compounds in the ionic liquid. The strong coulomb interactions between the $[BF_4]^-$ anion and $[Bmim]^+$ cation are weakened upon mixing with the neutral organic compounds, which leads to a higher mobility of the ions and a lower viscosity of the mixtures.

Conclusions

The values of V_m^E are negative in all the ranges of compositions, and all the V_m^E values in every $[Bmim][BF_4]$ + organic solute system have minimum values at about $x \approx 0.3$. The filling effect and the ion−dipole interactions are suggested to predominate for the experimental V_m^E values when methyl formate, methyl acetate, ethyl formate, or acetone is mixed with $[Bmim][BF_4]$.

The viscosity deviations $\Delta\eta$ are negative and very large values due to the big differences between ionic liquid's and other compound's viscosity. The minium values are observed at about mole fraction of the ionic liquid, $x \approx 0.7$.

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