Volumetric Properties and Conductivities of 1-Butyl-3-methylimidazolium Tetrafluoroborate + Sucrose + Water Mixtures[†]

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Densities, limiting molar conductivities (Λ_0), and Walden products ($\Lambda_0\eta$) for 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF$_4$])−sucrose−water solutions were determined at 298.15 K. The measured densities were used to calculate the apparent molar volumes of sucrose ($V_{\Phi,S}$) and [Bmim][BF$_4$] ($V_{\Phi,IL}$) in the studied solutions. Infinite dilution apparent molar volumes, $V_{\Phi,S}^{\infty}$ and $V_{\Phi,IL}^{\infty}$, have been evaluated, together with the standard transfer volumes of the sucrose ($\Delta_t V_S^{\infty}$) from water to aqueous solutions of [Bmim][BF$_4$] and those of [Bmim][BF$_4$] ($\Delta_t V_{IL}^{\infty}$) from water to aqueous sucrose solution. It was shown that the $\Delta_t V_S^{\infty}$ and $\Delta_t V_{IL}^{\infty}$ values are positive and increase with increasing molalities of [Bmim][BF$_4$] and sucrose, respectively. The volumetric interaction parameters for [Bmim][BF$_4$]−sucrose pairs in water were also obtained and interpreted by the structural interactions model. Additionally, the Λ_0 values for [Bmim][BF$_4$] decrease with the molality of sucrose (m_S), as well as Walden products ($\Lambda_0\eta$), due to the preferential solvation of ions by sucrose molecules.

Introduction

Aqueous biphasic systems (ABS) have been widely used as a powerful technique for purification, extraction,and enrichment.[1−3] Recently, we have proposed ionic liquids (ILs)−sugars−water ABS[4,5] since Rogers and co-workers[6] demonstrated that the addition of potassium phosphate to an aqueous solution of a hydrophilic IL produces aqueous two-phase systems. The increasing utilization of ionic liquids in chemical processes and separation processes requires reliable and systematic data of thermodynamic properties such as densities and conductivities. Undeniably, a considerable amount of density and conductivity data of pure ILs are available in the literature; however, there exist very few reliable data of liquid densities and conductivities for IL + sugar + water and/or IL + salt + water systems, besides some systematic work done on IL-containing mixtures.[7−15]

To understand the physicochemical process occurring in IL + sugar + water systems, it is necessary to investigate their volumetric properties because they can provide information about the structural interactions in solutions. In our previous work,[4,5] we explained why ABS can form by addition of sugars to an aqueous solution of 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF$_4$]). As a continuation, we report here studies on the interaction of [Bmim][BF$_4$] with sucrose by densimetry and conductometry at 298.15 K. These results will be valuable in chemical engineering.

Experimental

Materials. The sucrose (≥ 99.5 %), chlorobutane (≥ 99 %), 1-methylimidazole (≥ 99 %), ethyl acetate (99 %), acetone (99 %), and NaBF$_4$ (≥ 99 %) were all purchased from Shanghai Chemical Reagents Company. They are of analytic grade and used as received. Doubly distilled water was used in all experiments.

Synthesis of [Bmim][BF$_4$]. [Bmim][BF$_4$] was prepared based on the reported procedures[16] and dried under vacuum at 373.15 K for 24 h. The purity of the [Bmim][BF$_4$] was verified in terms of NMR analysis (> 99 %), and the Cl^{-1} content is smaller than 130 ppm. The water content of [Bmim][BF$_4$] (0.18 %) was determined by Karl Fischer titration (ZSD-2 KF with an uncertainty of 0.05 %, Cany Precision Instruments Co., Ltd.).

Measurement of Density. All aqueous solutions to be studied were freshly prepared by weight with correction for air buoyancy. The solutions were based on molality with respect to 1 kg of pure water. Relative uncertainties in molality are less than ± 0.03 %. Before measuring the densities of [Bmim][BF$_4$] + sucrose + water mixtures, a Westphal balance (PZ-D-5) was corrected with pure water at 298.15 K. The uncertainty in density was estimated to be $\pm 2.0 \cdot 10^{-6}$ g·cm^{-3}.

Measurement of Conductivity. The conductivity measurements were carried out with a DDSJ-308A conductometer (Shanghai Optical Instrument Factory, cell constant = 1.0 cm^{-1}) with an uncertainty of 0.5 %. The temperature of the sample was maintained at (298.15 ± 0.05) K with a DC-2006 low-temperature thermostat (Shanghai Hengping Instrument Factory). Each measurement was repeated thrice, and the average values were calculated and reported. It was estimated that the accuracy of the conductivity data was better than ± 3 %. The specific conductance for pure water is 0.03 mS·cm^{-1}.

Results and Discussion

Apparent Molar Volume. The densities of [Bmim][BF$_4$] + sucrose + water mixtures are given in Table 1. The apparent molar volumes of sucrose, $V_{\Phi,S}$, and [Bmim][BF$_4$], $V_{\Phi,IL}$, respectively, were calculated from[17]

$$V_{\Phi,S} = \frac{M_S}{d} - \frac{(1000 + m_{IL}M_{IL})(d - d_{IL})}{m_S d d_{IL}} \quad (1)$$

$$V_{\Phi,IL} = \frac{M_{IL}}{d} - \frac{(1000 + m_S M_S)(d - d_S)}{m_{IL} d d_S} \quad (2)$$

where M_{IL} and M_S are the molar masses of [Bmim][BF$_4$] and sucrose; m_{IL} and m_S are the molalities of [Bmim][BF$_4$] and

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Table 1. Densities and Apparent Molar Volumes of Sucrose and [Bmim][BF$_4$] in Sucrose−Water, [Bmim][BF$_4$]−Water, and Sucrose−[Bmim][BF$_4$]−Water Systems at 298.15 K

m_{IL} / mol·kg^{-1}	d / g·cm^{-3}	$V_{\Phi,S}$ / cm^3·mol^{-1}	$V_{\Phi,IL}$ / cm^3·mol^{-1}	m_E / mol·kg^{-1}	d / g·cm^{-3}	$V_{\Phi,S}$ / cm^3·mol^{-1}	$V_{\Phi,IL}$ / cm^3·mol^{-1}
	m_S = 0.0200 mol·kg^{-1}				m_S = 0.1500 mol·kg^{-1}		
0	0.999720	210.978	--	0	1.016060	212.126	--
0.0500	1.001580	211.124	188.034	0.0500	1.017790	211.724	188.412
0.1000	1.003400	211.310	188.297	0.1000	1.019380	211.974	188.416
0.1500	1.005150	211.539	188.570	0.1500	1.020910	212.195	188.669
0.2500	1.008550	211.747	188.813	0.2500	1.023930	212.396	188.906
0.5000	1.016510	211.939	189.059	0.5000	1.031030	212.573	189.150
0.7500	1.023760	212.133	189.222	0.7500	1.037490	212.819	189.336
1.0000	1.030320	212.337	189.438	1.0000	1.043350	213.038	189.545
	m_S = 0.0600 mol·kg^{-1}				m_S = 0.2000 mol·kg^{-1}		
0	1.004870	211.394	--	0	1.022120	212.144	--
0.0500	1.006680	211.312	188.183	0.0500	1.023760	211.940	188.499
0.1000	1.008420	211.524	188.360	0.1000	1.025280	212.132	188.520
0.1500	1.010100	211.778	188.615	0.1500	1.026740	212.313	188.756
0.2500	1.013390	211.963	188.859	0.2500	1.029620	212.514	189.040
0.5000	1.021070	212.175	189.110	0.5000	1.036400	212.742	189.256
0.7500	1.028070	212.394	189.271	0.7500	1.042580	212.969	189.417
1.0000	1.034410	212.574	189.479	1.0000	1.048190	213.154	189.610
	m_S = 0.1000 mol·kg^{-1}				m_S = 0.2500 mol·kg^{-1}		
0	1.009900	211.830	--	0	1.027950	212.599	
0.0500	1.011670	211.571	188.375	0.0500	1.029600	212.114	188.552
0.1000	1.013350	211.756	188.362	0.1000	1.031040	212.325	188.588
0.1500	1.014960	211.983	188.632	0.1500	1.032420	212.533	188.770
0.2500	1.018120	212.232	188.904	0.2500	1.035160	212.756	189.114
0.5000	1.025540	212.427	189.135	0.5000	1.041650	212.934	189.272
0.7500	1.032300	212.595	189.299	0.7500	1.047560	213.148	189.426
1.0000	1.038420	212.804	189.511	1.0000	1.052920	213.351	189.620
			[Bmim][BF$_4$]−water				
0	0.997100		--	0.2500	1.006100		188.743
0.0500	0.999000		188.077	0.5000	1.014200		189.016
0.1000	1.000850		188.239	0.7500	1.021570		189.197
0.1500	1.002630		188.530	1.0000	1.028250		189.408

sucrose; and d, d_S, and d_{IL} are the densities of the [Bmim][BF$_4$] + sucrose + water, sucrose + water, and [Bmim][BF$_4$] + water solutions, respectively. The calculated $V_{\Phi,S}$ and $V_{\Phi,IL}$ values are also included in Table 1. The values of $V_{\Phi,IL}$ for [Bmim][BF$_4$] are in line with the results by Malham.[18]

To analyze the structure of these ternary solutions through examining the volumetric behavior of [Bmim][BF$_4$] in the presence of sucrose, the $V_{\Phi,IL}$ values for [Bmim][BF$_4$] in aqueous solutions of sucrose and $V_{\Phi,S}$ values for sucrose in aqueous [Bmim][BF$_4$] solutions have been plotted in Figures 1 and 2. A significant increase in $V_{\Phi,IL}$ ($V_{\Phi,S}$) values with the molality of sucrose ([Bmim][BF$_4$]) was observed. This can be explained by the structure-breaking effect of [Bmim][BF$_4$] which decreases due to its interaction with the sucrose molecules, and thus more water molecules are released to the bulk water in the presence of sucrose and then contribute to the positive volume changes observed.[19]

Furthermore, it has been found that both plots of $V_{\Phi,S}$ against m_S and $V_{\Phi,IL}$ against $m_E^{1/2}$ are completely linear. Therefore, infinite-dilution apparent molar volumes, $V_{\Phi,S}^{\infty}$ and $V_{\Phi,IL}^{\infty}$, which are equal to the standard partial molar volume values (V_S^{∞} and V_{IL}^{∞}), are obtained from least-squares weighed fits of the experimental data by the following equations[20,21]

$$V_{\Phi,S} = V_{\Phi,S}^{\infty} - S_S^{*} m_S \tag{3}$$

$$V_{\Phi,IL} = V_{\Phi,IL}^{\infty} - S_{IL}^{*} m_{IL}^{1/2} \tag{4}$$

where S_S* and S_{IL}* are the experimental slopes. The infinite dilution apparent molar volumes for the systems studied are given in Tables 2 and 3. The V_{Φ}^{∞} ([Bmim][BF$_4$]) is consistent with the results by Malham (188 cm^3·mol^{-1}).[18]

Volume of Transfer. Standard transfer volumes for [Bmim][BF$_4$], $\Delta_t V_{IL}^{\infty}$, from water to sucrose−water solutions

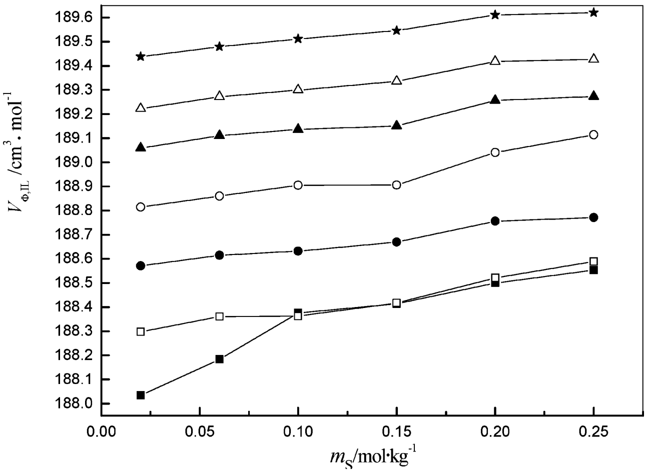

Figure 1. Apparent molar volume, $V_{\Phi,IL}$, of [Bmim][BF$_4$] plotted against the molality of the sucrose. ■, 0.05 mol·kg^{-1}; □, 0.1 mol·kg^{-1}; ●, 0.15 mol·kg^{-1}; ○, 0.25 mol·kg^{-1}; ▲, 0.50 mol·kg^{-1}; Δ, 0.75 mol·kg^{-1}; ★, 1 mol·kg^{-1}.

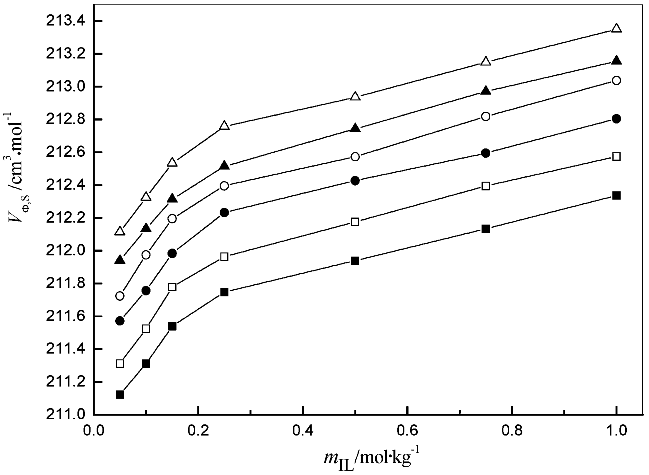

Figure 2. Apparent molar volume, $V_{\Phi,IL}$, of [Bmim][BF$_4$] plotted against the molality m_S of the sucrose. ■, 0.02 mol·kg^{-1}; □, 0.06 mol·kg^{-1}; ●, 0.10 mol·kg^{-1}; ○, 0.15 mol·kg^{-1}; ▲, 0.20 mol·kg^{-1}; Δ, 0.25 mol·kg^{-1}.

Table 2. Infinite-Dilution Apparent Molar Volumes ($V_{\Phi,S}^{\infty}$/cm^3·mol^{-1}) of Sucrose in Aqueous [Bmim][BF$_4$] Solutions and Slopes (S_S*/cm^3·kg·mol^{-2}) of Equation 3 at 298.15 K

	m_{IL}/mol·kg^{-1}							
quantities	0	0.0500	0.1000	0.1500	0.2500	0.5000	0.7500	1.0000
$V_{\Phi,S}^{\infty}$	211.00 (± 0.02)[a]	211.07 (± 0.04)	211.26 (± 0.02)	211.53 (± 0.02)	211.70 (± 0.03)	211.92 (± 0.03)	212.14 (± 0.02)	212.34 (± 0.01)
S_S*	6.42 (± 0.04)	4.29 (± 0.03)	4.36 (± 0.01)	4.04 (± 0.01)	4.2 (± 0.02)	4.18 (± 0.02)	4.16 (± 0.01)	4.082 (± 0.01)[a]

[a] Uncertainty.

Table 3. Infinite-Dilution Apparent Molar Volumes ($V_{\Phi,IL}^{\infty}$/cm^3·mol^{-1}) of [Bmim][BF$_4$] in Aqueous Sucrose Solutions and Slopes (S_{IL}*/cm^3·kg·mol^{-2}) of Equation 4 at 298.15 K

	m_S/mol·kg^{-1}						
quantities	0	0.0200	0.0600	0.1000	0.1500	0.2000	0.2500
$V_{\Phi,IL}^{\infty}$	187.78 (± 0.01)[a]	187.81 (± 0.01)	187.91 (± 0.02)	188.08 (± 0.04)	188.11 (± 0.01)	188.21 (± 0.02)	188.28 (± 0.03)
S_{IL}*	1.67 (± 0.01)	1.69 (± 0.01)	1.61 (± 0.03)	1.45 (± 0.05)	1.44 (± 0.02)	1.42 (± 0.01)	1.37 (± 0.04)

[a] Uncertainty.

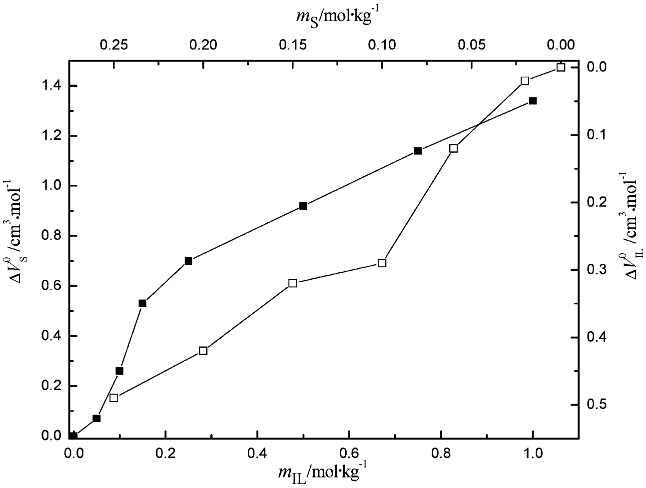

Figure 3. ■, Variation of the standard transfer volumes, $\Delta_t V_S^0$, of sucrose from water to aqueous [Bmim][BF$_4$] solutions with the molality of [Bmim][BF$_4$]; □, Variation of the standard transfer volumes, $\Delta_t V_{IL}^0$, of [Bmim][BF$_4$] from water to aqueous sucrose solutions with the molality of sucrose.

Table 4. Volumetric Interaction Parameters for [Bmim][BF$_4$]−Sucrose−Water Systems at 298.15 K

	$2\upsilon\nu_{IS}$	$3\upsilon\nu_{ISS}$	$3\upsilon^2\nu_{IIS}$	σ
IL	cm^3·mol^{-2}·kg	cm^3·mol^{-3}·kg^2	cm^3·mol^{-3}·kg^2	cm^3·mol^{-1}
[Bmim][BF$_4$]	2.208 ± 0.032[a]	−1.882 ± 0.015	−0.971 ± 0.035	0.03

[a] Uncertainty.

and those for sucrose, $\Delta_t V_S^{\infty}$, from water to [Bmim][BF$_4$] + water solutions were calculated by using values of $V_{\Phi,S}^{\infty}$ and $V_{\Phi,IL}^{\infty}$, respectively. Plots of $\Delta_t V_S^{\infty}$ and $\Delta_t V_{IL}^{\infty}$ against the molalities of [Bmim][BF$_4$] and sucrose are represented in Figure 3, respectively.

As shown in Figure 3, the values of $\Delta_t V_S^{\infty}$ and $\Delta_t V_{IL}^{\infty}$ for both systems studied are positive and increase with increasing molalities of [Bmim][BF$_4$] and sucrose, respectively. This can be interpreted in terms of the structural interaction model proposed by Desnoyers et al.[22] and the group additivity model.[23] According to these models, the interactions between sucrose and [Bmim][BF$_4$] can be classified into four types of interactions: (i) hydrophobic−ionic interactions between the hydrophobic parts of sucrose and [Bmim]$^+$/BF$_4^-$ ions; (ii) hydrophilic−ionic interactions between the hydrophilic −OH, −C═O, and −O− groups of sucrose and [Bmim]$^+$/BF$_4^-$ ions; (iii) hydrophobic−hydrophobic interactions between the hydrophobic parts of sucrose and [Bmim]$^+$; and (iv) hydrophilic−hydrophobic interactions between the hydrophilic parts of sucrose and the hydrophobic parts of [Bmim]$^+$.

According to the structural interaction model,[22] the interactions of types (i), (iii), and (iv) are repulsive because these two groups are incompatible in their structural influence or their tendencies to orient water and consequently contribute a negative volume. Only interactions of type (ii) contribute a positive volume owing to the overlap of the hydration cosphere of the ion ([Bmim]$^+$/BF$_4^-$) and a hydrophilic −OH, −C═O, and −O− group, which leads to a decrease in the structure-breaking tendency of the ion and a reduction in the electrostriction of the water caused by these ions. Thus, there are competing interactions that result in both negative and positive values to $\Delta_t V_{IL}^{\infty}$ for the systems studied. These values can be rationalized by considering these interactions and various other characteristics of the [Bmim][BF$_4$] and sucrose. The positive $\Delta_t V_{IL}^{\infty}$ observed indicated that the interaction of type (ii), i.e., hydrophilic−ionic interactions, predominates over those of the other types. Furthermore, the increase in their values with an increase in the concentration of sucrose points toward a strengthening of the hydrophilic−ionic interactions over the concentration range studied.

The standard partial molar volume, $V_{\Phi,S}^{\infty}$, of sucrose can also be expressed as[19,24]

$$V_{\Phi,S}^{\infty} = V_{v,w} + V_{void} - V_{shrinkage} \tag{5}$$

where $V_{v,w}$ is the van der Waals volume; V_{void} is the associated void or empty volume; and $V_{shrinkage}$ is the shrinkage in volume caused by interactions of hydrogen bonding groups with water molecules. If $V_{v,w}$ and V_{void} are assumed to have the same magnitudes in water and aqueous [Bmim][BF$_4$] solutions, positive values of $\Delta_t V_S^{\infty}$ might arise from $V_{shrinkage}$ in aqueous [Bmim][BF$_4$] solutions. Since ions of [Bmim][BF$_4$] can be hydrated, the presence of [Bmim][BF$_4$] in water will decrease the hydration effects of hydroxyl groups of sucrose molecules, thus causing the decrease in $V_{shrinkage}$. This is a reason why $\Delta_t V_S^{\infty}$ rises with increasing molalities of [Bmim][BF$_4$].

Volumetric Interaction Parameters. Volumetric interaction parameters can be obtained by separately fitting experimental data by the following equations[17,25]

$$\Delta_t V_{\Phi,S} = 2\upsilon\nu_{IS} m_{IL} + 3\upsilon^2\nu_{IIS} m_{IL}^2 + 3\upsilon\nu_{ISS} m_{IL} m_S + \cdots \tag{6}$$

$$\Delta_t V_{\Phi,IL} = 2\upsilon\nu_{IS} m_S + 3\upsilon^2\nu_{IIS} m_{IL} m_S + 3\upsilon\nu_{ISS} m_S^2 + \cdots \tag{7}$$

where $\Delta_t V_{\Phi,S}$ and $\Delta_t V_{\Phi,IL}$ are, respectively, the transfer volumes of sucrose at molality m_S from water to a solution of electrolyte at molality m_{IL} and of [Bmim][BF$_4$] at molality m_{IL} from water to a solution of saccharides at m_S. Here, υ is the number of ions into which the electrolyte dissociates, and ν_{IS}, ν_{IIS}, and

Table 5. Molar Conductivity of [Bmim][BF_4] in Water and Water−Sucrose Mixtures at 298.15 K

$m_S = 0.0200\ \mathrm{mol \cdot kg^{-1}}$		$m_S = 0.0600\ \mathrm{mol \cdot kg^{-1}}$		$m_S = 0.1000\ \mathrm{mol \cdot kg^{-1}}$	
c $(\mathrm{mol \cdot L^{-1}})$	Λ $(\mathrm{S \cdot cm^2 \cdot mol^{-1}})$	c $(\mathrm{mol \cdot L^{-1}})$	Λ $(\mathrm{S \cdot cm^2 \cdot mol^{-1}})$	c $(\mathrm{mol \cdot L^{-1}})$	Λ $(\mathrm{S \cdot cm^2 \cdot mol^{-1}})$
0.0500	86.57	0.0500	83.75	0.0500	80.24
0.1000	81.54	0.1000	78.75	0.1000	75.42
0.1500	78.14	0.1500	72.35	0.1500	69.12
0.2500	69.29	0.2500	67.65	0.2500	62.98
0.5000	53.69	0.5000	52.85	0.5000	51.74
0.7500	41.28	0.7500	40.73	0.7500	39.71
1.0000	38.34	1.0000	37.84	1.0000	36.94
$m_S = 0.1500\ \mathrm{mol \cdot kg^{-1}}$		$m_S = 0.0200\ \mathrm{mol \cdot kg^{-1}}$		$m_S = 0.2500\ \mathrm{mol \cdot kg^{-1}}$	
c $(\mathrm{mol \cdot L^{-1}})$	Λ $(\mathrm{S \cdot cm^2 \cdot mol^{-1}})$	c $(\mathrm{mol \cdot L^{-1}})$	Λ $(\mathrm{S \cdot cm^2 \cdot mol^{-1}})$	c $(\mathrm{mol \cdot L^{-1}})$	Λ $(\mathrm{S \cdot cm^2 \cdot mol^{-1}})$
0.0500	74.42	0.0500	69.03	0.0500	60.22
0.1000	70.43	0.1000	62.40	0.1000	57.52
0.1500	65.23	0.1500	60.16	0.1500	54.15
0.2500	56.82	0.2500	54.67	0.2500	51.89
0.5000	49.56	0.5000	47.49	0.5000	45.10
0.7500	38.87	0.7500	37.66	0.7500	36.67
1.0000	36.12	1.0000	34.98	1.0000	33.77
		pure water			
0.0500	90.60	0.2500	71.41	1.0000	38.86
0.1000	84.95	0.5000	54.67		
0.1500	80.00	0.7500	41.89		

Table 6. Values of Limiting Molar Conductivity (Λ_0), Viscosity (η), and the Walden Product ($\Lambda_0\eta$) for [Bmim][BF_4] in Water and Water−Sucrose Mixtures at 298.15 K

m_S $\mathrm{mol \cdot kg^{-1}}$	Λ_0 $\mathrm{S \cdot cm^2 \cdot mol^{-1}}$	η $\mathrm{mPa \cdot s}$	$\Lambda_0\eta$ $\mathrm{S \cdot cm^2 \cdot mol^{-1} \cdot mPa \cdot s}$
0	111.65 ± 0.18^a	0.8904	99.42
0.0200	105.18 ± 0.15	0.9014	94.82
0.0600	100.92 ± 0.21	0.9427	95.15
0.1000	97.57 ± 0.71	0.9726	94.91
0.1500	91.75 ± 0.32	1.0152	93.15
0.2000	80.75 ± 0.44	1.0659	86.08
0.2500	66.84 ± 0.27	1.1161	74.60

[a] Uncertainty.

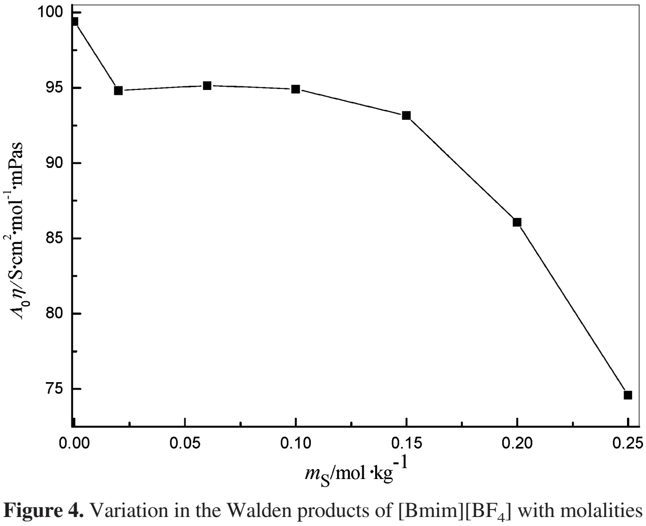

Figure 4. Variation in the Walden products of [Bmim][BF_4] with molalities of sucrose.

ν_{ISS} are pair and triplet interaction parameters. The interaction parameters were obtained by least-squares regression from these two equations, respectively. Since the values from eqs 6 and 7 are in good agreement with each other within experimental error, their mean values are taken as the final values and are given in Table 4 together with their standard deviations.

The results show that both ν_{IS} values are positive. This can be interpreted on the basis of the structural interaction model proposed by Desnoyers et al.[22] and the hydration model by Conway.[26] The positive ν_{IS} values are mainly due to the hydrophilic−ionic interactions since the dehydration of ions and −OH, −C=O, and −O− groups contribute a positive value to the volume. Meanwhile, this also corroborates our previous explanation.[5]

Conductivity. Limiting molar conductivity (Λ_0) of [Bmim][BF_4] was obtained by least-squares fitting the experimental data (Table 5) to the expression[27]

$$\Lambda = \Lambda_0 - \frac{A\sqrt{c}}{1 + B\sqrt{c}} \tag{8}$$

where Λ_0, A, and B are fitting parameters and c is the molarity of [Bmim][BF_4] in $\mathrm{mol \cdot dm^{-3}}$ and was obtained by converting molality with density. The resulting values are given in Table 6.

As shown in Table 6, the Λ_0 values for [Bmim][BF_4] decrease with the increase of m_S. This can be ascribed to the facts that (i) with the decrease in dielectric constant of the mixtures, the electrostatic attraction between the ions increases, and hence the ions in the free state decrease; (ii) the increased size of ions caused by the possible association of $[\mathrm{Bmim}]^+$ and sucrose reduces the ionic mobility;[28] and (iii) with the increase in microscopic viscosity of the mixtures, the mobility of ions decreases.

To eliminate the influence of macroscopic viscosity on the ionic mobility, the viscosity of the mixture was determined according to the method reported in the literature.[29] The values of the Walden product ($\Lambda_0\eta$) were calculated and given also in Table 6. An increase in viscosity leads to a decrease in conductivity. This effect was formulated quantitatively by the Walden rule,[30] which states that the product ($\Lambda_0\eta$) should be approximately constant for a given electrolyte, irrespective of the nature of the solvent, provided that the radius of the ion remains unchanged. As shown in Figure 4, the Walden products decrease as m_S increases. This suggests that these ions do not have the same effective radius in different solvent compositions and consequently provides evidence for the solvation of ions in solution. It seems to be caused by preferential solvation of ions by sucrose molecules. Furthermore, with m_S increasing, the interactions of ions with sucrose are stronger, leading to a larger radii of solvated ions, and thus the mobility of ions decreases.

Conclusions

Values of $\Delta_t V_S^\infty$ and $\Delta_t V_{IL}^\infty$ are positive and increase with increasing molalities of [Bmim][BF$_4$] and sucrose, respectively. It could be concluded that the hydrophilic−ionic interactions are predominant since they contribute a positive volume. The volumetric interaction parameter ν_{IS} is positive, suggesting that the interactions between the sucrose and [Bmim][BF$_4$] are mainly pair wise. Additionally, the Λ_0 values for [Bmim][BF$_4$] decrease with the increase of m_S, as well as Walden products ($\Lambda_0\eta$), due to the preferential solvation of ions by sucrose molecules.

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