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Volumetric Properties of 1-Butyl-3-methylimidazolium Tetrafluoroborate−Glucose−Water Systems

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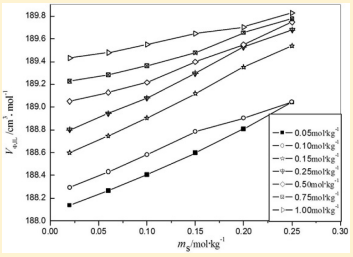
ABSTRACT: Densities for 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4)−glucose−water solutions were determined at 298.15 K. The measured densities were used to calculate the apparent molar volumes of glucose ($V_{\Phi,S}$) and [Bmim]BF_4 ($V_{\Phi,IL}$) in the studied solutions. Infinite 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 glucose 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 glucose, respectively, and the values of $V_{\Phi,S}^{\infty}$ have the order of glucose < sucrose. The volumetric interaction parameters for [Bmim]BF_4−glucose pairs in water were also obtained and interpreted by the structural interactions model.



INTRODUCTION

In recent years, aqueous biphasic systems (ABS) have been highly regarded due to their applications as a powerful technique for purification, extraction and enrichment. Recently, Wu and co-workers have demonstrated that the addition of saccharides to an aqueous solution of a hydrophilic ionic liquid (IL) produces aqueous two-phase systems (ABS),[1−3] which have great potential use for purification, extraction, and enrichment. Chen et al. have investigated the effect of temperature and IL structure on this type of ABS systems.[4,5] These chemical separation processes require reliable and systematic data of thermodynamic properties, such as densities. Actually, there exist very few reliable data of liquid densities for IL−sugar−water systems,[6−9] beside of some systematic work done on IL-containing mixtures.[10−17] In our previous works, we investigated the volumetric properties of [Amim]Cl−sucrose−water mixtures and made a comparison with the system of [Bmim]BF_4−sucrose−water.[18]

As a continuation, densities of 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4)−glucose−water systems have been measured at 298.15 K. The standard partial molar volumes of glucose and the corresponding transfer volumes were calculated. These parameters have been interpreted in terms of the various structural interactions, solute−solvent interactions, and the hydration model of glucose molecules in aqueous IL solutions. These results were compared with that of the 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]-BF_4)−sucrose−water system,[6] and their similarities and differences were explained.

EXPERIMENTAL SECTION

Materials. The D-glucose (≥ 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 analytical 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.[19] Equal molar amounts of chlorobutane and 1-methylimidazole were added to a round-bottomed flask fitted with a reflux condenser for 72 h at 70 °C. The unreacted starting material was extracted with ethyl acetate. Any remaining ethyl acetate was removed by rotating evaporation at 70 °C, and the product [Bmim]Cl was obtained. Then, equal molar amounts of [Bmim]Cl and $NaBF_4$ were mixed in a round-bottomed flask for 48 h at 25 °C, using acetone as the solvent. The product [Bmim]BF_4 was obtained after filtration and rotating evaporation 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 prepared in glass vials by weight using a MS204 analytical balance with an uncertainty of ± $2{\cdot}10^{-4}$ g. The solutions were based on molality with respect to 1 kg of pure water. The uncertainty for molalities of the solutions is less than $2.0{\cdot}10^{-4}$ mol·kg^{-1}. Before measuring the densities of [Bmim]BF_4 + glucose + water mixtures, a Westphal balance (PZ-D-5) was corrected with pure water at 298.15 K.

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Table 1. Densities and Apparent Molar Volumes of Glucose and [Bmim]BF_4 in Glucose−Water, [Bmim]BF_4−Water, and Glucose−[Bmim]BF_4−Water Systems at 298.15 K

m_{IL}	d	$V_{\Phi,S}$	$V_{\Phi,IL}$	m_E	d	$V_{\Phi,S}$	$V_{\Phi,IL}$
mol·kg^{-1}	g·cm^{-3}	cm^3·mol^{-1}	cm^3·mol^{-1}	mol·kg^{-1}	g·cm^{-3}	cm^3·mol^{-1}	cm^3·mol^{-1}
	m_S = 0.0200 mol·kg^{-1}				m_S = 0.1500 mol·kg^{-1}		
0	0.99850	110.112		0	1.00737	110.668	
0.0500	1.00038	110.258	188.136	0.0500	1.00912	110.842	188.597
0.1000	1.00221	110.428	188.294	0.1000	1.01082	111.037	188.784
0.1500	1.00397	110.621	188.598	0.1500	1.01245	111.256	189.118
0.2500	1.007405	110.810	188.799	0.2500	1.01562	111.758	189.295
0.5000	1.01543	110.947	189.050	0.5000	1.02317	111.931	189.398
0.7500	1.02273	111.223	189.227	0.7500	1.03005	112.062	189.476
1.0000	1.02935	111.306	189.432	1.0000	1.03628	112.248	189.646
	m_S = 0.0600 mol·kg^{-1}				m_S = 0.2000 mol·kg^{-1}		
0	1.00126	110.476		0	1.01069	110.818	
0.0500	1.00310	110.632	188.265	0.0500	1.01239	111.000	188.808
0.1000	1.00489	110.812	188.432	0.1000	1.01405	111.154	188.903
0.1500	1.00661	111.014	188.746	0.1500	1.01562	111.434	189.352
0.2500	1.00997	111.309	188.944	0.2500	1.01869	111.954	189.528
0.5000	1.01785	111.402	189.127	0.5000	1.02607	112.096	189.548
0.7500	1.02502	111.533	189.282	0.7500	1.03281	112.132	189.653
1.0000	1.03152	111.649	189.479	1.0000	1.03890	112.291	189.703
	m_S = 0.1000 mol·kg^{-1}				m_S = 0.2500 mol·kg^{-1}		
0	1.00399	110.608		0	1.01394	111.046	
0.0500	1.00579	110.772	188.406	0.0500	1.01559	111.238	189.040
0.1000	1.00754	110.960	188.582	0.1000	1.01721	111.371	189.044
0.1500	1.00922	111.170	188.904	0.1500	1.01873	111.650	189.537
0.2500	1.01251	111.444	189.078	0.2500	1.02175	112.147	189.676
0.5000	1.02024	111.607	189.216	0.5000	1.02887	112.506	189.746
0.7500	1.02727	111.846	189.362	0.7500	1.03541	112.553	189.775
1.0000	1.03365	111.996	189.547	1.0000	1.04141	112.718	189.826
			[Bmim]BF_4−Water[6]				
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

The uncertainty in density was estimated to be ± 2.0·10^{-6} g·cm^{-3}.

RESULTS AND DISCUSSION

Apparent Molar Volume. The densities of [Bmim]BF_4 + glucose + water mixtures are summarized in Table 1. The apparent molar volumes of glucose, $V_{\Phi,S}$, and [Bmim]BF_4, $V_{\Phi,IL}$, respectively, were calculated from[20]

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

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

where M_{IL} and M_S are the molar masses of [Bmim]BF_4 and glucose, m_{IL} and m_S are the molalities of [Bmim]BF_4 and glucose, and d, d_S, and d_{IL} are the densities of the [Bmim]BF_4 + glucose + water, glucose + 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 average uncertainty of V_Φ values is about 0.035 cm^3·mol^{-1}. The values of $V_{\Phi,IL}$ for [Bmim]BF_4 are in line with the results by Malham et al.[21]

To analyze the structure of these ternary solutions through examining the volumetric behavior of [Bmim]BF_4 in the presence of glucose. The $V_{\Phi,IL}$ values for [Bmim]BF_4 in aqueous solutions of glucose and $V_{\Phi,S}$ values for glucose in aqueous [Bmim]BF_4 solutions have been plotted in Figures 1 and 2, where $V_{\Phi,IL}$ ($V_{\Phi,S}$) values increase with a rise in the molality of glucose ([Bmim]BF_4). It can be explained that the

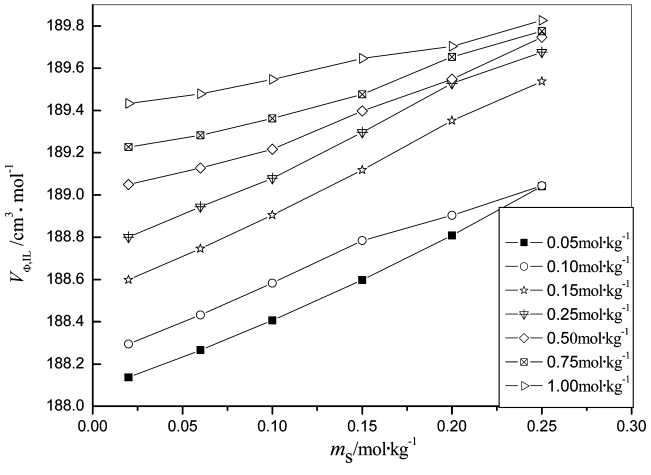

Figure 1. Apparent molar volume, $V_{\Phi,IL}$, of [Bmim]BF_4 plotted against the molality of the glucose.

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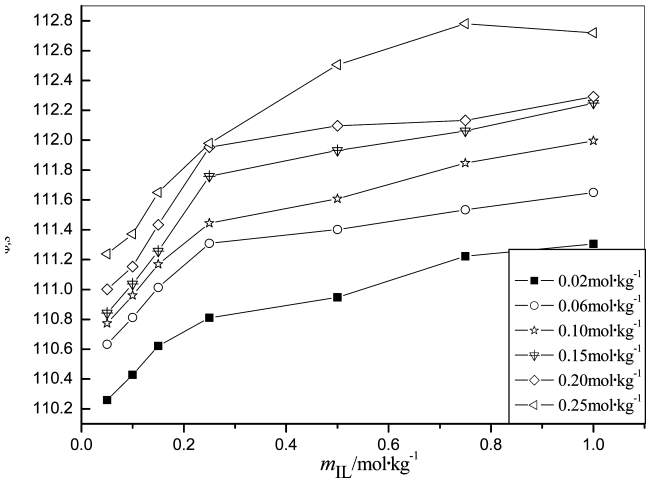

Figure 2. Apparent molar volume, $V_{\Phi,S}$, of glucose plotted against the molality of the [Bmim]BF_4.

structure-breaking effect of [Bmim]BF_4 decreases due to its interaction with the glucose molecules and thus more water molecules are released to the bulk water in the presence of glucose and then contribute to the positive volume changes observed.[22]

Furthermore, it has been found that both plots of $V_{\Phi,S}$ against m_S and $V_{\Phi,IL}$ against $m_{IL}^{1/2}$ 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:[23,24]

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

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

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) in pure water is 187.78, which is consistent with the results by Malham et al. (188 cm^3·mol^{-1}).[21]

More interestingly, it was shown that $V_{\Phi,S}^{\infty}$ of glucose in aqueous [Bmim]BF_4 solutions were lower than that of sucrose in aqueous [Bmim]BF_4 solutions.[6] This is ascribed to the fact that glucose contains less OH groups on its molecule (glucose (4.56) <sucrose (6.2)). The less the OH groups on saccharide molecules fit into the water structure, the more they break the water structure.[2] That is why the $V_{\Phi,S}^{\infty}$ is in the order of glucose < sucrose.

Volume of Transfer. Standard transfer volumes for [Bmim]BF_4, $\Delta_t V_{IL}^{\infty}$, from water to glucose−water solutions and those for glucose, $\Delta_t V_S^{\infty}$, from water to [Bmim]BF_4−water solutions were calculated as follows 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 glucose are represented in Figure 3, respectively.

$$\Delta_t V_{IL}^{\infty} = V_{IL}^{\infty}(\text{glucose−water}) - V_{IL}^{\infty}(\text{water}) \quad (5)$$

$$\Delta_t V_S^{\infty} = V_S^{\infty}([\text{Bmim}]BF_4\text{−water}) - V_S^{\infty}(\text{water}) \quad (6)$$

As shown in Figure 3, the values of $\Delta_t V_S^{\infty}$ and $\Delta_t V_{IL}^{\infty}$ for both system studied are positive and increase with increasing molalities of [Bmim]BF_4 and glucose, respectively. This can be interpreted in terms of the structural interaction model proposed by Desnoyers et al.[25] and the group additivity model.[26] According to these models, the interactions between glucose and [Bmim]BF_4 can be classified into four types of interactions: (i) hydrophobic−cation interactions between the hydrophobic parts of glucose and [Bmim]$^+$; (ii) hydrophilic−cation interactions between the hydrophilic −OH, −C═O, and −O− groups of glucose and [Bmim]$^+$; (iii) hydrophobic−anion interactions between the hydrophobic parts of glucose and BF_4^-; and (iv) hydrophilic−hydrophobic interactions between hydrophilic −OH, −C═O, and −O− groups of glucose and BF_4^-.

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]$^+$) 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 glucose. The positive $\Delta_t V_{IL}^{\infty}$ observed indicated that the interaction of type (ii), that is, hydrophilic−cationic interactions, predominate over those of the other types. Furthermore, the increase in their values with an increase in the concentration of glucose points toward a strengthening of the hydrophilic−ionic interactions over the concentration range studied.

The standard partial molar volume, $V_{\Phi,S}^{\infty}$, of glucose can also be expressed as[22,27]

$$V_{\Phi,S}^{\infty} = V_{v,w} + V_{void} - V_{shrinkage} \quad (7)$$

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

Table 2. Infinite-Dilution Apparent Molar Volumes ($V_{\Phi,S}^{\infty}$/cm^3·mol^{-1}) of Glucose 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
$V_{\Phi,S}^{\infty}$	110.16 (±0.02)[a]	110.31 (±0.04)	110.50 (±0.02)	110.68 (±0.02)	110.86 (±0.03)	110.93 (±0.03)	111.20 (±0.02)	111.30 (±0.01)
S_S*	3.52 (±0.04)	3.71 (±0.03)	3.54 (±0.01)	3.96 (±0.01)	5.47 (±0.02)	6.26 (±0.02)	5.31 (±0.01)	5.65 (±0.01)[a]

[a]Uncertainty.

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Table 3. Infinite-Dilution Apparent Molar Volumes ($V_{\Phi,IL}^{\infty}$/cm^3·mol^{-1}) of [Bmim]BF_4 in Aqueous Glucose 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]	187.87 (±0.01)	188.05 (±0.02)	188.24 (±0.04)	188.51 (±0.01)	188.78 (±0.02)	188.95 (±0.03)
S_{IL}*	1.67 (±0.01)	1.61 (±0.01)	1.47 (±0.03)	1.35 (±0.05)	1.20 (±0.02)	1.00 (±0.01)	0.99 (±0.04)

[a]Uncertainty.

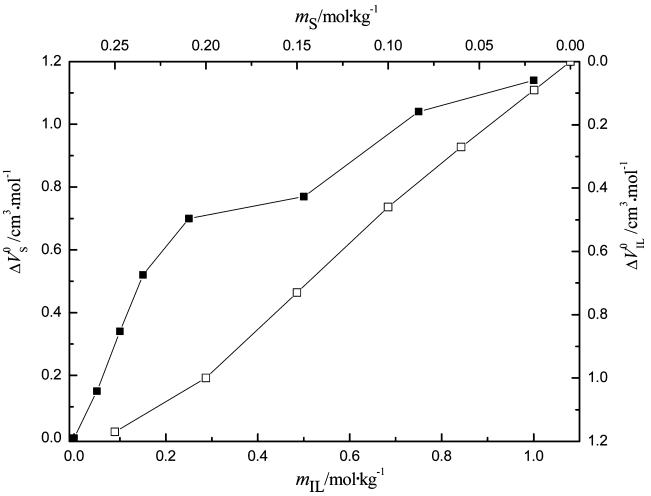

Figure 3. Variation of the standard transfer volumes, $\Delta_t V_S^0$, of glucose from water to aqueous [Bmim]BF_4 solutions (■) with the molality of [Bmim]BF_4; variation of the standard transfer volumes, $\Delta_t V_{IL}^0$, of [Bmim]BF_4 from water to aqueous glucose solutions (□) with the molality of glucose.

hydrated, the presence of [Bmim]BF_4 in water will decrease the hydration effects of hydroxyl groups of glucose 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[20,28]

$$\Delta_t V_{\Phi,S} = 2\upsilon\nu_{IS}m_{IL} + 3\upsilon^2\nu_{IIS}m_{IL}^2 + 3\upsilon\nu_{ISS}m_{IL}m_S + \ldots \quad (8)$$

$$\Delta_t V_{\Phi,IL} = 2\upsilon\nu_{IS}m_S + 3\upsilon^2\nu_{IIS}m_{IL}m_S + 3\upsilon\nu_{ISS}m_S^2 + \ldots \quad (9)$$

where $\Delta_t V_{\Phi,S}$ and $\Delta_t V_{\Phi,IL}$ are, respectively, the transfer volumes of glucose 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 glucose at m_S. Here, υ is the number of ions into which the electrolyte dissociates, and ν_{IS}, ν_{IIS}, and 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 8 and 9 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 interactions model proposed Desnoyers et al.[25] and the hydration model by Conway.[29] The positive ν_{IS} values are mainly due to the hydrophilic−ionic interactions, since the dehydration of ions and −OH, −C═O, and −O− group contribute a positive value to the volume.

In addition, we found that the ν_{IS} of the [Bmim]BF_4−glucose−water system (3.30) is larger than that of the [Bmim]BF_4−sucrose−water system (2.20),[6] which indicates that the interaction between [Bmim]BF_4 and glucose is more significant than [Bmim]BF_4−sucrose. More importantly, it was shown that ν_{ISS} is positive, which means glucose and [Bmim]BF_4 have not only pairwise, but triplet interaction. This was not found in the [Bmim]BF_4−sucrose−water system.[6]

■ CONCLUSIONS

In this work, we investigated the volumetric properties of [Bmim]BF_4−glucose−water mixtures. It was found that 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 glucose, respectively, and $V_{\Phi,S}^{\infty}$ have the order of glucose < sucrose. It could be concluded that the interaction of cation−O (O represents OH, C═O, and −O− groups of glucose) is predominant. Furthermore, we found that the volumetric interaction parameters ν_{IS} and ν_{ISS} are positive, suggesting that the interactions between the glucose and the [Bmim]BF_4 are mainly pair and triplet interaction, which is different from the [Bmim]BF_4−sucrose−water system.

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Notes

The authors declare no competing financial interest.

Table 4. Volumetric Interaction Parameters for the [Bmim]BF_4−Glucose−Water System 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	3.300 ± 0.015[a]	2.115 ± 0.012	−2.165 ± 0.018	0.03

[a]Uncertainty.

REFERENCES

(1) Wu, B.; Zhang, Y. M.; Wang, H. P. Aqueous biphasic systems of hydrophilic ionic liquids sucrose for separation. *J. Chem. Eng. Data* **2008**, *53*, 983−985.

(2) Wu, B.; Zhang, Y. M.; Wang, H. P. Phase behavior for ternary systems composed of ionic liquid + saccharides + water. *J. Phys. Chem. B* **2008**, *112*, 6426−6429.

(3) Wu, B.; Zhang, Y. M.; Wang, H. P. Temperature dependence of phase behavior for ternary systems composed of ionic liquid + sucrose + water. *J. Phys. Chem. B* **2008**, *112*, 13163−13165.

(4) Chen, Y. H.; Zhang, S. M. Phase behavior of 1-alkyl-3-methyl imidazolium tetrafluoroborate + 6-hydroxymethyloxane-2,3,4,5-tetrol + water. *J. Chem. Eng. Data* **2010**, *55*, 278−282.

(5) Chen, Y. H.; Meng, Y. S.; Zhang, S. M. Liquid-liquid equilibria of aqueous biphasic systems composed of 1-butyl-3-methyl imidazolium tetrafluoroborate−sucrose/maltose−water. *J. Chem. Eng. Data* **2010**, *55*, 3612−3616.

(6) Wu, B.; Zhang, Y. M.; Wang, H. P. Volumetric properties and conductivities of 1-butyl-3-methylimidazolium tetrafluoroborate + sucrose + water mixtures. *J. Chem. Eng. Data* **2009**, *54*, 1430−1434.

(7) Shekaari, H.; Kazempour, A. Effect of ionic liquid, 1-octyl-3-methylimidazolium bromide on the thermophysical properties of aqueous D-glucose solutions at 298.15 K. *Fluid Phase Equilib.* **2011**, *309*, 1−7.

(8) Shekaari, H.; Kazempour, A. Solution properties of ternary D-glucose + 1-ethyl-3-methylimidazolium ethyl sulfate + water solutions at 298.15 K. *J. Solution Chem.* **2011**, *40*, 1582−1595.

(9) Zhuo, K. L.; Chen, Y. H.; Chen, J. Interactions of 1-butyl-3-methylimidazolium carboxylate ionic liquids with glucose in water: a study of volumetric properties, viscosity, conductivity and NMR. *Phys. Chem. Chem. Phys.* **2011**, *13*, 14542−14549.

(10) Seddon, K. R.; Stark, A.; Torres, M. J. Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure Appl. Chem.* **2000**, *72*, 2275−2287.

(11) Heintz, A.; Klasen, D.; Lehmann, J. K. Excess molar volumes and viscosities of binary mixtures of methanol and the ionic liquid 4-methyl-n-butylpyridinium tetrafluoroborate at 25, 40, and 50 °C. *J. Solution Chem.* **2002**, *31*, 467−476.

(12) Nishida, T.; Tashiro, Y.; Yamamoto, M. Physical and electrochemical properties of 1-alkyl-3-methylimidazolium tetrafluoroborate for electrolyte. *J. Fluorine Chem.* **2003**, *120*, 135−141.

(13) Zhang, S.; Li, X.; Chen, H.; Wang, J.; Zhang, J.; Zhang, M. Determination of physical properties for the binary system of 1-ethyl-3-methylimidazolium tetrafluoroborate + H_2O. *J. Chem. Eng. Data* **2004**, *49*, 760−764.

(14) Lu, X.; Xu, W. G.; Gui, J. S.; Li, H. W.; Yang, J. Z. Volumetric properties of room temperature ionic liquid 1. The system of 1-methyl-3-ethylimidazolium ethyl sulfate + water at temperature in the range (278.15 to 333.15) K. *J. Chem. Thermodyn.* **2005**, *37*, 13−19.

(15) Zhang, Q. G.; Xue, F.; Tong, J. Studies on volumetric properties of concentrated aqueous solutions of the ionic liquid $BMIBF_4$. *J. Solution Chem.* **2006**, *35*, 297−309.

(16) Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H.; Hayamizu, K.; Watanabe, M. How ionic are room-temperature ionic liquids? An indicator of the physicochemical properties. *J. Phys. Chem. B* **2006**, *110*, 19593−19600.

(17) Shekaari, H.; Zafarani-Moattar, M. T. Volumetric properties of the ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate, in organic solvents at T = 298.15 K. *Int. J. Thermophys.* **2008**, *29*, 534−545.

(18) Jin, H. X.; Chen, H. Y. Volumetric properties for ionic liquid−sucrose−water mixtures. *J. Chem. Eng. Data* **2011**, *56*, 4392−4395.

(19) Huddleston, J. G.; Visser, A. E.; Rogers, R. D. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem.* **2001**, *3*, 156−164.

(20) de Visser, C.; Perron, G.; Desnoyers, J. E. Volumes and heat capacities of ternary aqueous systems at 25 °C. Mixtures of urea, tert-butyl alcohol, dimethylformamide, and water. *J. Am. Chem. Soc.* **1977**, *99*, 5894−5900.

(21) Malham, I. B.; Letellier, P.; Mayaffre, A. Part I: Thermodynamic analysis of volumetric properties of concentrated aqueous solutions of 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-2,3-dimethylimidazolium tetrafluoroborate, and ethylammonium nitrate based on pseudo-lattice theory. *J. Chem. Thermodyn.* **2007**, *39*, 1132−1143.

(22) Banipal, P. K.; Dhanjun, H. S.; Sharma, S.; Hundal, H. Effect of sodium sulphate on the volumetric, rheological and refractometric properties of some disaccharides in aqueous solutions at different temperature. *Z. Phys. Chem.* **2008**, *222*, 177−204.

(23) Hedwig, G. R. Thermodynamic properties of peptide solutions III. Partial molar volumes and partial molar heat capacities of some tripeptides in aqueous solution. *J. Solution Chem.* **1988**, *17*, 383−397.

(24) Zielenkiewicz, W.; Perlovich, G. L.; Nikitina, G. E.; Semeykin, A. S. Volumetric properties of tetraphenylporphine, their metallo-complexes and some substituted tetraphenylporphines in benzene solution. *J. Solution Chem.* **1996**, *25*, 135−153.

(25) Desnoyers, J. E.; Joly, M.; Perron, G.; Jolicoeur, C. Apparent molal volumes of alkali halides in water at 25 °C. Influence of structural hydration interactions on the concentration dependence. *J. Phys. Chem.* **1969**, *73*, 3346−3351.

(26) Savage, J. J.; Wood, R. H. Enthalpy of dilution of aqueous mixtures of amides, sugars, urea, ethylene glycol, and pentaerythritol at 25 °C: Enthalpy of interaction of the hydrocarbon, amide, and hydroxyl functional groups in dilute aqueous solutions. *J. Solution Chem.* **1976**, *5*, 733−750.

(27) Shahidi, F.; Farrell, P. G.; Edward, J. T. Partial molar volumes of organic compounds in water. III. Carbohydrates. *J. Solution Chem.* **1976**, *5*, 807−816.

(28) Perron, G.; Joly, D.; Desnoyers, J. E.; Avedikian, L.; Morel, J. P. Thermodynamics of the salting effect; free energies, enthalpies, entropies, heat capacities, and volumes of the ternary systems electrolyte-alcohol-water at 25 °C. *Can. J. Chem.* **1978**, *56*, 552−559.

(29) Conway, B. E. *Ionic Hydration in Chemistry and Physics*; Elsevier: Amsterdam, 1980.