Journal of chemical & engineering data

Article

Cite This: *J. Chem. Eng. Data* XXXX, XXX, XXX−XXX

pubs.acs.org/jced

Vapor Pressure Osmometry Studies of Aqueous Ionic Liquid−Carbohydrate Systems

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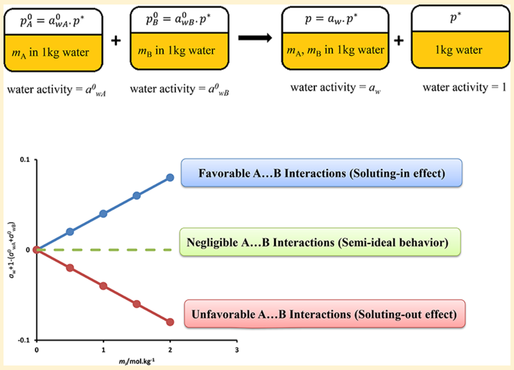
Supporting Information

ABSTRACT: Precise vapor pressure osmometry (VPO) measurements at 308.15 K were conducted for solutions of three ILs, 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]), 1-butyl-3-methylimidazolium bromide ([Bmim][Br]), and 1-butyl-3-methylimidazolium hydrogen sulfate ([Bmim][HSO_4]), in aqueous solutions of three carbohydrates, sucrose, maltose, and maltitol, as well as for solutions of the carbohydrates in aqueous solutions of these ILs. Because of the unfavorable IL−carbohydrate interactions, all the investigated IL + carbohydrates aqueous systems show the soluting-out effect and vapor−liquid equilibria behavior of these systems in the monophasic region show the negative deviation from the semi-ideal behavior ($a_w + 1 < a_{wIL}{}^\circ + a_{wC}{}^\circ$ and $\Delta p < \Delta p_{IL}{}^\circ + \Delta p_C{}^\circ$). For a certain carbohydrate and at the same molality of IL, the magnitude of the departures for the investigated ILs follows the order: [Bmim][BF_4] > [Bmim][HSO_4] ≫ [Bmim][Br]. In the case of [Bmim][BF_4]/carbohydrate aqueous systems, which have a phase separation capability, the soluting-out power of the carbohydrates on [Bmim][BF_4] in aqueous solutions (or negative deviation from the semi-ideal behavior) reduced by decreasing the hydrophilicity of the carbohydrates. Aqueous [Bmim][Br]/carbohydrate and [Bmim][HSO_4]/carbohydrate systems are unable to form the ABS, and the soluting-out effect of the ILs on the aqueous carbohydrate solutions appears in the form of precipitation of sugars from the aqueous solutions.



1. INTRODUCTION

After introducing the aqueous biphasic systems (ABS) and their applications in bioseparation processes by Albertson,[1] a lot of work has been conducted to introduce the new ABSs, to obtain thermodynamic information about the soluting effect phenomenon, and effective applications of ABS in biotechnology. ABS are formed of two aqueous A-rich and B-rich phases and both the phases have a water content above 70% that can provide the gentle environment for biomolecules. These systems are categorized based on ionic liquid/salt,[2] ionic liquid/polymer,[3] polymer/salt,[4] polymer/amino acid,[5] polymer/carbohydrate,[6] or ionic liquid/amino acid[7] compositions. These systems can be used for the extraction and purification of different types of valuable materials from biomolecules to metal ions.[7−9] In recent years, ionic liquids gained attention for their interesting properties such as negligible vapor pressures, nonflammability, and good thermal and electrochemical stabilities. Rogers and co-workers in 2003 established that these electrolytes are capable of ABS formation in the presence of the salts.[10] In 2007, Zhang et al. reported the ability of carbohydrates to solute-out ionic liquids from aqueous solution.[11] Carbohydrates are nontoxic, renewable feedstock and biodegradable organic molecules and use of them in the formation of IL/carbohydrate ABS has various advantages.[12,13] The soluting effect in aqueous ternary solute A + solute B solutions resulted from the quality of solute-water and solute A−solute B interactions. The difference between vapor−liquid equilibria (VLE) data for a certain aqueous ternary IL−carbohydrate system and its corresponding aqueous binary IL and carbohydrate solutions can provide some valuable information about soluting effect produced by addition of one solute to aqueous solution of another solute and therefore explain phase-forming ability of these systems.[3,6,14,15] The activity coefficient, osmotic coefficient, water activity, and Gibbs energy of transfer can be obtained from different technics such as direct vapor pressure measurements, isopiestic method, membrane osmometry, electromotive force measurements, headspace chromatography, and vapor pressure osmometry (VPO).[16] In this work, we used the VPO method because of its reliability, performance at ambient pressure, easier and cheaper, and shorter time measurements. In recent years various thermodynamic studies have been conducted on the aqueous solutions containing some imidazolium based ILs or carbohydrates.[3,17−25] However, as far as we know there is very limited information about the ternary aqueous carbohydrate−IL solutions in the literature.[11,13,26−30] In ternary aqueous IL + solute solutions, ILs can act as both soluting-out agent and a component that is soluted-out from the solution depending on the hydrophilicity differences

Received: August 8, 2017
Accepted: January 9, 2018

DOI: 10.1021/acs.jced.7b00719
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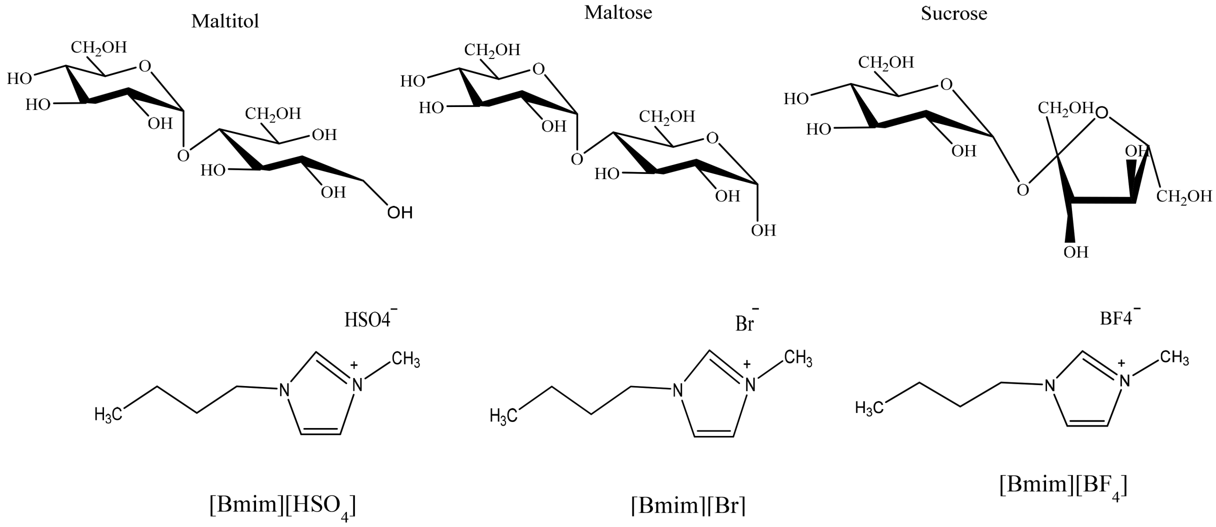
Table 1. Specification of Chemicals Used in this Work

chemical	source	CAS registry number	mass fraction purity	water content (mass fraction)
maltitol	Alfa Aesar	585-88-6	≥0.97	
sucrose	Merck	57-50-1	≥0.98	
maltose monohydrate	Merck	6363-53-7	≥0.99	
NaCl	Merck	7647-14-5	≥0.995	
sodium tetrafluoroborate	Merck	13755-29-8	≥0.97	
1-methylimidazole	Merck	616-47-7	≥0.99	
1-bromobutane	Merck	109-65-9	≥0.98	
$[Bmim][HSO_4]$	IoLiTec	262297-13-2	>0.99	<0.003
[Bmim][Br]	synthetic[33]		≥0.98	<0.003
$[Bmim][BF_4]$	synthetic[33]		≥0.98	<0.001

Scheme 1. Chemical Structures of the Carbohydrates and Ionic Liquids Studied



between the IL and the secondary solute. In order to study both situations, we chose three ILs and three sugars that their hydrophilicity powers follow the order: $[Bmim][HSO_4]$ > [Bmim][Br] ≥ carbohydrates ≫ $[Bmim][BF_4]$.[31,32] Therefore, $[Bmim][BF_4]$, which is more hydrophobic than the selected carbohydrates, and $[Bmim][HSO_4]$ and [Bmim][Br], which are more hydrophilic than the investigated carbohydrates, were selected. In order to study the effects of some parameters, such as number of hydroxyl groups, stereochemical properties of carbohydrate molecules, and anion of ionic liquids, on the vapor–liquid equilibria behavior of these systems, three ionic liquids mentioned above and three carbohydrates including disaccharides maltose and sucrose and a polyol (maltitol) were selected and the thermodynamic properties of their ternary aqueous systems were studied at 308.15 K.

2. EXPERIMENTAL SECTION

2.1. Materials. The properties of chemicals used in this work were listed in Table 1. Sodium chloride was dried in an electrical oven at 383.15 K for 24 h prior to use. The water content of the ionic liquids were determined by Karl Fischer titration. The purities of the ILs were determined by Karl Fischer titration and NMR spectroscopy. Double distilled and deionized water were used for the preparation of the solutions. The structures of studied carbohydrates and ionic liquids have been presented in Scheme 1.

2.1.1. Synthesis of Ionic Liquids. Ionic liquids [Bmim][Br] and $[Bmim][BF_4]$ were synthesized and purified according to standard procedures described in the literature.[33]

Synthesis of [Bmim][Br]. Equimolar quantities of butyl bromide (slightly excess) and 1-methylimidazole with an appropriate amount of ethyl acetate as solvent were added to a round-bottomed flask connected to a reflux condenser for 48 h at 70 °C with stirring until two phases formed. The reaction was conducted under an argon atmosphere. The top phase, containing unreacted starting materials along with ethyl acetate, was decanted and fresh ethyl acetate was again added, this process was repeated six times. Finally the bottom phase was vacuum-dried at 90 °C for 3 h to remove the traces of ethyl acetate. Yield of reaction was 95%. The ionic liquid was analyzed by FT-IR and ^1H NMR and ^{13}C NMR spectroscopy. The FT-IR spectrum of the synthesized IL contains the peaks at ν/cm^{-1} 3076 Br, 2960 (s, aliphatic C–H stretch), 1628 (w, C=C), 1568 (s, sym. ring stretch), 1463 (s, sym ring stretch), 1114 (w, sym. ring stretch), 1380 (m, CH_3 bending vibration), 1168 (s, C–N vibration). ^1H NMR spectrum contains peaks at δ(ppm): 0.53 (t, J = 7.3, 3H), 0.89–1.03 (m, 2H), 1.44–1.56 (m, 2H), 3.72 (s, 3H), 3.95 (t, J = 7.13, 2H), 7.3 (s, 1H), 7.4 (s, 1H), 9.82 (s, 1H). ^{13}C NMR: 13, 19, 31.8, 36.3, 49.4, 122, 123.6, 136.6.

Synthesis of $[Bmim][BF_4]$. In total, 0.1 mol (22 g) of [Bmim][Br] and an appropriate amount of acetone (about 100 mL) as solvent were added to the single-mouth flask connected to a reflux condenser until the IL was dissolved completely. Then 0.1 mol (11 g) of $NaBF_4$ was added to the obtained IL

Table 2. Experimental Water Activity, a_w, and vapor pressure, p, against IL Molality, m_{IL},[a] for Ternary Solutions of the ILs in Aqueous Solution of 1 mol kg^{-1} of the Carbohydrates at 308.15 K

m_{IL}/(mol kg^{-1})	a_w	p/(kPa)	m_{IL}/(mol kg^{-1})	a_w	p/(kPa)	m_{IL}/(mol kg^{-1})	a_w	p/(kPa)
[Bmim][BF$_4$] in sucrose			[Bmim][BF$_4$] in maltose			[Bmim][BF$_4$] in maltitol		
0.0000	0.9811	5.520	0.0000	0.9818	5.524	0.0000	0.9813	5.521
0.4772	0.9680	5.446	0.2571	0.9738	5.479	0.2561	0.9731	5.475
0.9290	0.9609	5.406	0.5665	0.9668	5.440	0.3863	0.9698	5.456
1.5150	0.9551	5.375	1.0799	0.9593	5.397	0.7878	0.9623	5.414
2.0601	0.9524	5.359	1.5394	0.9556	5.377	1.3730	0.9561	5.379
2.6400	0.9526	5.360	1.8066	0.9552	5.374	1.5135	0.9565	5.382
2.7012	0.9526	5.360	1.8117	0.9557	5.377	2.0728	0.9559	5.378
3.2435	0.9520	5.356	2.0676	0.9553	5.375			
			2.5288	0.9544	5.370			
[Bmim][Br] in sucrose			[Bmim][Br] in maltose			[Bmim][Br] in maltitol		
0.0000	0.9814	5.522	0.0000	0.9829	5.530	0.0000	0.9813	5.521
0.3095	0.9725	5.472	0.3292	0.9735	5.477	0.3053	0.9725	5.471
0.5262	0.9668	5.439	0.5639	0.9673	5.442	0.5183	0.9668	5.439
0.7610	0.9609	5.407	0.7710	0.9623	5.414	0.7629	0.9608	5.406
			0.9929	0.9571	5.385			
			1.4629	0.9470	5.328			
[Bmim][HSO$_4$] in sucrose			[Bmim][HSO$_4$] in maltose			[Bmim][HSO$_4$] in maltitol		
0.0000	0.9813	5.521	0.0000	0.9816	5.523	0.0000	0.9814	5.522
0.3440	0.9678	5.445	0.3351	0.9690	5.452	0.6116	0.9591	5.396
1.1305	0.9418	5.299	0.6151	0.9594	5.398	1.1172	0.9430	5.306
1.9503	0.9175	5.162	1.2209	0.9400	5.289	1.1335	0.9425	5.303
2.7635	0.8954	5.038	1.8604	0.9210	5.182	1.5263	0.9307	5.237
			2.6014	0.9016	5.073	2.5753	0.9023	5.077

[a] m_{IL} (ionic liquid molality) = the number of moles of IL per kilogram of water.The standard uncertainty in the measurement of water activity, temperature, vapor pressure, and molality were found to be 2 × 10^{-4}, 5 × 10^{-3} K, 1 × 10^{-3} kPa, and 0.01 mol kg^{-1}, respectively.

solution and then stirred for 48 h at 55 °C. Because of the presence of white precipitate, the reaction mixture was filtered and vacuum distilled. Dichloromethane as the extraction solvent was added to the residue liquid (in order to removal of the bromide salt), and the white precipitated NaBr salt was obtained. Then, the solid precipitate was separated by filtration and the product solution was dissolved in an excess amount of dichloromethane and was washed 3−5 times with deionized water to ensure complete removal of the bromide salt. Aqueous phase was tested with a saturated solution of $AgNO_3$. The product was dried for more than 5 h under vacuum conditions at 120 °C to remove the traces of dichloromethane and water. Finally, a colorless to pale yellow liquid with a yield of 75% was obtained. The compound was analyzed by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. The FT-IR spectrum of [Bmim][BF$_4$] contains the peaks at ν/cm^{-1} 2938 and 2876 (aliphatic asymmetric and symmetric (C−H) stretching vibrations), 1171 and 1059 (inplane bending vibrations for methyl groups), a broad peak at 3122−3162 (for quaternary amine salt formation with tetrafluoroborate), 1657 (stretching C═C), 1466 (stretching C═N), 757 and 623 (stretching vibration C−N). ^{1}H NMR spectrum contains peaks at δ(ppm): 0.89 (t, J = 7.1, 3H), 1.25−1.36 (m, 2H), 1.77−1.89 (m, 2H), 3.91 (s, 3H), 4.17 (t, J = 7.3, 2H), 7.44 (s, 2H), 8.67 (s, 1H). ^{13}C NMR: 13, 19, 31.6, 35.8, 49.4, 122.3, 123.6, 135.8. The NMR spectra of both the synthesized ILs are presented in the Supporting Information (Figures S1−S4).

2.2. Experimental Procedures. All the solutions were prepared freshly by mass using a Sartorius CP124S balance precise to within ±1.10^{-7} kg. The VPO measurements performed with the help of an Osmomat K-7000 (Knauer Inc.) at 308.15 K. The instrument has two thermistors (1 and 2) placed in an airtight cell which measure resistance changes aroused from the changes in temperature. The cell temperature was controlled electronically within ±1 × 10^{-3} K. Initially, a droplet of pure water is placed on each thermistor, and after equilibration (about 5 min), the reading is adjusted to zero. Then, the pure water on the thermistor 1 is replaced by the under study solution. Because of the heat of condensation of water from the vapor phase into the solution droplet, the thermistor 2 will be warmed until the vapor pressure of the droplet on the thermistor 2 equals that of the pure water droplet. Generally, the times of 4−8 and 15−20 min suffice to reach this steady state, respectively, for monophasic and biphasic samples. In this steady state, a bridge circuit measures the resistance differences aroused from the temperature difference between the two thermistors. Before analysis of the samples, the apparatus was calibrated with the help of reference aqueous NaCl solutions in the proper concentration range, resulting a function which correlates the panel readings to the corresponding concentrations of the sodium chloride aqueous solutions (Figure S5 of the Supporting Information). The following relation was used to correlate instrument panel reading (signal, SI) and NaCl molality (m_{NaCl}):

$$m_{NaCl} = a_0 + a_1\mathrm{SI} + a_2\mathrm{SI}^2 + a_3\mathrm{SI}^3 \tag{1}$$

where a_0, a_1, a_2, and a_3 are calibration constants and their values along with the standard deviation are reported in Table S1 of the Supporting Information. For a certain aqueous solution which has the same instrument reading as a sodium chloride solution with molality m_{NaCl}, the water activity, a_w, was obtained according to[34]

$$a_w = \exp(-0.001\nu_{NaCl}m_{NaCl}\Phi_{NaCl}M_w) \tag{2}$$

Table 3. Experimental Water Activity, a_w, and Vapor Pressure, p, against Carbohydrate Molality, m_C,[a] for Ternary Solutions of the Carbohydrates in Aqueous Solution of the ILs at 308.15 K

m_C/(mol kg^{-1})	a_w	p/(kPa)	m_C/(mol kg^{-1})	a_w	p/(kPa)	m_C/(mol kg^{-1})	a_w	p/(kPa)
carbohydrates in aqueous solution of 1 mol kg^{-1} of [Bmim][Br]								
	sucrose			maltose			maltitol	
0.0000	0.9737	5.478	0.0000	0.9737	5.478	0.0000	0.9737	5.478
0.5116	0.9630	5.418	0.5843	0.9616	5.410	0.7093	0.9588	5.394
1.5644	0.9398	5.288	0.8966	0.9552	5.375	0.8365	0.9559	5.378
2.5600	0.9165	5.157	1.1163	0.9509	5.350	1.1777	0.9482	5.335
						1.3042	0.9453	5.319
						1.9174	0.9312	5.239
crbohydrates in aqueous solution of 1 mol kg^{-1} of [Bmim][HSO$_4$]								
	sucrose			maltose			maltitol	
0.0000	0.9697	5.456	0.0000	0.9697	5.456	0.0000	0.9697	5.456
0.2070	0.9631	5.418	0.1627	0.9659	5.435	0.1735	0.9658	5.434
0.6429	0.9510	5.351	0.4920	0.9584	5.392	0.5318	0.9574	5.387
0.8307	0.9463	5.324	0.7948	0.9516	5.354	0.9077	0.9484	5.336
1.1873	0.9361	5.267	1.1258	0.9443	5.313			
crbohydrates in aqueous solution of 1.5 mol kg^{-1} of [Bmim][BF$_4$]								
	sucrose			maltose			maltitol	
0.0000	0.9786	5.506	0.0000	0.9786	5.506	0.0000	0.9786	5.506
0.2608	0.9727	5.473	0.4289	0.9683	5.448	0.4292	0.9678	5.445
0.7540	0.9623	5.414	0.7778	0.9609	5.407	0.8164	0.9591	5.396
1.2818	0.9500	5.345	1.2022	0.9517	5.355	1.1046	0.9544	5.370
1.5832	0.9446	5.315	1.3889	0.9500	5.345	1.6086	0.9477	5.332
2.0081	0.9371	5.272	1.7899	0.9445	5.314	1.9741	0.9396	5.287

[a] m_C (carbohydrate molality) = the number of moles of carbohydrate per kilogram of water. The standard uncertainty in the measurement of water activity, temperature, vapor pressure, and molality were found to be 2×10^{-4}, 5×10^{-3} K, 1×10^{-3} kPa, and 0.01 mol kg^{-1}, respectively.

where ν_{NaCl} is the stoichiometric number of reference electrolyte and M_w is the molar mass of water. Φ_{NaCl} is the osmotic coefficient for aqueous solutions of NaCl with molality m_{NaCl} calculated from the correlation of Clarke and Glew.[35] From the water activity values, the vapor pressures of aqueous solutions, p, were determined according to

$$\ln(a_w) = \ln\left(\frac{p}{p_w^0}\right) + \frac{(B_w^0 - V_w^0)(p - p_w^0)}{RT} \quad (3)$$

where $B_w{}^0$ and $V_w{}^0$ are the second virial coefficient and molar volume of pure water, respectively. $p_w{}^0$ is the vapor pressure of pure water calculated using the Saul and Wagner's equation of state.[36] By taking into account all the factors (X_i) affecting the quantity Y, such as repeatability of instrument, purity of sample, composition, and temperature, the combined uncertainty in quantity Y was obtained by $u(Y)^2 = \Sigma(u(X_i)\partial Y/\partial X_i)$, in which $u(Y)^2$ is the combined uncertainty and $u(X_i)$ is the experimental uncertainty in the measured quantity X_i.

3. RESULTS AND DISCUSSION

In order to study of relation between the VLE behavior and the soluting effect phenomenon in aqueous IL/carbohydrate systems, VPO measurements were conducted for aqueous [Bmim][BF$_4$]/sucrose, [Bmim][BF$_4$]/maltose, [Bmim][BF$_4$]/maltitol, [Bmim][Br]/sucrose, [Bmim][Br]/maltose, [Bmim][Br]/maltitol, [Bmim][HSO$_4$]/sucrose, [Bmim][HSO$_4$]/maltose, and [Bmim][HSO$_4$]/maltitol systems at 308.15 K. The experimental water activity and vapor pressure data were obtained for solutions of the ILs in aqueous solutions 1 mol kg^{-1} of the carbohydrates and for solutions of the carbohydrates in aqueous solutions 1 mol kg^{-1} of [Bmim][Br] and [Bmim][HSO$_4$] and 1.5 mol kg^{-1} of [Bmim][BF$_4$]. Since the used maltose was in a monohydrate form, in the case of solutions of maltose in aqueous IL solutions, because of the water molecules released from maltose monohydrate crystals, the molality of the ILs in the solutions cannot be constant and in fact it slightly decreases by increasing molality of maltose. The changes in the molalities of ILs for maltose + [Bmim][BF$_4$], maltose + [Bmim][Br], and maltose + [Bmim][HSO$_4$] systems were in the range of 1.5000−1.4517, 0.9997−0.9796, and 0.9998−0.9795 mol kg^{-1}, respectively. In the case of aqueous [Bmim][BF$_4$]/sugar systems, with the ability to form ABS, the water activity and vapor pressure data were obtained in both mono and biphasic regions. However, for [Bmim][Br]/carbohydrate and [Bmim][HSO$_4$]/carbohydrate systems that cannot form ABS, the vapor−liquid equilibria behavior was studied only in the monophasic region.

Tables 2 and 3 present the experimental water activity and vapor pressure values of the investigated systems. In Figure 1, the experimental values of water activities for solutions of sucrose in aqueous solutions of 1 mol kg^{-1} [Bmim][Br] have been compared with the literature values.[27] As can be seen, there is a good agreement between our experimental water activity data and those taken from the literature.

In order to study the soluting effect occurring in a ternary A + B + water solution, we consider deviations from the following ideal behavior equations:[15,37]

$$(a_w + 1) - (a_{wA}^0 + a_{wB}^0) = 0 \quad (4)$$

$$\Delta p - (\Delta p_A^0 + \Delta p_B^0) = 0 \quad (5)$$

where a_w and $\Delta p = p - p^*$, respectively, are the water activity and vapor pressure depression in the aqueous ternary A + B solution with solute molalities m_A and m_B. In these equations $a_i{}^\circ$ and $\Delta p_i{}^\circ = p_i{}^\circ - p^*$, respectively, are the water activity and

DOI: 10.1021/acs.jced.7b00719

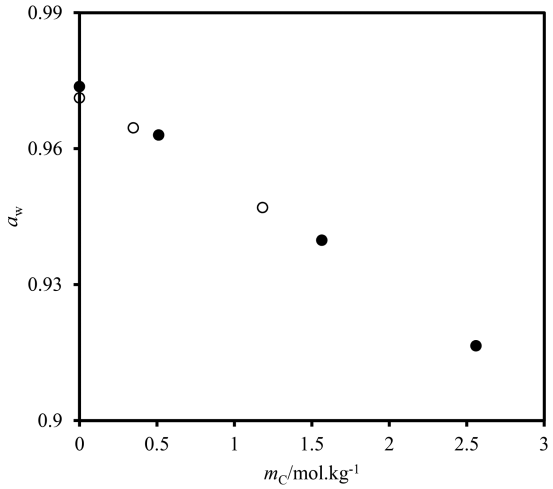


Figure 1. Plot of a_w against carbohydrate molality, m_C, for solutions of sucrose in aqueous solutions of 1 mol kg^{-1} [Bmim][Br]. ●, This work at T = 308.15 K; ○, ref 27 at T = 298.15 K.

vapor pressure depression in the binary i + water solutions with the same solute molalities as the aqueous ternary solution. Equations 4 and 5 are established for the ternary semi-ideal solutions that the A–B interactions can be either mutually self-canceled or neglected. In such systems the A–water and B–water interactions in the ternary solutions are the same as those in the corresponding binary solutions.

Departures from eqs 4 and 5, Δa_w and $\Delta \pi_w$ are calculated from the following equations:

$$\Delta a_w = a_w + 1 - (a_{wA}^0 + a_{wB}^0) \tag{6}$$

$$\Delta \pi_w = \Delta p - (\Delta p_A^0 + \Delta p_B^0) \tag{7}$$

The water activity and vapor pressure of the investigated binary carbohydrate–water and IL–water solutions were obtained from the our previous work.[19,30] The soluting effect phenomenon, which resulted from the quality of A–B and solute–solvent interactions, leads to the negative or positive deviations from the semi-ideal behavior. This effect can increase and decrease the mutual solubilities of each solute in the presence of another solute which, respectively, is known as the soluting-in and soluting-out effects. For A + B + water systems which show the soluting-in effect, as a consequence of preferential A–B interactions, the interaction of each solute with water molecules becomes weaker in the presence of the other solute. Therefore, water molecules released from the hydration shell of solutes to the bulk state and more free water molecules would be available with respect to the semi-ideal behavior in which the solute–water interactions in the ternary solution are the same as those in the binary solutions and therefore $\Delta a_w > 0$ and $\Delta \pi_w > 0$ (positive deviation). In these systems, the activity coefficient of solute A in aqueous solution is lowered by the presence of solute B.[38] On the other hand, for A + B + water systems which show the soluting-out effect, because of the unfavorable A–B interactions, the interaction of each solute with water becomes stronger in the presence of another solute, and therefore, in these ternary systems, less free water molecules would be available with respect to the semi-ideal behavior, and then these systems show negative departures from eqs 4 and 5 ($\Delta a_w < 0$ and $\Delta \pi_w < 0$). Because of the unfavorable A–B interactions, they exclude themselves from the vicinity of each other due to their preferential hydration. At higher concentrations, this exclusion will increase, and ultimately, the system could reach a state where, for entropic reasons, phase formation would become favorable and these systems separate into an A-rich aqueous phase and a B-rich aqueous phase. By phase separation, the partial dehydration of solutes leads to increasing the free water molecules in systems and therefore increasing the entropy of system.

The plots of Δa_w and $\Delta \pi_w$ against solutes molality for the investigated [Bmim][BF$_4$] + carbohydrate + water systems are shown in Figures 2 and 3. In these systems since the carbohydrates are more hydrophilic than the IL, the IL is soluted out by the carbohydrates and the soluting-out effect appears with ABS formation (visual observation).

As can be seen from these figures, for aqueous [Bmim][BF$_4$] + carbohydrate systems, which are capable of phase separation, the slopes of the plots of Δa_w and $\Delta \pi_w$ against solute molality in the before and after of phase separation points are negative and positive, respectively. In fact, all of these plots showed a shape of two lines, respectively, with negative and positive slopes intersecting at the break point, which corresponds to a point on the binodal curve. Comparison of parts a and b of Figure 2 for [Bmim][BF4]–sugars systems shows that in the case of solutions of [Bmim][BF$_4$] in aqueous solution of the sugars (Figure 2a), the break point of the maltose containing system is close to that of the maltitol containing system. However, in the case of solutions of carbohydrates in an

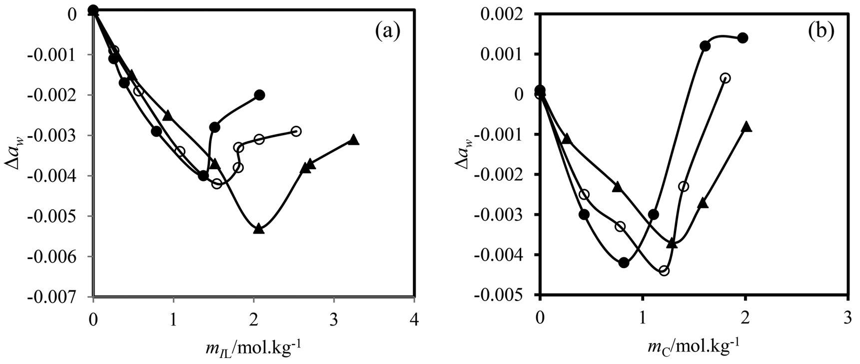


Figure 2. Plot of Δa_w against solute molality, m_{IL} or m_C, for [Bmim][BF$_4$] + carbohydrate + water systems at 308.15 K. (a) [Bmim][BF$_4$] in aqueous solution of 1 mol kg^{-1} of carbohydrates and (b) carbohydrates in aqueous solution of 1.5 mol kg^{-1} of [Bmim][BF$_4$]. ●, maltitol; ○, maltose; ▲, sucrose.

DOI: 10.1021/acs.jced.7b00719
J. Chem. Eng. Data XXXX, XXX, XXX–XXX

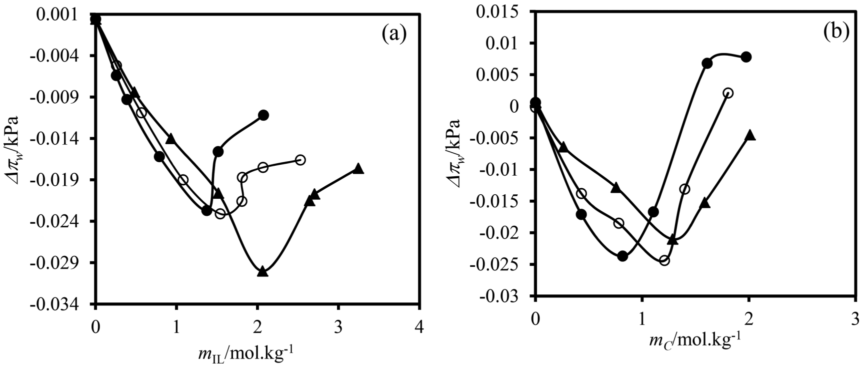


Figure 3. Plot of $\Delta\pi_w$ against solute molality, m_{IL} or m_C, for [Bmim][BF_4] + carbohydrate + water systems at 308.15 K. (a) [Bmim][BF_4] in aqueous solution of 1 mol kg^{-1} of carbohydrates and (b) carbohydrates in aqueous solution of 1.5 mol kg^{-1} of [Bmim][BF_4]. ●, maltitol; ○, maltose; ▲, sucrose.

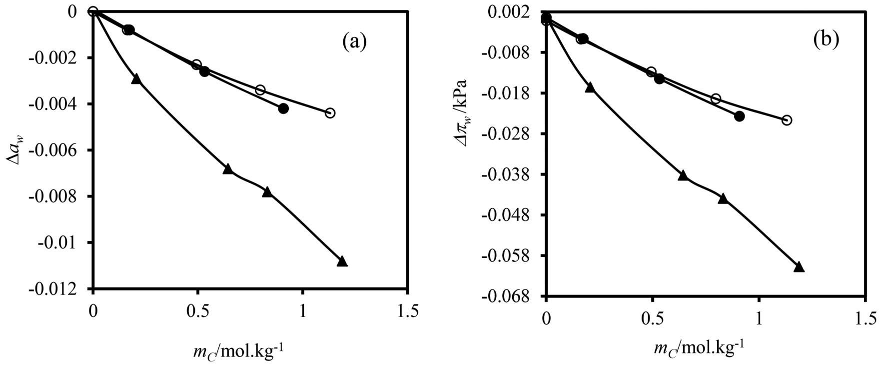


Figure 4. Plots of Δa_w (a) and $\Delta\pi_w$ (b) against carbohydrate molality, m_C, for solutions of the carbohydrates in aqueous solutions of 1 mol kg^{-1} [Bmim][HSO_4] at T = 308.15 K. ●, maltitol; ○, maltose; ▲, sucrose.

aqueous solution of [Bmim][BF_4] (Figure 2b), the break point of the maltose containing system is close to that of sucrose containing system (the phase separation occurs in the higher concentration of maltose in relative to those we expect from Figure 2a). As mentioned above, in the IL + maltose systems in which maltose acts as solute, the molality of [Bmim][BF_4] is not constant and decreases with increasing the molality of maltose. Therefore, a higher concentration of maltose is needed for phase separation.

In the monophasic region, the large negative deviation from the semi-ideal behavior was observed (soluting-out effect). Because of the unfavorable [Bmim][BF_4]−carbohydrate interactions, the solutes in ternary solutions exclude themselves by strengthening their interactions with water molecules, and therefore, the solute−water interaction in the ternary solutions is stronger than those in the corresponding binary solutions with the same molalities. This phenomenon reduces the amount of free water molecules in the bulk state compared to the semi-ideal solution, and therefore $a_w + 1 < a_{wIL}^\circ + a_{wC}^\circ$ ($\Delta a_w < 0$) and $\Delta p < \Delta p_{IL}^\circ + \Delta p_C^\circ$ ($\Delta\pi_w < 0$). By increasing the concentration of the solutes, the extent of the exclusion zone increases and thus the entropy of the system decreases, and eventually above a critical concentration, phase separation occurs and an aqueous biphasic system is formed. In fact by phase separation, the extent of the exclusion zones decreases and then the entropy of system increases. In other words, entropy increase is the driving force for ABS formation. By phase separation, the solutes in each phase is slightly dehydrated that leads to increasing of water activity and vapor pressure of the aqueous biphasic solution and therefore reducing magnitude of departure from the semi-ideal behavior. As can be seen from Figure 2, at each solute molality in the monophasic region, the magnitude of the negative departure follows the order: maltitol > maltose > sucrose. This trend is quite in agreement with the liquid−liquid equilibria behavior of aqueous [Bmim][BF_4]−carbohydrate systems in which the biphasic region decreases in the order: maltitol > maltose > sucrose.

The observed trend for the magnitude of the negative departure from the semi-ideal behavior shows that the unfavorability of interactions of [Bmim][BF_4] with the investigated carbohydrates follows the order: maltitol > maltose > sucrose. It was shown that the solubility of monosaccharides in pure [Bmim][BF_4][39,40] follows the order: fructose > glucose, and therefore the [Bmim][BF_4]−maltose (which contains two glucose molecules) interaction is more unfavorable than [Bmim][BF_4]−sucrose (which contains two monosaccharides glucose and fructose) interaction, and consequently maltose has a higher soluting-out power than sucrose. The magnitude of negative deviation for maltitol is larger than maltose. Maltitol, which has one additional hydroxyl group instead of etheric oxygen, has more capability for hydrogen bounding with water molecules and therefore shows a higher strength for phase separation. There is two different and quit reverse orders for magnitude of Δa_w and $\Delta\pi_w$ in the mono and biphasic regions of [Bmim][BF_4]−carbohydrate aqueous systems: maltitol > maltose > sucrose, in the monophasic region, and sucrose > maltose > maltitol, in the biphasic region. In the case of systems which have more unfavorable IL−carbohydrate interactions, more partial dehydration occurs by ABS formation.

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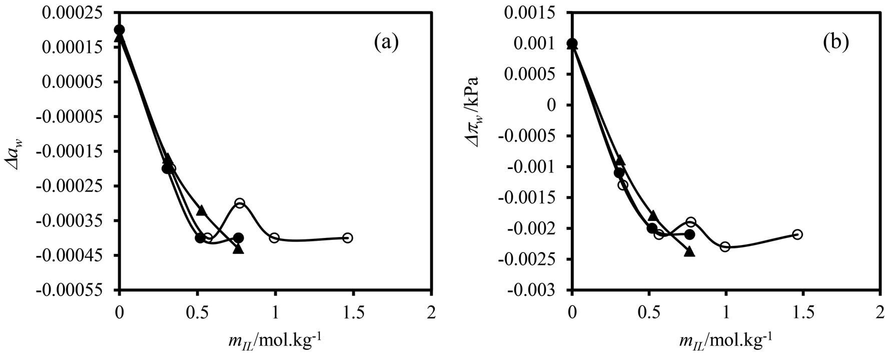

Figure 5. Plots of Δa_w (a) and $\Delta \pi_w$ (b) against IL molality, m_{IL}, for solutions of [Bmim][Br] in aqueous solutions of 1 mol kg^{-1} different carbohydrates at T = 308.15 K. ●, maltitol; ○, maltose; ▲, sucrose.

The plots of Δa_w and $\Delta \pi_w$ against solutes molality for the investigated [Bmim][HSO_4] + carbohydrate + water and [Bmim][Br] + carbohydrate + water systems are shown in Figures 4 and 5, respectively. Figure 4 shows that the magnitude of the departures from the semi-ideal behavior for [Bmim][HSO_4]−carbohydrate systems follows the order: sucrose ≫ maltitol ≅ maltose. As can be seen from Figure 5, for [Bmim][Br]−carbohydrate systems the negative departures are very small and the VLE behavior of these systems are close to the semi-ideal behavior. In these systems, the magnitude of the deviations are equal for all the [Bmim][Br]−carbohydrate systems. The small hydrophilicity differences between [Bmim][Br] and the investigated carbohydrates and favorable interactions between Br^- and the hydroxyl groups of carbohydrates[41] lead to reducing the soluting-out effect of [Bmim][Br] on the aqueous solutions of the carbohydrates.

Figure 6 shows that the magnitude of the negative departure from the semi-ideal behavior for a certain carbohydrate and at the same molality of IL follows the order: [Bmim][BF_4] > [Bmim][HSO_4] ≫ [Bmim][Br]. For the other IL−carbohydrate systems, similar behaviors were obtained.

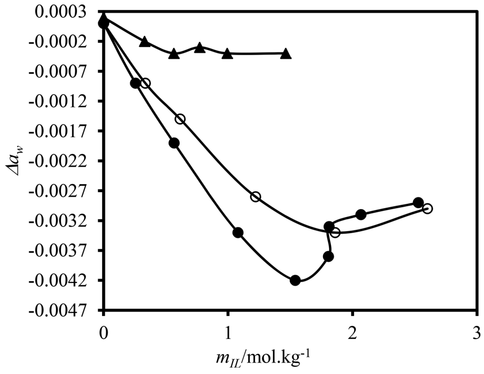

Figure 6. Plots of Δa_w, against IL molality, m_{IL}, for solutions of different ILs in aqueous solutions of 1 mol kg^{-1} of maltose at T = 308.15 K.●, [Bmim][BF_4]; ○, [Bmim][HSO_4]; ▲, [Bmim][Br].

All the investigated aqueous IL−carbohydrate systems (capable or not of ABS formation) show the negative departure from the semi-ideal behavior and therefore soluting-out effect has been observed in these systems. The investigated ILs in this work are different in their anions. The values of hydrogen bond accepting (HBA) strength β[42] and Gibbs free energies of hydration (ΔG_{hyd})[43] for the anions of the investigated ILs show that the ability of these anions to create hydration complexes follows the order: HSO_4^- > Br^- > BF_4^-, and therefore BF_4^- anion is less hydrated than the other anions (Table 4). In the case of HSO_4^-, protonation/deprotonation equilibria leads to the production of SO_4^{2-}, which forms the more stable hydration complexes with water molecules. On the other hand, the hydrophilicity power of the investigated carbohydrates and ILs obey the order: [Bmim][HSO_4] > [Bmim][Br] ≥ carbohydrates ≫ [Bmim][BF_4]. This trend explains the observed negative departures from the semi-ideal behavior (soluting-out effect) for all investigated IL−carbohydrate systems. In aqueous [Bmim][Br]/carbohydrate and [Bmim][HSO_4]−carbohydrate systems, the ILs (more hydrophilic solutes) act as the soluting-out agent and they reduce the solubility of carbohydrates (more hydrophobic solutes) in aqueous solutions. In fact, in these systems the soluting-out effect appears with solid−liquid equilibria formation. In the case of [Bmim][Br] and [Bmim][HSO_4] + carbohydrate + water systems, in the concentration range studied in this work, there is no any solid−liquid equilibria observation. In fact, the solubility of the carbohydrates in the aqueous solutions of these ILs is higher than the concentration range studied here. [Bmim][HSO_4] is more hydrophilic than [Bmim][Br] and thereby shows the larger deviation from the semi-ideal behavior. From the solubility data,[32] it was found that for a certain carbohydrate, [Bmim][HSO_4] has a stronger soluting-out power than [Bmim][Br]. However, for the IL−carbohydrate systems including the most hydrophobic IL in this work ([Bmim][BF_4]), the extreme departure is due to the soluting-out effect of carbohydrates (more hydrophilic solutes) on the IL in aqueous solutions. In this case, the soluting-out effect appears with liquid−liquid equilibria formation.

Table 4. Values of Gibbs Free Energies of Hydration (ΔG_{hyd})[43] and the Hydrogen Bond Accepting Strength (β)[42] of the Various Anions

anion	ΔG_{hyd}/kJ mol^{-1}	β
BF_4^-	−190	0.55
Br^-	−315	0.87
HSO_4^-	−330	

ΔG is the free energy change of the water in the following process: a solution of m_{IL} moles of IL in 1 kg of water is mixed isothermally with a solution of m_C moles of carbohydrate in 1 kg of water; then 1 kg of liquid water is isothermally separated via an osmotic membrane. This quantity can be defined as[44]

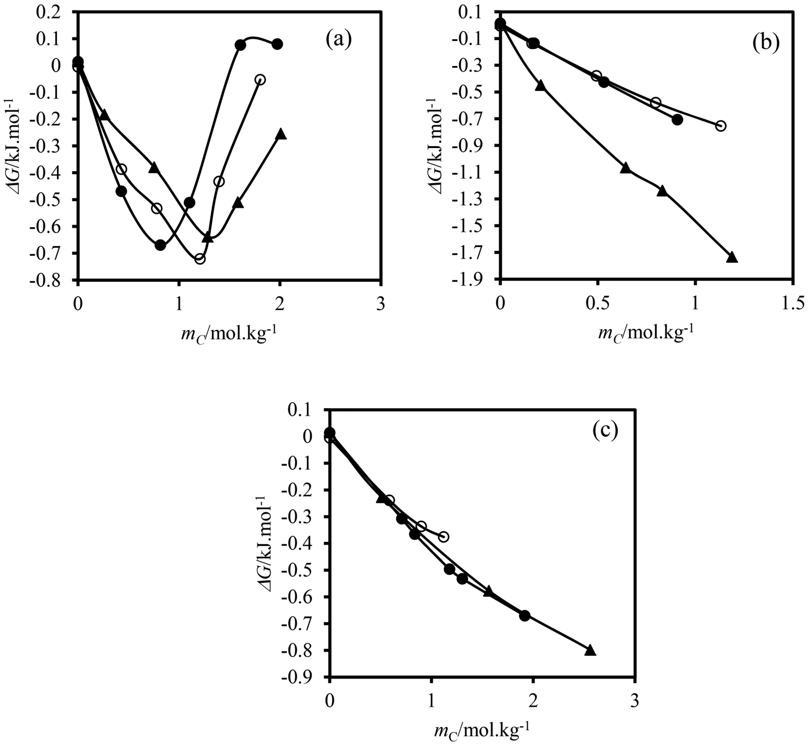

Figure 7. Plots of ΔG against carbohydrate molality, m_C, for solutions of different carbohydrates in aqueous solution of the investigated ILs at T = 308.15 K: (a) [Bmim][BF$_4$] + carbohydrate + water, (b) [Bmim][HSO$_4$] + carbohydrate + water, and (c) [Bmim][Br] + carbohydrate + water systems. ●, maltitol; ○, maltose; ▲, sucrose.

$$\Delta G = 55.5RT\ \ln\left(\frac{a_w}{a^0_{wIL}a^0_{wC}}\right) \tag{8}$$

In this equation, a_w, $a_{wIL}°$ and $a_{wC}°$ have been defined previously. As it can be seen from Figure 7, in the monophasic region of the [Bmim][BF$_4$]−carbohydrate systems, the values of ΔG are negative and become more negative by increasing the concentration and soluting-out power of the carbohydrates. For these systems, the magnitude of ΔG become smaller after ABS formation. Above the critical concentration, since the aqueous solution of each solute is an unsuitable cosolvent for another solute, the mixing process becomes a more undesirable process and therefore values of ΔG become less negative. ΔG for [Bmim][Br]−carbohydrate and [Bmim][HSO$_4$]−carbohydrate systems have the same trend as that observed in Figures 4 and 5 for deviations from eqs 4 and 5.

4. CONCLUSION

Vapor−liquid equilibria behavior of aqueous ternary IL + carbohydrate (sucrose, maltose, and maltitol) systems were studied at 308.15 K by means of the VPO method. The results show that, in the case of aqueous solutions of [Bmim][BF$_4$] (the most hydrophobic IL)−carbohydrate systems which form ABSs, because of the unfavorable IL−carbohydrate interactions, the interaction of each solute with water becomes more favorable in the presence of the other solute and therefore reduces the amount of free water molecules in the bulk state in compared to the semi-ideal solution and thus $a_w + 1 < a_{wIL}° + a_{wC}°$ and $\Delta p < \Delta p_{IL}° + \Delta p_C°$ (negative deviation). The magnitude of deviations in the monophasic region increases by increasing the concentration and soluting-out power of the carbohydrates (maltitol > maltose > sucrose) and decreases by ABS formation. Maltose and sucrose are structural isomers so that maltose has a glucose unit instead of fructose and therefore has more negative values of Δa_w and $\Delta \pi_w$ than sucrose. However, for the other investigated systems, the magnitude of deviations were smaller than that of [Bmim][BF$_4$]−carbohydrate systems and for a certain carbohydrate follow the order: [Bmim][HSO$_4$]−carbohydrate ≫ [Bmim][Br]−carbohydrate, which is in agreement with hydrophilicity of ILs. The soluting-out effect of [Bmim][HSO$_4$] on aqueous solutions of carbohydrates follows the order: sucrose ≫ maltitol ≅ maltose, but in the case of [Bmim][Br] no significant difference was found between sugars. For [Bmim][BF$_4$]−carbohydrate systems, the carbohydrates act as soluting-out agent and the soluting-out effect appears with liquid−liquid equilibria formation, and in aqueous [Bmim][Br]−carbohydrate and [Bmim][HSO$_4$]−carbohydrate systems, the ILs act as soluting-out agent and the soluting-out effect is appears with solid−liquid equilibria formation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.7b00719.

^{1}H and ^{13}C NMR spectra, calibration plot of VPO instrument, and calibration coefficients of eq 1with standard deviation of correlation (PDF)

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Notes

The authors declare no competing financial interest.

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