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Phase behavior for the [Bmim]BF_4 aqueous two-phase systems containing ammonium sulfate/sodium carbonate salts at different temperatures: Experimental and correlation

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ABSTRACT

The phase-forming salts and their corresponding phase-forming abilities for 1-butyl-3-methylimidazolium-tetrafluoroborate ([Bmim]BF_4)-based aqueous two-phase were discussed. The phase-forming abilities of $(NH_4)_2SO_4$ and Na_2CO_3 for [Bmim]BF_4-based aqueous two-phase were compared and discussed. Phase diagrams were experimentally determined for aqueous two-phase systems containing [Bmim]BF_4 and $(NH_4)_2SO_4$ at T = 298.15, 308.15, and 318.15 K. The Merchuk equation was used to correlate the binodal data of these systems. Simultaneously, the effect of temperature on the phase-forming ability in the investigated system has also been studied on the basis of a salting-out coefficient obtained from fitting the tie-line data to a Setschenow-type equation for each temperature.

1. Introduction

Aqueous two-phase system (ATPS) usually consisting of combining either two incompatible polymers or a polymer and a salt in water above a certain critical concentration [1] is considered to be environmentally friendly because traditional volatile organic solvents (VOCs) are not used in the whole process [2]. Therefore, ATPS has already been used to separate and purify various biological products [3,4], metal ions, dyes, drug molecules and small organic species [5,6] from the complex mixtures. However, most of the phase-forming polymers have high viscosity, form an opaque solution, and sometimes interfere with the analysis of analytes. In this respect, it is urgent to establish a new and favored ATPS process.

Ionic liquids (ILs) have many properties of conventional organic solvents, such as excellent solvation qualities, a variable viscosity range, a wide temperature range, being non-volatile, and excellent chemical and thermal stabilities [7]. These features of ILs offer promising alternative for the replacement of volatile organic solvents (VOS) in chemical/biochemical processes and numerous opportunities for the development of new extraction processes.

In recent years, a new type of aqueous two-phase system (ATPS) containing K_3PO_4 inorganic salt and ionic liquid [Bmim]Cl was introduced by Rogers and co-workers in 2003 for the first time [8]. This new type of ionic liquid aqueous two-phase systems (ILATPSs) have many advantages, such as low viscosity, little emulsion formation, no need of using volatile organic solvent, quick phase separation, high extraction efficiency, and gentle biocompatible environment, which have been successfully used to separate protein [9], antibiotics [10–12], incretion [13] and organic pollutants [11].

ILs tend to be chaotropic salts, having depressed melting points as a result of low symmetry ions which contain charge delocalization, and weak directional intermolecular interactions. Such salts should be water-destructuring and thus, capable of being salted-out by kosmotropic salts. The most common salts employed by different research groups [8,14–21] on the IL-based aqueous two-phase extraction technique consist of selective cations (ammonium, potassium, or sodium) and anions (phosphate, sulfate, hydroxide, or carbonate). This type of IL-based ATPS can be formed when a hydrophilic IL, such as 1-butyl-3-methylimidazolium chloride, [C_4mim]Cl, is contacted with the concentrated solutions of the water-structuring salts, forming an upper IL-rich phase and a lower salt-rich phase, both of which are aqueous [7]. A fundamental understanding of biomolecule partitioning and phase equilibrium in ionic liquid aqueous two-phase systems could lead to improvements in the design and optimization of large-scale purification processes.

A thermodynamic analysis (densities, pressure, excess molar volumes, liquid–liquid phase diagrams and so on) for [Bmim][BF_4]

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solutions was taken by Rebelo et al. [22]. Results showed that deuteration of water decreased the miscibility of [Bmim][BF_4], pressure effects were very subtle (taken at atmospheric pressure) and more complicated. In the case of H_2O as solvent, data showed that, while for off-critical concentrations pressurization helps miscibility, the opposite was true for near-critical concentrations.

Lin et al. [23] discussed the solubility of three dibasic carboxylic acids (adipic acid, glutaric acid, and succinic acid) in water and [Bmim][BF_4]. And the binodal curve of water + [Bmim][BF_4] was also determined experimentally. Results showed that all the investigated binary systems were simple eutectic. As evidenced from the experimental results of water (1) +[Bmim][BF_4] (2) system, solid–liquid–liquid equilibria (SLLE) existed in the composition ranging from water = 0.30 to 0.75 and the upper critical solution point was estimated as T = 278.6 K and $w_{\text{water}} = 0.4963$.

Zafarani-Moattar et al. [7] have studied the effects of the type of salt on the basis of Gibbs free energy of hydration of salt constituent ions on the binodal and tie-lines for the 1-butyl-3-methylimidazolium bromide [C_4mim]Br + salts + water aqueous two-phase systems. It was found that for the studied systems an increase in the charge of the anion (with the same size) causes the expansion of the two-phase area and an increase of slopes of tie-lines. And in 2009, Zafarani-Moattar and Hamzehzadeh [2] examined liquid–liquid equilibria (LLE) for [C_4mim]Br + tripotassium citrate system and investigated the effects of temperature on the phase-forming ability on the basis of a salting-out coefficient obtained from fitting the tie-line data to a Setschenow-type equation for each temperature. Results showed that for the studied system the value of salting-out coefficient K_S increases with decreasing temperature and the temperature with higher phase-forming ability has a larger value of K_S, and that two-phase area is expanded with a decrease in temperature.

This work is devoted to the study of the phase-forming salts for [Bmim]BF_4-based ATPSs and their corresponding phase-forming abilities. Moreover, the phase diagrams and the effects of temperature on phase-forming of [Bmim]BF_4–$(NH_4)_2SO_4$–water ATPS were discussed in detail. As far as we know, while there are scarce reports in the literature on the LLE data for the binary aqueous ionic liquid solutions, and there is no report on the corresponding LLE data for [Bmim]BF_4-based ATPSs. The obtained results are necessary for the design of extraction processes, understanding of general factors determining partition of solutes and particles in [Bmim]BF_4-based ATPSs, and development and testing of both thermodynamic and mass transfer models of ionic liquid aqueous two-phase systems [7].

2. Experimental

2.1. Material

[Bmim]BF_4 (99%, mass%) was obtained from Cheng Jie Chemical Co., Ltd. and used without further purification. Na_2CO_3, $(NH_4)_2SO_4$ and other salts (99%, mass%) were supplied from Chinese Medicine (Group) Shanghai Chemical Reagent Company and used without further purification. Double-distilled deionized water was used for the preparation of solutions.

2.2. Apparatus

The DHG-9140 aelectric heating constant temperature wind drum drying oven (Shanghai Yiheng Technology Co., Ltd.). Electronic balance (BS124S, Beijing Saiduolisi Instrument Co., Ltd.). Solar-type heating temperature magnetic stirrer DF-101S (Gongyi Yuhua Instrument Co., Ltd.). UV-Vis spectrometer Model UV-2450 (Shimadzu Corporation, Japan).

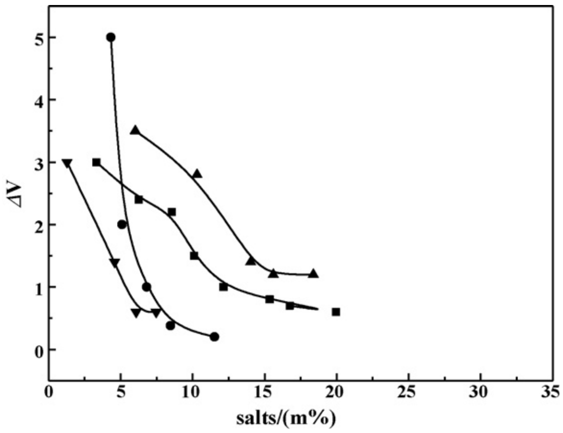

Fig. 1. The phase-forming ability of different salts ((■) Na_2CO_3; (▼) $(NH_4)_2SO_4$; (▲) Na_2SO_3; (●) NaH_2PO_4).

2.3. Procedure

The experimental apparatus employed is essentially similar to the one previously used [24–26]. The temperature was controlled to within 0.5 K. The binodal curves were determined by the cloud-point method [1]. A salt solution of known concentration was titrated with the IL solution or vice versa until the solution turned turbid, which indicated the formation of two liquid phases. In accordance with the amount of titrant added until turbidity was observed, the composition of the mixture for each point on the binodal curve was calculated by mass using an analytical balance with an uncertainty of 1×10^{-7} kg.

For the determination of the tie-lines, we prepared feed samples by mixing appropriate amounts of [Bmim]BF_4, salt, and water in the vessel. After sufficient mixing, the samples were placed in a water bath at the desired temperature and allowed to settle for at least 48 h to separate into two clear phases. The contents of [Bmim]BF_4 was determinate by UV–vis spectrometer at 211 nm, and the salt content was determinate by titrant, and water in both phases were calculated according to the material balance equation of the top and bottom phase.

3. Results and discussion

3.1. Experimental equilibrium compositions and correlation

For investigating the phase behavior of [Bmim]BF_4-based ATPSs, first, the salting-out agents for this system were studied. The experiment showed that Na_2CO_3, $(NH_4)_2SO_4$, NaH_2PO_4, $MgSO_4$, Na_2SO_3 and NaOH can be salting-out agents which made the aqueous and [Bmim]BF_4 form two phases, and Na_3PO_4, Na_2HPO_4, K_2HPO_4, NH_4Cl, CH3COONa, $NaNO_3$, NaCl and KCl cannot.

The binodal curves and data of Na_2CO_3, $(NH_4)_2SO_4$, NaH_2PO_4, and Na_2SO_3 were shown in Fig. 1 and Tables 1 and 2. The two-phase area was larger when Na_2CO_3 was taken as a salting-out agent than that of other salts by comparing the binodal curves. This was reflected by an increase in the critical concentration of Na_2CO_3 required to form a two-phase system, which in turn indicated the effectiveness of the salts in inducing the formation of two phases. The phase-forming ability followed the order: $Na_2CO_3 > Na_2SO_3 > (NH_4)_2SO_4 > NaH_2PO_4$. The salting-out ability of salts also can be related to the ions' Gibbs free energy of hydration (ΔG_{hyd}) [27,28]. Salts Na_2CO_3, Na_2SO_3, NaH_2PO_4 shared a common cation (Na^+) but contained different anions of charge, and the anion with higher charge (with the same size [29]) is a better salting-out agent because the higher charge anion hydrates more

Table 1
Phase-forming ability of different salts for $[Bmim]BF_4$-based ATPS ($T = 298.15$ K).

$[Bmim]BF_4–Na_2CO_3$ ATPS				$[Bmim]BF_4–NaH_2PO_4$ ATPS		$[Bmim]BF_4–Na_2SO_3$ ATPS	
$100W_1$	$100W_2$	$100W_1$	$100W_2$	$100W_1$	$100W_2$	$100W_1$	$100W_2$
79.64	0.2200	13.85	4.760	84.77	0.5700	75.05	0.4200
77.55	0.2500	12.72	5.120	76.48	0.5800	66.30	0.5800
75.87	0.2800	12.35	5.560	56.96	0.8400	60.18	0.6900
69.37	0.3400	11.74	5.640	48.49	1.480	48.00	1.250
67.61	0.3900	11.60	5.890	47.23	1.630	43.61	1.420
65.91	0.4100	11.29	5.900	45.07	1.810	39.28	1.690
62.63	0.4400	10.75	6.440	43.02	1.980	35.33	2.060
52.29	0.7300	10.29	6.830	40.70	2.260	33.51	2.120
49.70	0.8300	10.28	6.970	40.04	2.290	28.09	2.630
40.60	1.010	9.870	7.170	37.64	2.540	26.30	2.870
45.40	0.910	9.610	7.360	36.66	2.720	17.45	5.450
43.48	0.9600	9.390	7.550	34.97	2.800	15.17	6.470
37.00	1.360	9.200	7.690	34.81	2.860	13.82	7.150
32.81	1.510	9.010	7.800	33.50	2.930	12.57	7.900
31.27	1.660	8.470	8.040	32.96	3.020	11.18	8.550
28.58	1.870	8.14	8.620	32.02	3.070	9.330	9.610
27.12	1.92	7.730	8.830	31.28	3.250	6.920	13.10
27.08	2.02	7.500	9.330	29.16	3.530	3.950	18.91
26.95	2.080	6.940	9.630	27.34	3.790	2.430	22.99
26.01	2.180	6.570	9.980	26.62	3.940		
25.38	2.370	6.280	10.11	24.06	4.630		
25.36	2.170	6.220	10.52	20.25	5.650		
24.79	2.290	5.820	10.93	19.18	5.950		
24.38	2.420	5.510	12.08	18.03	6.480		
24.06	2.390	4.650	12.60	17.56	6.920		
23.49	2.340	4.400	12.79	15.56	7.850		
23.40	2.670	4.220	13.3	14.58	8.530		
22.60	2.700	4.060	13.48	14.48	8.680		
21.37	2.750	3.940	13.70	14.29	8.670		
20.47	3.140	3.830	14.21	13.94	9.210		
19.13	3.250	3.820	14.65	12.33	10.35		
18.07	3.480	3.570	15.71	10.77	12.21		
17.56	3.590	3.350	16.01	11.85	11.60		
16.25	3.950	2.910	16.75	10.39	13.06		
15.61	3.990	2.790	17.22	9.470	14.43		
15.46	4.06	2.480	17.92	8.780	15.62		
15.09	4.200	13.85	4.760	8.200	16.62		
13.68	4.730	12.72	5.120	7.730	17.35		

water than the lower charge anion. Thus, it is easy to see that the anion with a higher salting-out ability has a more negative ΔG_{hyd} value, CO_3^{2-}, −1476 kJ/mol > SO_3^{2-} (−1301 kJ/mol) > $H_2PO_4^-$ [19], for NH_4^+, the ΔG_{hyd} value is −292 kJ/mol, which shows that the NH_4^+ salts are poor at salting-out when compared to Na^+ (−374 kJ/mol) [30].

For $[Bmim]BF_4 + (NH_4)_2SO_4$ + water ATPS, the binodal curve representing the minimum concentration required for the formation of two phases at different temperatures ($T = 298.15$, 308.15 and 318.15 K) and tie-line data were shown in Tables 2 and 3, respectively, and the binodal curves were shown in Fig. 2.

The phase diagrams of three different temperatures of $[Bmim]BF_4 + (NH_4)_2SO_4$ + water ATPS were illustrated in Figs. 3–5. An attempt was made to fit the binodal data using different expressions, used previously for ATPSs. For representing the binodal data of the present $[Bmim]BF_4$-salts systems, the following non-linear expression (Eq. (1)) developed by Merchuk et al. [31] was used.

Recently, the Merchuk equation had been successfully used for the correlation of binodal data of some aqueous IL + salts systems [16,19]. Using Eq. (1), the coefficients a, b, and c obtained from the correlation of experimental binodal data along with the corresponding standard deviations were given in Table 4. Comparison between the experimental and correlated binodal was shown in Fig. 6 for the $[Bmim]BF_4 + (NH_4)_2SO_4 + H_2O$ at 298.15 K, as an example. On the basis of obtained standard deviations, we concluded that Eq. (1) can be satisfactorily used to correlate the binodal curves of the investigated systems.

In this work, the three fitting parameters of the Merchuk equation (Eq. (1)), a, b, and c, are further expressed as a function of temperature in the linear form with $(T - T_0)$ K as a variable, as Eqs. (1a)–(1c).

These fitting parameters obtained from the correlation of the experimental binodal data along with the corresponding standard deviations were given in Table 5. On the basis of the obtained

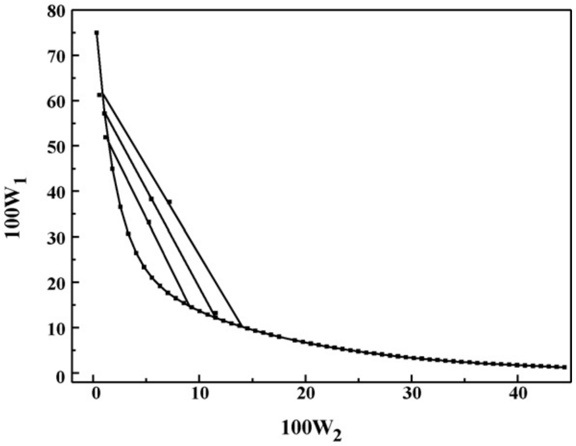

Fig. 2. Binodal curves for the $[Bmim]BF_4(1) + (NH_4)_2SO_4(2) + H_2O$ system at different temperature: (■) binodal at 298.15 K; (○) binodal at 308.18 K; (△) binodal at 318.15 K.

Table 2
Binodal data for the [Bmim]BF_4(1) + $(NH_4)_2SO_4$(2) + H_2O system at T = 298.15, 308.15, and 318.15 K.

T = 298.15 K		T = 308.15 K		T = 318.15 K	
$100W_1$	$100W_2$	$100W_1$	$100W_2$	$100W_1$	$100W_2$
75.00	0.3363	44.05	2.818	7.393	21.09
57.14	1.083	41.87	3.150	8.426	18.82
44.96	1.830	39.12	3.361	9.319	17.08
36.56	2.577	37.39	3.590	10.53	15.59
30.67	3.324	34.70	4.107	11.24	14.60
26.45	4.071	31.99	4.464	12.36	13.64
23.35	4.818	29.56	4.780	12.87	12.96
21.00	5.565	27.44	5.060	15.20	11.52
19.17	6.312	24.95	5.688	16.31	10.69
17.69	7.059	23.99	5.957	17.73	9.956
16.46	7.806	22.42	6.303	19.17	9.238
15.41	8.553	21.28	6.624	20.87	8.425
14.48	9.300	19.85	7.274	22.36	7.817
13.65	10.05	18.51	7.981	24.11	7.276
12.89	10.79	16.79	8.789	16.14	10.52
12.20	11.54	15.87	9.483	19.85	8.859
11.55	12.29	14.71	10.17	22.23	7.779
10.94	13.04	13.83	10.87	26.34	6.725
10.38	13.78	11.70	12.94	29.55	5.906
9.844	14.53	72.03	0.6035	33.65	5.131
9.339	15.28	80.82	0.3934	36.67	4.627
8.863	16.02	68.11	0.7398	39.63	4.157
8.412	16.77	3.342	38.66	42.40	3.757
7.985	17.52	3.748	30.59	45.05	3.315
7.580	18.26	4.607	26.83	47.53	2.981
7.200	19.01	5.385	25.16	49.83	2.696
6.832	19.76	6.633	22.51	51.87	2.455
6.487	20.51	7.009	21.10	53.68	2.253
6.159	21.25	8.786	17.71	55.53	2.059
5.849	22.00	9.150	16.90	57.26	1.877
5.553	22.75	9.901	15.96	59.00	1.701
5.274	23.49	10.49	15.08	0.4007	48.80
5.008	24.24	10.78	14.66	0.7961	41.94
4.756	24.99	11.12	14.24	1.168	39.36
4.517	25.73	11.85	13.45	1.557	36.42
4.290	26.48	12.43	12.77	1.909	34.35
4.075	27.23	12.91	12.43	1.974	32.46
3.871	27.98	13.66	11.64	2.451	31.60
3.677	28.72	1.672	44.25	2.898	30.39
3.493	29.47	2.184	39.71	3.436	28.62
3.319	30.22	2.680	36.57	3.863	27.06
3.153	30.96	3.058	34.13	5.882	23.24
2.996	31.71	3.320	32.14	4.771	24.56
2.847	32.46	1.682	48.18		
2.706	33.20	2.360	43.09		
2.571	33.95	2.535	37.75		
2.444	34.70	2.749	35.67		
2.323	35.45	3.102	34.12		
2.209	36.19	61.43	1.389		
2.099	36.94	53.80	1.693		
1.996	37.69	45.54	2.526		
1.898	38.43	40.30	3.049		
1.805	39.18	34.73	3.688		
1.717	39.93	30.61	4.195		
1.633	40.67				
1.554	41.42				
1.479	42.17				
1.407	42.92				
1.339	43.66				
1.275	44.41				

standard deviations, we concluded that Eqs. (1a)–(1c) can be satisfactorily used to reproduce the binodal curves of the investigated system.

3.2. *Effects of temperature on binodal curves*

The effects of temperature on the phase-forming ability of the studied system were illustrated in Fig. 2. The locuses for the experimental binodals were shown in Fig. 2 demonstrated that the two-phase area was expanded with a decrease in temperature for [Bmim]BF_4 + $(NH_4)_2SO_4$ + H_2O. In other words, if we take a sample with a known composition on the binodal curve, this mixture becomes a two-phase system at decreasing temperature as has been observed experimentally. This phenomena was attributed to the decrease in solubility of IL or the increase in the phase-forming ability of salt in the studied system. The experimental results of the present aqueous two-phase systems were in good agreement with the other similar ATPS binodal curves reported in the literatures [2,7].

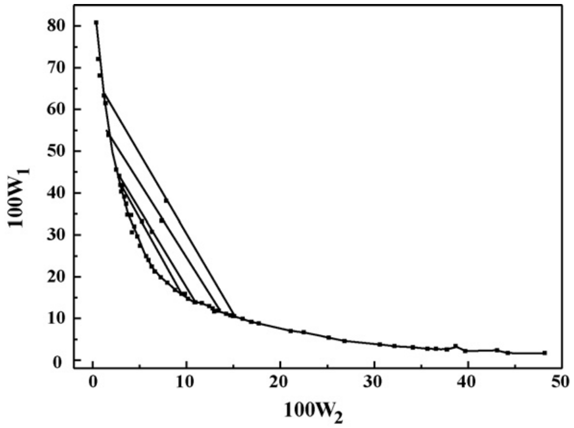

Fig. 3. The phase diagram of [Bmim]BF_4(1) + $(NH_4)_2SO_4$(2) + H_2O at 298.15 K.

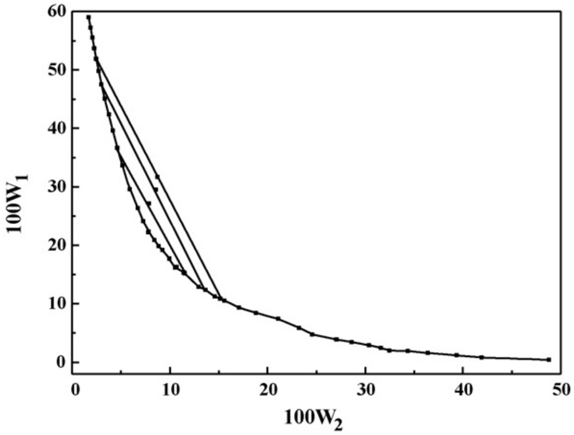

Fig. 4. The phase diagram of [Bmim]BF_4(1) + $(NH_4)_2SO_4$(2) + H_2O at 308.15 K.

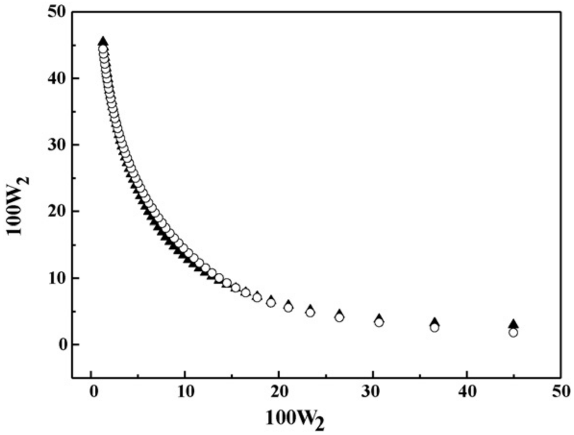

Fig. 5. The phase diagram of [Bmim]BF_4(1) + $(NH_4)_2SO_4$(2) + H_2O at 318.15 K.

Table 3
Experimental phase equilibrium compositions and tie-line data for the [Bmim]BF_4(1) + $(NH_4)_2SO_4$(2) + H_2O System at T = 278.15, 298.15, and 318.15 K.

Total composition		Top phase: ionic liquid-rich phase		Bottom phase: salt-rich phase		s	TLL
$100W_1$	$100W_2$	$100W_1$	$100W_2$	$100W_1$	$100W_2$		
T = 298.15 K							
37.68	7.20	61.22	0.5929	9.834	14.53	−3.68	53.24
38.28	5.506	57.14	1.073	13.19	11.54	−4.20	45.17
33.21	5.258	51.90	1.189	13.78	10.38	−4.15	39.20
T = 308.15 K							
30.68	6.331	63.34	1.203	10.57	14.97	−3.83	54.54
33.39	7.367	53.80	1.694	11.82	13.35	−3.60	43.57
38.10	7.84	43.97	2.823	13.82	10.92	−3.72	31.22
33.21	5.258	41.85	2.953	15.87	9.843	−3.978	26.79
T = 318.15 K							
27.13	7.861	51.92	2.449	11.77	15.27	−3.13	42.14
29.48	8.571	47.53	2.981	13.33	13.68	−3.20	35.83
31.68	8.737	36.67	4.627	15.52	11.28	−3.17	22.17
33.21	5.258	–	–	–	–		

Table 4
Values of parameters of Eq. (2) for [Bmim]BF_4(1) + salt(2) + H_2O.

System	a	b	c	SD[a]
[Bmim]BF_4 + $(NH_4)_2SO_4$ + H_2O (298.15 K)	0.905	−6.096	−7.510	0.016
[Bmim]BF_4 + $(NH_4)_2SO_4$ + H_2O (308.15 K)	1.125	−6.031	−2.307	0.016
[Bmim]BF_4 + $(NH_4)_2SO_4$ + H_2O (318.15 K)	1.0982	−6.034	−2.903	0.017
[Bmim]BF_4 + Na_2CO_3 + H_2O (298.15 K)	0.8557	−7.888	−10.92	0.019

[a] $SD = (\sum_{i=1}^{N} (w_2^{caled} - w_2^{exptl})^2/N)^{0.5}$ where N is the number of binodal data. These parameters were obtained from the correlation of the experimental binodal data of the investigated system at T = 298.15, 308.15 and 318.15 K.

Table 5
Values of parameters of Eqs. (1a)–(1c) for [Bmim]BF_4(1) + $(NH_4)_2SO_4$(2) + H_2O at T = 298.15, 308.15, and 318.15 K.

T (K)	a^0	a^1	b^0	b^1	c^0	c^1	SD[a]
298.15	0.3550	0.0220	−6.259	0.0065	20.52	0.5203	0.016
308.15							0.016
318.15							0.017

[a] $SD = [\sum_{j=1}^{3} \sum_{i=1}^{N} ((w_{i,j,cal}^{top} - w_{i,j,\exp}^{top})^2 + (w_{i,j,cal}^{bot} - w_{i,j,\exp}^{bot})^2)/6N]^{0.5}$ where N is the number of tie-lines, and j is the number of components in each phase.

As shown in Table 3, the slope, S, and the tie-lines length, TLL was calculated by Eqs. (2) and (3), respectively. The comparison between the tie-lines for the temperatures T = 298.15, 308.15 and 318.15 K, the slope S, and the length of the tie-lines showed that the slope and the length of the tie-lines decreased with an increase in temperature. This trend means that when the temperature decreased, water is driven from the [Bmim]BF_4-rich phase to the salt-rich phase, so the [Bmim]BF_4 concentration at the [Bmim]BF_4-rich phase increases, whereas the salt-rich phase will be somewhat more diluted (i.e., the salt concentration will be decreased). In other words, water becomes a poorer solvent for [Bmim]BF_4 as the temperature decreased. Depression of the solubility of the hydrophilic IL, [Bmim]BF_4, in water with decreasing temperature may be related to the salting-out phenomenon because a decrease in the solubility of [Bmim]BF_4 in water with a decrease in temperature.

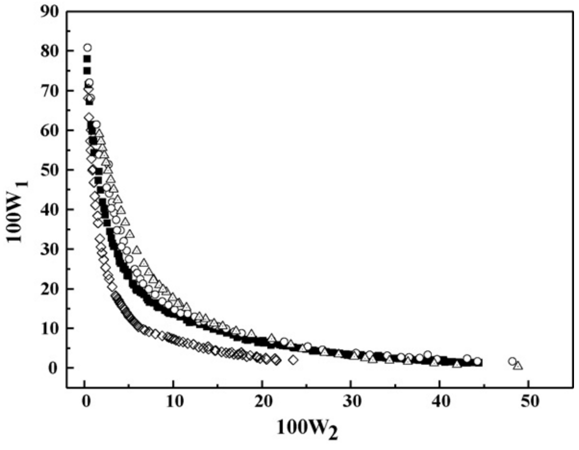

Fig. 6. Experimental and calculated binodal data calculated from eq1 for system [Bmim]BF_4 + $(NH_4)_2SO_4$ + H_2O at 298.15 K: (▲) experimental binodal; (○) calculated binodal using Eq. (1).

Salting-out effects are usually quantified by fitting solubility data to the empirical equation of Setschenow-type equation derived by Hey et al. [32] as Eq. (4) which was used successfully for IL-bases ATPSs [2].

The experimental tie-line compositions for the aqueous [Bmim]BF_4 + $(NH_4)_2SO_4$ + H_2O system given in Table 3 were fitted by a least-squares linear regression method to Eq. (4) (i.e., the logarithm of the ratio between the molality of [Bmim]BF_4 for the top phase and the one for the bottom phase, $\ln(C_I'/C_I'')$, was considered to be a linear function of (C_S''/C_S'), the difference in the salt concentrations between the bottom and top phases, respectively), and the obtained slopes that give the salting-out coefficients, K_S were listed in Table 6. From Table 6, we concluded that the equilibrium compositions of the investigated system at the studied temperatures can be satisfactorily characterized by Setschenow-type behavior. We can see that the value of K_S was decreased with the increase of temperature. It appears that in the studied system there was a

Table 6
Setschenow-type plots of the tie-line data for $[Bmim]BF_4(1) + (NH_4)_2SO_4(2) + H_2O$ at $T = 298.15$, 308.15, and 318.15 K.

298.15 K		308.15 K		318.15 K	
$C''{}_S - C'_S$	$\ln(C'_I/C''_{II})$	$C''_S - C'_S$	$\ln(C'_I/C''_{II})$	$C''_S - C'_S$	$\ln(C'_I/C''_{II})$
13.95	−3.500	13.77	−3.630	12.82	−3.940
10.47	−3.930	11.66	−3.900	10.70	−4.150
9.188	−4.095	8.097	−4.260	6.653	−4.561
$K_S = 0.1247$		$K_S = 0.1101$		$K_S = 0.1008$	
$R^2 = 0.9999$		$R^2 = 0.9959$		$R^2 = 0.9999$	

close relationship between the salting-out coefficient of the phase-forming salt and the working temperature.

The phenomenon of the two phases forming in an aqueous IL + salt system may be considered to be the competition between the hydrophilic IL and the salt for the water molecules. The competition is finally won by the salt ions because of their stronger affinity for the water. In other words, this occurrence results in a migration of water molecules away from the ions of the IL to those of the inorganic salt, which, in turn, decreases the hydration and hence the solubility of the ions of the IL. Consequently, a phase rich in the salted-out IL separates from the rest of the solution.

The formation of aqueous two-phase systems, clearly indicate the mutual exclusion of the ions and the IL and their high affinity for the solvent. It is possible that even in homogeneous systems (below the phase boundary) the ions are excluded from the near surface region of the IL in solution. With increase in the concentration of the IL or the salt, the extent of exclusion will increase. Ultimately, the system could reach a state, where for entropic reasons, phase formation would become favorable.

4. Conclusions

The phase-forming salts for $[Bmim]BF_4$-based ATPS was discussed, and results showed the salting-out ability of Na_2CO_3 was stronger than $(NH_4)_2SO_4$ by comparing the binary phase area and the ΔG_{hyd} value. Binodal curves and tie-line compositions were measured for the $[Bmim]BF_4 + (NH_4)_2SO_4 + H_2O$-based ATPSs at three different temperatures (298.15, 308.15, 318.15 K), and it was found that as the temperature decreases the binodal curve shifts down due to a decrease of IL in solubility, resulting in an increase in the two-phase region in $[Bmim]BF_4 + (NH_4)_2SO_4 + H_2O$-based ATPSs. The tie-line data were correlated to Setschenow-type equation for each temperature, results showed that the salting-out coefficient K_s was increased with the decrease of temperature. It appears that in the studied system there is a close relationship between the salting out coefficient of the phase-forming salt and the working temperature.

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Appendix A. Formulates

$$w_1 = a\exp(bw_2^{0.5} - cw_2^3) \tag{1}$$

where a, b, and c represent fit parameters and w_2 and w_1 represent the concentrations (in wt%) of salt and IL, respectively.

$$a = a^0 + a^1(T - T_0) \tag{1a}$$

$$b = b^0 + b^1(T - T_0) \tag{1b}$$

$$c = c^0 + c^1(T - T_0) \tag{1c}$$

In Eqs. (1a)–(1c), T_0 is assumed to be the reference temperature, $T_0 = 273.15$ K, and a_0, a_1, b_0, b_1, c_0, and c_1 are independent temperature-adjustable parameters.

$$\mathrm{TLL} = [(W_1^t - W_1^b)^2 + (W_2^t - W_2^b)^2]^{0.5} \tag{2}$$

$$S = \frac{W_1^t - W_1^b}{W_2^t - W_2^b} \tag{3}$$

where $W_1^t - W_1^b$ represents the IL concentrations (in wt%) in top/bottom phase and $W_2^t - W_2^b$ represents the salt concentrations (in wt%) in top/bottom phase.

$$\ln\left(\frac{C'_I}{C''_I}\right) = K_I(C''_I - C'_I) + K_S(C''_S - C'_S) \tag{4}$$

where C_I, C_S, K_I, and K_S, represent the molality of IL, the molality of the salt, a parameter relating the activity coefficient of IL to its concentration, and the salting-out coefficient, respectively. Single and double primes also refer to the upper and lower phases, respectively.

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