Research Article

Liquid-Liquid Equilibrium Data for the Ionic Liquid N-Ethyl-Pyridinium Bromide with Several Sodium Salts and Potassium Salts

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The liquid-liquid equilibrium (LLE) data for systems containing N-ethyl-pyridinium bromide ([EPy]Br), salt (Na_2HPO_4 , K_2HPO_4 , K_2SO_4 , $\text{C}_4\text{O}_6\text{H}_4\text{KNa}$), and water have been measured experimentally at $T = 298.15\text{ K}$ and the formations of these four aqueous two-phase systems (ATPSs) have been discussed. Also, the effective excluded volume (EEV) values obtained from the binodal models for the four systems were determined and the salting-out abilities of different salts follow the order of $\text{K}_2\text{SO}_4 > \text{K}_2\text{HPO}_4 > \text{Na}_2\text{HPO}_4 > \text{C}_4\text{O}_6\text{H}_4\text{KNa}$. The solubility data were correlated by the Merchuk and other equations while the tie-line data by the Othmer-Tobias, Bancroft, two-parameter, and Setschenow-type equations. The correlation coefficients evidenced that experimental data fitted well to all these equations. These four salts were proved successfully to form ATPSs with N-ethyl-pyridinium bromide, making a significant contribution to the further study of this kind of ATPS.

1. Introduction

Aqueous two-phase systems (ATPSs) [1] extraction, an economical and efficient technique for separation, extraction, and purification, have found wide application in comprehensive separation, concentration, and fractionation of biological solutes and particles such as cells and proteins [2, 3] for the past few years. An ATPS is essentially a mixture that exists in two phases and is usually formed by two high polymers, a high polymer and a salt, or a hydrophilic organic solvent and a salt [4]. Compared with traditional organic solvent extractions, ATPSs are more effective and can be carried out under mild processing conditions [5].

In recent years, a new type of ATPS based on ionic liquids (ILs) has been investigated, the ILATPS. The ILs are entirely composed of organic cation and organic or inorganic anion, which hold attention because of their chemical and physical properties such as a good thermal, chemical, and electrochemical stability, negligible volatility, a high ionic conductivity, and tenability [6, 7]. Thus, ILATPSs, combining both the advantages of traditional ATPSs and the aforementioned benefits of ILs, have been successfully used in

the separation, concentration, and purification of proteins [8], heavy metal ions [9], and small organic molecules [10]. ILATPSs have also been applied to extract antibiotics, such as penicillin G [11] and roxithromycin [12].

Consequently, further work is necessary for the development, optimization, and scale-up of extraction process using ILATPSs. Recently, an aqueous biphasic system (ABS) containing 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_4\text{mim}]\text{BF}_4$) + saccharides + water [13, 14] has been reported in the literature. In addition, ATPSs composed of $[\text{C}_n\text{mim}]\text{X}$ ($\text{X} = \text{Br}$ and Cl) + salts (KOH , K_2HPO_4 , KH_2PO_4 , K_2CO_3 , K_3PO_4 , $\text{K}_3\text{C}_6\text{H}_5\text{O}_7$ and sucrose) [13, 15–18] and $[\text{Bmim}]\text{BF}_4$ + salts (Na_3PO_4 , Na_2CO_3 , Na_2SO_4 , Na_2SO_3 , $(\text{NH}_4)_2\text{SO}_4$, NaH_2PO_4 , NaCl , $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$, $\text{NaC}_2\text{H}_3\text{O}_2$, and $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$) [19–22] also have been reported. For ATPSs containing pyridinium-based ionic liquids, there are 4-methyl-N-butyl pyridinium tetrafluoroborate + cyclohexane [23]. Furthermore, Bridges et al. described the phase diagrams for imidazolium-, pyridium-, and quaternary ammonium- and phosphonium-based chloride salts (all chaotropic salts) salted out by K_3PO_4 , K_2HPO_4 , K_2CO_3 ,

KOH, and $(\text{NH}_4)_2\text{SO}_4$ (all kosmotropic salts) [24]. Phase diagrams of ATPS composed of Mpy CH_3SO_4 and Na_2CO_3 have also been experimentally ascertained at $T = 298.15\text{ K}$ [25] and the effects of the cation core such as methylimidazolium, methylpyridinium, methylpyrrolidinium and methylpiperidinium, the length of the alkyl side chain, and the positional isomerism on ATPS formation ability of chloride-based ionic liquids such as $[\text{1-C}_4\text{-2-C}_1\text{py}]\text{Cl}$, $[\text{1-C}_4\text{-3-C}_1\text{py}]\text{Cl}$, $[\text{1-C}_4\text{-4-C}_1\text{py}]\text{Cl}$ have been investigated [26].

However, to our knowledge, the experimental work devoted to ILATPSs is far from enough. Compared to the existing imidazolium-based ionic liquids, pyridine-based ionic liquids provide lower cost, lower vapor pressure, better thermal, and chemical stability and are less polluting. An ATPS formed from an ionic liquid which is water soluble at room temperature, $[\text{BPy}]\text{BF}_4$ (nitrogen-butyl pyridine tetrafluoroborate) and a phase-forming salt $(\text{NH}_4)_2\text{SO}_4$ was studied for the extraction and separation of rutin [27]. The ATPS formed by the $[\text{EPy}]\text{Br}$ and K_2HPO_4 for extracting and separating chloramphenicol (CAP) in eggs has also been reported [28]. However, studies regarding this type of ILATPSs are insufficient and require further development.

In this work, phase diagrams and liquid-liquid equilibrium (LLE) data for the $[\text{EPy}]\text{Br}$ and four kosmotropic salts (Na_2HPO_4 , K_2HPO_4 , K_2SO_4 , $\text{C}_4\text{O}_6\text{H}_4\text{KNa}$) have been investigated. The solubility curves were fitted to three nonlinear equations, and the tie-lines were described using the Othmer-Tobias, Bancroft, and Setschenow-type equations and a two-parameter equation. Moreover, the effective excluded volume (EEV) values obtained from the binodal models for the four systems were determined, and the effect of salts on solubility curves and tie-lines were discussed. The as-obtained results are necessary for the design and optimization of extraction processes as well as the development of both thermodynamic and mass transfer models of ILATPSs.

2. Experimental Section

2.1. Materials. The $[\text{EPy}]\text{Br}$ was purchased from Chengjie Chemical Co., Ltd. (Shanghai, China) with a quoted purity of a mass fraction above 0.99 and was dried under high vacuum at 343.15 K using a semi-microdistiller with slow heating to remove impurities, mainly water. To prevent contact with the ambient air, the IL was kept in a sealed vessel and placed in refrigerator. The $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, K_2SO_4 and $\text{C}_4\text{O}_6\text{H}_4\text{KNa} \cdot 4\text{H}_2\text{O}$ were analytical grade reagents which were purchased from the Guanghua Chemical Factory Co., Ltd. (Guangdong, China). Double-distilled deionized water was also used in the experiments.

2.2. Experimental Procedure. The solubility curves were determined using the cloud point method. First, an IL solution of known mass fraction was added into a vessel, and the salt solution of known mass fraction was added dropwise until the mixture became cloudy. The composition of the mixture was calculated and the water content of the ionic liquid was calculated into the water mass fraction in the experiment mass balance. Then water was added dropwise

until the mixture became clear. The procedure was repeated to obtain all the points on the solubility curves until there was little precipitation at the bottom of the vessel. The vessel was placed in a DC-2008 water thermostat throughout the process, so that the temperature of the system could be kept constant (at $T = 298.15\text{ K}$). The temperature was controlled to within $\pm 0.05\text{ K}$. An analytical balance (model BS 124S, Beijing Sartorius Instrument Co., China) with a precision of $\pm 1.0 \times 10^{-7}\text{ kg}$ was used to measure the composition of the mixture at each point.

To determine the tie-lines, a series of ATPSs formed from three known compositions (including salt and water) were placed in a temperature-controlled bath. The system was held for at least 24 h to allow the formation of two phases. Both the upper and the lower phases were sampled for analysis. The concentrations of the salts in the two phases were determined via flame photometry. The uncertainty in the mass fractions of the salts was estimated to be ± 0.001 . The mass fraction of $[\text{EPy}]\text{Br}$ in both the top phase and bottom phase was determined using a UV-vis spectrophotometer (model UV-2450, Shimadzu Corporation, Japan) and the uncertainty was determined to be less than 7.5%. A suitable sample of the top phase or bottom phase was removed and placed into a vessel to be mixed with an appropriate quantity of water. The absorbance of the solution was then measured at a wavelength of 211 nm to obtain the mass fraction of the ionic liquid according to a standard curve.

The tie-line length (TLL), which reflects the differences between composition of top and bottom phase and the slope of the tie-line (S), which reflects the ability of phase formation to ATPS, were also calculated at different compositions, using the following two equations, respectively, [29]:

$$\begin{aligned} \text{TLL} &= \left[(w_1^t - w_1^b)^2 + (w_2^t - w_2^b)^2 \right]^{0.5} \\ S &= (w_1^t - w_1^b) / (w_2^t - w_2^b), \end{aligned} \quad (1)$$

where w_1^t , w_1^b , w_2^t , and w_2^b represent the equilibrium mass fraction of the $[\text{EPy}]\text{Br}$ and salt in the top and bottom phases, respectively. The tie-line data are provided in Table 1.

3. Results and Discussion

3.1. Solubility Data and Correlation. The solubility data determined at $T = 298.15\text{ K}$ are listed in Table 2. The data were fitted using the empirical nonlinear expression developed by Merchuk et al. [30] as follows:

$$w_1 = a \exp(bw_2^{0.5} - cw_2^3), \quad (2)$$

where w_1 and w_2 are the mass fractions of the $[\text{EPy}]\text{Br}$ and the salt, respectively. This expression has been used for the correlation of IL + salt ATPSs [31, 32] and IL + sugars ATPSs [14]. The parameters for this equation were determined from the experimental data obtained by the cloud point method. Coefficients a , b , and c obtained from the correlation of the experimental solubility data with the corresponding standard deviations (sd) and correlation coefficient (R^2) are given in Table 3.

TABLE 1: Tie-line data for the [EPy]Br (1) + salt (2) + water (3) ATPS at $T = 298.15$ K.

System	Total system		IL-rich phase		Salt-rich phase		TLL	S
	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$		
[EPy]Br + Na_2HPO_4	30.98	20.46	1.75	59.45	45.09	1.63	72.26	-1.33
	20.29	30.19	2.74	53.24	41.17	2.77	63.44	-1.31
	10.09	41.67	3.16	51.07	37.73	4.17	58.05	-1.36
[EPy]Br + K_2HPO_4	3.00	44.00	0.42	60.27	3.90	38.33	22.21	-6.32
	4.44	38.00	0.20	64.80	4.74	36.11	29.05	-6.31
	1.77	50.00	0.65	57.07	3.32	40.23	17.05	-6.30
[EPy]Br + K_2SO_4	6.15	17.00	0.24	67.93	6.45	14.45	53.84	-8.62
	4.83	24.00	0.42	62.20	5.36	19.42	43.06	-8.66
	3.63	30.00	0.79	54.37	4.11	25.86	28.70	-8.57
[EPy]Br + $\text{C}_4\text{O}_6\text{H}_4\text{KNa}$	9.77	62.95	0.30	81.03	31.62	21.24	67.50	-1.91
	6.99	57.11	1.80	67.59	19.21	32.48	39.19	-2.02
	8.32	62.16	0.52	77.83	26.59	25.45	58.51	-2.01

To obtain a more accurate fit, a nonlinear empirical expression [33] of the following form was proposed to correlate the solubility data

$$w_1 = \exp(a + bw_2^{0.5} + cw_2 + dw_2^2), \quad (3)$$

where w_1 is the mass fraction of the IL, w_2 is the mass fraction of the salts, and the coefficients a , b , c , and d are fitting parameters. These parameters, along with the correlation coefficient (R^2) and standard deviations (sd), are given in Table 4.

The following equation was also successfully used in this work to correlate the data:

$$w_1 = a_1 \exp\left(-\frac{w_2}{b_1}\right) + a_2 \exp\left(-\frac{w_2}{b_2}\right) + c, \quad (4)$$

where w_1 and w_2 are the mass fractions of the IL and salts, respectively. This equation has been extended to fit the results of the ATPSs based on hydrophilic organic solvents [34, 35]. The coefficients a_1 , a_2 , b_1 , b_2 , and c along with the correlation coefficient (R^2) and the standard deviations (sd) are listed in Table 5.

The solubility curves determined at $T = 298.15$ K for the [EPy]Br (1) + salt (2) (Na_2HPO_4 , K_2HPO_4 , K_2SO_4 , $\text{C}_4\text{O}_6\text{H}_4\text{KNa}$) + water (3) systems, which provided the minimum concentration required for the formation of these four ATPSs, are plotted in Figure 1, from which it can be observed that an ATPS can be produced by adding an appropriate amount of one salt to an aqueous solution of [EPy]Br. Moreover, one can easily conclude that the phase-separation abilities of the salts follow the order of $\text{K}_2\text{SO}_4 > \text{K}_2\text{HPO}_4 > \text{Na}_2\text{HPO}_4 > \text{C}_4\text{O}_6\text{H}_4\text{KNa}$ by comparing different curves in the phase diagram.

Based on the as-obtained R^2 and standard deviation values in Tables 3–5, it can be concluded that (2)–(4) are satisfactory for correlating the solubility curves of the investigated systems. The same levels of satisfactory results were obtained in other ILATPS as well [36]. Furthermore, the Merchuk equation performs best of the three while it possesses only three adjustable parameters.

3.2. Effective Excluded Volume (EEV) and Salting-out Ability. A binodal model based on the statistical geometry method developed by Guan et al. [37] for aqueous polymer systems was applied to correlate the experimental solubility data of ATPSs containing Na_2HPO_4 , K_2HPO_4 , K_2SO_4 , and $\text{C}_4\text{O}_6\text{H}_4\text{KNa}$ in this paper. The binodal equation can be written as follows:

$$\ln\left(V_{213}^* \frac{w_2}{M_2} + f_{213}\right) + V_{213}^* \frac{w_1}{M_1} = 0 \quad (5a)$$

$$\ln\left(V_{213}^* \frac{w_2}{M_2}\right) + V_{213}^* \frac{w_1}{M_1} = 0, \quad (5b)$$

where V_{213}^* , f_{213} , M_1 , and M_2 are the scaled EEV of the salts, the volume fraction of the unfilled effective available volume after tightly packing the salt molecules into the network of ionic liquid molecules in the ionic liquid aqueous solutions, and the molar masses of the ionic liquid and salt, respectively. The values of V_{213}^* and f_{213} derived from the correlation of the experimental solubility data and the corresponding correlation coefficients (R^2) and standard deviations (sd) are given in Tables 6 and 7.

The salting-out ability of the salt could be related to the EEV [38–40]. The salt with higher salting-out ability has a larger EEV value at the same temperature. This is because with a increase in EEV, the solubility line moves to the left of the phase diagram and the single-phase area decreases correspondingly, resulting in the decline of salts content forming ILATPS, which means that salting-out ability becomes stronger. The EEV represents the smallest spacing of the individual ionic liquid that will adopt an individual salt, reflecting the compatibility of both components in a system. In this study, the EEVs have been calculated using the binodal model developed by Guan et al. [37]. In the original application, (7) was used to correlate the solubility data of polymer-polymer systems because the two components significantly vary in size. The f_{213} value is so small that it can be neglected without obvious influence. From Table 7, it can be found that the parameter f_{213} was small enough to be neglected for the investigated systems, and the standard

TABLE 2: Solubility Data for [EPy]Br (1) + salt (2) + water (3) ATPS at $T = 298.15$ K.

Salt	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$
	0.39	75.96	2.65	54.63	8.37	34.17	15.96	23.49
	0.53	72.39	2.67	54.30	8.50	33.98	16.05	23.39
	0.63	70.30	2.68	54.47	8.61	33.74	16.20	23.13
	0.68	68.79	2.71	54.15	8.71	33.60	16.30	23.00
	0.69	68.13	2.72	53.74	8.84	33.38	16.70	22.53
	0.78	66.87	2.73	54.33	8.95	33.21	16.84	22.25
	0.80	66.11	2.74	53.91	9.05	33.03	16.95	22.13
	0.95	65.96	2.75	53.59	9.17	32.83	17.05	22.01
	0.96	66.23	2.76	53.76	9.28	32.66	17.15	21.91
	0.99	65.67	2.79	53.44	9.41	32.39	17.36	21.71
	1.02	65.43	2.80	53.61	9.53	32.17	17.56	21.41
	1.05	65.18	2.82	53.36	9.65	31.96	17.78	21.15
	1.09	64.76	2.83	53.54	9.77	31.75	18.02	20.90
	1.14	64.30	2.86	53.16	9.90	31.54	18.19	20.62
	1.17	64.06	2.87	53.35	10.03	31.32	18.31	20.47
	1.20	63.74	2.90	53.02	10.16	31.11	18.49	20.15
	1.23	63.50	2.91	53.20	10.29	30.87	18.62	19.99
	1.27	63.28	2.93	52.88	10.47	30.44	18.74	19.86
	1.30	62.99	2.94	53.06	10.59	30.30	18.87	19.73
	1.35	62.71	3.00	52.62	10.71	30.14	19.00	19.59
	1.39	62.67	3.01	52.81	10.83	30.14	19.13	19.45
	1.45	62.13	3.04	52.44	10.97	29.99	19.27	19.31
	1.52	61.54	3.05	52.63	11.08	29.77	19.42	19.17
	1.56	61.25	3.08	52.26	11.17	29.67	19.62	18.82
	1.63	60.68	3.10	52.45	11.28	29.45	19.75	18.66
	1.68	60.32	3.12	51.50	11.40	29.23	19.89	18.50
	1.74	59.92	3.17	52.27	11.52	29.01	20.02	18.34
	1.79	59.51	3.41	49.90	11.62	28.90	20.16	18.17
	1.84	59.14	3.99	47.46	11.77	28.73	20.30	18.00
	1.89	58.56	4.61	45.13	11.89	28.50	20.45	17.85
	1.90	58.69	5.04	40.83	12.00	28.38	20.59	17.67
	1.92	58.35	5.15	40.62	12.11	28.20	20.89	17.32
	1.93	58.48	5.16	41.91	12.24	27.96	21.20	16.98
	1.96	58.12	5.29	40.81	12.35	27.83	21.52	16.62
	1.97	58.25	5.37	40.83	12.49	27.59	21.85	16.22
	2.00	57.95	5.45	40.51	12.63	27.35	22.19	15.84
	2.01	58.09	5.48	40.33	12.74	27.23	22.54	15.43
	2.04	57.71	5.52	40.41	12.88	26.96	22.90	14.99
	2.05	57.85	5.60	40.15	13.00	26.82	23.25	14.56
	2.09	57.46	5.75	39.45	13.13	26.69	23.62	14.10
	2.10	57.60	5.77	39.01	13.28	26.40	24.00	13.67
	2.14	57.20	5.85	39.26	13.41	26.25	24.46	13.23
	2.15	57.35	5.95	38.89	13.57	25.97	24.88	12.78
	2.19	56.87	6.10	38.85	13.73	25.72	25.29	12.31
	2.20	57.02	6.22	38.67	13.83	25.70	25.75	11.83
	2.24	56.69	6.32	38.40	13.93	25.68	26.49	11.01
	2.25	56.84	6.43	38.18	14.04	25.62	26.85	10.76
	2.28	56.26	6.56	37.72	14.21	25.61	27.10	10.48
	2.29	56.41	6.66	37.41	14.35	25.40	27.46	10.20
	2.33	55.80	6.77	37.22	14.42	25.31	27.99	9.64
	2.34	55.95	6.87	37.19	14.49	25.26	28.62	9.06

TABLE 2: Continued.

Salt	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$
	2.36	55.84	6.99	37.00	14.60	25.01	29.31	8.52
	2.37	56.00	7.10	36.69	14.72	24.97	30.02	7.93
	2.40	55.89	7.21	36.50	14.80	24.88	30.97	7.34
	2.41	56.05	7.33	36.15	14.87	24.78	31.78	6.69
	2.45	55.62	7.43	35.91	14.95	24.69	32.63	6.01
	2.46	55.78	7.54	35.81	15.08	24.45	33.14	5.68
	2.51	55.36	7.63	35.74	15.20	24.40	33.66	5.35
	2.52	55.53	7.73	35.55	15.29	24.34	34.39	5.05
	2.56	54.95	7.82	35.45	15.38	24.25	35.15	4.71
	2.57	55.12	7.94	35.10	15.50	24.01	35.90	4.39
	2.61	54.59	8.03	34.87	15.58	23.90	36.81	4.02
	2.62	54.76	8.14	34.65	15.68	23.80	37.75	3.57
	2.64	54.46	8.27	34.41	15.77	23.69	39.04	3.17
K_2HPO_4	1.24	51.48	1.72	47.66	2.53	43.64	3.70	38.59
	1.26	51.29	1.77	47.21	2.62	43.11	3.80	38.28
	1.30	50.97	1.82	46.95	2.76	42.32	3.89	38.05
	1.34	50.68	1.88	46.75	2.86	42.07	3.94	38.02
	1.38	50.28	1.93	46.41	3.02	41.38	4.04	37.73
	1.41	50.02	2.00	46.07	3.19	40.64	4.18	37.35
	1.44	49.83	2.06	45.66	3.24	40.42	4.33	36.85
	1.47	49.54	2.12	45.22	3.30	40.17	4.44	37.02
	1.51	49.28	2.20	44.97	3.36	39.94	4.55	36.49
	1.56	48.82	2.28	44.71	3.43	39.72	4.70	36.10
	1.60	48.63	2.34	44.43	3.48	39.45	4.88	35.93
	1.64	48.25	2.38	44.18	3.55	39.37	5.00	35.30
	1.68	47.99	2.42	43.91	3.63	39.11	5.17	34.74
	7.36	10.51	4.56	23.33	3.33	30.28	2.46	36.40
K_2SO_4	6.74	13.54	4.32	24.69	3.18	31.45	2.34	37.26
	6.15	15.80	4.14	25.71	3.03	32.45	2.24	37.88
	5.70	17.96	3.94	26.70	2.92	33.20	2.14	38.80
	5.41	19.19	3.77	27.79	2.80	33.79		
	5.18	20.37	3.63	28.73	2.68	34.89		
	4.84	21.91	3.49	29.41	2.57	35.51		
$C_4O_6H_4KNa$	0.48	78.95	3.40	59.50	7.67	48.26	14.41	37.88
	0.70	77.03	3.55	58.99	8.06	47.57	15.45	36.29
	0.80	75.16	3.75	58.28	8.23	47.19	16.20	34.94
	0.82	75.03	4.10	57.11	8.72	46.26	16.75	34.77
	0.98	73.40	5.19	54.71	9.49	44.88	17.19	34.17
	1.17	71.64	5.45	53.74	10.39	43.43	17.34	33.96
	1.34	70.30	5.49	53.55	11.09	42.35	17.79	33.54
	1.98	66.65	5.81	52.73	12.12	40.77	18.26	33.07
	2.19	64.97	6.04	52.08	12.68	39.86	18.78	32.53
	2.38	64.09	6.23	51.73	13.32	39.11	19.22	32.18
	2.67	62.83	6.64	50.68	13.68	38.94	19.31	31.97
	2.82	61.98	6.82	50.35	13.95	38.49	19.38	31.81
	2.99	61.25	7.08	49.62	14.18	38.20		
	3.21	60.31	7.28	49.23	14.27	38.27		

TABLE 3: Parameters of (2) for the [EPy]Br (1) + salt (2) + water (3) ATPS at $T = 298.15$ K.

System	a	b	c	R^2	sd ^a
[EPy]Br + Na ₂ HPO ₄	92.2445	-0.3321	$1.9677E - 5$	0.9978	0.84
[EPy]Br + K ₂ HPO ₄	75.9749	-0.3544	$-2.5871E - 5$	0.9991	0.88
[EPy]Br + K ₂ SO ₄	89.4813	-0.5691	$1.4900E - 3$	0.9997	0.12
[EPy]Br + C ₄ O ₆ H ₄ KNa	91.7650	-0.2277	$5.7919E - 6$	0.9994	0.17

^asd = $(\sum_{i=1}^N (w_i^{\text{cal}} - w_i^{\text{exp}})^2 / N)^{0.5}$. Where w_i^{exp} is the experimental mass fraction of IL and w_i^{cal} is the corresponding data calculated using (2). The term "N" represents the number of solubility data.

TABLE 4: Parameters of (3) for the [EPy]Br (1) + salt (2) + water (3) ATPS at $T = 298.15$ K.

System	a	b	c	d	R^2	sd ^a
[EPy]Br + Na ₂ HPO ₄	4.5736	-0.4040	0.0271	-0.0011	0.9972	0.96
[EPy]Br + K ₂ HPO ₄	4.7432	-1.0384	0.3074	-0.0157	0.9992	0.14
[EPy] + K ₂ SO ₄	4.9165	-1.2750	0.3488	-0.0303	0.9996	0.15
[EPy]Br + C ₄ O ₆ H ₄ KNa	4.5676	-0.2982	0.0246	$-7.0600E - 4$	0.9995	0.30

^asd = $(\sum_{i=1}^N (w_i^{\text{cal}} - w_i^{\text{exp}})^2 / N)^{0.5}$. Where w_i^{exp} is the experimental mass fraction of IL and w_i^{cal} is the corresponding data calculated using (3). The term "N" represents the number of solubility data.

deviation in (7) differed significantly from that in (6) for the solubility data fitting, rendering (7) unusable.

According to Table 6, the salting-out ability of the salts at a constant temperature follows the order: K₂SO₄ > K₂HPO₄ > Na₂HPO₄ > C₄O₆H₄KNa, which is in agreement with the phase-separation abilities determined from Figure 1. Apparently, (6) satisfactorily reproduce the solubility curves of the investigated systems. However, when compared to the Merchuk and two other equations, there see a big gap.

Some also insist that salting-out abilities of different salts have something to do with ion hydration free energy (ΔG_{hyd}) [41], the more negative the ions, the stronger their salting-out abilities. K₂HPO₄ and Na₂HPO₄ share the same anion, the cation radius of cation K⁺ exceeds that of Na⁺, and ΔG_{hyd} of K⁺ and Na⁺ are -295 and -365 kJ·mol⁻¹, respectively. In accordance with the ion hydration free energy theory, the salting-out ability of Na₂HPO₄ should be stronger than K₂HPO₄. However, we found that in our study that although ΔG_{hyd} of K⁺ is greater than Na⁺, the salting-out ability is much higher. Still, the anions promote the formation of ATPSs in the following order: SO₄²⁻ (ΔG_{hyd} = -1080 kJ·mol⁻¹) > HPO₄²⁻ (ΔG_{hyd} = -1789 kJ·mol⁻¹), which also deviates from the ion hydration free energy theory.

3.3. Tie-Line Data and Correlation. The tie-line compositions, tie-line length (TLL), and average slopes (S) determined at $T = 298.15$ K are listed in Table 1 and Figures 2 and 3. In this work, the tie-line compositions are closely connected by the Othmer-Tobias equation (6) and Bancroft equation (7) [42, 43] as follows:

$$\left(\frac{1 - w_1^t}{w_1^b} \right) = k_1 \left(\frac{1 - w_2^b}{w_2^b} \right)^n \quad (6)$$

$$\left(\frac{w_3^b}{w_2^b} \right) = k_2 \left(\frac{w_3^t}{w_1^t} \right)^r \quad (7)$$

In these equations, w_1^t is the mass fraction of the IL in the top phase; w_2^t is the mass fraction of the salt in the bottom phase; w_3^b and w_3^t are the mass fractions of water in the bottom and top phases, respectively. Recently, (6) and (7) have been successfully verified by other ATPS researchers, indicating that the two equations can accurately correlate the tie-line data of the systems. The plots of $\log[(1 - w_1^t)/w_1^b]$ against $\log[(1 - w_2^b)/w_2^b]$ and $\log(w_3^b/w_2^b)$ against $\log(w_3^t/w_1^t)$ shows linear relationships, indicating acceptable consistency of the results. The values of the fit parameters k_1 , n , k_2 , and r , the coefficient values (R^2), and the standard deviations (sd) are listed in Table 8.

For further confirmation, the Setschenow-type equation [44] was used to correlate the tie-line compositions of the [EPy]Br + Na₂HPO₄/K₂HPO₄/K₂SO₄/C₄O₆H₄KNa ATPSs at $T = 298.15$ K:

$$\ln \left(\frac{c_1^t}{c_1^b} \right) = k_{\text{IL}} (c_1^b - c_1^t) + k_s (c_2^b - c_2^t). \quad (8)$$

In the above equation, c_1 , c_2 , k_{IL} , and k_s represent the molality of the IL, the molality of the salt, a parameter relating the activity coefficient of the IL to its concentration, and the salting-out coefficient, respectively. The two superscripts "t" and "b" represent the IL-rich phase and the salt-rich phase, respectively. Assuming that the first term on the right side of this equation is negligible in comparison with the second term, a Setschenow-type equation can be obtained, implying that $k_{\text{IL}} \ll k_s$ because the absolute values of $(c_1^b - c_1^t)$ exceed those of $(c_2^b - c_2^t)$. This equation was successfully used for the correlation of tie-line data for the IL + salt ATPSs [42]. The salting-out coefficients, k_s , with the corresponding intercepts, correlation coefficient (R^2) as well as standard deviations (sd) are all listed in Table 9.

In our study, a correlating equation with two parameters has also been used to determine the tie-line data which can be

TABLE 5: Parameters of (4) for the [EPy]Br (1) + salt (2) + water (3) ATPS at $T = 298.15$ K.

System	a_1	b_1	a_2	b_2	c	R^2	sd ^a
[EPy]Br + Na ₂ HPO ₄	23.3946	-3.4874E19	61.9954	11.0376	-16.9351	0.9859	2.14
[EPy]Br + K ₂ HPO ₄	9.4472	-8.8659E22	32.6463	2.7530	20.9157	0.9968	0.27
[EPy] + K ₂ SO ₄	9.0913	-2.2954E19	73.7805	7.5619	-26.0714	0.9996	0.49
[EPy]Br + C ₄ O ₆ H ₄ KNa	9.8253	-2.8063E23	49.0484	8.0236	19.4759	0.9911	1.28

^asd = $(\sum_{i=1}^N (w_i^{\text{cal}} - w_i^{\text{exp}})^2 / N)^{0.5}$. Where w_i^{exp} is the experimental mass fraction of IL and w_i^{cal} is the corresponding data calculated using (4). The term “N” represents the number of solubility data.

TABLE 6: Parameters of (5a) for the [EPy]Br (1) + salt (2) + water (3) ATPS at $T = 298.15$ K.

System	V_{213}^*	f_{213}	R^2	sd ^a
[EPy]Br + Na ₂ HPO ₄	5.2183	0.2018	0.9828	0.64
[EPy]Br + K ₂ HPO ₄	5.6397	0.1259	0.9824	2.39
[EPy]Br + K ₂ SO ₄	11.4851	-0.0575	0.9814	1.10
[EPy]Br + C ₄ O ₆ H ₄ KNa	4.7262	0.1524	0.9730	2.26

^asd = $(\sum_{i=1}^N (w_i^{\text{cal}} - w_i^{\text{exp}})^2 / N)^{0.5}$. Where w_i^{exp} is the experimental mass fraction of IL and w_i^{cal} is the corresponding data calculated using (6). The term “N” represents the number of solubility data.

TABLE 7: Parameters of (5b) for the [EPy]Br (1) + salt (2) + water (3) ATPS at $T = 298.15$ K.

System	V_{213}^*	R^2	sd ^a
[EPy]Br + Na ₂ HPO ₄	8.4568	0.0758	21.75
[EPy]Br + K ₂ HPO ₄	8.5867	0.8820	38.25
[EPy]Br + K ₂ SO ₄	10.2939	0.9601	2.57
[EPy]Br + C ₄ O ₆ H ₄ KNa	7.4313	0.1268	160.50

^asd = $(\sum_{i=1}^N (w_i^{\text{cal}} - w_i^{\text{exp}})^2 / N)^{0.5}$. Where w_i^{exp} is the experimental mass fraction of IL and w_i^{cal} is the corresponding data calculated using (7). The term “N” represents the number of solubility data.

TABLE 8: Parameters of (6) and (7) for the [EPy]Br (1) + salt (2) + water (3) ATPS at $T = 298.15$ K.

System	k_1	n	R_1^2	sd ₁ ^a	k_2	r	R_2^2	sd ₂ ^a
[EPy]Br + Na ₂ HPO ₄	0.5605	1.1210	0.8815	2.24	1.6422	0.8044	0.8802	0.06
[EPy]Br + K ₂ HPO ₄	0.0309	0.8786	0.9946	0.08	22.7372	0.9823	0.9950	0.16
[EPy]Br + K ₂ SO ₄	0.0190	1.2043	0.9984	0.07	19.0417	0.5867	0.9978	0.11
[EPy]Br + C ₄ O ₆ H ₄ KNa	0.0956	1.1154	0.9828	0.85	4.5475	0.7426	0.9868	0.06

^asd = $(\sum_{i=1}^N (100w_{i,j,\text{cal}}^{\text{top}} - 100w_{i,j,\text{exp}}^{\text{top}})^2 + (100w_{i,j,\text{cal}}^{\text{bot}} - 100w_{i,j,\text{exp}}^{\text{bot}})^2 / 2N)^{0.5}$. Where N is the number of tie-lines and $j = 1$ and $j = 2$, sd₁ and sd₂ represent the mass percent standard deviations for [EPy]Br and the salt, respectively.

TABLE 9: Parameters of (8) for the [EPy]Br (1) + salt (2) + water (3) ATPS at $T = 298.15$ K.

System	k_s	Intercept	R^2	$\delta(k_s)^b$	$\delta(\text{intercept})^c$	100sd ^a
[EPy]Br + Na ₂ HPO ₄	2845.9	-1.8166	0.9981	88.60	0.1512	0.09
[EPy]Br + K ₂ HPO ₄	1781.0	0.0146	0.9999	9.71	0.0025	0.60
[EPy]Br + K ₂ SO ₄	4837.4	-0.1873	0.9963	208.70	0.0590	2.41
[EPy]Br + C ₄ O ₆ H ₄ KNa	1231.1	-0.0241	0.9996	18.37	0.0167	2.45

^asd = $(\sum_{i=1}^N (100w_{i,j,\text{cal}}^{\text{top}} - 100w_{i,j,\text{exp}}^{\text{top}})^2 + (100w_{i,j,\text{cal}}^{\text{bot}} - 100w_{i,j,\text{exp}}^{\text{bot}})^2 / 6N)^{0.5}$. Where N is the number of tie-lines and j is the number of components in each phase. $\delta(k_s)^b$ is the standard deviation for the fitting parameters of “ k_s ”. $\delta(\text{intercept})^c$ is the standard deviation of the fitting parameters of the “intercept”.

TABLE 10: Parameters of (9) for the [EPy]Br (1) + salt (2) + water (3) ATPS at $T = 298.15$ K.

System	k	β	R^2	sd ^a
[EPy]Br + Na ₂ HPO ₄	0.0709	0.8535	0.9981	0.02
[EPy]Br + K ₂ HPO ₄	0.1300	0.5822	0.9956	0.05
[EPy]Br + K ₂ SO ₄	0.0656	0.2329	0.9984	0.03
[EPy]Br + C ₄ O ₆ H ₄ KNa	0.0926	0.8957	0.9991	0.04

^asd = $(\sum_{i=1}^N (100w_{i,j,\text{cal}}^{\text{top}} - 100w_{i,j,\text{exp}}^{\text{top}})^2 + (100w_{i,j,\text{cal}}^{\text{bot}} - 100w_{i,j,\text{exp}}^{\text{bot}})^2 / 6N)^{0.5}$. Where N is the number of tie-lines and j is the number of components in each phase.

TABLE II: Parameters of (10) for the [EPy]Br (1) + salt (2) + water (3) ATPS at $T = 298.15$ K.

System	f	g	R^2	$100w_1$	$100w_2$	sd
[EPy]Br + Na_2HPO_4	56.8201	-1.8603	0.8777	23.77	15.06	39.64
[EPy]Br + K_2HPO_4	54.9576	-4.2020	0.9644	46.67	1.89	0.84
[EPy]Br + K_2SO_4	49.0957	-5.4588	0.9904	40.03	1.94	0.62
[EPy]Br + $\text{C}_4\text{O}_6\text{H}_4\text{KNa}$	69.0866	-2.1286	0.9203	47.75	8.15	14.64

^asd = $(\sum_{i=1}^N (w_i^{\text{cal}} - w_i^{\text{exp}})^2 / N)^{0.5}$. Where w_i^{exp} is the experimental mass fraction of IL and w_i^{cal} is the corresponding data calculated using (10). The term “N” represents the number of solubility data.

FIGURE 1: Solubility curves of [EPy]Br(1) + salts (2)+water (3) ATPS at $T = 298.15$ K: *, Na_2HPO_4 ; □, K_2HPO_4 ; △, K_2SO_4 ; ▼, $\text{C}_4\text{O}_6\text{H}_4\text{KNa}$.

derived using the binodal theory [37]. The equation has the following form:

$$\ln\left(\frac{w_2^t}{w_2^b}\right) = \beta + k(w_1^b - w_1^t), \quad (9)$$

in which k is the salting-out coefficient, and β is the constant most closely related to the activity coefficient. The superscripts “t” and “b” represent the IL-rich phase and the salt-rich phase, respectively. Recently, (9) was successfully used to correlate the tie-line data for a polymer-salt ATPS [45, 46]. The fitting parameters of this equation, the correlation coefficient values (R^2), and the standard deviations (sd) are provided in Table 10.

The standard deviations in Tables 8–10 are small, indicating that (6)–(9) are appropriate for correlating the tie-line data of the ATPSs especially the Setschenow-type equation. For more details about the relationship between the Setschenow-type behavior and the phase diagrams, the Setschenow-type plots of the tie-line data for the investigated systems are also shown in Figure 4. The Setschenow-type plots with data from Table 9 indicate that the larger the slope, the larger the k_s . When combining with Figure 1, the

FIGURE 2: Tie-lines of [EPy]Br (1) + salts (2) + water (3) ATPS at $T = 298.15$ K: •, Na_2HPO_4 ; △, K_2SO_4 .

larger the k_s , the higher salting-out ability. This behavior is in agreement with the reported results for other ATPSs [47].

3.4. Calculation of the Plait Point. Plait points are points on the solubility curves where the length of tie-lines shrank to almost zero, indicating that the two liquid phases become identical [48]. The plait points data for the investigated ATPSs in this study were calculated via the following linear equation:

$$w_1 = f + gw_2 \quad (10)$$

in which f and g are the fitting parameters. For the four systems, the estimated values of the plait points along with the fitting parameters obtained from (10) and the corresponding correlation coefficients are given in Table 11.

3.5. Effect of Salts on Solubility Curves and Tie-Lines. Figure 1 presents the effect of different salts on the solubility curves. It is clear that different salts possess two-phase areas of different sizes. In this study, K_2SO_4 owns the largest area of two phase; therefore, the phase-separation ability of K_2SO_4 precedes the other three.

Considering that the salts Na_2HPO_4 and K_2HPO_4 share a common anion HPO_4^{2-} but contain different cations, one can conclude that the salting-out ability of K^+ is higher than

FIGURE 3: Tie-lines of [EPy]Br (1) + salts (2) + water (3) ATPS at $T = 298.15$ K: $\square$, K_2HPO_4 ; $\blacktriangledown$, $C_4O_6H_4KNa$.

FIGURE 4: Tie-lines of [EPy]Br (1) + salts (2) + water (3) ATPS fitted by Setschenow-type equation at $T = 298.15$ K: $\blacksquare$, Na_2HPO_4 ; $\bullet$, K_2HPO_4 ; $\star$, K_2SO_4 ; $\blacktriangledown$, $C_4O_6H_4KNa$.

that of Na^+ at a constant temperature, which is contrary to what Chen and Wang [49] obtained from their research. This may be due to the relatively large radius of HPO_4^{2-} . Also, the K_2HPO_4 and K_2SO_4 share a common cation K^+ , but the EEV for K_2SO_4 is higher than that of K_2HPO_4 ; therefore, the salting-out ability of SO_4^{2-} is higher than that of HPO_4^{2-} at the same temperature. When it comes to $C_4O_6H_4KNa$, which owns both K^+ and Na^+ , it might be the organic ion $C_4O_6H_4^{2-}$ that brings about the weakest salting-out ability.

Figures 2 and 3 present the effect of different salts on the phase compositions, from which it can be informed that the slopes of tie-lines differ greatly towards different salt types.

The slopes of tie-lines for ATPS containing K_2SO_4 are of the largest value, illustrating that K_2SO_4 hydrates the most water, thus decreasing the amount of water available to hydrate [EPy]Br.

4. Conclusions

The liquid-liquid equilibrium data have been determined for [EPy]Br + salt (Na_2HPO_4 , K_2HPO_4 , K_2SO_4 and $C_4O_6H_4KNa$) ATPSs at $T = 298.15$ K. The effect of salt on solubility curves as well as tie-lines was studied. The volume (EEV) values obtained from the binodal model together with the phase diagram indicated the order of phase separation abilities of the four salts. The Merchuk equation and two other equations were used to correlate the solubility data and the Othmer-Tobias, Bancroft, and Setschenow-type equations and a two-parameter equation were used to correlate the tie-line data. The results indicate that the calculation method and the corresponding tie-line data are reliable. At fixed temperatures, the salting-out ability of K^+ is higher than that of Na^+ , and that of anions follows $SO_4^{2-} > HPO_4^{2-} > C_4O_6H_4^{2-}$.

List of Symbols

N :	Number of solubility data
N :	Number of tie-lines
T :	Temperature (K)
TLL:	Tie-line length
S :	Slope of the tie-line
w :	Mass fraction
k_s, k_{IL} :	Salting-out coefficient
β :	Interaction parameter
V_{213}^* :	Scaled EEV of salt
f_{213} :	Volume fraction
M :	Molar mass
$a, b, c, d, a_1, b_1, a_2, b_2, k_1, n, k_2, r, k$:	Fitting parameters
R^2 :	Correlation coefficient
sd :	Standard deviation.

Super/Subscript

b :	Bottom phase
t :	Top phase
cal:	Calculated value
exp:	Experimental value
1:	[EPy]Br
2:	Salt
3:	Water.

Conflict of Interests

None of the authors for this paper have a direct financial relation with the commercial identity mentioned in this paper.

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