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Measurement and Correlation of Phase Diagram Data for Aqueous Two-Phase Systems Containing 1-Ethyl-3-methylimidazolium Dimethyl Phosphate + K_3PO_4/K_2HPO_4/K_2CO_3 + H_2O Ionic Liquids at (298.15, 308.15, and 318.15) K

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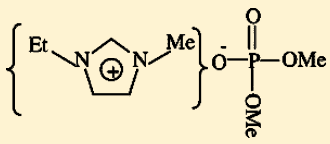
ABSTRACT: Binodal data for the 1-ethyl-3-methylimidazolium dimethyl phosphate ([Emim]DMP) + salt (K_3PO_4, K_2HPO_4, and K_2CO_3) + H_2O systems were experimentally determined at T = (298.15, 308.15, and 318.15) K, respectively. The Merchuk equation was used to correlate the binodal data. The abilities of the different salts for phase separation follow the order K_3PO_4 > K_2HPO_4 > K_2CO_3, which may be related to the Gibbs free energy of hydration of the ions ($\Delta_{hyd}G$). The two-phase area expands with a decrease in temperature, whereas the slope of the tie lines slightly decreases with an increase in temperature. The reliability of the calculation method and corresponding tie-line data was described by the Othmer−Tobias and Bancroft equations, as well as the two-parameter equation. [Emim]DMP is a familiar ionic liquid, extensively used for the extractive desulfurization of fuel oils. This study is the first to report data on the phase diagrams of [Emim]DMP + salt + water systems.



INTRODUCTION

Liquid−liquid extraction (LLE) is popular, well established, versatile, and easy to use for separation processes.[1] Aqueous two-phase systems (ATPSs), which are usually formed with two incompatible polymers or a polymer and a salt in water above a certain critical concentration, are improved LLE systems.[2−4] Aqueous two-phase extraction (ATPE) is an economical and efficient downstream processing method widely used for the separation, preconcentration, and purification of biomolecules,[5] metallic ions,[6] dye molecules,[7] drug molecules,[8] small organic molecules,[9] and nanoparticulates.[10]

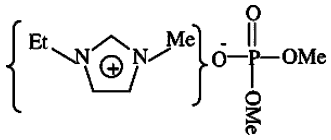


Figure 1. Structure of [Emim]DMP.

In recent years, ATPSs based on ionic liquids (ILs) as a new type of LLE have been investigated since Gutowski et al.[11] demonstrated that hydrophilic ILs could form ATPSs when potassium phosphate was added to the aqueous solution. ILs, being typically nonflammable and nonvolatile compounds, may help design environmentally safe processes.[12] Hence, IL-based aqueous two-phase systems (ILATPSs) have been successfully used to separate antibiotics,[13−16] drugs,[17,18] and proteins.[19] These new ATPSs present promising prospects for green extraction and separation processes.[20]

The most common kosmotropic salts employed by different research groups in the IL-based ATPE technique consist of selective cations (ammonium, potassium, or sodium) and anions (phosphate, sulfate, hydroxide, or carbonate).[21,22] Neves and Ventura[23,24] evaluated cation and anion influence on the formation and extraction capabilities of ILATPSs. The results indicate that the ability of an IL to induce ATPS closely follows the decrease in the hydrogen bond accepting strength or the increase in the hydrogen bond acidity of the IL anion. In the same way, an IL cation also has a significant influence on the behavior of the biondal curves and in the promotion of ATPS. Increasing the alkyl chain length (for mono- or disubstituted ILs) increases the phase separation ability, whereas the insertion of a double bond, a benzyl group, or a hydroxyl group leads to a decrease of ATPS promotion capability. Choosing ILs and salt for ILATPSs is important. Wu and coworkers[25,26] researched the phase diagrams of 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim]BF_4$) + saccharides + water. Pei et al.[27] reported liquid−liquid equilibrium data for imidazolium IL ($[C_4mim]Cl$, $[C_6mim]Cl$, $[C_4mim]Br$, $[C_6mim]Br$, $[C_8mim]Br$, and $[C_{10}mim]Br$) + salt (KOH, K_2HPO_4, K_2CO_3, and K_3PO_4). Deng et al.[28] measured the binodal curves and tie-line data of [Amim]Cl + salt (K_3PO_4, K_2HPO_4, and K_2CO_3) + water, which correlated satisfactorily with the Merchuk, Othmer−Tobias, and Bancroft equations, respectively.

1-Ethyl-3-methylimidazolium dimethyl phosphate ([Emim]-DMP) is a common and chaotropic IL. The structure of [Emim]-DMP is shown in Figure 1. [Emim]DMP was effectively used for the extractive desulfurization of fuel oils.[29,30] It is theoretically composed of ILATPS with conformable kosmotropic salt solutions. The vapor pressure data for water, methanol, ethanol, and their binary mixtures in the presence of [Emim]DMP were measured by

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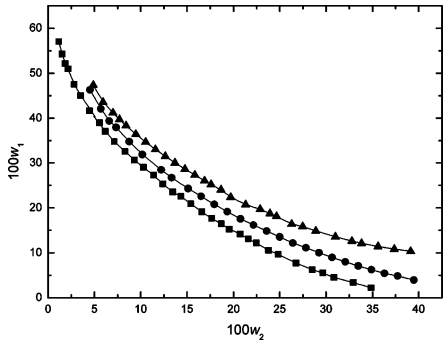

Figure 2. Effect of temperature on binodal curves of the [Emim]DMP (1) + K_3PO_4 (2) + H_2O (3) ATPS: ■, 298.15 K; ●, 308.15 K; ▲, 318.15 K.

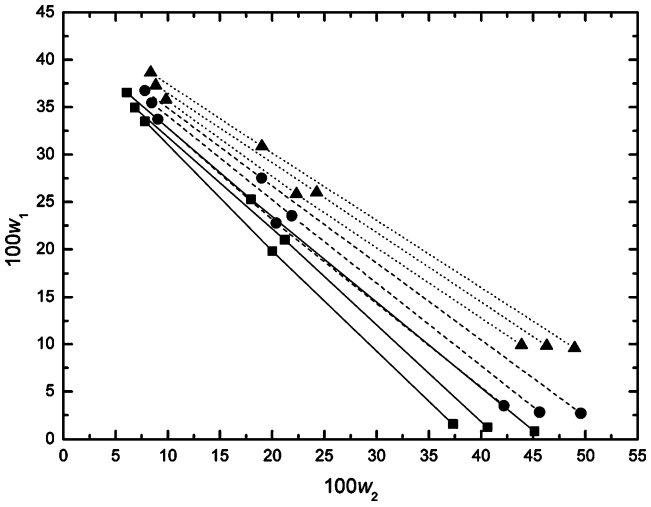

Figure 3. Effect of temperature on the equilibrium phase compositions of the [Emim]DMP (1) + K_3PO_4 (2) + H_2O (3) ATPS: ■, 298.15 K; ●, 308.15 K; ▲, 318.15 K; —, tie lines at 298.15 K; --, tie lines at 308.15 K; ···, tie lines at 318.15 K. These tie lines were obtained by connecting the experimental equilibrium phase composition data.

Wang et al.[31] However, data on the phase diagrams of [Emim]DMP + salt + water systems have not been reported.

In the present work, the ILATPS of [Emim]DMP + salt (K_3PO_4, K_2HPO_4, and K_2CO_3) + H_2O was designed. The results show that the ILATPS system is easy to construct. The binodal curves were fitted to the Merchuk equation, and the tie lines were described using the Othmer−Tobias and Bancroft equations, as well as the two-parameter equation. The effects of temperature on the binodal curves and tie lines were also studied. In addition, the ability of the three different salts for phase separation was examined. These results confirm very good correlation and provide a possible basis for the prediction of phase composition when such data are unavailable.

■ EXPERIMENTAL SECTION

Materials. [Emim]DMP was purchased from Chengjie Chemical Co., Ltd. (Shanghai, China) with a quoted purity greater than 0.99 mass fraction and was used without further purification. K_3PO_4, K_2CO_3, and K_2HPO_4 were analytical-grade reagents (GR, min. 99 % by mass fraction), supplied by Sinopharm Chemical Reagent Co., Ltd. Double-distilled deionized water was used for the experiments.

Apparatus and Procedures. The binodal curves were determined by the cloud point method (titration method).

Table 1. Binodal Data for the Hydrophilic [Emim]DMP (1) + K_3PO_4 (2) + H_2O (3) Systems at T = (298.15, 308.15, and 318.15) K and Pressure p = 0.1 MPa[a]

T = 298.15 K		T = 308.15 K		T = 318.15 K	
100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1
1.15	57.03	4.52	46.27	4.88	47.34
1.51	54.26	5.70	42.03	5.94	43.56
1.84	52.14	6.60	39.34	7.00	41.14
2.15	50.97	7.35	37.90	7.70	39.68
2.82	47.46	8.76	34.72	8.41	38.31
3.52	44.99	10.17	31.85	9.47	36.41
5.55	38.97	12.21	28.46	10.53	34.66
4.48	41.58	13.35	26.69	11.59	33.02
6.16	37.03	15.12	24.27	12.65	31.48
7.14	34.74	16.53	22.56	13.70	30.02
8.29	32.57	17.94	20.75	14.76	28.63
9.31	30.65	19.35	19.15	15.82	27.30
10.29	29.01	20.77	17.53	16.88	26.03
11.38	27.28	22.18	16.18	17.59	25.21
12.38	25.30	23.59	14.81	18.65	24.01
13.45	23.51	25.01	13.51	19.71	22.36
14.32	22.58	26.42	12.17	21.33	20.70
15.41	20.89	27.83	11.10	22.89	19.68
16.59	19.12	29.24	9.99	23.95	18.72
17.64	17.65	30.66	8.95	24.65	18.10
18.69	16.42	32.07	7.97	26.27	16.37
19.56	15.21	33.48	7.05	27.48	15.84
20.73	14.16	34.89	6.20	28.89	14.85
21.60	13.06	36.31	5.42	31.01	13.53
22.48	12.16	37.72	4.81	32.78	12.59
23.79	10.53	39.48	3.90	33.83	12.10
24.81	9.66			35.60	11.38
26.76	7.72			37.36	10.79
28.50	6.22			39.13	10.32
29.64	5.53				
30.84	4.45				
32.94	3.35				
34.89	2.20				

[a]Standard uncertainties u are $u(w)$ = 0.001, $u(T)$ = 0.05 K, and $u(p)$ = 10 kPa.

From stock, a salt solution of known concentration was placed into a vessel. The pure IL of [Emim]DMP was then added dropwise to the vessel until the mixture became turbid or cloudy. This phenomenon indicates the formation of two liquid phases. Then, water was added dropwise to the vessel to obtain a clear one-phase system, and the above-mentioned procedure was repeated. The vessel was immersed in a jacketed glass vessel, and the system temperature was maintained and controlled within ±0.05 K using a DF-101S water thermostat (Gongyi Yuhua Instrument Factory, China). The composition of the mixture for each point on the binodal curve was calculated by mass using an analytical balance (BS 124S, Beijing Sartorius Instrument Co., China) with a precision of ± 0.0001 g.

For the determination of the tie lines, a series of ATPSs with at least three different known total compositions, mixed with appropriate amounts of [Emim]DMP, salt, and water, were prepared in the vessel. After vigorously stirring for at least 30 min, the system was placed in a thermostatted bath for 12 h. Then, a TDL-4 centrifuge (Shanghai Anke Instrument Factory, China) operated at 2000 rpm was used for 20 min in each test to ensure complete phase separation. The systems were placed

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Table 2. Binodal Data for the Hydrophilic [Emim]DMP (1) + K_2HPO_4 (2) + H_2O (3) Systems at T = (298.15, 308.15, and 318.15) K and Pressure p = 0.1 MPa[a]

T = 298.15 K		T = 308.15 K		T = 318.15 K	
100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1
1.76	62.77	2.33	64.21	2.13	69.11
2.75	54.17	3.27	56.53	2.51	66.22
3.79	48.83	4.02	52.80	3.43	59.65
4.70	44.95	5.15	48.35	4.40	56.19
5.64	41.74	6.46	44.81	5.91	50.91
6.56	39.21	7.04	42.79	7.80	45.97
7.59	36.40	8.17	40.13	8.93	43.55
8.61	34.21	9.31	37.80	9.85	42.09
9.54	32.45	10.06	36.40	10.82	40.09
10.58	30.54	11.19	34.47	11.95	38.27
11.64	28.95	12.33	32.70	12.71	37.14
12.68	27.24	13.08	31.60	13.84	35.55
13.46	26.11	14.22	30.05	14.93	34.31
14.90	24.06	15.26	28.12	15.73	33.12
15.41	23.49	17.24	26.34	16.86	31.77
16.68	21.95	19.12	24.29	17.99	30.50
17.57	20.93	20.63	22.75	19.80	28.51
18.56	19.92	22.14	21.11	21.01	27.38
19.71	18.63	24.03	19.63	22.90	25.62
20.29	18.01	25.17	18.67	24.88	23.99
21.92	16.34	26.30	17.77	26.68	22.47
22.73	15.63	27.43	16.89	27.81	21.61
23.60	14.91	28.56	16.06	28.94	20.80
24.97	13.96	29.70	15.27	30.83	19.52
25.90	13.08	31.21	14.28	32.72	18.54
26.99	12.26	32.34	13.79	33.85	17.71
28.15	11.47	34.23	12.49	35.74	16.70
29.33	10.59	35.37	11.89	36.87	16.14
31.67	9.08	36.12	11.51	38.59	15.29
33.41	7.98	37.63	10.79	40.47	15.16
35.04	7.03	38.38	10.45		
37.04	6.08	40.33	10.06		
39.14	5.09				

[a]Standard uncertainties u are $u(w)$ = 0.001, $u(T)$ = 0.05 K, and $u(p)$ = 10 kPa.

again into the thermostatted bath and allowed to settle for at least 2 h to enable separation into two clear phases. After reaching phase equilibrium, the volumes of the top and bottom phases were noted. The samples of the top and bottom phases were retrieved carefully for analysis. The concentrations of salts in the top and bottom phases were determined by inductively coupled plasma−optical emission spectrometry (VISTA-MPX, US Varian Co., USA). The uncertainty in the measurement of the mass fraction of the salts was estimated to be ± 0.00001. The mass fraction of [Emim]DMP in both phases was determined at 210 nm (absorption peak) using a UV−vis spectrometer (model UV-2450, Shimadzu Corporation, Japan). The uncertainty of the mass fraction of [Emim]DMP was better than 0.001. The mass fraction of water was then calculated.

The tie-line length (TLL) and tie-line slope S at different compositions were calculated using eqs 1 and 2, respectively.

$$\mathrm{TLL} = [(w_1^{\,t} - w_1^{\,b})^2 + (w_2^{\,t} - w_2^{\,b})^2]^{0.5} \quad (1)$$

$$S = (w_1^{\,t} - w_1^{\,b})/(w_2^{\,t} - w_2^{\,b}) \quad (2)$$

Table 3. Binodal Data for the Hydrophilic [Emim]DMP (1) + K_2CO_3 (2) + H_2O (3) Systems at T = (298.15, 308.15, and 318.15) K and Pressure p = 0.1 MPa[a]

T = 298.15 K		T = 308.15 K		T = 318.15 K	
100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1
1.20	77.12	2.98	80.16	2.61	94.96
1.53	73.21	3.72	74.43	3.56	85.43
1.86	70.36	4.84	67.01	4.37	80.22
2.24	68.29	5.95	61.12	5.11	75.06
2.61	65.97	6.69	57.8	6.03	70.08
3.01	63.18	7.80	54.27	7.26	64.43
3.51	60.95	8.64	51.83	8.96	58.50
4.32	56.74	9.66	48.88	10.01	55.34
5.07	54.07	10.77	45.81	11.63	51.20
5.68	51.57	11.80	42.97	14.19	46.34
6.81	48.09	12.92	40.73	16.28	42.70
7.79	45.29	13.73	39.51	18.39	39.63
8.81	42.94	14.85	37.80	20.37	36.81
9.81	40.58	15.96	35.80	22.24	34.59
10.62	38.98	17.11	33.62	24.38	32.08
11.83	36.76	18.92	31.37	27.13	30.07
13.04	34. 70	20.78	28.80	29.51	28.08
13.86	33.23	21.89	27.65	31.79	26.56
14.99	31.69	23.43	25.63	33.74	25.75
16.28	29.81	24.55	24.90	35.66	24.54
16.94	28.49	25.97	23.62	37.01	23.89
17.60	27.46	27.82	21.16	39.31	22.66
18.07	26.70	28.93	20.36		
19.36	25.10	30.86	18.54		
20.49	23.38	32.64	17.09		
21.51	22.23	34.64	15.75		
22.16	21.38	35.98	15.02		
23.74	19.24	37.83	14.05		
24.72	18.34	38.94	13.81		
25.60	17.18				
27.05	15.28				
28.11	14.40				
29.37	12.99				
30.88	11.53				
33.10	9.68				
35.97	7.20				
38.06	5.95				

[a]Standard uncertainties u are $u(w)$ = 0.001, $u(T)$ = 0.05 K, and $u(p)$ = 10 kPa.

where $w_1^{\,t}$, $w_1^{\,b}$, $w_2^{\,t}$, and $w_2^{\,b}$ represent the equilibrium mass fraction of [Emim]DMP (1) and salt (2) in the top (t) and bottom (b) phases, respectively.

RESULTS AND DISCUSSION

Binodal Data and Correlation. For the [Emim]DMP (1) + salt (K_3PO_4, K_2HPO_4, and K_2CO_3) (2) + H_2O (3) systems, the binodal data determined at T = (298.15, 308.15, and 318.15) K are given in Tables 1, 2, and 3, respectively. The binodal data were correlated using the Merchuk equation

$$w_1 = a \exp(b w_2^{\,0.5} - c w_2^{\,3}) \quad (3)$$

where w_1 is the mass fraction of hydrophilic ILs [Emim]DMP, w_2 is the mass fraction of salts, and a, b, and c represent the fitting parameters. The parameters for this equation were determined by least-squares regression of the cloud point data.

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Table 4. Values of Parameters of Eq 3 for the Hydrophilic [Emim]DMP (1) + K_3PO_4/K_2HPO_4/K_2CO_3 (2) + H_2O (3) Systems at T = (298.15, 308.15, and 318.15) K[a]

T/K	a	b	c	R^2	100 SD
		[Emim]DMP + K_3PO_4 + H_2O			
298.15	78.5560	−0.2984	4.0932×10^{-5}	0.9999	0.1668
308.15	93.1704	−0.3304	1.7820×10^{-5}	0.9999	3.6412
318.15	93.3979	−0.3064	6.6189×10^{-6}	0.9981	1.4872
		[Emim]DMP + K_2HPO_4 + H_2O			
298.15	98.8349	−0.3573	1.1736×10^{-5}	0.9995	0.3045
308.15	103.1037	−0.3268	4.5731×10^{-6}	0.9992	1.5548
318.15	103.6012	−0.2875	2.0711×10^{-6}	0.9993	3.3271
		[Emim]DMP + K_2CO_3 + H_2O			
298.15	106.4949	−0.3000	1.8473×10^{-5}	0.9999	0.2443
308.15	145.3200	−0.3500	3.3300×10^{-6}	0.9995	0.9795
318.15	160.9302	−0.3349	-2.6946×10^{-6}	0.9993	18.1146

[a]SD = $(\Sigma_{i=1}^{n} (w_1^{cal} - w_1^{exp})^2/N)^{0.5}$, where w_1 and N represent the mass fraction of [Emim]DMP and the number of binodal data, respectively. w_1^{exp} is the experimental mass fraction of [Emim]DMP listed in Table 1, and w_1^{cal} is the corresponding data calculated using eq 3.

Table 5. Tie Line Data of [Emim]DMP (1) + K_3PO_4 (2) + H_2O (3) at T = (298.15, 308.15, and 318.15) K and Pressure p = 0.1 MPa[a]

	total system		IL-rich phase		salt-rich phase			
T/K	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	TLL	S
298.15	21.20	21.00	6.82	34.95	40.61	1.23	47.73	−1.00
	20.03	19.82	7.81	33.50	37.33	1.57	43.49	−1.08
	17.99	25.28	6.08	36.54	45.13	0.80	52.93	−0.92
308.15	21.88	23.53	8.48	35.43	45.61	2.83	49.41	−0.88
	20.39	22.78	9.05	33.72	42.22	3.52	44.86	−0.91
	18.99	27.52	7.81	36.74	49.57	2.70	53.88	−0.82
318.15	24.27	26.21	8.85	37.31	46.30	9.82	46.46	−0.73
	22.33	25.83	9.83	35.81	43.86	9.91	42.77	−0.76
	19.01	30.86	8.35	38.64	48.97	9.60	49.93	−0.72

[a]Standard uncertainties u are $u(w)$ = 0.001, $u(T)$ = 0.05 K, and $u(p)$ = 10 kPa.

Table 6. Tie Line Data of [Emim]DMP (1) + K_2HPO_4 (2) + H_2O (3) at T = (298.15, 308.15, and 318.15) K and Pressure p = 0.1 MPa[a]

	total system		IL-rich phase		salt-rich phase			
T/K	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	TLL	S
298.15	25.96	26.98	4.22	44.87	57.04	0.43	69.02	−0.84
	22.01	26.43	6.00	39.99	49.66	2.22	57.73	−0.87
	19.99	30.50	5.11	42.57	53.88	1.24	63.93	−0.85
308.15	24.57	34.03	4.42	50.87	56.04	8.03	67.07	−0.83
	20.08	33.33	5.80	46.00	50.66	8.62	58.40	−0.83
	23.09	28.00	7.61	41.00	45.88	9.31	49.68	−0.83
318.15	26.57	36.82	4.82	54.69	56.04	12.93	66.08	−0.82
	21.21	36.33	6.64	49.00	50.16	13.62	56.09	−0.81
	20.10	43.90	4.02	57.32	58.58	13.26	70.13	−0.81

[a]Standard uncertainties u are $u(w)$ = 0.001, $u(T)$ = 0.05 K, and $u(p)$ = 10 kPa.

Recently, the above equation has been successfully used for the correlation of binodal data of IL + salt[21,22,25,27] ATPSs. Using eq 3, the coefficients a, b, and c obtained from the correlation of experimental binodal data along with the correlation coefficients (R) and standard deviations (SD) are given in Tables 4. On the basis of obtained standard deviations, we concluded that eq 3 can be satisfactorily used to correlate the binodal curves of the investigated systems.

Effect of Temperature on Binodal Curves. The effects of temperature on the phase-forming ability of the studied system are illustrated in Figure 2. The loci of the experimental binodals demonstrate that the two-phase area expands with a decrease in temperature for [Emim]DMP + K_3PO_4 + H_2O. This phenomenon is attributed to the decrease in the solubility of IL or the increase in the phase-forming ability of salt in the studied system. More recently, the effect of temperature on the phase-forming ability in the [Bmim]BF_4 + $(NH_4)_2SO_4$ two-phase system[32] has also demonstrated that the two-phase area expands with a decrease in temperature.

Effect of Salts on Binodal Curves. The phase diagrams in Figure 2 also provide information on the concentration of phase-forming components required to form two phases and

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Table 7. Tie Line Data of [Emim]DMP (1) + K_2CO_3 (2) + H_2O (3) at T = (298.15, 308.15, and 318.15) K and Pressure p = 0.1 MPa[a]

	total system		IL-rich phase		salt-rich phase			
T/K	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	TLL	S
298.15	19.98	35.18	4.98	53.35	48.57	3.45	66.26	−1.14
	18.07	41.06	3.88	57.48	52.35	2.92	72.98	−1.13
	22.02	40.16	2.77	62.45	55.74	2.33	80.13	−1.14
308.15	21.84	39.28	7.08	56.05	47.72	12.05	59.89	−1.08
	19.17	45.16	6.19	59.48	51.60	11.52	66.04	−1.06
	22.92	45.96	5.47	63.85	56.54	11.03	73.48	−1.03
318.15	21.69	50.88	6.48	67.15	52.87	20.55	65.75	−1.00
	19.57	57.86	5.59	72.38	57.10	20.02	73.45	−1.02
	24.02	56.66	4.67	77.35	61.54	19.53	81.11	−1.02

[a]Standard uncertainties u are $u(w)$ = 0.001, $u(T)$ = 0.05 K, and $u(p)$ = 10 kPa.

Table 8. Values of the Parameters of Eqs 4 and 5 for the [Emim]DMP (1) + K_3PO_4/K_2HPO_4/K_2CO_3 (2) + H_2O (3) ATPS at T = (298.15, 308.15 and 318.15) K[a]

	Othmer−Tobias equation				Bancroft equation			
T/K	k_1	n	R	δ	k_2	r	R	δ
	[Emim]DMP + K_3PO_4 + H_2O				[Emim]DMP + K_3PO_4 + H_2O			
298.15	1.5994	0.4112	0.9923	0.0015	0.3298	2.8650	0.9976	0.0019
308.15	1.7011	0.4441	0.9700	0.0029	0.3619	2.4183	0.9423	0.0087
318.15	1.5462	0.5905	0.9918	0.0014	0.4275	2.1646	0.9992	0.0008
	[Emim]DMP + K_2HPO_4 + H_2O				[Emim]DMP + K_2HPO_4 + H_2O			
298.15	1.4899	0.6708	0.9966	0.0015	0.6144	1.5069	0.9967	0.0019
308.15	1.2177	0.9760	0.9955	0.0033	0.7517	1.1849	0.9953	0.0036
318.15	1.0482	0.9812	0.9996	0.0009	0.8299	1.3724	0.9975	0.0026
	[Emim]DMP + K_2CO_3 + H_2O				[Emim]DMP + K_2CO_3 + H_2O			
298.15	0.8195	1.2988	0.9835	0.0060	1.1928	0.7993	0.9788	0.0050
308.15	0.7215	0.9200	0.9999	0.0004	1.4049	1.2237	0.9996	0.0010
318.15	0.5774	1.4462	0.9999	0.0003	1.2110	0.9363	0.9985	0.0024

[a]R, corresponding correlation coefficient values; δ, standard deviation.

Table 9. Values of Parameters of Eq 6 for the [Emim]DMP (1) + K_3PO_4/K_2HPO_4/K_2CO_3 (2) + H_2O (3) ATPS at T = (298.15, 308.15 and 318.15) K[a]

T/K	k	β	R	δ
	[Emim]DMP + K_3PO_4 + H_2O			
298.15	0.1158	2.1294	0.9977	0.0061
308.15	0.0782	0.8349	0.9313	0.0234
318.15	0.0871	0.7541	0.9845	0.0099
	[Emim]DMP + K_2HPO_4 + H_2O			
298.15	0.0733	0.6624	0.9960	0.0089
308.15	0.0665	0.3145	0.9996	0.0043
318.15	0.0740	0.6044	0.9842	0.0242
	[Emim]DMP + K_2CO_3 + H_2O			
298.15	0.0709	1.2645	0.9999	0.0022
308.15	0.0483	0.2116	0.9934	0.0100
318.15	0.0427	−0.1009	0.9951	0.0097

[a]R, corresponding correlation coefficient values; δ, standard deviation.

the concentration of phase components in the top and bottom phases. The diagrams show that ILATPS can be formed by mixing an appropriate amount of salts with aqueous [Emim]DMP solution. Thus, the abilities of the salts for phase separation follow the order K_3PO_4 > K_2HPO_4 > K_2CO_3. The kosmotropic ions, PO_4^{3-}, HPO_4^{2-}, and CO_3^{2-}, which exhibit stronger interaction with water molecules, are beneficial to ILATPS formation. The salting-out ability may be related to the Gibbs energy of hydration of the ions ($\Delta_{hyd}G$).[33,34] Considering that these salts share a common cation but contain different anions, better salting-out of [Emim]DMP was observed when the ions of the salt have a more negative Gibbs free energy {$\Delta_{hyd}G(PO_4^{3-})$ = −2765 kJ·mol^{-1} 26 > $\Delta_{hyd}G(HPO_4^{2-})$ = −1789 kJ·mol^{-1} 27 > $\Delta_{hyd}G(CO_3^{2-})$ = −1315 kJ·mol^{-1}}.[35,36]

LLE Data and Effect of Temperature on Tie Lines. The tie-line compositions, TLL, and S for the [Emim]DMP + salt (K_3PO_4, K_2HPO_4, and K_2CO_3) + H_2O systems determined at T = (298.15, 308.15, and 318.15) K are given in Tables 5, 6, and 7, respectively. Additionally, to show the effect of temperature on the equilibrium phase compositions in the investigated system, the experimental tie lines are compared in Figure 3 for the temperatures T = (298.15, 308.15, and 323.15) K. Figure 3 shows that the slope of the tie lines slightly decreases with an increase in temperature. This trend indicates that when temperature decreases, water is driven from the [Emim]DMP-rich phase to the salt-rich phase, so that the [Emim]DMP concentration at the [Emim]DMP-rich phase increases. Conversely, that at the salt-rich phase is somewhat more diluted. In other words, water becomes a poorer solvent for [Emim]DMP as temperature decreases.

Correlation of LLE Data. The Othmer−Tobias (eq 4) and Bancroft (eq 5) equations were used to evaluate the reliability of the calculation method and corresponding tie-line data.

$$[(1 - w_1^{t})/w_1^{t}] = k_1[(1 - w_2^{b})/w_2^{b}]^n \quad (4)$$

$$(w_3^{b}/w_2^{b}) = k_2(w_3^{t}/w_1^{t})^r \quad (5)$$

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where w_1^t is the mass fraction of ILs in the top phase; w_2^b denotes the mass fraction of 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; and k_1, n, k_2, and r represent the fit parameters. Recently, eqs 4 and 5 have been successfully used for the correlation of the tie-line compositions of the imidazolium ILs + salt + water ATPSs.[37,38] A linear dependency of the plot log $[(1 - w_1^t)/w_1^t]$ 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), indicates acceptable consistency of the results. The values of k_1, n, k_2, and r with the corresponding correlation coefficient values (R) and SDs (δ) are given in Table 8. Equations 4 and 5 can be satisfactorily used to correlate the tie-line data of the investigated systems.

In this work, a relatively simple two-parameter equation was used to correlate the tie-line data, which can be derived from the binodal theory.[39] The equation used has the following form:

$$\ln(w_2^t/w_2^b) = \beta + k(w_1^b - w_1^t) \quad (6)$$

where k is the salting-out coefficient and β is the constant related to the activity coefficient. Superscripts t and b denote the IL-rich and salt-rich phases, respectively. Recently, eq 6 has been successfully used for the correlation of tie-line data for the polymer-salt ATPSs.[40] The fitting parameters of eq 6 with the corresponding correlation coefficient values (R) and SDs (δ) for the investigated systems are presented in Table 9. On the basis of the SDs reported, eq 6 reveals good accuracy for the experimental LLE data.

CONCLUSIONS

The binodal data of the [Emim]DMP + salt (K_3PO_4, K_2HPO_4, and K_2CO_3) + H_2O systems were determined at T = (298.15, 308.15, and 318.15) K, respectively. The experimental binodal data directly calculated using the Merchuk equation exhibits optimum accuracy. The abilities of the kosmotropic salts for phase separation follow the order $K_3PO_4 > K_2HPO_4 > K_2CO_3$, which can be explained by the Gibbs free energy of hydration of anions. The two-phase area expands with a decrease in temperature, whereas the slope of the tie lines slightly decreases with an increase in temperature. Finally, the tie lines were correlated with the Othmer−Tobias and Bancroft equations, as well as with the two-parameter equation, which show satisfactory accuracy for the investigated systems.

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