Phase Diagrams for the Aqueous Two-Phase Ternary System Containing the Ionic Liquid 1-Butyl-3-methylimidazolium Bromide and Tri-potassium Citrate at T = (278.15, 298.15, and 318.15) K

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Liquid−liquid equilibria (LLE) for the aqueous 1-butyl-3-methylimidazolium bromide ([C_4mim]Br) + tri-potassium citrate system have been experimentally determined at T = (278.15, 298.15, and 318.15) K. An empirical nonlinear expression developed by Merchuk was used for reproducing the experimental binodal data. In this work, the three fitting parameters of the Merchuk equation were obtained with the temperature dependence expressed in the linear form with ($T - T_0$) K as a variable. 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. The values of the salting-out coefficients may reflect the extent of the preferential hydration of the ionic liquid. Furthermore, the kosmotropicity of tri-potassium citrate for the exclusion of [C_4mim][Br] in an aqueous solution has been examined in comparison with the previously studied kosmotropic salts on the basis of the ionic viscosity B coefficients of salt constituent anions and the preferential hydration of the ionic liquid.

Introduction

Liquid−liquid extraction has often been a favored choice of the process engineer for the development of separation processes.[1] Meanwhile, liquid−liquid extraction utilizing aqueous two-phase systems (ATPSs) that are usually formed by combining either two incompatible polymers or a polymer and a salt in water above a certain critical concentration[2−4] is considered to be environmentally friendly because traditional volatile organic solvents (VOCs) are not used in the whole process; therefore, it has already been used to separate and purify various biological products,[2−4] metal ions, dyes, drug molecules, and small organic species[5,6] from the complex mixtures in which they are produced. For large-scale enzyme extraction, the aqueous polymer−salt systems are more attractive than the aqueous polymer−polymer systems because of their greater selectivity, lower viscosity, lower cost, rapid phase disengagement, and the availability of commercial separators, which allow a faster and continuous protein separation.

Poly(ethylene glycol) (PEG) or poly(propylene glycol) (PPG), which is a hydrophilic polymer, are the most common polymers used with a kosmotropic (water-structuring) salt to form the polymer−salt ATPSs. The applications of the polymer-based ATPSs have been well documented.[2−8] 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, in mixtures with aqueous solutions of kosmotropic salts, the hydrophilic ionic liquids (ILs) have been investigated as an alternative to hydrophilic polymers in recent years.[9−19] These new ATPSs have many advantages shared by ILs and ATPSs, such as low viscosity, little emulsion formation, no need of using VOC, quick phase separation, high extraction efficiency, and gentle biocompatible environment and have been successfully used to separate testosterone,[19] epitestosterone,[19] opium alkaloids,[20] and bovine serum albumin.[21]

The most common kosmotropic salts employed by different research groups[9−21] on the IL-based aqueous two-phase extraction technique consist of selective cations (ammonium, potassium, or sodium) and anions (phosphate, sulfate, hydroxide, or carbonate). For the first time, Vernau and Kula[22] have investigated citrates as a substitute for inorganic salts in polymer−salt ATPSs. Citrates are biodegradable and nontoxic and could be discharged into biological wastewater treatment plants. For analogical reasons, we decided here to examine citrate as an alternative to inorganic salts in IL-based ATPSs. In this respect, this work is devoted to the study of the phase behavior of the [C_4mim]Br + tri-potassium citrate aqueous two-phase system. Here we report liquid−liquid equilibrium (LLE) data for the aqueous [C_4mim]Br + tri-potassium citrate system at T = (278.15, 298.15, and 318.15) K that have not been previously published. The obtained results are necessary for the design and optimization of extraction processes, the understanding of general factors determining the partition of solutes and particles in such ATPSs, and the development and testing of both thermodynamic and mass transfer models of ATPSs.

The effect of temperature on the phase-forming ability in the investigated aqueous IL + salt two-phase system has also been studied on the basis of a salting-out coefficient obtained from fitting the tie-line data to a Setschenow-type[23] equation. ILs tend to be chaotropic (water-destructuring) salts and thus are capable of being salted-out by kosmotropic (water-structuring) salts, as stated by Bridges et al.[18] In the further analysis, the phenomenon of the two phases forming in an aqueous IL + salt two-phase system may be considered to be the competition between the hydrophilic IL and the kosmotropic salt for the water molecules. The competition is finally won by the kosmotropic 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

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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. From this point of view in which the salting-out concept is directly correlated to the hydration strength of the inorganic salt, the values of the obtained salting-out coefficients for the used Setschenow-type equation may be related to the extent of the preferential hydration (or the preferential exclusion) of the IL. Therefore, to provide a quantitative perspective for the salting-out phenomenon that occurred in the investigated IL-based ATPS, our interest lies here in examining the Setschenow-type behavior of phase diagrams for the studied IL + salt system at different temperatures and the possibility of using the recently derived Setschenow-type equation[23] in the correlation of experimental LLE data of the investigated system. Furthermore, the kosmotropicity of tri-potassium citrate for the exclusion of [C_4mim][Br] in an aqueous solution has been examined in comparison with the previously studied kosmotropic salts[15,16] on the basis of the ionic viscosity *B* coefficients of salt constituent anions and the preferential hydration of the IL.

Experimental Section

Material. [C_4mim]Br was obtained from Merck with a quoted purity of greater than 0.98 mass fraction and was used without further purification. Water content in the IL was determined by the use of the Karl Fischer method to be 0.0095 mass fraction, which was in good agreement with the value quoted by the suppliers, approximately less than 0.01 mass fraction. This water content in the IL was taken into account during the preparation of the aqueous solutions for the treatment of the experimental data. Tri-potassium citrate with purity of min. 99 % by mass was supplied by Fluka and used without further purification. Double-distilled deionized water was used for the preparation of solutions.

Apparatus and Procedure. The experimental apparatus employed is essentially similar to the one previously used.[16,24,25] The temperature was controlled to within ± 0.05 K. The binodal curves were determined by the cloud-point method. 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 (Shimatzu, 321-34553, Shimatzu Co., Japan) with an uncertainty of $\pm 1 \cdot 10^{-7}$ kg. For the determination of the tie lines, we prepared feed samples (about $2 \cdot 10^{-5}$ m^3) by mixing appropriate amounts of IL, 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 overnight to separate into two clear phases. After separation of the two phases, the concentrations of salts in the top and bottom phases were determined by potassium analysis using flame photometry. Following Cheluget et al.,[26] the concentration of IL in both phases was also determined by refractive index measurements performed at 298.15 K using a refractometer (ATAGO DR-A1, Atago, Japan) with a precision of ± 0.0001. The uncertainties in the refractive index measurements are ± 0.0002. For dilute aqueous solutions containing an IL and a salt, the relation between the refractive index, n_D, and the mass fractions of IL, w_1, and salt, w_2, is given by[26]

$$n_D = n_0 + a_1 w_1 + a_2 w_2 \tag{1}$$

where n_0 is the refractive index of pure water, which is set to 1.3325 at 298.15 K. This equation has been used for phase analysis of the PPG + NaCl + H_2O system by Cheluget et al.[26]

In regard to the validity of the above procedure in the determination of tie-line compositions, it must be noted that similar to what was observed by Gutowski et al.[9] for the aqueous [C_4mim]Cl + K_3PO_4 two-phase system, because of the existence of equilibria of ions in two phases, the distribution ratios for the imidazolium and bromide ions are not exactly 1:1. However, to justify whether the amounts of salts and IL used to create the feed sample corresponded to the amounts in the top and bottom phases, we performed mass balance calculations and found that our procedure for the determination of the concentrations of salts in both phases using potassium analysis and those of IL by refractive index measurements is consistent with the mass balance calculations within ± 1 %. Therefore, we concluded that the same method of calibration plots and evaluation of parameters given by Cheluget et al.[26] can also be used for the analysis of the [C_4mim]Br + tri-potassium citrate + water system. Therefore, the values of coefficients a_1 and a_2 in eq 1 for the applied system were obtained at 298.15 K as 0.1586 ± 0.0002 and 0.1537 ± 0.0001, respectively. The standard uncertainties in the a_1 and a_2 values were evaluated using the method of least-squares to fit a linear curve to the refractive index calibration plots to estimate the parameters of the curve and their standard deviations.[27] However, it should be noted that this equation is only valid for dilute solutions ($w_1 \leq 0.1$ and $w_2 \leq 0.05$) for which linear calibration plots of the refractive index of ternary solutions with a fixed mass fraction of salt or IL against IL or salt are obtained. Therefore, before the refractive index measurements, it was necessary to dilute the samples to the above mass fraction ranges.

Furthermore, to see the reliability of the above procedure employed in the determination of the tie-line compositions of the investigated system more closely, we arbitrarily determined the water contents or the IL concentrations in some phases, respectively, by Karl Fischer method using a Karl Fischer titrator (751 GPD Titrino- Metrohm, Herisau, Switzerland) and by nitrogen analysis performed by an element analyzer instrument (Vario EL III, elementar Analysensysteme GmbH, Hanau, Germany). The obtained results were in good agreement with the results obtained using the method given by Cheluget et al.[26]

The tie-line length, TLL, and the slope of the tie line, *S*, at different compositions and temperatures were also calculated, respectively, using eqs 2 and 3 as follows[4]

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

$$S = (w_1^t - w_1^b)/(w_2^t - w_2^b) \tag{3}$$

where $w_1{}^t$, $w_1{}^b$, $w_2{}^t$ and $w_2{}^b$ represent the equilibrium compositions (in weight percent) of IL (1) and salt (2), in the top, t, and bottom, b, phases, respectively.

Results and Discussion

Phase Diagrams. For the aqueous [C_4mim]Br + tri-potassium citrate system, the binodal data and the tie-line compositions determined experimentally at T = (278.15, 298.15, and 318.15) K are given in Tables 1 and 2, respectively. The standard uncertainties in the experimental tie-line compositions (Table 2) were evaluated using the method of propagation of uncertainties.[27]

For the studied system, the experimental binodal data were fitted by a least-squares regression method to the following empirical nonlinear expression developed by Merchuk[28]

$$w_1 = a \exp\left(b w_2^{0.5} - c w_2^3\right) \quad (4)$$

where a, b, and c represent fit parameters and w_1 and w_2 represent the concentrations (in weight percent) of IL and salt, respectively. Recently, the above equation has been successfully used for the correlation of binodal data of some aqueous IL + salt systems.[9,16−18] In this work, the three fitting parameters of the Merchuk equation, 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 follows

$$a = a^0 + a^1(T - T_0) \quad (4a)$$

$$b = b^0 + b^1(T - T_0) \quad (4b)$$

$$c = c^0 + c^1(T - T_0) \quad (4c)$$

In eqs 4a, 4b, and 4c, 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. These fitting parameters obtained from the correlation of the experimental

Table 1. Binodal Data for the [C_4mim]Br (1) + Tri-potassium Citrate (2) + H_2O (3) System at T = (278.15, 298.15, 308.15, and 318.15) K

T/K = 278.15				T/K = 298.15		T/K = 308.15		T/K = 318.15	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
62.13	2.22	17.08	27.92	49.98	6.48	48.01	8.10	52.71	6.17
57.56	3.15	16.36	28.63	47.38	7.84	46.00	8.96	44.37	10.50
54.70	4.20	15.68	29.22	41.44	11.20	41.29	11.71	41.65	12.02
52.72	4.90	14.97	29.91	37.15	13.76	39.01	13.24	39.56	13.32
50.68	5.65	14.42	30.45	33.99	15.97	36.95	14.63	37.11	14.91
49.10	6.37	13.99	30.90	29.14	19.61	34.20	16.52	35.51	16.14
47.65	7.01	13.36	31.50	27.12	20.96	31.87	18.09	33.97	17.08
46.25	7.66	12.80	32.14	25.05	22.55	29.33	20.11	31.77	18.72
44.95	8.22	12.10	32.96	23.25	24.02	27.59	21.27	30.22	19.87
43.88	8.85	11.27	33.89	21.47	25.56	26.61	22.09	28.58	21.22
42.90	9.41	10.46	34.94	19.80	26.88	25.17	23.06	26.31	22.86
40.90	10.42	9.64	35.97	18.69	27.76	24.04	23.96	22.88	25.67
39.41	11.43	8.81	37.08	17.75	28.69	23.36	24.60	21.08	27.14
37.82	12.37	7.76	38.76	16.66	29.68	22.03	25.62	19.91	28.04
35.78	13.67	6.35	41.44	15.69	30.56	20.85	26.55	18.93	28.91
34.04	14.94			15.03	31.22	19.55	27.68	17.87	29.93
32.50	16.05			14.56	31.59	18.31	28.61	16.94	30.72
31.09	17.10			13.98	32.18	17.32	29.49	15.42	32.23
29.73	17.98			13.44	32.73	16.03	30.91	14.29	33.39
28.79	18.68			12.85	33.38	15.10	31.76	13.52	34.24
27.35	19.76			12.14	34.31	14.09	32.75	12.41	35.43
25.72	21.04			11.61	34.95	13.02	33.92	11.45	36.65
24.22	22.10			11.06	35.47	12.12	34.90	10.44	37.95
22.94	23.11			10.30	36.48	11.34	35.88	9.60	39.18
21.99	23.81			9.72	37.46	10.48	36.93	8.81	40.34
20.95	24.67			9.35	37.92	9.53	38.23	6.70	44.09
19.59	25.80			8.63	38.98	8.50	39.90		
18.80	26.48			8.01	40.03	7.58	41.51		
17.91	27.26			7.05	41.80				

Table 2. Experimental Phase Equilibrium Compositions, Tie-Line Lengths (TLLs), and Slopes of Tie Lines (S) for the [C_4mim]Br (1) + Tri-potassium Citrate (2) + H_2O (3) System at T = (278.15, 298.15, and 318.15) K

total composition		top phase: ionic liquid-rich phase			bottom phase: salt-rich phase				
100 w_1	100 w_2	100 w_1	100 w_2	100 w_3[a]	100 w_1	100 w_2	100 w_3[a]	TLL	S
				T = 278.15 K					
31.12	20.19	51.93 ± 0.08 51.49[b]	5.01 ± 0.02		9.03 ± 0.17	36.90 ± 0.13		53.46	− 1.35
39.52	16.06	55.92 ± 0.18 57.92[b]	3.46 ± 0.11		5.90 ± 0.27	42.17 ± 0.24		63.25	− 1.29
39.65	20.36	63.89 ± 0.13	1.50 ± 0.06		2.63 ± 0.27	49.04 ± 0.24		77.54	− 1.29
38.25	23.64	67.07 ± 0.37	1.06 ± 0.29		1.84 ± 0.30	52.06 ± 0.27		82.80	− 1.28
37.70	27.02	70.78 ± 0.16 70.09[b]	0.55 ± 0.09	28.66	0.77 ± 0.22	55.95 ± 0.19	42.83	89.28	− 1.26
38.30	26.71	71.15 ± 0.31	0.69 ± 0.23		0.64 ± 0.32	57.26 ± 0.29		90.40	− 1.25
37.48	30.36	73.83 ± 0.28 74.01[b]	0.37 ± 0.19	24.89	0.37 ± 0.33	60.24 ± 0.30	38.41	94.77	− 1.23
37.68	30.01	75.01 ± 0.16 75.56[b]	0.29 ± 0.06	23.93	0.48 ± 0.25	59.61 ± 0.21	39.27	95.25	− 1.26
				T = 298.15 K					
35.61	18.76	54.40 ± 0.19	4.75 ± 0.12		7.38 ± 0.28	40.06 ± 0.25		58.80	− 1.33
35.59	22.22	62.43 ± 0.10	2.57 ± 0.02		4.27 ± 0.29	46.31 ± 0.27		72.77	− 1.33
34.76	25.17	66.52 ± 0.09	1.65 ± 0.01		2.50 ± 0.33	50.78 ± 0.31		80.70	− 1.30
38.46	27.82	73.30 ± 0.11	0.71 ± 0.02		1.14 ± 0.37	57.95 ± 0.35		92.10	−1.26
38.72	30.71	76.15 ± 0.11	0.42 ± 0.01		0.49 ± 0.45	63.03 ± 0.41		98.21	−1.21
				T = 318.15 K					
33.98	21.07	56.15 ± 0.06	4.74 ± 0.03		7.06 ± 0.37	43.02 ± 0.34		62.25	− 1.28
34.76	20.21	56.23 ± 0.07 56.64[b]	4.50 ± 0.03	38.28	6.63 ± 0.35	43.03 ± 0.33	51.42	62.81	− 1.29
43.68	17.54	62.09 ± 0.07	2.36 ± 0.02		4.09 ± 0.47	50.90 ± 0.45		75.64	− 1.19
43.58	20.97	67.98 ± 0.08	1.33 ± 0.01		2.82 ± 0.53	54.21 ± 0.50		83.92	− 1.23
43.61	24.40	72.37 ± 0.09	0.82 ± 0.01		2.33 ± 0.56	57.59 ± 0.53		90.15	− 1.23
43.70	27.85	76.48 ± 0.10	0.46 ± 0.01		1.42 ± 0.60	62.95 ± 0.57		97.67	− 1.20

[a] Were determined by the Karl Fischer method. [b] Were determined by nitrogen analysis using an element analyzer instrument.

Table 3. Values of Parameters of Equation 4 for [C_4mim]Br (1) + Tri-potassium Citrate (2) + H_2O (3) at T = (278.15, 298.15, and 318.15) K

T/K	a^0	a^1	b^0	b^1	$10^4 \cdot c^0$	$10^4 \cdot c^1$	sd[a]
278.15	87.09	0.1774	− 0.2312	− 2.734	1.879	− 9.786	0.28
298.15							0.30
308.15							0.28[b]
318.15							0.28

[a] sd = $(\sum_{i=1}^{N} (w_1^{\text{calcd}} - w_1^{\text{exptl}})^2/N)^{0.5}$, where w_1 and N represent the concentration (in weight percent) of IL and the number of binodal data, respectively. [b] Obtained from the comparison of the experimental IL compositions, w_1, on the binodal curve of the [C_4mim]Br (1) + tri-potassium citrate (2) + H_2O (3) system at T = 308.15 K reported in Table 1 and the corresponding data predicted using eq 4 and the fitting parameters given in Table 3. These parameters were obtained from the correlation of the experimental binodal data of the investigated system at T = (278.15, 298.15, and 318.15) K.

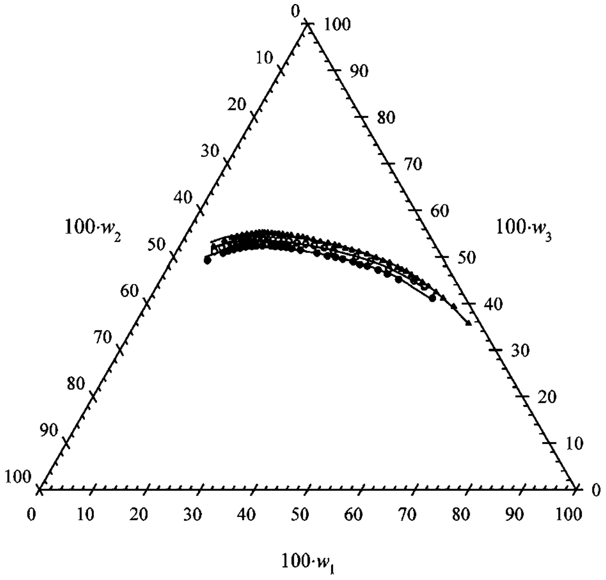

Figure 1. Binodal curves for the [C_4mim]Br (1) + tri-potassium citrate (2) + H_2O (3) two-phase system at different temperature: ▲, 278.15 K; ○, 298.15 K; ●, 318.15 K; —, calculated from eq 4.

binodal data along with the corresponding standard deviations are given in Table 3. The binodals reproduced from eq 4 at different temperatures are also shown in Figure 1. On the basis of the obtained standard deviations, we conclude that eq 4 can be satisfactorily used to reproduce the binodal curves of the investigated system. Furthermore, to examine the performance of eq 4 in the prediction of the locus of the binodal curves for the investigated system at temperatures where no experimental data are available, we attempted to compare the experimental IL compositions, w_1, on the binodal curve of the [C_4mim]Br + tri-potassium citrate + H_2O system at T = 308.15 K with those predicted using eq 4 at the corresponding temperature. The necessary experimental binodal data at T = 308.15 K that evidently have no contribution to obtaining the fitting parameters for eq 4 were also determined in this work and are collected in Table 1. The standard deviation obtained from this comparison is also given in Table 3. As can be seen, eq 4 can also accurately predict the characteristics of the binodal curves for the investigated system at temperatures at which no experimental data are available.

The effect of temperature on the phase-forming ability of the studied system is also illustrated in Figure 1. The locus for the experimental binodals shown in Figure 1 demonstrates that the two-phase area is expanded with a decrease in temperature, which is attributed to the decrease in solubility of IL or the increase in the phase-forming ability in the studied system. This is because the effects of a decrease in temperature on the structure of water is qualitatively similar to that of a kosmotropic (structure-making) ion[4] and therefore can promote the phase-forming ability in the investigated system as a favorable factor for salting-out of IL. More recently, the effect of temperature on the phase-forming ability in the aqueous [C_4mim]Br + K_2HPO_4 two-phase system has also been examined at T = (298.15, 308.15, and 318.15) K by Pei et al.[15] Unlike the binodal curves for the aqueous [C_4mim]Br + K_2HPO_4 system,[15] the relative difference observed for the salting-out ability of the K_3-citrate salt in the aqueous [C_4mim]Br + K_3-citrate system with a decrease in temperature from T = 318.15 K to T = 298.15 K is less suppressed. A possible reason is that the hydration sheath around the [C_4mim]Br in the aqueous [C_4mim]Br + K_3-citrate system is more sensitive to temperature because of a decreased kosmotropicity of the citrate ion (the relative kosmotropicity of the K_2HPO_4 and K_3-citrate salts is discussed in detail in the last section). Additionally, to show the effect of temperature on the equilibrium phase compositions for the investigated system, the experimental tie lines are compared in Figure 2 for the temperatures T = (278.15 and 318.15) K, as an example. As shown in Figure 2, the slope, S, and the length of the tie lines, TLL, are not sensitive to an increase in temperature. In the further analysis, the comparison between the two third tie lines for the temperatures T = (278.15 and 318.15) K in Table 2 that have nearly the same position in the phase diagram (Figure 2) or, similarly, the two second last tie lines shows that the slope and the length of the tie lines slightly decrease with an increase in temperature. This trend means that when the temperature is decreased, water is driven from the [C_4mim]Br-rich phase to the salt-rich phase, so the [C_4mim]Br concentration at the [C_4mim]Br-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 [C_4mim]Br as the temperature is decreased. Depression of the solubility of the hydrophilic IL, [C_4mim]Br, in water with decreasing temperature may be related to the salting-out phenomenon because a decrease in the

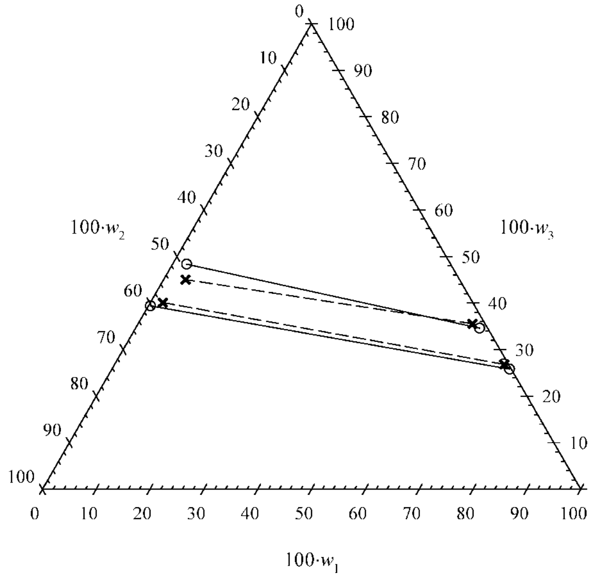

Figure 2. Effect of temperature on the equilibrium phase compositions for the [C_4mim]Br (1) + tri-potassium citrate (2) + H_2O (3) system: ○, 278.15 K; ×, 318.15 K; —, tie lines at 278.15 K; ---, tie lines at 318.15 K. These tie lines were obtained by connecting the experimental equilibrium phase composition data.

solubility of [C$_4$mim]Br in water with a decrease in temperature, as shown in Figure 1, is reflected by a decrease in the critical concentration of a salt required to form a two-phase system, which in turn indicates the effectiveness of the salt in inducing the formation of two phases (i.e., the salting-out strength of the salt). Salting-out effects are usually quantified by fitting solubility data to the empirical equation of Setschenow[29]

$$\ln \frac{S_0}{S} = k_S c_S \tag{5}$$

where S_0 and S refer to the solubility of a given nonelectrolyte in pure water and in a salt solution of concentration c_S, respectively, and k_S, defined as the salting-out coefficient, is specific for a particular nonelectrolyte−salt pair. In earlier studies, on the basis of eq 5 or the salting-out concept, the Setschenow-type behavior of the phase diagrams for a number of aqueous PEG + salt two-phase systems have been substantiated by some authors,[30,31] but with only limited success. In this regard, in recent years, Hey et al.[23] proposed a new derivation of Setschenow-type equations from which a characteristic parameter, k_S, for the salting-out effect of an electrolyte on ethylene oxide (EO) groups in PEG + salt ATPSs can be satisfactorily determined. More recently,[32] we have also successfully applied this equation to introduce a quantitative measure for the salting-out effects of the tri-potassium citrate salt on propylene oxide (PO) units in the investigated PPG + tri-potassium citrate ATPS at different temperature.

The same Setschenow-type equation derived by Hey et al.[23] for characterizing the phase diagrams of the typical aqueous nonelectrolyte−salt two-phase systems may be applied to the aqueous IL−salt two-phase systems because in these systems, the extent of the water-structure-enforced hydrophobic ion associations is remarkable.[33−35] Using statistical mechanical theories,[33,36] these extensive water-structure-enforced hydrophobic ion associations may reflect the considerable nonelectrolyte contributions to the aqueous IL solutions. This means that, as stated by Grover and Ryall,[37] for all practical purposes, the electrolytes and nonelectrolytes usually used in the definition of the salting-out phenomenon are the salts that have, respectively, high and low solubilities (or as ions with a relatively strong and less affinity for the solvent). In recent years, for the aqueous solutions of some hydrophilic ILs such as [C$_2$mim][Br] and [C$_4$mim][Cl], the formation of the extensive water-structure-enforced hydrophobic ion pairs, which, in turn, shows that in these solutions the solute−solute interactions have a greater contribution than the solute−solvent interactions, has been verified by some thermodynamic studies.[33] The overall picture of this thermodynamic analysis[33] reveals that the low charge density of constituent ions and their hydrophobic nature is responsible for the formation of the water-structure-enforced ion pairs in the studied IL[33] solutions. From these studies,[33] we may conclude that the extent of ion association and thus the nonelectrolyte contribution in aqueous [C$_4$mim][Br] solution is higher than that in [C$_2$mim][Br] or [C$_4$mim][Cl] aqueous solutions because of the lower charge density of [C$_4$mim][Br] constituent ions. In this respect, we decided here to examine this Setschenow-type equation to describe the salting-out effects of the tri-potassium citrate salt on [C$_4$mim]Br in the investigated IL + salt ATPS at different temperature. The equation[23] used has the following form

$$\ln\left(\frac{c'_I}{c''_I}\right) = k_I(c''_I - c'_I) + k_S(c'_S - c'_S) \tag{6}$$

Table 4. Values of Parameters from Least-Squares Linear Fits to the Setschenow-Type Equation (Equation 6) for [C$_4$mim]Br (1) + Tri-potassium Citrate (2) + H$_2$O (3) at T = (278.15, 298.15, and 318.15) K

T/K	k_S/(kg·mol^{-1})	intercept	R^2	10^2·Dev[a]
278.15	1.2384	− 0.3729	0.996	0.06
298.15	0.9222	0.4123	0.995	0.11
318.15	0.6489	0.7986	0.988	0.12

[a] Dev = $(\sum_p \sum_l \sum_j (w_{p,l,j}^{\text{calcd}} - w_{p,l,j}^{\text{exptl}})^2/6N)$, where $w_{p,l,j}$ is the weight fraction of the component j (i.e., IL, salt, or water) in the phase p for lth tie line and the superscripts "calcd" and "exptl" refer to the calculated and experimental values, respectively. N is the number of tie-line data.

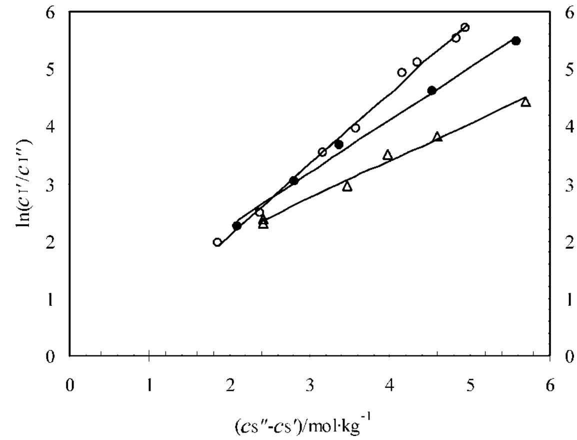

Figure 3. Setschenow-type plots for the tie-line data of the [C$_4$mim]Br (1) + tri-potassium citrate (2) + H$_2$O (3) system. Upper and lower phase concentrations are denoted by single and double primes, respectively: ○, 278.15 K; ●, 298.15 K; △ 318.15 K.

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. If the first term on the right-hand side of this equation is small compared with the second term, then a Setschenow-type equation is obtained. This would imply that $k_I \ll k_S$ because the absolute values of $(c''_I - c'_I)$ exceed the $(c''_S - c'_S)$ values.[23]

The experimental tie-line compositions for the aqueous [C$_4$mim]Br + tri-potassium citrate system given in Table 2 were fitted by a least-squares linear regression method to eq 6 (i.e., the logarithm of the ratio between the molality of [C$_4$mim]Br 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, together with corresponding intercepts and correlation coefficients, R, are listed in Table 4 for each working temperature. To examine the relation between the Setschenow-type behavior and the phase diagrams more closely, the Setschenow-type plots of the tie-line data for the studied system have also been shown in Figure 3. On the basis of correlation coefficients, R, given in Table 4 and Setschenow-type plots shown in Figure 3, we conclude that the equilibrium compositions of the investigated system at the studied temperatures can be satisfactorily characterized by Setschenow-type behavior.

For the studied system, as shown in Table 4, the values of k_S increase with decreasing temperature. The increase in k_S is reflected in the phase diagram by a shift in the position of the binodal curve to the top corresponding to a decrease in the area representing the single-phase mixture, as shown in Figure 1, indicating an increasing phase-forming ability. Furthermore, Figure 4 shows the k_S and the corresponding intercept values

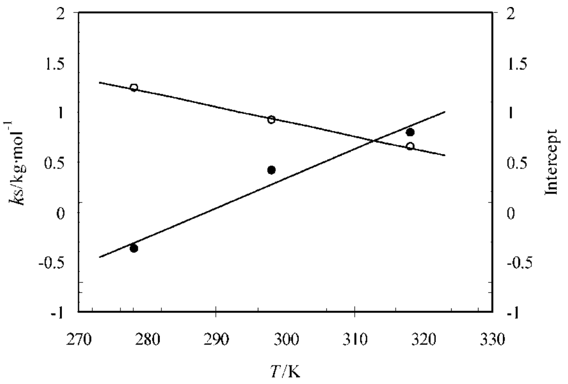

Figure 4. Relationship between the values of the fit parameters, k_S, and the corresponding intercept listed in Table 4 and the working temperatures: ○, salting-out coefficients obtained from fitting the tie-line data to eq 6; —, best fit line using the linear function $k_S = f + gT$ with the obtained fit parameters ($f = 5.33$ and $g = -0.01$) and correlation coefficient, $R^2 = 0.998$; ●, fit parameter specified as intercept; —, best fit line using a similar linear function with corresponding fit parameters ($f = -8.45$ and $g = 0.03$) and correlation coefficient, $R^2 = 0.963$.

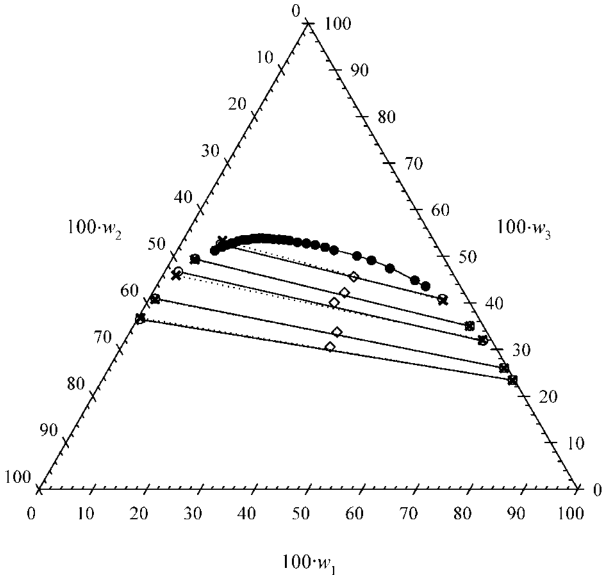

Figure 5. Phase diagram of the [C$_4$mim]Br (1) + tri-potassium citrate (2) + H_2O (3) two-phase system at 298.15 K: ●, experimental binodal; —, calculated binodal from eq 4; ◇, total composition of tie lines; —○—, experimental tie lines; ···×···, calculated tie lines using eq 6.

Table 5. Values of Parameters of Equation 7 and the Plait Points for [C$_4$mim]Br (1) + Tri-potassium Citrate (2) + H_2O (3) at T = (278.15, 298.15, and 318.15) K

T/K	f	g	R^2	plait point (100 w_1, 100 w_2, 100 w_3)
278.15	26.72	− 0.2045	0.861	(21.78, 24.18, 54.04)
298.15	29.19	− 0.2371	0.925	(23.52, 23.94, 52.54)
318.15	25.65	− 0.1840	0.942	(20.54, 27.76, 49.82)

in relation to the working temperatures. 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.

Furthermore, by the use of the parameters given in Table 4, the performance of eq 6 in representing the tie-line data of the investigated system has been examined, and the corresponding standard deviations are also given in Table 4. On the basis of the obtained standard deviations given in Table 4, we conclude that eq 6 can be satisfactorily used to correlate the tie-line data of the investigated system. To show the reliability of the model, a comparison between the experimental and reproduced tie-lines at T = 298.15 K is also shown in Figure 5, as an example.

The location of the plait point for the studied system at each working temperature was also estimated by extrapolation from the auxiliary curve satisfactorily fitted with the following linear equation

$$w_1 = f + g w_2 \tag{7}$$

where f and g represent fit parameters. For the studied system, the estimated values for the plait points along with the obtained fitting parameters for eq 7 and the corresponding correlation coefficients are listed in Table 5. As an example, the locus of the estimated plait point for the temperature 298.15 K along with the used procedure is illustrated in Figure 6.

Effect of Temperature on the Exclusion of [C$_4$mim]Br. The phenomenon of the two phases forming in an IL-based ATPS, as mentioned earlier, clearly indicates the mutual exclusion of a kosmotropic salt and a chaotropic IL, which in turn results from their competition for the water. The preferential exclusion of one solute from the hydration shell of another solute can be described in terms of a local excess of water molecules by analogy to the Gibbs surface excess defined in connection with macroscopic interfaces.[38] Therefore, we decided to estimate the excess number of water molecules adjacent to the chaotropic [C$_4$mim]Br pairs to get some information in regard to the effect of temperature on the exclusion of the [C$_4$mim]Br pairs. As stated by Hey et al.,[23] the excess number of water molecules can be related to the magnitude of the salting-out coefficient, k_S, for a given electrolyte as follows

$$\frac{k_S}{v} = 0.018 N_{ew} \frac{d(\phi c_S)}{dc_S} \tag{8}$$

where k_S represents the salting-out coefficient, v is the number of moles of ions in the fully dissociated mole of kosmotropic electrolyte, ϕ and c_S are, respectively, the molal osmotic coefficient and the molality of the salt, and N_{ew} is the excess number of water molecules per IL particles in the salt-depleted region. N_{ew} is related to the actual number of water molecules, N_w, in this region by[23]

$$N_{ew} = N_w\left(1 - \frac{n_w/n_s}{N_w/N_s}\right) \tag{9}$$

where n_w/n_s and N_w/N_s represent water/electrolyte ratios from regions unaffected by and influenced by IL, respectively. The other relevant equations together with the procedure[23] for deducing eq 8 are not given here.

The necessary molal osmotic coefficients, ϕ, for tri-potassium citrate at T = 298.15 K have been calculated from the corresponding water activity data[39] using the following equation

$$\phi = -\frac{\ln(a_w)}{v m M_w} \tag{10}$$

where a_w, and M_w represent the activity and molecular weight of water, respectively. For the temperatures 278.15 and 318.15 K, we predicted the necessary molal osmotic coefficients, ϕ, by employing the Wilson model used successfully by Sadeghi and Ziamajidi[39] for the correlation of the water activity data of the binary tri-potassium citrate + water[39] system at T = (293.15, 298.15, 303.15, 308.15, and 313.15) K. We used the obtained molal osmotic coefficients for aqueous tri-potassium citrate to determine d(ϕc_S)/dc_S by plotting ϕc_S against c_S at three studied temperatures. The plots are generally linear for concentrations up to about 1 molal. Therefore, we can estimate N_{ew} values at

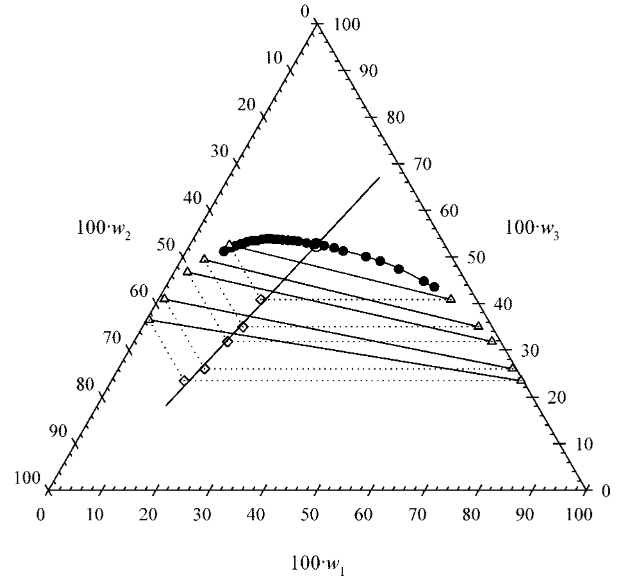

Figure 6. Binodal curve, tie lines, and plait point for the [C$_4$mim]Br (1) + tri-potassium citrate (2) + H_2O (3) system at 298.15 K: ●, binodal curve data; —, calculated binodal from eq 4; △, tie-line data; ···, tie lines; ◇, auxiliary curve data; —, calculated from eq 7; ○, plait point.

different temperatures by substituting the values obtained for d(ϕc_S)/d$c_S$and k_S/v into eq 8. The estimated values for N_{ew} along with the corresponding values for d(ϕc_S)/dc_S and k_S/v are listed in Table 6. The obtained N_{ew} values, which may give a quantitative measure of the preferential hydration of [C$_4$mim]Br, show that the increasing number of water molecules around [C$_4$mim]Br pairs with a decrease in the temperature may be related to the enhancement of the exclusion of [C$_4$mim]Br in the investigated ATPS (Figure 1). It seems that because of the hydration sheath increment per [C$_4$mim]Br pairs by decreasing temperature, the near-surface region of the [C$_4$mim]Br pairs may be less accessible to structure-making ions and hence the extent of exclusion will increase. In a further analysis, the interactions of the chaotropic [C$_4$mim]Br pairs with surrounding water molecules weakened because of the formation of water structure, which in turn resulted from the presence of the studied kosmotropic salt, are further diminished as a result of a decrease in temperature. Therefore, for a given concentration of the investigated water-structure-making salt, the water-structuring forces preferably dominate the interaction between structure-making electrolyte and [C$_4$mim]Br pairs, leading to the hydration sheath increment around [C$_4$mim]Br pairs and therefore the ability of the system to produce a [C$_4$mim]Br-rich, salt-deficient local composition increase.

Effect of Salt on the Exclusion of [C$_4$mim]Br. As mentioned earlier, because of its low-symmetry constituent ions that contain charge delocalization and its weak directional intermolecular interactions, [C$_4$mim]Br should be a chaotropic salt and thus could be salted-out by a kosmotropic salt to form the IL-based ATPSs.[15,16] The same chaotropic [C$_4$mim]Br in an aqueous solution salted-out by kosmotropic K_2CO_3, KOH, K_2HPO_4, K_3PO_4, or K$_3$-citrate salt as that in the phase diagrams for the aqueous [C$_4$mim]Br + K_2CO_3,[15] [C$_4$mim]Br + KOH,[15] [C$_4$mim]Br + K_2HPO_4,[16] [C$_4$mim]Br + K_3PO_4,[16] and [C$_4$mim]Br + K$_3$-citrate (this work), respectively, two-phase systems at $T = 298.15$ K is shown in Figure 7 as a criterion by which the differences in kosmotropicity of the used salts may be illustrated. The ion kosmotropicity can also be reflected by ionic viscosity B coefficients. The ionic viscosity B coefficients in aqueous solutions allow us to understand the interactions involved in the hydration of the ions and their effects on the structure of the water in the near environment of the solute particles.[40] Positive B values typically suggest ions as kosmotropes because strongly hydrated ions exhibit a larger change in viscosity with concentration, whereas negative B coefficients suggest chaotropes for weakly hydrated ions.[41] From Figure 7, it is easy to see that the studied salts shared a common cation (K^+) but contained different anions; the higher kosmotropicity of the salt for the exclusion of [C$_4$mim]Br is observed when the anions of the salt have more positive B-coefficient values: PO_4^{3-}, 0.495 $dm^3 \cdot mol^{-1}$ > HPO_4^{2-}, 0.382 $dm^3 \cdot mol^{-1}$ > citrate^{3-}, 0.333 $dm^3 \cdot mol^{-1}$ > CO_3^{2-}, 0.294 $dm^3 \cdot mol^{-1}$ > OH^-, 0.122 $dm^3 \cdot mol^{-1}$. This is because the anions with a more positive B coefficient value hydrate more water than do the anions with a less-positive B coefficient value, thus decreasing the amount of water available to hydrate [C$_4$mim]Br. The anions' viscosity B coefficients were taken from Jenkins and Marcus[41] and Zhao et al.[42] In Figure 7, the concentrations for the salts are given in molality. This is because the values for the viscosity B coefficients are expressed per one mole of the ionic species. In the further analysis, by the use of eqs 6, 8, 9, and 10, the excess number of water molecules in the vicinity of [C$_4$mim]Br, N_{ew}, in the ATPSs containing K_3PO_4 or K_2HPO_4, for which the tie-line data at $T = 298.15$ K are available,[16] has been estimated to be 48 and 25, respectively and is compared with the corresponding value for K$_3$-citrate reported as 18 in Table 6. The necessary molal osmotic coefficients, ϕ, for K_3PO_4 and K_2HPO_4 at $T = 298.15$ K have been taken from Robinson and Stokes.[43] In fact, the interaction between water and [C$_4$mim]Br, which is preferably decreased in the presence of a salt with a higher kosmotropicity (i.e., K_3PO_4) as a result of the increased formation of water structure in the vicinity of [C$_4$mim]Br, results in the hydration sheath increment (preferential hydration) per [C$_4$mim]Br. This preferential hydration is also reflected by the increasing N_{ew} values in the order K$_3$-citrate, 18 < K_2HPO_4, 25 < K_3PO_4, 48. This trend is consistent with the enhancement of the exclusion of [C$_4$mim]Br in the investigated ATPSs (Figure 7).

Table 6. Excess Number of Water Molecules Per [C$_4$mim]Br Pairs

T/K	k_S/v ($kg \cdot mol^{-1}$)	d(ϕc_S)/dc_S	N_{ew}
278.15	0.31	0.75	23
298.15	0.23	0.73	18
318.15	0.16	0.74	12

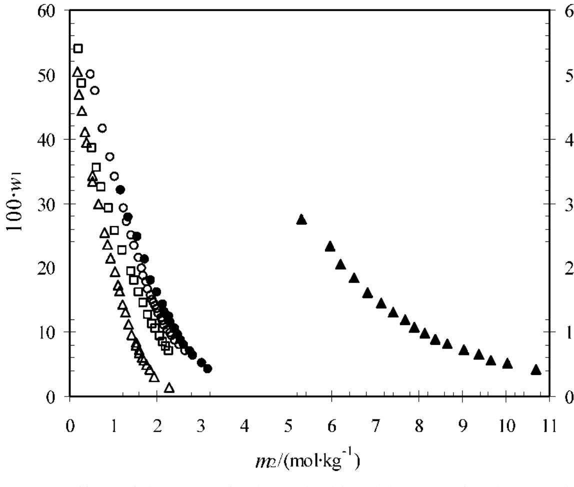

Figure 7. Effect of the type of salt on the binodal curves for the [C$_4$mim]Br (1) + salt (2) + H_2O (3) two-phase systems at 298.15 K: △, K_3PO_4 (ref 16); □, K_2HPO_4 (ref 16); ○, K3Cite (this work); ●, K_2CO_3 (ref 15); ▲, KOH (ref 15).

Conclusions

Liquid−liquid equilibrium data for the [C_4mim]Br (1) + tri-potassium citrate (2) + H_2O (3) system were obtained at T = (278.15, 298.15, and 318.15) K. The experimental binodal data were satisfactorily correlated with the Merchuk equation for which the three fitting parameters, a, b, and c, are further expressed as a function of temperature in the linear form with $(T - T_0)$ K as a variable. The effect of temperature on the phase-forming ability of the studied system was also successfully explained on the basis of salting-out coefficient of the salt, k_S, obtained from fitting the tie-line data to a Setschenow-type equation. It was shown that for the studied system the value of k_S increases with decreasing temperature and the temperature with higher phase-forming ability has a larger value of k_S. Additionally, the tie-line data for the investigated system can be successfully represented by the Setschenow-type equation. Furthermore, by using the k_S values obtained for the studied electrolyte, we estimated the number of water molecules adjacent to [C_4mim]Br and showed that the enhancement of the exclusion of [C_4mim]Br in the investigated ATPS may be related to the increasing number of water molecules around the [C_4mim]Br as the temperature is decreased. Finally, the kosmotropicity of tri-potassium citrate for the exclusion of [C_4mim][Br] in an aqueous solution in comparison with that of the salts K_2CO_3, KOH, K_2HPO_4, and K_3PO_4 was also discussed on the basis of the viscosity B coefficients of salt constituent anions and the preferential hydration of the [C_4mim][Br].

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