J. Chem. Eng. Data **2010,** *55,* 5621–5626

Liquid−Liquid Equilibrium of Potassium Phosphate/Potassium Citrate/Sodium Citrate + Ethanol Aqueous Two-Phase Systems at (298.15 and 313.15) K and Correlation

Yun Wang,*,[†] Yanli Mao,[‡] Juan Han,[†] Yan Liu,[†] and Yongsheng Yan[†]

School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 201013, People's Republic of China, and Environment and Municipal Engineering Department, Henan University of Urban Construction, Henan, 467001, People's Republic of China

Binodal data for the ethanol + $K_3PO_4/K_3C_6H_5O_7/Na_3C_6H_5O_7$ + water systems were experimentally determined at (298.15 and 313.13) K. On the basis of the binodal data fitting equation with the highest accuracy and the Lever rule, the liquid−liquid equilibrium data for the investigated systems at 298.15 K were directly calculated by MATLAB. The Othmer−Tobias equation and Bancroft equation were used to correlate tie-line data and evaluate the reliability of the calculation method and the corresponding tie-line data. The salting-out strength of salt ions was compared by the parameter of effective excluded volume and the binodal curves plotted in molality, while the salting-out strength of salts was compared by the parameter of salting-out coefficient and the binodal curves plotted in mass fraction. The salting-out strength of the investigated salts is in the order $K_3PO_4 > Na_3C_6H_5O_7 > K_3C_6H_5O_7$. As for salt ions, the salting-out strength of anions is in the order $PO_4^{3-} < C_6H_5O_7^{3-}$, while the salting-out strength of Na^+ is similar to K^+. The effects of salt, hydrophilic alcohol, and temperature on liquid−liquid equilibria were also discussed. The shapes and locations of binodal curves are not sensitive to the investigated temperature range. The additions of salt and ethanol both increase the tie-line length and the absolute value of the tie-line slope.

Introduction

Aqueous two-phase systems (ATPS), as novel liquid−liquid extraction systems, have become the research hotspot in the biochemical fields, especially in the separation and purification of biological products due to its mild extraction environment. Compared with the polymer−polymer/salt ATPS and the ionic liquid (IL)−salt ATPS, besides the advantage of low cost, it is easier to recover the products and recycle the phase-forming substances for the hydrophilic alcohol−salt ATPS. Liquid−liquid equilibrium (LLE) data for the IL−salt ATPS,[1,2] polymer−salt ATPS,[3,4] and hydrophilic alcohol−salt ATPS[5,6] have been determined in recent years. These data are essential to the design of liquid−liquid extraction, the crystallization of salt, and the establishment of thermodynamic models. On the basis of reported phase diagrams, it can be seen that potassium phosphate shows a higher salting-out strength than other phase-forming salts in the polymer−salt ATPS[7,8] and IL−salt ATPS,[2,9,10] including K_2HPO_4, $(NH_4)_2SO_4$, K_2CO_3, Na_2CO_3, Li_2SO_4, $MnSO_4$, and $ZnSO_4$. However, phase diagram data of the ethanol−K_3PO_4 ATPS at (298.15 and 313.15) K have not been reported. Citrates have the advantages of biodegradability and nontoxicity over the traditional phase-forming inorganic salts. Recently, citrates have been investigated as a substitute for the inorganic salts with polymer or IL to form aqueous two-phase systems.[1,11,12] Zafarani-Moattar et al.[13] studied the phase diagrams of some hydrophilic alcohols + $Na_3C_6H_5O_7/K_3C_6H_5O_7$ + water systems at 298.15 K; however, they only determined a small part of the binodal data. To compare the salting-out strength of phase-separation salts and salt ions, overall binodal data should be determined.

The study of the salting-out effect of salts is of industrial interest. The excluded volume theory proposed by Guan et al.[14] has been used in evaluating the salting-out strength of salts for the exclusion of polymer,[2,8,12] while the application of this theory in hydrophilic alcohol−salt systems is rare. In this theory, each system on a binodal curve is treated as a geometrically saturated solution of one solute in the presence of another, and each composition in a solution is distributed at random. Effective excluded volume (EEV) represents the acceptability of one component by a network constructed of the other. We extended the application of this theory in hydrophilic alcohol−salt systems to correlate binodal data and evaluate the salting-out strength of salt ions. Meanwhile, the salting-out coefficient (k) was calculated to evaluate the salting-out strength of salts.

In the present paper, binodal data for the ethanol + $K_3PO_4/K_3C_6H_5O_7/Na_3C_6H_5O_7$ + water systems were determined at (298.15 and 313.15) K. Tie-line data were directly calculated by MATLAB on the basis of binodal data-fitting equations and the Lever rule,[8,10] which significantly simplify traditional operations. For industrial application, reliable LLE data and a convenient determination method are both beneficial to the design of aqueous two-phase extraction. The Othmer−Tobias equation and Bancroft equation[15,16] were used to evaluate the reliability of the calculation method as well as the calculated tie-line compositions.

Experimental Section

Materials. Ethanol, $K_3PO_4\cdot3H_2O$, $K_3C_6H_5O_7\cdot H_2O$, and $Na_3C_6H_5O_7\cdot2H_2O$ were supplied by the Sinopharm Chemical Reagent Co., Ltd. with a minimum purity of 99.7 %, 99.0 %,

---

* Corresponding author. E-mail: yunwang@ujs.edu.cn.
[†] Jiangsu University.
[‡] Henan University of Urban Construction.

10.1021/je100501f

Table 1. Binodal Data for the Ethanol (1) + $K_3PO_4/K_3C_6H_5O_7/Na_3C_6H_5O_7$ (2) + Water (3) Systems at 298.15 K

ethanol−K_3PO_4				ethanol−$K_3C_6H_5O_7$				ethanol−$Na_3C_6H_5O_7$			
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	100 w_1	100 w_2
0.68	39.74	24.45	9.93	2.04	56.22	42.48	7.25	8.81	31.71	44.42	3.95
0.89	39.13	27.28	8.29	2.13	55.30	45.27	5.89	11.42	28.16	45.41	3.61
1.70	34.02	29.53	7.11	3.27	49.48	51.87	3.42	14.02	25.22	48.91	2.64
2.74	30.99	32.09	5.91	3.45	48.91	51.91	3.40	16.56	22.71	52.23	1.92
3.37	29.41	34.40	5.07	5.09	43.23	55.93	2.35	18.75	20.65	53.25	1.75
4.38	27.53	37.87	3.78	7.25	38.30	57.75	1.94	20.01	19.51	54.80	1.48
5.55	25.63	41.70	2.75	9.80	34.11	61.39	1.31	21.54	18.16	57.18	1.15
5.98	25.17	43.21	2.42	12.40	30.62	61.66	1.28	25.57	14.91	60.01	0.84
9.95	20.82	44.58	2.13	13.01	29.77	63.04	1.09	28.67	12.58	62.24	0.65
13.15	17.94	48.65	1.47	20.73	22.45	67.10	0.66	31.31	10.72		
13.90	17.50	52.08	1.04	26.49	17.80	69.24	0.49	31.90	10.26		
17.02	15.07	54.21	0.83	30.77	14.65			33.43	9.27		
19.65	13.18	58.47	0.52	33.67	12.58			38.72	6.28		
20.97	12.22			38.78	9.30			42.48	4.62		

Table 2. Binodal Data for the Ethanol (1) + $K_3PO_4/K_3C_6H_5O_7$ (2) + Water (3) Systems at 313.15 K

ethanol−K_3PO_4				ethanol−$K_3C_6H_5O_7$			
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
0.65	40.33	27.31	8.64	1.95	57.65	18.30	23.93
1.91	33.29	30.57	6.98	3.10	50.55	24.22	19.13
2.67	31.63	35.85	4.74	3.81	47.77	30.34	14.94
6.29	24.49	36.65	4.48	5.02	44.49	40.42	8.57
11.62	19.12	41.47	3.03	6.07	40.46	45.97	5.79
15.41	16.24	44.96	2.24	8.80	34.83	49.87	4.23
16.44	15.39	46.92	1.79	10.86	31.60	52.26	3.42
22.60	11.41			17.36	24.93	60.27	1.58

99.5 %, and 99.0 %, respectively. All chemicals were used without further purification. Double distilled and deionized water was used throughout the entire experiment.

Apparatus and Procedures. The binodal curves were determined by the titration method (cloud point method). A K_3PO_4, $K_3C_6H_5O_7$, or $Na_3C_6H_5O_7$ solution of known concentration was titrated with ethanol until the clear solution turned turbid. The compositions of the mixture were determined by a Sartorious analytical balance (model BS 124S) with a precision of 0.0001 g. A conical flask (50 cm^3) was used to carry out the experiment, and the temperature was maintained within ± 0.1 K in a water bath.

The phase equilibrium experiments were carried out in a separating funnel (60 mL). The feed samples were prepared by mixing an appropriate mass of ethanol (m_1), $K_3PO_4/K_3C_6H_5O_7/Na_3C_6H_5O_7$ (m_2)m and water (m_3) in a vessel (50 mL), and the mass of each composition was determined by the same Sartorious analytical balance mentioned above. After sufficient mixing, the samples were placed in a water bath at (298.15 or 313.15) K for more than 6 h until it separated into two clear phases. After the phase separation, the mass of the bottom phase (m_b) and top phase (m_t) was determined.

Results and Discussion

Binodal Data and Correlation. For the ethanol (1) + $K_3PO_4/K_3C_6H_5O_7/Na_3C_6H_5O_7$ (2) + water (3) systems, binodal data determined at 298.15 K are listed in Table 1. Binodal data for the ethanol (1) + $K_3PO_4/K_3C_6H_5O_7$ (2) + water (3) systems at 313.15 K are given in Table 2. The binodal curves are plotted in Figure 1. As shown in Figure 1, there is no significant difference in the locations and shapes of binodal curves with an increase of temperature. The binodal data at 298.15 K were correlated by the following equations

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

$$w_1 = a + bw_2^{0.5} + cw_2 \qquad (2)$$

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

where w_2 is the mass fraction of salt; w_1 is the mass fraction of hydrophilic alcohol; and *a*, *b*, *c*, and *d* are fitting parameters. In these three different equations, eqs 1 and 2 have often been used to correlate binodal data of IL−salt systems[17] and PEG−salt systems.[12] Equation 3 has been applied in the binodal data fitting of hydrophilic alcohol−salt systems,[5] but its application is relatively small compared to the other two equations. The fitting parameters, coefficients of determination (R^2), and standard deviations (sd) of eqs 1 and 2 as well as eq 3 for binodal data fitting are given in Table 3 and Table 4, respectively. Comparing the values of R^2 and sd, it can be concluded that eq 3 shows a higher accuracy in binodal data fitting than eqs 1 and 2.

We have investigated many hydrophilic alcohol−salt ATPS, including 2-propanol−$Li_2SO_4/Na_2SO_4/Na_2CO_3/K_2CO_3/Na_2HPO_4/K_2HPO_4$ ATPS. For all the investigated systems, binodal data were correlated by the above three equations, and eq 3 also shows the highest accuracy in binodal data fitting. Therefore, eq 3 can be taken as a widely suitable equation for the binodal data fitting of the hydrophilic alcohol−salt ATPS.

Liquid−Liquid Equilibrium Data and Correlation. On the basis of eq 3 and the Lever rule, the equilibrium compositions were calculated by MATLAB, using eqs 1, 5, 6, and 7 as follows

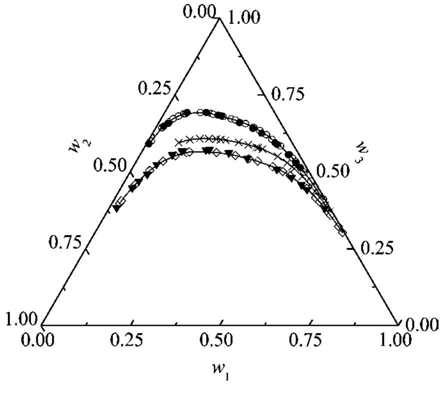

Figure 1. Binodal curves for the ethanol (1) + $K_3PO_4/K_3C_6H_5O_7/Na_3C_6H_5O_7$ (2) + H_2O (3) aqueous two-phase systems at (298.15 and 313.15) K. ○, K_3PO_4 (298.15 K); ●, K_3PO_4 (313.15 K); ◇, $K_3C_6H_5O_7$ (298.15 K); ▼, $K_3C_6H_5O_7$ (313.15 K); ×, $Na_3C_6H_5O_7$ (298.15 K); —, obtained by connecting experimental binodal data.

Table 3. Values of Parameters of Equations 1 and 2 for the Ethanol + $K_3PO_4/K_3C_6H_5O_7/Na_3C_6H_5O_7$ + Water Systems at 298.15 K

salt	*a*	*b*	*c*	R^2	100sd
K_3PO_4	0.73623^a	-3.37172^a	49.16208^a	0.9998^a	0.27^a
	0.69342^b	-1.79501^b	1.09538^b	0.9983^b	0.75^b
$K_3C_6H_5O_7$	0.81833^a	-2.46080^a	15.69968^a	0.9992^a	0.65^a
	0.78905^b	-1.56031^b	0.68840^b	0.9984^b	0.95^b
$Na_3C_6H_5O_7$	0.76201^a	-2.67452^a	20.92335^a	0.9997^a	0.30^a
	0.71927^b	-1.46289^b	0.62794^b	0.9982^b	0.69^b

[a] Values of parameters of eq 1. [b] Values of parameters of eq 2. sd = $(\sum_{i=1}^{n}(w_1^{\text{cal}} - w_1^{\text{exp}})^2/N)^{0.5}$, where w_1 and N represent the mass fraction of ethanol and the number of binodal data, respectively. w_1^{exp} is the experimental mass fraction of ethanol listed in Table 1, and w_1^{cal} is the corresponding data calculated using eq 1 or 2.

Table 4. Values of Parameters of Equation 3 for the Ethanol + $K_3PO_4/K_3C_6H_5O_7/Na_3C_6H_5O_7$ + Water Systems at 298.15 K

salt	*a*	*b*	*c*	*d*	R^2	100sd
K_3PO_4	−0.21034	−4.95774	6.42496	−27.15580	1.0000	0.13
$K_3C_6H_5O_7$	−0.17793	−2.91450	2.15402	−9.82933	0.9998	0.30
$Na_3C_6H_5O_7$	−0.19339	−3.82414	4.12531	−13.94020	1.0000	0.04

$$w_1^{\text{t}} = \exp(a + b(w_2^{\text{t}})^{0.5} + cw_2^{\text{t}} + d(w_2^{\text{t}})^2) \qquad (4)$$

$$w_1^{\text{b}} = \exp(a + b(w_2^{\text{b}})^{0.5} + cw_2^{\text{b}} + d(w_2^{\text{b}})^2) \qquad (5)$$

$$\frac{w_1^{\text{t}} - w_1}{w_1 - w_1^{\text{b}}} = \frac{m_{\text{b}}}{m_{\text{t}}} \qquad (6)$$

$$\frac{w_2 - w_2^{\text{t}}}{w_2^{\text{b}} - w_2} = \frac{m_{\text{b}}}{m_{\text{t}}} \qquad (7)$$

where w_1^{t}, w_1^{b}, w_2^{t}, and w_2^{b} represent the equilibrium compositions (in mass fraction) of alcohol (1) and salt (2), in the top, t, and bottom, b, phases, respectively. w_1 and w_2 represent the total compositions (in mass fraction) of alcohol (1) and salt (2), respectively. The results are given in Table 5.

The Othmer−Tobias equation (eq 8) and Bancroft equation (eq 9)[15,16] were used to evaluate the reliability of the calculation method and tie-line data. In fact, eqs 8 and 9 have been successfully used in correlation of the tie-line compositions of PEG−salt systems,[12] ionic liquid−salt systems,[9] and hydrophilic alcohol−salt systems.[15]

$$\frac{1 - w_1^{\text{t}}}{w_1^{\text{t}}} = k_1\left(\frac{1 - w_2^{\text{b}}}{w_2^{\text{b}}}\right)^n \qquad (8)$$

$$\frac{w_3^{\text{b}}}{w_2^{\text{b}}} = k_2\left(\frac{w_3^{\text{t}}}{w_1^{\text{t}}}\right)^r \qquad (9)$$

where w_1^{t}, w_1^{b}, w_2^{t}, w_2^{b}, w_3^{t}, and w_3^{b} represent the equilibrium compositions (in mass fraction) of alcohol (1), salt (2), and water (3) in the top, t, and bottom, b, phases, respectively. k_1, k_2, n, and r are fitting parameters. The fitting parameters of eq 8 are given in Table 6. A linear dependence of $\log((1 - w_1^{\text{t}})/w_1^{\text{t}})$ against $\log((1 - w_2^{\text{b}})/w_2^{\text{b}})$ as well as $\log(w_3^{\text{b}}/w_2^{\text{b}})$ against $\log(w_3^{\text{t}}/w_1^{\text{t}})$ also indicates good fitting properties of the experimental results to eqs 8 and 9. The linear correlation coefficients of eq 9 for the ethanol−K_3PO_4 system, ethanol−$K_3C_6H_5O_7$, system and ethanol−$Na_3C_6H_5O_7$ system are 0.9987, 0.9994, and 0.9986, respectively. The results proved the reliability of the calculation method and the corresponding tie-line data.

Table 5. Phase Equilibrium Compositions for the Ethanol (1) + $K_3PO_4/K_3C_6H_5O_7/Na_3C_6H_5O_7$ (2) + Water (3) Systems at 298.15 K

	total composition		alcohol-rich phase		salt-rich phase		tie-line
No.	100 w_1	100 w_2	100 w_1^{t}	100 w_2^{t}	100 w_1^{b}	100 w_2^{b}	slope (*k*)
			Ethanol (1) + K_3PO_4 (2)				
I ①	26.78	16.04	51.00	1.16	2.88	30.72	−1.6279
I ②	31.08	17.98	61.35	0.37	1.40	35.27	−1.7190
I ③	31.21	12.00	47.77	1.58	3.44	29.49	−1.5886
I ④	31.13	15.97	56.87	0.63	1.93	33.34	−1.6774
I ⑤	24.04	15.99	46.07	1.85	3.63	29.10	−1.5578
			Ethanol (1) + $K_3C_6H_5O_7$ (2)				
II ①	31.00	16.01	42.08	7.41	14.10	29.15	−1.2868
II ②	30.97	18.00	48.58	4.55	10.46	33.66	−1.3095
II ③	30.97	22.03	58.19	1.89	6.38	40.24	−1.3510
II ④	34.00	22.00	62.62	1.16	5.03	43.10	−1.3729
II ⑤	36.02	22.01	65.11	0.85	4.20	45.18	−1.3741
			Ethanol (1) + $Na_3C_6H_5O_7$ (2)				
III ①	30.98	14.00	42.89	4.49	8.56	31.93	−1.2511
III ②	29.00	16.05	44.27	3.99	8.15	32.53	−1.2657
III ③	30.97	16.00	48.33	2.78	7.07	34.20	−1.3132
III ④	28.96	18.00	49.70	2.45	6.83	34.60	−1.3334

Table 6. Values of Parameters of Equation 8 for the Ethanol (1) + $K_3PO_4/K_3C_6H_5O_7/Na_3C_6H_5O_7$ (2) + H_2O (3) Systems at 298.15 K

salt	k_1	*n*	*R*	100sd[a]
K_3PO_4	0.17281	2.1276	0.9987	0.29
$K_3C_6H_5O_7$	0.41284	1.3691	0.9995	0.27
$Na_3C_6H_5O_7$	0.24403	2.2457	0.9988	0.14

[a] sd = $(\sum_{i=1}^{N}(w_1^{\text{t,cal}} - w_1^{\text{t,exp}})^2/N)^{0.5}$, where w_1^{t} and N represent the mass fraction of ethanol in the top phase and the number of tie-lines, respectively. $w_1^{\text{t,exp}}$ is the experimental mass fraction of ethanol in the top phase listed in Table 5, and $w_1^{\text{t,cal}}$ is the corresponding data calculated using eq 8.

Excluded Volume Theory. In this paper, the excluded volume theory developed by Guan et al.[14] was used to correlate binodal data and calculate the effective excluded volume of salt. It is based on the concept that macroscopically any molecular species in a solution is distributed at random, and every system composition on the binodal is a geometrically saturated solution of one solute in the presence of another. The binodal model developed by Guan et al. was originally used in the polymer−polymer aqueous two-phase systems, while we extended the application of this model to hydrophilic alcohol−salt systems. As for a hydrophilic alcohol (1) + salt (2) + water (3) ternary system, two equations can be given, respectively[18]

$$\ln\left(V_{213}^{*}\frac{w_2}{M_2} + f_{213}\right) + V_{213}^{*}\frac{w_1}{M_1} = 0 \qquad (10)$$

$$\ln\left(V_{213}^{*}\frac{w_2}{M_2}\right) + V_{213}^{*}\frac{w_1}{M_1} = 0 \qquad (11)$$

In the original application, eq 11 was used to correlate binodal data of the polymer−polymer system due to the marked difference in size between these two components. The f_{213} value will be very small and consequently can be neglected. The parameter f_{213} depends on the relative geometric shape, size, and interaction of unlike molecules. The effective excluded volume reflects the compatibility of components in the same system.

Table 7. Values of Parameters of Equations 10 and 11 for the Ethanol (1) + $K_3C_6H_5O_7$/$Na_3C_6H_5O_7$ (2) + H_2O (3) Systems at 298.15 K

salt	$10^2 v^*_{213}$ g·mol^{-1}	$10^{-3} f_{213}$	R	sd[a]
$K_3C_6H_5O_7$	3.1232	2.6972	0.9896	0.043
	3.2191		0.9844	0.045
$Na_3C_6H_5O_7$	3.1158	6.3753	0.9944	0.019
	3.2757		0.9883	0.026

[a] sd = $(\sum_{i=1}^{N}(w_1^{\mathrm{cal}} - w_1^{\mathrm{exp}})^2/N)^{0.5}$, where N represent the number of binodal data. w_1^{exp} is the experimental mass fraction of ethanol listed in Table 1, and w_1^{cal} is the corresponding data calculated using eq 10 or 11.

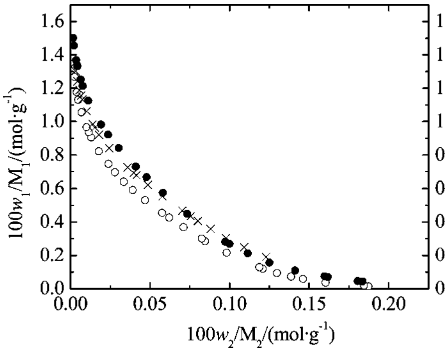

Figure 2. Binodal curves in molality for the ethanol (1) + K_3PO_4/$K_3C_6H_5O_7$/$Na_3C_6H_5O_7$ (2) + H_2O (3) systems at 298.15 K. ○, K_3PO_4; ×, $Na_3C_6H_5O_7$; ●, $K_3C_6H_5O_7$.

Effective Excluded Volume and Salting-Out Strength of Salt Ions. In many published papers, the salting-out strength of salt ions has always been compared by the binodal curves plotted in mass fraction. In fact, it cannot exactly reflect the nature of interaction between ions and water molecules in the systems. In this paper, the scaled EEV of salts and the binodal curves plotted in molality were used to evaluate the salting-out strength of salt ions in the hydrophilic alcohol−water component solvent.

Equations 10 and 11 were both used to calculate the scaled EEV of K_3PO_4, $K_3C_6H_5O_7$, and $Na_3C_6H_5O_7$ in ethanol−water component solvent. In comparison of the fitting results, we found that there is no significant difference between these two equations for binodal data fitting of the ethanol−K_3PO_4 ATPS. The scaled EEV of K_3PO_4 calculated by eqs 10 and 11 are 362.49 g·mol^{-1} and 360.74 g·mol^{-1}, respectively. The corresponding standard deviations are 0.032 and 0.033, respectively. So the simplified equation (eq 11) can also be used to correlate binodal data of the ethanol−K_3PO_4 system. However, for the ethanol−$K_3C_6H_5O_7$/$Na_3C_6H_5O_7$ systems, eq 10 should be used to calculate the scaled EEV of $K_3C_6H_5O_7$ and $Na_3C_6H_5O_7$ due to the significant difference in calculated EEV, as shown in Table 7. The scaled EEV is in the order K_3PO_4 (360.74 g·mol^{-1}) > $K_3C_6H_5O_7$ (312.32 g·mol^{-1}) ≈ $Na_3C_6H_5O_7$ (311.58 g·mol^{-1}), which indicates that the salting-out strength of anions is in the order PO_4^{3-} > $C_6H_5O_7^{3-}$ and that of cations (Na^+ and K^+) is similar to each other. As for the investigated salts, the influence of the anion was dominant, whereas that of the cation was of little consequence. It may be because the size of $C_6H_5O_7^{3-}$ is larger than K^+ and Na^+. Thus, the influence of the cation is weakened.

The bindal curves of the investigated systems are plotted in molality in Figure 2. The increase in the scaled EEV value is reflected by a decrease in the concentration of salt required for the formation of aqueous two-phase systems, which indicates a higher salting-out ability of salt ions. This relationship can also be deduced from eqs 10 and 11. To have an intuitive comparison, the binodal curves in Figure 1 are plotted in Cartesian coordinates in Figure 3. Comparing Figure 2 and Figure 3, it can be seen that the locations of binodal curves are different in the two figures. As shown in Figure 2, Na^+ only shows a slightly higher salting-out strength than K^+ as the concentration of salts is below 0.070 mol·g^{-1}. When the concentration is between 0.070 mol·g^{-1} and 0.080 mol·g^{-1}, their salting-out strength is similar. Then, K^+ shows slightly higher salting-out strength than Na^+ as the concentration of salts is higher than 0.080 mol·g^{-1}. In summary, PO_4^{3-} shows a higher salting-out strength than $C_6H_5O_7^{3-}$ under all the investigated concentrations, and the salting-out strength of Na^+ and K^+ is similar under the concentrations forming aqueous two-phase systems.

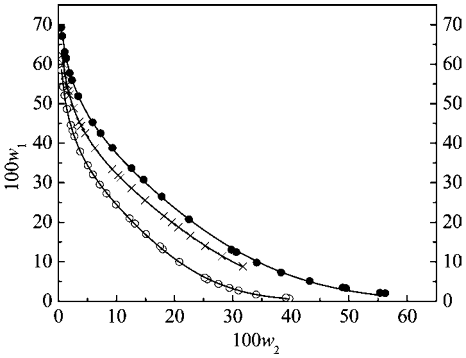

Figure 3. Binodal curves in mass fraction for the ethanol (1) + K_3PO_4/$K_3C_6H_5O_7$/ $Na_3C_6H_5O_7$ (2) + H_2O (3) systems at 298.15 K. ○, K_3PO_4; ×, $Na_3C_6H_5O_7$; ●, $K_3C_6H_5O_7$; —, obtained by eq 3.

Table 8. Values of Parameters of Equation 12 for the Ethanol (1) + K_3PO_4/$K_3C_6H_5O_7$/$Na_3C_6H_5O_7$ (2) + H_2O (3) Systems at 298.15 K

salt	k	β	R	100sd[a]
K_3PO_4	10.232	1.6142	0.9990	0.55
$K_3C_6H_5O_7$	7.8651	0.91510	0.9965	1.75
$Na_3C_6H_5O_7$	8.0264	0.79749	0.9999	0.08

[a] sd = $(\sum_{i=1}^{2}((w_i^{\mathrm{t,cal}} - w_i^{\mathrm{t,exp}})^2 + (w_i^{\mathrm{b,cal}} - w_i^{\mathrm{b,exp}})^2)/4N)^{0.5}$, where N is the number of tie-lines.

Salting-Out Coefficient and Salting-Out Strength of Salts. In many practical applications, the salting-out strength of salts is always compared by the extraction coefficients of target products through adding the same mass of phase-separation salts. Therefore, the salting-out strength of salts was compared by the salting-out coefficients calculated on the basis of LLE data as well as the binodal curves plotted in mass fraction in this paper.

A two-parameter equation, which had been used in the correlation of tie-line data of polymer−polymer systems and polymer−salt systems, was also used to correlate tie-line data of the investigated systems in this paper. The equation is given as[7,14]

$$\ln\left(\frac{w_2^{\mathrm{t}}}{w_2^{\mathrm{b}}}\right) = \beta + k(w_1^{\mathrm{b}} - w_1^{\mathrm{t}}) \tag{12}$$

where k is the salting-out coefficient and β is the constant related to the activity coefficient. The fitting parameters of eq 12 are given in Table 8. On the basis of the salting-out coefficients listed in Table 8, it can also be concluded that the salting-out strength of the investigated salts is in the order K_3PO_4 >

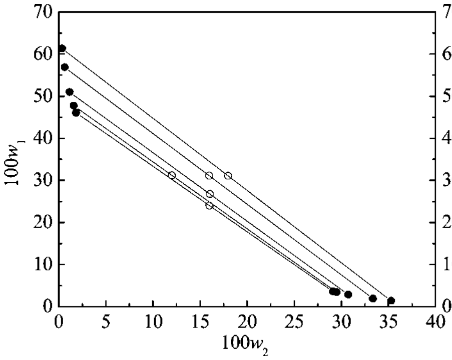

Figure 4. Effects of salt and alcohol on the LLE of the ethanol (1) + K_3PO_4 (2) + H_2O (3) systems at 298.15 K. ○, total compositions of tie-line; ●, liquid−liquid equilibrium compositions of tie-line; —, tie-lines.

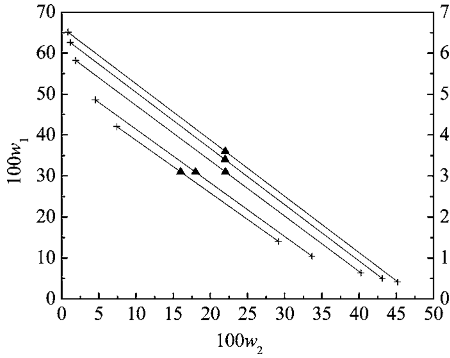

Figure 5. Effects of salt and alcohol on the LLE of ethanol (1) + $K_3C_6H_5O_7$ (2) + H_2O (3) systems at 298.15 K. ▲, total compositions of tie-line; +, liquid−liquid equilibrium compositions of tie-line; —, tie-lines.

$Na_3C_6H_5O_7 > K_3C_6H_5O_7$, which is also proved by the binodal curves plotted in mass fraction in Figure 3.

Effect of Temperature and Phase-Forming Substance on LLE. A relation between excluded volume theory and thermodynamics was also established by Guan et al.[14] Assuming there is no change in the total volume of the system with temperature, the following relationship applies

$$\left(\frac{\partial V^*_{210}}{\partial T}\right)_V = -\frac{\rho N_a}{k v_i}\frac{\Delta U_{210}}{T^2} \qquad (13)$$

where ΔU_{210} is the internal energy change of the system to create an empty region with volume V_{210}. For the polymer−polymer system they investigated, they proposed that ΔU_{210} must be greater than zero, and then $(\partial V^*_{210}/\partial T)_V$ must always be negative at any temperature suitable for the binodal model. So the EEV value will decrease when the temperature increases. The locations of binodal curves will shift with an increase of temperature for the polymer−polymer ATPS. For the hydrophilic alcohol−salt systems in this paper, as shown in Figure 1, the locations and shapes of binodal curves are not sensitive to temperature, which is different from the polymer−polymer/salt ATPS and IL−salt ATPS.

Figures 4, 5, and 6 show that increasing amounts of ethanol and salts both increase the tie-line length; meanwhile, the absolute value of tie-line slope also slightly increases with additions of salts and ethanol. The addition of salts to the aqueous ethanol solution leads to the migration of water molecules away from ethanol to ions of salts. Then, more ethanol molecules will be excluded from the salt-rich phase to the ethanol-rich phase. Meanwhile, in comparison of tie-lines with the same total compositions for these three different ATPS, such as I ②, II ②, II ①, and III ③ in Table 5, it can also be concluded that K_3PO_4 shows the highest salting-out strength for the exclusion of ethanol, and the salting-out strength of salts is also in the same order as the salting-out coefficients.

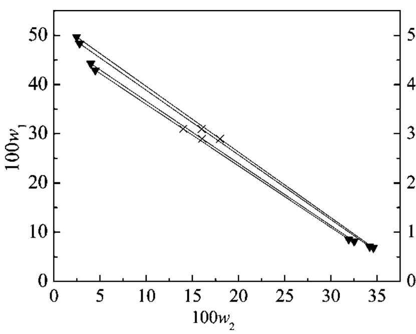

Figure 6. Effects of salt and alcohol on the LLE of ethanol (1) + $Na_3C_6H_5O_7$ (2) + H_2O (3) systems at 298.15 K. ×, total compositions of tie-line; ▼, liquid−liquid equilibrium compositions of tie-line; —, tie-lines.

Conclusion

Binodal data for the ethanol + $K_3PO_4/K_3C_6H_5O_7/Na_3C_6H_5O_7$ + water systems were experimentally determined at (298.15 and 313.13) K. Liquid−liquid equilibrium data for the investigated systems at 298.15 K were directly calculated by MATLAB, which significantly simplifies the traditional operations. The reliability of the calculation method and the corresponding LLE data was proved by the Othmer−Tobias equation and Bancroft equation.

The series of salting-out strengths of salts and salt ions are very useful for the design of aqueous two-phase extraction and the recovery of hydrophilic alcohols or salts. In this paper, the scaled EEV and the binodal curves plotted in molality were used to evaluate the salting-out strength of salt ions, while the salting-out coefficient and the binodal curves plotted in mass fraction were used to evaluate the salting-out strength of salts. It can be concluded that the salting-out strength of the investigated salts is in the order $K_3PO_4 > Na_3C_6H_5O_7 > K_3C_6H_5O_7$. Although the salting-out strength of $Na_3C_6H_5O_7$ and $K_3C_6H_5O_7$ is not as strong as K_3PO_4, these two citrates also show satisfactory phase-separation abilities. Citrate shows great potential in the aqueous two-phase extraction process due to its biodegradable and nontoxic properties. As for the investigated salts, the influence of anions was dominant, whereas that of cations was of little consequence. The salting-out strength of cations is in the order $PO_4^{3-} > C_6H_5O_7^{3-}$, and the salting-out strengths of Na^+ and K^+ are similar. These two parameters can also be extended to evaluate the salting-out strength of other phase-separation salts and salt ions.

Literature Cited

(1) Zafarani-Moattar, M. T.; Hamzehzadeh, S. 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. *J. Chem. Eng. Data* **2009**, *54*, 833–841.

(2) Zafarani-Moattar, M. T.; Hamzehzadeh, S. Liquid-Liquid Equilibria of Aqueous Two-Phase Systems Containing 1-Butyl-3-methylimidazolium Bromide and Potassium Phosphate or Dipotassium Hydrogen Phosphate at 298.15 K. *J. Chem. Eng. Data* **2007**, *52*, 1686–1692.

(3) Sadeghi, R. Measurement and Correlation of Phase Equilibria for Several PVP + Salt Aqueous Two-phase Systems at 303.15K. *Fluid Phase Equilib.* **2005**, *237*, 40–47.

(4) Salabat, A. The Influence of Salts on the Phase Composition in Aqueous Two-Phase Systems: Experiments and Predictions. *Fluid Phase Equilib.* **2001**, *187* (188), 489–498.

(5) Katayama, H.; Miyahara, M. Liquid-Liquid Phase Equilibria of (Ethanol or Methanol + Water) Containing either Dipotassium Hydrogen Phosphate or Sodium Dihydrogen Phosphate. *J. Chem. Eng. Data* **2006**, *51*, 914–918.

(6) Wang, J.; Zhang, Y.; Wang, Y. Liquid-Liquid Equilibria for 1-Propanol (or 2-Propanol) -Water Systems Containing Potassium Fluoride. *J. Chem. Eng. Data* **2002**, *47*, 110–112.

(7) Zafarani-Moattar, M. T.; Seifi-Aghjekohal, P. Liquid-Liquid Equilibria of Aqueous Two-phase Systems Containing Polyvinylpyrrolidone and Tripotassium Phosphate or Dipotassium Hydrogen Phosphate: Experiment and Correlation. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **2007**, *31*, 553–559.

(8) Huddleston, J. G.; Willauer, H. D.; Rogers, R. D. Phase Diagram Data for Several PEG + Salt Aqueous Biphasic Systems at 25 °C. *J. Chem. Eng. Data* **2003**, *48*, 1230–1236.

(9) Pei, Y.; Wang, J.; Liu, L.; Wu, K.; Zhao, Y. Liquid-Liquid Equilibria of Aqueous Biphasic Systems Containing Selected Imidazolium Ionic Liquids and Salts. *J. Chem. Eng. Data* **2007**, *52*, 2026–2031.

(10) Deng, Y.; Chen, J.; Zhang, D. Phase Diagram Data for Several Salt + Salt Aqueous Biphasic Systems at 298.15 K. *J. Chem. Eng. Data* **2007**, *52*, 1332–1335.

(11) Sadeghi, R. Aqueous Two-phase Systems of Poly(vinylpyrrolidone) and Potassium Citrate at Different Temperatures—Experimental Results and Modeling of Liquid-Liquid Equilibrium Data. *Fluid Phase Equilib.* **2006**, *246*, 89–95.

(12) Regupathi, I.; Murugesan, S.; Govindarajan, R.; Amaresh, S. P.; Thanapalan, M. Liquid- Liquid Equilibrium of Poly(ethylene glycol) 6000 + Triammonium Citrate + Water Systems at Different Temperatures. *J. Chem. Eng. Data* **2009**, *54*, 1094–1097.

(13) Zafarani-Moattar, M. T.; Banisaeid, S.; Beirami, M. A. S. Phase Diagrams of Some Aliphatic Alcohols + Potassium or Sodium Citrate + Water at 25 °C. *J. Chem. Eng. Data* **2005**, *50*, 1409–1413.

(14) Guan, Y.; Lilley, T. H.; Treffry, T. E. A New Excluded Volume Theory and its Application to the Coexistence Curves of Aqueous Polymer Two-phase Systems. *Macromolecules* **1993**, *26*, 3971–3979.

(15) Zafarani-Moattar, M. T.; Tolouei, S. Liquid-Liquid Equilibria of Aqueous Two-phase Systems Containing Polyethylene Glycol 4000 and Di-Potassium Tartrate, Potassium Sodium Tartrate, or Dipotassium Oxalate: Experiment and Correlation. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **2008**, *32*, 655–660.

(16) Othmer, D. F.; Tobias, P. E. Liquid-Liquid Extraction Data-Toluene and Acetaldehyde Systems. *Ind. Eng. Chem.* **1942**, *34*, 690–692.

(17) Merchuk, J. C.; Andrews, B. A.; Asenjo, J. A. Aqueous Two-phase Systems for Protein Separation: Studies on Phase Inversion. *J. Chromatogr. B* **1998**, *711*, 285–293.

(18) Wang, Y.; Yan, Y.; Hu, S.; Han, J.; Xu, X. Phase Diagrams of Ammonium Sulfate + Ethanol/1-Propanol/2-Propanol + Water Aqueous Two-Phase Systems at 298.15 K and Correlation. *J. Chem. Eng. Data* **2010**, *55*, 876–881.

Received for review May 12, 2010. Accepted October 23, 2010. Financial support from the Natural Science Foundation of Jiangsu Province (BK2010349) and the National Natural Science Foundation of China (21076098; 20976074) is gratefully acknowledged.

JE100501F