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Liquid–liquid equilibrium of aqueous two-phase systems containing poly(propylene glycol) and salt ($(NH_4)_2SO_4$, $MgSO_4$, KCl, and KAc): experiment and correlation

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ABSTRACT

Binodal data of poly(propylene glycol) PPG_{400} + salt ($(NH_4)_2SO_4$, $MgSO_4$, and KCl) + H_2O systems were determined at T = 298.15 K, and binodal data of PPG_{400} + KAc + H_2O system was determined at T = (298.15, 308.15, and 318.15) K. Moreover, the binodal curves were fitted to Merchuk equation, and the tie-lines were fitted to both the Othmer–Tobias and Bancroft equations. The effects of temperature and salts on the binodals and tie-lines of the investigated ATPSs were also studied. Finally, the salting-out ability of salts on the polymer was obtained by fitting the Setschenow-type equation to the tie-line data to derive a salting-out coefficient (k_S) for each salt. For potassium salts, the relative effectiveness of the anions in inducing the phase segregation in ATPSs follows the Hofmeister series. The relative salting-out effectiveness of the sulfate salts is influenced by complexation of the cations by PPG.

1. Introduction

Liquid–liquid extraction has often been a favored choice in separation and purification processes. However, it faced some challenge such as toxicity, volatility, and flammability. Aqueous two-phase systems (ATPSs) have been of increasing importance as a method for the separation and purification of biological material [1–3] in biochemistry and biotechnology. It has been established that ATPSs can be formed by combining hydrophilic solutes (polymer–polymer or polymer–salt) in aqueous solution above critical concentrations. Low molecular weights of polypropylene glycol (PPG) are completely soluble in water, while high molecular weights are only partially soluble. This polymer can also be used for the separation of biomolecules, since its aqueous solutions form a two-phase system. A few years ago, Salabat et al. used ATPS of PPG425 + $MgSO_4$ + H_2O at 298.15 K to separate amino acids [4]. Now they investigated the applicability of the systems composed of PPG and some inorganic salts to proteomic analysis [5]. Reliable liquid–liquid equilibrium (LLE) data are necessary for the design of a separation process, understanding of general factors determining partition of solutes and particles in such ATPSs, and development and testing of both thermodynamic and mass transfer models of ATPSs. However, LLE data of PPG-based ATPSs are relatively scarce. The LLE data of PPG-based ATPSs containing phosphates, sulphates, carbonates, and citrates have been studied [6–10].

Ananthapadmanabhan et al. [11–13] systematically investigated the phenomenon of aqueous two-phase formation in mixtures of PEO and electrolytes in water. They found that two-phase formation occurs with anions such as sulfate which have a marked salting-out effect on non-electrolytes but for singly charged ions such as iodide only one phase exists. The formation of the two phases in polymer–salt system is due to the "salting-out" effect of salt, in other words, polymer and salt are strongly associated with the water molecules but exclude each other by separating into two phases. In many previous studies, the salting-out ability of salts or ions is always compared by binodal curves plotted in mass fraction [14–16]. In fact, it cannot exactly reflect the nature of interaction between molecules in the system. Wang et al. investigated the salting-out abilities of organic salts in several hydrophilic alcohol + citrate ATPSs at 298.15 K by the binodal curves plotted in molality [17]. Many ionic liquid + salt ATPSs also used binodal curves plotted in molality to discuss salting-out abilities of salts [18,19]. Zafarani-Moattar et al. used Setschenow-type equation to describe the salting-out effects of the tri-potassium citrate salt on 1-butyl-3-methylimidazolium bromide in the IL + salt ATPS at different temperatures [19]. Therefore, we decided to use the binodal curves plotted in molality and salting-out coefficient (k_s) of Setschenow-type equation to evaluate the salting-out ability of different salts in the investigated PPG_{400} + salt ATPS.

In this research, LLE binodal curves and tie-lines for the aqueous PPG_{400} + salt ($(NH_4)_2SO_4$, $MgSO_4$, KCl, and KAc) + H_2O ATPSs

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Table 1
Binodal curve data as the mass fraction for the PPG_{400} (1) + salt (2) + H_2O (3) systems at T = (298.15, 308.15, and 318.15) K.

$MgSO_4$ (298.15 K)		$(NH_4)_2SO_4$ (298.15 K)		KCl (298.15 K)		KAc (298.15 K)		KAc (308.15 K)		KAc (318.15 K)	
$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$
46.15	0.55	61.92	0.45	91.12	0.36	89.47	0.29	86.94	0.15	65.32	0.14
44.40	0.61	57.53	0.76	86.01	0.60	85.09	0.36	83.30	0.27	49.03	0.70
43.10	0.71	55.59	0.92	78.75	0.95	77.16	0.64	58.42	1.49	44.69	0.82
39.79	1.00	52.65	1.22	74.11	1.38	69.81	1.27	54.99	1.71	41.05	0.99
37.61	1.34	48.83	1.71	70.81	1.68	57.41	2.49	52.10	1.90	29.46	1.82
34.41	1.78	45.98	2.11	64.17	2.51	43.00	4.17	47.96	2.24	27.18	1.97
32.07	2.14	37.24	3.77	56.53	3.57	35.78	5.24	36.44	3.14	23.17	2.36
30.48	2.43	34.83	4.29	47.05	4.94	32.07	5.82	23.11	4.97	21.43	2.57
27.26	3.23	32.80	4.77	41.73	5.72	26.39	6.89	20.65	5.36	17.47	3.21
24.87	3.86	31.04	5.16	34.65	6.86	23.24	7.69	18.21	5.93	16.10	3.47
21.62	4.91	29.44	5.51	30.05	7.66	19.66	8.69	12.45	7.77	14.03	3.89
18.36	6.07	27.95	5.86	25.06	8.98	18.03	9.22	10.87	8.44	9.29	5.48
16.58	6.71	25.07	6.65	22.23	9.73	14.07	10.76	9.07	9.15	7.61	6.27
14.30	7.63	17.65	8.68	20.89	10.07	13.12	11.19	9.03	9.25	4.20	9.01
11.75	8.67	10.41	11.35	17.00	11.72	6.13	14.99	8.14	9.78	3.65	9.82
9.85	9.50	7.27	12.66	15.05	12.37	4.30	16.74	6.14	11.5	2.96	10.85
8.39	10.18	5.14	13.79	12.25	13.62	3.17	18.38	5.01	12.57	2.68	11.35
6.13	11.48	3.48	15.34	10.38	14.96	2.19	19.84	3.78	13.79	2.01	13.07
4.97	12.26	2.80	16.08	7.73	16.69	1.58	21.63	3.32	14.58	1.54	14.55
4.01	12.89	1.86	17.34	5.80	18.22	1.09	23.45	2.95	15.23	1.35	15.58
3.50	13.36	1.12	19.96	4.31	19.90					1.19	16.11
3.12	13.70			3.47	20.59						
2.69	14.19			2.19	22.57						
2.27	14.80			0.99	24.55						

have been studied. The obtained binodal data and tie-lines were correlated using empirical equations. Moreover, the effect of temperature on the binodal curves and tie-lines were studied. Finally, the influence of salts on the phase-forming ability has also been studied.

2. Experimental

2.1. Chemicals

PPG with a quoted molar mass of 400 g mol^{-1} was obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). Potassium acetate (KAc), $(NH_4)_2SO_4$, $MgSO_4$, and KCl were purchased from Sinopharm Chemical Reagent Co., Ltd. (Nanjing, China) with a minimum mass fraction purity of 0.985, 0.990, 0.990, 0.990, and 0.995, respectively. The polymer and salts were used without further purification. Double distilled deionized water was used in the experiments.

2.2. Apparatus and procedure

The phase diagram includes the binodal curve and tie-lines. The titration method was used to determine the phase equilibrium concentrations for establishing binodal curves. From the stock, a polymer solution of known mass fraction was filled into the vessel. A salt solution of known concentration was then added to the vessel until the mixture became turbid or cloudy, which indicates the two-phase formation. Then, water was added until the disappearance of turbidity and the procedure was repeated and so on. The composition of the mixture was measured on an analytical balance with a precision of ±0.0001 g. The system temperature was maintained constant and controlled to within ±0.05 K.

The phase equilibrium experiments were carried out in glass separators (25 mL). The feed samples were prepared by mixing appropriate amounts of PPG_{400}, salt, and H_2O in the vessel. The samples were stirred for 1 h at a desired temperature, and then the mixture was allowed to settle for at least 24 h at constant temperature using a thermostat. When phases were separated, they were properly diluted to determine PPG_{400} and salts equilibrium concentrations. The concentrations of $MgSO_4$, KCl, and KAc in the top and bottom phases were determined by flame photometry. The uncertainty in the measurement of the mass fraction of the salts was estimated to be ±0.001. The concentrations of $(NH_4)_2SO_4$ were determined by the formaldehyde method:

$$4NH_4^+ + 6HCHO \rightarrow (CH_2)_6N_4 + 4H^+ + 6H_2O$$

The H^+ formed was titrated using a sodium hydroxide solution. Titration of solution of known concentration indicated that this method is very accurate and reproducible. The uncertainty in the measurement of the salt was estimated to be ±0.002. Following Cheluget et al. [20] the concentration of PPG in both phases was determined by refractive index measurements performed at 298.15 K using a refractometer. Because the refractive index of the phase samples depends on polymer and salt concentration and it is an additive property, we obtained the PPG concentration by subtracting the salt concentration from the total solution composition. The uncertainty of the mass fraction of PPG was better than 0.002.

3. Results and discussion

3.1. Binodal data and correlation

For PPG_{400} + salt ($(NH_4)_2SO_4$, $MgSO_4$, KCl, and KAc) + H_2O systems, the binodal data determined at T = 298.15 K, and in part at T = (308.15–318.15) K are shown in Table 1. For correlation of binodal data for the studied systems, the following non-linear expression developed by Merchuk [21] has been successfully used by Huddleston et al. [22]:

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

where w_1 and w_2 are the mass fractions of PPG_{400} and salt, respectively. Recently, this equation has been successfully used for the correlation of the binodal data of polymer-based ATPSs [23,24] and ionic liquid-based ATPSs [25,26]. Using Eq. (1), the coefficients a, b and c along with the corresponding standard deviations for the investigated systems were obtained, and the results are listed in Table 2. On the basis of the standard deviations obtained, we conclude that Eq. (1) can be satisfactorily used to correlate the binodal curves.

Table 2
Values of *a*, *b*, *c*, and standard deviation of Eq. (1) for the PPG_{400} (1) + salt (2) + H_2O (3) systems at T = (298.15, 308.15, and 318.15) K.

Salt	a	b	c	R^2	sd[a]
$(NH_4)_2SO_4$ (298.15 K)	81.31	−0.40	0.00049	0.9995	0.50
$MgSO_4$ (298.15 K)	64.29	−0.47	0.00050	0.9998	0.23
KCl (298.15 K)	120.50	−0.43	0.00029	0.9954	1.91
KAc (298.15 K)	116.18	−0.49	0.00041	0.9961	1.70
KAc (308.15 K)	113.60	−0.60	0.00095	0.9896	2.55
KAc (318.15 K)	96.26	−0.90	0.00051	0.9918	1.55

[a] $sd = \left(\sum_{i=1}^{N} \frac{(100w_{1,i}^{cal} - 100w_{1,i}^{\exp})^2}{N} \right)^{0.5}$, where *N* is the number of binodal data.

3.2. Tie-line data and correlation

The liquid–liquid equilibrium data for the PPG_{400} + salt ($(NH_4)_2SO_4$, $MgSO_4$, KCl, and KAc) + H_2O systems determined at T = 298.15 K, and in part at T = (308.15–318.15) K are shown in Table 3. Empirical equations have been proposed to model the equilibrium results of traditional liquid–liquid extraction, the most used being those of The Othmer–Tobias equation (Eq. (2)) and Bancroft equation (Eq. (3)) [27,28].

$$\left[\left(\frac{1-w_1^t}{w_1^t}\right)\right] = k\left[\left(\frac{1-w_2^b}{w_2^b}\right)\right]^n \tag{2}$$

$$\left(\frac{w_3^b}{w_2^b}\right) = k_1\left(\frac{w_3^t}{w_1^t}\right)^r \tag{3}$$

where k, n, k_1, and r are the fitting parameters; w_1^t, w_1^b, w_2^t, w_2^b, w_3^t, and w_3^b are the mass fraction of PPG, salt, and water in the top and bottom phases, respectively. Recently, the equations have been successfully used for assessment and correlation of tie-line compositions of polymer-based ATPSs [24], hydrophilic organic solvents-based ATPSs [29], and ionic liquid-based ATPSs [25,26], hence these equations were used to correlate the liquid–liquid equilibrium data of the investigated systems. A linear dependency of the plots $\log((1-w_1^t)/w_1^t)$ against $\log((1-w_2^b)/w_2^b)$ and $\log(w_3^b/w_2^b)$ against $\log(w_3^t/w_1^t)$ indicated an acceptable consistency of the results. The fitting parameters, R^2 and the standard deviations are given in Table 4, from which we conclude that Eqs. (2) and (3) can satisfactorily correlate the tie-line compositions of the investigated systems.

3.3. Effect of salts on binodal curves and tie-lines

To see the effectiveness of the salts in forming ATPSs with PPG, the experimental binodal curves of the PPG_{400} + salt ($(NH_4)_2SO_4$, $MgSO_4$, KCl, and KAc) + H_2O systems at T = 298.15 K are shown in Fig. 1. The binodal curves for the PPG_{400} + salt (K_3PO_4, K_2HPO_4, K_2CO_3) + H_2O systems [30] studied previously were also collected in Fig. 1. The salting-out ability of salts or ions is always compared by binodal curves plotted in mass fraction. In fact, it cannot exactly reflect the nature of interaction between molecules in the system. Therefore, we decided to use the binodal curves plotted in molality to see the effect of the type salt on the phase-forming ability. As seen in Fig. 1, the effect of potassium salts in salting-out the PPG to form the two-phase system essentially

Table 3
Tie-line compositions as mass fraction for the PPG_{400} (1) + salt (2) + H_2O (3) systems at T = (298.15, 308.15, and 318.15) K.

Total composition		Top phase: polymer-rich phase		Bottom phase: salt-rich phase	
$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$
PPG_{400} + $(NH_4)_2SO_4$ + H_2O (298.15 K)					
18.07	10.03	44.24	2.46	5.18	13.78
20.01	10.97	48.35	1.75	2.16	16.67
20.92	11.91	50.68	1.46	1.25	18.70
22.53	13.01	53.69	1.18	0.48	21.48
PPG_{400} + $MgSO_4$ + H_2O (298.15 K)					
18.50	6.50	26.53	3.43	7.60	10.62
19.09	6.98	32.16	2.11	5.14	12.19
20.08	6.98	34.67	1.76	4.08	12.81
22.39	7.93	41.89	0.84	2.09	15.06
PPG_{400} + KCl + H_2O (298.15 K)					
20.27	13.00	78.75	0.95	9.11	15.50
17.30	14.02	80.26	0.84	8.84	15.73
19.95	14.02	84.59	0.62	8.36	16.30
PPG_{400} + KAc + H_2O (298.15 K)					
18.08	13.50	78.26	0.82	6.33	16.15
24.56	14.04	81.56	0.58	3.56	19.55
27.63	15.27	83.00	0.54	2.00	22.03
PPG_{400} + KAc + H_2O (308.15 K)					
24.34	7.02	73.82	0.75	10.01	8.86
26.02	8.00	77.90	0.48	6.50	10.80
28.05	9.52	82.50	0.28	4.07	13.68
PPG_{400} + KAc + H_2O (318.15 K)					
27.04	3.29	53.02	0.55	10.56	5.01
28.04	4.20	62.55	0.25	7.88	6.47
30.96	4.98	70.89	0.10	5.44	8.17

Table 4
Values of parameters of Eqs. (2) and (3) for PPG$_{400}$ (1) + salt (2) + H$_2$O (3) systems at T = (298.15, 308.15, and 318.15) K.

Salt	k	n	R^2	k_1	r	R^2	dev[a]
(NH$_4$)$_2$SO$_4$ (298.15 K)	0.35	0.70	0.9998	4.62	1.33	0.9993	0.04
MgSO$_4$ (298.15 K)	0.069	1.73	0.9995	4.72	0.51	0.9987	0.05
KCl (298.15 K)	3.78×10^{-6}	6.66	0.9982	5.79	0.13	0.9988	1.18
KAc (298.15 K)	0.074	0.80	0.9970	20.39	1.09	0.9973	0.60
KAc (308.15 K)	0.031	1.05	0.9998	22.44	0.84	0.9999	0.01
KAc (318.15 K)	0.012	1.47	0.9996	18.20	0.61	0.9995	0.11

[a] $dev = (\sum_p \sum_l \sum_j (100w_{p,l,j}^{cal} - 100w_{p,l,j}^{\exp})^2/6N)$, where $w_{p,l,j}$ is the mass fraction of the component j (i.e. polymer, salt or water) in the phase p for lth tie-line. N is the number of tie-line data.

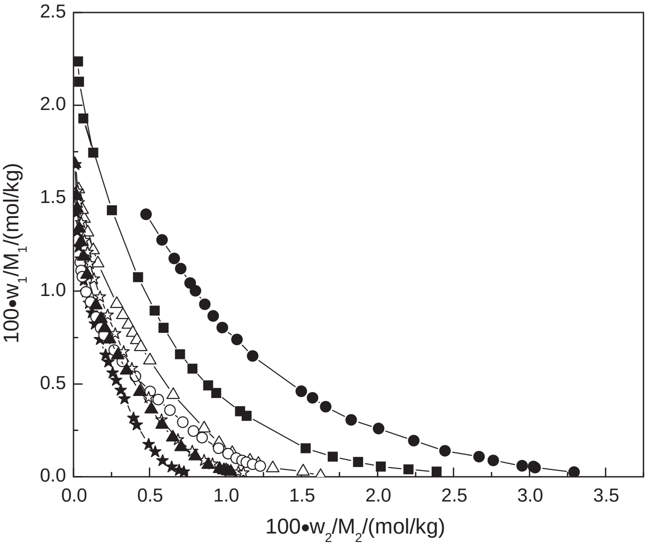

Fig. 1. Effect of the type of salt on the binodal curves for the PPG$_{400}$ (1) + salt (2) + water (3) ATPSs at T = 298.15 K: ★, K$_3$PO$_4$; ▲, K$_2$HPO$_4$; ☆, K$_2$CO$_3$; ○, MgSO$_4$; △, (NH$_4$)$_2$SO$_4$; ■, KAc; ●, KCl.

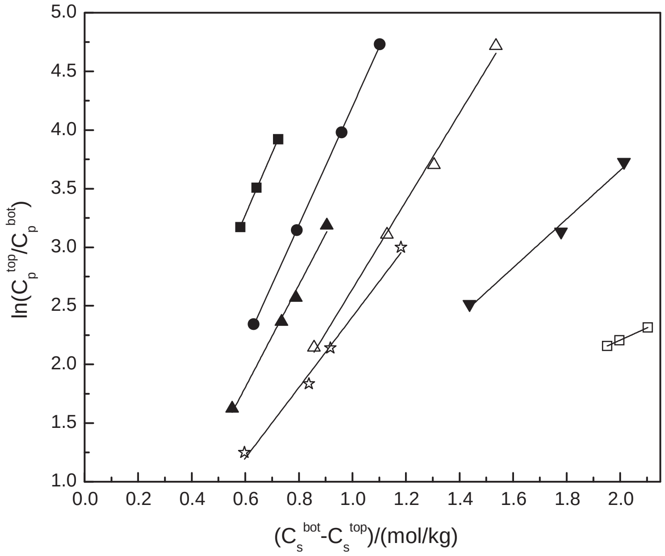

Fig. 2. Experimental and calculated tie-lines with the Setschenow-type plots of the PPG$_{400}$ (1) + salt (2) + H$_2$O (3) systems: ■ K$_3$PO$_4$; ●, K$_2$HPO$_4$; ▲, K$_2$CO$_3$; ▼, KAc; □, KCl; ☆, MgSO$_4$; △, (NH$_4$)$_2$SO$_4$.

follows the order: K$_3$PO$_4$ > K$_2$HPO$_4$ > K$_2$CO$_3$ > KAc > KCl. It implies that anions with a higher valence are better salting-out agents than anions with a lower valence, because higher-valence anions hydrate more water than lower-valence anions, thus decreasing the amount of water available to hydrate PPG. The salting-out ability can also be related to the Gibbs free energy of hydration of ions($\Delta_{hyd}G$), as proposed by Marcus [31]. It was found that better salting-out of PPG is observed when the ions have a more negative Gibbs free energy {$\Delta_{hyd}G$(PO$_4^{3-}$) = −2765 kJ/mol > $\Delta_{hyd}G$ (HPO$_4^{2-}$) = −1789 kJ/mol > $\Delta_{hyd}G$ (CO$_3^{2}$) = −1315 kJ/mol > $\Delta_{hyd}G$ (Ac$^-$) = −365 kJ/mol > $\Delta_{hyd}G$ (Cl$^-$) = −340 kJ/mol} [31,32].

The effectiveness of cations to form aqueous two-phase systems with PPG was also investigated. When comparing the salts having the same anion, we can conclude that the salting-out ability of the cations follows the ordering Mg^{2+} > NH$_4^+$ from Fig. 1. This can be explained by the different Gibbs energies of hydration of Mg^{2+} ($\Delta_{hyd}G$ = −1830 kJ/mol) and NH$_4^+$ ($\Delta_{hyd}G$ = −285 kJ/mol) [31].

The salting-out strength of salts could also be evaluated by the salting-out coefficient (k_S). In this paper, Setschenow-type equation proposed by Hey et al. [33] for PEG + salt ATPSs was used to correlate the experimental tie-line compositions for the investigated systems. The salting-out coefficient (k_S) can be determined using the following Setschenow-type equation.

$$\ln\left(\frac{C_p^t}{C_p^b}\right) = k_p\left(C_p^b - C_p^t\right) + k_s\left(C_s^b - C_s^t\right) \qquad (4)$$

where C_p, C_s, k_p, and k_s represent the molality of polymer, the molality of salt, a parameter relating the activity coefficient of polymer to its concentration, and the salting-out coefficient, respectively. If the first term on the right-hand side of this equation is very small compared with the second term, then a Setschenow-type equation is obtained. This would say the second term in Eq. (4) is greater than the first term. The fitting parameters along with the corresponding

Table 5
Values of k_s and intercept from least-squares linear fits to the Setschenow-type equation (Eq. (4)) for PPG$_{400}$ (1) + salt (2) + H$_2$O (3) systems at T = (298.15, 308.15, and 318.15) K.

Salt	k_S/(kg mol^{-1})	Intercept	R^2	dev[a]
(NH$_4$)$_2$SO$_4$ (298.15 K)	3.75	−1.11	0.9945	1.19
MgSO$_4$ (298.15 K)	3.02	−0.61	0.9882	0.77
KCl (298.15 K)	1.04	0.14	0.9997	0.14
KAc (298.15 K)	1.91	−0.50	0.9825	1.56
KAc (308.15 K)	1.86	0.48	0.9897	0.93
KAc (318.15 K)	2.59	0.43	0.9999	0.11

[a] $dev = (\sum_p \sum_l \sum_j (100w_{p,l,j}^{cal} - 100w_{p,l,j}^{\exp})^2/6N)$, where $w_{p,l,j}$ is the mass fraction of the component j (i.e. polymer, salt or water) in the phase p for lth tie-line. N is the number of tie-line data.

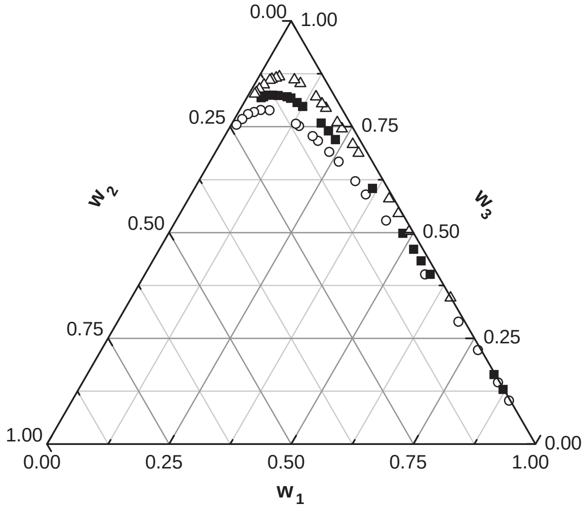

Fig. 3. Effect of temperature on the binodal curves for the PPG_{400} (1) + KAc (2) + H_2O (3) systems: ■, 298.15 K;■, 308.15 K; ■, 318.15 K.

standard deviations are presented in Table 5 for the investigated systems.

To see more closely the relation between the Setschenow-type behavior and the phase diagrams, the Setschenow-type plots of the tie-line data for the investigated systems have also been shown in Fig. 2. The increase in k_s is reflected in the phase diagram by a shift in the position of binodal curve to the top corresponding to a decrease in the area representing single-phase mixture. For the potassium salts mentioned previously, the rank order of the k_s values can be established: PO_4^{3-} (5.28 kg mol^{-1}) > HPO_4^{2-} (5.06 kg mol^{-1}) > CO_3^{2-} (4.36 kg mol^{-1}) > Ac^- (1.91 kg mol^{-1}) > Cl^- (1.04 kg mol^{-1}), indicating their interactions with water molecules become stronger. The relative effectiveness of the anions in inducing the phase segregation in ATPSs follows the Hofmeister series (HS) [31].

For sulfate salts, the k_s values are in the order of $NH_4^+ > Mg^{2+}$. From studied effects of inorganic salts on the cloud points, critical micelle concentrations and surface tensions of non-ionic surfactants in aqueous solution, Schott et al. [34–37] shown that polyoxyethylene chains act as polydentate ligands in the complexation of di- and trivalent cations, which lead to a salting-in effect opposes the salting-out associated with the sulfate ions. This may be the reason for the decreased curvatures of the binodals for mixtures containing $MgSO_4$ compared to those for $(NH_4)_2SO_4$.

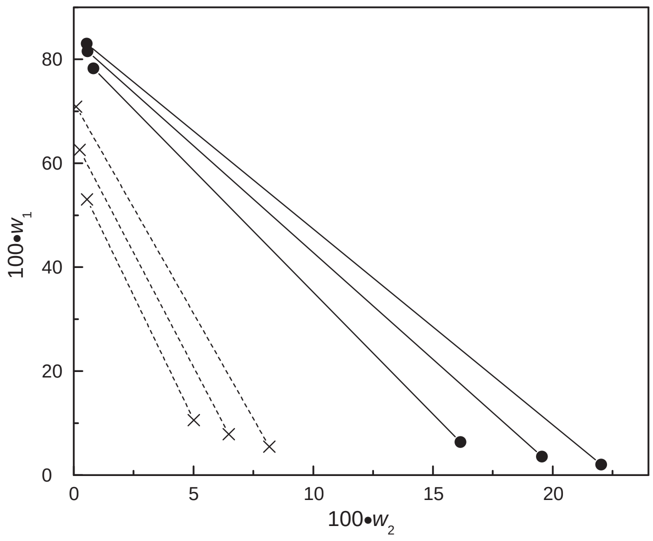

Fig. 4. Effect of temperature on the tie-lines for the PPG_{400} (1) + KAc (2) + H_2O (3) systems: ●, 298.15 K; ×, 308.15 K.

3.4. *Effect of temperature on binodal curves and tie-lines*

As an example, the effect of temperature on phase separation of PPG_{400} + KAc + H_2O were determined at T = (298.15, 308.15, and 318.15) K. The results are illustrated in Fig. 3. The locus for the experimental binodals shown in Fig. 3 demonstrates that the two-phase area is expanded with an increase in temperature, in other words, if we take a sample on the binodal with a known composition, this mixture becomes a two-phase system by increase in temperature. With increasing temperature, PPG becomes more hydrophobic [10], that is, the solubility of PPG in water decreases, which results a decrease in the critical concentration of a salt required to form two-phase system.

Fig. 4 shows the effect of temperature on the equilibrium phase compositions. In the temperature range considered, the absolute values of slopes of the tie-lines increase with increasing temperature. A possible explanation for this change is that PPG becomes more hydrophobic with increasing temperature. Thus, by increasing temperature, water is driven from the polymer-rich phase to the salt-rich phase, so the PPG_{400} concentration at the polymer-rich phase increases, whereas the salt-rich phase will somewhat be diluted.

4. Conclusions

Experimental binodal data and liquid–liquid equilibrium data have been determined for the PPG_{400} + salt ($(NH_4)_2SO_4$, $MgSO_4$, KCl, and KAc) + H_2O aqueous two-phase systems at T = 298.15 K, and in part at T = (308.15–318.15) K. The binodal curves were fitted to Merchuk equation relating the concentrations of PPG and salt. Moreover, the effect of temperature on phase-forming ability has been studied, and it was observed that the two-phase area increased with increase in temperature. The influence of salts on phase-forming ability have been studied, and it was found that ions with a higher valence are better salting-out agents than ions with a lower valence, which may be related to the Gibbs free energy of hydration of ions($\Delta_{hyd}G$). Finally, tie-line compositions were estimated and correlated with Othmer–Tobias and Bancroft equations.

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