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Phase equilibrium in aqueous two-phase systems containing poly(vinylpyrrolidone) and sodium citrate at different temperatures—Experimental and modeling

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Abstract

The phase diagrams and compositions of coexisting phases have been determined for aqueous two-phase systems containing poly(vinylpyrrolidone) (PVP) and sodium citrate at various temperatures of 298.15, 308.15, 318.15 and 328.15 K. The effect of temperature on the salting-out effect of poly(vinylpyrrolidone) by sodium citrate has been studied. It was found that, an increasing in temperature caused the expansion of two-phase region. Increasing temperature also increases the concentration of PVP in the PVP-rich phase, while the salt-rich phase will be somewhat mole diluted. Furthermore, it was found that, as temperature is increased, this aqueous two-phase system exhibits a phase inversion. Specifically, the PVP-rich phase – which at low temperatures is the less dense top phase – becomes the lower phase at elevated temperatures. The results have been discussed on the basis of the effect of temperature on the hydrophobicity of the polymer. Furthermore, the Wilson model has been used for the correlation of the experimental liquid–liquid equilibrium data.

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Keywords: Aqueous two-phase systems; Liquid–liquid equilibrium; Sodium citrate; Polyvinylpyrrolidone; Wilson

1. Introduction

Ternary aqueous solutions of poly(vinylpyrrolidone) (PVP) and certain electrolytes separate into a PVP-rich and a salt-rich phase over part of the composition space. Aqueous two-phase systems of this nature are useful for the separation and purification of biomaterials where the employment of a nonpolar solvent/aqueous phase system would lead to degradation of biological activity [1,2]. Liquid–liquid equilibrium (LLE) data for some aqueous PVP + inorganic salt two-phase systems have been reported in the literature [3–5]. In these studies [3–5], salting out of PVP has been accomplished by the use of either phosphates or sulfates. These salts, however, lead to high phosphate or sulfate concentration in the effluent streams and therefore, to environmental concern. Citrate is biodegradable and nontoxic and could be discharged into biological wastewater treatment plants and therefore the citrates can be considered as a substitute for inorganic salts, because the citrate forms aqueous two-phase system with PVP which are suitable for protein extraction. In our previous work [6], the phase diagrams and compositions of coexisting phases were determined for aqueous two-phase systems containing PVP and potassium citrate at various temperatures of 298.15, 308.15 and 318.15 K. As far as we know, there is no report on the phase diagram of the PVP + sodium citrate + water system in the literature. In this work, the phase diagrams and LLE data have been determined for aqueous two-phase systems containing PVP and sodium citrate at various temperatures of 298.15, 308.15, 318.15 and 328.15 K. Also, the extended segment-based local composition Wilson model [6] has been used to correlate the experimental LLE data of investigated aqueous two-phase systems.

2. Experiments

2.1. Materials

PVP (K15), of molecular weight 10,000, was obtained from Aldrich. Sodium citrate was obtained from Merck (GR,

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Nomenclature

c	concentration
E	binary parameter in the Wilson model
k	salting-out coefficient
OF	objective function
S	solubility
T	temperature
x	mole fraction
Greek letter	
γ	activity coefficient
Subscripts	
a	anion
c	cation
ca	salt
j	any species, polymer, salt and water
l	tie-line
p	top and bottom phase or polymer
s	segment
w	water
0	pure water
Superscripts	
bot	bottom phase
cal	calculated value
exp	experimental value
top	top phase

min 99.5%). The polymer and salt were used without further purification, and double distilled, deionized water was used.

2.2. Apparatus and procedure

The experimental apparatus employed is essentially similar to the one used previously [6]. The binodal curves were determined by a titration method. A salt solution of known concentration was titrated with the polymer solution or vise versa, until the solution turned turbid. The composition of the mixture was determined by mass using an analytical balance with a precision of ±1 × 10^{-7} kg. To determine the compositions of coexisting phases, feed samples (about 20 cm^3) were prepared by mixing appropriate amounts of polymer, salt and water in the vessel. The thermostat was set at a desired temperature, and the sample was stirred for 1 h. Then the mixture was allowed to settle for 96 h. After separation of the two transparent phases, the concentrations of the salts 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 ±0.0002. The concentration of PVP in both phases was determined by refractive index measurements performed at 298.15 K. The uncertainty of the mass fraction of PVP achieved using this method was estimated to be 0.001.

Table 1
Binodal data for PVP (p) + Na_3cit (ca) + H_2O (w) systems at 298.15, 308.15, 318.15 and 328.15 K

298.15 K		308.15 K		318.15 K		328.15 K	
w_p	w_{ca}	w_p	w_{ca}	w_p	w_{ca}	w_p	w_{ca}
0.3574	0.0441	0.3632	0.0444	0.3511	0.0457	0.3669	0.0423
0.3502	0.0469	0.3452	0.0480	0.3392	0.0482	0.3564	0.0441
0.3304	0.0509	0.3188	0.0526	0.3235	0.0507	0.3326	0.0478
0.3078	0.0566	0.3069	0.0564	0.3052	0.0554	0.3153	0.0507
0.2753	0.0642	0.2777	0.0633	0.2792	0.0613	0.2921	0.056
0.2448	0.0729	0.2446	0.0714	0.2466	0.0686	0.2645	0.0616
0.2131	0.0817	0.2155	0.0794	0.2125	0.0762	0.2332	0.0683
0.2058	0.0841	0.1845	0.0871	0.1798	0.0836	0.201	0.0754
0.1760	0.0917	0.1538	0.0947	0.1758	0.0844	0.1763	0.0807
0.1492	0.0988	0.1278	0.1007	0.1516	0.0902	0.1410	0.0885
0.1250	0.1047	0.1252	0.1012	0.1390	0.0929	0.1090	0.0950
0.1017	0.1096	0.1184	0.1022	0.1248	0.0955		
		0.1070	0.1047	0.1103	0.0977		
				0.1019	0.0997		

3. Results and discussion

3.1. Experimental results

For the aqueous PVP + sodium citrate two-phase system the binodal data obtained from turbidimetric titrations and the tie line data for the compositions of conjugate solutions at 298.15, 308.15, 318.15 and 328.15 K are shown in Tables 1 and 2, respectively. The complete phase diagrams of all studied systems are shown in Figs. 1–4.

The formation of aqueous two-phase systems, clearly indicates the mutual exclusion of the ions and the polymer and their high affinity for the solvent. It is possible that even in homogeneous systems (below the phase boundary) the ions are excluded from the near surface region of the polymer in solution. With increase in the concentration of the polymer or the salt, the extent of exclusion will increase. Ultimately, the system could reach a

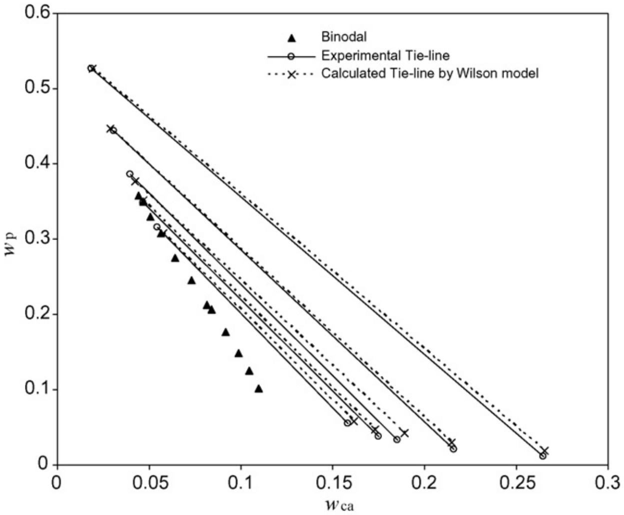

Fig. 1. Phase diagram of the PVP (p) + sodium citrate (ca) + H_2O (w) aqueous two-phase system at 298.15 K.

Table 2
Experimental phase equilibrium compositions for the PVP (p) + Na_3cit (ca) + H_2O (w) at 298.15, 308.15, 318.15 and 328.15 K

298.15 K				308.15 K				318.15 K				328.15 K			
Top		Bottom		Top		Bottom		Top		Bottom		Top		Bottom	
w_p	w_{ca}	w_p	w_{ca}	w_p	w_{ca}	w_p	w_{ca}	w_p	w_{ca}	w_p	w_{ca}	w_p	w_{ca}	w_p	w_{ca}
0.3152	0.0543	0.0545	0.1581	0.3480	0.0465	0.0462	0.1559	0.3630	0.0439	0.0404	0.1547	0.0616	0.1212	0.2635	0.0615
0.3490	0.0468	0.0375	0.1747	0.3741	0.0435	0.0309	0.1774	0.4010	0.0381	0.0228	0.1765	0.0400	0.1395	0.3309	0.0487
0.3862	0.0398	0.0330	0.1852	0.4447	0.0312	0.0204	0.2062	0.4114	0.0374	0.0252	0.1781	0.3807	0.0404	0.0356	0.1513
0.4436	0.0309	0.0200	0.2163	0.5152	0.0189	0.0098	0.2476	0.4567	0.0276	0.0241	0.1904	0.4157	0.0350	0.0309	0.1667
0.5271	0.0188	0.0116	0.2650									0.4921	0.0222	0.0264	0.1970

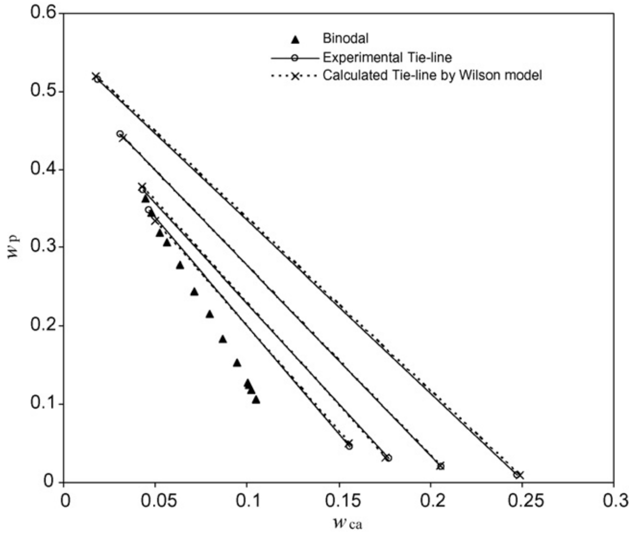

Fig. 2. Phase diagram of the PVP (p) + sodium citrate (ca) + H_2O (w) aqueous two-phase system at 308.15 K.

state where, for entropic reasons, phase formation would become favorable. In fact, salting-out effects are related to a reduction in entropy resulting from the exclusion of ions from volume elements immediately adjacent to the solute molecules. Exclusion of ions from the polymer molecule–water interface itself can occur for a number of reasons. Both the polymer and the ion are strongly hydrated in solution. Because of the hydration sheath, the near-surface region of the polymer may not be accessible to structure-making ions. Exclusion can occur also by repulsive interaction between the anions and the anionic-like imide group on the pyrrolidone ring especially in the presence of nonbonding cations like K^+, NH_4^+ and Na^+. In this respect, further details can be found in our previous work [6].

The binodal curves at different temperatures are given in Fig. 5. Fig. 5 shows that the two-phase area is expanded with increasing temperature. In other words, if we take a sample with a known composition on the binodal curve, this mixture becomes a two-phase system at increasing temperature as has been observed experimentally. It was found that, at higher temperatures, hydrogen bond interactions of PVP are weakened [7]. Depression of the cloud point by increasing temperature is may be related to the salting-out phenomenon resulting from the weakening of the PVP–solvent interaction. Salting-out effects are usually quantified by fitting solubility data of polymer to the empirical equation of Setschenow [8]:

$$\ln \frac{S_0}{S} = k_{ca} c_{ca} \tag{1}$$

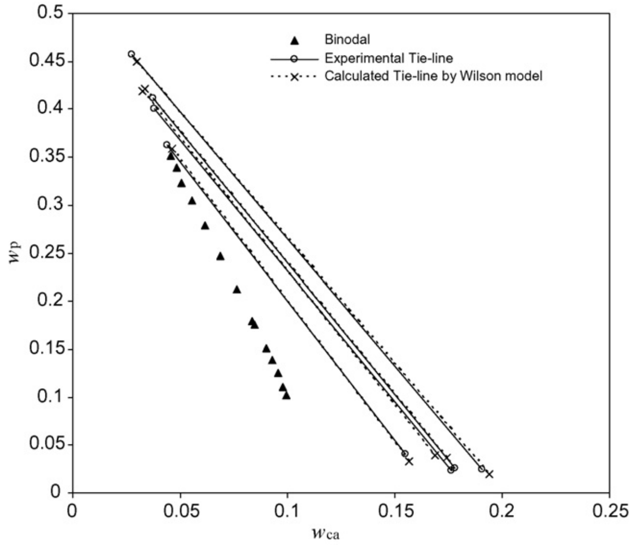

Fig. 3. Phase diagram of the PVP (p) + sodium citrate (ca) + H_2O (w) aqueous two-phase system at 318.15 K.

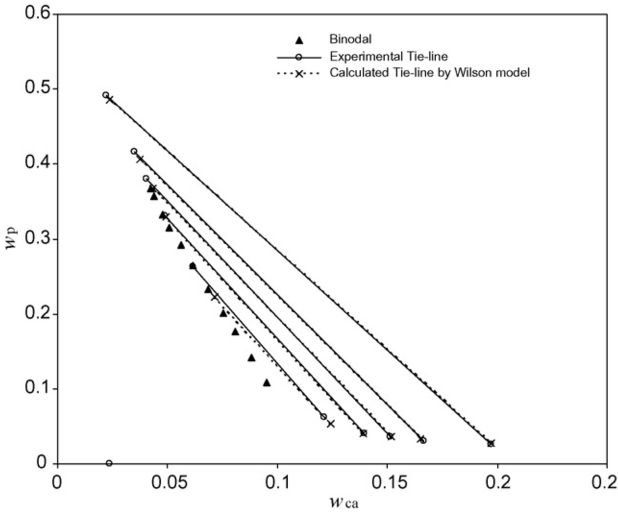

Fig. 4. Phase diagram of the PVP (p) + sodium citrate (ca) + H_2O (w) aqueous two-phase system at 328.15 K.

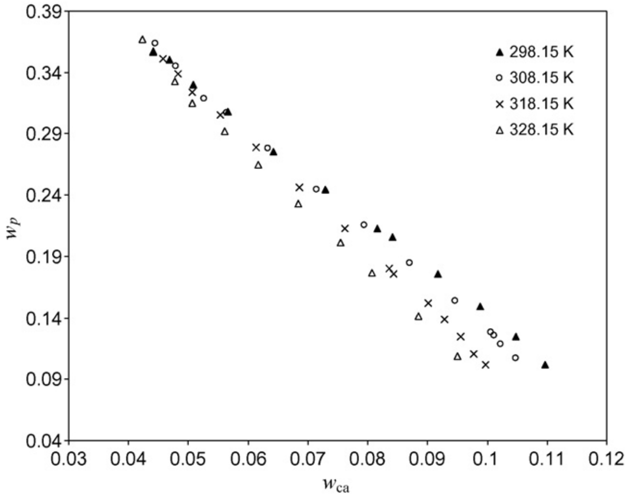

Fig. 5. Effect of temperature on the binodal curve of the PVP (p) + sodium citrate (ca) + H_2O (w) aqueous two-phase system.

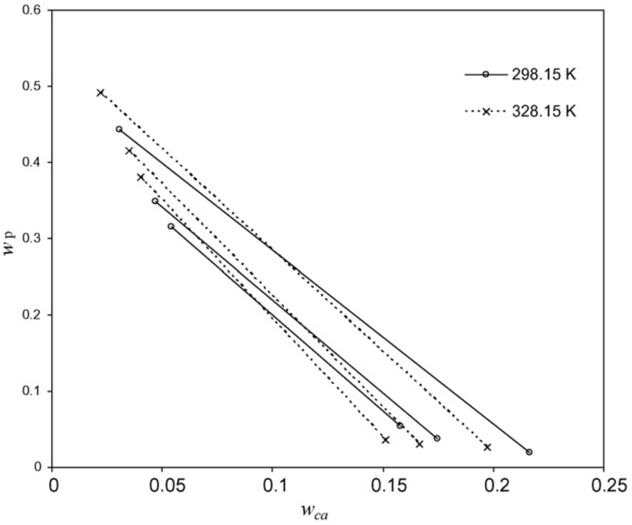

Fig. 6. Effect of temperature on the tie-lines for the PVP (p) + sodium citrate (ca) + H_2O (w) aqueous two-phase system.

where S_0 and S refer to the solubilities of the polymer in pure water and in a salt solution of concentration c_{ca}, respectively, and k_{ca}, the salting-out coefficient, is specific for a particular non-electrolyte/salt pair. In this work, a Setschenow-type equation has been applied for compositions on the binodal line separating the two-phase and one-phase regions in the phase diagram for PVP-salt solution i.e. the logarithm of the PVP concentration (weight fraction) against the salt concentration (weight fraction). The plots are linear for salt concentration up to about 0.088 and therefore at each temperature the binodal data in this regions were used for the calculation of k_s values. The values of the salting-out coefficient at 298.15, 308.15, 318.15 and 328.15 K were obtained as 14.0087, 15.4865, 17.7052 and 18.5998, respectively. Increasing of the salting-out coefficient by increasing temperature is in agreement with our experimental observations in which at higher temperatures, aqueous two-phase formation occurs at lower levels of the polymer and salt.

As shown in Fig. 6, the slope of the equilibrium tie-lines increase with increasing temperature. Also, by increasing temperature the volume of salt-rich phase increases at the expense of the PVP-rich phase, as we observed experimentally. This is because the compositions of the phases in equilibrium change with varying temperature. Increasing the temperature of the aqueous PVP-salt two-phase system will cause an increase of the concentration in the PVP-rich phase and a decrease of the concentration in the salt-rich phase. As mentioned above, the attraction between PVP and water will decrease with an increase in temperature and therefore by increasing temperature of the aqueous PVP-salt two-phase system water is driven from the PVP-rich phase to the salt-rich phase, so the PVP concentration of the PVP-rich phase increases, while the salt-rich phase will be somewhat more diluted (i.e. the salt concentration will be decreased), and the volume of the salt-rich phase increases at expense of the PVP-rich phase. Close examination of the tie-line data given in Table 2 indicate that, the PVP has been observed to enrich the upper phase, while the salt has been observed to enrich the lower phase for the aqueous PVP-salt systems at temperatures 298.15, 308.15 and 318.15 K. However, at 328.15 K the investigated system exhibit phase inversion. Specifically, the PVP-enriched phase-which is the less dense upper phase-becomes the lower phase at elevated temperatures. In fact inversion occurs at lower concentrations of either phase-forming constituent. As mentioned above, by increasing temperature water is driven from the PVP-rich phase to the salt-rich phase, so the PVP-rich phase is concentrated, while the salt-rich phase will be somewhat more diluted. Thus, by increasing temperature the density of PVP-rich phase increases while the density of salt-rich phase decreases and we expect there should be a temperature in which density of PVP-rich to be more than density of salt-rich phase and thus the phase inversion is occurred.

3.2. Theoretical results

In our previous work [9], we extended the Wilson model to represent the excess Gibbs energy of polymer-electrolyte solutions. The extended Wilson model was used for correlation of water activity data of some aqueous polymer-salt systems [9]. In our another previous work [6], a simple modification was done on this model and then used to correlate the experimental LLE data of PVP–potassium citrate aqueous two-phase systems. In this work, this extended Wilson model [6] is applied to correlation of liquid–liquid equilibrium data of the investigated aqueous two-phase systems. The model parameters of the extended Wilson model was estimated by minimizing the following objective function by the simplex method:

$$\mathrm{OF} = \sum_{p}\sum_{l}\sum_{j}(w_{p,l,j}^{\mathrm{cal}} - w_{p,l,j}^{\mathrm{exp}})^2 \tag{2}$$

where $w_{p,l,j}$ is the weight fraction of the component j in the phase p for lth tie-line. In this equation the species j can be polymer molecule, salt or solvent molecule. The liquid–liquid

Table 3
Values of parameters of the extended Wilson model for PVP (p) + Na3cit (ca) + H_2O (w) at different temperatures

T (K)	E_{sw} (J/mol)	E_{ws} (J/mol)	$E_{ca,w}$ (J/mol)	$E_{w,ca}$ (J/mol)	E_{cs} (J/mol)	E_{as} (J/mol)	$E_{sc,ac}$ (J/mol)	$E_{sa,ca}$ (J/mol)	Dev[a]
298.15	−5236.97	5979.24	−12619.04	7682.52	1442.84	1442.84	54.22	54.22	0.17
308.15	−1706.80	2725.17	−11754.83	15919.87	15482.15	15480.54	56.54	56.54	0.17
318.15	−1036.25	1954.23	−7613.92	1859.88	723.03	723.03	13.56	13.56	0.64
328.15	−528.50	2068.03	−9892.79	18937.00	26125.51	26125.51	56.84	56.84	1.08

[a] Dev = (OF/6N) × 100; where N is the number of tie-lines.

equilibrium data of Table 2 were correlated using the equilibrium condition:

$$(x_j\gamma_j)^{\text{top}} = (x_j\gamma_j)^{\text{bot}} \quad (3)$$

The fitting parameters of the extended Wilson model along with the corresponding deviations are given in Table 3. On the basis of the obtained deviations, given in Table 3, we conclude that the model represents the experimental liquid–liquid equilibrium data of the investigated aqueous two-phase systems with good accuracy. To show the reliability of the model, comparison between the experimental and correlated tie-lines are also shown in Figs. 1–4. As can be seen from Table 3, the energy parameters E_{ws} and E_{sw} have positive and negative values, respectively. From Eq. (16) of reference [6], we conclude that the interaction between two segments is stronger than the interaction between the solvent molecules and the segments which, in turn, is stronger than the interaction between two solvent molecules. Table 3 also shows that, the energy parameter $E_{ca,w}$ has negative values and energy parameter $E_{w,ca}$ has positive values. This result is not surprising since the interaction between the cation and the anion is stronger than the interaction between the solvent molecules and the ionic species which, in turn, is stronger than the interaction between two solvent molecules. Furthermore, Table 3 shows that the energy parameters between the cation and segment is same as those between the anion and segment. This is because the ions in the solution remain strongly associated with the solvent and therefore the ions do not have any interaction with the polymer segments.

4. Conclusions

The binodal curves and liquid–liquid equilibrium data for the aqueous two-phase PVP–sodium citrate system have been determined experimentally at 298.15, 308.15, 318.15 and 328.15 K. It was found that the salting-out of PVP by sodium citrate is increased with increasing temperature and therefore at higher temperatures, aqueous two-phase formation occurs at lower levels of the polymer and salt. Also it was found that, for the studied system increasing temperature caused an increase of the concentration in the PVP-rich phase and a decrease of the concentration in the salt-rich phase. Furthermore, the extended local composition model Wilson has been used to correlate the phase behavior of the investigated system.

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