

Aqueous two-phase systems of poly(vinylpyrrolidone) and potassium citrate at different temperatures—Experimental results and modeling of liquid–liquid equilibrium data

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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 potassium citrate at various temperatures of 298.15, 308.15 and 318.15 K. The effect of temperature on the salting-out effect of poly(vinylpyrrolidone) by potassium citrate has been studied. 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. The agreement between the correlation and the experimental data is good.

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1. Introduction

Ternary aqueous solutions of water-soluble polymers and certain electrolytes separate into a polymer-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].

Polyethylene glycol (PEG), which is a hydrophilic polymer, is often used in aqueous two-phase partitioning studies. In earlier studies, salting out of PEG 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 [3] and therefore, to environmental concern. On way to reduce the salt discharged in the wastewater is to recycle the chemicals. In this regard, Hustedt [3] and Greve and Kula [4] have published useful papers. Recently, as an alternative approach Vernau and Kula [5] have investigated citrates as a substitute for inorganic salts and found that citrate forms aqueous two-phase

system with PEG which are suitable for protein extraction. Citrate is biodegradable and nontoxic and could be discharged into biological wastewater treatment plants. Liquid–liquid equilibrium data for some aqueous PEG + sodium citrate [5–7] and PEG + potassium citrate [8] systems have been reported in the literature.

Poly(vinylpyrrolidone) (PVP) is a water-soluble polymer that can also be used for the separation of biomolecules, since its aqueous solutions with a suitable polymer or a salt forms a two-phase system. Liquid–liquid equilibrium (LLE) data for some aqueous PVP + salt two-phase systems have been reported in the literature [9–13]. As far as we know, there is no report on the phase diagram of the PVP + potassium 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 potassium citrate at various temperatures of 298.15, 308.15 and 318.15 K.

There are mainly two kinds of models describing the phase behavior of aqueous two-phase systems proposed in the literature, one based on osmotic virial expansions and the other on lattice theories. Osmotic virial expansions, derived from knowledge of the osmotic pressure of a solvent in the solution, have been used in various versions and achieved some success in describing the phase behavior of polymer–salt aque-

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ous two-phase systems [14–17]. Among the most familiar lattice models that have been extended to represent phase diagrams of polymer–salt aqueous two-phase systems are the UNIQUAC model [18,6], the UNIFAC model [19] and the NRTL model [9,20].

Recently, the Wilson model [21] was extended to represent the excess Gibbs energy of aqueous polymer–electrolyte solutions [22]. This model has three contributions. The Flory–Huggins expression for the configurational entropy of mixing is used as a combinatorial contribution to the excess Gibbs energy. The Pitzer–Debye–Hückel model is used for long-range electrostatic interactions between ions and the modified Wilson equation is used for short-range interactions between all species. This extended model successfully was used to correlate the vapor–liquid equilibrium data of several polymer–salt–water systems [22]. In the present work, a simple modification has been done on this model and then 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. Potassium citrate with a minimum purity of 99% was obtained from Fluka. 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 [6,10,23]. A glass vessel, volume 50 cm³, was used to carry out the phase equilibrium determinations. The glass vessel was provided with an external jacket in which water at constant temperature was circulated using a thermostat. The temperature was controlled to within ± 0.05 K. The binodal curves were determined by a titration method. A salt solution of known concentration was titrated with the polymer solution or vice versa, until the solution turned turbid. The composition of the mixture was determined by mass using an analytical balance with a precision of $\pm 1 \times 10^{-7}$ kg. To determine the compositions of coexisting phases, feed samples (about 20 cm³) 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 as weight fraction for PVP (p) + potassium citrate (ca) + H₂O (w) at different temperatures

298.15 K		308.15 K		318.15 K	
w_p	w_{ca}	w_p	w_{ca}	w_p	w_{ca}
0.4003	0.0430	0.3930	0.0421	0.3849	0.0413
0.3855	0.0458	0.3846	0.0440	0.3656	0.0456
0.3563	0.0536	0.3669	0.0483	0.3593	0.0470
0.3405	0.0572	0.3506	0.0522	0.3459	0.0497
0.3209	0.0623	0.3296	0.0571	0.3279	0.0540
0.2968	0.0691	0.3037	0.0635	0.3037	0.0598
0.2699	0.0766	0.2756	0.0710	0.2836	0.0649
0.2420	0.0848	0.2462	0.0796	0.2663	0.0693
0.2163	0.0926	0.2193	0.0873	0.2448	0.0752
0.1906	0.1007	0.1952	0.0939	0.2242	0.0808
0.1736	0.1058	0.1781	0.0992	0.2085	0.0850
0.1300	0.1221	0.1278	0.1168	0.1919	0.0888
0.0950	0.1403	0.0980	0.1305	0.1598	0.0992
				0.1265	0.1110
				0.1010	0.1218
				0.0852	0.1305

3. Results and discussion

3.1. Experimental results

For the aqueous PVP + potassium 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 and 318.15 K are shown in Tables 1 and 2, respectively. The complete phase diagrams of all studied systems are shown in Figs. 1–3.

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

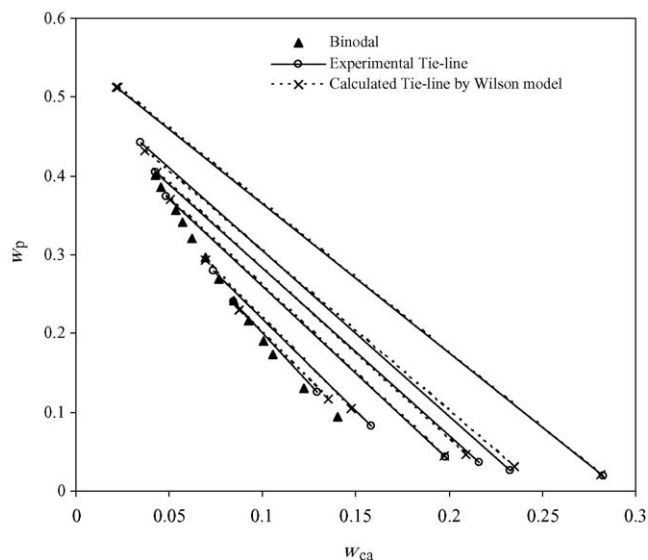


Fig. 1. Phase diagram of the PVP (p) + potassium citrate (ca) + H₂O (w) aqueous two-phase system at 298.15 K.

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