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Thermodynamic studies on the complete phase diagram of the ternary aqueous system containing polyvinylpyrrolidone 3500 and sodium sulfate at different temperatures: Experiment and correlation

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ABSTRACT

The complete phase diagram for the {polyvinylpyrrolidone (PVP) + sodium sulfate (Na_2SO_4) + water} with PVP of molar mass 3500 g · mol^{-1} was determined at $T = 298.15$ K and atmospheric pressure (≈95 kPa). (Liquid + liquid) equilibria (LLE) of {PVP_{3500} + sodium sulfate + water} was also studied at $T = (298.15, 308.15$ and $318.15)$ K. Furthermore for this system and some previously studied systems containing PVP_{3500} the free energies, enthalpies and entropies of cloud points were calculated at the mentioned temperatures in order to investigate the driving force formation of these two-phase systems. In addition, the calculated free energies for phase separation of the studied systems were used to investigate the salting-out ability of the salts having different anions. The effect of temperature on the salting-out effect of polyvinylpyrrolidone by sodium sulfate has been studied. For representing the experimental binodal data the Merchuk equation in the original form and with the temperature dependency and an empirical equation were used. A temperature dependent Setschenow and the extended NRTL were used to fit the tie-line data of this system. Also, we estimated plait point, slope and the length of tie-lines at $T = (298.15, 308.15$ and $318.15)$ K.

1. Introduction

(Liquid + liquid) extraction utilizing aqueous two-phase systems (ATPS's) has often been a favoured choice in both industry and academia for the development of separation processes because these systems are considered to be environmentally safe and benign due to the lack of use of traditional volatile organic compounds in the whole process. ATPS's usually form when an aqueous solution exceeds specific threshold concentrations of two water-soluble, but mutually incompatible (*e.g.*, a polymer *versus* a polymer, a polymer *versus* a salt, or an ionic liquid *versus* a salt), components [1–4].

Polymer-based (*i.e.* (polymer + polymer) or (polymer + salt)) ATPS's have been widely used to separate and purify various biological products [1–3,5], metal ions [6,7], dyes, drug molecules, small organic species [8,9], and nano and micro solid particles [10,11] from the complex mixtures in which they are produced. For large-scale extractions, the (polymer + salt) ATPS's are more attractive because of their greater selectivity, lower viscosity, lower cost, rapid phase disengagement, and availability of commercial separators, which allow a faster and continuous separation.

Polyvinylpyrrolidone (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. In regard to aqueous (PVP + salt) systems, the LLE of aqueous (PVP + ammonium sulfate) and (PVP + sodium phosphate) systems have been studied by Franks [12] and Zafarani-Moattar and Sadeghi [13], respectively. Recently, LLE data for aqueous (PVP + salt) systems with PVP of molar mass 3500 g · mol^{-1} containing tri-potassium phosphate/di-potassium hydrogen phosphate [14], di-potassium tartrate/di-potassium oxalate [15] have been reported. Also, phase compositions for aqueous (PVP + salt) systems with PVP of molar mass 10,000 g · mol^{-1} containing sodium citrate [16], magnesium sulfate [17], potassium citrate [18], disodium hydrogen phosphate/tri-sodium phosphate [19], sodium carbonate/sodium sulfate/sodium succinate at $T = 303.15$ K [20] and $(NH_4)_2HPO_4$/$(NH_4)H_2PO_4$ [21], sodium sulfite [22] have been reported.

In this work, we reported the binodal curves and the tie-lines for an aqueous two-phase system containing PVP_{3500} and Na_2SO_4 at $T = (298.15, 308.15$ and $318.15)$ K and atmospheric pressure (≈95 kPa). For this system a complete phase diagram also was

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obtained at $T = 298.15$ K, which has not been published previously. Furthermore, plait points of phase diagram have also been calculated at $T = (298.15, 308.15$ and $318.15)$ K using the linear least squares regression method.

The effect of temperature on the binodal curves and the tie-lines for the investigated aqueous two-phase system were also studied and two empirical statistic equations [23,24] as a function of temperature in the linear form with $(T - T_0)$ K as a variable were used for reproducing the experimental binodal data. The experimental tie-line compositions obtained at the noted temperatures were fitted to a temperature dependent Setschenow-type equation [25] and osmotic virial model [26] and extended NRTL [13] models. Correlation coefficients for all equations have been reported. Additionally, the free energies of cloud points for this system were calculated in each temperature.

2. Materials and methods

2.1. Materials

Polyvinylpyrrolidone (PVP) (K12), of molar mass 3500, with CAS number 9003-39-8, was obtained from Across Organics. Sodium sulfate with CAS Registry No. 7757-82-6 was obtained from Merck, Germany. The purity of the materials is shown in table 1. The polymer and salt were used without further purification, and double distilled deionised water was used.

2.2. Apparatus and procedure

2.2.1. (Liquid + Liquid) equilibrium (LLE)

The experimental apparatus employed is essentially similar to the one used in previous work [13]. A glass vessel with volume about 50 cm^3 was used to collect the binodal equilibrium values. An external jacket was placed in the glass vessel and water at constant temperature was circulated using a thermostat around this jacket. The temperature was controlled to be within ±0.05 K. The binodal curves were determined by the clouding point titration method. In this method, a salt solution of known concentration was titrated with the polymer solution or vice versa, until the solution turned turbid. This point indicates the formation of two immiscible liquid phases. In accordance with the amount of added titrant 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 a precision of $\pm 1 \cdot 10^{-7}$ kg. The standard uncertainty of mass fraction was found to be 0.002 for both PVP_{3500} and Na_2SO_4 using this method.

For determination of the tie-lines, feed samples (about $2 \cdot 10^{-5}$ m^3) were prepared by mixing appropriate amounts of polymer, salt and water in the vessel. The thermostat was set at the desired temperature, and the samples were stirred for 1 h. Then, the samples were placed in the thermostat and allowed to settle for at least 48 h so that they could be separated into two clear phases. After the separation of the two phases, the concentrations of sodium sulfate in the top and bottom phases were determined by flame photometry (JENWAY PFP7, England). The concentration of PVP in both phases was determined by refractive index measurements performed at $T = 298.15$ K using a refractometer (ATAGO DR-A1, Japan). The uncertainty in refractive index measurement is ±0.0002. For dilute aqueous solutions containing a polymer and a salt, the relation between the refractive index, n_D, and the mass fractions of polymer, w_p, and salt, w_s is given by:

$$n_D = n_w + a_p w_p + a_s w_s, \tag{1}$$

where, n_w is the refractive index of pure water which is set to 1.3325 at $T = 298.15$ K. a_p and a_s are constants of polymer and salt, respectively, for which linear calibration plots of refractive index of the solution are obtained. However, it should be noted that equation (1) is only valid for dilute solutions. Therefore, before refractive index measurements, it was necessary to dilute the samples to be in the mass fraction range (*C range*) presented in table 2. The uncertainty of the mass fraction of PVP achieved using equation (1) was better than 0.002. The values of these constants and respective correlation coefficient values, *R*, are given in table 2.

TABLE 1
Provenance and mass fraction purity of the materials studied.

Material	Source	Molecular formula	Mass fraction purity
Polyvinylpyrrolidone 3500	Acros organics	$(\text{C}_6\text{H}_9\text{NO})_n$	>0.99
Sodium sulfate	Merck	$\text{Na}_2\text{SO4}$	>0.99
Sodium phosphate	Merck	$\text{Na}_2\text{PO4}$	>0.99

2.2.2. (Liquid + solid) equilibrium (LSE)

Various series of solutions of the three components were prepared in order to delimit the three-phase region from the two-phase region. A total composition in the two liquid and one solid (2L + 1S) region was selected. Then, it was titrated with water until the solid phase in the system disappeared; again the sample was placed in the water bath at the desired temperature ($T = 298.15$ K) and allowed to settle for at least 120 h so that they could be separated into two clear phases. The procedure used to determine this border tie-line is exactly the same as the one we used to determine the other tie-lines in the LLE region.

Also, to determine the boundary between (1L + 1S) and (1L + 2S) regions, a total composition in one liquid and two solid (1L + 2S) region was selected. Then, the temperature was increased up to about 318.15 K in order to dissolve the solid phases. After that, the temperature was slowly decreased to the working temperature $T = 298.15$ K. To establish thermodynamic equilibrium between phases, the samples were placed in the water bath at the desired temperature and allowed to settle for at least 120 h. After reaching the thermodynamic equilibrium, extracted polymer and salt can be observed as solid phases on top and bottom of liquid phase, respectively. To determine the polymer concentration at saturated solution first the sample was titrated with water until the solid polymer in the system disappeared then the refractive index of obtained saturated solution was measured as described in Section 2.2.1. The mentioned procedure was repeated to determine the components concentration. This procedure was performed at least for three times at $T = 298.15$ and the data had good reproducibility. The maximum deviation between these series of the measured data was better than ±0.006.

2.2.3. XRD analyses

To identify the bottom solid phase (salt) composition, the salt sedimentations that were in equilibrium with one liquid and one solid phases were filtered off and analyzed by X-ray diffraction using an automatic, computerized X-ray diffractometer (Siemens

TABLE 2
Values of the parameters of the equation (1) for $\{\text{PVP}_{3500}\,(\text{p}) + \text{Na}_2\text{SO}_4\,(\text{s}) + \text{H}_2\text{O}\,(\text{w})\}$ system.

Material	Constant	Value	*C range* (w/w)	R^2
PVP_{3500}	a_p	0.1755	0 to 0.10	0.9995
Na_2SO_4	a_s	0.1405	0 to 0.09	0.9999

Where, *R*, represents the respective correlation coefficient value of the linear calibration plot of the refractive index against mass fraction for PVP_{3500} or Na_2SO_4 at the mass fraction range (*C range*) of each material.