



Measurement and correlation of aqueous two-phase systems of polyvinylpyrrolidone (PVP) and manganese sulfate: Effects of molecular weight and temperature



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ABSTRACT

Aqueous two-phase systems (ATPS) are a substitute for conventional liquid-liquid extraction systems and, are usually composed of a salt solution and the polymer polyethylene glycol (PEG). Polyvinylpyrrolidone (PVP) is an alternative polymer, inexpensive, stable, and it has great potential for ATPS. This study aimed to investigate the effect of the molecular weight of the polymer (10 000 and 40 000) and the temperature (298.15, 318.15 and 338.15 K) in the system composed of PVP10 or PVP40 + manganese sulfate + water. The Merchuk equation has been used to correlate the experimental binodal data. For all systems, the higher the temperature, the higher the two-phase region and the slope of the tie-line. The increase in the molecular weight of the polymer resulted in the expansion of the two-phase region. Furthermore, the UNIQUAC model was used to fit the experimental LLE data.

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1. Introduction

Liquid-liquid extraction using aqueous two-phase systems (ATPS) has attracted interest from industry and academia to the development of alternative separation process. ATPS, in general, are environmentally safe and non-toxic considering the absence of organic solvents in this type of process [1,2]. The ATPS can consist of polymer/polymer, polymer/salt or salt/salt aqueous mixtures above the critical concentration [3]. The relative phase separation efficiency of each salt is correlated according to the Hofmeister series [4], which corresponds to a classification of ions present in the salts and it is based on their ability to cause the salting-out effect [5–9].

ATPS application to partition species was initiated by Albertsson [10], who investigated the separation of biological particles. From the Albertsson work, due to its biocompatibility, ATPS has been evaluated in the separation of biomolecules, such as antibiotics [11,12], vitamin [13], protein [14,15], alkaloids [16–18] and enzymes [19,20]. For large-scale extractions, polymer/salt ATPS are considered more advantageous because of their higher selectivity, lower viscosity, lower energy consumption, lower cost, and faster phase separation [21]. Due to these characteristics, the use of ATPS in the

separation of organic molecules, such as dyes [22], and inorganics, such as metallic ions [23–25], have recently been proposed. In these cases, the evaluation of the phase behavior of these systems at temperatures higher than those used when separating biomolecules has been considered.

The polymer/salt ATPS is composed of aqueous mixtures of different water-soluble polymers such as polyethylene glycol (PEG) and dextran or inorganics salts [10]. Polyvinylpyrrolidone (PVP) is a water-soluble polymer, inexpensive, stable and as well as PEG has great potential for extraction/purification of biomolecules in aqueous two-phase systems [26]. Several authors have reported the suitable use of PVP as a substitute for PEG in ATPS. Zafarani-Moattar and Abdizadeh-Aliyar [27] reported the equilibrium data of PVP35 ($M_w = 3500$) and sodium sulfate using a temperature dependent equation of Merchuk methodology [28]. Wang et al. [26] studied the PVP30 and different ammonium salts systems, obtaining experimental data and correlations. Phases diagrams of ATPS composed of PVP and salt was also obtained to the systems composed of PVP10 and sodium pentane-1-sulfonate [29], and PVP24 with potassium dihydrogen phosphate/dipotassium hydrogen phosphate [30].

In this context, the aim of this work is to report data of binodal curves, and tie-lines for the new aqueous two-phase systems composed of PVP10 + $MnSO_4$ and PVP40 + $MnSO_4$. For these systems, complete phase diagrams were obtained at 298.15, 318.15 and

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338.15 K in the atmospheric pressure. The effect of the molecular weight of the polymer and the temperature on the binodal curves and the tie-lines were studied. Also, the thermodynamic modeling of the experimental data was performed using the UNIQUAC model. Also, the polyvinylpyrrolidone substitution by polyethylene glycol was discussed in these systems.

2. Experimental section

2.1. Materials

Polyvinylpyrrolidone, PVP10 ($M_W = 10000$) and PVP40 ($M_W = 40000$), were obtained from Sigma Aldrich (St. Louis, MO, USA). Manganese sulfate $MnSO_4 \cdot H_2O$ (99.0 wt % pure) were obtained from Neon (São Paulo, SP, BR) and was dried in a laboratory stove at 105 °C for 2 h previous it uses. The water used in the experiments was undergone by a reverse osmosis system purification apparatus (Vexer, Smart VOS 106).

2.2. Apparatus and procedure

The experimental apparatus is similar to the one used in previous work [31]. A jacketed-glass cell with temperature control was used to obtain the binodal equilibrium data at 298.15, 318.15 and 338.15 K. Temperature was controlled by a thermostatic water bath (Lab Companion, RW – 1025G). The binodal curves were determined by the clouding point titration method [32]. In this method, salts or PVP solutions were added drop-wise to each other until the visual detection of a cloudy solution (biphasic region). The composition of the mixture for each point on the binodal curve was calculated by mass using an analytical balance (Mettler Toledo, AL204, São Paulo, BR) with a precision of ± 0.0002 g.

For determination of tie-lines, aqueous solutions in the heterogeneous region were prepared by mixing appropriate amounts (around 12 g) of salt, polymer, and water in graduated centrifuge tubes (15 mL) with an uncertainty of the ± 0.0002 g. The centrifuge tubes were vigorously stirred for approximately 5 min in vortex stirrer (Fisatom, MD722). Then, the samples were placed in the thermostatic water bath and allowed to settle for at least 24 h so that they could be separated into two well-defined phases. After this period, the phases were cautiously separated with a Pasteur pipette and weighed.

2.3. Binodal curve correlation

For the correlation of binodal data, the Merchuk equation [28] was used. The experimental binodal curves were fitted using Eq. (1) by the regression and minimization of the objective function (Eq. (2)) [28]. For this, a generalized reduced gradient optimization method in Solver tool (Microsoft Excel™) was used, and the parameters A , B , and C were obtained.

$$Y = A \cdot \exp(B \cdot X^{0.5} - C \cdot X^3) \quad (1)$$

$$OF = 10^{10} \sum_{i=1}^N (Y_i^{exp} - Y_i^{mod})^2 \quad (2)$$

where X and Y are the salt and PVP weight fractions percentages, respectively.

In order to evaluate the correlation of the Merchuk equation (Eq. (1)) to the binodal experimental data, the root mean square deviation ($rmsd$) was used (Eq. (3)).

$$rmsd (\%) = 100 \cdot \sqrt{\frac{\sum_i^N (Y^{exp} - Y^{calc})^2}{N}} \quad (3)$$

where exp and $calc$ refer to the experimental and calculated value of Y , respectively.

2.4. Tie-line correlation

For the determination of TLs, a system of four equations (Eqs. (4)–(7)) and four variables (Y_T , Y_B , X_T , and X_B) was solved by the Solver tool in Microsoft Excel™, applying the generalized reduced gradient optimization method as described by Sampaio et al. [16].

$$Y_T = \left(\frac{Y_M}{\alpha} \right) - \left(\frac{(1-\alpha)}{\alpha} \right) \cdot Y_B \quad (4)$$

$$Y_T = A \cdot \exp(B \cdot X_T^{0.5} - C \cdot X_T^3) \quad (5)$$

$$Y_B = A \cdot \exp(B \cdot X_B^{0.5} - C \cdot X_B^3) \quad (6)$$

$$X_T = \left(\frac{X_M}{\alpha} \right) - \left(\frac{(1-\alpha)}{\alpha} \right) \cdot X_B \quad (7)$$

where M , T , and B denote the mixture, the top phase, and the bottom phase, respectively, X is the weight fraction of manganese sulfate, Y is the weight fraction of PVP, and α is the ratio between the mass of the top phase and the total mass of the mixture.

With the finality to check the accuracy of the results obtained with the systems of equations (Eqs. (4)–(7)), some tie-lines were reproduced and analyzed by thermogravimetric analysis (TGA) to quantify the phases composition (see Fig. S1 in Supporting Information). More details about this validation method and the technique used are presented in the Supporting Information.

3. Results and discussion

3.1. Effect of temperature on ATPS

The effect of temperature on the binodal curves of the investigated aqueous systems (PVP + $MnSO_4$) is illustrated in Fig. 1. As one can see the two-phase region of the systems formed by PVP + $MnSO_4$ expand with increasing temperature. However, in the polymer-rich region, the effect of temperature is lower than in the salt-rich region. This behavior was also observed for the system PVP + Na_2SO_4 [2].

Additionally, the effect of temperature on tie-lines was evaluated. The slope of the tie line (STL) (Eq. (8)) and the tie-line length (TLL) (Eq. (9)), for both systems, are shown in Tables 1 and 2, as well as the tie-line compositions.

$$STL = \frac{Y_T - Y_B}{X_T - X_B} \quad (8)$$

$$TLL = \sqrt{(X_T - X_B)^2 + (Y_T - Y_B)^2} \quad (9)$$

in which X_T , X_B , Y_T , and Y_B represent the equilibrium compositions of the salt and PVP in the top and bottom phases, respectively.

It was observed in Tables 1 and 2, as well in Fig. 2, a direct relationship between temperature, slope (in absolute values) and length of the tie-lines. This occurs due the PVP becomes more hydrophobic with increasing temperature, as well as observed by

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