



Liquid-liquid equilibrium of the ternary ammonium salt + poly(propylene glycol) + water system



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ABSTRACT

Aqueous two-phase systems (ATPS) have been investigated as alternative systems for liquid-liquid extraction. Many ATPS phase diagrams for poly(ethylene glycol) (PEG) have been reported, but little information is available regarding liquid-liquid equilibrium data for poly(propylene glycol) (PPG). In the present work, the phase diagrams for PPG425 + ammonium acetate + H₂O, PPG425 + ammonium tartrate + H₂O, PPG425 + ammonium citrate + H₂O, PPG425 + ammonium formate + H₂O, and PEG900 + ammonium citrate + H₂O were experimentally determined at 283.2, 298.2, and 313.2 K. The study of statistic treatment was introduced by a computation method NRTL model. This program is a method to estimate the energetic parameters of the studied systems. The binary interaction of the calculated parameters are very important for designing or optimizing industrial process. The results were considered very satisfactory with global root mean square deviations of 1.82%. Factors affecting the phase-forming capability of the polymer + electrolyte + water ATPS, such as anion structure, temperature, polymer hydrophobicity were evaluated. For all the systems, the increase in temperature enlarges the area of the phase diagram, indicating the enthalpic contribution to the formation of the biphasic system. The ability of the different anions to induce ATPS formation with PPG425 followed the order: C₄H₄O₆²⁻ (tartrate) > C₆H₆O₇³⁻ (citrate) > C₂H₃O₂⁻ (acetate) > CHO₂⁻ (formate). The ATPS involving PPG425 showed a larger two-phase area than that observed in the system formed by PEG900, which is more hydrophilic than PPG425.

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1. Introduction

Liquid-liquid extraction using aqueous two-phase systems (ATPS) has been used to extract metals [1–3], dyes [4–6], biomolecules [7–9], and phenolic compounds [10,11]. These systems can be formed by the mixture of aqueous solutions of incompatible polymers [12–14], by a polymer and an electrolyte [4,15–18], or by two electrolytes [4,19–21] at specific conditions of temperature, pressure, and composition. The resultant system is composed of two phases, a polymer-rich phase (PRP) and an electrolyte-rich phase (ERP).

The most commonly used ATPS contain hydrophilic macromolecules of poly(ethylene glycol) (PEG) [3,9,10,22]. This polymer is

used in partitioning studies of water soluble compounds, since the selective distribution of substances between the phases at equilibrium is a consequence of the interactions established between the solutes and the phase-forming constituents [1,2,5,23]. In order to extend the applicability of the system to hydrophobic compounds, a possibility is to use poly(propylene glycol) (PPG) as the ATPS-forming component. There are several reports detailing the liquid-liquid equilibrium data for PEG, but the literature still lacks the phase diagrams for PPG. This macromolecule displays hydrophobic characteristics due to the presence of one additional methyl group per monomer when compared to PEG [24]. This remarkable property enables the handling of strategic hydrophobic compounds in ATPS systems [24]. Moreover, PPG is biodegradable [25], can be recovered by heating [25], and is safe [25,26], enabling its use in the food and cosmetics industry [26].

In the present work, we report the determination of the experimental liquid-liquid equilibrium data for ATPS containing

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PPG with an average molar mass of 425 g mol⁻¹ (PPG425) and different electrolytes: PPG425 + NH₄C₂H₃O₂ + H₂O, PPG425 + (NH₄)₂C₄H₄O₆ + H₂O, PPG425 + (NH₄)₂C₆H₆O₇ + H₂O, and PPG425 + NH₄CHO₂ + H₂O at 283.2, 298.2, and 313.2 K. One ATPS containing poly(ethylene glycol) with an average molar mass of 900 g mol⁻¹ (PEG900) + (NH₄)₂C₆H₆O₇ + H₂O was investigated at 298.2 K.

The non-random two-liquid (NRTL) model was developed to represent the energy parameters of the system. The temperature is the dependent variable of this model. The experimental data were correlated with the modified NRTL model [27] for the activity coefficient, with estimation of new interaction parameters.

2. Materials and methods

2.1. Materials

Deionized water (Millipore, Milli-Q) was used for preparing all the solutions. Analytical-grade reagents were used as received without further purification as shown in Table 1.

2.2. Preparation of the aqueous two-phase systems

Aqueous stock solutions of PPG425 and the electrolyte were prepared using an analytical balance (AY 220, Shimadzu; uncertainty of ±0.0001 g). Appropriate quantities of these stock solutions were weighed in glass vessels to obtain the desired global compositions. The samples were stirred in a vortex mixer (CertomatMV, B. Braun Biotech International) until the system became cloudy, and were placed in a temperature controlled bath (MQBTC 99-20, Micro-química; uncertainty of ±0.1 K) at 283.2, 298.2, or 313.2 K for at least 48 h. The thermodynamic equilibrium was characterized by the presence of two clear phases that were collected and appropriately diluted for quantification.

2.3. Determination of equilibrium composition

The electrolyte concentration (ammonium acetate, ammonium citrate, ammonium formate, and ammonium tartrate) was determined by conductivity (DM-32, Digimed) after obtaining the analytical curves ($R^2 \geq 0.999$) of the electrolyte in the dynamic range of 1.00×10^{-3} to $300 \times 10^{-3}\%$ (w/w). The electrolyte solutions show the same conductivity in water and in the diluted polymer solution. A refractometer (Abbe 09-2011, Analytik Jena) was used to measure the PPG425 and PEG900 concentrations. Aqueous polymer solutions (or electrolyte aqueous solutions) were prepared, analyzed in a refractometer, and analytical curves with similar linear adjustments for PPG425/PEG900 and electrolyte were obtained. Thus, the refractive index was considered an additive property, i.e., the refractive index value is proportional to the sum of the concentration of electrolyte and polymer for the ATPS phases. The total concentration of the phase components (polymer

and electrolyte) was determined by the refractive index, and the PPG425/PEG900 concentration was obtained by subtracting the electrolyte concentration (acquired by conductivity). The water content was determined from the mass balance. All analytical measurements were performed in duplicate.

2.4. NRTL (non-random, two-liquid) model and parameter estimation

The NRTL model is based on local composition concept and it is applicable to partially miscible systems. This model was used to study the experimental liquid-liquid equilibrium of all systems in this work. The equations of the original NRTL model were altered for systems containing electrolytes and polymers [27]. This model has five adjustable parameters for each binary pair (A_{0ij} , A_{0ji} , A_{1ij} , A_{1ji} and α_{ij}). The parameters A_{0ij} , A_{0ji} , A_{1ij} , A_{1ji} are related to the characteristic energy of interaction between the molecules of type i and j , while the parameter α_{ij} is related to the non-randomness of the mixture.

The estimation of the new binary interaction parameters was performed using the software FORTRAN code WTML-LLE [27] (weight temperature-maximum likelihood – liquid-liquid equilibrium).

3. Results and discussion

3.1. Aqueous two-phase system compositions

In general, ATPS containing a macromolecule, electrolyte, and water are more efficient than ATPS formed by two macromolecules and water, for the extraction and purification of different solutes. Therefore, the modification of the ATPS-forming polymer or electrolyte allows modulation of the characteristics of the phases, to enable their application for different compounds. The phase compositions for new aqueous two-phase systems formed by PPG425 + NH₄C₂H₃O₂ + H₂O, PPG425 + (NH₄)₂C₄H₄O₆ + H₂O, PPG425 + (NH₄)₂C₆H₆O₇ + H₂O, PPG425 + NH₄CHO₂ + H₂O, and PEG900 + (NH₄)₂C₆H₆O₇ + H₂O at different temperatures (283.2, 298.2, and 313.2 K) and the tie-line lengths (TLL) are shown in Tables 2–6 (The standard uncertainties were calculated using the compositions of the polymer-rich phase and electrolyte-rich phase at 298.2 K and 313.2 K. The measures performed at 283.2 K were difficult to carry out and less precise). The phase compositions were presented in mole fraction (x).

The tie-lines were obtained by linear regression fitting of the values of overall composition, and the compositions of the PPG425-rich phase and electrolyte-rich phase. The TLLs presented in Tables 2–6, express the difference in phase composition between both ATPS phases, and at constant pressure and temperature could be considered related to the difference in intensive thermodynamic properties between the polymer-rich phase and the concentrated salt phase [27]. The TLL can be calculated by Eq. (1):

$$TLL = \left[\left(x_p^{PRP} - x_p^{ERP} \right)^2 + \left(x_E^{PRP} - x_E^{ERP} \right)^2 \right]^{1/2} \quad (1)$$

where x_p^{PRP} and x_p^{ERP} are the polymer mole fractions in the polymer- and electrolyte-rich phases, respectively, and x_E^{PRP} and x_E^{ERP} are the corresponding electrolyte mole fractions in the polymer- and electrolyte-rich phases, respectively.

As is normally observed for other salt-polymer ATPS, an increase in the TLL promotes the enrichment of polymer content along with a decrease of water and electrolyte quantity in the PRP, while in the ERP, water and electrolyte concentration increases along with a

Table 1
Specification of chemical samples.

Chemical name	Source	Initial mole fraction purity
PPG425 ^a	Aldrich	0.999
PEG900 ^b	Aldrich	0.999
Ammonium citrate dibasic	Fluka	0.990
Ammonium acetate	Neon	0.980
Ammonium tartrate	Vetec	0.990
Ammonium formate	Vetec	0.960

^a Poly(propylene glycol) with an average molar mass of 425 g mol⁻¹.

^b Poly(ethylene glycol) with an average molar mass of 900 g mol⁻¹.

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