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Phase equilibrium of aqueous two-phase systems composed by L35 triblock copolymer + organic and inorganic ammonium electrolytes + water at 298.2 and 313.2 K

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ABSTRACT

Liquid-liquid equilibrium data of aqueous two-phase systems (ATPS) composed by L35 triblock copolymer + ammonium electrolytes (nitrate, NO_3^-; tartrate, $C_4H_4O_6^{2-}$; phosphate, HPO_4^{2-}; acetate, $C_2H_3O_2^-$) + water, at different temperatures (298.2 and 313.2 K) are presented in this paper. The experimental ATPS data were correlated with the original and modified non-random two-liquid (NRTL) for predicting energetic parameters of the studied systems. The results were satisfactory with global root mean square deviations (33 tie-lines) of the 2.36% and 2.53% for the original and modified models, respectively. The effect of the temperature and electrolyte nature on the biphasic area position was investigated. The increase of the temperature promoted a slight increase in the two-phase region indicating the endothermic character of the phase splitting. The increase in the temperature also promoted a rise in the module of the slope of the tie-lines. The anions ability to promote phase separation followed the order: $HPO_4^{2-} > C_4H_4O_6^{2-} > NO_3^- > C_2H_3O_2^-$.

1. Introduction

Aqueous two-phase systems (ATPS) have been investigated as environmentally safe and promising alternative extraction systems. These systems can be formed by the mixture of aqueous solutions of a polymer and an electrolyte [1], two electrolytes [2] or two structurally different polymers [3], under specific thermodynamic conditions [4]. The resulting systems have two immiscible liquid phases mainly formed by water [3].

The ATPS researches involving metal ions [5–7], dyes [8,9], phenolic compounds [10,11] and enzymes [12,13] have focused on the use of systems composed by polymer and electrolyte. The poly(ethylene oxide) polymer (PEO) is one of the main used macromolecules since it contributes to some ATPS advantages as low cost [14], rapid phase separation [15], low interfacial tension [3], possibility to scale-up, and low toxicity [12]. On the other hand, for a long time, the hydrophilicity of the PEO-based systems limited the ATPS application for water soluble compounds. Da Silva et al., in 2005, were one of the firsts scientists to fine-tuned the polymer-rich phase characteristic with the use of triblock copolymer macromolecules and expand the application of the ATPS to hydrophobic compounds [16].

The triblock copolymer used in ATPS formation (commercially available as pluronic) is composed by units of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), denoted as (PEO)n-(PPO)m-(PEO)n or (EO)n(PO)m(EO)n [17]. The usual nomenclature for the triblock copolymer starts with the letters L, P or F, that means liquid, paste and flakes, respectively. The first one or the two first numbers are indicative of the molecular weight of the PPO block, and the last number represents the weight fraction of the PEO block [17]. The advantage of using triblock copolymers is that, in aqueous solution, at specific temperature and concentration, these

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substances have the ability of self-association to form micelles with a core dominated by hydrophobic units (PPO), surrounded by a crown of hydrophilic units (PEO) [18,19]. These micelles provide amphiphilic characteristics for the ATPS [19], allowing the partitioning of hydrophilic and hydrophobic compounds [20]. Another advantage is that triblock copolymers are thermosensitive, presenting a lower cloud point temperature than PEO polymer [21]. Consequently, these macromolecules are easier recycled by the phase separation induced by the temperature increase [21]. Despite the advantages presented by the triblock copolymer in the literature still has few ATPS equilibrium data for systems composed by triblock copolymers [16,20,22–26]. In addition, liquid-liquid equilibrium data with ammonium electrolytes are also scarce, despite these salts are environmentally safe and compatible with different analytical techniques. Finally, ATPS constituted by triblock copolymer and ammonium salt will allow that the applications of the ATPS are more extended.

In this paper, we report the phase equilibrium data for systems containing L35 triblock copolymer ($(EO)_{11}(PO)_{16}(EO)_{11}$), which has an average molar mass of 1900 g mol^{-1} and different ammonium electrolytes: L35 + NH_4NO_3 + H_2O, L35 + $(NH_4)_2C_4H_4O_6$ + H_2O, L35 + $(NH_4)_2HPO_4$ + H_2O, and L35 + $NH_4C_2H_3O_2$ + H_2O. Phase equilibria were obtained at 298.2 and 313.2 K because these temperatures are more using to separate different analytes thus widening the applications of the aqueous biphasic systems. Equilibrium data were correlated using the original and modified NRTL models to estimate new interaction parameters.

2. Materials and methods

2.1. Materials

L35 copolymer and all the electrolytes were analytical-grade and used as received without further purification, as shown in Table 1. Deionized water (Millipore Corp., Molsheim/Bas-Rhin, France) was used for preparing all the solutions.

2.2. Preparation of the aqueous two-phase systems

Aqueous stock solutions of L35 and electrolyte were prepared using an analytical balance (AY 220, Shimadzu, Rosário/Cavite, Phillippines) with uncertainty of ±0.0001 g. The stock solutions of copolymer and electrolyte were weighed in glass vessels to obtain the appropriated amount of each component to form biphasic systems. The glass vessels were stirred in a vortex mixer (CertomatMV, B. Braun Biotech International, Melsungen/Hesse, Germany) until the system became turbidity. They were left in a controlled bath (MQBTC 99-20, Microquimica, Palhoça/Santa Catarina, Brazil) with uncertainty of ±0.1 K at 298.2 or 313.2 K for at least 48 h, to reach the thermodynamic equilibrium. The equilibrium state was characterized by the presence of two clear phases. Aliquots of the both phases were collected and appropriately diluted for quantification.

Table 1
Specification of chemical samples.

Chemical name	Source	Initial mole fraction purity
L35[a]	Aldrich	0.999
Ammonium nitrate	Aldrich	0.980
Ammonium tartrate	Vetec	0.990
Ammonium phosphate dibasic	Vetec	0.980
Ammonium acetate	Aldrich	0.980

[a] Triblock copolymer ($(EO)_{11}(PO)_{16}(EO)_{11}$) with average molar mass of 1900 g mol^{-1}.

2.3. Determination of equilibrium composition

The electrolyte concentration (NH_4NO_3, $(NH_4)_2C_4H_4O_6$, $(NH_4)_2HPO_4$ or $NH_4C_2H_3O_2$) was determined by conductivity (DM-32, Digimed, São Paulo/São Paulo, Brazil, with uncertainty of ±0.001) after obtaining the analytical curves [22] The electrolytes dynamic range was 1.00×10^{-3} to 300×10^{-3}% (m/m) with $R^2 \geq 0.999$. The conductivity measurement of diluted triblock copolymer solutions was the same obtained for deionized water, indicating that the concentration of the macromolecule does not contribute to the conductivity value. So, the conductivity represents only the concentration of the electrolyte. The uncertainty of the electrolyte composition by this method was ±0.44%. In order to determine the concentration of the copolymer, standard copolymer aqueous solutions (or electrolyte aqueous solutions) were prepared and analyzed in a refractometer (Abbe 09–2011, Analytik Jena, Thuringia/Jena, Germany, with uncertainty of ±0.0001). Analytical curves with similar linear adjustments for L35 and electrolytes were obtained, confirming the additivity of the refractive index. So, the measurement of the refractive index of the samples provide the sum of the concentration of copolymer and electrolyte. The concentration of the copolymer can be obtained by the difference between the refractive index value (which corresponds to the sum of the copolymer and electrolyte concentration) and conductivity value (which corresponds only to the electrolyte concentration), according to Eq. (1):

$$[Cp] = [IR] - [E] \tag{1}$$

where Cp is the concentration of the copolymer in % (m/m), IR is the refractive index and E is the electrolyte concentration in % (m/m). The uncertainty of the copolymer composition by this method was ±0.61%. The water content was determined by mass balance. The uncertainty of the water composition by this method was ±0.48%. The determination of the concentration of the copolymer, electrolyte and water was carried out in the same way in both phases. All analytical measurements were performed in duplicate.

3. Results and discussion

3.1. Equilibrium data of aqueous two-phase systems

Phase composition for ATPS is great important for studying the partition of strategic solutes in these environmental safe systems. Tables 2–5 show the phase composition and the tie-line lengths (TLL) of the new systems formed by L35 + NH_4NO_3 + H_2O, L35 + $(NH_4)_2C_4H_4O_6$ + H_2O, L35 + $(NH_4)_2HPO_4$ + H_2O, and L35 + $NH_4C_2H_3O_2$ + H_2O at 298.2 and 313.2 K. The standard uncertainties were calculated using the compositions of the macromolecule-rich phase (MRP) and electrolyte-rich phase (ERP) at 298.2 and 313.2 K. The phase compositions were presented in mass percent (w).

The tie-lines are diagram connecting lines between the composition of the two phases at constant pressure, temperature and concentration. The TLL is an important parameter that is a numerical indicator of the difference in phase composition between ERP and MRP, and when the systems are in thermodynamic equilibrium, it is related to the difference in intensive thermodynamic properties of the coexisting phases [27]. The TLL can be calculated by the difference between the macromolecule and electrolyte concentration in both phases in equilibrium, as shown in Eq. (2):

$$TLL = \left[\left(w_M^{MRP} - w_M^{ERP}\right)^2 + \left(w_E^{MRP} - w_E^{ERP}\right)^2\right]^{1/2} \tag{2}$$

where w_M^{MRP} and w_M^{ERP} are the macromolecule concentration in the