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Measurement and correlation of phase equilibria in aqueous two-phase systems containing polyethyleneglycol (2 000, 4 000, and 6 000) and sulfate salts (manganese sulfate and copper sulfate) at different temperatures (298.15, 318.15, and 338.15 K)

Filipe Hobi Bordón Sosa [a], Daniela de Araujo Sampaio [b], Fabiane Oliveira Farias [a], Andrea Briones Gonçalves Bonassoli [a], Luciana Igarashi-Mafra [a], Marcos Rogério Mafra [a, *]

[a] Chemical Engineering Department, Federal University of Parana, 81531-980, Curitiba, PR, Brazil
[b] Food Engineering Department, Federal University of Rondônia, 76872-848, Ariquemes, RO, Brazil

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ABSTRACT

Liquid–liquid equilibrium (LLE) data were obtained for polyethylene glycol (PEG)-salt aqueous two-phase system (ATPS) at 298.15, 318.15 and 338.15 K. Two salts, copper sulfate and manganese sulfate, and PEG with different molecular weights, 2 000, 4000 (manganese sulfate only), and 6 000, were used. The effects of the molecular weight of PEG and temperature on phase separation and the salting-out effect were studied. For all aqueous two-phase systems, the increase in the polymer molecular weight provides a larger biphasic region. The temperature promoted an increase in the biphasic region, and the slope of tie-lines tended to decrease with increasing temperature. The Setschenow-type equation was used to evaluate the salting-out effect of $MnSO_4$ and $CuSO_4$, as well as the temperature and molecular weight of the PEG influence on the phase formation. The rank order of salting-out coefficients is $Mn^{2+} > Cu^{+2}$ since the cation Mn^{2+} is more kosmotropic than Cu^{2+}. NRTL and UNIQUAC models have been used to fit the 18 experimental LLE data. The interaction parameters of the models were estimated. The results show that the quality of fitting is better with the UNIQUAC model.

1. Introduction

Aqueous two-phase systems (ATPSs) have great potential to substitute for the conventional extraction methods (organic solvent [1], supercritical [2]) in extraction and separation systems. The conventional ATPSs are formed by a combination of polymer/polymer, polymer/inorganic-salt, or salt/salt solutions at critical concentrations [3].

In 1956, Albertsson pioneered the application of ATPSs for the separation of biological materials such as proteins [4]. Since then, polymer–salt ATPSs have been used to separate biomolecules because they create a suitable and non-aggressive environment for this type of material due to the significant presence of water in the composition. Separation/extraction using ATPSs has been applied to several systems such biological membranes [5], stem cells [6], phenolic compounds [7], enzymes [8], and metallic ions [9].

In general, ATPSs have numerous advantages when compared to conventional extraction/separation systems, such as low energy consumption in the process of separation, fast separation, ease of use, low cost, and easy scale-up [10].

The application of ATPSs in the extraction of metals started in the mid-1980's, and the first work was reported by Zvarova et al. [9], who studied the partitioning of radionuclide metals such as ^{22}Na and ^{42}K. The application of ATPSs for partitioning of metal ions suggests that other systems that are unsuitable (manganese sulfate) for the separation of biomolecules can be studied for this purpose.

Currently, few studies of the application of ATPSs for partitioning of metal ions have been performed compared to those applied to the separation of biomolecules. However, the advantages presented by these systems have encouraged studies of the partitioning of metal ions, which allows its application to samples of industrial and environmental interest [3].

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* Corresponding author. Federal University of Paraná, Jardim das Américas, 81531-990, Curitiba, PR, Brazil.
E-mail addresses: marcos.mafra@ufpr.br, marcos.mafra@gmail.com (M.R. Mafra).

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New ATPSs composed of $CuSO_4$ + PEG 2000 + H_2O, $CuSO_4$ + PEG 6000 + H_2O, $MnSO_4$ + PEG 2000 + H_2O, $MnSO_4$ + PEG 4000 + H_2O, and $MnSO_4$ + PEG 6000 + H_2O were obtained and their phase compositions were determined. PEG 2 000, 4000 and 6000 were chosen due to its non-toxic, low-cost and suitable balance between the hydrophobicity and viscosity. Manganese sulfate and copper sulfate salts have a high kosmotropicity, which facilitates the phase separation. The temperatures studied in this work (298.15, 318.15 and 338.15 K) are conditions normally employed in the separation processes. With these systems, the influence of temperature, salt type, and the molecular weight of PEG on the liquid–liquid equilibrium (LLE) behavior is evaluated. The empirical Setschenow-type equation [11] was used to evaluate the kosmotropic effect of the salts $MnSO_4$ and $CuSO_4$, as well the temperature and molecular weight of the PEG influence on the phase formation. NRTL (NonRandom Two-Liquid) and UNIQUAC (UNIversal QUAsiChemical) models were used to correlate the LLE for aqueous two-phase polymer–salt solutions.

2. Experimental section

2.1. Materials

Polyethylene glycols (PEG 2 000, 4 000, and 6000 g mol^{-1}) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Chemicals were employed without further purification. Copper sulfate ($CuSO_4$, 99.0%, anhydrous, granular) and manganese sulfate ($MnSO_4 \cdot H_2O$, 99.0%, monohydrate, granular) were obtained from Neon (São Paulo, SP, Brazil). They were dried in an oven at 378.15 K for 1 h before use. In the case of manganese sulfate, the boundary water was counted both in the determination of the binodal and the tie-line. Also, TGA (Perkin Elmer, TGA 4000) analysis was performed to ensure that in the drying conditions only the free water was evaporated. Water that had been passed through a reverse osmosis system purification apparatus (Vexer Smart VOS 106) was used in all experiments. The CAS number (CAS), supplier, and purity of the chemicals are listed in Table 1.

Table 1
Source and purity of the materials.

Name	CAS	Supplier	Purity assay (%)
PEG 2000	25322-68-3	Sigma-Aldrich	–
PEG 4000	25322-68-3	Sigma-Aldrich	–
PEG 6000	25322-68-3	Sigma-Aldrich	–
Copper sulfate	7758-98-7	Neon	99.0
Manganese sulfate monohydrate	10034-96-5	Neon	99.0
Water		Lab made	–

2.2. Apparatus and procedure

2.2.1. Determination of aqueous two-phase diagrams

The experimental determination of the binodal curves at a temperature of 298.15, 318.15, and 338.15 K was accomplished using the cloud point method [12]. This method employs an LLE cell with a controlled temperature and volume of 30 cm^3 as previously described by Sampaio et al. [13]. The solution was kept well-mixed within the jacketed glass cell using a magnetic stirrer (Nova Ética, AGI 114), and the temperature was controlled by water flow from a thermostatic water bath (Lab Companion RW − 1025G). Scheme of experimental apparatus used in the determination of binodal curves and tie-lines are provided in Supplementary Information.

Solutions of knowing compositions prepared by gravimetric analysis (Shimadzu, AUX320) were titrated with each other until the cloud point was found. A Pasteur pipette was used to add water to the system to make it homogeneous again. The amount of water added was also quantified by gravimetric analysis. This procedure was repeated until enough points for construction of the binodal curve were obtained. The experimental procedure was validated by comparison of the phase diagram obtained for the aqueous systems PEG 1000/1500/2000 and $(NH_4)_2SO_4$ at $T = 298.15$ K with the literature [14] and was found to be in close agreement with it (Fig. S2 - Supplementary Information). All LLE assays were performed at a local atmospheric pressure (about 91 kPa) measured by a calibrated manometer (Greisinger, GDH 12 vacuum gauge model).

2.2.2. Determination of tie-lines (TLs)

The determination of the TL compositions was based on the gravimetric method proposed by Merchuk [15]. This method consists of choosing different concentrations (overall compositions) situated within the partial miscibility region. After the overall compositions had been chosen, the system was prepared in centrifuge tubes, into which appropriate amounts of PEG solution, salt, and water were added to obtain a total system mass of 12 g. The mixture was agitated (Gomixer, MX-S) for 5 min, producing a homogeneous mixture. Then the samples were placed in a thermostatic bath at constant temperature (298.15, 318.15, and 338.15 K) for 24 h. After this time, the phases were carefully separated with a Pasteur pipette and then weighed.

The experimental binodal curves were fitted using Eq. (1) [15]. The parameters *A*, *B*, and *C* were obtained by regression and minimization of the objective function (Eq. (2)) with the Solver tool in Microsoft Excel using the generalized reduced gradient optimization method.

$$Y = A exp\left[\left(BX^{0.5}\right) - \left(CX^{3}\right)\right] \tag{1}$$

where *Y* and *X* are the PEG and salt weight percentages, respectively.

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

The Solver function employs the Generalized Reduced Gradient (GRG) optimization method considering the experimental values of the PEG mass fraction (Y_i^{exp}) in the system and the PEG mass fraction computed from the model equation (Y_i^{mod}), where 10^{10} is a coefficient used to enhance objective function, allowing the correct calculation of the PEG mass fraction in the system as described by Sampaio et al. [13].

For determination of the TLs, a system of four equations (Eq. (3–6) and four variables (Y_T, Y_B, X_T, and X_B) was solved by the Solver tool in Microsoft Excel, applying the GRG optimization method.

$$Y_T = A exp\left(B{X_T}^{0.5} - C{X_T}^{3}\right) \tag{3}$$

$$Y_F = A exp\left(B{X_F}^{0.5} - C{X_F}^{3}\right) \tag{4}$$

$$Y_T = \left(\frac{Y_M}{\propto}\right) - \left[\left(\frac{1-\propto}{\propto}\right)Y_B\right] \tag{5}$$

$$X_T = \left(\frac{X_M}{\propto}\right) - \left[\left(\frac{1-\propto}{\propto}\right)X_B\right] \tag{6}$$

where *M*, *T*, and *B* denote the mixture, the top phase, and the bottom phase, *X* is the weight fraction of an inorganic salt, *Y* is the weight fraction of PEG, and α is the ratio between the mass of the