



# Aqueous two-phase system of poly(ethylene glycol) 4000 and ferrous sulfate at different temperatures



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## ABSTRACT

Liquid–liquid equilibrium (LLE) data for a  $\text{FeSO}_4$  + polyethylene glycol 4000 (PEG 4000) +  $\text{H}_2\text{O}$  system were experimentally determined at  $T = (288.15, 298.15 \text{ and } 308.15) \text{ K}$ . The effects of temperature on the solubility curves and tie-lines were studied to show in this case that an increasing the temperature expanded the two-phase region. The UNIQUAC model was used to correlate the experimental tie-line data, which yielded a good representation of the equilibrium.

Additionally, experimental density, sound velocity, refractive index, viscosity and electrical conductivity data were also determined at  $T = (288.15, 298.15 \text{ and } 308.15) \text{ K}$  over a wide composition range in the monophasic zone. Othmer's rule was used to correlate the experimental density, sound velocity, refractive index and viscosity data. The electrical conductivity data were transformed to molar conductivity data and correlated with the percentage of poly(ethylene glycol). The experimental and correlated values were similar.

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## 1. Introduction

Systems containing two aqueous liquid phases at certain concentrations are very useful to extract and recover many types of molecules and ions. These systems are usually formed by combining polymer/polymer, polymer/salt or salt/salt dissolved in water [1]. Aqueous two-phase systems (ATPSs) have been widely studied [2–5] and are recognized as an economical and efficient downstream processing method that offers several advantages, such as low cost, environmentally friendliness, low viscosity and short phase splitting times [6,7], in contrast with conventional solvent extraction stages.

One of the most common polymers used to form ATPSs is poly(ethylene glycol) (PEG), which is a hydrophilic polymer. This polymer is mixed with a kosmotropic (water structuring) salt to form an ATPS. This type of ATPS can be applied to separate, concentrate or fractionate biological solutes and particles, such as cells and proteins [8–10]. ATPSs can also be applied to selectively separate metal ion species [3,7,11].

Pathak et al. [12] reported the phase diagram of the studied

$\text{FeSO}_4$  + PEG 4000 +  $\text{H}_2\text{O}$  system at  $T = (290.15, 303.15 \text{ and } 313.15) \text{ K}$ , but did not note the physical properties at equilibrium or in the monophasic zone, nor is analyzed the pH effect, nor did they model the equilibrium data.

Furthermore, the physical and chemical properties of aqueous solutions, including poly(ethylene glycol) and sulfate salt solutions, have rarely been reported. Gonzáles-Tello et al. [13] studied the effect of  $\text{MgSO}_4$  on the viscosity of PEG (8000 and 1000) +  $\text{H}_2\text{O}$  at (277 and 298) K. Mei et al. [14] reported the density and viscosity experimental data of aqueous solutions of PEG +  $(\text{NH}_4)_2\text{SO}_4$  at 298.15 K for several molecular weights of PEG (1000, 2000, 4000, 6000 and 20000 g/mol). The density, electrical conductivity, viscosity and refractive index of the aqueous system formed by lithium sulfate + PEG 4000 were measured by Silva et al. [15] over a temperature range of (278.15–318.15) K. Zafarani-Moattar et al. [16] measured the densities of aqueous solutions for several PEG + salt systems at (298.15, 308.15 and 318.15) K. These experiments used salts of sodium sulfate, sodium carbonate, ammonium sulfate and a mixture of dipotassium hydrogen phosphate and potassium dihydrogen phosphate, and the experimental results were correlated with a semi-empirical equation. Similar work was also reported by Zafarani-Moattar and Mehrdad [17].

In the future, the liquid–liquid equilibrium (LLE) data reported herein could allow metal ion separation processes to be planned.

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Furthermore, the phase diagram of this system has not yet been reported at  $T = (288.15, 298.15 \text{ and } 308.15) \text{ K}$ . The refractive index, density, sound velocity and kinematic viscosity of each phase at equilibrium and  $T = (288.15, 298.15 \text{ and } 308.15) \text{ K}$  were also measured. Complementing the work, density, sound velocity, refractive index, kinematic viscosity and electrical conductivity of the monophasic zone were measured at the three temperatures mentioned above.

The LLE phase diagrams of polymer-salt ATPs are usually modeled based on local composition concepts and their modifications [5,18,19]. In the present work, the extended UNIQUAC [20] model was applied to correlate the experimental LLE data of the aqueous  $\text{FeSO}_4 + \text{PEG 4000} + \text{H}_2\text{O}$  system at  $T = (288.15, 298.15 \text{ and } 308.15) \text{ K}$ . The Pitzer–Debye–Hückel equation [21] was used to account for the long-range electrostatic interactions of the ions.

## 2. Experimental

### 2.1. Chemicals

Synthesis-grade polyethylene glycol with an average molar mass of 4000 (3500–4500)  $\text{g mol}^{-1}$  and analytical grade reagent ferrous sulfate heptahydrate with a purity  $>0.99$  mass fraction were procured from Sigma–Aldrich and Riedel-de Haën, respectively. The water content in the PEG 4000 was determined to be 0.0031 mass fraction by the Karl Fisher method and was neglected in the calculus of total solution mass. Sulfuric acid, with a purity of 0.95–0.97 mass fraction (density:  $1.84 \text{ g cm}^{-3}$ ), was procured from Merck. All chemicals were used without further purification. Milli-Q quality deionized water was used in all experiments ( $\kappa = 0.054 \text{ mS cm}^{-1}$ ).

### 2.2. Apparatus and procedure

The pH values of the aqueous solutions of  $\text{FeSO}_4$  must be acidic, preferably less than 3, to prevent ferrous ions from being oxidized to ferric ions and precipitating [22]. At pH values below 3, these solutions are stable for several days. Thus, we utilized acidified water to ensure that the ferrous ions remained stable.

The deionized water was acidified in a jacketed vessel by adding sulfuric acid at a constant temperature until the solution reached a pH value of 1.06. The pH values were measured using an Accumet pH meter 50 with a measurement range from  $-2$  to  $20$  between  $(268.15 \text{ and } 378.15) \text{ K}$  and a relative accuracy of  $\pm 0.002$ . To maintain a constant temperature, a thermostatically controlled Julabo bath F25-ME Refrigerated/Heating Circulator was used with working temperature range  $245.15\text{--}473.15 \text{ K}$  and an uncertainty of  $\pm 0.01 \text{ K}$ . The solutions were agitated using a VWR® Professional magnetic stirrer with operating conditions from  $278.15$  to  $313.15 \text{ K}$  and a speed range from  $60$  to  $1600 \text{ rpm}$ . The acidified water needed to be prepared at each temperature under study because the pH value is a function of the temperature (more sulfuric acid was necessary at higher temperatures).

The turbidimetric method was used to determine the solubility curve; this procedure consisted of adding a small amount of  $\text{FeSO}_4$  or PEG (approximately  $0.01 \text{ g}$ ) to the respective acidified aqueous solution of  $\text{FeSO}_4$  or PEG with known mass composition. The solutions were prepared by mass in a Mettler Toledo analytical balance (model AX204) with a precision of  $\pm 0.1 \text{ mg}$ . These solutions were then agitated for two minutes using a Vortex Mixer Classic Model F202A0173 (Velp Scientific). Subsequently, the solutions were placed in a thermostatic bath (F25-ME Julabo) at constant temperature ( $\pm 0.1 \text{ K}$ ) for several minutes; this procedure was repeated until a change in the turbidity appeared, which indicated the formation of a second liquid phase. The procedure was similar

for the three tested temperatures.

Once the solubility curve was determined, the properties in the monophasic zones of density, sound velocity, refraction index and kinematic viscosity were determined. Approximately  $40 \text{ g}$  of a solution of known composition was prepared by mass. The densities and sound velocities of the solutions were measured using a density and sound velocity meter (Anton Paar DSA 5000M, measuring range from  $0$  to  $3 \text{ g cm}^{-3}$ , resolution  $1 \cdot 10^{-6} \text{ g cm}^{-3}$ ) with a precision of  $\pm 0.001 \text{ K}$ . The obtained uncertainties were  $\pm 1 \cdot 10^{-5} \text{ g cm}^{-3}$  and  $\pm 0.03 \text{ m s}^{-1}$  for the density and sound velocity, respectively. The density and sound velocity meter was calibrated using air and deionized water as reference substances. Two milliliters of solution was used for each measurement, and measurements were conducted in triplicate. The reported data represent the average. Density and sound velocity were measured simultaneously.

The refractive indices were measured using a refractometer (Anton Paar Abbemat 550, measuring range from  $1.30$  to  $1.72 n_D$  units, resolution  $1 \cdot 10^{-6} n_D$  units, accuracy  $\pm 2 \cdot 10^{-5} n_D$  units, temperature probe accuracy  $0.03 \text{ K}$ , temperature probe stability  $0.002 \text{ K}$ ). Each measurement was conducted in triplicate and utilized  $0.5 \text{ ml}$  of solution; the average of these measurements is reported. The uncertainty of these measurements was  $\pm 1 \cdot 10^{-4}$ .

The kinematic viscosities were measured with calibrated micro-Ostwald viscometers. A Schott-Gerate automatic measuring unit (model AVS 310) equipped with a thermostat (Schott-Gerate, model CT 52) in which the temperature was regulated to within  $\pm 0.05 \text{ K}$  was used for the measurements. We obtained the absolute viscosity by multiplying the kinematic viscosity by the corresponding density. The uncertainty of the kinematic viscosity measurements was  $\pm 5 \cdot 10^{-3} \text{ mm}^2 \cdot \text{s}^{-2}$ . The measurements were conducted in triplicate, and  $2 \text{ ml}$  were used for each experiment.

The electrical conductivities were measured in a conductivity meter (Orion Orion, model 19700-27, accuracy  $<0.5\%$  and reproducibility  $\pm 0.07\%$ ). Forty milliliters of solution were incubated in a jacketed vessel maintained at the working temperature by a thermostatically controlled bath. The solutions were continuously stirred with a magnetic stirrer. The above-described thermostatically controlled bath and magnetic stirrer were used. The average of three measurements is reported. The uncertainty of these measurements was  $\pm 0.01 \text{ mS cm}^{-1}$ .

The tie-lines were determined for mixtures of known overall composition (typically  $80 \text{ g}$ ), which were agitated for  $48 \text{ h}$  in a rotatory bath, whose temperature was controlled within  $\pm 0.1 \text{ K}$ . The obtained biphasic solutions were allowed to settle for  $24 \text{ h}$  at constant temperature, and extending the time periods of agitation and sedimentation did not affect the results.

Once equilibrium was reached, the top and bottom phases were withdrawn using syringes and needles to determine the ion  $\text{Fe}^{2+}$  concentration of each phase and measure the physical properties (density, sound velocity, refractive index and kinematic viscosity) in the same way as explained above.

The concentration of  $\text{FeSO}_4$  was determined by analyzing the iron content using atomic absorption spectroscopy (AAS). The AAS measurements were performed using a Varian Atomic Absorption Spectrophotometer, model 220; using acetylene gas burner, at wavelengths of  $248.3 \text{ nm}$  and a lamp current of  $5 \text{ mA}$ . The PEG concentration was determined using the Merchuk equation (equation 15), which related the concentrations of ferrous sulfate and PEG, and the water content is given by the difference between the iron and PEG concentrations.

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