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Measurement and correlation of phase equilibrium of the aqueous two-phase system formed by $Fe_2(SO_4)_3$ + PEG 4000 + H_2O at different temperatures

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ABSTRACT

Liquid-liquid equilibrium (LLE) data for the $Fe_2(SO_4)_3$ + polyethylene glycol 4000 (PEG 4000) + H_2O system were determined experimentally at $T = (323.15, 333.15 \text{ and } 343.15)$ K. The effect of temperature on the binodal curves and tie-lines were studied and it was found that an increasing in temperature caused the expansion of two-phase region.

Additionally, experimental density, sound velocity, refractive index and viscosity data were also reported at $T = (323.15, 333.15 \text{ and } 343.15)$ K.

The Chen-NRTL, modified Wilson and extended UNIQUAC models and the Othmer-Tobias and Bancroft equations were used to correlate the experimental tie-line data obtaining a good representation of the equilibrium. Furthermore, the Merchuk equation was used to correlate the binodal curves.

1. Introduction

From previous studies in the hydrometallurgy field, where the solvent extraction stage uses highly volatile and polluting organic solvents, the aqueous two-phase systems (ATPS) arise as an alternative for replace these organic solvents. Since, the ATPSs have many advantages such as low cost, low viscosity, short process time, low energy consumption and are environmentally friendly [1].

The ATPSs are usually formed by combining polymer/polymer, polymer/salt or salt/salt dissolved in water. These systems have been previously studied in the extraction of biological material such as proteins and cells, the recovery of biomolecules and in the extraction of inorganic salts and metal ions [2–5].

Liquid–liquid equilibrium data of ATPSs composed of polyethylene glycol supply relevant information for potential applications, especially studies that investigate the influence of the temperature on the phase diagram, parameter that influence the extraction or partition of analytes, as the above mentioned [6]. Also, the physical and chemical properties of the constituent phases of an ATPS are of great relevance in chemical engineering to understand the fundamentals of separation processes and fluid transport, among others. Properties, such as density and viscosity, are also crucial for pipe sizing, mass balance calculations, and equipment design [7].

As a continuation of the previous works, the liquid-liquid equilibrium data for the ATPS formed by $Fe_2(SO_4)_3$ + PEG 4000 + H_2O at $T = (323.15, 333.15 \text{ and } 343.15)$ K are reported. The physical properties as density, sound velocity, refractive index and kinematic viscosity of both phases were also measured. In the future, the liquid-liquid equilibrium (LLE) data and the physical properties reported herein could allow metal ion separation processes to be planned, because in the hydrometallurgy process of copper, the ferric sulfate is present at high concentrations, so this compound could be used to form an ATPS and study the partition of metal ions as copper, molybdenum, among others. It is noteworthy that there is no record of this system at any temperature.

The LLE phase diagrams of polymer-salt ATPSs are usually modeled based on local composition concepts and their modifications [8–10]. In the present work, the experimental data of the tie-lines were correlated by Chen-NRTL [11], modified Wilson [12] and extended UNIQUAC [13] models and with the Othmer-Tobias [14] and Bancroft [15] equations. The binodal curves were correlated by the Merchuk equation [16].

2. Experimental

2.1. Chemicals

Synthesis grade PEG with an average molar mass of 4000 (3500–4500) was procured by Merck and ferric sulfate hydrate with a purity of >0.985 was procured by Winkler, both reagents were used without further purification. Deionized water was used in all experiments

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Table 1
General description of the chemicals used.

Chemical	Source	Purity	Purification method
PEG 4000	Merck	Synthesis grade	None
$Fe_2(SO_4)_3 \cdot nH_2O$	Winkler	≥0.985 (mass fraction)	None

(Milli-Q, Millipore, $\kappa = 0.055$ μS·cm^{-1}). Table 1 shows the general descriptions of the salt and polymer used.

2.2. Apparatus and procedure

The binodal curves were determined by the turbidimetric method [10]; this procedure consisted in adding small amount of PEG or $Fe_2(SO_4)_3 \cdot nH_2O$ (typically 0.001 g) to the respective aqueous solution. Later, the solution was shaken and put it in a thermostatic bath at constant temperature (±0.1 K) by some minutes. The 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.

The tie-lines were determined at constant temperature for mixtures of known overall composition (typically 60 g), which were agitated for 48 h in a rotatory bath, whose temperature was controlled within ±0.1 K. The biphasic solutions obtained were allowed to settle for 24 h at constant temperature. After reaching equilibrium, samples were taken from top and bottom phases to determine the composition of each phase and measure the physical properties (density, sound velocity, refractive index and kinematic viscosity) by triplicate.

All solutions were prepared by mass in a Mettler Toledo analytical balance (model AX-204) with a precision ±0.1 mg.

The densities and sound velocities of the solutions were measured in a density and sound velocity meter (Anton Paar: DSA 5000 M) with uncertainties of $\pm 5 \cdot 10^{-5}$ g·cm^{-3} and 0.05 m·s^{-1} for the density and sound velocity, respectively. The equipment was calibrated using distilled deionized water and air as reference substances.

A refractometer (Anton Paar Abbemat 550) was used to measure refractive indices with an uncertainty of $\pm 1 \cdot 10^{-4} nD$ units. A calibrated micro-Ostwald viscometer was used to measure the kinematic viscosities. This viscometer is constituted by 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 ±0.05 K. To obtain the absolute viscosity values, the kinematic viscosity can be multiplied by the corresponding density; the uncertainty obtained was $\pm 8 \times 10^{-3}$ mPa·s.

The concentration of $Fe_2(SO_4)_3$ 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. The PEG concentration of the Tie-lines was determined using the Merchuk equation (Eq. (18)), which related the concentrations of ferric sulfate and PEG, and the water content is given by the difference between the iron and PEG concentrations.

Table 2
Binodal curve data of the $Fe_2(SO_4)_3$ (ca) + PEG 4000 (p) + H_2O (w) system at T = (323.15, 333.15 and 343.15) K[a].

w_{ca} $T = 323.15$ K	w_p	w_{ca} $T = 333.15$ K	w_p	w_{ca} $T = 343.15$ K	w_p
0.4082	0.0111	0.3507	0.0063	0.4052	0.0028
0.3407	0.0142	0.3107	0.0104	0.3358	0.0044
0.3150	0.0202	0.2868	0.0159	0.2232	0.0279
0.2971	0.0245	0.2390	0.0423	0.2266	0.0266
0.2839	0.0280	0.2275	0.0521	0.2290	0.0255
0.2723	0.0332	0.1983	0.0878	0.2323	0.0244
0.2638	0.0381	0.1923	0.0968	0.2359	0.0228
0.2550	0.0446	0.1839	0.1048	0.2359	0.0228
0.2390	0.0638	0.1766	0.1112	0.2323	0.0244
0.2299	0.0739	0.1699	0.1192	0.2290	0.0255
0.2205	0.0849	0.1592	0.1426	0.2266	0.0266
0.2131	0.0942	0.1553	0.1474	0.2232	0.0279
0.2061	0.1023	0.1501	0.1548	0.2153	0.0285
0.1971	0.1144	0.1446	0.1615	0.2135	0.0310
0.1892	0.1267	0.1365	0.1853	0.2080	0.0334
0.1808	0.1380	0.1320	0.1914	0.2045	0.0353
0.1747	0.1469	0.1273	0.1991	0.2024	0.0370
0.1660	0.1606	0.1215	0.2051	0.1984	0.0419
0.1577	0.1754	0.1165	0.2130	0.1980	0.0451
0.1493	0.1912	0.1118	0.2186	0.1928	0.0492
0.1413	0.2072	0.1019	0.2599	0.1889	0.0538
0.1284	0.2630	0.0985	0.2658	0.1840	0.0567
0.1208	0.2911	0.0949	0.2719	0.1836	0.0600
0.1145	0.3079	0.0910	0.2823	0.1786	0.0663
		0.0869	0.2934	0.1734	0.0766
		0.0842	0.2993	0.1561	0.1027
		0.0825	0.3037	0.1541	0.1054
				0.1520	0.1082
				0.1498	0.1111
				0.1474	0.1142
				0.1457	0.1179
				0.1432	0.1216
				0.1407	0.1253
				0.1377	0.1293
				0.1348	0.1334
				0.1317	0.1380
				0.1283	0.1429
				0.1226	0.1485
				0.1143	0.1549
				0.1117	0.1606
				0.1062	0.1676
				0.1039	0.1739
				0.1023	0.1807
				0.0961	0.1886
				0.0911	0.1923
				0.0849	0.2015
				0.0789	0.2156
				0.0715	0.2309
				0.0660	0.2478
				0.0602	0.2617
				0.0534	0.3006

[a] The standard uncertainties, u, are $u(w_i) = 0.003$ and $u(T) = 0.1$ K.

Previously, the parameters of Merchuk equation were determined by fitting the binodal data and then the equation was used to determine the PEG concentration [17].

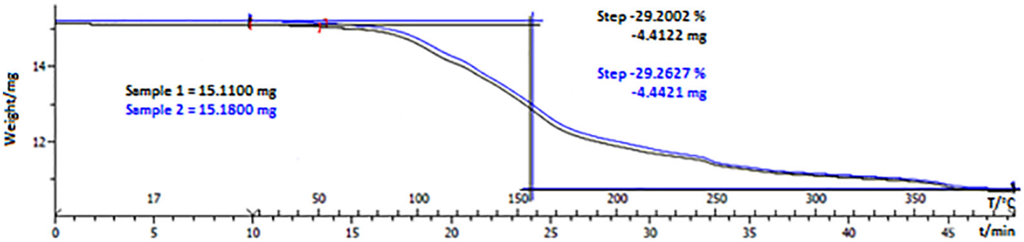

Fig. 1. Thermal decomposition curve of $Fe_2(SO_4)_3 \cdot nH_2O$ to determine the water molecules.