Molybdate ion partition in the aqueous two-phase system formed by CuSO₄ + PEG 4000 + H₂O at different pH and temperatures

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ABSTRACT

In this study, the aqueous two-phase system (ATPS) formed by $CuSO_4$ + PEG 4000 + H_2O, for the partition of the molybdate ion at different pH values (1.5, 2.0 and 2.5) and at five different temperatures, T = (298.15, 308.15, 318.15, 328.15 and 338.15) K was studied. Two different salts, Na_2MoO_4 and $(NH_4)_6Mo_7O_{24}$, were used for the experimental partition tests. The extraction percent for the molybdate ion in the ATPS was studied as a function of pH and temperature. The experimental results indicate that the extraction percent increases with increasing temperature. The maximum extraction reached was 93.07% at pH = 2.5 and T = 338.15 K, for the $CuSO_4$ + PEG + H_2O + Na_2MoO_4 system, and 92.66% in the $CuSO_4$ + PEG + H_2O + $(NH_4)_6Mo_7O_{24}$ system at pH = 2.5 and T = 318.15 K.

In addition, the pH effect on the liquid-liquid equilibria of the ATPS $CuSO_4$ + PEG + H_2O at T = 308.15 K was studied, where no significant influence was observed in the working pH range (from 1.5 to 2.5). However, if it is compared with the literature data, it has a relevant importance. With decreasing pH, the two-phase area decreases, thus the tie-line slope also varied.

Chen-NRTL and Wilson modified models were applied to correlate the liquid-liquid equilibrium. A good agreement between experimental data and correlated results was obtained.

1. Introduction

The ATPSs are generally formed by combining polymer/polymer, polymer/salt or salt/salt dissolved in water, which separate into two phases above a critical thermodynamic condition. Beijerinck [1] reported the first ATPS in 1896, afterwards Albertsson [2] applied these systems for recovery of biological molecules such as proteins and cells. Last years, ATPSs have been also used in the extraction of ions [3–10]. Rogers et al. [3] applied crown ethers 1, 4, 7, 10, 13-pentaoxacyclopentadecane (15-crown-5) and 1, 4, 7, 10, 13, 16-hexaoxacyclooctadecane (18-crown-6) to study the partitioning of Group 1 and 2 cations in the aqueous biphasic system formed by polyethylene glycol of 2000 and NaOH. The partitioning behavior of Sr^{2+} and Cs^+ in aqueous biphasic systems formed by the addition of polyethylene glycol (PEG)-2000 to either NaOH, $(NH_4)_2SO_4$, or K_2CO_3 was investigated by Rogers et al. [5]. The authors reported that the distribution ratios in the presence or absence of extractants and regardless of salt system appear to be governed by cation enthalpy of hydration and system composition. Griffin et al. [8] reported that iodide partitions to the PEG-rich phase of a PEG-2000/salt ATPS and onto ABEC-5000 and ABEC-2000 resins, while iodate does not. Iodide can

be separated from IO_3^- using these methods. The partitioning of iodide can also be enhanced by derivatization with 2,6-dimethylphenol to 4-iodo-2,6-dimethylphenol or complexation with I_2, increasing its preference for the PEG-rich phase. Recently, Jimenez et al. [10] reported the partition of the perchlorate anion on the ATPS $NaNO_3$ + PEG 4000 + H_2O, concluding that the partition coefficient is proportional to the difference concentration of PEG of the tie-lines and to the temperature.

Molybdenum is a mineral that is present in nature associated to sulfide minerals, although it is also presented in oxidized minerals in the form of rock. It can be found in minerals such as molybdenite, MoS_2, or associated with others such as wolframite or certain copper minerals. It is a valuable metal and has been widely used in many applications, in steel and iron alloys [11], chemical industry and agriculture [12]. The solvent extraction process to recover this metal from leach solutions has been investigated previously. Where several extraction reactants where reported such as bis(2-ethylhexyl)phosphoric acid (D2EPHA) [13], alkylphosphonic and β-hydroxyoxime [14], tertiary amines [15], among several other volatile organic solvents (VOCs).

Contrary to a regular solvent extraction process, ATPS are environmentally friendly, of low cost, low viscosity and short phase separation [16]. To our knowledge, there are only one reported ATPS for molybdenum partitioning. Zhang et al. [17] studied the selective extraction and separation of molybdenum (VI) from aqueous media by ATPS formed by Triton X-100 + $(NH_4)_2SO_4$ + H_2O. The authors reported that the

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extraction percentage and distribution coefficient of molybdenum have relationship with molybdenum species in aqueous phase and reach the maximum of 97% and 75, respectively, at pH = 3.0.

Chile is one of the largest world producers of copper and molybdenum concentrates. In the production of these concentrates, the molybdenum is one of the most important products. Therefore, it is interesting to study the probability of partitioning molybdate ion in an ATPS formed by poly(ethylene glycol) and copper sulfate that could constitute an alternative process for the production of molybdate salts. As part of a long-term study, the partitioning of molybdate ion in the ATPS formed by $CuSO_4$ + PEG 4000 + H_2O at pH = (1.5, 2.0 and 2.5) and T = (298.15, 308.15, 318.15, 328.15 and 338.15) K is reported.

It is noteworthy that there is no record concerning to the partitioning of molybdate ion on the ATPS $CuSO_4$ + PEG 4000 + H_2O. Moreover, thermodynamic parameters of transference, $\Delta_{tr}G°$, $\Delta_{tr}H°$ and $\Delta_{tr}S°$ were determined from partition experimental tests for the pH and temperature values under study.

The liquid–liquid equilibrium (LLE) data can be accurate correlated generally with two kinds of models, one based on osmotic virial expansions and the other on lattice theories. Zafarani-Moattar and Sadeghi [18], determined that an extension of the NRTL model can be made to express short-range interaction for aqueous polymer-salt system, applying the local composition concept to solvent, segments and ions, instead than solvents, polymer and salt. Additionally, two assumptions of local electro-neutrality and like-ion repulsion proposed by Chen [19] and Chen and Evans [20], are incorporated. Sadeghi [21], presented the electrolyte Wilson model combined with the polymer Wilson model to represent the excess Gibbs energy of aqueous polymer-electrolyte solutions. The integrated model has three contributions. For the configurational entropy of mixing the Flory-Huggins is used as a combinatorial contribution to the excess Gibbs free energy. The Pitzer-Debye-Hückel model is used for long-rage electrostatic interactions and the modified Wilson equation is used for short-range interactions.

LLE data at T = (288.15, 298.15 and 308.15) K were previously reported by Claros et al. [22]. This information was used to plan the molybdate ion partition tests, and to complement this study, the effect of the pH on the LLE at 308.15 K was studied. Chen-NRTL [18] and Wilson modified [21] models were applied for the correlation of LLE data.

2. Experimental

2.1. Chemicals

Poly(ethylene glycol) was purchased from Sigma-Aldrich with synthesis grade and an average molar mass of 4000 g·mol^{-1} (3500–4500 g·mol^{-1}). Copper (II) sulfate pentahydrate, sodium molybdate dihydrate and ammonium heptamolybdate tetrahydrate with a purity of >0.99, >0.995 and >0.995, respectively, were procured by Merck and used without further purification. Milli-Q quality deionized water (κ = 0.054 μS·cm^{-1}) was used in all experiments. Sulfuric acid with a purity of 0.95–0.97 mass fraction was procured from Merck. The specifications of the chemical products are described in Table 1.

Table 1
General description of the chemicals used.

Reagent	Supplier	Purity (mass fraction)	Purification method
PEG 4000	Merck	BioUltra	None
$CuSO_4 \cdot 5H_2O$	Sigma – Aldrich	>0.99	None
$Na_2MoO_4 \cdot 2H_2O$	Merck	>0.995	None
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	Merck	>0.995	None
H_2SO_4	Merck	0.95–0.97	None

2.2. Methods and procedures

2.2.1. Liquid/liquid partitioning studies for molybdate ion

For the partition of molybdate ion in the biphasic $CuSO_4$ + PEG 4000 + H_2O system, the salts of $Na_2MoO_4 \cdot 2H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were used, separately. The pH was modified with the addition of sulfuric acid, which was not included in the calculation since the amounts were insignificant, for each temperature the pH was fixed to a determined value. The composition of the tie-line used for the partition tests was based on literature [22]. For each partition test, the global composition of the system was 0.1130 of $CuSO_4$ and 0.1405 of PEG 4000 mass fractions (tie-line midpoint). 0.05 g of molybdate salts expressed as anhydrous in all solutions was added. The total weight of each solution was 30 g. All solutions were prepared using an analytical balance Mettler Toledo C. AX-204 with a precision of ± 0.07 mg.

The solutions were prepared in a jacketed vessel of 70 ml. The jacketed vessel was connected to a thermostatically controlled Julabo bath F25-ME Refrigerated/Heating Circulator to maintain a constant temperature, with an uncertainty of ± 0.01 K. The agitation was made with a professional magnetic stirrer VWR® with speed range from 60 to 1600 rpm. For pH solutions measurement, a pH meter Accumet 50 with a relative accuracy of ± 0.002 was used (uncertainty ± 0.02). Equilibrium time of each solution was of 1 h approximately. Once equilibrium was reached, the biphasic solution was left to settle under controlled temperature until the system was completely divided in two-phases. Both phases were separated using syringes and needles to determine the ion concentration in each phase of the partitioned salts. The concentration of sodium and molybdenum was determined by atomic absorption spectroscopy (AAS) and ammonium by direct potentiometric analysis by Ion-selective electrode. A Varian Atomic Absorption Spectrophotometer model 220 was used to realize the AAS measurements and a Fischer Scientific Accumet model 25 pH/Ion meter with Ion-selective electrode was used to realize the direct potentiometric analysis. All partition studies were realized in duplicate.

2.2.2. Physical properties

Physical properties of each phase were measured in triplicate. Densities and sound velocities were measured in an Anton Paar DSA 5000 M density and sound velocity meter, with an uncertainty of ± 5 × 10^{-5} g·cm^{-3} and 0.05 m·s^{-1}, for the density and sound velocity, respectively. Refractive indices were measured in an Anton Paar: Model Abbemat 550 refractometer (uncertainty ± 1 × 10^{-4} n$_D$).

2.2.3. Liquid/liquid equilibria at different pH values

For the study of pH influence on liquid/liquid equilibria, the literature data reported by Claros et al. [22] were used as reference. In the biphasic area, four tie-lines were determined for mixtures of known overall composition. The solutions were prepared by mass with a total weight of 30 g in a 70 ml jacketed vessel to control a constant temperature of 308.15 K for all the tie-lines.

Sulfuric acid was added to adjust the pH values to 1.5, 2.0 and 2.5. The equilibrium was reached after 1 h, then, the phases were separated using syringes and needles. Samples are later analysed with Atomic Absorption Spectrophotometry to determine copper concentration. Water concentration was obtained by evaporation at 313.15 K in a stove, and by mass difference the concentration of PEG in each solution was calculated.

2.3. Partition coefficient and extraction percent

The partition coefficient is calculated by:

$$K = \frac{C_{ca}^{top}}{C_{ca}^{bot}}, \tag{1}$$

where C is the concentration and the subscript "ca" stands for salt. The