



Aqueous two-phase system of poly(ethylene glycol) 4000 and sodium molybdate at different temperatures



Yahaira Barrueto, Katherine Muñoz, Katuska Garnica, Islamán Villalobos, Yecid P. Jimenez*

Department of Chemical and Mineral Process Engineering, Universidad de Antofagasta, Av. Angamos 601, Antofagasta, Chile

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ABSTRACT

Liquid–liquid equilibrium (LLE) data for the Na_2MoO_4 +polyethylene glycol 4000 (PEG 4000)+ H_2O system were determined experimentally at $T=(288.15, 298.15$ and $308.15)$ K. Additionally, experimental data of density, sound velocity, refractive index and viscosity are also reported at $T=(288.15, 298.15$ and $308.15)$ K.

The effect of temperature on the binodal curves and tie-lines was studied and it was found that an increasing in temperature caused the expansion of two-phase region. The extended UNIQUAC model and the Othmer–Tobias and Bancroft equations were used to correlate the experimental tie-line data obtaining a good representation of the equilibrium. Moreover, the Merchuk equation was used to correlate the binodal curves. A good agreement between experimental and correlated values of the tie-lines was obtained.

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1. Introduction

In the copper hydrometallurgical process and in its concentration process, one of the most important stages to remove impurities is the solvent extraction stage, but one of the main disadvantages is the use of highly volatile and polluting organic solvents.

In recent times, the called aqueous two-phase systems (ATPS) have been investigated as alternative systems of extraction, these systems have many advantages such as low cost, low viscosity, short process time, low energy consumption and are environmentally friendly [1].

The aqueous two-phase systems are constituted of two immiscible aqueous solutions; these can be formed by mixing two polymers and water or an inorganic salt, a polymer and water. The ATPSs have been previously studied in the recovery of biomolecules, extraction of biological material such as proteins and cells, also the last years in the extraction of inorganic salts and metal ions [2–5].

As part of a long-term study, the liquid–liquid equilibrium data for the ATPS formed by Na_2MoO_4 +PEG 4000+ H_2O at $T=(288.15, 298.15$ and $308.15)$ K are reported. The physical properties as

density, sound velocity, refractive index and kinematic viscosity of both phases were also measured. In a future, these liquid–liquid equilibrium (LLE) data and the physical properties will allow to plan the partition experiences of metal ions of our interest. It is noteworthy that there is no record of this system at the three temperatures above mentioned.

The experimental data of the tie-lines were correlated by the extended UNIQUAC model [6] and with the Othmer–Tobias [7] and Bancroft [8] equations. The binodal curves were correlated by the Merchuk equation [9].

2. Experimental

2.1. Chemicals

Synthesis grade PEG with an average molar mass of 4000 (3500–4500) and sodium molybdate dihydrate with a purity of >0.995 were procured by Merck, both reagents were used without further purification. Deionized water was used in all experiments (Milli-Q, Millipore, $\kappa=0.055 \mu\text{S cm}^{-1}$). Table 1 shows the general descriptions of the salt and polymer used.

2.2. Apparatus and procedure

The turbidimetric method [10] was used to determine the binodal curves, this procedure consisted in adding small amount of

* Corresponding author. Tel.: +56 55 2637902.

E-mail address: yecid.jimenez@uantof.cl (Y.P. Jimenez).

Nomenclature

a	Fit parameter, Eq. (20)
a_{ij}	Binary interaction parameter for the extended UNIQUAC model
A_x	Pitzer–Debye–Hückel constant
b	Fit parameter, Eq. (20)
c	Fit parameter of the Merchuk equation
d	Fit parameter of the Merchuk equation
e	Electronic charge
F_{ob}	Objective function
f	Fit parameter of the Merchuk equation
G^E	Excess Gibbs energy
I_x	Ionic strength in mole fraction scale
K	Boltzmann's constant
k	Fit parameter of the Othmer–Tobias equation
k_1	Fit parameter of the Bancroft equation
l_i	Size parameter in UNIQUAC equation
N_A	Avogadro's number
n	Fit parameter of the Othmer–Tobias equation
q_i	Surface parameter of the component I
R	Gas constant
r_1	Volume parameter of the component I
r	Fit parameter of the Bancroft equation
STL	Slope of the tie-line
T	Absolute temperature
TLL	Tie-line length
V_s	Molar volume of the mixed solvents
w_i	Mass fraction of species I
x_i	Mole fraction of species I
Z_i	Absolute charge of ion i
z	Coordination number

Greek symbols

ΔG_c	Free energy of phase separation
ΔH_c	Enthalpy of phase separation
ΔS_c	Entropy of phase separation
γ_i	Activity coefficient of species I
ϵ	Permittivity of vacuum
ϵ_T	Dielectric constant of the mixed solvents
ϕ_i	Volume fraction of component I
ρ	Closest distance parameter
φ	Segment fraction
θ_i	Surface area fraction of component I
τ_{ij}	Boltzmann factor

Subscripts

ca	Salt
cal	Calculated value
exp	Experimental value
i, j	Any species, polymer, ions and solvent
I, J	Any species, polymer, ions and solvent
p	Polymer
w	Water

Superscripts

B	Bottom
ex	Excess property
LR	Long-range
PDH	Pitzer–Debye–Hückel
T	Top
UQ	UNIQUAC

Table 1

General description of the chemicals used.

Chemical	Source	Purity	Purification method
PEG 4000	Merck	Synthesis grade	None
Na ₂ MoO ₄ ·2H ₂ O	Merck	≥0.995 (mass fraction)	None

Na₂MoO₄·2H₂O or PEG (approximately 0.001 g) to the respective aqueous solution. After, the solution was shaken in a vortex and put it in a thermostatic bath at constant temperature (± 0.1 K) by some minutes; this procedure is repeated until a change in the turbidity appears, indicative of the formation of a second liquid phase. The procedure for the three temperatures established was similar.

The tie-lines were determined at constant temperature from mixtures of known overall composition above the binodal curve (typically 60 g), which were agitated for 48 h in a rotatory bath with the temperature controlled to within ± 0.1 K. The biphasic solutions obtained were allowed to settle for 24 h at the desired temperature. All solutions were prepared by mass in a Mettler Toledo C. AX-204 analytical balance of precision ± 0.1 mg. Once the equilibrium was achieved, the top and bottom phases were withdrawn using syringes and needles to determine the composition of each phase and measuring the physical properties by triplicate.

The concentration of Na₂MoO₄ was determined by sodium analysis using atomic absorption spectroscopy (AAS). The AAS measurements were performed using Varian Atomic Absorption Spectrophotometer, model 220. The PEG concentration was determinate using the Merchuk equation, which related the concentrations of sodium molybdate and PEG, and then the water content is given by the difference.

The physical properties measured were density, sound velocity, refractive index and kinematic viscosity, each one of the equipments was previously calibrated at each temperature in study.

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 $\pm 5 \times 10^{-5}$ g cm⁻³ and 0.5 m s⁻¹ for the density and sound velocity, respectively. The equipment was calibrated using air and distilled deionized water as reference substances.

The refractive indices were measured using a refractometer (Mettler Toledo RE50) with an uncertainty of $\pm 1 \times 10^{-4} n_D$ units. Kinematic viscosities were measured using a calibrated micro-Ostwald viscometer; this equipment has a Schott-Gerate automatic measuring unit, model AVS 310, equipped with a Schott-Gerate CT 52 thermostat with a temperature control of ± 0.05 K. The absolute viscosity values were obtained by multiplying the kinematic viscosity by the corresponding density and the uncertainty obtained was $\pm 5 \times 10^{-3}$ mPa s.

3. Thermodynamic framework

For the extend UNIQUAC model, the excess Gibbs energy, G^E , is calculated as a sum of two contributions [6,11]:

$$G^E = G^{E,LR} + G^{E,UQ}, \quad (1)$$

where $G^{E,LR}$ and $G^{E,UQ}$ are the long-range interaction contribution and the value from the UNIQUAC equation, respectively.

The expression for the activity coefficient of the component I (polymer, ions, water), is also considered as the sum of two contributions:

$$\ln \gamma_i = \ln \gamma_i^{LR} + \ln \gamma_i^{UQ}. \quad (2)$$

The terms, $G^{E,LR}$ and $G^{E,UQ}$ are calculated by the Pitzer–Debye–Hückel equation (PDH) [12] and the UNIQUAC equation [6], respectively.

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