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Thermodynamic model for tungstic acid extraction from sodium tungstate in sulfuric acid medium by primary amine N1923 diluted in toluene

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ABSTRACT

A thermodynamic model for the extraction of tungstic acid from sodium tungstate in sulfuric acid using the primary amine N1923 diluted in toluene has been developed. The liquid–liquid extraction equilibrium data were determined by performing a series of experiments at 293.15 K. The activity coefficients of the ions and molecules in the aqueous and organic phases were calculated using the Pitzer equations. Nonlinear regression, based on the balance equations of chemical, mass and charge equilibria and the experimental data, was used as the optimization method. Next, the thermodynamic equilibrium constant and the new Pitzer parameters for sodium tungstate electrolytes in the aqueous phase and the binary interactions between the species in the organic phase were obtained. The new model was used to predict the extraction efficiency from different initial conditions. Experiments were performed to verify the new model. The results indicated that the model could moderately predict this extraction system. Furthermore, the extraction reaction mechanism was investigated using the new model, and the scope of the new model is discussed.

1. Introduction

Molybdenum has been widely used in metallurgical applications in recent decades. In part, the common usage of this element is due to its intrinsic characteristics, such as its ability to withstand extreme temperatures without significantly expanding or softening, its ability to significantly resist corrosion, its high degree of weldability, and its low density. In addition, Mo has had a very stable market price (Considine, 2005; Emsley, 2001). However, molybdenum and tungsten (W) often coexist in natural minerals and other recovery materials due to lanthanide contraction. Thus, developing an efficient method for the separation of these two metals is of particular importance and highly desirable in extractive metallurgy (Cao et al., 2011).

Most researchers have addressed the problem of separating molybdenum and tungsten by primarily focusing on removing molybdenum from tungstate solutions (Gong et al., 1996; Guan et al., 2012; Li et al., 2003; Mohamed et al., 1996; Xiao et al., 2001; Zhao et al., 2010; Zheng and Fan, 1986). However, there have been very few reports on methods for removing tungsten from molybdate solutions. The reports that exist have focused mainly on the utilization of ion exchange, extraction, precipitation, and adsorption methods. Blokhin et al. (2005) used a PK-S cation exchanger to remove tungsten (VI) (0.1 wt.% relative to molybdenum) from ammonium molybdate solution. This cation exchange resulted in a decrease in tungsten content by a factor of no less than 100. Batueva et al. (2010) reported that using *N*′,*N*′-dialkylhydrazides of 2-ethylhexanoic and octanoic acids as the extractant worked well for the separation of tungsten from molybdate solution. Cao et al. (2011) proposed a precipitation route for the separation of W and Mo using divalent metal salts as the precipitating agents. The best results showed that the separation factor can reach 110.9. Srivastava et al. (2012) proposed a simple and effective inorganic adsorption process to separate W and Mo. Their results showed that 91% of W can be removed using the best adsorption reagent, HFO. Unfortunately, there are drawbacks to using these methods for tungsten extraction; these drawbacks include the use of large amounts of acid, residual amounts of W present in the extractant, and the loss of Mo. These shortcomings have hindered the adoption of the aforementioned methods for tungsten extraction in large-scale industrial applications. Thus, other methods need to be developed for the removal of tungsten from molybdate.

Our group previously proposed a method for the removal of tungsten from sodium molybdate solution using primary amine N1923 as

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an extractant (Ning et al., 2009). We systematically studied the effects of different factors on the separation of W and Mo under fixed initial concentrations of W, Mo, and extractant. However, the influence of the different feed solutions on the distribution coefficient and separation factor has not been investigated due to the size of the experiments required for such a study. Additionally, the corresponding fundamental thermodynamic constants, which serve as the basis for simulating and designing extraction processes, have not yet been reported. To research these constants in detail, a thermodynamic model needs to be constructed. The construction of such a model would greatly aid in predicting the extraction performance under various initial conditions without requiring additional experiments. To date, thermodynamic studies of tungsten, molybdenum and other metal extraction using N1923 have been rather limited. Thus, the extraction thermodynamics of W and Mo using a primary amine need be investigated. The new models are expected to predict the separation factor of the two metals.

In this paper, the extraction of tungsten from sodium tungstate using primary amine N1923 was investigated. We subsequently established a thermodynamic model to predict the performance of this extraction process.

2. Experiments

2.1. Materials

A feed solution of W was prepared by dissolving sodium tungstate dihydrate (analytical grade, Beijing Chemical Works, Beijing, China) in ultra-pure water. Dilute sulfuric acid, prepared from concentrated sulfuric acid (95%–98%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), was used as the pH modifier. The extractant, primary amine N1923, i.e., C_{19}–C_{23} secondary alkyl primary amine, with a purity of 98% was purchased from Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The molar mass of N1923 is 310.30 g/mol (Yang et al., 2012). Analytical grade toluene was used as the diluent in this study (Beijing Chemical Works, Beijing, China). All reagents were used without further purification.

2.2. Experimental apparatus and procedure

As shown in Fig. 1, the liquid–liquid extraction equilibrium was determined in a homemade measuring apparatus (Yang et al., 2012). The equilibrium vessel was placed in a magnetic agitator (B4-1A, Shanghai Sile Instrument Co., Ltd., China), connected to a thermostat (DC-0510, Ningbo Scientz Biotechnology Polytron Technologies Inc., China) that held the temperature constant within ±0.1 K.

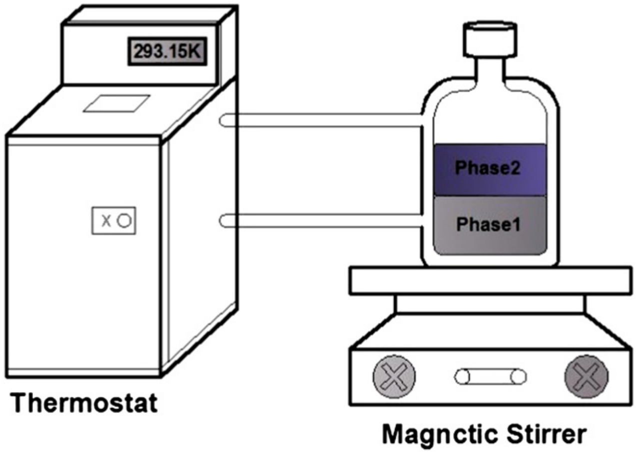

Fig. 1. Apparatus for the liquid–liquid extraction equilibrium.

The initial pH of the aqueous solution of tungsten was adjusted to the desired value using dilute sulfuric acid and measured using a pH meter (Delta320, Mettler, Switzerland) with an accuracy of ±0.01. Samples containing equal volumes (10 mL) of an aqueous phase and organic phase were first placed in the equilibrium vessel at 293.15 K for more than 10 min, rigorously stirred for 1 h and then allowed to settle for 1 h. Next, the samples were transferred to separating funnels. After phase separation, the raffinate was separated, and the equilibrium pH was measured using the pH meter. The metal concentration in the aqueous phase was analyzed using an OPTIMA 5300DV inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer, USA). The wavelength used for tungsten analysis was 207.912 nm. The metal concentration in the organic phase was calculated from the mass balance. The solubilities of the primary amine N1923 and toluene in the aqueous phase, as well as water in the organic phase, were small and, therefore, neglected.

The mass concentration of W ranged from 0.1 g/L to 1.0 g/L, and the mass concentration of N1923 ranged from 0.4 g/L to 3.3 g/L. All experiments were performed in duplicate at least.

3. Chemical, mass and charge equilibria

3.1. Chemical equilibria

According to our previous report (Ning et al., 2009), when the equilibrium pH of the aqueous phase is approximately 7.00 and the initial mass concentration of W is less than 1.0 g/L, the chemical reaction equilibrium can be described as follows:

$$2H^{+}+{WO_4}^{2-}+RNH_2^{org.}\overset{K}{\rightleftarrows}H_2WO_4\cdot {RNH_2}^{org.}. \tag{1}$$

The corresponding thermodynamic equilibrium constant, K, is expressed as:

$$K=\frac{a^{org.}_{H_2WO_4\cdot RNH_2}}{a^2_{H^+}a_{{WO_4}^{2-}}a^{org.}_{RNH_2}}=\frac{m^{org.}_{H_2WO_4\cdot RNH_2}\gamma^{org.}_{H_2WO_4\cdot RNH_2}}{a^2_{H^+}\cdot m_{{WO_4}^{2-}}\gamma_{{WO_4}^{2-}}\cdot m^{org.}_{RNH_2}\gamma^{org.}_{RNH_2}} \tag{2}$$

where a_i is activity of species i, m_i is the molality of species i, γ_i is the activity coefficient of species i and RNH_2 stands for the primary amine N1923 throughout the paper.

3.2. Mass and charge equilibria

According to the general experimental procedure, dilute sulfuric acid was slowly added to the feed solution of W to adjust the initial pH of the aqueous phase. Therefore, the following reaction equilibria should be taken into consideration in the aqueous phase (Eqs. (3)–(7)):

$$Na_2WO_4\rightarrow 2Na^{+}+{WO_4}^{2-} \tag{3}$$

$$H_2SO_4\rightarrow H^{+}+{HSO_4}^{-} \tag{4}$$

$${HSO_4}^{-}\overset{K_s}{\rightleftarrows}H^{+}+{SO_4}^{2-} \tag{5}$$

$$H_2WO_4\overset{K_1}{\rightleftarrows}H^{+}+{HWO_4}^{-} \tag{6}$$

$${HWO_4}^{-}\overset{K_2}{\rightleftarrows}H^{+}+{WO_4}^{2-}. \tag{7}$$