Hydrometallurgy 100 (2010) 110–115

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Kinetics and mechanism of Re(VII) extraction with mixtures of tri-alkylamine and tri-n-butylphosphate

Ying Xiong *, Zhenning Lou, Suang Yue, Junjun Song, Weijun Shan, Guangxi Han

College of Chemistry, Liaoning University, Shenyang 110036, PR China

ARTICLE INFO

Article history:
Received 5 September 2009
Received in revised form 20 October 2009
Accepted 27 October 2009
Available online 5 November 2009

Keywords:
Interfacial extraction kinetics
Tri-alkylamine
Tri-n-butylphosphate
Rhenium(VII)
Molybdenum(VI)

ABSTRACT

The extraction kinetics of rhenium(VII) with mixtures of tri-alkylamine (N235, R_3N, $R=C_8-C_{10}$) and tri-n-butylphosphate (TBP) dissolved in heptane has been investigated by constant interfacial cell with laminar flow. The influence of stirring speed, temperature, specific interfacial area, extractant concentration and chloride concentration on the extraction rate has been studied. It is concluded that the extraction of Re(VII) takes place at the liquid–liquid interface, while the extraction regime belongs to kinetic control by chemical reaction. The extraction rate equations and the rate-determining step have been obtained under the experimental conditions, and the extraction rate constant is calculated. The results are also compared with the system with N235 alone as extractant which shows that the Re(VII) extraction rate is enhanced and the activation energy is decreased with the mixtures of N235 and TBP. The separation of Re(VII) from Mo(VI) by kinetics with the mixtures of N235 and TBP is similar to that with N235 alone. Nevertheless, the separation of Re (VII) from Mo(VI) is better under kinetic conditions than under thermodynamic equilibrium conditions.

1. Introduction

Rhenium is usually recovered from molybdenite concentrates through roasting or direct reduction of the concentrates (Sutulov, 1970). With the ever increasing demands of high purity rhenium and its compounds in the petrochemical industry, national defense and aviation and other specialized applications, many methods are used to purify and separate rhenium and molybdenum, such as chemical deposition, ion exchange, capillary electrophoresis, liquid chromatography and solvent extraction. Among them, liquid–liquid extraction provides an effective and simple separation method (Jordanov et al., 1968; Karagiozov and Vasilev, 1979; Almela et al., 1998). However, it is often complicated by multi-stage cycles, extractant loss and formation of stable emulsions etc. Thus, it is important to explore some new extraction systems or separation methods superior to the current extraction process which has been widely applied to the recovery of rhenium (Gerhardt et al., 2000; Cao et al., 2009).

It is well known that separation by extraction kinetics is possible for the quantitative separation of metal ions which cannot be separated in the equilibrium state (Itabashi et al., 1997). Although the thermodynamics of extraction are relatively well known, there is a lack of comprehensive information on the kinetics of mass transfer in biphasic solvent extraction systems (Chitra et al., 1995; Biswas et al., 1997; Corsi et al., 1998). Thus, kinetics studies on the extraction of individual element are necessary for the development of the experimental procedure and to understand the mechanism and mass-transfer models.

The revised Lewis cell, called the constant interfacial-area cell with laminar flow, developed by Zheng et al. (1998) was previously used in our work (Wang et al., 2002; Xiong et al., 2004). The operation is carried out under laminar flow, which keeps the interface as stable as possible, keeping no flow between two phases. But to date, little research has been reported on the extraction kinetics of rare metals by constant interfacial cell with laminar flow.

In our earlier work, the kinetics of Re(VII) extraction and separation from Mo(VI) with N235 was investigated (Lou et al., 2009), which indicates that the separation of Mo(VI) and Re(VII) could be easier to carry out by kinetics rather than equilibrium extraction. In the present work, research results on the extraction kinetics of Re(VII) with the mixtures of N235 and TBP dissolved in heptane using a constant interfacial cell with laminar flow are reported. The extraction controlling regime is carefully evaluated, and the reaction zone is determined by considering different effects on the extraction process. The purpose is to provide useful information towards developing more efficient and economical hydrometallurgy process for rhenium separation and purification from molybdenum.

2. Experimental

2.1. Reagents

Tri-alkylamine (N235, R_3N, $R=C_8-C_{10}$) was kindly supplied by organic chemical factory Shanghai China. Tri-n-butylphosphate (TBP) was

---

* Corresponding author. Tel./fax: +86 24 62202006.
E-mail address: xiongying_1977@hotmail.com (Y. Xiong).

0304-386X/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.hydromet.2009.10.014

kindly supplied by Tianjin Chemical Reagent No 1 plant. All the reagents were used without further purification. Rhenium stock solutions were prepared by dissolving NH_4ReO_4 (99.9%) in HCl and molybdenum stock solutions were prepared by dissolving $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in HCl. All other reagents were of analytical grade.

2.2. Procedure

N235 was pre-equilibrated with the same volume of 3 M HCl solution in the absence of the metal ions. It was separated and washed with distilled water until neutral pH for the following experiments. The concentration of the mixtures of N235 and TBP (at a ratio of 1:3) in the organic phase was 0.06 mol L^{-1} and the chloride concentration in aqueous phase was kept at 0.1 mol L^{-1} except for the experiments of their effect of concentration on the extraction rate. The aqueous phases contained 5.0×10^{-4} mol L^{-1} rhenate, together with 0.1 mol L^{-1} HCl. The interfacial area was 1.94×10^{-3} m^2 (19.4 cm^2). Both the volumes of aqueous and organic phase were 98 mL. The extraction kinetics was investigated by using a constant interfacial area cell with laminar described previously (Zheng et al., 1998). The concentrations of Re(VII) and Mo(VI) in the aqueous phase were measured by using a 7230 model grating spectrophotometer and PE-700 atomic absorption spectrophotometer, respectively. The concentrations of metal ions in the organic phase were determined by difference.

The interfacial tension experiments were carried out by using JYZ-200 auto-tensiometer.

For the equilibrium experiments, equal volumes (5 mL each) of aqueous and organic phases were mixed and shaken for 30 min at 298 ± 1 K (except for the temperature experiments). The distribution coefficient (D) was taken as the ratio of the metal concentration in the organic phase to the concentration in the aqueous phase.

2.3. Theoretical

Assuming that the mass-transfer process could be formally treated as a pseudo-order reversible reaction with respect to the metal cation (Danesi and Vandergrift, 1981):

$$M^{n+}_{(a)} \Leftrightarrow M(N)_{(o)} \tag{1}$$

The following rate equation can be obtained as described in Eqs. (9) and (10):

$$R_{F(f)} = -\frac{d[M^{n+}]_{(a)}}{dt} = k_f[M^{n+}]^b[Cl^-]^c[\text{Extractant}]^d \tag{2}$$

$$-\frac{d[M^{n+}]_{(a)}}{dt} = -\frac{Q}{V}(k_{oa}[M]_{(o)}-k_{ao}[M]_{(a)}) \tag{3}$$

$$\ln\left(1-\frac{[M]_{(o)}}{[M]^e_{(o)}}\right) = -\frac{Q}{V}(1+K_d)k_{oa}t \tag{4}$$

$$\ln\left(1-\frac{[M]_{(o)}}{[M]^e_{(o)}}\right) = -\frac{Q}{V}\left(1+\frac{1}{K_d}\right)k_{ao}t \tag{5}$$

The slopes of the plots $\ln(1-[M]_{(o)}/[M]^e_{(o)})$ vs. t have been used to evaluate k_{oa} and k_{ao}. All plots are straight lines in the present work, indicating that above assumption is reasonable.

3. Results and discussion

3.1. Stoichiometry of the heterogeneous complex formation reactions for Re(VII)

The equilibrium equation corresponding to the extraction of rhenium ion with the mixtures of N235 and TBP in heptane has been investigated. As shown in Fig. 1, the plots of log D vs. log [Cl^-] at fixed extractant concentrations give straight lines with the slope of about −1.0. Similarly, keeping the concentration of chloride ions and one of the extractants as constant, the plots of log D vs. log C are linear with slopes of about 1.0 and 0.5 for N235 and TBP, respectively. Thus, the equilibrium equation of extraction reaction for Re(VII) can be proposed as follows:

$$ReO_4^- + R_3NHCl + 0.5TBP = R_3NHReO_4\cdot 0.5TBP + Cl^- \tag{6}$$

Where $R_3NHReO_4\cdot 0.5TBP$ is the organic complex.

3.2. Extraction regime

For extraction kinetics, the criterion generally used to identify the extraction regime is independence of the extraction rate on the stirring speed in constant interfacial area cell. Fig. 2 shows the effect of the stirring rate on k_{ao} for rhenium extraction with the mixtures of N235 and TBP keeping the other conditions fixed. It shows an initial linear dependence when the stirring speed is less than 250 r/min. because the thickness of the stagnant interfacial films is relatively large so that the process of diffusion is slow. When the chemical reaction is slow enough to be competitive with the diffusional processes, the progressive increase of the stirring rate (>250 r/min) reduces the thickness of the stationary diffusional film and a “plateau region” appears indicating that the extraction rate is most likely kinetically controlled by chemical reaction. Nevertheless, a “plateau region” can be also generated by other phenomena and it is necessary to explore other approaches to identify the extraction regime.

Another criterion that distinguishes between diffusion control and kinetic control is the experimental determination of the activation energy of the extraction process. The effect of the temperature on the rhenium extraction rate is studied in the temperature range of 289 K to 313 K. The apparent activation energy (Ea) for the extraction is calculated from the slope of log k_{ao} vs. 1000/T, as shown in Fig. 3, and Ea is calculated as 40.6 kJ/mol for rhenium extraction. In general, if the rate is controlled by a chemical reaction, Ea is >40 kJ/mol but if the

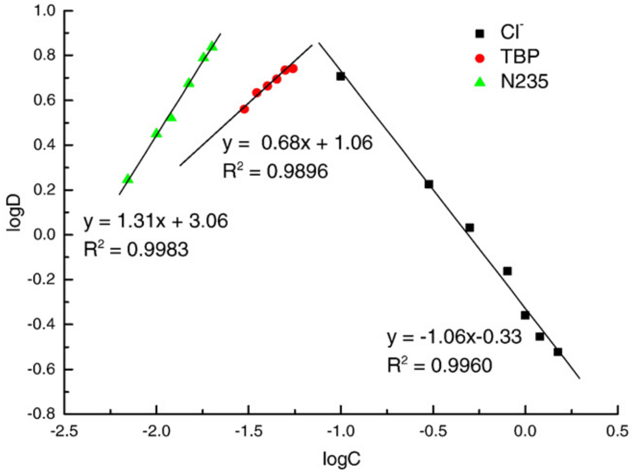

Fig. 1. Dependence of distribution coefficient on the species concentration. [NH_4ReO_4] = 5×10^{-4} M, [HCl] = 0.01 M, T = 298 K. ■, [N235] = 1.5×10^{-2} M, [TBP] = 4.5×10^{-2} M; ●, [N235] = 1.5×10^{-2} M, [Cl^-] = 0.1 M; and ▲, [TBP] = 4.5×10^{-2} M, [Cl^-] = 0.1 M.