Extraction kinetics of neodymium(III) from chloride medium in the presence of two complexing agents by D2EHPA using a constant interfacial area cell with laminar flow

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ABSTRACT

Kinetic studies of the extraction of neodymium (Nd) from chloride medium in the presence of two complexing agents lactic acid (HLac) and citric acid (H$_3$Cit) by D2EHPA (H$_2$A$_2$) in kerosene have been investigated using a constant interfacial area cell with laminar flow. The different parameters affecting the extraction rate such as stirring speed, temperature, specific interface area, hydrogen ion concentration, and H$_2$A$_2$ concentration are separately studied and a rate equation is deduced. The experimental results demonstrate that, the rate of Nd(III) extraction is a diffusion controlled process at the interface rather than in the bulk phase, and it is first order with respect to H$_2$A$_2$ and H$^+$ concentrations. The rate-determining step is proposed on the basis of predictions derived from interfacial reaction models, and is in good agreement with the analysis of the experimental results.

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1. Introduction

Neodymium (Nd) as catalyst, additive, and permanent-magnet material has been applied extensively in the rare earths industry, with its use NdFeB accounting for the majority of its consumption (He et al., 2008). During the last few decades, solvent extraction has been the most effective unit operation, playing a main role in the production of neodymium compounds in the hydrometallurgical flowsheets (Lee et al., 2005). At present, organophosphorous extractants like di-2-ethylhexyl phosphoric acid (D2EHPA, H$_2$A$_2$) and 2-ethylhexyl phosphonic acid mono-(2-ethyl hexyl) ester (HEH/EHP) have been applied extensively to extract rare earths on an industrial scale (Ioannou et al., 1972; Ahmed et al., 2002). However, even with the above extractants, the separation selectivity for the lanthanides is not satisfactory due to the similar physicochemical properties of some adjacent lanthanide pairs like Pr–Nd, Eu–Gd and Yb–Lu (Wu et al., 2007; Fontana and Pietrelli, 2009). Also, the need for higher acidity for stripping (>1.0 mol L^{-1}) is another disadvantage due to higher acid consumption. Therefore, there is growing interest in developing new extraction systems to separate lanthanides into groups or individual ions.

Currently, the chelating extraction has attracted considerable attention based on the different complex formation constants for the effective separation of lanthanides. Much effort has been devoted to studying the extraction system in the presence of complexing agents such as ethylenediaminetetraacetic acid (EDTA) (Nishihama et al., 2000), diethylenetriaminepentaacetic acid (DTPA) (Nishihama et al., 2003), 2-ethyl-2-hydroxy butyric acid (Bhattacharyya and Ganguly, 1993), acetic acid (Chang et al., 2010), citric acid (H$_3$Cit) (Kumbhar et al., 2003) and lactic acid (HLac) (Zalupski et al., 2010). The results showed that the extraction method including EDTA and DTPA has succeeded in enhancing the selectivity of the rare earth elements. Our group has studied the extraction and separation of the light rare earths from chloride medium in the presence of citric acid or lactic acid, and found that the complexing extraction system containing citric acid or lactic acid could not only improve the extraction capacity of D2EHPA, but also heighten the selectivity among some adjacent rare earths (Yin et al., 2013a, 2014).

In order to develop a novel separation technology and to enhance the selectivity of element pairs superior to the HEH/EHP or D2EHPA system for commercialization, the extraction kinetics data are prerequisites to clarify the extraction mechanism and the chemical reaction rate. The extraction kinetics of lanthanides in the presence of citric acid and lactic acid has not been reported. They are important for understanding the nature of the separation process and predicting the extraction rate. Currently, a constant interfacial area cell with laminar flow is widely

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used to obtain solvent extraction kinetics data, because it could keep the interface steady and smooth (Wang et al., 2002; Zhao et al., 2006).

In the present work, the extraction kinetics of Nd(III) in the presence of citric acid and lactic acid by D2EHPA was studied using constant interfacial area cell with laminar flow. As the main aspects, the determination of the extraction regime, chemical reaction zone, and extraction rate equation were studied. The research results will provide useful information for developing more efficient separation processes.

2. Experimental

2.1. Reagents and apparatus

The D2EHPA extractant and sulfonated kerosene were purchased from Luoyang Zhongda Chemical Industry Co., Ltd. The extractant was used without further purification and dissolved in sulfonated kerosene to the required concentrations. In general, D2EHPA extractant diluted by sulfonated kerosene is capable of forming the dimer H_2A_2 [2HA $\underset{K_d}{\overset{K_d}{\rightleftharpoons}}$ H_2A_2, where dimerization constant (K_d) is defined as: $K_d = [H_2A_2]/[HA]^2$, log $K_d = 4.42$ (Szymanowski et al., 1997), at T = 25 °C; HA $\overset{K_a}{\rightleftharpoons}$ $H^+ + A^-$, dissociation constant (K_a) is defined as: $K_a = [H^+][A^-]/[HA]$, p$K_a = 1.27$ (Szymanowski et al., 1997), at T = 25 °C]. The Nd(III) stock solutions were prepared by dissolving Nd_2O_3 (purity ≥ 99.9%) in hydrochloric acid and standardized by EDTA titration using xylenol orange as an indicator. The ionic strength of the aqueous phase was maintained at 1.0 mol L^{-1} by the addition of NaCl. Lactic acid (HLac, p$K_a = 3.86$, at T = 25 °C) and citric acid (H_3Cit, p$K_{a1} = 3.13$, p$K_{a2} = 4.76$, p$K_{a3} = 6.40$, at T = 25 °C) were obtained from Sinopharm Chemical Reagent Co. Ltd. All other reagents were of analytical reagent grade.

A pHS-3C digital pH meter (Shanghai Rex Instruments Factory) was used for pH measurements. A Prodigy high dispersion inductively coupled plasma spectrometer (Leeman labs, America) was employed to measure the neodymium ion concentration in the extraction process.

2.2. Experimental procedures and analysis

A constant interfacial area cell with laminar flow was made by our laboratory according to the literature (Zheng and Li, 1996) and employed for kinetic measurements. The interfacial area was 15 cm² unless otherwise stated. An aliquot of the aqueous phase (84 mL) followed by another aliquot of organic phase was added carefully to the cell chambers using a syringe, and stirring experiment was started. The stirring speed for both phases in the majority of experiments was kept constant at 300 rpm unless otherwise stated. After commencing the stirring, 0.2 mL samples of the aqueous phase was taken for analysis every 10 min. The kinetic experiments were carried out at 298 K unless otherwise stated.

2.3. Treatment of experimental data

The experimental data were treated according to the method used by Danesi (Danesi and Vandegrift, 1981). Assuming that the mass transfer process could be formally treated as a pseudo first order reversible reaction with respect to the neodymium ion (Nd^{3+}), one could write the following equation:

$$Nd^{3+}_{(a)} \underset{k_{oa}}{\overset{k_{ao}}{\rightleftharpoons}} Nd^{3+}_{(o)} \tag{1}$$

where a, o, k_{ao} (cm s^{-1}) and k_{oa} (cm s^{-1}) represent the aqueous phase, organic phase, forward and backward mass transfer coefficients, respectively.

The rate that the number of moles, n, enters into the organic phase, dn/dt, is given by Eq. (2) (Vandegrift and Horwitz, 1977):

$$\frac{dn}{dt} = Q\left(k_{ao}\left[Nd^{3+}\right]_{(a)} - k_{oa}\left[Nd^{3+}\right]_{(o)}\right) \tag{2}$$

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

where t, V and Q represent time, either the aqueous or organic phase and the interfacial area, respectively.

At steady state, the left hand side or right hand side is equal to zero in Eq. (3), that is:

$$-\frac{d\left[Nd^{3+}\right]_{(o)}}{dt} = 0 \tag{4}$$

and then, the distribution ratio, K_d, is defined as follows:

$$K_d = \frac{\left[Nd^{3+}\right]^e_{(o)}}{\left[Nd^{3+}\right]^e_{(a)}} = \frac{k_{ao}}{k_{oa}}. \tag{5}$$

According to the conservation of mass, and integrating Eq. (3), it follows that:

$$\ln\left(1 - \frac{\left[Nd^{3+}\right]_{(o)}}{\left[Nd^{3+}\right]^e_{(o)}}\right) = -\frac{Q}{V}(1 + K_d)k_{oa}t. \tag{6}$$

The slopes of the plots of $\ln\{1 - ([Nd^{3+}]_{(o)}/[Nd^{3+}]^e_{(o)})\}$ against t are used to evaluate k_{oa} and k_{ao}. A linear relationship will indicate that the mass transfer process could be treated as a pseudo-first-order reversible reaction with respect to Nd^{3+}.

The distribution ratio K_d value was determined using Eq. (5) after determining Nd^{3+} concentrations following contacting the two phases (20 mL each) for 30 min.

3. Results and discussion

3.1. Dependence of log k_{ao} on the stirring speed

In the Lewis cell technique, one of the common criteria generally used to identify the extraction rate is the stirring speed. When the
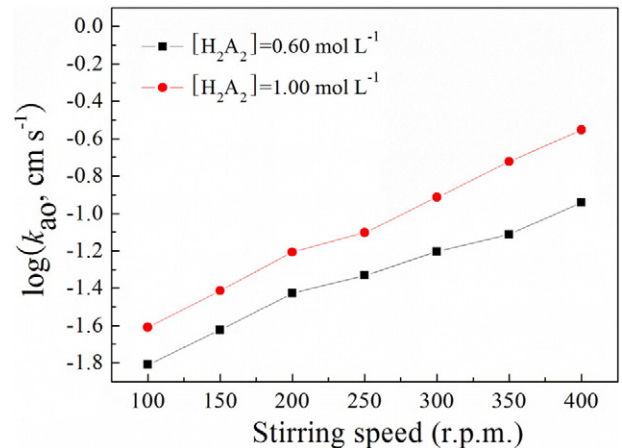
Fig. 1. Effect of stirring speed on mass transfer rate. Aqueous phase: [NdCl₃] = 0.10 mol L^{-1}, pH = 2.00, [HLac] = 0.3 mol L^{-1}, [H₃Cit] = 0.03 mol L^{-1}; organic phase: [H₂A₂] = 0.60 mol L^{-1} or [H₂A₂] = 1.00 mol L^{-1}; Q = 15 cm², T = 298 K.