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Kinetics of ytterbium(III) extraction with Cyanex 272 using a constant interfacial cell with laminar flow

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Abstract

Studies have been made on the kinetics of ytterbium(III) with bis-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272, HA) in *n*-heptane using a constant interfacial cell with laminar flow. The stiochiometry and the equilibrium constant of the extracted complex formation reaction between Yb^{3+} and Cyanex 272 are determined. The extraction rate is dependent of the stirring rate. This fact together with the E_a value suggests that the mass transfer process is a mixed chemical reaction–diffusion controlled at lower temperature, whereas it is entirely diffusion controlled at higher temperature. The rate equations for the ytterbium extraction with Cyanex 272 have been obtained. The rate-determining step is also made by predictions derived from interfacial reaction models, and through the approximate solutions of the flux equation, diffusion parameters and thickness of the diffusion film have been calculated.

Keywords: Extraction kinetics; Ytterbium(III); Cyanex 272

1. Introduction

It is well known that kinetics separation is a possibility for the quantitative separation of metal ions, which cannot be separated in the equilibrium state [1]. It exists unresolved fundamental problems on the kinetics of mass transfer in the bi-phasic liquid/liquid extraction system. Thus, the kinetics studies of the extraction of individual elements are definitely necessary for the development of the experimental procedure and accumulation of data. In our experiments, constant interfacial cell with laminar flow developed by Zheng and Li was used because it is carried out under laminar flow, which can keep the interface steady and smooth as the result of no flow towards the interface. The previous work of our group using this apparatus has been reported in literature [2–3].

Cyanex 272 containing bis(2,4,4-trimethylpentyl) phosphinic acid as the main constituent and trioctylphosphine oxide as impurities has several advantages including high selectivity, low aqueous acidity in extraction and stripping and high separation factors of rare earth ions by contrast with DEHPA and HEH/EHP [4–5]. Golding et al. investigated extraction kinetics of nickel with Cyanex 272 using the rising drop method [6]. Saleh et al. also studied kinetics of lanthanum (III) with Cyanex 272 using the single drop technique [7]. But to date, few literatures reported the extraction kinetics of rare earth with Cyanex 272 by constant interfacial cell with laminar flow. In earlier work, we reported the kinetics of Y(III) with Cyanex 272 using this apparatus [8]. As part of our continuing interest in the kinetics mechanism and mass transfer models, we investigated the kinetics of ytterbium(III) with Cyanex 272, and find that it is different from the kinetics mechanism of Y(III). In this paper, the research results on the extraction kinetics of Yb(III) with Cyanex 272 dissolved in heptane using a constant interfacial cell with laminar flow are reported. The extraction regime and rate determining stage are determined and extraction reaction models are brought.

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2. Experimental

2.1. Reagent

Di-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272, HA) was kindly supplied by CYTEC Canada Inc., and it was used without purification. All other reagents were of analytical grade. Ytterbium stock solutions were prepared by dissolving ytterbium oxide (99.9%) in hydrochloric acid and standardized by EDTA titration using xylenol orange as an indicator.

2.2. Procedure

The concentration of Cyanex 272 in the organic phase and pH value of aqueous phase used in all experiments were 3.0×10^{-2} mol l^{-1} and 2.69, respectively, and varied when studying their effect on the rate. The aqueous phases contained 3.0×10^{-3} mol l^{-1} ytterbium ion. The interfacial area was 19.4 cm^2. Both aqueous and organic phase volumes were 98 cm^3. The extraction kinetics was investigated by using a constant interfacial area cell with laminar described previously [2].

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 [9], one can write the following equation:

$$\mathrm{Yb}^{3+} \Leftrightarrow \mathrm{Yb(III)}_{(\mathrm{o})} \tag{1}$$

The following equation can be obtained as:

$$-\frac{\mathrm{d}[\mathrm{Yb}]_{(\mathrm{o})}}{\mathrm{d}t} = -\frac{Q}{V}(k_{\mathrm{r}}[\mathrm{Yb(III)}]_{(\mathrm{o})} - k_{\mathrm{f}}[\mathrm{Yb}^{3+}]_{(\mathrm{a})}) \tag{2}$$

$$K_{\mathrm{e}} = \frac{[\mathrm{Yb(III)}]_{(\mathrm{o}),\mathrm{e}}}{[\mathrm{Yb}^{3+}]_{(\mathrm{a}),\mathrm{e}}} = \frac{k_{\mathrm{f}}}{k_{\mathrm{r}}} \tag{3}$$

$$\ln\left(1 - \frac{[\mathrm{Yb}]_{(\mathrm{o})}}{[\mathrm{Yb}]^{\mathrm{e}}_{(\mathrm{o})}}\right) = -\frac{Q}{V}(1 + K_{\mathrm{e}})k_{\mathrm{r}}t \tag{4}$$

$$\ln\left(1 - \frac{[\mathrm{Yb}]_{(\mathrm{o})}}{[\mathrm{Yb}]^{\mathrm{e}}_{(\mathrm{o})}}\right) = -\frac{Q}{V}\left(1 + \frac{1}{K_{\mathrm{e}}}\right)k_{\mathrm{f}}t \tag{5}$$

where “a” refers to the aqueous phase, “o” is the organic phase, “e” indicates the equilibrium of extraction, “k_{f}” and “k_{r}” are respectively the forward as well as reverse pseudo-first-order rate constants, “K_{e}” represents the equilibrium constants of ytterbium, “Q” stands for the interfacial area, and “V” is the volume of the aqueous phase or the organic phase.

The slopes of the plots $\ln(1 - [\mathrm{Yb}]_{(\mathrm{o})}/[\mathrm{Yb}]^{\mathrm{e}}_{(\mathrm{o})})$ versus t have been used to evaluate k_{r} and k_{f}. All plots were straight lines in the work, indicating that above assuming was reasonable.

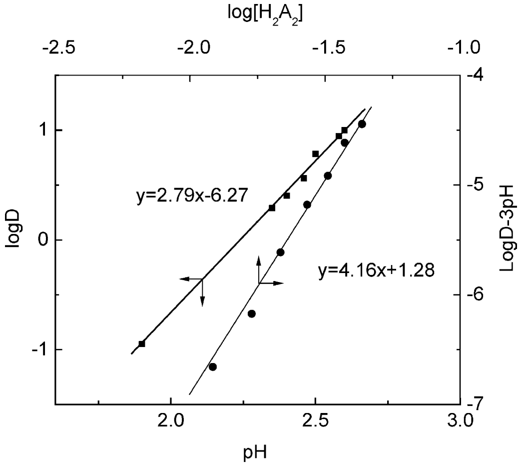

Fig. 1. Dependence of distribution coefficient on equilibrium pH and extractant concentration. [Cyanex 272] = 3.0×10^{-2} M, [Yb^{3+}] = 3.0×10^{-3} M, T = 303 K.

3. Results and discussion

3.1. Extraction equilibrium

The stoichiometry of the complex formation reaction between the ytterbium ion and Cyanex 272 in heptane has been evaluated by studying the dependence of log D on pH at constant extractant concentration and log D – 3 pH on the logarithmic Cyanex 272 concentration at constant pH. The slopes (shown in Fig. 1) are approximately equal to 3 and 4, respectively. Thus, the equilibrium equation can be proposed as follows:

$$\mathrm{Yb}^{3+}_{(\mathrm{a})} + 4\mathrm{H_2A}_{2(\mathrm{o})} \xleftrightarrow{K_{\mathrm{e}}} \mathrm{YbA_3(HA)}_{5(\mathrm{o})} + 3\mathrm{H}^+ \tag{6}$$

where $\mathrm{H_2A_2}$ represents the dimer of Cyanex 272; $\mathrm{YbA_3(HA)_5}$ is the organic complex of the metal cation. From the slope and intercept values shown in Fig. 1, the values of K_{e} is calculated to be $10^{0.54}$.

3.2. Extraction regime

3.2.1. Dependence of log k_f on the stirring speed

In extraction kinetics experiments, the criterion generally used to identify the extraction regime is the dependence of the extraction rate on the stirring speed in constant interfacial area cell [10]. The influence of the stirring rate of the two phases on k_{f} has been studied for Yb(III) at other constant conditions (shown in Fig. 2). The extraction rate is dependent on the stirring rate indicates that it is diffusion controlled in the range from 150 to 350 rpm. Nevertheless, a “no plateau region” can be also generated by other phenomena, and it is still possible that in spite of the experimentally determined dependence of extraction rate on the stirring speed, the rate of extraction is still kinetics controlled or, at least not fully kinetics controlled. So, it is necessary

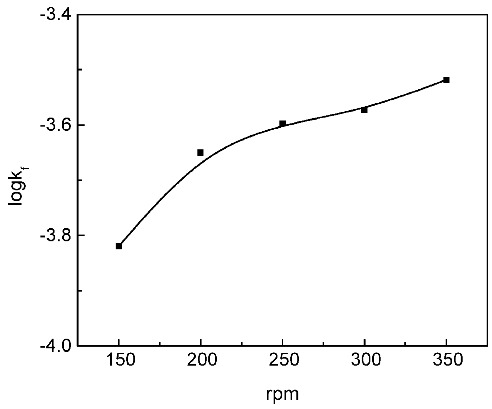

Fig. 2. The effect of the stirring speed on the extraction rate. pH = 2.69, [NaCl] = 1 M, T = 303 K, $[\mathrm{Yb}^{3+}] = 3.0 \times 10^{-3}$ M, [Cyanex 272] = 3.0×10^{-2} M.

with the help of other approach to identify the extraction regime.

3.2.2. Dependence of log k_f on the temperature

A further criterion that enables distinguishing between a diffusion-controlled and a kinetics regime is the experimental determination of the activation energy of the extraction process. The effect of the temperature on the extraction rate is studied in the temperature range of 293–313 K. From the slope of log k_f versus 1000 T^{-1} shown in Fig. 3, the apparent activation energy (E_a) for Yb(III) extraction is calculated to be 35.58 kJ mol^{-1} in the temperature range 293–303 K, and 8.76 kJ mol^{-1} from 303 to 313 K. According to the theory by Yu et al. [8,11], the obtained value of E_a suggests a possible mixed reaction control regime in the temperature range of 293–303 K and a diffusion regime from 303 to 313 K.

According to consistent estimate from two ways, we can conclude that the extraction rates which are either controlled by interfacial film diffusion or interfacial chemical reaction [12]. Therefore, the two limiting and alternative possibility, which is mass-transfer rate controlled by chemical reaction and mass-transfer rate controlled by interfacial film diffusion, will both be discussed and as follows. All other kinetics experiments are measured at 250 rpm/min and 303 K in order to maintain the same hydrodynamic conditions.

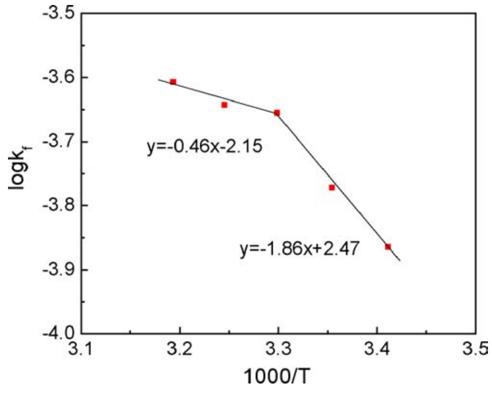

Fig. 3. The effect of the temperature on the extraction rate. pH = 2.69, [NaCl] = 1 M, rpm = 250 r/min, $[\mathrm{Yb}^{3+}] = 3.0 \times 10^{-3}$ M, [Cyanex 272] = 3.0×10^{-2} M.

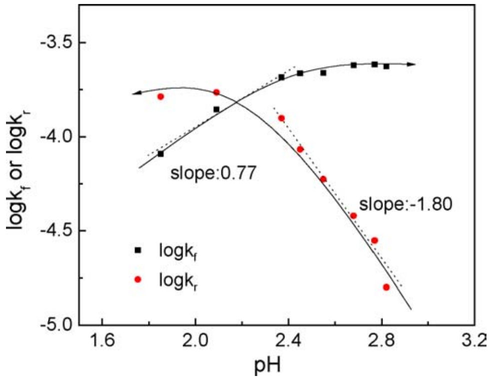

Fig. 4. The effect of pH on the extraction rate. [NaCl] = 1 M, rpm = 250 r/min, T = 303 K, $[\mathrm{Yb}^{3+}] = 3.0 \times 10^{-3}$ M, [Cyanex 272] = 3.0×10^{-2} M.

3.3. Extraction rate equation and chemical mass-transfer model

The influence of extraction rate on the concentration of extractant and hydrogen ion is shown in Figs. 4 and 5, respectively. The relationship between extraction rate and extractant concentration remains linear. However, the relationship between extraction rate and pH does not remain linear with increasing the bulk aqueous pH. The reason is that the rate is proportional to the hydrogen ion concentration at the interface rather than its bulk concentration [13]. Thus, from the slopes of log k_f and log k_r versus pH with a linear range, one can calculate that the orders of hydrogen ion concentration are 0.77 and −1.80, respectively, and the orders of extractant concentration at a constant pH are 0.46 and −3.33, respectively. The extraction rate constants of the forward as well as reverse are calculated to be $10^{-3.99}$ and $10^{-4.54}$ m s^{-1}, respectively, and give an K_e value of $10^{0.55}$. So the K_e value obtained from the rate study is in agreement with that obtained from the equi-

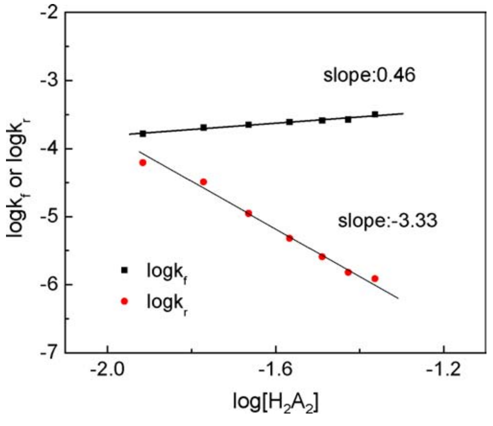

Fig. 5. The effect of the extractant concentration on the extraction rate. [NaCl] = 1 M, rpm = 250 r/min, T = 303 K, pH = 2.69, $[\mathrm{Yb}^{3+}] = 3.0 \times 10^{-3}$.

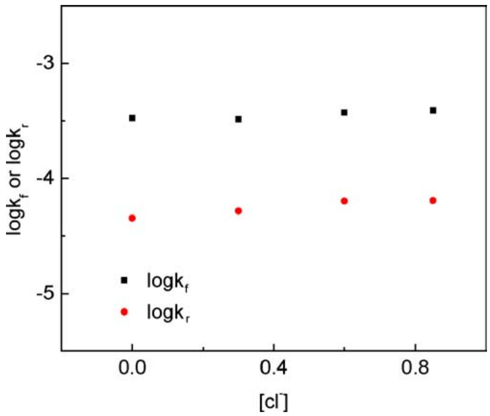

Fig. 6. The effect of chlorine ion concentration on the extraction rate. pH = 2.69, rpm = 250 r/min, $T = 303$ K, $[\mathrm{Yb}^{3+}] = 3.0 \times 10^{-3}$ M, [Cyanex 272] = 3.0×10^{-2} M.

librium study ($10^{0.54}$). Moreover, the extraction rate does not change with varying concentration of chloride ion (shown in Fig. 6).

According to the above results, the forward and reverse rate equations for the extraction of Yb(III) with Cyanex 272 can be written as:

$$R_\mathrm{f} = -\frac{\mathrm{d}[\mathrm{Yb(III)}]_{(\mathrm{o})}}{\mathrm{d}t} = 10^{-3.99}[\mathrm{Yb}^{3+}]_{(\mathrm{a})}[\mathrm{H_2A_2}]^{0.46}_{(\mathrm{o})}[\mathrm{H}^+]^{-0.77}_{(\mathrm{a})}\ \mathrm{kmol\,m^{-2}\,s^{-1}} \tag{7}$$

$$R_\mathrm{r} = -\frac{\mathrm{d}[\mathrm{Yb}^{3+}]}{\mathrm{d}t} = 10^{-4.54}[\mathrm{Yb(III)}]_{(\mathrm{o})}[\mathrm{H_2A_2}]^{-3.33}_{(\mathrm{o})}[\mathrm{H}^+]^{1.80}_{(\mathrm{a})}\ \mathrm{kmol\,m^{-2}\,s^{-1}} \tag{8}$$

A simple rate equation for the mixed regime can be derived by assuming that the reaction zone is represented by a surface, which lies parallel to the interface and located in the aqueous phase at a distance from the interface that is negligible compared to the thickness of the diffusion films. Thus, referring to the interfacial reaction model proposed by Danesi et al. [10], the following reactions will be considered:

$$\mathrm{H_2A_{2(o)}} \overset{K_1}{\longleftrightarrow} \mathrm{2HA_{(o)}} \tag{9}$$

$$\mathrm{HA}_{(i')} \overset{K_2}{\longleftrightarrow} \mathrm{H}^+_{(\mathrm{a})} + \mathrm{A}^-_{(i')} \tag{10}$$

$$\mathrm{Yb}^{3+}_{(\mathrm{a})} + \mathrm{A}^-_{(i')} \overset{k_1 k_{-1}}{\longleftrightarrow} \mathrm{YbA}^{2+}_{(i')} \tag{11}$$

$$\mathrm{YbA}^{2+}_{(i')} + \mathrm{HA}_{(i')} \overset{K_3}{\longleftrightarrow} \mathrm{YbA}^+_2 + \mathrm{H}^+_{(\mathrm{a})} \tag{12}$$

$$\mathrm{YbA}^+_{2(i')} + \mathrm{HA}_{(i')} \overset{K_4}{\longleftrightarrow} \mathrm{YbA}_{3(i')} + \mathrm{H}^+_{(\mathrm{a})} \tag{13}$$

$$\mathrm{YbA}_{3(i')} + 5\mathrm{HA}_{(\mathrm{o})} \overset{K_5}{\longleftrightarrow} \mathrm{YbA_3(HA)}_{5(\mathrm{o})} \tag{14}$$

Considering equilibrium (11) as the rate-controlling step, one can write the following equations, where i' is the reaction surface; k_1, k_{-1} are the forward and the reverse reaction rate constants for step (11), respectively; and K_1, K_2, K_3, K_4, K_5 represent the equilibrium constants, respectively.

Based on Eqs. (9)–(14), one can write the following equation:

$$K_1 = \frac{[\mathrm{HA}]^2_{(\mathrm{o})}}{[\mathrm{H_2A_2}]_{(\mathrm{o})}} \tag{15}$$

$$K_2 = \frac{[\mathrm{H}^+]_{(\mathrm{a})}[\mathrm{A}^-]_{(i')}}{[\mathrm{HA}]_{(i')}} \tag{16}$$

$$K_3 = \frac{[\mathrm{YbA}^+_2]_{(i')}[\mathrm{H}^+]_{(\mathrm{a})}}{[\mathrm{YbA}^{2+}]_{(\mathrm{a})}[\mathrm{HA}]_{(i')}} \tag{17}$$

$$K_4 = \frac{[\mathrm{YbA_3}]_{(\mathrm{o})}[\mathrm{H}^+]_{(\mathrm{a})}}{[\mathrm{YbA}^+_2]_{(i')}[\mathrm{HA}]_{(i')}} \tag{18}$$

$$K_5 = \frac{[\mathrm{YbA_3(HA)_5}]_{(\mathrm{o})}}{[\mathrm{YbA_3}]_{(\mathrm{o})}[\mathrm{HA}]^5_{(\mathrm{o})}} \tag{19}$$

Base on Eqs. (15) and (16), we obtain then for the forward initial rate of extraction:

$$R_\mathrm{f} = k_1[\mathrm{Yb}^{3+}]_{(\mathrm{a})}[A-]_{(i')} = k_1 a K_1^{0.5} K_2 [\mathrm{Yb}^{3+}]_{(\mathrm{a})}[\mathrm{H_2A_2}]^{0.5}_{(\mathrm{o})}[\mathrm{H}^+]^{-1}_{(\mathrm{a})} \tag{20}$$

where a is the adsorption constant of extractant. Base on Eqs. (17)–(19), one can write the following equation:

$$R_\mathrm{r} = k_{-1}[\mathrm{YbA}^{2+}]_{(i')} = k_{-1} a^{-2} K_1{}^{-3.5} K_3{}^{-1} K_4{}^{-1} K_5{}^{-1} [\mathrm{H}^+]^2_{(\mathrm{a})} \times [\mathrm{YbA_3(HA)_5}]_{(\mathrm{o})}[\mathrm{H_2A_2}]^{-3.5}_{(\mathrm{o})} \tag{21}$$

Eqs. (20) and (21) can be simplified as follows:

$$R_\mathrm{f} = k_\mathrm{f}[\mathrm{Yb}^{3+}]_{(\mathrm{a})}[\mathrm{H_2A_2}]^{0.5}_{(\mathrm{o})}[\mathrm{H}^+]^{-1}_{(\mathrm{a})} \tag{22}$$

$$R_\mathrm{r} = k_\mathrm{r}[\mathrm{H}^+]^2_{(\mathrm{a})}[\mathrm{YbA_3(HA)_5}]_{(\mathrm{o})}[\mathrm{H_2A_2}]^{-3.5}_{(\mathrm{o})} \tag{23}$$

where $k_\mathrm{f} = k_1 a K_2 K_1^{0.5}$, and $k_\mathrm{r} = a^{-2} k_{-1} K_1^{-3.5} K_3^{-1} K_4^{-1} K_5^{-1}$.

Above mechanism is consistent with the rate equations (7) and (8) obtained from experimental results. Comparing the result of Yb(III) with Y(III) [8], we can find that the kinetics mechanism of Yb(III) is different from that of Y(III) by Cyanex 272. The extraction rate equation of yttrium-Cyanex 272 in heptane is:

$$R_\mathrm{f} = 10^{-4.41}[\mathrm{Y(OH)}^{2+}]_{(\mathrm{a})}[\mathrm{H_2A_2}]^{0.79}_{(\mathrm{o})}[\mathrm{H}^+]^{-1.06}_{(\mathrm{a})}\ \mathrm{kmol\,m^{-2}\,s^{-1}}$$

which is only controlled by interfacial chemical reaction, but not controlled by the mixed reaction.

3.4. Mass-transfer rate controlled by interfacial film diffusion

The rate-determining processes would then be diffusion of each species to and from the interface through stagnant organic and aqueous diffusion zones of thickness δ_o and δ_w, then [12,14]:

$$J = k_f([\mathrm{Yb}^{3+}]_{(a)} - J\Delta)([\mathrm{H_2A_2}]^4_{(o)} - (1/4)J\Delta) - k_r([\mathrm{YbA_3(HA)_5}]_{(o)} + J\Delta)([\mathrm{H}^+]^3_{(a)} + (1/3)J\Delta) \quad (24)$$

where $\Delta_o = \Delta_w = \delta_o/D_o = \delta_w/D_w$ are the diffusional parameter, that is the ratios between the thickness of the diffusion films and the diffusion coefficients D, assumed to depend only on the nature of the liquid phase. In this case the rate-determining step in the extraction is considered to be diffusional instead of chemical, and local chemical equilibrium at the interface is assumed, i.e.

$$K_e = \frac{[\mathrm{YbA_3(HA)_5}]_{(o,i)}[\mathrm{H}^+]^3_{(a,i)}}{[\mathrm{Yb}^{3+}]_{(o,i)}[\mathrm{H_2A_2}]^4_{(o,i)}} \quad (25)$$

$$K_e = \frac{([\mathrm{YbA_3(HA)_5}]_o + J\Delta)([\mathrm{H}^+]_a + (1/3)J\Delta)^3}{([\mathrm{Yb}^{3+}]_o - J\Delta)([\mathrm{H_2A_2}]_o - (1/4)J\Delta)^4} \quad (26)$$

An approximate and explicit form of J can be easily obtained from Eqs. (24) and (26) by neglecting the terms be containing J^2, $[\mathrm{Yb}^{3+}]J$, $[\mathrm{YbA_3(HA)_5}]J$ because of the low fluxes (10^{-6} kmol m^{-2} s^{-1}) and the tracer-metal concentrations (10^{-3} mol l^{-1}) used in our experiments

$$k_f = \frac{J_0}{[\mathrm{Yb}^{3+}]_{(a)}} = \frac{1}{\Delta}\frac{[\mathrm{H_2A_2}]^4_{(o)}}{[\mathrm{H_2A_2}]^4_{(o)} + K_e^{-1}[\mathrm{H}^+]^3_{(a)}} \quad (27)$$

Using Eq. (27), we can obtain the following values for the diffusional parameter $\Delta = 0.23$ cm s^{-1}. If one assumes a diffusion coefficient $D = 5 \times 10^{-6}$ cm^2 s^{-1} [13], the thickness of the diffusion film δ is calculated to be 1.15×10^{-6} cm at 250 rpm.

4. Conclusion

The extraction of Yb(III) with Cyanex 272 is a complex kinetics process with an interfacial reaction. The stoichiometry of the extracted complex and the equilibrium constant are been determined to be $\mathrm{YbA_3(HA)_5}$ and $10^{0.54}$, respectively. The mass transfer process is a mixed chemical reaction–diffusion controlled at lower temperature, whereas it is entirely diffusion controlled at higher temperature. The extraction rate constants of the forward as well as reverse are calculated to be $10^{-3.99}$ and $10^{-4.54}$ m s^{-1}, respectively. The rate equations are obtained, and the formation of 1:1 complex of Yb^{3+} with A^- at the reaction surface is the rate-determining step when mass-transfer rate is controlled by chemical reaction. Through the approximate solutions of the flux equation that we obtained when mass-transfer rate is controlled by partly interfacial film diffusion, diffusion parameters and thickness of the diffusion film is calculated to be 0.23 cm s^{-1} and 1.15×10^{-6} cm, respectively.

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