Kinetics and Mechanism on Removal of Aluminum from Phosphoric Medium by Solvent Extraction using Lewis Cells

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The kinetics of the forward extraction of aluminum ion had been investigated using Lewis cells. The influences of the aluminum concentration, temperature, and interfacial area were studied. The extracted species was demonstrated to be $AlL_3 \cdot (HL)_3$ by stoichiometry studies and the mechanism of the extraction was explained. The results indicated that the extraction process was under mixed-control by the extraction reaction at the interface and the diffusion of the resultant in the organic phase. The activation energy was calculated to be 23.26 kJ/mol and was concordant with the mixed-control regime. Further analysis suggested that the reaction orders with respect to aluminum and extractant were 1 and 2, respectively, and the extraction rate constant was $10^{-4.526} \text{ L}^2 \cdot \text{g}^{-2} \cdot \text{s}^{-1}$. The total rate of the extraction reaction for $AlL_3 \cdot (HL)_3$ was given based on kinetic steps.

1. Introduction

Phosphoric acid is universally used to produce phosphate and compound fertilizer as chemical raw material [1,2]. The wet process in sulfuric acid route is the main method for producing phosphoric acid and the most economic method of production. However, it suffers from the fact that a larger number of metal impurities were introduced due to the low quality and complexity of phosphate rock [2-4]. Unlike iron and magnesium ions, which are essential elements for plant growth, soluble aluminum ions usually show strong toxicity to the root growth of plant [5-8]. It has been reported that the exposure to aluminum will restrain mineral uptake [7-9], cell division [5,8,10], and cell elongation [6,8] of plant growth. Therefore, decreasing the content of aluminum in phosphoric acid is a pressing concern of the phosphate fertilizer industry and agriculture.

Current major technologies of aluminum removal from phosphoric acid are chemical precipitation [4,11], crystallization process [12,13], ion exchange [14,15], and solvent extraction. Solvent extraction is widely used in several industries, such as purification, pharmacy, agrochemicals, and hydrometallurgy [1-3,16]. The virtues of high yield, convenient operation and technological-mature make it suitable for aluminum removal from phosphoric acid solution.

Kinetic investigation is necessary to acquire extraction behaviors such as extraction rate and extraction mechanism, and it is crucial to the design and selection of extraction equipment for industrial production in the future. Primary techniques such as Lewis cells and single drops [17-19] are available to the investigation of extraction kinetics. Because of the stability and simplicity of constant-interfacial-area cell, it is considered

the most effective method for kinetic studies and already used by many researchers in their investigations [20-25].

In this study, the P-15 extractant was selected because of its high efficiency in removing impurity ions, low phosphorus loss, and low price. The P-15 extractant is a kind of organophosphorus acid extractant, and our research group has conducted sufficient research on this extractant. For example, Huang *et al.* have researched the mechanism of removing manganese from phosphoric acid using P-15 extractant [26].

The purpose of this paper is to research the extraction rate on removal of aluminum from phosphoric acid solution by P-15 extractant using the Lewis cells technique. The equilibrium studies were conducted to determine the stoichiometry of equilibrium reaction and the composition of extraction complex. The extraction conditions, such as aluminum concentration, temperature, and interfacial area were studied to determine the influence factors of extraction rate and put forward a reasonable extraction mechanism. Finally, total reaction rate equation was calculated based on the mechanism.

2. Experimental

2.1 Reagents

Phosphoric acid and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, supplied by Kelong Corp. LTD. (Sichuan, China) were used to prepare stock $\text{Al-H}_3\text{PO}_4$ solution of aqueous phase. Sulfonated kerosene, provided by Chengdu Max-Top New Energy Lubricating Materials Corp. LTD, is a diluent to alter the viscosity and concentration of extractant. P-15 extractant was purchased from Kelong Corp. LTD. The organic phase containing P-15 extractant and sulfonated kerosene was saturated with deionized water before the experiment. Deionized water was utilized throughout this experiment.

2.2 Procedure with Lewis cells

The extraction kinetics data was obtained by the technique of Lewis cells in the experiments. The main characteristics and sketch of the Lewis cells utilized in this study are presented in Table 1 and Figure 1, respectively. A stirring paddle is set in each phase to achieve differential stirring. A circular ring is set in the middle of the Lewis cells, and interface areas can be changed by replacing circular rings with different diameters. A heat retaining jacket is used to maintain a certain temperature.

Identical volumes (135 mL) of the aqueous phase and organic phase containing P-15 extractant and sulfonated kerosene, preheated to a prearranged temperature, were introduced into the Lewis cells in succession. Aqueous phase was added into the container, and then organic phase was introduced slowly to maintain the interface steady. The paddles were concurrently activated at presupposed speed respectively. A stopwatch was used to record time. 10 μL aqueous phase was withdrawn for analysis by micro syringe at fixed time interval of 2 minutes, and about 0.3 mL within 1 hour was used to analysis in total, which is less than 0.23% of the global aqueous volume with negligible disturbance to the investigation system.

Table 1. The main characteristics of the Lewis cells.

Height of cell	Volume of each phase	Internal diameter	Blades length	Blades distance	Rings diameter
9 cm	135 mL	7 cm	2 cm	4.5 cm	5.0, 5.5, 6.0, 6.5, 7.0 cm

Figure 1. The sketch of the Lewis cells. 1-interface, 2-water input, 3-water output, 4-stirring paddle, 5-stirring paddle, 6-interfacial ring, 7-thermostatic jacket, 8- micro syringe.

2.3 Analytical methods

The concentration of aluminum in the aqueous phase was analyzed by ICP-OES (Perkin Elmer Optima 7000DV). The extraction ratio E can be expressed as followed:

$$E = \frac{\omega_1 - \omega_2}{\omega_1} \times 100\% \quad (1)$$

where ω_1 and ω_2 denote the mass fractions of aluminum in aqueous phase before and after extraction, respectively.

3. Results and Discussion

3.1 Influence of experimental conditions

3.1.1 Effect of aluminum concentration

Extraction experiments were carried out with different initial concentrations of aluminum, and the plots of aluminum concentration in phosphoric acid versus time are shown in Figure 2A. It is shown that at the beginning of the reaction, the extraction rate increases with the increase of the initial concentrations of aluminum. When the aluminum concentration is 0.78%, the extraction speed is relatively fast, and is close to the aluminum concentration in most wet-process phosphoric acid, so the aluminum concentration is selected as 0.78% in the subsequent experiments.

3.1.2 Effect of temperature

The influence of temperature on the extraction rate was studied in the range of 303.15 – 333.15 K, and the removal curves of mass fractions of aluminum versus time at different temperatures are given in Figure 2B. Comparing vertically, the extraction rates are augmented with the increasing temperature at the same reaction time, indicating that the extraction of aluminum may be an endothermic process.

3.1.3 Effect of interfacial area

Figure 2C shows the concentrations of aluminum versus time at different interfacial diameters, varied from 5 to 7 cm. With the increase of interfacial area, the concentrations of aluminum in phosphoric acid

solutions decrease and extraction rate increases constantly at identical reaction time, indicating that interfacial reaction may be one of the controlling steps of the extraction process.

Figure 2. The results of preliminary experiments. (A) Effect of aluminum concentration. Conditions: $T = 323.15$ K, $\omega_{HL} = 33.3\%$, $D = 7.0$ cm, $V_o = V_a = 135$ mL, $N_o = N_a = 120$ rpm. (B) Effect of temperature. Conditions: $[Al]_{ini} = 0.78$ wt.%, $\omega_{HL} = 33.3\%$, $D = 7.0$ cm, $V_o = V_a = 135$ mL, $N_o = N_a = 120$ rpm. (C) Effect of interfacial area. Conditions: $T = 323.15$ K, $[Al]_{ini} = 0.78$ wt.%, $\omega_{HL} = 33.3\%$, $V_o = V_a = 135$ mL, $N_o = N_a = 120$ rpm.

3.2 Stoichiometry of the extraction complex

In weakly polar solvent sulfonated kerosene, organophosphorus acid extractant mainly exists in the form of dimer. In the extraction process, the dimer of the extractant is broken, and cation exchange reactions usually take place [27,28]. Meanwhile, the electron donor phosphoryl groups $P=O$ also participate in the extraction reaction. Aluminum ions usually exist in solution as hydroxy or hydrated aluminum ions. Since the pH value of the phosphoric acid system studied in this paper is less than 1, there is no hydroxy aluminum ion, i.e., reactive extraction is mainly the exchange reaction between hydrated aluminum ion and hydrogen ion.

To confirm the extraction mechanism, the composition of the extraction complex of aluminum with the P-15 extractant was measured via the slope method extensively adopted in literature [16,29,30]. In the

reaction extraction of aluminum, L denotes the P-15 extractant, and then the equation of extraction reaction can be described as:

where the subscripts o and a denote the organic phase and aqueous phase, respectively, and x is the stoichiometric coefficient of the extractant.

The equilibrium constant (K_{eq}) of Equation (2) is

$$K_{eq} = \frac{[ALL_x \cdot (HL)_{x(o)}^{3-x}][H^+]_{(a)}^x}{[Al^{3+}]_{(a)}[(HL)_2]_{(o)}^x} \quad (3)$$

The distribution coefficient of aluminum can be described as

$$D = \frac{[ALL_x \cdot (HL)_{x(o)}^{3-x}]}{[Al^{3+}]_{(a)}} = K_{eq} \frac{[(HL)_2]_{(o)}^x}{[H^+]_{(a)}^x} \quad (4)$$

Equation (4) takes the logarithmic operation, and the following expression can be obtained

$$\lg D = \lg K_{eq} + x \lg [(HL)_2]_{(o)} - x \lg [H^+]_{(a)} \quad (5)$$

Since the concentration of hydrogen ions generated by the extraction reaction is much lower than that produced by the ionization of phosphoric acid, the concentration of hydrogen ion in the phosphoric acid solution is approximately a constant. Therefore, the stoichiometric x can be acquired by obtaining the distribution rules of the distribution coefficient with the concentration of the extractant in the phosphoric acid solution. The plot of $\lg [(HL)_2]_{(o)}$ against $\lg D$ is shown in Figure 3.

The stoichiometric coefficient x is suggested to be 3. Thus, the equilibrium equation of reactive extraction can be proposed as:

3.3 Kinetic studies

3.3.1 Extraction rate equation

The reaction rate of the extraction process can be written as:

$$r = k_f [Al^{3+}]_{(a)}^\alpha [(HL)_2]_{(o)}^\beta - k_b [ALL_3 \cdot (HL)_3]_{(o)}^\gamma [H^+]_{(a)}^\delta \quad (7)$$

Figure 3. The distribution coefficient variation with $[(HL)_2]_{(o)}$. Conditions: $T = 323.15$ K, $D = 7.0$ cm, $N_o = N_a = 120$ rpm.

In the incipient stage of the reactive extraction, the amount of the extracted compound $AlL_3 \cdot (HL)_3$ is so little that the reverse reaction is almost not carried out [23,28]. As a result, Equation (7) can be simplified to the following expression

$$r = k_f [Al^{3+}]_{(a)}^\alpha [(HL)_2]_{(o)}^\beta \quad (8)$$

Take the logarithm of both sides of the Equation (8) and get Equation (9).

$$\ln r = \ln k_f + \alpha \ln [Al^{3+}] + \beta \ln [(HL)_2] \quad (9)$$

The reaction orders α and β can be determined by change the concentration of Al^{3+} and $(HL)_2$ severally. The plots between $\ln r$ versus $\ln [Al^{3+}]_{(a)}$ and $\ln [(HL)_2]_{(o)}$ are shown in Figure 4.

Figure 4. The effect of the Al^{3+} and extractant concentration on the extraction rate. Conditions: $T = 323.15$ K, $D = 7.0$ cm, $N_o = N_a = 120$ rpm.

According to equation (9), the slopes of those two curves are 1.065 and 2.235 respectively, which indicates that the reaction orders of aluminum and $(HL)_2$ approximately equal 1 and 2 respectively. Furthermore, the intercepts of two lines are -10.339 and -10.538 respectively, therefore the constant of forward rate k_f is calculated to be $10^{-4.526}$ at 323.15 K.

Hence, the rate equation at 323.15 K can be expressed as followed:

$$r = -\frac{d[Al^{3+}]_{(a)}}{dt} = 10^{-4.526} [Al^{3+}]_{(a)} [(HL)_2]_{(o)}^2 \quad (10)$$

3.3.2 Reaction region

In Lewis cells, the extractant phase and the phosphoric acid phase are separated, and the contact area of Lewis cells can be changed by replacing interface rings with different diameters. The area of the constant interface pool used in this experiment varied from 19.6 to 38.5 cm². The regularity of the initial reaction rate with different interface areas is shown in Figure 5.

In the reactive extraction, the relationship between extraction rate of a reaction occurring at the interface and interfacial area is a straight line passing through the origin. From Figure 5, we can observe that the extraction reaction rate is basically linearly related to the interfacial area without crossing the origin. The

result indicates that the extraction of aluminum ions in the phosphate aqueous solution is restrained by interface reaction, but it is not simple mode of interface reaction control.

3.3.3 Diffusion resistance region

According to the discussion in 3.3.2, the process of extraction reaction is controlled by the interfacial reaction. The aluminum ion and P-15 extractant migrate to the interface, and the extraction complex and hydrogen ions produced by the interfacial reaction migrate to the bulk phase respectively. During the migration process, substances with a low rate of diffusion play a leading role in the entire extraction reaction. Increasing the stirring speed is one of the main methods to eliminate the mass-transfer resistance.

Figure 5. Effect of interfacial area on the extraction rate of aluminum. Conditions: $T = 323.15 \text{ K}$, $[\text{Al}]_{(\text{ini})} = 0.78 \text{ wt.}\%$, $\omega_{\text{HL}} = 33.3\%$, $N_o = N_a = 120 \text{ rpm}$.

Figure 6. Effect of agitation speed on the extraction rate of aluminum. Conditions: $T = 323.15 \text{ K}$, $D = 7.0 \text{ cm}$, $\omega_{\text{HL}} = 33.3\%$, $[\text{Al}]_{(\text{ini})} = 0.78 \text{ wt.}\%$.

Using a Lewis cell, we separate the phosphoric acid phase from the extraction phase and realize the differential agitation of two phases in the independence. By studying the effect of the rotation rate of each phase on the extraction reaction rate, the diffusion resistance zone can be determined.

From Figure 6, the extraction rate increased linearly as the agitation speed of organic phase increased from 0 to 160 rpm, but the extraction rate did not change with the increase of stirring rate of aqueous phase. The results indicate that aluminum ions diffuse quickly in aqueous phase, and the mass-transfer resistance in aqueous phase can be ignored. Instead, the diffusion resistance in the organic phase is much higher than that in the aqueous phase. That is to say, the process of extraction reaction is controlled by the diffusion of organic phase.

3.3.4 Thermodynamics analysis

Activation energy (E_a) is another criterion to distinguish the extraction regime. Activation energy below 20 KJ/mol indicates a diffusion controlled regime, while E_a above 40 KJ/mol indicates a chemical reaction controlled process. E_a values between 20 kJ/mol and 40 kJ/mol indicating that both diffusion and extraction reactions influence extraction process, i.e., the process of extraction reaction is a mixed-control process[31,32].

The Arrhenius formula is usually used to calculate the activation energy.

$$k = Ae^{-\frac{E_a}{RT}} \quad (11)$$

Combining with Equation (9) and (11) leads to the followed expression:

$$r = -\frac{d[Al^{3+}]_{(a)}}{dt} = e^{-\frac{E_a}{RT}} [Al^{3+}]_{(a)}^\alpha [(HL)_2]_{(o)}^\beta \quad (12)$$

By taking logarithms, Equation (12) converts to:

$$\ln r = -\frac{E_a}{RT} + \ln A + \alpha \ln [Al^{3+}]_{(a)} + \beta \ln [(HL)_2]_{(o)} \quad (13)$$

According to the slope of the straight line in Figure 7, the calculated activation energy is 23.25 kJ/mol, and the result indicates that the extraction process may be a mixed-control process.

Next, we use “*” to indicate transition state. Based on the transition state theory, the following equation can be acquired

$$\Delta G^* = \Delta H^* - T\Delta S^* = -RT \ln K^* \quad (14)$$

The basic theory of transition state can be expressed as

$$k = \frac{k_B T}{h} K^* (C^\theta)^{1-n} \quad (15)$$

where h is Planck's constant, and k_B stands for the Boltzmann constant.

Figure 7. Effect of temperature on the extraction rate of aluminum. Conditions: $D = 7.0$ cm, $\omega_{HL} = 33.3\%$, $[Al]_{(ini)} = 0.78$ wt.%, $N_o = N_a = 120$ rpm.

Inserting equation (15) into (14) gives

$$k = \frac{k_B T}{h} (C^\theta)^{1-n} e^{\frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}} \quad (16)$$

The derivative of equation (16) is obtained

$$\ln \frac{kh}{k_B T} = \lg(C^\theta)^{1-n} - \frac{\Delta H^*}{2.303RT} + \frac{\Delta S^*}{2.303R} \quad (17)$$

As seen in Figure 8, the plot of $\ln(kh/k_B T)$ against $1/T$ yields a straight line with slope $= -1.116$, and ΔH^* can be calculated to be 21.37 kJ/mol. The correlation between the reaction enthalpy $\Delta_r H_m$ and the equilibrium constant K can be obtained.

$$\ln K = -\frac{\Delta_r H_m}{RT} + \frac{\Delta_r S_m}{R} \quad (18)$$

Equilibrium constant K can be written as

$$K = \frac{[ALL_3 \cdot (HL)_3]_{(eq)} [H^+]_{(eq)}^3}{[Al^{3+}]_{(eq)} [(HL)_2]_{(eq)}^3} \quad (19)$$

If the removal rate of aluminum ion at equilibrium is E , then the K can be expressed as

$$K = \frac{E \{ [H^+]_{(eq)} + 3E[Al^{3+}]_{(ini)} \}^3}{(1-E) \{ [(HL)_2] - 3E[Al^{3+}]_{(ini)} \}^3} \quad (20)$$

The concentration of H^+ is much larger than Al^{3+} in the phosphoric acid solution. Then substituting equation (20) into (18) gives

$$\ln \frac{E}{(1-E) \{ [(HL)_2] - 3E[Al^{3+}]_{(ini)} \}^3} = -\frac{\Delta_r H_m}{RT} + \frac{\Delta_r S_m}{R} - 3 \ln \{ [H^+]_{(eq)} + 3E[Al^{3+}]_{(ini)} \} \quad (21)$$

The plot of $\ln \{ E \cdot (1-E)^{-1} \cdot \{ [(HL)_2] - 3E[Al^{3+}]_{(ini)} \}^{-3} \}$ against $1/T$ is summarized in Figure 8.

According to the slope, the calculation value of $\Delta_r H_m$ is 3.07 kJ/mol, which manifests that the extraction reaction is an endothermic reaction. Furthermore, a low value of $\Delta_r H_m$ indicates that the extractant process is just slightly affected by temperature. Based on the intercept of the straight line, $\Delta_r S_m$ and $\Delta_r G_m$ in the 303.15 K can be founded to be 30.02 J·mol⁻¹·K⁻¹ and -6.04 kJ·mol⁻¹, respectively. In summary, the extraction is a spontaneous process with increased endothermic entropy.

3.4 Mixed-control regime

Through the above solvent extraction kinetics studies, the extraction complex is demonstrated to be $ALL_3 \cdot (HL)_3$ and the extraction reaction process is under mixed control by the extraction reaction at the

Figure 8. Effect of temperature on the extraction rate of aluminum. Conditions: $D = 7.0$ cm, $[Al]_{(ini)} = 0.78$ wt.%, $\omega_{HL} = 33.3\%$, $N_o = N_a = 120$ rpm.

interface and the diffusion in the organic phase. As a consequence, the concentration distribution of the research system shown in Figure 9 can be obtained, and extraction process consists of the following steps.

Figure 9. The Concentration profile of the extraction process.

The rate equation of mass transfer of $(HL)_2$, Al^{3+} , $AlL_3 \cdot (HL)_3$ and H^+ can be obtained respectively as

$$r_{(HL)_2} = D_{(HL)_2} \frac{[(HL)_2]_{(o)} - [(HL)_2]_{(i)}}{V_o \delta_o} \quad (29)$$

$$r_{Al^{3+}} = D_{Al^{3+}} \frac{[Al^{3+}]_{(a)} - [Al^{3+}]_{(i)}}{V_a \delta_a} \quad (30)$$

$$r_{AlL_3 \cdot (HL)_3} = D_{AlL_3 \cdot (HL)_3} \frac{[AlL_3 \cdot (HL)_3]_{(i)} - [AlL_3 \cdot (HL)_3]_{(o)}}{V_o \delta_o} \quad (31)$$

$$r_{H^+} = D_{H^+} \frac{[H^+]_{(i)} - [H^+]_{(o)}}{V_a \delta_a} \quad (32)$$

where D is the mass transfer coefficient; V represents the volume and δ is the thicknesses of the boundary layer.

At a given temperature, D can be treated as a constant if it is only related to the nature of the phase [33]. Letting $k=D/V\delta$, then the concentrations of the substances in the interface can be represented as follows:

$$[(HL)_2]_{(i)} = [(HL)_2]_{(o)} - \frac{r_{(HL)_2}}{k_{(HL)_2}} \quad (33)$$

$$[Al^{3+}]_{(i)} = [Al^{3+}]_{(a)} - \frac{r_{Al^{3+}}}{k_{Al^{3+}}} \quad (34)$$

$$[ALL_3 \cdot (HL)_3]_{(i)} = [ALL_3 \cdot (HL)_3]_{(o)} + \frac{r_{ALL_3 \cdot (HL)_3}}{k_{ALL_3 \cdot (HL)_3}} \quad (35)$$

$$[H^+]_{(i)} = [H^+]_{(a)} + \frac{r_{H^+}}{k_{H^+}} \quad (36)$$

To determine the reaction mechanism, it is crucial to confirm the rate-controlling step of the extraction reaction. For the convenience of expression, equations (24)-(26) are called R1, R2 and R3 respectively. Assuming R1 is the rate-determining step, R2 and R3 quickly reach the reaction equilibrium. Therefore, the rate equation of extraction reaction and the equilibrium equations of R2 and R3 are given by equations (37)-(39)

$$r = -\frac{d[Al^{3+}]_{(a)}}{dt} = k_f[Al^{3+}]_{(i)}[(HL)_2]_i - k_b[ALL_2^+ \cdot (HL)]_{(i)}[H^+]_i \quad (37)$$

$$K_{eq2} = \frac{[ALL_2^+ \cdot (HL)_2]_{(i)}[H^+]_{(i)}}{[(HL)_2]_{(i)}[ALL_2^{2+} \cdot (HL)]_{(i)}} \quad (38)$$

$$K_{eq3} = \frac{[ALL_3 \cdot (HL)_3]_{(i)}[H^+]_{(i)}}{[(HL)_2]_{(i)}[ALL_2^+ \cdot (HL)_2]_{(i)}} \quad (39)$$

Combining with equations (33)-(39) lead to the rate equations of extraction reaction:

$$r = k_f \left\{ [Al^{3+}]_{(a)} - \frac{r_{Al^{3+}}}{k_{Al^{3+}}} \right\} \left\{ [(HL)_2]_{(o)} - \frac{r_{(HL)_2}}{k_{(HL)_2}} \right\} - k_b \frac{\left\{ [ALL_3 \cdot (HL)_3]_{(o)} + \frac{r_{ALL_3 \cdot (HL)_3}}{k_{ALL_3 \cdot (HL)_3}} \right\} \left\{ [H^+]_{(a)} + \frac{r_{H^+}}{k_{H^+}} \right\}^3}{K_{eq2} K_{eq3} \left\{ [(HL)_2]_{(o)} - \frac{r_{(HL)_2}}{k_{(HL)_2}} \right\}^2} \quad (40)$$

Similarly, assuming R2 and R3 are rate-determining steps respectively, the rate equations of extraction reaction can be solved respectively as

$$r = k_f K_{eq1} \frac{\left\{ [Al^{3+}]_{(a)} - \frac{r_{Al^{3+}}}{k_{Al^{3+}}} \right\} \left\{ [(HL)_2]_{(o)} - \frac{r_{(HL)_2}}{k_{(HL)_2}} \right\}^2}{\left\{ [H^+]_{(a)} + \frac{r_{H^+}}{k_{H^+}} \right\}} - k_b \frac{\left\{ [ALL_3 \cdot (HL)_3]_{(o)} + \frac{r_{ALL_3 \cdot (HL)_3}}{k_{ALL_3 \cdot (HL)_3}} \right\} \left\{ [H^+]_{(a)} + \frac{r_{H^+}}{k_{H^+}} \right\}}{K_{eq3} \left\{ [(HL)_2]_{(o)} - \frac{r_{(HL)_2}}{k_{(HL)_2}} \right\}} \quad (41)$$

$$r = k_f K_{eq1} K_{eq2} \frac{\left\{ [Al^{3+}]_{(a)} - \frac{r_{Al^{3+}}}{k_{Al^{3+}}} \right\} \left\{ [(HL)_2]_{(o)} - \frac{r_{(HL)_2}}{k_{(HL)_2}} \right\}^3}{\left\{ [H^+]_{(a)} + \frac{r_{H^+}}{k_{H^+}} \right\}^2} - k_b \left\{ [ALL_3 \cdot (HL)_3]_{(o)} + \frac{r_{ALL_3 \cdot (HL)_3}}{k_{ALL_3 \cdot (HL)_3}} \right\} \left\{ [H^+]_{(a)} + \frac{r_{H^+}}{k_{H^+}} \right\} \quad (42)$$

In this extraction system, the hydrogen ions produced by the extraction reaction are much lower than those in the phosphoric acid solution, i.e., $[H^+]_{(a)} \gg r_{H^+}/k_{H^+}$. Hence, the concentration of hydrogen ions at the interface remains unchanged. According to the research in 3.3.3, the mass-transfer resistance is mainly focus on the organic phase, and the mass-transfer rate of P-15 extractant in sulfonated kerosene is very fast, so the mass transfer resistance is mainly existed in the diffusion process of extraction complex. Therefore, equations (40)-(42) can be simplified as

$$r = k_f [Al^{3+}]_{(a)} [(HL)_2]_{(o)} - k_b \frac{\left\{ [ALL_3 \cdot (HL)_3]_{(o)} + \frac{r_{ALL_3 \cdot (HL)_3}}{k_{ALL_3 \cdot (HL)_3}} \right\} [H^+]_{(a)}^3}{K_{eq2} K_{eq3} [(HL)_2]_{(o)}} \quad (43)$$

$$r = k_f K_{eq1} \frac{[Al^{3+}]_{(a)} [(HL)_2]_{(o)}^2}{[H^+]_{(a)}} - k_b \frac{\left\{ [ALL_3 \cdot (HL)_3]_{(o)} + \frac{r_{ALL_3 \cdot (HL)_3}}{k_{ALL_3 \cdot (HL)_3}} \right\} [H^+]_{(a)}}{K_{eq3} [(HL)_2]_{(o)}} \quad (44)$$

$$r = k_f \frac{[Al^{3+}]_{(a)} [(HL)_2]_{(o)}^3 K_{eq2} K_{eq1}}{[H^+]_{(a)}^2} - k_b \left\{ [ALL_3 \cdot (HL)_3]_{(o)} + \frac{r_{ALL_3 \cdot (HL)_3}}{k_{ALL_3 \cdot (HL)_3}} \right\} [H^+]_{(a)} \quad (45)$$

At the beginning of the extraction reaction, the reverse reaction has not yet started, so the initial rate equation of the extraction reaction is

$$r = k_f [Al^{3+}]_{(a)} [(HL)_2]_{(o)} \quad (46)$$

$$r = \frac{k_f K_{eq1}}{[H^+]_{(a)}} [Al^{3+}]_{(a)} [(HL)_2]_{(o)}^2 \quad (47)$$

$$r = \frac{k_f K_{eq1}}{[H^+]_{(a)}} [Al^{3+}]_{(a)} [(HL)_2]_{(o)}^3 \quad (48)$$

According to the research of 3.3.1, the reaction orders of aluminum and $(HL)_2$ are 1 and 2 respectively. Obviously, Equation (47) has the same form with the conclusions in the section of 3.3.1, it can be acquired that the rate of extraction reaction is determined by R2.

At steady state

$$r_{ALL_3 \cdot (HL)_3} = - \frac{d[Al^{3+}]_{(a)}}{dt} = \frac{d[ALL_3 \cdot (HL)_3]_{(o)}}{dt} \quad (49)$$

Hence, the total rate equation of reactive extraction can be eventually calculated as

$$r = \frac{k_f K_{eq3} K_{eq1} k_{ALL_3 \cdot (HL)_3} [(HL)_2]_{(o)}^3 [Al^{3+}]_{(a)}}{k_b [H^+]_{(a)} + K_{eq3} k_{ALL_3 \cdot (HL)_3} [(HL)_2]_{(o)}} - \frac{k_b K_{eq3} k_{ALL_3 \cdot (HL)_3} [ALL_3 \cdot (HL)_3]_{(o)} [H^+]_{(a)}}{k_{ALL_3 \cdot (HL)_3} K_{eq3}^2 [(HL)_2]_{(o)} + k_b K_{eq3} [H^+]_{(a)}} \quad (50)$$

4. Conclusions

The extraction kinetics of aluminum ion from phosphoric acid solution by P-15 extractant using constant-interfacial-area cells was investigated, and the following results can be obtained:

1. Investigations on the influences of experimental conditions indicated that increasing the aluminum concentrations, temperature, interface area can improve extraction efficiency.
2. The extraction rate of $ALL_3 \cdot (HL)_3$ is deduced, and the reaction orders of aluminum and $(HL)_2$ are 1 and 2 respectively.
3. According to the results of kinetic studies, the extraction is a mixed-control process affected by interfacial reaction and the diffusion of the resultant in the organic phase
4. By thermodynamics analysis, the extraction process is a spontaneous process with increased endothermic entropy.
5. A mixed-control model is determined, and the rate-limited steps of extraction process are:

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