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Ca(II) extraction by D2EHPA from Calcium Lactate Solution to Produce Lactic Acid: Process and Kinetics

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Abstract

A new solvent extraction method that removing the Ca(II) from calcium lactate by Di-(2-ethylhexyl) phosphoric acid (D2EHPA) to produce lactic acid was proposed. The influences of composition of organic phase, phase ratio, temperature and calcium concentration, on extraction yield, were investigated. The optimal technological conditions of extraction were obtained: reaction temperature 323 K, phase ratio (O/W) 4:1, the initial calcium concentration 1.03 mol L^{-1}, the D2EHPA volume fraction 40%, and 5% 1-octanol as modifiers. The reaction occurs at the interfacial zone possibly, and the rate is mostly controlled by chemical reaction. Reaction order with respect to H_2A_2, pH and Ca^{2+} was determined and the rate of calcium extraction could be expressed as: $F = 10^{-6.81}[Ca^{2+}][H_2A_2]^{0.5}[H^+]^{-1}$.

Keywords: Calcium lactate, lactic acid, solvent extraction, kinetics

1. Introduction

Lactic acid is a chemical commodity utilized in chemical and pharmaceutical fields [1]. Approximately 90% of the total lactic acid produced worldwide is made by bacterial fermentation at present [2]. Solvent extraction was a kind of method to recovery lactic acid from fermentation broth, and the lactic acid was extracted to organic phase. However, this process has drawbacks of consuming extra chemicals and forming a waste salt.

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To resolve these shortcomings, the way of keeping lactic acid in aqueous phase was proposed in this paper. In this process, calcium lactate solution produced by the addition of calcium hydroxide to the aqueous fermentation broth was contacted with D2EHPA (H_2A_2) to remove cations to organic phase, while lactic acid retained in aqueous phase. For this new approach of separating lactic acid by solvent extraction of cations, it is necessary to perform detail experiments to optimize the extraction conditions and make some insight of kinetic mechanism for finding out the determining step of the solvent extraction process.

The aim of this study is to select an appropriate solvent composition for extraction of Ca(II) and optimize the extraction conditions, meanwhile, kinetic mechanism of solvent extraction was investigated. The effects of composition of organic phase, phase ratio, temperature, and concentration of calcium lactate were examined in solvent extraction runs. The kinetic equation of solvent extraction was derived by "F" method based on the effects of parameters on the extraction rate.

2. Experimental techniques

2.1. Materials

The materials used in this study were calcium lactate (kindly provided by Henan Jindan Lactic acid Tech CO., Ltd.) which has an analytical purity of 98 %. The content of D2EHPA (Tianjin Chemical Co.ltd,) was of 99 %. 1-octanol, 2-octanol and iso-octanol, aromatic free kerosene were of reagent grade and were used without pretreatment. Deionized water was produced by Millipore Milli-Q Water System.

The aqueous medium was prepared by dissolving calcium lactate in deionized water at desired temperature, and its concentrations were measured by EDTA complexometry using EBT (Eriochrome black T) as an indicator. All other reagents were of analytical grade.

2.2. Procedure

The experiments were carried out in 250 ml conical flask. Proportional volumes of aqueous and organic phases were shaken for 5 min at constant temperature on the magnetic stirring apparatus, unless for the tests about reaction time effect on the result. The phase separations were carried out in 250 ml separatory funnels.

After phase separation, the calcium ions concentrations in the aqueous phase were measured by EDTA complexometry using EBT (Eriochrome black T) as an indicator. The pH of aqueous phase was measured by a Mettler Toledo pH meter, and lactic acids concentrations could be calculated.

The construction of the Lewis cell and the working procedure with the Lewis cell used in this investigation was discussed before [3]. The stirring rate was controlled at 180 rpm except the effect of it on kinetic experiment. The aqueous concentration of calcium was estimated by sampling and complexometry. A Mettler Toledo pH meter was used for pH measurements. All experiment were carried out at 293 K, the interfacial area was kept at 1.776 cm^2 unless for the tests about temperature or interfacial area.

3. Results and discussion

3.1. The research of extraction process

The influences of H_2A_2 volume fraction, modifiers, phase ratio, temperature, and calcium concentration were researched, and the initial conditions were: reaction temperature 298 K, phase ratio (O/W) 4:1, the initial calcium concentration 0.68 mol L^{-1}, the H_2A_2 volume fraction 40 %, and 5% 1-octanol as modifiers. The major criterions to choose technological conditions were extraction yield and concentration of H$^+$.
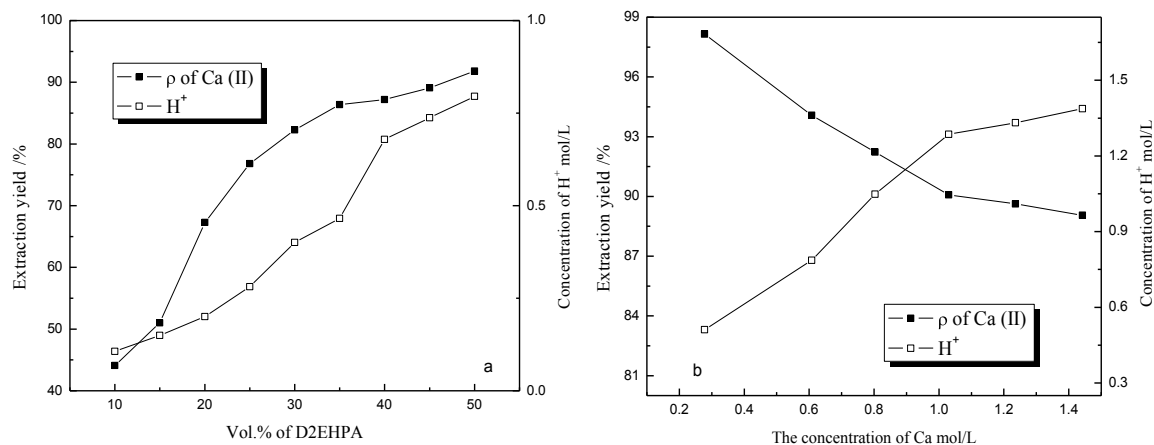
Fig. 1. (a) The effect of D2EHPAvolume fraction on extraction yield and concentration of H$^+$. *V(o)* = 120 ml, *V(a)* = 30 ml, *T* = 298 K, 1-octanol % = 5 (V/V), [Ca^{2+}] = 0.68mol/L, *t* = 5 min. (b) The effect of the calcium concentration on extraction yield and concentration of H$^+$. *V(o)* = 120 ml, *V(a)* = 30 ml, D2EHPA % = 40 (V/V), *T* = 298 K, 1-octanol % = 5 (V/V), *t* = 5 min.

3.1.1. Influence of D2EHPAvolume fraction on extraction yield and concentration of H$^+$

The D2EHPAvolume fraction ranged from 10 vol. % to 50 vol. % to research its influence on extraction yield and concentration of H$^+$, and the result was plotted in Fig. 1 (a).

Fig. 1 (a). shows that the calcium extraction yield and concentration of H$^+$ increased linearly with the increase of D2EHPA volume fraction, and inflection points appeared at 35 vol. % and 40 vol. %, respectively. These were because that more resultant was obtained. Considering the extraction yield and concentration of H$^+$, the H$_2$A$_2$ volume fraction was chosen as 40 vol. %.

3.1.2. Influence of calcium concentration on extraction yield and concentration of H$^+$

The calcium concentration was varied from 0.28 to 1.44 mol L^{-1}, to research its influence on extraction yield and concentration of H$^+$, and the result was shown in Fig. 1 (b).

Fig. 1 (b). shows that with the growth of calcium concentration, extraction yield fell from 98% to 89%, concentration of H$^+$ grew from 0.5 to 1.39 mol L^{-1}. These were because that more resultant was obtained. Considering the extraction yield, concentration of H$^+$, the calcium concentration was chosen as 1.03 mol L^{-1}.

3.1.3. Influence of modifiers on extraction yield and concentration of H$^+$

The volume fraction of three modifiers ranged from 5 vol. % to 25 vol. % respectively, to research their influence on extraction yield and concentration of H$^+$, and the result was shown in Fig. 2.
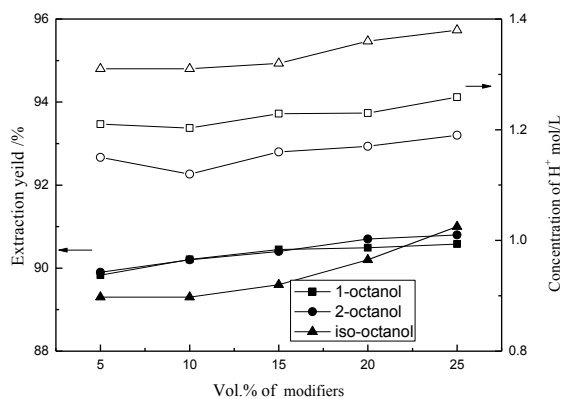
Fig. 2. The effect of volume fraction of modifiers on extraction yield and concentration of H$^+$. $V(o)$ = 120 ml, $V(a)$ = 30 ml, T = 298 K, [Ca^{2+}] = 1.03 mol/L, D2EHPA % = 40 (V/V), t = 5 min.
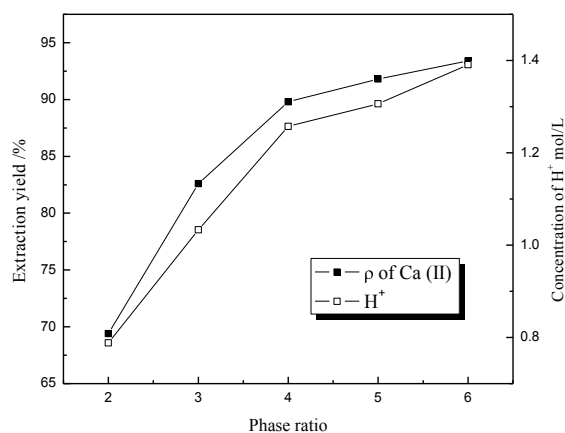

Fig. 3. The effect of phase ratio on extraction yield and concentration of H$^+$. $V(a)$ = 30 ml, T = 298 K, 1-octanol % = 5 (V/V), [Ca^{2+}] = 1.03 mol/L, t = 5 min, D2EHPA % = 40 (V/V).

Fig. 2 shows that the extraction yield and concentration of H$^+$ increased with the increase of three modifiers, but not observably. The reason was that the addition of modifiers changed the polarity of organic phase, and made more D2EHPA exist as monomers. Meanwhile, the solubility of extraction complex was higher with the existence of modifiers. Considering that the absence of modifier caused the solidification of organic phase when it cooled to room temperature, the modifier volume fraction was chosen as 5 vol. %. However, the influences of three modifiers on extraction process were similar, so all of them could be chosen. In this research, 1-octanol was chosen as modifier.

3.1.4. Influence of phase ratio on extraction yield and concentration of H^+

The phase ratio was varied from 2:1 to 6:1, to research its influence on extraction yield and concentration of H^+, and the result was plotted in Fig. 3.

Fig. 3. shows that the calcium extraction yield and concentration of H^+ increased with the increase of phase ratio, and both inflection points appeared at phase ratio of 4:1. The increase of phase ratio was actually to increase the amount of extractant, which conduced to increasing the extraction yield and concentration of H^+. Considering the extraction yield and concentration of H^+, the phase ratio was chosen as 4:1.

3.1.5. Influence of temperature on extraction yield and concentration of H^+

The temperature was varied from 293 to 353 K, to research its influence on extraction yield and concentration of H^+, and the result was shown in Fig. 4.
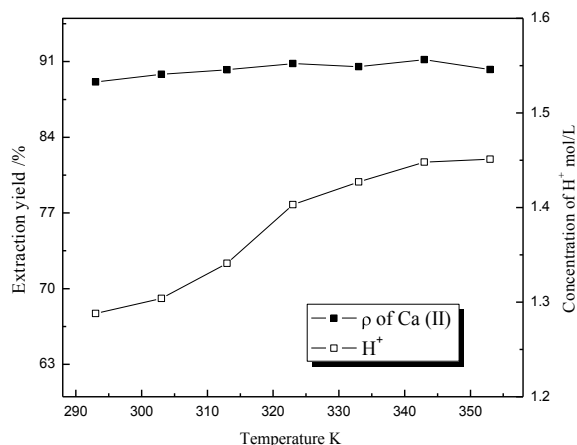

Fig. 4. The effect of temperature on extraction yield and concentration of H^+. $V(o)$ = 120 ml, $V(a)$ = 30 ml, D2EHPA % = 40 (V/V), $[Ca^{2+}]$ = 1.03mol/L, 1-octanol % = 5 (V/V), t = 5 min.

Fig. 4. shows that the temperature had a slight influence on extraction yield but a remarkable influence on concentration of H^+. The reason was that the distribution ratio of lactic acid changed with the change of temperature, so more lactic acid could stay in aqueous phase. Considering the extraction yield and concentration of H^+, the temperature was chosen as 323 K.

The optimal technological conditions of extraction by D2EHPA were obtained: reaction temperature 323 K, phase ratio (O/W) 4:1, the initial calcium concentration 1.03 mol L^{-1}, the H_2A_2 volume fraction 40%, and 5% 1-octanol as modifiers. Under these conditions, the extraction rate could reach 91%, and the concentration of H^+ could reach 1.4 mol L^{-1}.

3.2 Kinetic study

3.2.1. Extraction equilibrium

The expected thermodynamic extraction reaction could be represented as follows, where "a" refers to the aqueous phase; "o" refers to the organic phase.

$$Ca_{(a)}^{2+} + xH_2A_{2(o)} \Leftrightarrow CaA_y \cdot (2x - y)HA_{(o)} + yH_{(a)}^+ \tag{1}$$

By assuming ideal behavior for the reaction in Eq. (1) in organic and aqueous phases, the stoichiometric equilibrium constant could be written as:

$$K = \frac{[CaA_y(2x - y)HA][H^+]^y}{[Ca^{2+}][H_2A_2]^x} \tag{2}$$

And the distribution coefficient was equal to:

$$D = \frac{[Ca]_{(o)}}{[Ca]_{(a)}} = \frac{K[H_2A_2]^x}{[H^+]_y} \tag{3}$$

or

$$\log D = \log K + x * \log[H_2A_2] + y * pH \tag{4}$$

Coefficient "x" and "y" could be evaluated by studying the dependence of log D on concentration of H^+ at constant extraction concentration and the influence of D2EHPA concentration on log D at constant concentration of H^+. The plots of log D vs. concentration of H^+ and log D vs. log $[H_2A_2]$ (Fig. 5.) yielded straight lines: $y = -7.49 + 1.71x$, $y = 0.84 + 1.89x$ and the slopes were both approximately equal to 2.
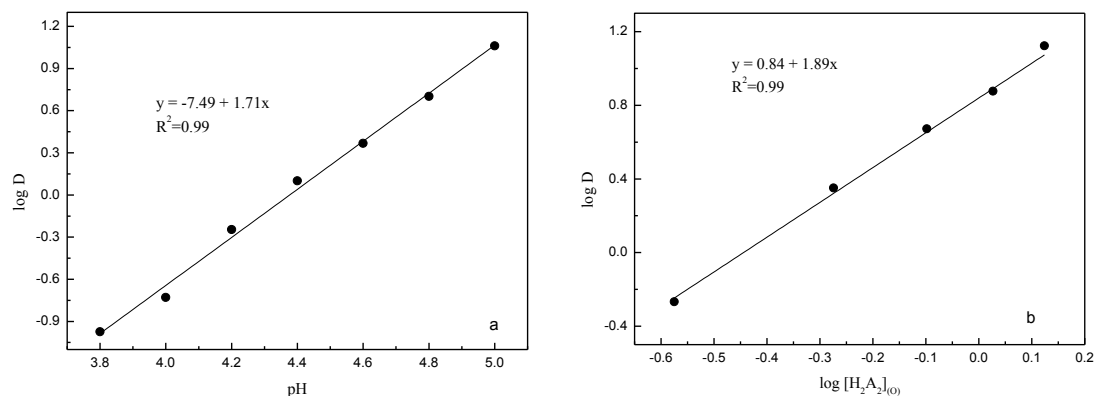

Fig. 5. (a) Dependence of distribution coefficient log D on concentration of H^+. [D2EHPA] = 1.33 mol/L, 1-octanol%= 5 (V/V), [Ca^{2+}] = 0.57 mol/L. (b0Dependence of distribution coefficient log D on extractant concentration. [Ca^{2+}] = 0.57 mol/L, 1-octanol% = 5 (V/V), pH = 5.

Reaction was obtained based on the results:

$$Ca^{2+} + 2H_2A_2 \Leftrightarrow CaA_2 \cdot 2HA + 2H^+ \tag{5}$$

3.2.2 Data treatment by 'F' method

The extraction rate of Ca(II) at a constant temperature could be written as:

$$Rate = ([Ca^{2+}]_{(O)}/dt) = k_f \, A[Ca^{2+}]^a \, [H_2A_2]_{(O)}^b \, [H^+]^c \tag{6}$$

Flux 'F' can be calculated by this:

$$F = \frac{m\, t\, (\text{Kmol})}{A\, (\text{m}^2)\, t\, (\text{s})} \tag{7}$$

Which is proportional to $[Ca^{2+}]^a$, $[H_2A_2]^b$ and $[H^+]^c$ as shown below:

$$F = k_f\, [Ca^{2+}]^a\, [H_2A_2]_{(O)}^{\,b}\, [H^+]^c \tag{8}$$

$$\log F = \log k_f + a \log[Ca^{2+}] + b \log[H_2A_2]_{(O)} + c \log[H^+] \tag{9}$$

With Eq (9), reaction orders (a, b, c) could calculated by the slopes of the linear relationship between $\log F$ and $\log[Ca^{2+}]$, $\log[H_2A_2]_{(O)}$, $\log[H^+]$, respectively, then k_f could be evaluated based on the intercepts [4].

3.2.3. Extraction rate equation

To obtain extraction rate equation, the influence of the parameters on should be studied [5].

With other chemical parameter constant, the concentration of calcium H_2A_2 and H^+ changed (Fig. 6.). With their linear relationships, the values of a, b, and c can be obtained, and $a = 1$, $b = 0.5$, $c = -1$. According to the intercepts, extraction rate constant could be evaluated and $k_f = 10^{-6.81}$. The following expression was obtained from the results above:
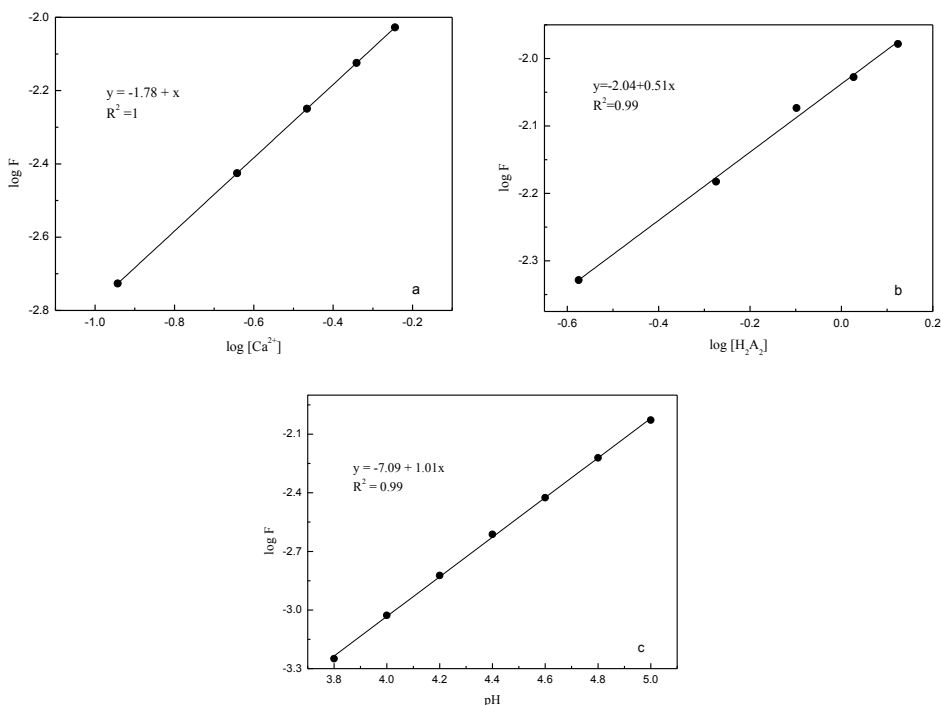
$$F = 10^{-6.81}[Ca^{2+}][H_2A_2]^{0.5}[H^+]^{-1} \tag{10}$$

Fig. 6. (a) Effect of concentration of Ca^{2+} on extraction rate. $A = 1.776$ cm^2, $V(o) = V(a) = 100$ ml, $T = 298$ K, [D2EHPA] = 1.33 mol/L, 1-octanol% = 5 (V/V), pH = 5. (b) Effect of concentration of D2EHPA on extraction rate. $A = 1.776$ cm^2, $V(o) = V(a) = 100$ ml, $T = 298$ K, $[Ca^{2+}] = 0.57$ mol/L, 1-octanol % = 5 (V/V), pH = 5. (c) Effect of concentration of concentration of H^+ on extraction rate. $A = 1.776$ cm^2, $V(o) = V(a) = 100$ ml, $T = 298$ K, $[Ca^{2+}] = 0.57$ mol/L, 1-octanol = 5 (V/V), [D2EHPA] = 1.33 mol/L.
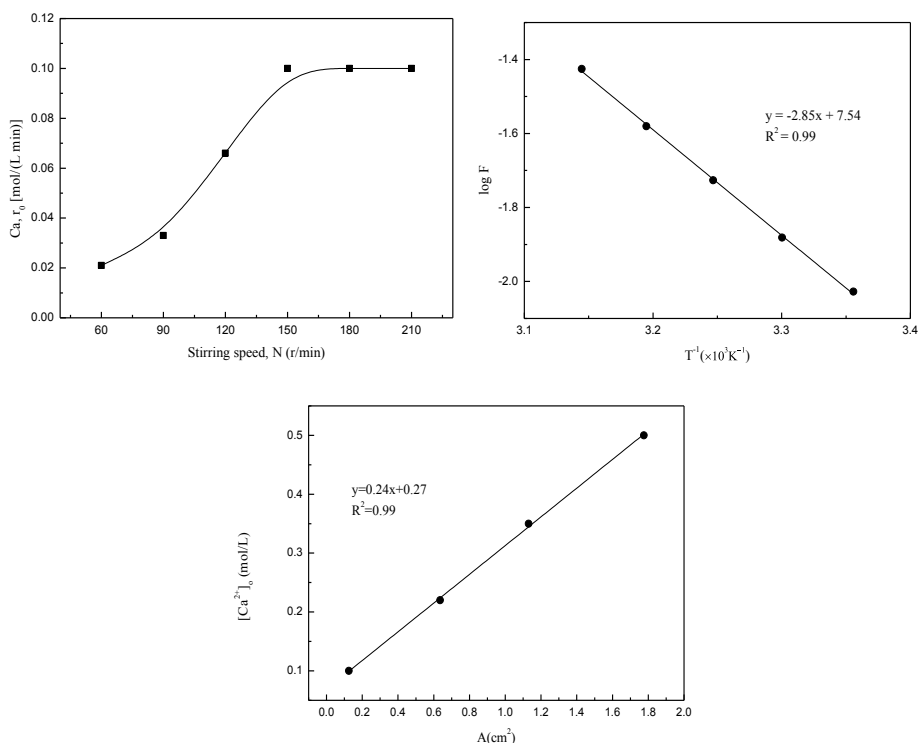
Fig. 7. (a) Effect of stirring speed on extraction rate. $A = 1.776$ cm^2, $V(o) = V(a) = 100$ ml, $T = 298$K, [D2EHPA] = 1.33 mol/L, 1-octanol% = 5 (V/V), [Ca^{2+}] = 0.57 mol/L, pH = 5. (b) Effect of temperature on extraction rate. $A = 1.776$ cm^2, $V(o) = V(a) = 100$ ml, [D2EHPA] = 1.33 mol/L,1-octanol % = 5 (V/V), [Ca^{2+}] = 0.57 mol/L, pH = 5. (c) Effect of specific interfacial area on concentration of Ca^{2+} in organic phase. $V(o) = V(a) = 100$ ml, $T = 298$K, [D2EHPA] = 1.33 mol/L, 1-octanol% = 5 (V/V), [Ca^{2+}] = 0.57 mol/L, pH = 5, $t = 5$min

3.2.4. Identification of the nature of the kinetic regime

The most important criterion that enabled to distinguish between a diffusion-controlled and a kinetics regime was the influence of extraction rate on the stirring speed, and to research it, the stirring speed was varied between 60 and 210 rpm (Fig.7. (a)).

When the stirring speed was lower than150 rpm, the extraction rate was influenced by stirring speed. When it was higher than 150 rpm, a plateau appeared, and the extraction rate is constant, demonstrating that the interfacial area and the global transfer coefficient were constant.

A further criterion was the experimental determination of the activation energy of the extraction process. Generally, when the rate is controlled by chemical reaction, Ea is above 40 kJ/mol; when the rate is controlled by a diffusion process, Ea is below 20 kJ/mol; and the rate might be a mixture controlled regime when the Ea value is between 20 kJ/mol and 40 kJ/mol [6].

The influence of temperature on the kinetics of calcium extraction was shown in Fig. 7 (b).The extraction rate increased with increasing temperature and the experimental data obeyed Arrhenius equation:

$$\log F = \frac{- Ea}{2.303RT} + C$$

(11)

The apparent activation energy of the reaction was 54.57 kJ/mol calculated from the Arrhenius plot, and it was above 40 kJ/mol. That suggested the extraction process was controlled by chemical reaction.

The effect of interfacial area on the rate of extraction was another important criterion to identify reaction mechanism. The relationship between interfacial area and extraction rate was showed in Fig. 7. (c), demonstrating the reaction occurring at the interfacial zone possibly[7].

4. Conclusion

The following conclusions have been obtained:

1. The optimal technological conditions of extraction by D2EHPA were obtained: reaction temperature 323 K, reaction time 5 min, phase ratio (O/W) 4:1, the initial calcium concentration 1.03 mol L^{-1}, the H_2A_2 volume fraction 40%, and 5% 1-octanol as modifiers. Under these conditions, the extraction rate could reach 91%, and the concentration of H^+ could reach 1.4mol L^{-1}.

2. In extraction equilibrium studies, the relationship between pH, log $[H_2A_2]$ and log D was investigated, and the thermodynamic extraction reactions is as follows:

$Ca^{2+} + 2H_2A_2 \Leftrightarrow CaA_2 \cdot 2HA + 2H^+$
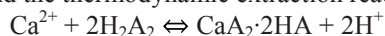
3. The reaction occurs at the interfacial zone possibly, and the rate is mostly controlled by chemical reaction. Under the conditions prevailed in the Lewis cell, the rate of extraction at 293 K can be expressed as:

$F = 10^{-6.81}[Ca^{2+}] [H_2A_2]^{0.5}[H^+]^{-1}$

Nomenclature

a,b,c	Reaction orders with respect to $[Ca^{2+}]$, $[H_2A_2]$ and $[H^+]$,respectively
Ea	Activation energy; kJ/mol
A	Interfacial area through which mass transfer occurs; m^2
D	Diffusion coefficient; m^2/s
F	Mass transfer flux of Ca(II); $Kmol/ m^2s$
k_f	Forward extraction rate constant
mt	Amount of mass transferred; Kmol
t	Phase contact time; s
T	Absolute temperature; K
ρ	Extraction yield

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