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# Thermodynamics and kinetics of lutetium extraction with HEH(EHP) in hydrochloric acid medium

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**Abstract:** Solvent extraction has been the most widely used technique for rare earths separation. In this study, thermodynamics and kinetics of lutetium extraction with HEH (EHP) in hydrochloric acid medium were investigated. The extraction mechanism and the relevant parameters were determined by experiment research which can guide the practical extraction process. The data indicated that chloride ion had no effect on lutetium extraction, the rate constant increased when stirring speed was enhanced. Effects of temperature, HEH (EHP) concentration, acidity, and chloride concentration were also studied. Thickness of the diffusion film was also calculated to be $4.66\times10^{-3}$ cm at 150 r/min.

**Keywords:** extraction; kinetics; thermodynamics; lutetium; HEH (EHP); rare earths

Rare earths have seventeen elements including fifteen lanthanides and yttrium and scandium. As a result of their unique physicochemical properties the lanthanides are used in many industrial fields and are strategic materials needed for the security and defense sectors. However, compared to light rare earths, heavy rare earths (gadolinium to lutetium and yttrium) are regarded as more critical strategic resources by many countries because of their extensive distribution, less reserves, wider application and more difficulty to be substituted. Lutetium, as one of the most valuable heavy rare earths due to its scarce abundance, has been widely used in petrochemical materials, special alloys, electroluminescent materials and scintillation crystals[1–5].

At present, solvent extraction has become the most widely used technique for rare earths separation owing to its advantages of high processing capacity, fast extraction kinetics and high separation efficiency. Therefore, rare earth extraction behaviors have been carried out by many investigations. Previously, researchers have made many efforts on equilibrium state direction. However, the kinetic studies on rare earth extraction are to a large extent insufficient[6,7]. Now a number of techniques for studying solvent extraction kinetics are available including the rotating-diffusion cell, single-drop technique, Lewis cell, the laminar jet and Lewis-Hahn cell[8]. As a result, it is not only important but also necessary to investigate extraction kinetics studies mechanism and optimize the extraction conditions.

HEH (EHP) (2-ethyl-hexyl phosphonic acid mono-2-ethylhexyl ester) has been widely used in rare earth separation processes. A number of studies have been carried out on the kinetics and mechanisms of rare earth extraction by acidic organophosphorus extractants. For instance, the extraction of heavy rare earths by Cyanex272[9], and by the mixture of Cyanex272 and HEH(EHP)[10], $Yb^{3+}$ extraction by HEH(EHP)[11], $La^{3+}$ extraction by Cyanex272[12], $Ce^{4+}$ extraction by DEHEHP[13], $Eu^{3+}$ extraction by HDEHP[14]. However, there are still many problems in the rare earth industrial productions requiring the technological improvement for separation process[15,16]. In the present paper, the thermodynamics and kinetics of lutetium extraction with HEH (EHP) in hydrochloric acid medium were studied, an improved Lewis cell with a known interfacial area was used. The improved Lewis cell was ready to control the extraction speed. The effect of various parameters on the extraction kinetics was investigated.

## 1 Experimental

### 1.1 Reagents and apparatus

HEH (EHP) was obtained from Shanghai Rare-earth Chemical Co., Ltd., China, and was purified to 99%. Kerosene (DT-100) used as a diluent in this study was supplied by Kopper Chemical Industry Co., Ltd., China.

The extraction rate of lutetium from the aqueous chlo-

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ride solution into the HEH (EHP) solution was measured using a stirred transfer cell of Lewis type, as illustrated in Fig. 1. It consists of a plastic container having a paddle in each phase. The upper and lower phases were stirred in the reverse rotation at the same rate, which allows equal individual mixing of each phase without disturbing the interface. Both initial aqueous and organic phase volume were 1.0 L with a constant temperature heating jacket. The contact area of the interface between two phases was 20.36 cm$^2$.

In this experiment, the interfacial tension experiments were performed on a Du Nouy tensiometer, which was used to measure the interfacial tension (Full Automatic Surface & Interface Tensiometer & Contact Angle Meter A60, USA Kino Industry) according to the Du Nouy ring method. All experiments were carried out at 298±0.2 K unless otherwise stated.

### 1.2 Procedures

Stock solution of lutetium chloride was prepared from lutetium oxide (99.995% purity) by dissolved in hot concentrated hydrochloric acid and diluted with deionized distilled water. All other chemicals used were of analytical grade.

Equal volume of 20 mL aqueous and 20 mL organic solution were mixed at 298±1 K and shaken for 30 min, the aqueous phase was then analyzed after phase separation by centrifugation for 5 min at 4000 r/min.

During the studies of extraction kinetics, the lutetium concentration was 0.02 mol/L. NaCl was used to maintain the solutions at a constant ionic strength of 0.2 mol/L. The aqueous phase was added to the bottom of the cell through a funnel and insulated for 60 min, which was sufficient to attain stable temperature. The organic phase was preheated in the thermostat bath and injected carefully into top of the cell in order to minimize the disturbance of the interface. Then the stirrer was started immediately, according to actual situations, samples were taken from the aqueous phase via a glass syringe at time intervals of 5–10 min. The amount of sample was 2 mL.

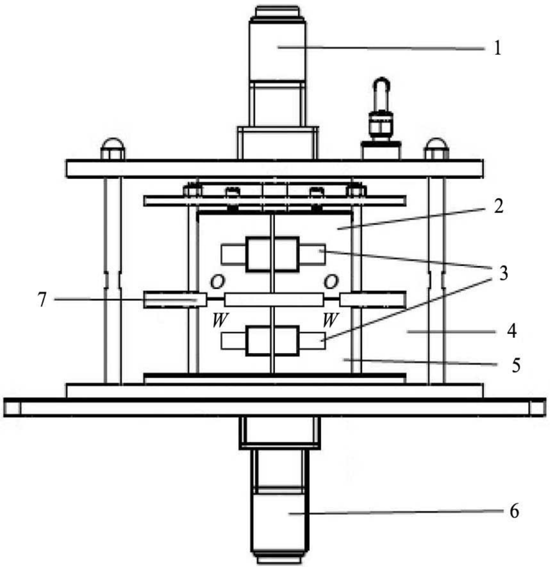

Fig. 1 A schematic diagram of the improved Lewis cell
1-Upper motor; 2-Organic phase; 3-Agitating paddle; 4-Insulating layer; 5-Aqueous phase; 6-Lower motor; 7-Interface of two phases

The Lu$^{3+}$ was analyzed by titration with a standard solution of EDTA with xylenol orange (XO) as indicator. Concentration of lutetium in the organic phase was calculated based on the mass balance of lutetium concentrations in the feed and in the raffinate. During the experiments, the pH of aqueous solution was first adjusted to the desired values with hydrochloric acid and monitored with Mettler Toledo pH electrode LE438 series coupled with the InLab Routine pH meter.

### 1.3 Data analysis

The mass transfer of lutetium from an organic to an aqueous phase can be described as a simple approach to equilibrium[17–21]:

$$\mathrm{Lu(III)}_{(a)} \underset{k_{oa}}{\overset{k_{ao}}{\rightleftarrows}} \mathrm{Lu(III)}_{(o)} \tag{1}$$

where subscripts a and o represent aqueous and organic phases, respectively, and $k_{ao}$ and $k_{oa}$ represent the interfacial mass transfer coefficients from the aqueous to organic phase and from the organic to aqueous phase, respectively.

Assuming the mass-transfer process could be formally treated as a pseudo-first-order reversible reaction with respect to the metal cation, the rate of extraction is given by the following equation:

$$-\frac{\mathrm{d}[\mathrm{Lu}]_{(o)}}{\mathrm{d}t} = -\frac{\mathrm{d}n_0}{V\mathrm{d}t} = \frac{A}{V}\times(k_{oa}[\mathrm{Lu}]_{(o)} - k_{ao}[\mathrm{Lu}]_{(a)}) \tag{2}$$

where $n_0$ is the number of moles of lutetium in the organic phase, $V$ (mL) is the volume of either aqueous or organic phase, and $A$ (cm$^2$) is the interfacial area, it follows upon integration that:

$$\ln\left(1-\frac{[\mathrm{Lu}]_{(o)}}{[\mathrm{Lu}]^{e}_{(o)}}\right) = -\frac{A}{V}\times(1+k_d)\times k_{oa}\times t \tag{3}$$

where $[\mathrm{Lu}]^{e}_{(o)}$ is the equilibrium concentration of Lu in organic phase, and the distribution coefficient $K_d=[\mathrm{Lu}]^{e}_{(o)}/[\mathrm{Lu}]^{e}_{(a)}=k_{ao}/k_{oa}$. Through the experiment, function $V/A\cdot\ln(1-[\mathrm{Lu}]^{e}_{(o)}/[\mathrm{Lu}]^{e}_{(a)})$ *vs.* time were all plotted for straight lines, indicating that the mass-transfer process could be formally treated as a pseudo-first-order reversible reaction with respect to the metal cation. Fig. 2 is an example of a typical first order plot of data collected in this fashion. The slopes of plots were used to evaluate $k_{oa}$ and $k_{ao}$ per experiment. By investigating the influences of various parameters on the extraction rate, the extraction regimes and reaction zone can be determined.

In this research, the following isotherms were also used for processing the interfacial tension data and esti-