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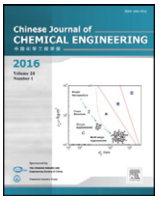

Separation Science and Engineering

Solvent extraction of lanthanum and cerium ions from hydrochloric acidic aqueous solutions using partly saponified 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester☆

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ABSTRACT

In order to clarify the extraction process with saponified extractant, the solvent extraction experiments of rare earth elements (REEs), lanthanum and cerium, by using partly saponified 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (EHEHPA, HL) from hydrochloric acidic solutions have been performed. The concentration of initial aqueous rare earth ion was in a range of 0.0010–0.1000 $\mathrm{mol\cdot L^{-1}}$; EHEHPA in a range of 0.2877–0.8631 $\mathrm{mol\cdot L^{-1}}$ with saponification rate of 0.3 (mole fraction), and the initial aqueous pH in a range of 1.00–4.00. Firstly, the extracted species were determined by the saturation extraction capacity method. Secondly, according to the equilibrium aqueous pH values, the extraction processes were divided into three different categories: extraction with saponified EHEHPA, extraction with un-saponified EHEHPA, and hydrolysis process. Finally, for the first two processes, in order to predict the distribution ratio, two semi-empirical calculation models were developed with. The calculation results are in good agreement well with the experimental data.

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1. Introduction

Rare earth elements (REEs) have been drawing great attention because of their extensive applications in permanent magnet [1], catalyst [2,3], metallurgy [4,5], and other high-technology domains [6]. Solvent extraction method has been broadly used to separate REEs. Organophosphorus acids, such as 2-ethylhexyl phosphoric acid-2-ethylhexyl ester (EHEHPA) [7,8], di-(2-ethylhexyl) phosphoric acid (D2EHPA) [9,10], and carboxylic acid [11,12], are widely used. Among these, EHEHPA is more preferable due to its high selectivity and low stripping acidity [13]. The mechanism with un-saponified EHEHPA is a cation exchange reaction [14], in which hydrogen ions are released. With the increase of acidity, the extraction process is inhibited. In order to enhance the extraction capability of the extractant, the saponified extractant is used in hydrometallurgy separation process. Thakur and coworkers [15] used 20% saponified alkylphosphonic acid, EHEHPA, to separate Nd (III), and some basic experimental data on the distribution of REEs against initial aqueous acidity were determined. Devi and coworkers [16] studied extraction process of Co (II)/Ni (II) from sulfate solutions with saponified extractants, D2EHPA, EHEHPA, and Cyanex 272. The optimal extraction conditions for separating the two elements were investigated. Sarangi and coworkers [17] separated Co (II)/Ni (II) from chloride solutions by using Cyanex 272 as an extractant, TBP as a phase modifier, and NaOH as a saponifier. Devi and coworkers [18] performed works on optimal conditions for the Co (II)/Mn (II) separation process with saponified extractant. Lee and coworkers [19] used 40% saponified EHEHPA to extract Nd (III) from chloride medium. The complex of saponified extraction was considered as $\mathrm{NdL_3}$. Although the saponification extraction process is very important in industrial process, the mechanisms of the processes, including the formation of the complex, and the accompanying phenomena, have not been thoroughly clarified.

In this paper, we attempt to clarify the mechanism of the rare earth elements extraction process with partly saponified EHEHPA. Firstly, the complex was determined by the saturation extraction capacity method. The REE aqueous solution with concentration in a range of 0.0010 to 0.10 00 $\mathrm{mol\cdot L^{-1}}$ was used as the aqueous phase. The EHEHPA with 0.3 (mole fraction) saponified with concentration in a range of 0.2877 to 0.8631 $\mathrm{mol\cdot L^{-1}}$ was the organic phase. Secondly, according to the relationship between the initial aqueous phase pH and equilibrium aqueous phase pH, the reaction mechanisms under different conditions were

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determined. Finally, on the basis of the mechanism determined, mathematical models were developed in order to predict the REE distribution ratio.

2. Experimental Procedures

2.1. Reagents

The aqueous phase was obtained by dissolving certain amount of the $LaCl_3 \cdot 7H_2O$ or $CeCl_3 \cdot 7H_2O$ in hydrochloric acid solution with different initial pH. The diluent, sulphonated kerosene and the acidic extractant, EHEHPA were used directly without having any further purification. The organic phase was prepared from mixing the EHEHPA in sulphonated kerosene with a certain amount of strong ammonia water. The mixture was kept stirring for 12 h until a single transparent phase formed. All the reagents and the material used in the experiments are listed in Table 1.

2.2. Measurements

The un-saponified EHEHPA was quantified by electronic scale (Mettler AL204), and then dissolved in alcohol solution (75 vol%). To determine the purity of the un-saponified EHEHPA, the EHEHPA alcohol solution was titrated by 0.1001 $mol \cdot L^{-1}$ standard NaOH solution with an intelligent titrator (Mettler T50). The concentration of lanthanum or cerium ions in the aqueous solution was determined by an inductively coupled plasma optical emission spectrometer (ICP-OES, IRIS Intrepid II XSP) at 295 K. The pH value in the aqueous phase was determined by Mettler Easy Five pH meter with a Mettler Toledo LE420 electrode and an ATC temperature probe. The pH meter was calibrated by using standard pH buffer solutions, before each round of pH measurement.

2.3. Extraction procedure

The extraction equilibrium experiments were carried out as follows: equal volumes (20 ml) of aqueous and organic phases were placed in conical flasks. These conical flasks were kept shaking for 1 h in water bath shaker (HZ-9212S purchased from Taicang Science and Education instrument Plant), which was sufficient to reach the thermodynamic equilibrium. The temperature of the water bath was controlled at (298 ± 1) K, and the vibration speed was at (203 ± 1) $r \cdot min^{-1}$. The REE concentrations in aqueous solutions before and after phase separation were measured by the ICP-OES, and the quantity of REE ions extracted into the organic phase was determined by mass balance. The distribution ratio is defined as the followings (Eq. (1)):

$$D = [RE]_{eo}/[RE]_{ea} \tag{1}$$

where D represents the distribution ratio. RE represents the REEs, La (III) or Ce (III). Square bracket refers to the concentration, $mol \cdot L^{-1}$. The subscripts eo and ea refer to the substance at the equilibrium state in the organic phase and aqueous phase respectively. All the experiments were conducted at ambient atmospheric pressure.

3. Results and Discussions

3.1. Determination of the extracted complexes

In this study, a saturation extraction capacity method was used to determine the complex formed during the extraction process by using the partly saponified EHEHPA. By computing EHEHPA to REE mole ratio in organic phase under the saturation extraction conditions, the formation of the complex was obtained.

The extraction capacities of different EHEHPA concentration solutions were evaluated by different REE concentration solutions with different initial aqueous pH. The extraction results of the lanthanum ion are shown in Fig. 1. It is clear that the lanthanum ion equilibrium concentration in the organic phase, $[La]_{eo}$, increased with the growth of initial concentration of lanthanum ion, $[La]_{ia}$, and became stable when $[La]_{ia}$ was larger than 0.0400 $mol \cdot L^{-1}$ for 0.2877 $mol \cdot L^{-1}$ [EHEHPA], and 0.0800 $mol \cdot L^{-1}$ for 0.5754 $mol \cdot L^{-1}$ [EHEHPA]. As for the results of 0.8631 $mol \cdot L^{-1}$ [EHEHPA], $[La]_{eo}$ did not reach any stable values. Fig. 1 also shows the effect of initial aqueous pH on $[La]_{eo}$. When $[La]_{ia}$ was less than 0.0100 $mol \cdot L^{-1}$ for 0.2877 $mol \cdot L^{-1}$ [EHEHPA] and 0.0400 $mol \cdot L^{-1}$ for 0.5754 $mol \cdot L^{-1}$ [EHEHPA], the pH effect was not obvious due to the high EHEHPA concentration. As the initial aqueous pH increased from 1.00 to 4.00, $[La]_{eo}$ increased and became stable when pH was larger than 2.50 for 0.2877 $mol \cdot L^{-1}$ [EHEHPA] and 2.00 for 0.5754 $mol \cdot L^{-1}$ [EHEHPA]. Fig. 2 shows the extraction results of cerium ion with similar trend found.

In order to obtain the molecular formula of the complex, the EHEHPA to REE mole ratio under the stable conditions was determined. To describe easily, $[RE]_{av}$ was defined as the mean value of $[RE]_{eo}$ of 0.080 and 0.100 $mol \cdot L^{-1}$ $[RE]_{ia}$ with the same initial aqueous pH values, at which the $[RE]_{eo}$ reached the maximum and stable values. Ratio R was calculated by dividing the [EHEHPA] with $[RE]_{av}$.

Table 2 shows the $[La]_{av}$ and R values with different $[La]_{ia}$ under different extraction conditions. It indicates that, as the initial aqueous pH increased, $[La]_{av}$ showed an increase trend, and stabilized at 0.042 $mol \cdot L^{-1}$ for 0.2877 $mol \cdot L^{-1}$ EHEHPA, and 0.085 $mol \cdot L^{-1}$ for 0.5754 $mol \cdot L^{-1}$ EHEHPA. R stabilized at 6.8. Table 3 shows the $[Ce]_{av}$ and R with different $[Ce]_{ia}$ under different extraction conditions. $[Ce]_{av}$ increased as the initial aqueous phase pH increased, and also stabilized at 0.041 $mol \cdot L^{-1}$ for 0.2877 $mol \cdot L^{-1}$ EHEHPA, and 0.077 $mol \cdot L^{-1}$ for 0.5754 $mol \cdot L^{-1}$ EHEHPA. R stabilized at 7.6. The difference of stabilized R between La and Ce may be caused by the initial aqueous pH.

Table 1
Chemical sample details

Chemical name	Source	Purity (Mass fraction)	Grade
$LaCl_3 \cdot 7H_2O$	Biam Alloys Co., Ltd (Beijing, China)	0.9999	–
$CeCl_3 \cdot 7H_2O$	Biam Alloys Co., Ltd (Beijing, China)	0.9999	–
Sulphonated kerosene	Hubei Prosperity Galaxy Chemical Co., Ltd (Hubei, China)	0.99	Tech①
EHEHPA	Luoyang Aoda Chemical Co., Ltd (Henan, China)	0.93	Tech
NaOH powder	Beijing Chemical Reagent Factory (Beijing, China)	–	AR②
HCl	Beijing Chemical Reagent Factory (Beijing, China)	–	AR
Strong ammonia water	Beijing Chemical Reagent Factory (Beijing, China)	–	AR

① Technical grade.
② Analytical grade.

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