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Synergistic extraction study of samarium(III) from chloride medium by mixtures of bis(2,4,4-trimethylpentyl)phosphinic acid and 8-hydroxyquinoline

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ABSTRACT

The extraction behavior of samarium(III) with mixtures of bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272, H_2A_2) and 8-hydroxyquinoline (HQ) in heptane has been investigated from chloride medium. The mixtures are proved to have higher selectivity when applied to the extraction of the samarium compared with single extractant, the largest synergistic enhancement factor can be calculated to be 233 at pH 4.0. The results show that Sm^{3+} is extracted into heptane as $Sm(OH)_2Q(HA)_{2(o)}$ or $Sm(OH)_2Q(HQ)_4(HA)_{2(o)}$ with synergistic mixture. The equilibrium constants have been determined. The result shows that the synergistic extraction system not only shows perfect capacity of synergistic extraction, but also overcomes emulsification of 8-hydroxyquinoline.

1. Introduction

Synergistic extraction systems show promise in the field of solvent extraction. It can not only improve the extraction efficiency and improve the extraction selectivity but also enhance the stability of the extracted complexes, improve the solubility of the extracted complexes in the organic phase, eliminate emulsification and the formation of the third phase, and increase the extraction reaction rate [1]. Thus, there is a growing interest in development of new synergistic systems for effective separation of rare earths (REs). The investigations devoted to the synergistic extraction of lanthanides with mixtures of extractants including Cyanex272 are numerous [2–9]. Yuan et al. [3] have used the mixture of EHEH-PA and Cyanex272 to separate heavy lanthanides, but it needs very high stripping acidity, potentially bring environmental pollution. Sun et al. [4,5] have investigated the synergistic extraction of some trivalent REs from chloride medium using mixtures of Cyanex272 and CA100 or CA12. The synergistic effect of lanthanides and Y using mixture of Cyanex272 and 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 (HPMBP) from chloride solution has been reported in detail [6]. Xiong et al. [7] studied the synergistic extraction and separation of heavy lanthanide by mixtures of Cyanex272 and HEH/EHP in chloride media, it was found that $\beta_{z/z+1}$ (separation factor) of heavy RE(III) using the mixture of Cyanex272 and HEH/EHP as an extractant is higher than that obtained with only HEH/EHP as the extractant. Freiser et al. and Saleh et al. reported the synergistic extraction of tervalent lanthanides by Cyanex272 combined with TOPO, CMPO, or MBDPO [8,9].

8-Hydroxyquinoline (HQ), which contains a nitrogen atom and an oxygen atom, and a lot of electrons exist in this molecule, is a widely applied chelate agent in analytical chemistry due to its metal-complex ability. The extraction of metals 8-hydroxyquinoline complex has been reported by several authors [10–12]. However, at present, quantitative data on the extraction or synergistic extraction of lanthanide elements are very scarce [10]. The present work is aimed for studying the solvent extraction Sm^{3+} by using Cyanex272 and HQ. The choice of this mixed extractant system is based essentially on Cyanex272, which has a high selectivity, high separation factors of rare earth ions, and a low aqueous acidity in extraction and stripping. However, the organic phase caused an increase in viscosity, and low extraction efficiency when Cyanex272 is used. In order to prevent the problems, one of the most effective methods is to modify organic phase by introducing one adduct into Cyanex272. In addition, although impurities that Cyanex272 contains may influence the extraction synergism [13,14], Cyanex272 is used without purification in this paper in order to combine with the practicality of production. The experimental results suggest synergistic extraction not only shows perfect capacity of synergistic extraction, but also overcomes emulsification of 8-hydroxyquinolin.

2. Experimental

2.1. Reagents and apparatus

Cyanex272 was kindly supplied by CYTEC Canada Inc. 8-Hydroxyquinoline was obtained from Aldrich and used without

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further purification. All extractants were used as received. The extractants were dissolved in heptane to the required concentration. Stock solutions of samarium(III) were prepared by dissolving its oxide with a purity 99.9% in hydrochloric acid and diluting with distilled water. All other reagents employed in this work were of analytical grade.

2.2. Extraction procedures

Distribution data of solutes were determined by mixing 5 mL of the organic phase and 5 mL of the aqueous phase and mechanically shaken at 25 ± 1 °C for 60 min. The concentration of metal ions in the aqueous phase after equilibration was determined spectrophotometrically using the RE(III)–Arsenazo III complex after dilution and that of in the organic phase was determined by difference. NaCl ($\mu = 0.1\ \mathrm{mol\,L^{-1}}$) was used to maintain constant ionic strength. A PHS-3 digital pH meter (Shanghai Rex Instrument Factory) was used for pH measurements. All the experimental work was carried out in duplicate and the average result was presented. Distribution ratios (D) were calculated from these concentrations, $D = [\mathrm{RE}]_{(o)}/[\mathrm{RE}]_{(a)}$.

3. Results and discussions

3.1. Extraction of Sm(III) with Cyanex272 and HQ, respectively

The solvent extraction of Sm^{3+} by Cyanex272 was studied earlier [15]. The extraction equilibrium is expressed as follows:

$$\mathrm{Sm}^{3+}_{(a)} + 3(\mathrm{HA})_{2(o)} \overset{k_{AQ}}{\Longleftrightarrow} \mathrm{Sm(HA_2)}_{3(o)} + 3\mathrm{H}^{+}_{(a)} \quad (1)$$

where $(HA)_2$ represent Cyanex272. ‘a’ denotes aqueous phase and ‘o’ denotes organic phase.

For elucidating the extraction mechanism with HQ alone, the conventional slope analysis method has been introduced. As shown in Fig. 1, the plot of $\log D$ versus pH at constant extractant concentration gives a straight line with a slope of about 0.89, that is $b = 0.89$–1.0, which can be seen that the transfer of a rare earth ion is accompanied by release of one hydrogen ions under these conditions. In addition, the influence of extractant concentration on the extraction is investigated, too. The plot of $\log D$ versus $\log[H_2A_2]$ at fixed aqueous concentrations gives a straight line with a slope of about 2.0 (Fig. 2). The extraction reaction do not changed with the content of the chloride ion concentration. Taking into account that the rare earths are easily hydrolyzed, the possible reason which release 1.0 hydrogen ions may be that hydroxide ion may take part in the extraction reaction [16]. Thus, the extraction equations for the extraction of Sm(III) with HQ can be written as:

$$[\mathrm{Sm(OH)}_2^{+}]_{(a)} + 2(\mathrm{HQ})_{(o)} \Longleftrightarrow [\mathrm{Sm(OH)}_2]\mathrm{Q(HQ)}_{(o)} + \mathrm{H}^{+} \quad (2)$$

3.2. Synergistic extraction of Sm(III) with mixtures of Cyanex272 and HQ

In order to gain insight into the synergistic effect of Sm^{3+} observed with mixtures of Cyanex272 and HQ, transformation of mole fraction of Cyanex272 ($X_{\mathrm{Cyanex272}}$) experiment has been performed with continuous variation method, in the extraction system changing with different mole fraction of Cyanex272 in the total fixed 0.04 mol/L Cyanex272 and HQ. The distribution ratios of Sm^{3+} in the mixing system change with changing mole fraction of Cyanex272. The synergistic effect for Sm^{3+} can be seen clearly (Fig. 3). According to Xu et al.’s theory [17], the synergistic enhancement coefficient R, ($R = D_{\mathrm{mix}}/(D_{\mathrm{Cyanex272}} + D_{\mathrm{HQ}})$) is calculated, which is used to evaluate whether a mixing system has synergistic extraction effect or not. The Table 1 gives the variation of R with different ratio of Cyanex272 and HQ. The largest synergistic coefficient of Sm(III) is obtained at the mole fraction $X_{\mathrm{Cyanex272}} = 0.5$ and the maximum value of R obtained at 233 and the obvious synergistic effect can be seen. The following extraction experiments are measured at a ratio of Cyanex272 to HQ of 1 to 1 in order to maintain synergistic effect. Thus, according to charge balance, the synergistic extraction reaction of Sm^{3+} from sulfuric acid medium with mixture of Cyanex272 + HQ can be expressed as following:

$$\mathrm{Sm}^{3+}_{(a)} + x(\mathrm{HA})_{2(o)} + y\mathrm{HQ}_{(o)} \overset{k_{12}}{\Longleftrightarrow} \mathrm{SmH}_{(2x+y-i)}\mathrm{A}_{2x}\mathrm{Q}_{y(o)} + i\mathrm{H}^{+}_{(a)} \quad (3)$$

where x and y represent unknown coefficients, then the equilibrium constant (k_{12}) and the distribution ratio (D_{12}) of the synergistic extraction system should be:

$$D_{12} = D_{\mathrm{mix}} - D_1 - D_2 = \frac{\mathrm{SmH}_{(2x+y-i)}\mathrm{A}_{2x}\mathrm{Q}_{y(o)}}{[\mathrm{Sm}^{3+}]_{(a)}} \quad (4)$$

Taking logarithms:

$$\log D_{12} = \log k_{12} + i\mathrm{pH(a)} + x\log[\mathrm{HA}]2(\mathrm{o}) + y\log[\mathrm{HQ}](\mathrm{o}) \quad (5)$$

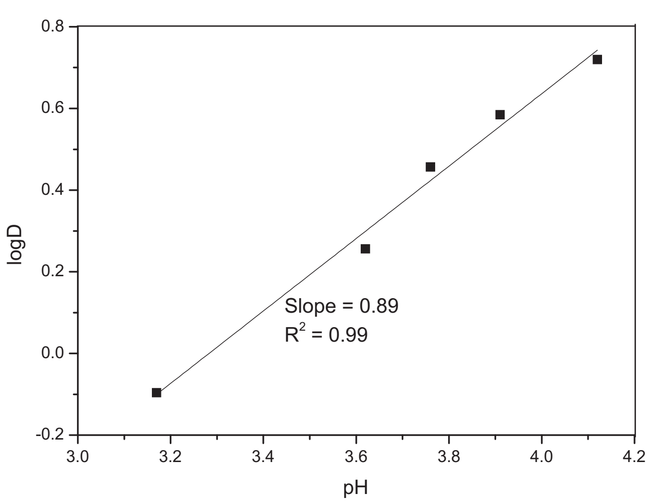

Fig. 1. Relationship between distribution ratio D and pH with HQ. $[\mathrm{HQ}] = 4.0 \times 10^{-2}$ mol/L, $[\mathrm{Sm^{3+}}] = 5.56 \times 10^{-4}$ mol/L; $\mu = 0.1$ mol/L.

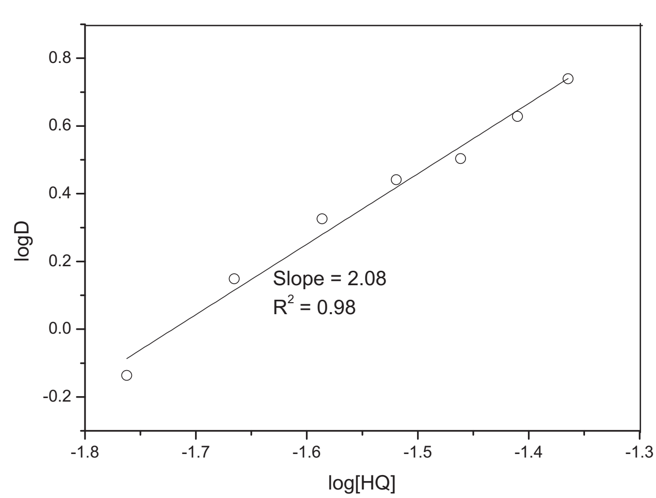

Fig. 2. Relationship between distribution ratio D and equilibrium concentration of extractant. $[\mathrm{Sm^{3+}}] = 5.56 \times 10^{-4}$mol/L; $\mu = 0.1$ mol/L; pH = 4.0.