

## MATLAB simulation of preparation of Sm-loaded extractant directly from HEH(EHP)

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**Abstract:** Computer simulation of the preparation process loading rare earth (RE) directly from acidic extractant and RE chloride was established using MATLAB software. The mechanism of the extraction reaction was assumed, and then an experiment was conducted to confirm the mechanism and the apparent equilibrium constant of the reaction was determined as well. Owing to the involvement of H<sup>+</sup> ion in the reaction between acidic extractant and RE chloride, the computer simulation of the process was more complicated than that of the extraction only between different rare earths. In the present work, MATLAB software was therefore introduced to handle the resolution of the complicated processing equation, and the simulation was performed by varying some key parameters including feed composition and phase ratio, etc. Consequently this work presented a simple method to simulate the H<sup>+</sup> ion involved countercurrent extraction process of rare earths and also provided the practical references for the relative process designing.

**Keywords:** rare earths; saponification; MATLAB; simulation

The acidic extractants used in rare earth (RE) countercurrent extraction processing are generally saponified by a certain base (NaOH or NH<sub>3</sub>·H<sub>2</sub>O). However all the base saponification processes cause raffinate emission with salt which is strictly controlled by Chinese Department of the Environment<sup>[1-4]</sup>, hence the saponification directly using RECl<sub>3</sub> as well as recycling resultant acid may be of great potential in the future. The conventional RE saponification reacts according to the exchange between RE<sup>3+</sup> and Na<sup>+</sup> or NH<sub>4</sub><sup>+</sup>, therefore the process of extraction and separation can be assumed to have a constant mixed extraction ratio, and some numerical methods<sup>[5-8]</sup> have been developed to deal with its simulation and parameter optimization. In contrast for the direct RE saponification by mixing fresh acidic extractant with RE chloride solution, RE ion will be loaded to the extractant along with H<sup>+</sup> ion released to the aqueous phase, which leads to a variable mixed extraction ratio, as a result calculation of the process based on its mass balance and reaction equilibrium shall be more complicated because it is necessary to solve a higher equation.

Computer is helping chemists more and more on data processing and simulation, however some advanced languages such as FORTRAN, PASCAL, C++ are usually used and programming is a complicated work with

higher theoretical level and stronger experience. MATLAB with concise language and rich pre-incorporated functional resources has become a big numerical calculation and graphic image processing software tool since developed in 1982 by MathWorks<sup>[9]</sup>. MATLAB is widely used in academic and research institutes as well as industrial enterprises abroad<sup>[10-14]</sup>, but has not attracted enough attention by chemists in China and few applications to simulation of countercurrent extraction processing were reported<sup>[15]</sup>. In the present work MATLAB was introduced to simulate the extraction process of samarium chloride and HEH(EHP) (popularly called as and hereafter denoted by P507) and to investigate the feasibility and optimization of base-free saponification.

## 1 Experimental

### 1.1 Reagents and apparatus

Both of P507 (industrial grade) and kerosene (industrial grade) were obtained from Tianjin Beichen Chemical Plant (China). Samarium oxide with the purity of 99.5% was provided by Dingnan Dahua Advanced Material Resources Co., Ltd.. EDTA and hydrochloride acid were reagents of A.R. grade. A pH meter produced by

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Mettler-Toledo Instruments (Shanghai) Co., Ltd. was used to measure acidity of the aqueous phase.

### 1.2 Measurement

The content of samarium was determined by complexometric titration with EDTA using xylenol orange-bromocresol green mixed indicator at pH of about 5.5, and that of H<sup>+</sup> ion in the aqueous phase was measured by a pH meter.

### 1.3 Determination of apparent equilibrium constant

Fresh P507 was mixed with kerosene at a volumetric ratio of 1:1. Samarium chloride was prepared by treating the samarium oxide with a slightly excess amount of hydrochloric acid, and titrated with EDTA to exactly determine the concentration of samarium.

Five aqueous feed solutions with the same samarium content, the same volume of 25 ml and variable acidities were equilibrated with 30 ml organic phases respectively in separate funnels by shaking the two phases vigorously for 15 min, then the funnels were allowed to remain undisturbed for 2 h before the phases were separated and the analysis begun. The samarium contents in the final aqueous phases and the organic phases after back-extraction were determined by titration with EDTA. The H<sup>+</sup> concentrations of the final aqueous phases were measured by a pH meter. All equilibrium data were obtained at a temperature of 25±1 °C.

## 2 Modeling and programming

### 2.1 Modeling of H<sup>+</sup>-involved extraction equilibrium

Usually P507 prefers to form dimer molecules in kerosene, thus can be expressed by H<sub>2</sub>A<sub>2</sub>. And there is little complex of Cl<sup>-</sup> ion lower than 8 mol/L with RE<sup>3+</sup> ion because of a weak complexation between RE<sup>3+</sup> and Cl<sup>-</sup> [7], therefore in the case of mixing RE chloride solution with P507 in kerosene, it can be considered that Cl<sup>-</sup> is not involved in the extraction reaction and the extraction reaction could be assumed to occur according to the following equation [8,16,17]:



in which the upper line denotes the species in organic phase, otherwise those without upper line exist in aqueous phase. And if the activity coefficients of all the species in Eq. (1) can be assumed to be constant, the extractant equilibrium constant (*K*) of the reaction (Eq. (1)) can

be expressed by:

$$K = \frac{\overline{[\text{RE}(\text{HA}_2)_3]} \times [\text{H}^+]^3}{[\text{RE}^{3+}] \times [\text{H}_2\text{A}_2]^3} \quad (2)$$

The items of the above equation should be the concentrations when the extraction reaction reaches an equilibrium state. *K* represents the apparent equilibrium constant on the basis of factors such as activity coefficients, and its value can be determined by experiment.

With respect to a countercurrent extraction process of RE chloride by fresh P507 in a cascade with a total stage number of *n* as illustrated in Fig. 1, P507 enters and raffinate discharges in the head (i.e. the 1<sup>st</sup> stage) while the RE-loaded extractant is obtained and RE solution is fed in the tail (i.e. the *n*<sup>th</sup> stage). The case of the *i*<sup>th</sup> stage shown in the figure is considered as a representative to create an equilibrium model, where the content with subscript *i* is used to denote those of the species in the aqueous phase entering the *i*<sup>th</sup> stage and also to denote those of the species in the organic phase flowing out from the *i*<sup>th</sup> stage and so on.

The extraction relation equilibrium of the species in the *i*<sup>th</sup> stage can be expressed as:

$$K = \frac{\overline{[\text{RE}(\text{HA}_2)_3]}_i \times [\text{H}^+]_{i-1}^3}{[\text{RE}^{3+}]_{i-1} \times [\text{H}_2\text{A}_2]_i^3} \quad (3)$$

If the increment of RE loading resulted in the *i*<sup>th</sup> stage by ion exchange reaction is set to be *x* at mol/L, then

$$\overline{[\text{RE}(\text{HA}_2)_3]}_i = \overline{[\text{RE}(\text{HA}_2)_3]}_{i-1} + x \quad (4)$$

$$[\text{H}^+]_{i-1} = [\text{H}^+]_i + 3rx \quad (5)$$

where *r* is the phase ratio which is defined as volumetric ratio of the organic phase to the aqueous phase. Combining Eqs. (4) and (5) together with Eq. (3), we obtain:

$$K = \frac{\overline{[\text{RE}(\text{HA}_2)_3]}_i \times ([\text{H}^+]_i + 3rx)^3}{([\text{RE}^{3+}]_i - rx) \times [\text{H}_2\text{A}_2]_i^3} \quad (6)$$

If

$$a = \frac{K[\text{H}_2\text{A}_2]_i^3}{\overline{[\text{RE}(\text{HA}_2)_3]}_i} \quad (7)$$

a cubic equation involving *x* can then be deduced as below:

$$27r^3x^3 + 27[\text{H}^+]_i r^2x^2 + (9r[\text{H}^+]_i^2 + ra)x +$$

$$([\text{H}^+]_i^3 - a[\text{RE}^{3+}]_i) = 0$$

Therefore if  $\overline{[\text{RE}(\text{HA}_2)_3]}_i$ ,  $[\text{H}_2\text{A}_2]_i$ ,  $[\text{H}^+]_i$ ,  $[\text{RE}^{3+}]_i$ ,

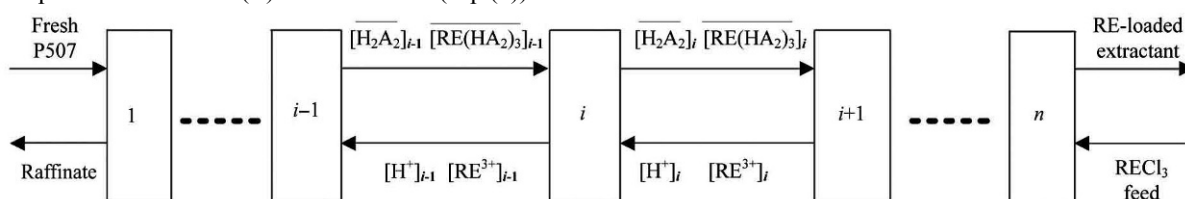


Fig. 1 Schematic flow of a countercurrent extraction cascade

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