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Kinetic model of actinides and lanthanides extraction in non-stationary conditions

M.A. Afonin*, A.A. Kopyrin, A.A. Fomichev

Saint-Petersburg Institute of Technology, 26 Moskovsky av., 190013 Saint-Petersburg, Russia

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Abstract

The influence of periodical oscillations of the temperature on extraction and stripping processes in the extraction systems is studied. Three extraction systems with tri-*n*-butyl phosphate (TBP) were investigated: No. 1, 6 M $NaNO_3$–$Nd(NO_3)_3$–$Pr(NO_3)_3$–TBP–kerosene; No. 2, $[Nd(NO_3)_3{\cdot}3TBP]$–$[Pr(NO_3)_3{\cdot}3TBP]$–kerosene–0.1 M HNO_3; No. 3, $NaNO_3$–$Nd(NO_3)_3$–$Pr(NO_3)_3$–TBP–kerosene–0.1 M HNO_3. Mathematical model of the non-stationary membrane extraction is enhanced including the dependence of extraction rate constants on temperature. The values of activation energy for direct and reverse reactions of extraction and stripping reactions of Pr and Nd were calculated. The mathematical model describes experimental data adequately. The optimal conditions of separation by liquid membrane were found.

Keywords: Rare earth alloys and compounds; Kinetics; Computer simulations

1. Introduction

Separation of similar elements in none steady state conditions are a prospective method to increase elements separation factor. Realisation of the process in non-stationary non-equilibrium conditions using phenomena of oscillating extraction allows the exploitation of differences in kinetics of ion complexation and extraction rates, using their transport through the boundary area in both directions for elements separation [1]. One of the possible procedures to deviate extraction system from equilibrium is oscillatory changing of the temperature of the extractors. However, the influence of oscillatory temperature changing in the extractor(s) is not described in the literature.

2. Experimental

The setup flow sheet (Fig. 1) is described as follows: the emulsion is pumped from thermostatic extractors 16 and 17 to centrifugal separators 5 and 6 through the turbidimeters 11 and 12 by peristaltic pump 10. After separation from the separator 5, the organic phase flows to the extractor 17 and from the separator 6 the organic phase flows to spectrophotometer 8 for analysis and it flows to the extractor 16, passing through both aqueous phases organic phase forms bulk liquid membrane. After spectrophotometers 7 and 9 the aqueous phases come back to their corresponding extractors. Data acquisition of pH, red/ox potential of the aqua phase, temperature and emulsion turbidity are performed with frequency above 1 Hz using the DAQ board in computer 18 and specially designed software. Diode-array spectrophotometers are used to obtain spectra every 6–15 s. By deconvolution of each spectrum, using specially designed software concentration of several elements can be obtained.

3. Mathematical model

As the basis of mathematical model of non-equilibrium extraction of actinides and lanthanides the skeletal mechanism of Field-Kõrös-Noyes (FKN) is used, known as Oregonator [2]. To use the classical model FKN to describe the metal extraction, we added the reactions R1–R10 to the model. It is supposed the first order reaction for all extraction rate constants:

$$Ce^{4+} + 4(NO_3{}^-) + 2TBP \rightleftarrows Ce(NO_3)_4{\cdot}2TBP \qquad (R1\text{–}R2)$$

$$Ce^{3+} + 3(NO_3{}^-) + 3TBP \rightleftarrows Ce(NO_3)_3{\cdot}3TBP \qquad (R3\text{–}R4)$$

$$Nd^{3+} + 3(NO_3{}^-) + 3TBP \rightleftarrows Nd(NO_3)_3{\cdot}3TBP \qquad (R5\text{–}R6)$$

$$Pr^{3+} + 3(NO_3{}^-) + 3TBP \rightleftarrows Pr(NO_3)_3{\cdot}3TBP \qquad (R7\text{–}R8)$$

$$UO_2{}^{2+} + 2(NO_3{}^-) + 2TBP \rightleftarrows UO_2(NO_3)_2{\cdot}2TBP \qquad (R9\text{–}R10)$$

Existing equation system of mathematical model was extended with dependence of extraction rate constant on temperature-

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* Corresponding author. Tel.: +7 8123627813; fax: +7 8127127791.
E-mail address: afonin1@lti-gti.ru (M.A. Afonin).

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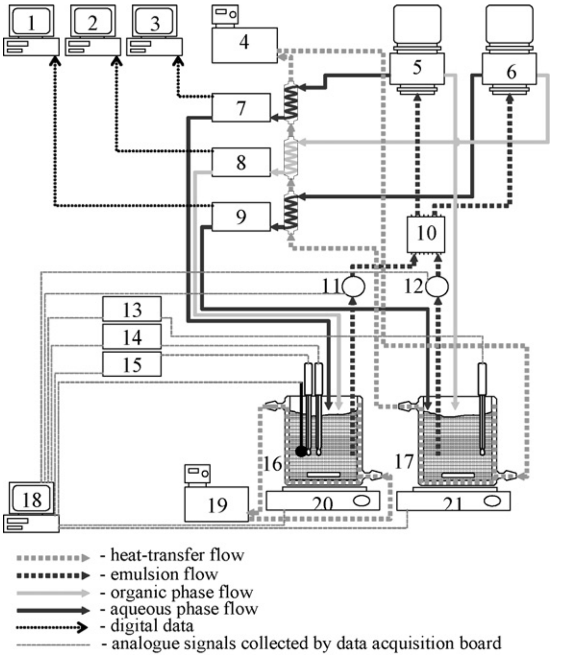

Fig. 1. Experimental setup: 1–3 and 18, computers; 4 and 19, thermostats; 5 and 6, centrifugal separators EC-33 NIKIMT; 7–9, spectrophotometers SF 2000 OKB Spectrum; 10, peristaltic pump; 11 and 12, turbidimeters; 13, pH-meter; 14 and 15, potentiometers; 16 and 17, extractors; 20 and 21, magnetic stirrers.

Arrhenius equation $k = k_0\, e^{-E_a/RT}$ or modified Arrhenius equation $k = BT^n\, e^{-E_a/RT}$.

4. Results and discussion

Dependence of rate constants of extraction on temperature according to Arrhenius equation has been included into existing mathematical model of none stationary membrane extraction. The values of activation energy and Arrhenius pre-exponential factor for the rate constants of extraction and stripping reactions of Pr and Nd were calculated from experimental temporal dependencies of metal concentration and temperature by solving reverse kinetics problem using proposed mathematical model and software package. The difference between the activation energy of extraction and the activation energy of stripping of Pr, and Nd from 6 mol/l $NaNO_3$ by TBP in the temperature range of 293–308 K were -25 ± 3 and -30 ± 3 kJ/mol, respectively. The rate constants of Pr and Nd extraction and stripping in 6 M $NaNO_3$ and 0.1 M HNO_3 were also calculated.

The series of experiments with influence of periodical oscillations of the temperature on the extraction system for separation of rare earth elements using bulk liquid membrane between two extractors are performed. The mathematical model describes experimental data adequately (Fig. 2).

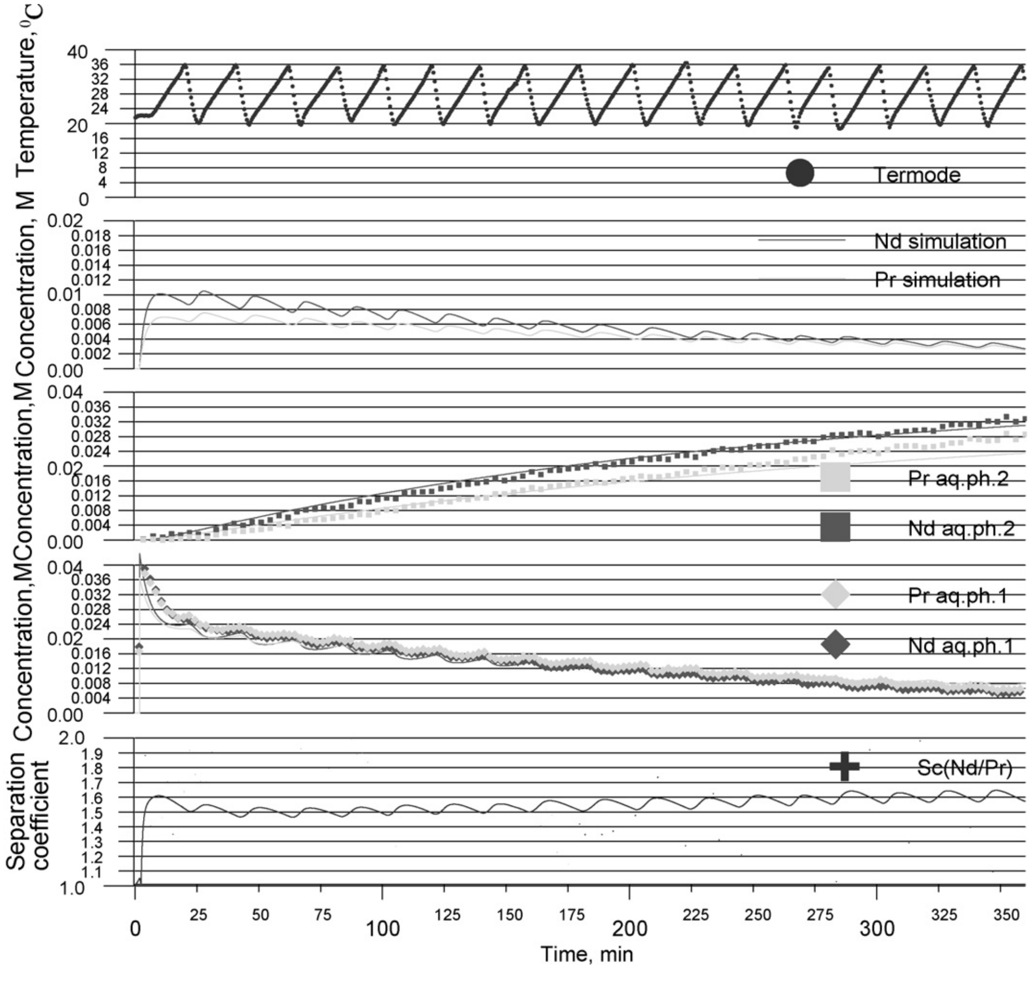

Fig. 2. Experimental data and mathematical simulation of extraction system behaviour under periodical temperature oscillations.

The parameters of modified Arrhenius equation for the system $Nd(NO_3)_3$–$Pr(NO_3)_3$–6 M $NaNO_3$–H_2O–0.7 M TBP–kerosene were estimated by solving reverse kinetics problem from the temporal dependence of the metal concentrations in aqueous and organic phases at temperature $T = 293$, 298, 303, and 308 K:

$$\frac{\vec{k}_{Pr}}{\overleftarrow{k}_{Pr}} = 1.88 \times 10^{-7} T^{9.03\times 10^{-1}} \mathrm{e}^{-25\,\mathrm{kJ}/RT},$$

$$\frac{\vec{k}_{\mathrm{Nd}}}{\overleftarrow{k}_{\mathrm{Nd}}} = 4.45 \times 10^{-6} T^{4.83\times 10^{-2}} \mathrm{e}^{-30\,\mathrm{kJ}/RT}$$

The following rate constants of Pr and Nd extraction in the system 0.1 M HNO_3–H_2O–0.7 M TBP–$Nd(NO_3)_3\cdot 3TBP$–$Pr(NO_3)_3\cdot 3TBP$ were estimated by solving reverse kinetics problem from the temporal dependence of the metal concentrations in aqueous and organic phases at constant temperature $T = 293.15$ K:

$$\vec{k}_{Pr} = (2.5 \pm 0.3) \times 10^{-5}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1},$$

$$\overleftarrow{k}_{Pr} = (1.8 \pm 0.2) \times 10^{-4}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1},$$

$$\vec{k}_{\mathrm{Nd}} = (2.2 \pm 0.2) \times 10^{-5}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1},$$

$$\overleftarrow{k}_{\mathrm{Nd}} = (2.0 \pm 0.2) \times 10^{-4}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$$

On the basis of the extraction and stripping rate constants and corresponding activation energies, the optimization of the extraction process of separation of rare earth elements by liquid membrane under the influence of periodical oscillation of the temperature is carried out. The optimal conditions of separation by liquid membrane were found: frequency and amplitude of thermal oscillations, effective boundary area and liquid membrane flow rate.

Acknowledgements

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