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Reactive extraction of europium(III) and neodymium(III) by carboxylic acid modified calixarene derivatives: Equilibrium, thermodynamics and kinetics

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ABSTRACT

In this paper, extraction behaviors of different carboxylic acid modified calixarenes towards Eu(III) and Nd(III) were performed. These extractants were extensively evaluated for the extraction abilities for extraction of Eu(III) and Nd(III) under different conditions, including pH, concentration of extractants and temperature. Carboxylic acid modified calix[6]arene (extractant-**2**) showed remarkably high extraction ability for Eu(III) and Nd(III). The thermodynamic parameters (enthalpy, entropy and Gibbs free energy) were determined. The extraction of Eu(III) with extractant-**2** occurred with a cation exchange reaction and this extraction reaction is an exothermic process. Kinetic studies of reactive extraction of Eu(III) with extractant-**2** were performed in a stirred cell. The value of mass-transfer coefficient of Eu (III) in chloroform was evaluated to be 3.35×10^{-6} m s^{-1}. The Hatta number was calculated and observed to vary in the range of 3.80×10^{-4}–9.10×10^{-4}. The effects of stirring speed, the phase volume ratio and species concentration on the initial extraction rate and Hatta number, demonstrate that the reaction is a very slow chemical reaction process occurring at the bulk of the organic phase. The rate constants of forward and backward reactions were determined to be 3.05×10^{-2} (kmol m^{-3})$^{-0.64}$ s^{-1} and 1.55×10^{-3} (kmol m^{-3})$^{-2.64}$ s^{-1}, respectively.

1. Introduction

To satisfy demand for more energy, numerous nuclear power plants have been built recently. As a result, large amount of nuclear waste has been generated. For a sustainable solution to global energy shortage, reprocessing of the nuclear wastewater is indispensable in the whole nuclear industry. In addition, the disclosure accidents of nuclear power plants in some part of the world resulted in water resource contamination and caused global concern [1]. It is a great challenge to extract key nuclides from either the contaminated water due to the disclosure of nuclear power plant or generated wastewater in the mining and refining processes efficiently for reduction the potential risk to environment and human health.

In view of the particularity of wastewater, the liquid-liquid extraction method is suitable for recovery of the key metals from aqueous solution in nuclear industry. Based on the industrial values and hazards of the nuclides, the selectivity of suitable extractant, which can extract the target nuclides from aqueous solution efficiently, has become an important research topic. Calixarenes, as the third generation of supramolecules after cyclodextrins and crownethers, have attracted much attention in the field of coordination chemistry and separation science [2–4]. They are known for their excellent physical and chemical properties such as low toxicities, high thermal and irradiation stabilities, and chemical modifiability [5]. Due to the enhanced binding and selectivity abilities, they have a potential to become excellent extractants towards different cations by changing the bridging atoms, altering the size of cavity, and substituting the upper/lower groups into the functional groups, namely, ester, amine, amide and etc. [6–8]. In addition, the extracting properties towards cations should be based on the hard and soft acids and bases theory (HSAB theory), extractants with hard donor atoms favor hard cations and the soft binding extractants prefer soft cations [9].

However, most of the extraction studies with calixarene derivatives, which exhibit excellent extractive performances, were carried out by picrate extraction method [10,11]. In this method,

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the highly organosoluble picrate ion can easily transport into an organic phase to maintain the electroneutrality of the complex and enhance the extracting efficiency. Nevertheless, the picrate method is not suitable for the application in the nuclear industry because most anions are highly hydrophilic in the wastewater. It is very difficult to force the anions to transfer from aqueous phase into organic phase. This situation will limit the extraction efficiency of non-proton-ionizable solvent extraction reagents towards polyvalent metal ions in the liquid-liquid extraction process [11]. To solve this problem, it is necessary to make proton-ionizable solvent extraction reagents act as cation exchanger liquid [12]. Some researchers have found that introduction of proton-ionizable group, such as carboxyl groups, can enhance the cations extractability efficiently [13,14]. Carboxylic acid modified calixarenes have excellent extraction ability to bind the key cations from contaminated water.

To date, the extraction capabilities of calixarenes modified by carboxylic acid towards strontium, plumbum and other metal ions using liquid-liquid extraction method have been reported [7,11,15,16]. The extraction experiments were all carried out with batch method. And the organic phase was mixed with inorganic phase by shaking in vessels for a certain period of time to reach the extraction equilibrium state in the extraction process. This extraction operation can supply enough extraction data to acquire the parameters about equilibrium isotherms and evaluate the extraction capacity of the extractant at different conditions such as pH, shaking time, temperature, and concentration of metal ions, conveniently [17,18]. However, kinetics of liquid-liquid extraction is also an important parameter for industrial application, but the equilibrium state cannot give the information about the rate of reaction or mass transfer process from one phase to the other [19]. The batch method is not convenient to study the kinetic effects and mass-transfer parameters for the extraction system. There are few reports on the study of extraction kinetics and mass-transfer process about calixarene. Hence, it is necessary to design an extraction process to gather data on the kinetics and mass-transfer of extraction system. In order to obtain the mass transfer characteristics and intrinsic kinetic from a rational extraction equipment, the extraction cell is an appropriate choice for the kinetics of liquid-liquid extraction process [19].

Because Europium (Eu) is similar to the elements of long-lived trivalent actinides, such as Am(III) and Cm(III), on physicochemical properties and comparable environmental behaviors, it is always used as a chemical analogue element for studying the properties of long-lived trivalent actinides [20]. Neodymium (Nd), which is representative of all of the most valuable rare earths (REs), can be selected for research of its behavior in the extraction process in order to investigate the recovery of rare earths from liquid waste [21]. Extraction of Eu(III) and Nd(III) from waste aqueous solution can help to complement the recycle of valuable metals from primary mining and refining processes and simplify the problem of water pollution from nuclear industry [22].

Based on the previous studies [15,23,24], four different carboxylic acid modified calixarene derivatives (compounds **1**–**4**) in Scheme 1 were selected to evaluate their extraction capacities towards radionuclides Eu(III) and Nd(III) from aqueous solution. The liquid-liquid extraction experiments were carried out using batch method for equilibrium and extraction cell for kinetics, respectively. The extraction efficiencies of Eu(III) and Nd(III) were investigated as functions of pH, concentrations of extractants and temperature. The extraction kinetics and thermodynamic parameters (the changes in entropy and enthalpy) of Eu(III) were determined. Besides, the mass transfer extraction behaviors in the influences of stirring rate, phase volume ratio and so on in the extraction cell were discussed.

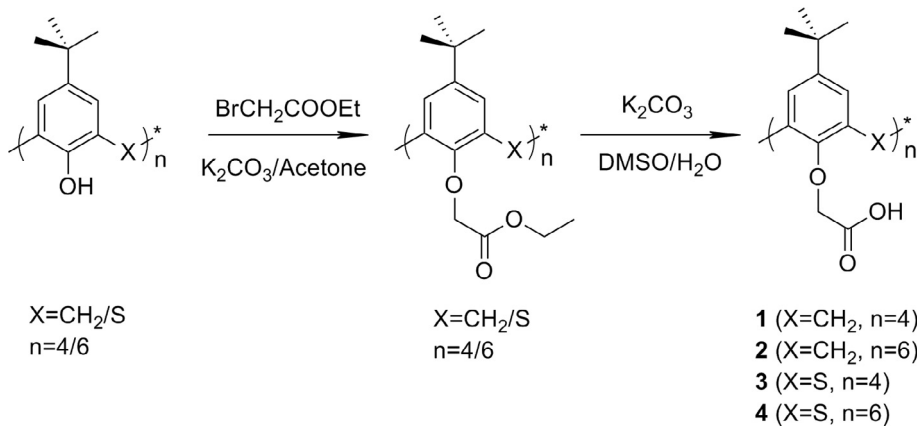
2. Experimental section

2.1. Materials and methods

Sodium hydroxide (NaOH), hydrochloric and nitric acids (HCl and HNO_3) were used to adjust pH of the solution. The alkali, acid and all reagents were purchased from Beijing chemical works, Beijing, China. All metal nitrates were purchased from Aladdin Co. Ltd., Beijing, China. All chemicals purchased from commercial sources were of analytical grade and used without further purification unless mentioned otherwise. Deionized water from a milli-Q plus water purification system (Millipore) was used in all experiments. An IS128 pH meter was used to measure the adjusted pH. The concentrations of metal ions were analyzed by microwave plasma-atomic emission spectroscopy (MP-AES). The synthesis of the compounds **1**–**2** [23], **3** [25], and **4** [26] were in accordance with previous literatures.

2.2. Equilibrium

The organic solution (different concentrations of extractant ranging from about 0.005 mM to 0.1 mM) was prepared by diluting extractant into chloroform to the desired concentration. Metal nitrate solutions (initial metal-ion concentration was about 0.05 mM) were prepared by dissolving the designed weights of the nitrates in nitric acid solutions. Deionized water was used for preparation of nitrate solutions. The desired pH was achieved by injecting negligible volumes of HNO_3 or NaOH. The extraction



Scheme 1. Synthesis of the four calixarene carboxylic acid derivatives.