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Extraction of neodymium from nitric acid feed solutions using an emulsion liquid membrane containing TOPO and DNPPA as the carrier extractants

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ABSTRACT

The transport of Nd(III) from nitric acid medium across emulsion liquid membrane (ELM) using di-nonyl phenyl phosphoric acid (DNPPA) as the carrier extractant and Span 80 (sorbitol monoleate) as the surfactant in Petrofin as the diluent and sulphuric acid as the internal phase has been systematically investigated. The effect of different physical and chemical parameters such as stirring speed, neodymium concentration, external phase nitric acid concentration, extractant concentration, external to internal phase volume ratio, stripping agent concentration has been investigated on the extraction of Nd(III). The synergistic extraction of the metal ion has also been studied using mixtures of DNPPA and tri-*n*-octylphenyl phosphine oxide (TOPO) as the carrier extractants in the ELM. Quantitative extraction (>97%) of Nd(III) was observed with 0.3 M DNPPA + 0.13 M TOPO and 1% (v/v) Span 80 liquid membrane at external to internal phase volume ratio of 10 for a feed having 500 mg/L Nd(III) at 0.5 M nitric acid concentration. The mechanism of extraction of Nd(III) has also been discussed in the light of the results obtained.

1. Introduction

The rare earth elements (REE) represent a group of 17 elements including 15 lanthanides, plus yttrium and scandium. All these elements have unique physicochemical properties, which make them essential for various applications, from batteries in hybrid cars and phosphors for illuminated screens of electronic devices to permanent magnets used in computer hard drives and wind turbines (Golev et al., 2014). High purity rare earth oxides, metals and alloys have been increasingly used in the field of chemical engineering, metallurgy, nuclear energy, optical, magnetic, luminescence and laser materials, superconductors, etc. Out of the rare earth oxides, importance of neodymium has dramatically increased since the development of a neodymium–iron–boron (Nd–Fe–B) permanent magnet (Sugimoto, 2001). Solvent extraction and ion exchange are employed to separate and purify REEs on an industrial scale for production of Nd (Banda et al., 2015; Wang et al., 2011). However, solvent extraction processes have many operational difficulties such as large inventory of extractants, loss of solvent due to the organic solubility in aqueous solutions, volatilization of diluents etc. Membrane processes, especially those involving liquid membranes, are gaining importance and are emerging as a viable alternative to above conventional separation processes (Bartsch et al., 1996; Kocherginsky et al., 2007; Mohapatra and Manchanda, 2003). The growing interest in membrane processes can be attributed towards its simplicity, requirement of small quantities of extractant and low energy consumption. One of the promising methods of liquid membrane processes is Emulsion Liquid Membrane (ELM)

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to recover metal ions such as uranium, rare earth from lean solutions (Kulkarni et al., 2002; Lee et al., 1994).

ELM process is a separation process which offers three advantages over solvent extraction: (a) high interfacial surface area for mass transfer, especially at the inner oil–water interphase, due to the small size of the aqueous phase droplets, (b) high diffusion rate of the metal ion through the membrane, and (c) simultaneous extraction (at the outer interphase) and stripping (at the inner interphase) in the same system (Frankenfield and Li, 1987). ELM contains three-phase dispersion system; the innermost phase is usually an aqueous phase (strippant solution), the intermediate phase is a membrane phase containing the organic extractant in a suitable diluent along with a surfactant to stabilize the emulsion droplet and the outer phase is aqueous feed solution (Prashant and Vijaykumar, 2002). The feed is often referred to as the external phase while the strippant solution is termed as the internal phase. The metal ion present in the feed solution forms a complex with the extractant at the interface of the emulsion globule and the external phase. The complex formed is transported through the membrane phase to the membrane phase-stripping phase interface from where it is stripped into the internal phase. Selectivity for the desired species is often enhanced by incorporating suitable carriers in the membrane.

The most widely used extractants for separating REE are organophosphorous acids due to their solvation properties as well as their chemical stability and low aqueous solubilities. Acidic organophosphorous extractants, such as 2-ethylhexyl 2-ethyhexylphosphonic acid (EHEHPA), di-2-ethyl hexyl phosphoric acid (D2EHPA) are widely used for the extraction and separation of rare earths (Sato, 1989; Thakur et al., 1993). However, even with the above extractants, separation and purification into individual REE is still known to be difficult due to their similar chemical and physical properties. Therefore, there is a growing interest in the development of new extractants for the separation of rare earths. Recently, dinonylnaphthalene phosphoric acid (DNNPA) was evaluated as an alternative extractant for REE extraction form chloride medium in our laboratory (Anitha et al., 2014). DNPPA is stronger cationic extractant compared to its homologues D2EHPA and EHEHPA. However, metal ion extraction at higher acidities was feasible in the case of DNPPA owing to its higher pK_a value. Singh et al., have reported the recovery of yttrium from phosphoric acid medium with DNPPA and TOPO (tri-*n*-octyl-phosphine oxide) by solvent extraction (Singh et al., 2012). DNPPA was also explored for neodymium separation by supported liquid membrane and hollow fibre membrane techniques (Anitha et al., 2013; Ambare et al., 2013). Due to inherent advantages associated with the membrane separation technique, coupled with scanty reports available in literature employing DNPPA as carrier in ELM, we have extended our research further, where DNPPA has been used as a carrier for preparing the emulsion liquid membrane for the transport study of Nd(III) and the present investigation highlights its role as a suitable carrier under wide range of experimental conditions. The effect of variables including extractant concentration, surfactant concentration (1–3% v/v), emulsifier speed (5000–7000 rpm) for the preparation of ELM, volume ratio of external phase to the internal phase, acidity of external aqueous phase (0.1–5 M), concentration of Nd (30–1000 mg/L), etc. on Nd(III) extraction was investigated. The scope of the present study is limited to the evaluation of technical feasibility for the separation of neodymium by ELM.

2. Experimental

2.1. *Reagents*

DNPPA was obtained from Heavy Water Board, Tuticorin, India and were used as procured. TOPO, Nd_2O_3 and Sorbitan monooleate (Span 80) were procured from E-Merck, IREL, India and Sigma-Aldrich, respectively while petrofin (normal heavy paraffin hydrocarbon C12–C14) was obtained from a local manufacturer. All the other chemicals used were of analytical reagent grade.

The di- and the mono-ester content of DNPPA was estimated by potentiometric titration as reported previously (Anitha et al., 2014). The Nd(III) solutions were prepared by dissolving an appropriate quantity of Nd_2O_3 in nitric acid. The Nd(III) concentration in the aqueous solutions was estimated by ICP-AES (JY Ultima 2) using appropriate standards. Dilute sulphuric acid was used as the stripping reagent.

2.2. *Procedure*

2.2.1. *Preparation of the ELM*

In a 100 mL stainless steel (SS 316) container, a 10 mL portion of DNPPA (1–13% v/v) and Span 80 (0.5–5% v/v) in organic solvent (petrofin) were emulsified at a stirring speed of 1000–7000 rpm by means of a motor-driven four-blade turbine impeller of 10 mm diameter. To this organic solution, H_2SO_4 (7 M) solution was added drop wise to the stirred organic phase until 1:1 volume ratio of organic membrane solution to stripping solution. The solution was stirred vigorously for 10 min at 25 °C to obtain the required emulsion.

2.2.2. *Extraction experiments*

In a 100 mL stoppered flask, 10 mL of the prepared ELM (organic phase and internal phase) was added to 100 mL of the external phase (Nd in nitric acid medium) so that the external phase to internal phase volume ratio was about 20. The contents were stirred by means of a magnetic stirrer at a speed of 250 rpm for different time intervals. The stirred solution was allowed to separate by gravity in a separatory funnel and the external phase was carefully separated and a known aliquot was removed for the analysis of neodymium metal ion by ICP-AES.

3. Results and discussion

3.1. *Extraction mechanism in ELM system*

Solvent extraction studies on DNPPA for the extraction of rare earths suggested that the extraction of Nd(III) from aqueous acidic medium with DNPPA dissolved in non-polar diluent takes place via a cation-exchange mechanism (Anitha et al., 2014) as per the following equation:

$$Nd^{3+}_{(a)} + 3H_2A_{2(o)} \overset{K_{ex}}{\longleftrightarrow} Nd(A_2H)_{3(o)} + 3H^+_{(a)} \qquad (1)$$

where K_{ex} is the extraction constant of the two phase reaction and the subscripts '(a)' and '(o)' represent species present in the aqueous and the organic phases, respectively. In view of the non-polar diluent (Petrofin) employed in the present study, DNPPA is supposed to be present as a dimeric species such as, H_2A_2. The back extraction was done in an analogous manner as reported previously (Ambare et al., 2013) and it is assumed