



Carrier facilitated transport of uranium across supported liquid membrane using dinonyl phenyl phosphoric acid and its mixture with neutral donors

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ABSTRACT

Carrier facilitated transport of U(VI) from nitric acid medium across supported liquid membrane (SLM) has been studied under varying experimental conditions, namely feed, carrier, receiver phase compositions, pore size and membrane thickness etc. Microporous polytetrafluoroethylene (PTFE) membranes were used as a solid support and dinonyl phenyl phosphoric acid (DNPPA) either alone or in combination with neutral donors dissolved in *n*-paraffin was used as carrier. Receiver phases like H₂SO₄, Oxalic acid, Citric acid and Na₂CO₃ were evaluated. 2 M H₂SO₄ appeared to be most effective as receiver for U(VI) transport across SLM under the conditions of these studies. The permeability coefficient (*P*) evaluated for 0.1 M DNPPA in combination with 0.05 M neutral donors showed the U(VI) transport order: Cyanex 923 ~ TOPO > TBP > TEHP. The permeability (*P*) of U(VI) decreased with increase in HNO₃ concentration and with metal ion concentration in feed solution. The variation of Cyanex 923 concentration at fixed DNPPA concentration (0.1 M) revealed that U(VI) permeation across SLM was maximum at 1:2.5 mole ratio. The synergistic mixture of 0.1 M DNPPA + 0.05 M Cyanex 923 was used for uranium recovery from uranyl nitrate raffinate (UNR) solution.

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1. Introduction

Uranium is one of the contaminants that can be found in environment at trace concentrations due to weathering effects and erosion of rocks and soil. In addition, the increased nuclear power production, predominantly based on the uranium fuel cycle, leads to the possibility of release of uranium and other radionuclides during different stages in the life history of uranium fuel. The uranium fuel cycle begins with mining of uranium ore, followed by its extraction and purification, fuel fabrication, irradiation in the reactor, spent fuel reprocessing, recycling of separated plutonium and uranium back into the reactor, and ending with the management of nuclear waste produced. These processes lead to release of uranium in various process streams encountered at different stages. Therefore, there is a growing interest in devising efficient methods for uranium separation from different effluents/wastes produced in the nuclear fuel cycle. Though majority of the processes are based solvent extraction methods, there is a preference for the development of green technologies namely membrane based separations in view of the growing environmental concern. Membrane based metal transport appears attractive particularly for dilute aqueous streams due to lower solvent inventory, and simultaneous extraction/stripping processes [1,2]. These methods can make use of the selectivity of the

solvent extraction and can be carried out with low energy requirements. However, the transport process is governed by kinetic rather than equilibrium parameters. Several Supported Liquid Membrane (SLM) based transport studies have been reported dealing with the role different experimental parameters such as (i) nature of membrane supports viz. polypropylene (PP), polyvinylidenedifluoride (PVDF), polytetrafluoroethylene (PTFE), (ii) feed acidity, and (iii) nature of strip solution [3–8]. The requirements for a good polymeric support are high porosity, small pore size, good mechanical strength, chemical resistance, thickness, hydrophobicity and low cost. Several organo-phosphorous solvents have been successfully used for the separation of actinides preferably uranium from different waste streams both in the front-end and in the back-end of nuclear fuel cycle. Extensive studies have been carried out in our laboratory as well as elsewhere to evaluate different types of extractants to optimize the conditions for the separation of actinides like uranium, plutonium, and americium etc. from solutions of different origin [7–17]. SLM based transport studies employing di(2-ethylhexyl) phosphoric acid (D2EHPA) with and without neutral oxodonors like tri-*n*-butyl phosphate (TBP), di-butyl butyl phosphonate (DBBP), tri-*n*-octyl phosphine oxide (TOPO), and Cyanex 923 (a mixture of four trialkyl phosphine oxides viz. R₃PO, R₂R'PO, RR'₂PO and R'₃PO where R: *n*-octyl and R': *n*-hexyl chain) have provided encouraging results for the recovery of uranium (VI) from phosphoric acid medium [17–19]. These studies were extended for uranium recovery from phosphoric acid medium using synergistic mixtures of 2-ethylhexyl phosphoric acid-mono-2-ethylhexyl ester

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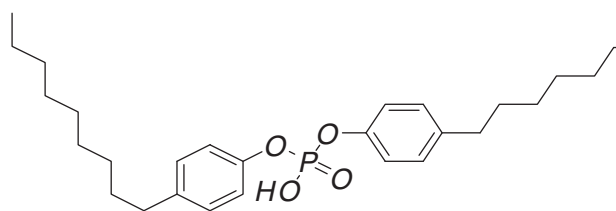
(PC88A) with either TOPO or octyl (phenyl)-*N,N*-diisobutylcarbamoyl methyl phosphine oxide (CMPO) as the carriers [20,21]. Uranium recovery was also performed from analytical waste solutions generated in the laboratory during uranium analysis in phosphoric acid medium under these conditions. Kedari et al. investigated the transport mechanism of U(VI) and Pu(IV) across a SLM and Emulsion Liquid Membrane (ELM) from nitric acid medium using PC88A as the carrier under varying experimental conditions such as stirring speed, carrier concentration, nature of anions and acidity of source phase [22–24]. Selectivity of Pu permeability over several cationic impurities was also investigated. Uranium transport studies from nitric acid solutions across SLMs containing PC88A suggested that transport process was diffusion controlled. The analytical as well as process applications of this method were evaluated by the transport of uranium across the SLM from solutions containing diverse ionic impurities [25]. Dinonyl phenyl phosphoric acid (DNPPA, Fig. 1), a close analog of D2EHPA was widely used for recovery of uranium from phosphoric acid medium by solvent extraction technique [26–29]. Our literature search suggested that no reports are available on uranium transport from acidic medium using DNPPA as carrier solvent.

In the present study it is our interest to investigate detail uranium permeation across SLM from nitric acid medium using synergistic mixture of DNPPA and various neutral donors like Cyanex 923, TOPO, TBP and tris(2-ethylhexyl) phosphate (TEHP) as the carrier solvent. In this context, the effects of various parameters such as nature/concentration of neutral donors, composition of receiver phase, concentration of receiver phase, optimization of carrier concentration, feed acidity, metal ion concentration, membrane pore size, membrane thickness etc. on U(VI) transport across SLM have been investigated. A simple kinetic model was proposed to evaluate the different membrane properties such as diffusion coefficient $D_{(o)}$ and mass transfer coefficient $\Delta^{-1}_{(a)}$ under the present experimental conditions.

2. Experimental

2.1. Materials and solutions

DNPPA (Heavy Water Board, India, 97% pure), TBP (B.D.H, 97% pure), TOPO (E-Merck), Cyanex 923 (E-Merck, >97% pure) and TEHP (E-Merck, >97% pure) were used without further purification. DNPPA exists as dimeric form (H_2A_2) in non polar diluents. All other reagents used in the experiments were of A.R. grade. Natural uranium oxide and uranyl nitrate raffinate (UNR) waste solutions were obtained from Uranium Metal Plant, BARC, Mumbai. Uranium oxide dissolved in nitric acid was diluted as per requirements. The free acidity of the solutions was determined by using standard method described elsewhere [30]. The carrier solutions of DNPPA or its mixture with TBP, TEHP, Cyanex 923 and TOPO in desired concentrations were prepared by weighing the required amounts and making up the volume with *n*-paraffin (a mixture of C_{12} – C_{14}). Unicam UV500 (UV-visible) spectrophotometer and Jobinyvon Emission, Model No JY 328 (ICPAES) instruments were used to determine the concentration of uranium and other trace impurities. Tables 1 and 2 show the compositions (minor/



DNPPA

Fig. 1. Structure of di-nonyl phenyl phosphoric acid (DNPPA).

Table 1

Major components of a typical raffinate solution (of uranium purification cycle).

Component	Concentration
U	0.35–1.4 g/L
Free acidity	1.1–2.0 M
Soluble solid ^a	6.43% (w/v)
Suspended solids ^a	0.23% (w/v)

^a Determined by gravimetry.

major components) of a typical UNR solution [31]. The uranium concentrations in strip as well as in feed solutions were determined by Br-PADAP as well as ICPAES method (as per requirements) with the relative standard deviation of ± 2 –5% [32]. Similarly, trace impurities in UNR as well as in feed and strip solutions were determined by ICP-AES with the relative standard deviation of 2–5%. The detection limit (3σ) of the instrument for non-transition elements: <0.2 ppb, transition elements: <1 ppb and rare earths elements: <3 ppb (for pure solution). For real sample solutions containing a number of elements and matrices the detection limit of the elements was 100 ppb. All the experiments were carried out at room temperature (25 °C).

2.2. Characterization and preparation of SLM

The hydrophobic polytetrafluoroethylene (PTFE) membranes (pore size: 0.45 μ m; diameter: 47 mm) procured from Sartorius, Germany, were used as a solid support. The porosity of the membranes was determined by taking membrane pieces of desired dimensions (~ 2 mm \times 2 mm) which were mounted on aluminum stubs employing a mixture of white glue and colloidal graphite paste. The samples from the stubs were viewed in an electroscan model 2020 environmental scanning electron microscope (ESEM) supplied by Electroscan Corporation, Wolmington, MA. The images taken by ESEM were analyzed by image analyzer. The filled portions of membrane were marked by using digital pad. The porosities of the membranes were calculated from the knowledge of filled portion and total area. In addition, the porosities in membrane with were also determined by measuring the volume of dodecane that the membrane could hold in the pores. The measured porosity value for the membranes used in this study was determined as $\sim 72\%$ by these methods, and the values agreed well with earlier reported values (within $\pm 5\%$) [8,33].

2.2.1. SLM preparation

The SLM was prepared by soaking overnight ca. 24 h the PTFE microporous host membrane in an organic phase having desired composition of the carriers in *n*-dodecane. The impregnated membrane was rinsed with a jet of distilled water to remove the excess of organic solution adhered to the surface of membrane.

Table 2

ICP-AES analysis of typical raffinate solution (of uranium purification cycle).

Element	Concentration, μ g/mL	Element	Concentration, μ g/mL
Al	257	Fe	238
B	0.37	Mg	37.5
Cd	0.53	Mn	3.84
Ce	0.65	Ni	6.75
Co	0.43	Sm	<0.1
Cr	9.27	Yb	<0.1
Dy	<0.10		
Eu	<0.1		

Detection limit (3σ) of non-transition elements: <0.2 ppb, transition elements: <1 ppb and rare earths elements: <3 ppb. Standard deviations of the measurements are within 2–5%.

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