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Extraction of uranium(VI) from sulfate solutions using a polymer inclusion membrane containing di-(2-ethylhexyl) phosphoric acid

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ABSTRACT

In this study a polymer inclusion membrane (PIM) for the extraction and separation of uranium (UO_2^{2+}) from acidic sulfate solutions is detailed. Poly(vinyl chloride) (PVC) based PIMs containing the following commercial extractants were screened for their ability to extract uranium: Alamine 336, Cyanex 272, Aliquat 336, di-(2-ethylhexyl) phosphoric acid (D2EHPA), and tri-*n*-butyl phosphate (TBP). The membrane containing 40% (m/m) D2EHPA is shown to be the most effective in the quantitative extraction and back extraction of uranium using sulfuric acid solutions. Facilitated transport of uranium across the membrane against its concentration gradient is demonstrated with uranium fluxes as high as $4.85 \times 10^{-7}\ \mathrm{mol\,m^{-2}\,s^{-1}}$. A new method for determining the stoichiometry of extracted complexes in both membrane and solvent extraction systems has revealed the composition of the UO_2^{2+}–D2EHPA complex to be $UO_2{\cdot}A_2{\cdot}(HA)_2$ where HA and A^- are D2EHPA and its conjugated base, respectively.

1. Introduction

The separation of uranium from its ores has been the subject of a considerable amount of research effort since the inception of nuclear power generation. A large body of work exists on separation techniques for uranium which largely relies on liquid–liquid extraction techniques; commonly known as solvent extraction (SX) [1]. Whilst these processes are usually efficient and cost-effective, they present environmental and occupational hazards as the extractants are commonly toxic and corrosive and the organic solvents (diluents) are often highly flammable [2].

Membrane technologies have shown potential to reduce these risks. Previous authors have reported on the development of bulk liquid membranes (BLMs) [3–6], emulsion liquid membranes (ELMs) [7–15] and supported liquid membranes (SLMs) [16–22] for the separation of uranium. However, despite the potential advantages offered by these membranes, their operational complexity and the sharing of some of the hazards inherent to SX techniques (BLMs and ELMs) or poor stability (SLMs) have seriously limited their commercial use [23].

Polymer inclusion membranes (PIMs) are a new and very promising type of visibly homogeneous extracting membranes. They are suitable for the separation of ions and small organic molecules which substantially reduces the hazards associated with SX-like techniques. PIMs entrap an extractant within a polymer matrix, often with the addition of a plasticizer or modifier to improve their extraction characteristics. As the extractant is wholly encapsulated in the polymer, the exposure of workers to toxic extractants is minimized. The polymer replaces the organic diluent which removes the fire hazard associated with conventional SX. PIMs are mechanically strong and stable, easy and safe to handle and reasonably simple to fabricate [24].

The possibility also exists for PIMs to be deployed for environmental remediation. Nghiem et al. [24] outlined their ability to selectively and completely extract heavy metals from aqueous solutions, even at trace concentrations, which makes them ideal candidates to clean up industrial wastewater or as an emergency rehabilitation procedure. We envisage that in situations where mine discharges pose a pollution risk, PIM technologies may provide an effective cleanup tool due to the ability to deploy prefabricated membrane modules in situ.

Surprisingly, whilst the body of knowledge on the extraction of uranium is voluminous, there are only four reports on PIM systems for the separation of uranium. Bloch et al. [25] reported in 1967 that a PIM-like membrane coating consisting of tri-*n*-butyl phosphate (TBP) and poly(vinyl chloride) (PVC) supported on Kraft paper was effective in separating uranyl nitrate from nitric acid solutions. However, it was noted that the thin supported membranes had short lifetimes of only 1–2 days (at which point the flux of uranium had dropped to below 20% of its original value).

Matsuoka et al. [26] reported on a PIM (which they termed a *liquid membrane*) consisting of cellulose triacetate (CTA) and TBP.

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Using this membrane, uphill transport of uranium was achieved by having a sufficiently high concentration of the counter-ion in the receiver phase. Again, this membrane suffered from poor stability due to the relatively high water solubility of TBP which led to leaking of this extractant from the membrane unless the aqueous phases contacting the membrane were saturated with TBP.

More recently, Sodaye et al. [27] described a PIM for the preconcentration of α-emitting actinides for scintillation purposes. This PIM was fabricated from di-(2-ethylhexyl) phosphoric acid (D2EHPA) and CTA, in combination with a number of plasticizers and scintillants, and showed almost complete extraction of uranium from acidic nitrate solutions. Although the authors appeared to overlook the possible application of their membrane system to larger scale separation processes, their work showed the potential for PIMs to be adapted to macro-scale uranium separation.

Nazarenko and Lamb [28] reported in 1997 on a wide range of CTA based PIMs with crown-ether carriers for the transport of various metals, including a PIM for the transport of uranium using tri-*n*-octyl phosphine oxide as the carrier. However, no details regarding these transport studies were given and the original conference publication does not seem to have been followed up with a more detailed journal publication.

This work is aimed at developing and characterizing a PIM that can quantitatively extract and transport uranium from acidic sulfate solutions.

2. Experimental

2.1. Reagents

High molecular weight PVC was supplied by Fluka. Tetrahydrofuran (THF), HPLC grade, was supplied by Scharlau. Alamine 336 and Cyanex 272 were of normal technical grade, kindly supplied by Cognis and Cytec, respectively, and were used as received. (Alamine 336 is a mixture of tri-alkyl amines, with the substituent chain length varying between 6 and 12 carbon atoms. Cyanex 272 is a mixture of phosphinic acid esters, with the main component being bis(2,4,4-trimethylpentyl)phosphinic acid). D2EHPA (97%) and Aliquat 336 were supplied by Sigma–Aldrich (Aliquat 336 is a mixture of tri-alkyl methyl ammonium chloride salts produced from the methylation of Alamine 336, with the substituent alkyl chain length varying between 6 and 12 carbon atoms). Tri-*n*-butyl phosphate (Unilab (LR)) was used as received. Uranyl nitrate hexahydrate (Alfa Products, USA), was standardized with a NIST-traceable 1000 mg/L U atomic absorption spectrometry standard (Accutrace, USA). Arsenazo III (99.9%) was supplied by Fluka. All other reagents were of analytical grade unless otherwise stated. Deionised water (18 MΩ cm, Millipore, Synergy 185, France) was used for the preparation of all aqueous solutions.

2.2. Instruments

Optical microscopy and membrane thickness measurements were conducted with a Motic SMZ-140 stereo microscope (Motic, China) with 60× magnification in combination with a MotiCam 1000 microscope camera (Motic, China).

Inductively coupled plasma optical emission spectrometry (ICP-OES) measurements were made using a Perkin-Elmer 3000DV spectrometer.

pH measurements were made using an Ionode IJ-44 pH electrode connected to a smartCHEM analyser (TPS, Australia).

Mass spectrometric measurements were performed using a Finnigan LCQ Deca XP Max liquid chromatograph mass spectrometer (LC-MS) (Thermo-Finnigan, San Jose, USA) after direct infusion. Mass spectra were evaluated using the Xcalibur software (Thermo-Electron, Manchester, UK).

Visible spectrophotometry was undertaken with a Libra S12 spectrophotometer (Biochrom, UK)

2.3. Transport cell

Transport experiments were conducted in a system similar to the one used previously by us [29–31] which consisted of two water jacketed glass cells with the PIM sandwiched between them. The water circulating through the two jackets was thermostated at 25 °C ± 1 °C (Ratek TH5 thermoregulator, Australia). The solutions in the two cells were mechanically stirred by a Velp Scientific B5-type stirrer motor using belt-driven stirrer glands. The area of membrane surface in contact with the solutions was 9.6 cm^2. The volume of solution in each cell was 220 mL.

2.4. Membrane preparation

Membranes were prepared similarly to the procedure used in our previous studies [29–31] which involved dissolving of the extractant, plasticizer or modifier (if used), and the base polymer (PVC), in THF (volume; 10 mL per gram of membrane components). The liquid components were mixed using a magnetic stirrer and the polymer was added slowly over approximately 15 min. Once the polymer was dissolved, 8 mL of the mixture was dispensed by autopipette into a glass ring with a ground bottom edge (internal diameter of ring = 7.6 cm), sitting on a flat glass plate. The combined mass of the polymer, extractant and plasticizer (if used) was 800 ± 20 mg. The ring and mixture were covered with a filter paper and watchglass to slow the evaporation of the solvent. The membrane solution was allowed to evaporate over 48 h and then was peeled from the glass plate.

The resulting membrane was evaluated for its strength, flexibility and visually apparent homogeneity. Successful membranes were transparent, flexible and reasonably resistant to simple mechanical stress, such as tearing and stretching. Additionally, membranes were considered to be homogenous if no residue could be removed from the surface of the membrane and no significant refractive index changes over the surface of the membrane could be visually observed.

The thickness of membranes composed of 40% (m/m) D2EHPA and 60% (m/m) PVC, which make up the bulk of the membranes used in this study, was measured using a digital image of the membrane cross section taken through an optical microscope and compared against a calibration slide with markings of known dimensions. The calculated density of the membrane segments was in the range 1.18–1.27 $g\,cm^{-3}$. Circular segments with a diameter of 45 mm were cut from the centre of the membranes and used in the extraction and transport experiments. As has been observed earlier, the thickness of the membrane appears to vary to a much lesser degree at the centre of PIMs than at their periphery [32]. The typical thickness of standard membrane segments cut from an 800 mg membrane was 100 ± 15 μm. This thickness could be varied by pouring less or more mixture into the casting ring, as desired.

2.5. Membrane screening experiments for the selection of a suitable carrier

The following commercially available extractants were screened for their suitability as PIM carriers for uranium extraction: Alamine 336, Aliquat 336, Cyanex 272, TBP, and D2EHPA. Those extractants that produced mechanically stable, transparent and homogeneous membranes were selected for further screening in uranium extraction experiments. In these experiments a membrane segment (220 ± 10 mg) was immersed in 100 mL of a solution containing 100 $mg\,L^{-1}$ U(VI), adjusted to pH 3 with sulfuric acid and 0.5 M Na_2SO_4. The solution was agitated on an