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Evaluation of polymer inclusion membranes containing calix[4]-bis-2,3-naptho-crown-6 for Cs recovery from acidic feeds: Transport behavior, morphology and modeling studies

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ABSTRACT

Transport of cesium across polymer inclusion membrane (PIM) containing calix[4]-bis-2,3-naptho-crown-6 (CNC) was investigated using acidic feed conditions. The PIMs were prepared using cellulose triacetate (CTA) as the polymer, 2-nitrophenyloctyl ether (NPOE) as the plasticizer and CNC as the carrier extractant. The studies included effects of nature of plasticizer, plasticizer concentration, CNC concentration, CTA fraction, feed acidity, and cesium concentration. Optimized membrane composition was found to be 33% CTA, 5% CNC and 62% NPOE which could result in ca. 85% Cs transport in 24 h. While significant Cs transport was seen with NPOE and TBP as the plasticizer, nearly no transport was noticed with TEHP (*tris*-2-ethylhexyl phosphate) and di-*n*-octyl phthalate (DOP). The transport behavior of Cs(I) was correlated with membrane morphology using Transmission Infrared Mapping Microspectroscopy (TIMM) plots and AFM profiles. Selectivity studies were also carried out which were found to be quite encouraging. A mathematical model was developed to simulate the transport process of Cs(I) ion from feed side to the strip side.

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1. Introduction

^{137}Cs (half-life: 30.1 y) is one of the important fission products present in the nuclear waste and responsible for the MANREM problems associated with radioactive waste management due to the 662 keV gamma ray emission. There is, therefore, a strategy evolving for the separation of radio-cesium prior to the vitrification of the high level waste (HLW). Moreover, the separated radio cesium can be used as a potential gamma ray source in place of ^{60}Co for different purposes like sterilization of foods, sterilization of medical accessories as well as sewage sludge treatment [1]. The separation of radio cesium from acidic radioactive waste solutions is achieved using three classes of reagents, viz., ion-exchangers such as AMP coated resins, cobalt dicarbollides, and macrocyclic compounds such as crown ethers and calix-crown derivatives [2–7]. Out of these, AMP based separations are really hard to be reversible while solvent extraction methods using cobalt dicarbollides use corrosive or hazardous diluents like nitrobenzene and FS-13 [8–10]. Crown ether based separations are attractive from the point of view of facile back extraction of Cs(I) using distilled water as the strippant [11]. The selectivity of a crown ether is derived by the cavity fitting parameter and cation–pi electron cloud interactions and hence can be tuned by synthesizing molecules of the required cavity size. Calix-crowns are reported to be more efficient extractants due to their high complexation ability with Cs$^+$ ion and display very high selectivity in the presence of large concentrations of other alkali metal ions [12]. Separation of Cs(I) from alkaline nuclear waste solutions has been extensively studied using calix[4]arene-bis(*tert*-octylbenzo-crown-6), better known as BOBCalixC6 [13,14]. However, degradation of this reagent in acidic conditions limits its use for Cs(I) recovery from the acidic wastes such as the high level waste (HLW) [15].

We have studied several commercial calix-bis-crown-6 ligands for Cs(I) recovery, out of which calix[4]-bis-2,3-naptho-crown-6 (CNC, Fig. 1) was found to be the most efficient [16]. Crystal structure and molecular dynamics calculations have revealed its excellent selectivity (1:45,000) over Na(I) [17]. The favorable cation–*pi* interactions between the cation and phenyl rings of ligand led to selective binding of the metal ion [18]. Using solvent extraction techniques we have demonstrated the selective extraction of Cs(I) employing the CNC as the extractant from acidic waste solutions with nitrobenzene–toluene mixture as the diluent [19]. Its radiation and chemical stability were found to be satisfactory suggesting its potential for long term applications [20].

Due to the concern for the environment and possibility of using very low inventory of the extractant, liquid membrane based

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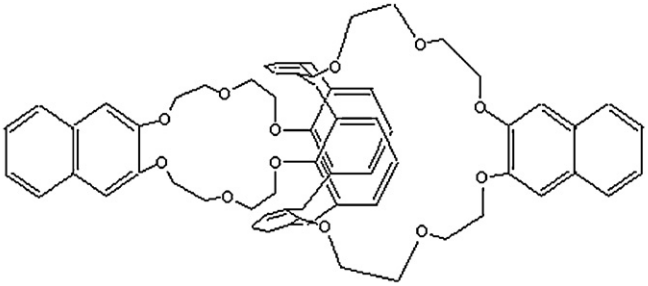

Fig. 1. Structural formula of calix[4]-bis-2,3-naphtho-crown-6 (CNC).

separation methods are considered viable alternatives to the solvent extraction methods [21–23]. We have carried out systematic investigations on the Cs transport using CNC as the carrier in flat sheet supported liquid membranes [24,25]. The flux, however, was low resulting in slow mass transfer rates. It was required, therefore, to evaluate alternative membrane separation methods such as polymer inclusion membranes which display high stability [26]. Schow et al. [27] reported higher fluxes for PIMs for K^+ ion using a crown ether as carrier than those for flat sheet supported liquid membranes. Miguel et al. [28] reported quantitative recovery of Au(III) using polymer inclusion membranes from concentrated hydrochloric media using Kelex-100 (7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline) as carrier. The transport mechanism in PIMs depends on factors like membrane composition, homogeneity of the membrane and surface morphology. Therefore, it is required to investigate the effects of membrane morphology on the transport rates.

In the present study, we have prepared several PIM compositions containing cellulose triacetate (CTA) as the polymeric material and calix[4]-bis-2,3-naptho-crown-6 as the carrier extractant. Several plasticizers such as TBP, NPOE, DOP and TEHP were evaluated and the Cs(I) transport rates were measured. Other transport studies included carrier concentration variation, CTA concentration variation, and effect of feed acidity. Selectivity and long term stability studies were also carried out. Role of membrane homogeneity and morphology on the Cs(I) transport rates were also investigated by carrying out TIMM (Transmission Infrared Mapping Microspectroscopy and AFM (Atomic Force Microscopy) measurements. Mathematical modeling of the transport data was also done and compared with the experimentally obtained data points.

2. Experimental

2.1. Materials

Calix[4]-bis-2,3-naptho-crown-6 (CNC) was purchased from Acros Organics, Belgium. ^{137}Cs tracer was procured from Board of Radiation and Isotope Technology (BRIT), Mumbai, and its radiochemical purity was ascertained by gamma ray spectrometry employing high resolution HPGe detector. 2-Nitrophenyloctyl ether (Fluka), *tris*-2-ethylhexyl phosphate (Fluka), tri-*n*-butyl phosphate (Aldrich), di-*n*-octyl phthalate (Aldrich) and cellulose triacetate (CTA) were used as obtained. All the other reagents used were of analytical reagent grade.

2.2. Preparation of PIM

The PIMs were prepared using previously reported literature methods [27,29]. A mixture of cellulose triacetate (CTA), extractant (CNC) and a plasticizer (TBP/NPOE/DOP/TEHP) was dissolved in dichloromethane and homogenized by sonication. The solution was poured into a flat petri dish and was allowed to evaporate at room temperature. The resulting PIM was peeled out by spreading a few mL of water on it and was subsequently used for the transport studies. Thickness of the membranes was measured using digimatic micrometer (Mitutoyo Corporation, Japan).

2.3. Transport studies of Cs(I)

The Cs(I) transport experiments were carried out by using a two-compartment Pyrex glass cell as reported earlier [29]. Volumes of the feed and the receiver compartments were 20 mL each and the exposed membrane area was 4.94 cm^2. The feed solution for these studies contained 1 M HNO_3 while distilled water was used as the strippant. Equal volumes of the feed (spiked with ^{137}Cs tracer) and receiver phase were transferred into the respective compartments and were stirred at 200 rpm by synchronous motors. Assay of ^{137}Cs in the feed as well as in the receiver phase was carried out at different time intervals to calculate the transport parameters. Counting was done by the NaI(Tl) detector and High Purity Germanium (HPGe) detector both coupled to multi-channel analyzers. All the transport studies were carried out at ambient temperature ($25 \pm 1\,^{\circ}$C). The material balance in these studies was found to be within ±5%.

2.4. Membrane characterization

2.4.1. TIMM measurements

Transmission Infrared Mapping Microspectroscopy (TIMM) plot measurements were performed by using a PERKIN ELMER auto image microscope coupled with FTIR. Scanning was performed using $25\,\mu m \times 25\,\mu m$ aperture areas with 16 cm^{-1} resolution having intervals of 8 cm^{-1} using 2 scans per point in the region, 4000–720 cm^{-1}. Membranes made of CTA served as blanks and all measurements were baseline corrected with the 4000 cm^{-1} line as the reference. The distribution of the components was measured using the following bands: NPOE: 1528 cm^{-1} for (asym. NO_2 stretching), TEHP: 1943 cm^{-1} (P=O stretching), DOP: 1730 cm^{-1} (C=O stretching), TBP: 1899 cm^{-1} (P=O stretching), CNC: 2356, 1198 cm^{-1} (C—H bending, C—H stretching, respectively), unless mentioned otherwise.

2.4.2. Atomic force microscopy

Surface morphology of the polymer inclusion membranes was characterized by atomic force microscopy (AFM). AFM measurements were carried out in contact mode using a scanning probe microscope (SPM-Solver P47, NT-MDT, Russia). Rectangular cantilevers of silicon nitride having force constant of 3 N/m was employed for measurement. The membrane surfaces were compared by means of roughness parameters, such as maximum height (R_{max}), mean height (R_{mean}), mean roughness (R_a) and root mean square (rms) of the z data (R_q) [30].

2.5. Mathematical modeling of Cs transport data

A mathematical model was developed to simulate the transport process of Cs(I) in a manner similar to that reported in a recent publication [25]. The model was developed based on carrier (ligand) mass balance in the membrane phase. Distribution ratio values were calculated by equilibrating a known volume and weight of piece of PIM with certain volume of nitric acid (1 M) containing ^{137}Cs. The membrane phase diffusivity ($\triangle_o$) was calculated by time-lag experiment and used to predict the transport data.

It is assumed that the facilitated transport of the Cs(I) takes place through the ion-pair mechanism similar to that of supported liquid membranes as given below,

$$Cs^+(a) + NO_3{}^-(a) + L(o) \overset{K_{ex}}{\rightleftarrows} (Cs \cdot L)^+ \cdot NO_3{}^-(o) \qquad (1)$$

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