Journal of Membrane Science 487 (2015) 127–134

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Pertraction of radio-cesium from acidic feeds across supported liquid membranes containing calix-crown-6 ligands in a fluorinated diluent

P. Jagasia [a], P.K. Mohapatra [b,*], D.R. Raut [b], P.S. Dhami [c], V.C. Adya [b], A. Sengupta [b], P.M. Gandhi [c], P.K. Wattal [d]

[a] Process Development Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India
[b] Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India
[c] Fuel Reprocessing Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India
[d] Nuclear Recycles Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

ARTICLE INFO

Article history:
Received 13 November 2014
Received in revised form
16 February 2015
Accepted 17 February 2015
Available online 20 March 2015

Keywords:
Calix-crown-6
Radio-cesium
Supported liquid membrane
Nuclear waste
Transport

ABSTRACT

Supported liquid membranes containing a solution of four calix-crown-6 ligands viz., calix[4]arene-bis-crown-6 (CC), calix[4]arene-benzo-bis-crown-6 (CBC), calix[4]arene-naphtho-bis-crown-6 (CNC), and bis-(octyloxy)calix[4]arene-mono-crown-6 (CMC) in a fluorinated diluent, phenyltrifluoromethyl sulfone (PTMS) along with small fraction of Alamine 336, were employed for the pertraction of radio-cesium from nitric acid feed solutions. The transport efficiency of the membranes followed the trend: CNC⩾CBC > CC⩾CMC. While 4.0×10^{-3} M solutions of CBC, CC and CMC were used for the transport studies and near quantitative Cs(I) transport was seen at tracer scale after 4 h using CBC, transport studies with CNC were carried out at 1.0×10^{-3} M due to solubility limitations. The mass transport rates for Cs(I) reported here is the fastest in a calix-crown-6 based SLM and shown to be promising for applications in nuclear waste remediation. Acid co-transport was observed with all the calix-crown-6 ligands which increased sharply if the membranes were used for longer time. ^{137}Cs spiked simulated high level waste (SHLW) was used as the feed to result in > 60% transport of the metal ion and < 3% acid co-transport after 5 h when the CBC based SLM was used to suggesting effectiveness of the transport system for applications in the back end of the nuclear fuel cycle. Transport parameters such as permeability coefficient (P) and diffusion coefficient (D_o) were also determined. The SLM was found to have limited stability to suggest that fresh membranes need to be used for better performance.

1. Introduction

The public acceptance of the nuclear power as an alternative to the conventional energy sources largely depends on the safe management of the radioactive high level waste. One of the major challenges in radioactive waste processing includes separation of heat generating fission products such as ^{137}Cs and ^{90}Sr. Removal of ^{137}Cs (half-life: 30.1 years) from the radioactive wastes is also required to solve the MANREM radiation risks due to the reasonably hard 662 keV gamma ray emission. It is, therefore, suggested to separate ^{137}Cs from the high level waste (HLW) prior to the vitrification of the latter. Furthermore, the recovered ^{137}Cs can be used as a potential source of gamma radiation in place of ^{60}Co for purposes such as sewage sludge treatment, sterilization of foods, sterilization of medical accessories, irradiation of hides, etc. [1,2]. Conventionally, the separation of radio cesium from HLW has been attempted using solvent extraction or ion-exchange based separation methods using reagents such as, AMP (ammonium molybdophosphate), cobalt dicarbollides, and calix-crown-6 [3–5] while that from alkaline wastes have been achieved using sodium tetraphenylborate, RFPR (resorcinol formaldehyde poly-condensate resin) resin [6,7]. Some of the other promising reagents are crystalline sillicotitanate, zeolite and Prussian blue [8–10].

Out of the reagents used for Cs separation from radioactive wastes, calix-crown-6 ligands have shown remarkable selectivity for radio-cesium from both acidic as well as alkaline feed solutions [11–14]. The calix-crown-6 ligands have shown very high selectivity towards Cs(I) as compared to Na(I) due to cation–pi electron interactions [15]. Furthermore, the radiation stability and reusability studies were found to be encouraging [16]. The now well known, BOBCalix6 (calix[4]arene-bis(t-octylbenzo-crown-6)) has been used by the researchers from Oak Ridge National Laboratory, USA for the separation of radio-cesium from the Savanna River Site alkaline

* Corresponding author. Fax: +91 22 25505151.
E-mail address: mpatra@barc.gov.in (P.K. Mohapatra).

http://dx.doi.org/10.1016/j.memsci.2015.02.037
0376-7388/

wastes and flow sheet has been developed for large scale processing [11]. The BOBCalix6 has not been successfully employed for the recovery of radio-cesium from acidic wastes and we have carried out extensive studies using CNC (calix[4]arene-naphtho-bis-crown-6) for such purpose with reasonably good success in our lab scale studies [17]. Our studies have shown that the diluents have a very significant role to play in the metal ion extraction [18]. However, the mixture of nitrobenzene and toluene used in a previous study was not acceptable due to the large inventory requirement of the toxic nitrobenzene as the diluent [15]. Though many diluents have been tested for this purpose, most of those were found to be unsuitable due to solubility limitations.

The UNEX process, developed for the simultaneous recovery of actinides, cesium and strontium from the HLW uses a fluorinated diluent with very encouraging results [19]. We have used the UNEX process diluent, FS-13 or phenyltrifluoromethyl sulfone (PTMS) along with CCD (chlorinated cobalt dicarbollide) for the extraction/transport of radio-cesium from acidic feed solutions [20]. Recently, we have developed novel solvent systems containing four calix-crown-6 ligands (Fig. 1), viz., calix[4]arene-bis-crown-6 (CC), calix[4]arene-benzo-bis-crown-6 (CBC), calix[4]arene-naphtho-bis-crown-6 (CNC), and bis-(octyloxy)calix[4]arene-mono-crown-6 (CMC) in PTMS for the selective extraction of radio-cesium from HLW [21]. The major advantage of the PTMS based solvent systems is significantly lower ligand inventory requirement as compared to other diluents reported for the same purpose. It was interesting to note that while CNC was reported in earlier publications to be the most efficient calix-crown-6 ligand as compared to the remaining three in nitrobenzene based solvent systems [14], CBC was found to be the most efficient amongst these ligands in PTMS [21]. Furthermore, CBC was reported to be having higher radiolytic stability compared to the other three calix-crown-6 extractants [22]. Sharma et al., used a mixture of *n*-dodecane and *iso*-decanol as diluent and modifier respectively for cesium extraction using a substituted calix-mono-crown-6 [23]. However, about 20 times more ligand concentration was needed for obtaining comparable distribution ratio values in the diluent mixture as compared to that reported by us using PTMS.

With a view to bring down the inventory of high cost extractants such as the calix-crown-6 ligands, it was thought of interest to use liquid membrane based separation methods which are considered viable alternatives to solvent extraction based separation methods [24–27]. The major advantages of liquid membranes, especially the supported liquid membranes include (apart from very low extractant inventory) simultaneous extraction and stripping, low power consumption and easy scaling up [27]. Furthermore, the disadvantages of solvent extraction methods such as feed entrainment, flooding, third phase formation, etc. can be easily alleviated [27].

There are several reports available on Cs transport using calix-crown ligands as the carrier in flat sheet supported liquid membranes [28,29]. Transport behavior of Cs(I) using the calix-crown-6 ligands, CC, CBC and CNC as the carrier extractants has been investigated by us using several diluents [18]. It was observed that quantitative transport was not possible in most cases and it was difficult to obtain transport rates beyond 50%. This was attributed to stripping limitations and acid transport as 6–8 M HNO_3 was used as the strippant in the receiver phase. On the other hand, our subsequent study involving a mixture of 20% *n*-dodecane and 80% 2-nitrophenyloctyl ether (NPOE) resulted in ca. 90% Cs(I) transport [30]. The relatively high viscosity of NPOE (13.417 mPa s at 25 °C) is not very conducive for faster mass transfer rates as it leads to slower diffusion of the metal–carrier complex in the liquid membrane phase. However, any attempt to decrease the viscosity by increasing *n*-dodecane fraction resulted in poor Cs(I) transport efficiency. In view of this, it was of interest to use diluents with low viscosity for the Cs(I) transport studies and PTMS with significantly low viscosity (3.4675 mPa s at 25 °C) compared to NPOE was chosen in the present study.

In the present work, we have studied the transport behavior of Cs(I) from nitric acid feed solutions using the four PTMS based solvent systems (containing a small fraction of Alamine 336 to facilitate Cs(I) stripping) and compared the transport parameters with those reported previously. The studies included the effect of feed nitric acid concentration and the transport of Cs(I) and co-transport of HNO_3 were measured. As the radioactive HLW is usually in 3 M HNO_3, major part of the studies is carried out in this acid concentration. The supported liquid membrane based transport studies were also carried out using a synthetic high level waste solution and information on the transport behavior of other components of HLW was thus, obtained. Finally, liquid membrane stabilities studies were also carried out to evaluate the possibility of application of the transport systems.

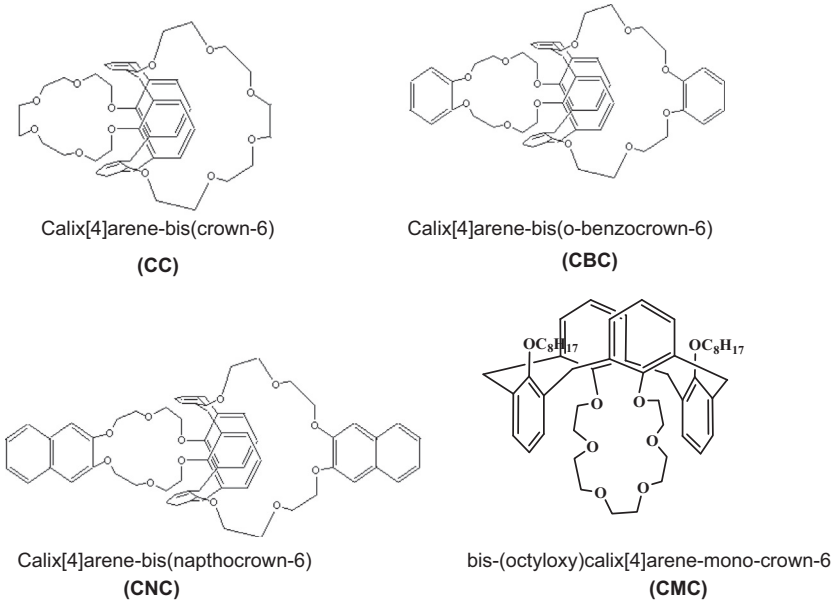

Fig. 1. Structural formulae of the calix-crown-6 ligands used in the present study.