



Evaluation of polymer inclusion membranes containing crown ethers for selective cesium separation from nuclear waste solution

P.K. Mohapatra, D.S. Lakshmi, A. Bhattacharyya, V.K. Manchanda*

Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

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ABSTRACT

Transport behaviour of ^{137}Cs from nitric acid feed was investigated using cellulose triacetate plasticized polymer inclusion membrane (PIM) containing several crown ether carriers viz. di-benzo-18-crown-6 (DB18C6), di-benzo-21-crown-7 (DB21C7) and di-*tert*-butylbenzo-18-crown-6 (DTBB18C6). The PIM was prepared from cellulose triacetate (CTA) with various crown ethers and plasticizers. DTBB18C6 and tri-*n*-butyl phosphate (TBP) were found to give higher transport rate for ^{137}Cs as compared to other carriers and plasticizers. Effect of crown ether concentration, nitric acid concentration, plasticizer and CTA concentration on the transport rate of Cs was also studied. The Cs selectivity with respect to various fission products obtained from an irradiated natural uranium target was found to be heavily dependent on the nature of the plasticizer. The present work shows that by choosing a proper plasticizer, one can get either good transport efficiency or selectivity. Though TBP plasticized membranes showed good transport efficiency, it displayed poor selectivities. On the other hand, an entirely opposite separation behaviour was observed with 2-nitrophenyloctylether (NPOE) plasticized membranes suggesting the possible application of the later membranes for the removal of bulk ^{137}Cs from the nuclear waste. The stability of the membrane was tested by carrying out transport runs for nearly 25 days.

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1. Introduction

Due to its long half-life (30.1 years) and reasonable thermal output (0.42 W/g), ^{137}Cs has potential application as an excellent source for gamma irradiators which are in use for the environmental pollution control, food preservation and sterilization of medical accessories, etc. However, economic considerations require ^{137}Cs recovery from the high level nuclear waste (HLW) to make it a viable alternative to Co-60, which at present is the mainstay in gamma irradiators. The world inventory of ^{137}Cs from spent nuclear fuel is estimated to be around 30 GCi by the year 2010. Removal of ^{137}Cs from HLW is also helpful for the safe disposal in deep geological repositories as vitrified mass [1]. Due to the presence of large concentration of sodium ions in HLW, removal of Cs from HLW requires particularly large separation factors of Cs over Na. Among the separation methods employed for Cs removal from waste solutions, solvent extraction methods have been particularly attractive

because of their rapidity, ease of operation and large throughput [2]. Rais et al. [3] and Miller et al. [4] used dicarbollide in nitrobenzene and diethyl benzene, respectively for the preferential removal of ^{137}Cs from nuclear waste solutions. Recent reports from the joint research programme of Khlopin Radium Institute and Idaho National Environmental and Engineering Laboratory have used fluorinated aryl diluents such as FS-13 for effective removal of Cs from acidic waste solutions which is also the basis of the UNEX process [5,6]. Solvent extraction methods involving the crown ethers have also shown great promise for Cs recovery from the acidic waste solutions [7–10].

Among the crown ethers, which are selective for alkali metal ions, derivatives of 21-crown-7 have been extensively used for Cs extraction [11] which has a good match between the cavity of the crown ether and the crystal ionic radius of the metal ion. However, there are several reports involving the extraction of Cs with the 18-membered crown ethers as well [12]. Kikuchi and Sakamoto [13] have investigated the influence of the substituents in the crown ether ring on the extent of complex formation with Cs by an ion-pair extraction study from picrate medium. It was observed that the stereochemistry of the crown ether governs the stoichiometry of the complexes. Dietz et al. [14] have carried out Cs extraction using crown ether solutions in oxo diluents such as alcohols, ketones, ethers and carboxylic acids. We [15] have also reported the extraction of ^{137}Cs from the nitric acid medium using several di-benzo-18-crown-6 (DB18C6) derivatives. Structures

Abbreviations: CTA, cellulose triacetate; DB18C6, di-benzo-18-crown-6; DB21C6, di-benzo-21-crown-7; DTBB18C6, di-*tert*-butylbenzo-18-crown-6; HLW, high level nuclear waste; HPGe, high purity germanium; PHWR, pressurized heavy water reactor; PIM, polymer inclusion membrane; NPOE, 2-nitrophenyloctylether; SLM, supported liquid membrane; SHLW, simulated high level waste; TBP, tri-*n*-butyl phosphate; TEHP, tris-2-ethylhexyl phosphate.

* Corresponding author. Tel.: +91 22 25593688; fax: +91 22 25505151.

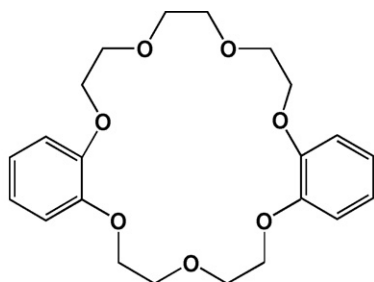
E-mail address: vkm@barc.gov.in (V.K. Manchanda).

Nomenclature

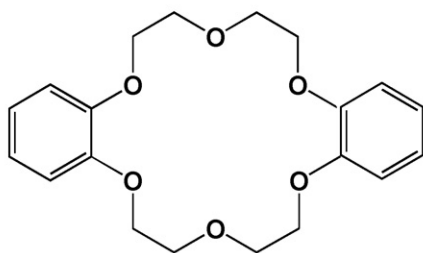
C_f	concentration of metal ion in the feed
$C_{f,0}$	concentration of metal ion in the feed at the beginning
$C_{f,t}$	concentration of metal ion in the feed at a given time
P	permeability coefficient
J	flux
k	Boltzmann constant
η	viscosity

of some crown ethers used in the present work are shown in Fig. 1.

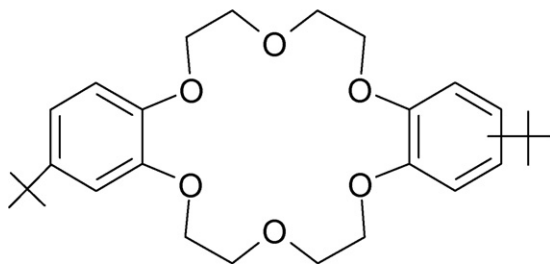
Though crown ethers have yielded promising results in studies related to the selective separation of Cs from complex mixtures including nuclear waste solutions, the prohibitive cost of these compounds has been a major hurdle in their use in large-scale process applications. Separation methods such as extraction chromatography (EC) and supported liquid membrane (SLM) have been suggested as alternatives to the solvent extraction methods. These methods have drawn the attention of separation chemists in view of the low inventory of extractant and low energy requirement. Dozol et al. [16] have studied the transport behaviour of Cs using SLM with benzo substituted 21-membered crown ethers while our work



(a) Di-benzo 21 crown 7 (DB21C7)



(b) Di-benzo 18 crown 6 (DB18C6)



(c) Di-tert-butyl benzo 18 crown 6 (DTBB18C6)

Fig. 1. Structural formulae of the crown ethers used in the present work.

using di-*tert*-butylbenzo-8-crown-6 (DTBB18C6) indicated reasonable transport efficiency and selectivity [17]. However, the SLMs have suffered from the serious drawbacks of stability and carrier compatibility [17,18] and are not suitable for continuous operation. Polymer inclusion membranes (PIMs), on the other hand, have been reported to have high stability with respect to carrier leaching and have been reported for continuous operation for long durations. The PIM entraps the macrocyclic carriers in the membrane matrix during the casting process, effectively inhibiting carrier loss to adjacent aqueous phases [19]. A comparison between SLM and PIM performance has been reported recently, where it was inferred that similar phenomena control metal ion transport in the two membrane systems [20]. A recent review gives a good account of the polymer inclusion membrane transport mechanisms [21].

An attempt has been made in the present work to develop a membrane-based method for the selective separation of ^{137}Cs from solutions of acidic origin (such as the HLW) using DTBB18C6 as the carrier. As will be discussed below, a proper choice of plasticizer is extremely important while deciding transport efficiency or selectivity. Though bulk of the present work was carried out using TBP plasticized membranes keeping transport efficiency in mind, the NPOE plasticized membranes showed better selectivity. The latter option can be used for Cs analysis in radioactive waste solutions.

2. Experimental

2.1. Materials

DTBB18C6 (Fluka), DB18C6 (Fluka), DB21C7 (Fluka), 2-nitrophenyloctylether (NPOE) (Fluka) and cellulose triacetate (Alfa Biochem) were used as procured. Analar grade TBP was procured from BDH and was used as such. ^{137}Cs tracer was procured from BRIT, Mumbai. All other reagents were of AR grade.

2.2. Preparation and characterization of CTA membranes

The PIMs were prepared using the method reported in the literature [22]. 5 ml of dichloromethane solution containing 12.5 mg/ml CTA, 6 mg/ml of macrocyclic ligand and 0.2 ml NPOE or TBP were casted in a glass culture dish (flat bottom, 9 cm diameter) after sonification for thorough mixing. Following the slow evaporation of the solvent and attendant setting of the CTA membrane, a few drops of water were swirled on the top of the film to help loosen it from the glass. The polymer film was then carefully peeled out from the dish. A typical composition of NPOE plasticized membrane was 25.97% CTA, 6.49% DTBB18C6 and 67.53% NPOE while that of a typical TBP plasticized membrane was 28.07% CTA, 7.02% DTBB18C6 and 64.91% TBP. Membranes with different concentrations of crown ether, plasticizer and CTA were prepared in a similar fashion. The membrane characterization studies involved X-ray diffraction (Philips, PW-1710 X-ray diffractometer using monochromatized $\text{Cu K}\alpha$ radiation), FT-IR (JASCO-610 model, Japan) and AFM (Solver, P-47 model, Russia) measurements.

2.3. Membrane transport experiments

The apparatus used for the transport experiment was a permeability cell consisting of two cylindrical glass compartments. The half cell volumes were 24 ml each and the effective membrane area was 4.94 cm². The CTA membrane was fixed between the two compartments of the cell using metallic clips. The feed (source) compartment or the source phase usually contained 1 M HNO_3 while distilled water was used as the stripping in the receiver compartment. The side of the film exposed to the air during evaporation was placed so as to face the vessel containing the source solution [23]. Equal volumes of source and receiver phase were

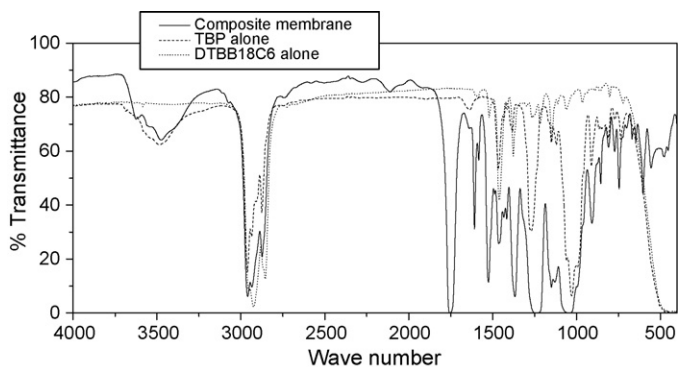


Fig. 2. IR spectra of PIM containing DTBB18C6, TBP and CTA along with those of DTBB18C6 and TBP alone.

transferred into the respective compartments and the source phase was spiked with ^{137}Cs tracer. Both sides were stirred with Teflon coated magnetic stirring bars at 200 rpm by synchronous motors. Samples (0.1 ml) from both the feed and receiver were periodically taken out and assayed radiometrically (661 keV gamma line) using a well-type NaI(Tl) scintillation counter interphased with a PC-based multichannel analyzer. The transport studies were carried out at ambient temperature (24–26 °C). The material balance in these studies was found to be within $\pm 5\%$.

2.4. Thickness measurement

Thickness of the membranes was measured with a Mitutoyo Digital micrometer. Thickness was also calculated from weight per unit area measurements. Both the values agreed within error limits ($\pm 5\%$).

2.5. Transport of nitric acid

The amount of nitric acid transported through PIM was determined by titration. A known aliquot of the receiver phase was titrated with standard NaOH using phenolphthalein as the indicator.

2.6. Studies with irradiated natural uranium target

Transport selectivity of the present PIM for Cs^+ with respect to other fission products was investigated by irradiating a natural uranium target (~ 2 mg) wrapped with Al foil at a thermal neutron

Table 1

Permeability coefficients of Cs(I) transport for membranes using different carrier ligands with TBP as plasticizer (200 μl); membrane composition: 15.2% carrier–24.2% CTA–60.4% TBP; feed: 2 M HNO_3 containing ^{137}Cs tracer ($\sim 10^{-5}$ M); strip phase: distilled water.

Ligand	$P \times 10^5$ (cm s^{-1})
DTBB18C6	8.46 ± 0.12
DB18C6	0.15 ± 0.08
DB21C7	0.13 ± 0.05

flux of 1×10^{12} neutrons $\text{cm}^{-2} \text{s}^{-1}$. Subsequently, the irradiated target containing the fission products was dissolved in 6 M HNO_3 and finally, the acidity was adjusted to 1 M HNO_3 prior to transfer into the feed compartment for the transport experiments. The fission product mixture was spiked with ^{137}Cs tracer for the convenient monitoring of Cs.

3. Results and discussion

3.1. Physical characterization of membranes

The membranes were characterized by several physico-chemical techniques viz., elemental analysis, FT-IR, TG-DTA and X-ray diffraction. The FT-IR spectrum of the TBP plasticized composite PIM is shown in Fig. 2. The possible leaching of the carrier/plasticizer molecules was monitored at regular intervals by FT-IR method and apparently the membranes were found to be stable. For example, the leaching of TBP can be monitored from the $>\text{P}=\text{O}$ group stretching frequency (1240–1250 cm^{-1}). The uniformity of the membranes was checked by thickness measurement as described above and the surface morphology was studied by atomic force microscopy (AFM). The surface morphology of the membrane appeared somewhat rough (Fig. 3) with well-defined pockets containing plasticizers in between swelled blobs of CTA chains. Similar surface roughness was observed by Scindia et al. [24] in their studies involving CTA membranes for Cr(VI) transport. The rough membranes may lead to faster mass transfer rates (due to localized plasticizer pockets), though it could also lead to relatively lower stability of the membranes. The X-ray diffraction pattern of the CTA membranes indicated a single maximum located at approximately 20° found in all polymers corresponding to the Van der Waals halo which suggested essentially amorphous characteristics. The absence of crystallization within the membrane ruled out the fixed site jumping mechanism of ion transport [25]. The TG-DTA analysis of the CTA membranes (Fig. 4) indicated 2 stage decomposition pattern suggesting volatilization of NPOE at around 138 °C and thermal degradation of the cellulose triacetate chains at 295 °C which slowly converted to gaseous products. The CTA membranes containing the macrocyclic carrier showed similar 2 stage decomposition patterns with steeper second weight losses. These data indicated reasonably good thermal stability of the membranes at ambient temperature.

3.2. Transport equations

The transport equations can be developed based on the following assumptions: (1) interfacial mass transfer is very fast leading to instantaneous establishment of chemical equilibria; (2) metal ion concentration in the membrane phase is negligible with regard to the carrier concentration suggesting that the carrier concentration is constant; (3) concentration of metal-carrier complex at feed-membrane interface is much larger as compared to that in the membrane-receiver interface; (4) mass transfer within the membrane follows the Fick's law of diffusion; (5) the aqueous diffusion layers in both the feed and receiver compartment are maintained very small by uniform stirring. Under steady state conditions, the

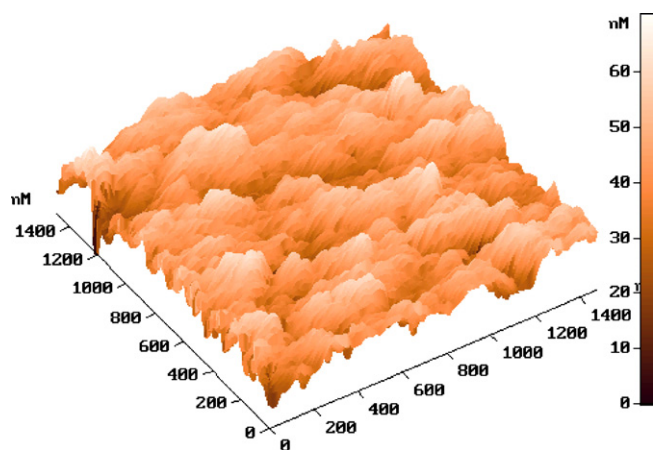


Fig. 3. AFM surface morphology picture of the PIM taken for the side exposed to the feed compartment.

permeability coefficient (P) is given by:

$$\ln \left(\frac{C_{f,t}}{C_{f,0}} \right) = - \left(\frac{Q}{V} \right) Pt \quad (1)$$

where $C_{f,t}$ and $C_{f,0}$ are the concentrations of metal ion in aqueous feed at time t and initial metal ion concentration (at $t=0$) respectively, Q is the surface area, V is the aqueous feed volume (in ml). The permeability coefficient is also related to the flux and concentration of metal ion in the feed compartment (C_f) as:

$$P = \frac{J}{C_f} \quad (2)$$

3.3. The effect of the nature of the carrier

From size consideration, the crystal ionic radius of Cs^+ is compatible with the cavity of 21-membered crown ethers. Structure of di-benzo-21-crown-7 (DB21C7) is shown in Fig. 1(a). However, several solvent extraction studies have indicated excellent selectivity with 18-member crown ethers viz. di-benzo-18-crown-6 (Fig. 1(b)) and DTBB18C6 (Fig. 1(c)) [14]. In the present study, it was decided to employ DB21C7, DB18C6 and DTBB18C6 for the studies involving Cs transport to understand the role of size selectivity and role of substituents, which affect the lipophilicity and basicity of the ligand. The data in Table 1 shows that transport rate of Cs(I) is poor (<1%) for both DB18C6 and DB21C7 while DTBB18C6 shows significant mass transfer. Higher transport rate observed for DTBB18C6 has been attributed to its higher complexation ability as well as lipophilicity. The increase in the electron density on the crown ether oxygens due to the +I effect of *tert*-butyl group and favourable stereochemistry in the presence of the *tert*-butyl group led to its higher complexation constants as compared to the respective cyclohexano derivative [26].

3.4. The effect of the carrier concentration

In order to model Cs transport through PIM, experiments were designed to establish the relationship between the carrier concentration in the membrane and the transport of Cs^+ ion. The crown ether content in the membrane was varied from 2 mg/ml to 20 mg/ml. However, as the increase in the ligand concentration resulted in increased thickness of the membranes (which affected

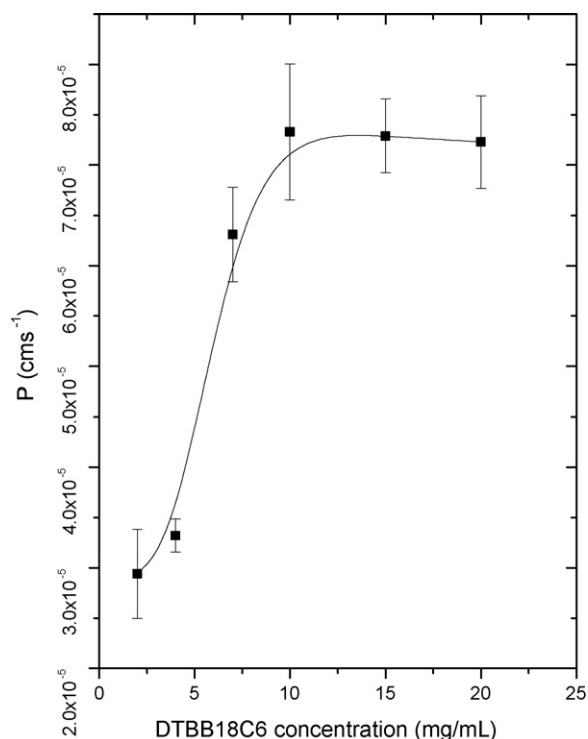


Fig. 5. Correlation between Cs(I) permeability coefficient (P) as a function of DTBB18C6 (carrier) concentration in the range 2–20 mg/ml. Feed: 1 M HNO_3 ; receiver: distilled water.

the transport rates), the ligand concentration was restricted to 10 mg/ml in all the transport experiments unless mentioned otherwise. As shown in the Fig. 5, the permeability coefficient values varied linearly up to a concentration of 8 mg/ml beyond and a plateau was observed. The plateau at higher ligand concentration was partly due to the increase in the membrane thickness which retarded the transport rate (Eq. (1)). This result was consistent with a diffusion-controlled transport mechanism for the SLMs as described by Yahaya [27]. Diffusion-controlled transport involves the formation of the metal ion complex at the surface of PIM and the whole complex diffuses to the opposite side of the PIM and

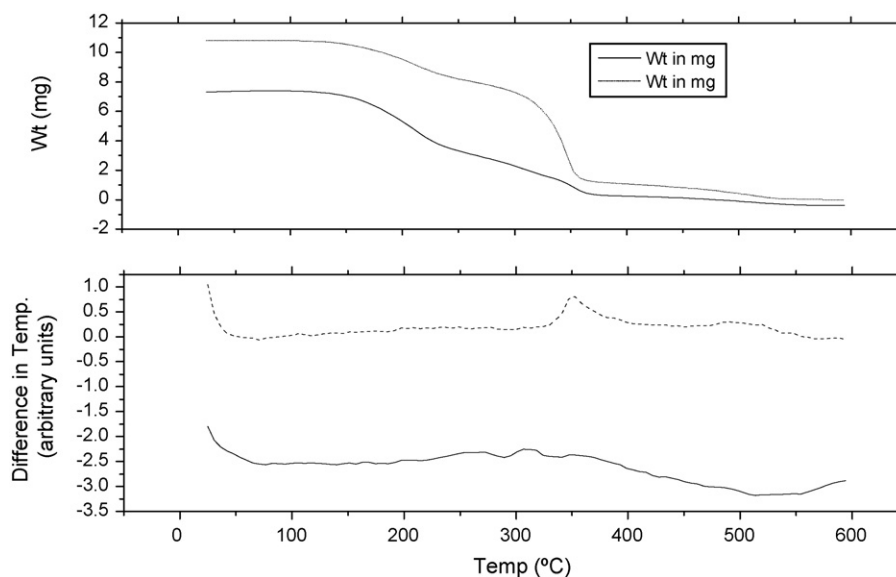


Fig. 4. Thermogravimetric analysis of the CTA–NPOE membrane (solid line) and CTA–NPOE–Crown ether membrane (dashed line). Upper: TG; lower: DTA.

Table 2

Permeability coefficients of Cs(I) transport for membranes using different plasticizers (200 μ l) along with physical parameters; membrane composition: 15.3% carrier–24.6% CTA–60.1% plasticizer; feed: 2 M HNO₃ containing ¹³⁷Cs tracer ($\sim 10^{-5}$ M); strip phase: distilled water.

Plasticizer	P (cm s ⁻¹)	Viscosity (cP)	Dielectric constant
NPOE	$(1.68 \pm 0.03) \times 10^{-5}$	13.8	24
TEHP	$(6.41 \pm 1.4) \times 10^{-6}$	10.2	–
TBP	$(8.07 \pm 0.11) \times 10^{-5}$	3.32	8.09
TBP ^a	$(2.77 \pm 0.07) \times 10^{-5}$	3.32	8.09

^a 100 μ l plasticizer was used.

finally liberation of the metal ion at the receiver phase. The plateau in the transport rates (as shown by the constant P values beyond DTBB18C6 concentration of 10 mg/ml) can also be partly due to ligand aggregation which is a common phenomenon with the crown ether carriers [28]. This observation is in sharp contrast to those by Fontàs et al. [29] who have explained the facilitated transport of metal ions on the basis of occurrence of liquid micro-domains where the carrier was solvated by the plasticizer, which at that stage acted as a solvating medium. Their suggestion of formation of the liquid micro-domains at higher carrier concentration in PIM though appears to enhance the facilitated transport with reagents such as Lasalocid A and Aliquat 336 as the carrier, which may in fact act in the opposite direction with crown ether carriers at higher ligand concentrations.

3.5. The role of plasticizer

The plasticizer is one of the most important components of the PIM and hence the nature of the plasticizer has a significant influence on the mass transfer rates. In order to understand this, membranes were prepared using a given concentration of different plasticizers, i.e., 2-nitrophenyloctylether, tris(2-ethylhexyl) phosphate (TEHP) and tri-*n*-butyl phosphate (TBP) while keeping the carrier as well as CTA concentration unchanged. Transport rate of Cs(I) from a feed of 1 M HNO₃ was monitored for 24 h using membranes made from various plasticizers and the measured permeability coefficient values are listed in Table 2. A reduction in the plasticizer concentration by 2 times had indicated a significant decrease in the P value suggesting the important role of the plasticizer in the preparation of the membrane. As seen from Table 2, TBP gave significantly higher transport rate as compared to NPOE, while TEHP was much inferior as a plasticizer. In view of this, the transport studies were carried out using the PIMs made with TBP as the plasticizer. While the transport rates were higher with the TBP-based PIMs, selectivity of such membranes as compared to the NPOE/TEHP based PIMs needed to be investigated.

According to the Stokes–Einstein equation,

$$D = \frac{kT}{6\pi r\eta} \quad (3)$$

the diffusion coefficient of the complex in the membrane is inversely proportional to the viscosity of the plasticizer present in the membrane phase, η , where k is the Boltzmann constant, T is the absolute temperature, and r is the radius of the complex molecule (assuming it to be spherical). On the other hand, the diffusion of the ion-pair species $[\text{CsL}]^+ \cdot [\text{NO}_3]^-$ is influenced by the dielectric constant of the medium. Table 2 lists the values of viscosity and dielectric constants of the plasticizers used in the present work. The diffusion of the complex in the membrane is mainly governed by the polarity of the plasticizer and probably to a lesser extent on the viscosity. Salazar-Alvarez et al. [30] showed that a PIM made without plasticizer had a reduced permeability and also indicated enhanced transport in the presence of the plasticizer. They had also reported that with increased plasticizer content, the permeability

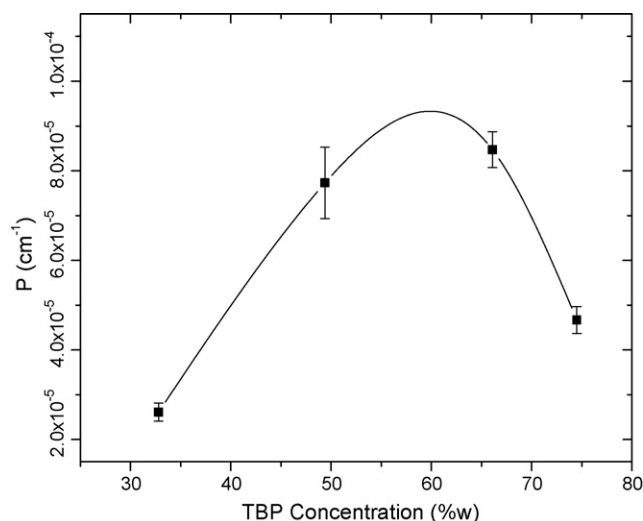


Fig. 6. Correlation between Cs(I) permeability coefficient (P) as a function of TBP concentration. [DTBB18C6]: 10 mg/ml. Feed: 1 M HNO₃; receiver: distilled water.

increased till a plateau was reached. They had proposed a carrier diffusion transport mechanism which also appears feasible for the present system.

3.6. Effect of TBP concentration

The plasticizer concentration has a positive influence on the transport rates of metal ions. Increasing the concentration of the plasticizer rendered enhanced mobility of the metal carrier complex resulting in an increase in the transport rates of the metal ions. In a detailed investigation, the plasticizer content in the membrane was varied from 32.8 wt.% to 74.5 wt.%. As seen in Fig. 6, the permeability coefficient initially increased with increasing TBP concentration from 32.8 wt.% ($P = (2.61 \pm 0.22) \times 10^{-5}$ cm s⁻¹) to 66.1 wt.% ($P = (8.47 \pm 0.42) \times 10^{-5}$ cm s⁻¹) but decreased thereafter up to the TBP concentration of 74.5 wt.% ($P = (4.67 \pm 0.31) \times 10^{-5}$ cm s⁻¹). It is ascribed to the relative decrease in the crown ether concentration and increase in the thickness of the membranes. Additionally, though greater plasticizer fraction can enhance transport rates due to less obstruction and high fluid content in the membrane phase, viscosity effects tend to affect them at even higher concentrations.

3.7. Optimization of membrane parameters

From the results of the above experiments, the membrane parameters are optimized for maximum Cs⁺ transport across the PIM. The transport rate increased with the crown ether concentration as well as TBP concentration (*vide supra*) and decreased with increasing CTA concentration (Fig. 7) which was due to an increase in the thickness of the resulting membrane. Though thinner membranes showed higher transport rates their mechanical stability was poor, especially so in the presence of dilute nitric acid. Based on all these aspects, the optimum concentrations of the three components for the subsequent experiments were arrived at as 24.6 wt.% CTA, 15.3 wt.% DTBB18C6 and 60.1 wt.% TBP. A comparison of different compositions along with the transport data is presented in Table 3.

3.8. Effect of feed acidity

The high level nuclear waste solution usually contains nitric acid in the concentration range of 1–3 M. It was of interest, therefore, to

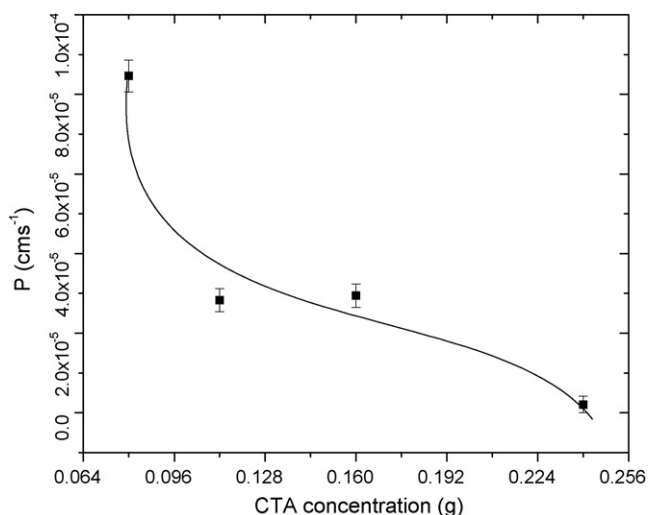


Fig. 7. Correlation between Cs(I) permeability coefficient (P) as a function of cellulose triacetate concentration. [DTBB18C6]: 10 mg/ml. Feed: 1 M HNO₃; receiver: distilled water.

investigate the transport rates as a function of nitric acid concentration. Transport of Cs(I) was investigated as a function of the feed nitric acid concentration in the range 0.5–3 M HNO₃ and the permeability coefficient is given in Table 4. The increase in the transport rate with nitric acid concentration is less significant at lower acidity as compared to that at higher acidity. Attempts to investigate the transport behaviour at 3 M HNO₃ medium were not successful as the membrane got ruptured after nearly 30 min of operation. It is ascribed to the acid hydrolysis of the CTA membrane. We have reported similar instability of the CTA membranes at higher acidities earlier [19]. Using 2 M HNO₃ as the feed, only about 62% Cs transport was observed. Though this is far below the quantitative transport required for Cs recovery from HLW, modifying the receiver phase to effect low acid transport can possibly enhance Cs transport.

Crown ethers are well-known scavengers of proton [31]. Due to favourable interaction with the hydronium ion, acid transport across the membrane and acid uptake by the membrane was also measured. It was found that apart from Cs trans-

Table 3
Optimization of membrane parameters for maximum Cs(I) transport.

CTA	DTBB18C6	TBP	$P \times 10^5$ (cm s ⁻¹)
24.2	15.2	60.6	8.07 ± 0.11
48.9	10.2	40.9	0.22 ± 0.02
26.7	6.7	66.4	2.94 ± 0.02
32.4	13.5	54.1	4.21 ± 0.17
39.8	11.7	49.5	7.70 ± 0.21*

Feed: 1 M HNO₃; receiver: distilled water.

* Though TBP fraction was least in this case, relatively higher transport was due to lower membrane thickness.

Table 4
Transport of Cs(I) and nitric acid as a function of the feed phase acidity.

HNO ₃ (M)	% Cs transport (24 h)	$P \times 10^5$ (cm s ⁻¹)	% H ⁺ transport (24 h)
0.5	4.23	0.61 ± 0.02	29.30
1.0	11.2	1.14 ± 0.21	29.79
1.5	37.4	4.49 ± 0.38	30.07
2.0	62.6	8.47 ± 0.42	29.65
3.0	3.35 ^a	–	–

PIMs used were having the composition 24.6 wt.% CTA, 15.3 wt.% DTBB18C6 and 60.1 wt.% TBP.

^a Data obtained after 30 min as membrane disintegrated.

port, significant amount of hydrogen ion was also transported across the membrane. Table 4 shows the amount of acid transported by the membranes during 24 h of operation. Surprisingly, in all cases, about 30% acid transport was observed. Our studies with Sr(II) transport using PIM containing and analogous crown ether ligand (DTBCH18C6 [19]) did not show the transport of acid to such a large extent. This is probably due to the transport of acid facilitated by TBP which is present at a significantly higher concentration as compared to the crown ether. In an experiment carried out using NPOE plasticized membrane, the acid transport decreased significantly to <3% in 20 h of operation.

In view of the instability of the membrane when the feed solution contained 3 M HNO₃, it was thought of interest to carry out transport studies with part neutralized acid solution. Therefore, a mixture of 2 M NaNO₃ + 1 M HNO₃ as well as 1 M NaNO₃ + 2 M HNO₃ was used as the feed solutions. However, in both these cases the transport rates were surprisingly low (<10%) even after 20 h of operation. This may be partially due to the complexation of the crown ether with the Na⁺ (present at >10⁵ times higher concentration as compared to Cs) which competes with the Cs⁺ ion. Though the complexation constant of Na⁺ with an 18-member crown ether ligand is much lower as compared to the corresponding complexation constant with Cs⁺ [26], the large excess of Na⁺ ion apparently affects the Cs⁺ ion transport rates. Interestingly, the effect of Na⁺ ion was to a much lower extent when Sr²⁺ transport was studied using an analogous membrane containing DTBCH18C6 (di-*tert*-butylcyclohexano-18-crown-6) as the carrier ligand.

3.9. Stability of the PIM

Transport experiments were carried out to evaluate the stability of the membranes. The experiments involved 30 ± 5 μm thick PIMs, containing 1 M as well as 2 M HNO₃ as the feed solutions and distilled water as receiver phase for 25 days. The PIM stability was reasonably good with 1 M HNO₃ as the feed, as the membrane could be used till 25 days without any significant change in the P values (±5% change). Stability with 2 M HNO₃ as the feed was reasonably good up to about 8 days of operation, after which there was membrane degradation. This is a significant improvement over the SLM instability reported by us earlier where the membrane stability was good only up to 24 h of operation [19]. In view of the higher stability of the PIM at 1 M HNO₃, these membranes can be used for acidic nuclear wastes containing lower acidity (for example, the Trombay HLW).

3.10. Studies with an irradiated U target solution

Our previous studies with PIM containing a Sr-selective crown ether have shown excellent selectivity for Sr²⁺ ion in the presence of fission products produced by neutron irradiation of a natural U target. Similar investigations were undertaken in the present study as part of the selectivity study. Though the fission products obtained by this method are of shorter half lives and are in much lower concentrations as compared to those present in the actual nuclear waste, they are used as true representatives as the chemistry remains the same. Most of the structural materials such as Fe, Cr, etc. were not used as their ionic sizes were not compatible with the cavity size of the crown ether used in the present work. The transport of various fission products along with that of Cs(I) (spiked with ¹³⁷Cs) was monitored at the end of 20 h. In two sets of experiments, the transport studies were carried out using TBP as well as NPOE plasticized membranes. Fig. 8 shows the gamma spectrum, of the results obtained using the TBP membrane, recorded by a HPGe detector connected to a multi channel analyzer. The high resolution gamma spectrum clearly showed that Cs(I) (as indicated

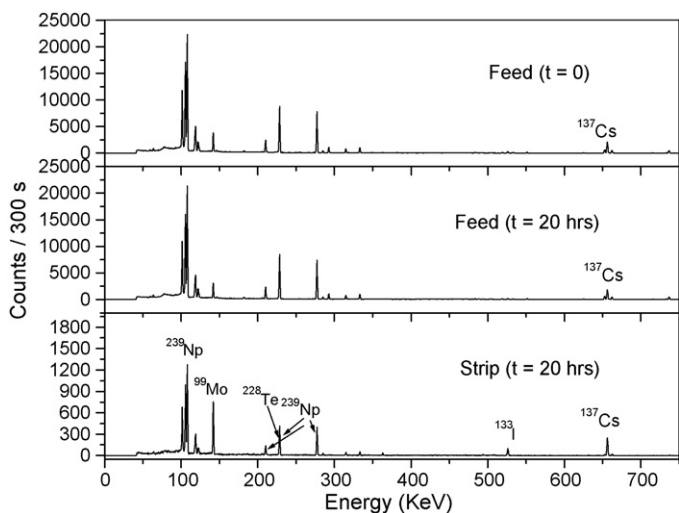


Fig. 8. High resolution gamma spectra of the feed and strip phases obtained using HPGe detector for the selectivity study. PIMs used were having the composition 24.6 wt.% CTA, 15.3 wt.% DTBB18C6 and 60.1 wt.% TBP. Feed: 1 M HNO₃; receiver: distilled water.

by the 661 keV gamma line) is not selectively transported as most of the other radionuclides also get transported. It is apparently due to the presence of TBP which extracts the solvated complexes of many other metal ions. In the second set of experiments, the PIM made from NPOE was used and the selectivity has improved significantly as evident from the high resolution gamma spectrum (Fig. 9). This indicated that though better transport rates are obtained with TBP as the plasticizer, for selective transport one needs to employ NPOE as the plasticizer.

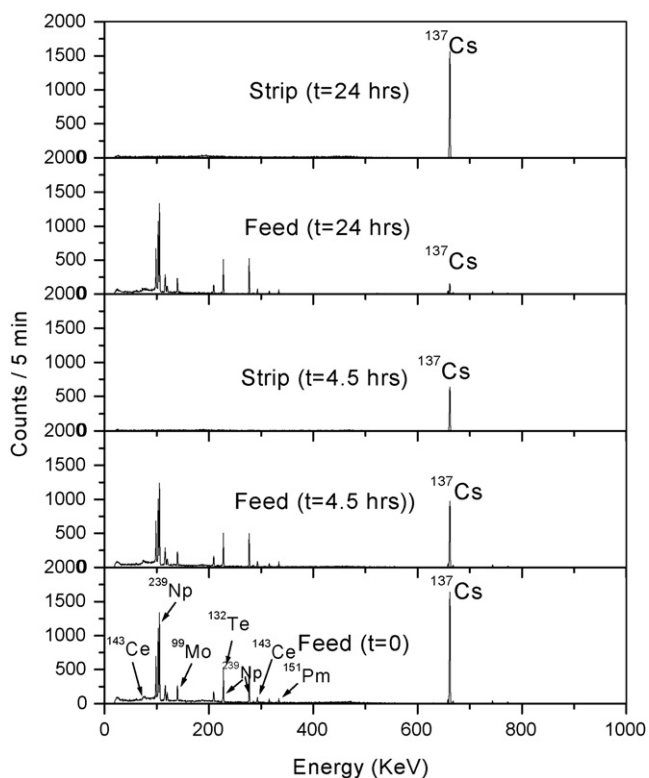


Fig. 9. High resolution gamma spectra of the feed and strip phases obtained using HPGe detector for the selectivity study. Plasticizer: NPOE. Feed: 1 M HNO₃; receiver: distilled water.

3.11. Analytical application

The present studies have indicated that though quantitative ¹³⁷Cs estimation is possible using the TBP plasticized membrane; selective pre-concentration of ¹³⁷Cs from a host of fission products is feasible using the NPOE plasticized membrane. This can certainly help the analysis of the ¹³⁷Cs activity in complex acidic radioactive wastes, such as the high level waste. Similar analytical application for ¹³⁷Cs analysis was reported by us using a calix-crown-6 ligand [32].

4. Conclusions

The plasticized polymeric membrane made from CTA, DTBB18C6 and TBP was efficient in transporting Cs from acidic solutions suggesting the applicability of this method as a viable option for radioactive waste remediation. The optimum concentrations of the three components were 24.6 wt.% CTA, 15.3 wt.% DTBB18C6 and 60.1 wt.% TBP. The stability of the membrane was good only for the feed at 1 M HNO₃, suggesting application of this membrane can be done for pre-concentration of radio-cesium from waste solutions of low acidity. However, selective pre-concentration requires utilization of membranes made from NPOE as the plasticizer.

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