



Cs(I) extraction / transport studies using irradiated calix [4]-bis 2,3-naphtho-crown-6

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ABSTRACT

Studies on the effects of irradiation of the Cs-selective extractant calix [4]-bis-2,3-naphtho-crown-6 (CNC) on its extraction as well as transport behaviour towards using acidic feed solutions has been investigated. While the extraction studies were carried out using a previously reported diluent composition of 50% toluene – 50% nitrobenzene, the transport studies were carried out using a diluent mixture of 20% n-dodecane – 80% 2-nitrophenyl octyl ether (NPOE). The transport studies were carried out using both polytetrafluoroethylene (PTFE) as well as polypropylene (PP) membrane filters. While an increase in the distribution ratio values for Cs were observed with the irradiated CNC, the transport studies indicated a decrease in the permeability coefficient values.

Keywords: Cesium; Calix-crown; Liquid membrane; Irradiation; Solvent extraction

1. Introduction

Removal of ^{137}Cs from high level waste (HLW) would not only facilitate its safe disposal in deep geological repository as vitrified mass, but also its application as a radiation source in gamma irradiators in the environmental pollution control, food preservation and sterilization of medical accessories, etc. [1,2]. It is, therefore, required to develop efficient separation methods for the recovery of ^{137}Cs from HLW.

A variety of methods based on precipitation, ion exchange and solvent extraction etc., have been reported in the literature for the recovery of ^{137}Cs . Liquid–liquid extraction methods based on the use of substituted cobalt dicarbonyl and crown ethers seems to offer good prospects for Cs recovery from acidic solutions [3,4]. Gerow et al. [4] have proposed the use of a mixture of TBP, dinonylnaphthalene sulphonic acid and kerosene

containing 0.05M bis-4,4'(5') [1-hydroxy-2-ethyl hexyl] benzo 18 crown 6 for the effective extraction of Cs from simulated waste solution. Dietz et al. [5] have carried out Cs extraction using various crown ethers in oxo solvents like alcohols, ketones, and carboxylic acids. Recent reports have indicated that calix-crowns are more efficient extractants for Cs(I) both from extraction efficiency as well as from selectivity point of view [6,7].

Calix-crown ligands, especially the bis-crown derivatives, have been used as complexing agents for the alkali/alkaline earth metal cations due to the presence of suitable pre-organized cavity in their frame work [6–11]. Calix[4]-bis-2,3-naphtho-crown-6 (CNC) was highly selective for Cs(I) cation over other alkali metal ions, making it possible to separate cesium from a solution containing 10^4 – 10^6 - fold higher concentration of Na(I) [12]. We have evaluated three commercial calix-crown ether ligands, viz. calix[4]arene-bis(crown-6) (CC), calix[4]arene-bis(o-benzocrown-6) (CBC) and calix[4]

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arene-bis(naphthocrown-6) (CNC) in nitrobenzene for effective Cs recovery from acidic solutions and observed that CNC was more efficient than the other two [13]. In another set of studies, CNC and its mixture with toluene was proposed for Cs recovery from high level waste [14]. Selective transport of ^{137}Cs from nitric acid feed solutions in to receiver solutions containing distilled water was also reported using CNC in 2-nitrophenyloctylether (NPOE) and n-dodecane mixture [15,16]. For both these studies, low concentration of the ligand CNC (2.5×10^{-3} M in nitrobenzene–toluene mixture for solvent extraction studies and 5×10^{-4} M in n-dodecane–NPOE mixture for transport studies) was required. However, it is of interest to understand the reusability, chemical and radiation stability of this reagent for its possible application in treatment of HLW.

The present study was taken up to investigate the effect of gamma irradiation on CNC with respect to its extraction (using 50% toluene–50% nitrobenzene as diluent) and transport (using 20% n-dodecane–80% NPOE) properties of Cs(I). All the studies were carried out after exposing the extractant to gamma irradiation as such and as its solution. Both solvent extraction and liquid membrane studies were carried out from the separation as well as the selectivity point of view.

2. Experimental

2.1. Materials

Calix[4]-bis-2,3-naphtho-crown-6 (.95, Fig. 1) was procured from Acros Organics, Belgium. The diluents nitrobenzene, n-dodecane, NPOE (2-nitrophenyl octyl ether) and toluene were of AR grade. Simulated HLW was supplied by WMD of BARC and its composition is represented in Table 1. The tracer ^{137}Cs was procured from Board of Radiation Isotope Technology (BRIT), India and was used after checking its radiochemical purity. Celgard-2500 PP membranes were obtained as a gift sample from Membrana, USA while the PTFE membranes were procured from Sartorius, Germany.

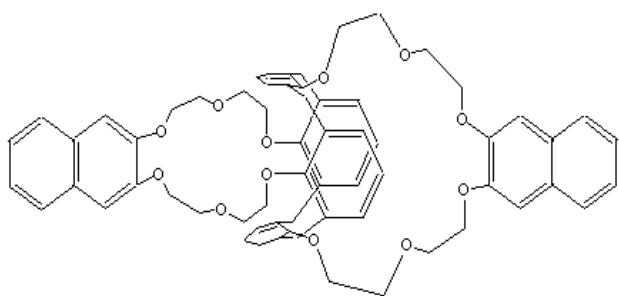


Fig. 1. Structural formula of calix [4]-bis-2,3-naphtho-crown-6 (CNC).

Table 1

Composition of a typical simulated high level waste (SHLW)

Metal ion	Concentration (g/L)
Na	5.500
K	0.224
Sr	0.031
Ba	0.064
Fe	0.720
Cr	0.119
Ni	0.107
Mn	0.426
Zr	0.004
Mo	0.137
Y	0.060
La	0.180
Ce	0.060
Cs	0.321
Pr	0.090
Nd	0.120
Sm	0.085
U	6.34
HNO_3	3.2 M

2.2. Irradiation studies

Irradiation was done in a gamma chamber at dose rate of 0.68 Rad/h (standardized by dosimetry experiments). The samples (both the ligand (CNC) and its solution in nitrobenzene–toluene mixture (1:1) and NPOE–n-dodecane mixture (4:1) were irradiated in glass vials for the requisite number of hours before carrying out the solvent extraction/transport experiments. The irradiation studies were carried out with an absorbed dose in the range of 5–100 MRad.

2.3. Solvent extraction studies

Solvent extraction experiments were performed by equilibrating equal volumes of organic and aqueous phases, i.e. with a volume ratio of 1, in stoppered glass tubes in a thermostated bath at $25 \pm 1^\circ\text{C}$. Usually, about 5000 cps activity was taken in an equilibration tube containing 1 mL organic and 1 mL aqueous phase. The distribution ratio value was defined as the ration of Cs-activity per unit volume in the organic phase to that in the aqueous phase.

2.4. Transport studies

Transport studies were carried out using a method reported earlier [17]. Celgard 2500 PP micro porous membrane filter containing the carrier solution (usually, 5.0×10^{-4} M CNC in 20% n-dodecane + 80% NPOE) was

interspersed between the feed and strip compartments (both of 20 mL capacity). Usually, the feed compartment contained 3.0 M HNO₃ while the strip solution was distilled water.

The permeability coefficients were calculated using the following equation:

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

where $C_{f,t}$ and $C_{f,0}$ are the concentrations of metal ion in the feed side at a given time interval and at the start of the experiment, respectively. Q is the effective membrane area, V is the volume of the feed solution in cm³ and t is the permeation time. The cumulative percentage transport (% T) at a given time is determined by the following equation:

$$\%T = 100 \cdot C_{s,t} / C_{f,0} \quad (2)$$

where $C_{s,t}$ is the concentration of the metal ion in the strip at a given time interval

Analysis of ¹³⁷Cs was carried out by radiometry employing NaI(Tl) scintillation detector. Reproducibility of the results was within ±5%.

3. Results and discussion

3.1. Solvent extraction studies

White et al. studied the irradiation stability of the CSSX (caustic side solvent extraction) solvent which contained 0.01 M calix[4]arene-bis(tert-octylbenzocrown-6) in 0.5 M 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol and 1.0×10⁻³ M tri-*n*-octylamine (used as modifier) in Isopar L up to a dose of 50 MRad and found it satisfactory [18]. On the other hand, Jankowski et al. have observed >90% degradation of calix-crowns in NPOE when irradiated (up to 300 MRad) in contact with nitric acid which decreased to about 50% in the absence of nitric acid [19]. Our earlier studies on solvent extraction of Cs(I) from HLW involved 2.5×10⁻³ M CNC + 0.4% alamine 336 in 50% toluene + 50% nitrobenzene as the solvent which yielded D_{Cs} values of 2.5 and 8.3 for simulated high level waste (HLW) and 3 M HNO₃, respectively [14]. The effect of varying irradiation dose on Cs(I) extraction was investigated in the present work using the same solvent at varying dose and the distribution data with 3 M HNO₃ as the feed are shown in Fig. 2.

It is evident that the D_{Cs} values showed an irregular trend, but an overall increase is observed from 0 to 100 MRad dose. Nearly 5 times increase in the D_{Cs} value was observed at 50 MRad but it decreased thereafter. Studies on Cs extraction with SHLW were also carried out and a comparison of results is presented in Table 2. The D_{Cs} value increased to >3 times for the irradiated CNC as compared to the unirradiated reagent. This is rather surprising and appears promising for long term reusability

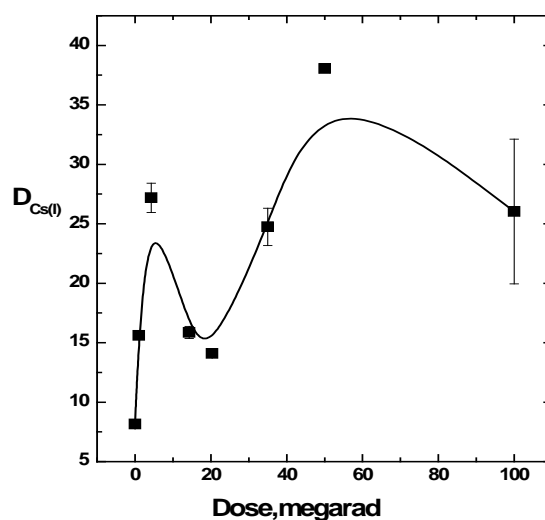


Fig. 2. Effect of gamma irradiation dose (MRad) on Cs(I) extraction using CNC.

Table 2

Comparison of D_{Cs} data with irradiated and unirradiated CNC. Diluent: 50% toluene + 50% nitrobenzene + 0.4 vol.% alamine 336

Unirradiated CNC	D_{Cs}	Irradiated CNC	D_{Cs}
3.0 M HNO ₃	8.91	3.0 M HNO ₃	26.2
SHLW	2.53	SHLW	8.72

of the reagent. Stripping studies were also carried out using the irradiated CNC solution in toluene–nitrobenzene mixture and found to be satisfactory.

3.2. Liquid membrane studies

Our previous studies on the liquid membrane transport of Cs from nitric acid feed solution using flat sheet membranes have indicated that nitrobenzene has poor stability and NPOE was an acceptable diluent in spite of its higher viscosity [15]. In addition, a mixture of NPOE and *n*-dodecane was reported to improve the transport efficiency [16]. Therefore, the effect of irradiation on the carrier solvent used for the flat sheet liquid membrane studies was investigated. For comparison purpose, the solvent extraction data using this diluent mixture is also reported in this paper.

Liquid membrane studies were also carried out using irradiated CNC and the carrier solvent contained 5×10⁻⁴ M CNC (irradiated to varying extent) in 20% *n*-dodecane + 80 NPOE mixture. As mentioned earlier, this solvent when impregnated into the pores of flat sheet membranes resulted in very high selectivity and stability of the membrane [16]. However, for long term application of

the liquid membrane technology, not only the irradiation stability of the membrane is needed to be evaluated, but also that of the carrier solvent is also extremely important. The present studies include the transport data obtained after using irradiated CNC in 20% n-dodecane + 80 NPOE mixture as the carrier in both PP and PTFE flat sheets. The feed was 3.0 M HNO₃ while the receiver phase was distilled water according to our previous report.

When the transport studies were carried out with unirradiated membranes, the transport rate was faster with PP membranes as compared to the PTFE flat sheets (Tables 3 and 4). Co-transport of nitric acid was also observed in both cases and was found to be 4.7% and 2.5% for the PP and PTFE membranes, respectively. As the wettability of the PP membranes was better as compared to the PTFE membranes, the diffusivity of the ligand as well as that of the complex is expected to be superior in case of the former.

The irradiated CNC when used in the carrier solvent resulted in an overall decrease in the transport rates with both PP (Fig. 3) and PTFE (Fig. 4) membranes. However, a closer look at the transport data indicates that after an absorbed dose of 5 MRad, the transport rates show an increase. This was also observed in case of the solvent

Table 3

Transport data with irradiated and unirradiated 5.0×10⁻⁴ M CNC in 20% n-dodecane + 80% NPOE as the carrier solvent. Support: PP flat sheet

Absorbed dose	D_{Cs}	$P \times 10^4$ (cm/s)	% T in 24 h	
			Cs	Acid
0	2.43	0.884 ± 0.05	89.89	4.73
5	4.47	1.465 ± 0.05	90.92	4.68
10	2.61	0.728 ± 0.02	66.24	5.79
20	3.66	0.891 ± 0.02	70.46	4.53
50	2.81	0.636 ± 0.03	80.75	8.39
98	2.43	0.546 ± 0.01	59.73	5.24

Table 4

Transport data with irradiated and unirradiated 5.0×10⁻⁴ M CNC in 20% n-dodecane + 80% NPOE as the carrier solvent. Support: PTFE flat sheets

Absorbed dose	D_{Cs}	$P \times 10^4$ (cm/s)	% T in 24 h	
			Cs	Acid
0	2.43	0.63 ± 0.06	55.7	2.53
5	4.47	1.34 ± 0.05	78.8	5.06
10	2.61	1.14 ± 0.05	62.2	3.42
20	3.66	1.31 ± 0.02	70.2	2.03
50	2.81	0.95 ± 0.03	77.0	2.85
100	2.43	1.08 ± 0.02	81.5	2.06

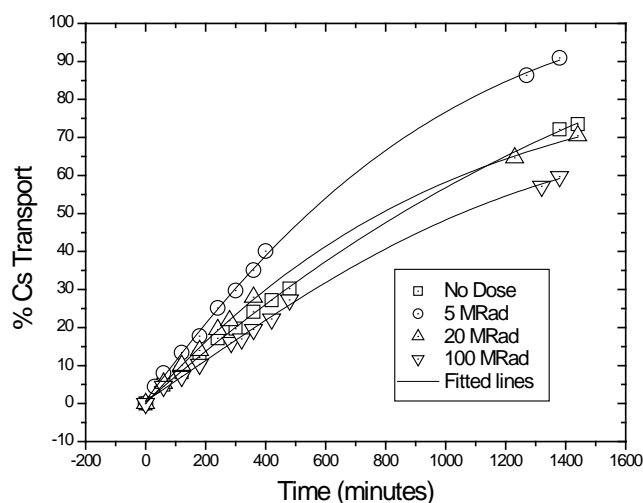


Fig. 3. Effect of gamma irradiation dose (MRad) on Cs(I) transport rates using PP membranes. Carrier: 5.0×10⁻⁴ M CNC in 20% n-dodecane + 80% NPOE; Feed: 3.0 M HNO₃; Strip: distilled water.

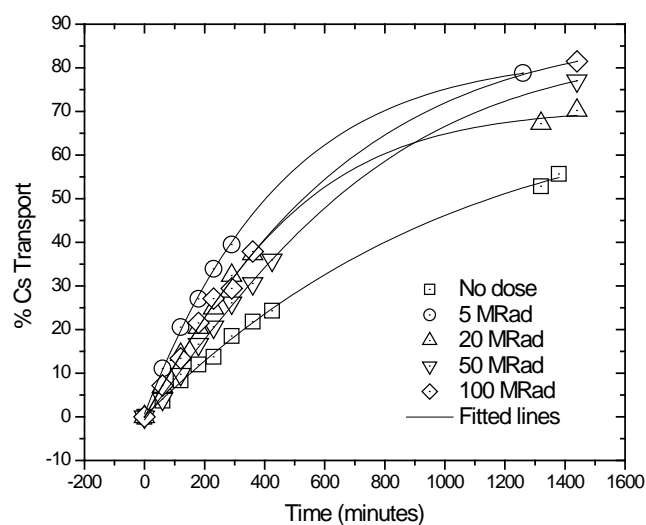


Fig. 4. Effect of gamma irradiation dose (MRad) on Cs(I) transport rates using PTFE membranes. Carrier: 5.0×10⁻⁴ M CNC in 20% n-dodecane + 80% NPOE; Feed: 3.0 M HNO₃; Strip: distilled water.

extraction studies carried out using 5.0×10⁻⁴ M CNC in 20% n-dodecane + 80% NPOE diluent mixture as the organic phase (Table 3).

In the case of PP membranes, the permeability coefficients expectedly increased after an irradiation up to 5 MRad beyond which no regular trend was observed (Table 3). The acid transport showed an increasing trend with increasing absorbed dose. In the case of PTFE membranes, an increase in the D_{Cs} , transport rate, permeability coefficient as well as acid transport were observed for the

case where CNC irradiated to 5 MRad dose was used as compared to the unirradiated ligand. With increasing absorbed dose up to 100 MRad, the Cs transport rate showed an overall increase while acid transport decreased. This suggested that PTFE membranes can be used for better Cs transport and poor acid co-transport as compared to the polypropylene membranes, thereby resulting in a more efficient transport process with increasing absorbed dose.

It remains to be seen, however, whether properties of the extractant such as loading characteristics and selectivities are not significantly affected by irradiation.

4. Conclusions

The extraction behaviour of the irradiated solvent containing 2.5×10^{-3} M CNC + 0.5% alamine 336 in toluene–nitrobenzene mixture (1:1) did not get affected by the irradiation dose to the extent to give lower D_{Cs} values as compared to unirradiated solvent mixture from acidic medium. On the contrary, several fold increase in the D_{Cs} values at 50 MRad absorbed dose have suggest long term recycling and reusability of the solvent. SLM data indicated that PTFE is a better choice as support as compared to PP for use with the irradiated solvents (5×10^{-4} M CNC in n-dodecane–NPOE mixture (1:4).

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