A new ion selective electrode for cesium (I) based on calix[4]arene-crown-6 compounds

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ABSTRACT

A polyvinylchloride (PVC) based liquid membrane ion selective electrode (ISE) for cesium has been developed. 25,27-Dihydroxycalix[4]arene-crown-6 (L1), 5,11,17,23-tetra-tert-butyl-25,27-dimethoxycalix[4]arene-crown-6 (L2) and 25,27-bis(1-octyloxy)calix[4]arene-crown-6 (L3) were investigated for their use as ionophores. The cation exchange resin DOWEX-50W was used to maintain low activity Cs^+ in inner filling solution to improve the performance. The best response for cesium was observed with L3 along with optimized membrane constituents and composition. Excellent Nernstian response (56.6 mV/decade of Cs(I)) over the concentration range 10^{-7} to 10^{-2} M of Cs(I) was obtained with a fast response time of less than 10 s. Detection limit for Cs(I) using the present ISE is 8.48×10^{-8} M Cs(I). Separate solution method (SSM) was applied to ascertain the selectivity for Cs(I) over alkali, alkaline earth and transition metal ions. The response of ISE for Cs(I) was fairly constant over the pH range of 4–11. The lifetime of the electrode is 10 months which is the highest life for any membrane based Cs-ISE so far developed. The concentration of cesium ion in two simulated high level active waste streams was determined and results agreed well with those obtained independently employing AAS.

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1. Introduction

Determination of trace amounts of cesium is important from many angles. Due to toxicity of cesium and its ability to displace potassium from muscles and red blood cells, its concentration in environment needs to be ascertained. Also, since nuclear power is an important energy source, many nuclear reactors have been installed throughout the world. The spent fuel from the reactors is reprocessed to recover U and Pu. Safe storage/disposal of radioactive wastes, generated in this process [1] is an important issue. In the context of nuclear waste management, removal of ^{137}Cs from medium and low level nuclear wastes gained importance, because it is one of the major radionuclides responsible for MANREM problems. For this, the extent of removal of ^{137}Cs needs to be ascertained by measuring the concentration of Cs. While radioactivity counting techniques based on gamma spectrometry offer a very sensitive measurement option, they cannot be deployed for measuring stable isotopes of Cs. Also measurement of the radioactivity may not also

be possible to all researchers. The other sensitive techniques such as atomic absorption spectroscopy (AAS) and fluorescence technique [2] used to determine Cs ions involves expensive instrumentation and cost of operation. Thus, it would be ideal to have a measurement technique which is reasonably sensitive, easily portable, and can measure stable cesium isotopes also.

One approach that offers rapid and reliable measurements in aqueous environments is the use of polymeric membrane ion selective electrodes (ISEs). Typically ISEs are composed of a highly selective ionophore, incorporated in a polyvinylchloride (PVC) matrix, plasticized with suitable plasticizer and a tetraphenylborate type ion exchanger. The measurement range of conventional membrane-based ISEs lies between 1 and 10^{-6} M. Extensive research has revealed that more than the ionophore, it is the small flux of primary ions from the organic sensing membrane into its aqueous surface layer, influences the detection limit. The composition of inner filling solution (IFS) of the ISEs is crucial, because it is the most important source of these fluxes due to the enhanced co-extraction or ion exchange processes at the inner solution/membrane interface. In addition to restricting attainment of lower DL, the trans-membrane ion fluxes also affect the potential measurement of solutions of even strongly discriminated pure ions. This reduces the ionophore-based selectivity of the ISEs, and the determined selectivity coefficients

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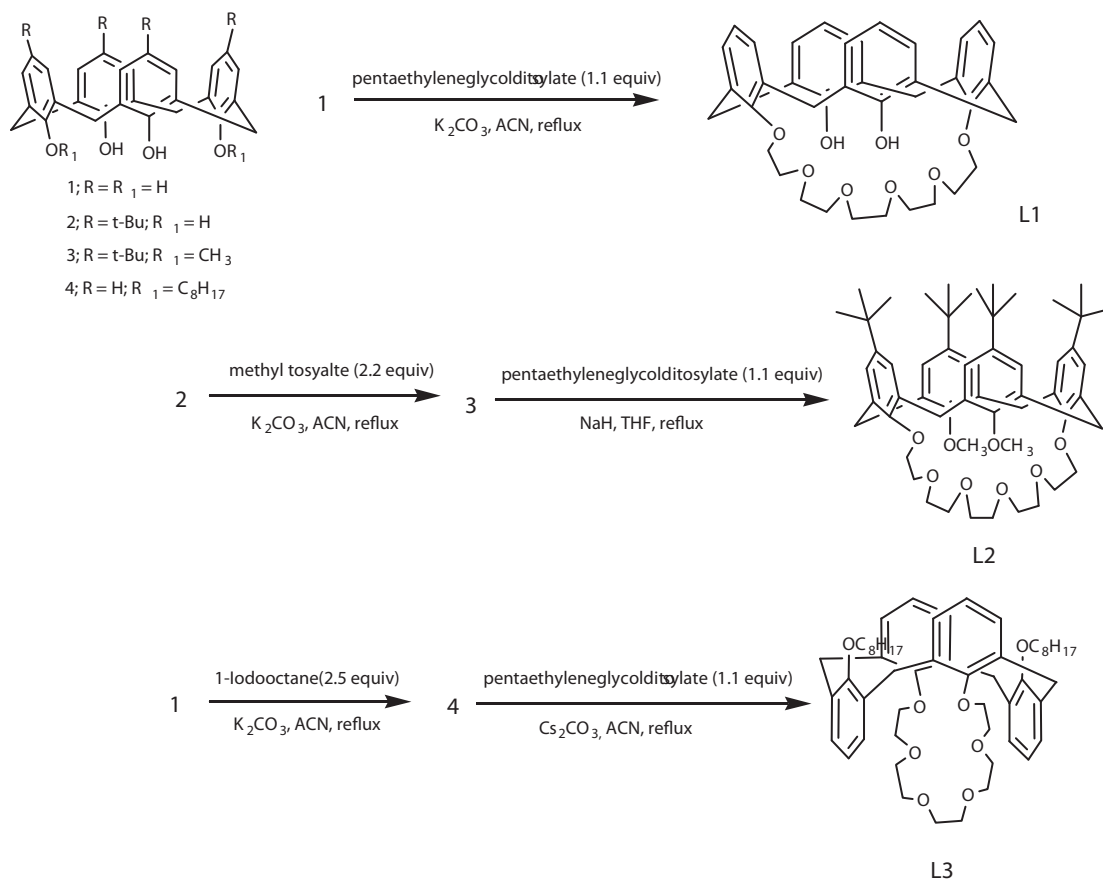(K.L. Ramakumar).

Fig. 1. Scheme of the synthesis of ionophores L1, L2 and L3 and their structures.

represent upper limits rather than the true (thermodynamic) values [3].

In recent years, the DLs and selectivity coefficients of several known ISEs have been improved by several orders of magnitude by introducing novel and non-classical response principles [4,5]. The minor ionic fluxes across the membrane, contaminating the sample solution in contact with the sensing membrane could be eliminated by employing non-equilibrium conditions with engineered concentration gradients [6] or external current [7,8]. This led to ISEs with much lower (nano- and picomolar) DLs. In view of this, a recent IUPAC technical report [9] emphasized the need for updated or refined IUPAC recommendations of performance evaluation criteria for preparation and measurement of macro and microfabricated ion selective electrodes. Use of strong chelating agents [10,11] or ion-exchangers [12] in the IFS set a very low primary ion concentration in the IFS and preclude the primary ion leaching toward the sample. Hence this approach is strongly recommended to improve the DLs and selectivity coefficients of ISEs. Although used initially, internal solutions with ion buffers (e.g., EDTA) are unsuitable for quantifying cations such as alkali metals and ammonium ions as well as many anions for which no appropriate complexing agents are available. Ion exchangers are best option for these ions.

Overall, the choice of ionophores and IFS play a crucial role in the performance of any ISE. A diverse range of molecular architectures including crown ethers [13,14], calix[4]arenes [15–20], thiacalix[4]arenes [21,22], calix[6]arenes [23,24], zeolite and acetonitrile compounds [25–27] has been used to design neutral Cs(I)-selective ionophores. Of these, the calixarenes are widely regarded as an important class of macrocyclic host molecules. The structural and electronic features in them allow a three

dimensional control of metal ion-selective complexation and efficient binding. Sachleben et al. used various dialkyloxycalix[4]arene-crown-6 compounds to study their selectivity in solvent extraction of cesium ions over other alkali ions [28]. Simon et al. reported good separation efficiency and selectivity for extracting cesium ions over other alkali metals (especially sodium) ions from acidic high level active waste [29].

The Cs-selective ISEs, available or reported in literature have limited lifetime, at best a couple of months only. Based on our own requirement, we were interested in developing an ISE for Cs(I) with a reasonably long life so that it can be used to determine Cs ions in nuclear waste streams where the Na ions concentration is very high. Earlier, we developed a Cs-ISE with 5-(4′-nitrophenylazo)25,27-bis(2-propyloxy)26,28-dihydroxycalix[4]arene as the ionophore that showed only a moderate Cs/Na selectivity coefficient ($\log K_{Cs,Na} = -3.13$) [20]. Using Dowex-C-350 as the cation exchange resin, Radu et al. [30] developed an ISE to detect cesium ions at nanomolar level. However, the resin is commercially unavailable, restricting the practical application of the Cs-ISE.

Hence, in the present studies, we used three different calix[4]arene-crown-6 compounds, viz. 25,27-dihydroxycalix[4]arene-crown-6 (L1), 5,11,17,23-tetra-tert-butyl-25,27-dimethoxycalix[4]arene-crown-6 (L2) and 25,27-bis(1-octyloxy)calix[4]arene-crown-6 (L3) as the ionophores to develop PVC based membrane electrodes for the Cs⁺ ions. The inexpensive commercial cation exchange resin, Dowex-50W was used as the IFS to maintain low and constant activity of Cs(I). The plasticizers and ion additives were also varied to optimize the membrane composition for obtaining the best performance for the Cs(I) ions.

2. Experimental

2.1. Instrument

The Orion model 720A potentiometer was used to measure the potentials and pH. The Orion double junction Ag/AgCl (model 9002) was used as the reference electrode. A pH electrode (Eutech instruments, Singapore) was used to measure the pH of the solution.

2.2. Ionophores, membrane components and chemicals

Scheme of the synthesis of all ionophores L1, L2 and L3 and their structures are given in Fig. 1.

2.2.1. Synthesis and characterization of L1

To a suspension of calix[4]arene (**1** (Fig. 1), 0.85 g, 2 mmol) and K_2CO_3 (0.69 g, 5 mmol) in acetonitrile (30 ml), pentaethyleneglycol di(*p*-toluenesulfonate) (1.20 g, 2.2 mmol) was added and the mixture was refluxed (10 h). After completion of the reaction (monitored by TLC), acetonitrile was removed and the pale yellow mass was quenched with ice-water, acidified with aqueous 1N HCl and extracted with chloroform (3×15 ml). The organic layer was washed with water, brine and dried (Na_2SO_4). Solvent was removed to get a thick oil which was recrystallized from chloroform/hexane to get pure 25,27-dihydroxy-calix[4]arene-crown-6 (**L1**) (0.514 g, 41%).

25,27-Dihydroxy-calix[4]arene-crown-6 (**L1**): colorless solid, mp 221–222 °C (mp 224–225 °C [31]); IR (neat): ν 3358 (OH) cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.42 (s, 2 H), 7.09 (d, *J* = 7.6 Hz, 4 H), 6.82 (d, *J* = 7.6 Hz, 4 H), 6.71 (t, *J* = 7.6 Hz, 2 H), 6.65 (t, *J* = 7.6 Hz, 2 H), 4.45 (d, *J* = 13.1 Hz, 4 H), 3.70–4.15 (m, 20H), 3.38 (d, *J* = 13.1 Hz, 4 H); ^{13}C NMR (50 MHz, CDCl$_3$): δ 153.3, 152.1, 133.1, 128.2, 129.0, 128.5, 125.3, 118.9, 76.4, 71.6, 71.0, 69.9, 31.1.

2.2.2. Synthesis and characterization of L2

A suspension of 4-*tert*-butyl-calix[4]arene (**2** (Fig. 1) 1.30 g, 2 mmol), K_2CO_3 (0.304 g, 2.2 mmol) and methyl tosylates (0.782 g, 4.2 mmol) in acetonitrile (30 mL) was refluxed (12 h) when TLC showed complete consumption of calix[4]arene. Acetonitrile was removed and the yellow mass was quenched with ice-water, acidified with aqueous 1N HCl and extracted with chloroform (3×15 ml). The organic layer was washed with water, brine and dried (Na_2SO_4). Solvent was removed to get a thick oil which was recrystallized from chloroform/methanol to get pure 25,27-dimethoxy-26,28-dihydroxy-4-*tert*-butyl-calix[4]arene (**3** (Fig. 1)) (0.74 g, 55%).

A mixture of **3** (0.68 g, 1.00 mmol) and NaH (0.22 g, 9 mmol) in dry THF (100 ml) was heated under reflux (0.5 h). It was cooled to ambient temperature and a solution of pentaethyleneglycol di(*p*-toluenesulfonate) (0.60 g, 1.1 mmol) in THF (10 mL) was added drop wise. The reaction mixture was refluxed for 10 h when TLC showed completion of the reaction. Then THF was removed and the thick mass was quenched with water, acidified with 1N aqueous HCl and extracted with chloroform. The organic layer was washed with water, brine and dried (Na_2SO_4). The solvent was removed under vacuum to leave an off-white residue which was purified by silica gel chromatography (gradient elution with hexane-THF mixture) to afford a colorless solid which was recrystallized from chloroform/methanol to get pure crystals of crystals of 25,27-dimethoxy-4-*tert*-butyl-calix[4]arene-crown-6 (**L2**) (0.41 g, 47%).

25,27-Dimethoxy-4-*tert*-butyl-calix[4]arene-crown-6 cone (**L2**) [32]: colorless solid; mp 252–253 °C; IR (neat): ν 2960 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.12 (s, 4 H), 6.45 (s, 4 H), 4.40 (d, *J* = 13.0 Hz, 4 H), 4.1–4.3 (m, 26 H), 3.13 (d, *J* = 13.0 Hz, 4 H), 1.35 (s, 18 H), 0.80 (s, 18 H).

2.2.3. Synthesis and characterization of L3

A suspension of **1** (Fig. 1) (1.27 g, 3.00 mmol), K_2CO_3 (1.04 g, 7.5 mmol) and 1-iodooctane (2.16 g, 9.0 mmol) in acetonitrile (40 mL) was refluxed (5 d) when TLC showed complete consumption of calix[4]arene. Acetonitrile was removed and the yellow mass was quenched with ice-water, acidified with aqueous 1N HCl and extracted with chloroform (3×15 ml). The organic layer was washed with water, brine and dried (Na_2SO_4). Solvent was removed to get a thick oil which was recrystallized from hexane to get pure 25,27-dioctyloxycalix[4]arene (**4** (Fig. 1)) (1.02 g, 52%).

A mixture of **4** (Fig. 1) (0.65 g, 1.00 mmol), Cs_2CO_3 (0.98 g, 3 mmol) and pentaethyleneglycol di(*p*-toluenesulfonate) (0.6 g, 1.1 mmol) in acetonitrile (30 mL) was refluxed for 16 h when TLC showed completion of the reaction. Then acetonitrile was removed and the thick mass was quenched with water, acidified with 1N aqueous HCl and extracted with chloroform. The organic layer was washed with water, brine and dried (Na_2SO_4). The solvent was removed under vacuum to leave an off-white residue which was purified by silica gel chromatography (gradient elution with hexane–THF mixture) to afford a colorless solid which was recrystallized from chloroform/methanol to get pure crystals of crystals of 25,27-bis(1-octyloxy)-calix[4]arene-crown-6, 1,3-alternate (**L3**) (0.38 g, 45%).

25,27-Bis(1-octyloxy)calix[4]arene-crown-6, 1,3-alternate (**L3**): colorless solid; yield 45%; mp 92–93 °C (mp 94–95 °C [31]); IR (KBr): ν 3008, 2926, 1458, 1216, 667 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.00 (d, 4H, *J* = 7.5 Hz), 6.93 (d, 4H, *J* = 7.5 Hz), 6.66–6.80 (m, 4H), 3.70 (s, 8H), 3.63 (s, 4H), 3.49–3.60 (m, 8H), 3.29–3.44 (m, 12H), 1.11–1.21 (m, 24H), 0.85 (t, 6H, *J* = 6.8 Hz); ^{13}C NMR (CDCl$_3$, 50 MHz): δ 156.9, 156.4, 133.9, 133.6, 129.7, 129.5, 122.0, 71.1, 71.0, 70.9, 70.5, 69.8, 37.8, 31.8, 29.6, 29.3, 25.8, 22.6, 14.0.

2.2.4. Other membrane components

The other membrane components, 2-nitrophenyl octyl ether (oNPOE), potassium tetrakis (perchlorophenyl) borate (KTpClPB), and high molecular weight polyvinylchloride were procured from Fluka, Switzerland. Bis(2-ethylhexyl) sebacate (DOS, BDH, UK), sodium tetraphenyl borate (NaTPB, Merk, India), and tetrahydrofuran (THF, G-Merk, Germany) were also used. AR grade CsCl, RbCl, KCl, NaCl, SrCl$_2$, BaCl$_2$, MgCl$_2$, CaCl$_2$, NH$_4$NO$_3$, Pb(NO$_3$)$_2$, Ce(NO$_3$)$_3$, CuSO$_4$, ZnSO$_4$, NiSO$_4$, HCl, and NaOH were used as such, when required. The standard CsCl solution was prepared using the salt, heated at 383 K for 2 h followed by cooling in a desiccator. High purity de-ionized water, obtained from milli Q academic apparatus (Millipore, India) was used to prepare all solutions and dilutions.

2.3. Membrane composition and electrode fabrication

The composition of PVC matrix membrane was ~1.0 wt% ionophore, ~33 wt% PVC, ~65.5 wt% plasticizer, and ~0.5 wt% KTpClPB as the ion additive. The components were dissolved in 6.0 ml of freshly distilled THF by stirring for 10 min with a magnetic stirrer. The solution was homogenized in an ultra-sonic bath for 10 min, and poured into a 5.0 cm inner diameter Petri dish. On gradual evaporation of THF at room temperature for 48 h, a transparent membrane was obtained. The resulting membrane was gently peeled off from the Petri dish and a disc of 7 mm diameter was cut out using a punch borer. This membrane was attached to an ion selective electrode body (Fluka, cat. No. 45137). Keeping the same membrane composition, various ISEs were made with different ionophores, plasticizers and different amounts of ion additive, as detailed in Table 1.

Table 1
Comparison of response of ISE with different ionophores, plasticizers and amount of ion additive.

	ISE no.								
	ISE 1	ISE 2	ISE 3	ISE 4	ISE 5	ISE 6	ISE 7	ISE 8	ISE 9[a]
Ionophore	L1	L1	L2	L2	L3	L3	L3	L3	L3
Plasticizer	oNPOE	DOS	oNPOE	DOS	oNPOE	DOS	oNPOE	oNPOE	oNPOE
Ion additive (mol%)	50	50	50	50	50	50	40	30	40
Linear range	10^{-5} to 10^{-2}	10^{-5} to 10^{-2}	5×10^{-6} to 10^{-2}	10^{-5} to 10^{-2}	5×10^{-7} to 10^{-2}	10^{-6} to 10^{-2}	10^{-7} to 10^{-2}	5×10^{-7} to 10^{-2}	10^{-5} to 10^{-2}
Nernstian slope (mV/decade of Cs)	55.8	50.3	53.3	53.7	57.0	55.6	56.3	57.3	55.8
DL	3.72E−6	4.46E−6	3.16E−6	3.54E−6	2.82E−7	8.62E−7	8.48E−8	3.9E−7	5.45E−6

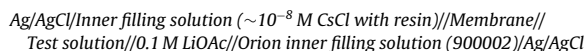[a] Inner filing of this ISE is 10^{-3} M CsCl.

2.4. Inner filling solution preparation

About 5 g of the cation exchange resin Dowex-50W (H$^+$ form), taken in a glass beaker was equilibrated with aqueous NaOH (50 ml, 1 M) for about 14 h under constant stirring. The resulting Na$^+$ form of resin was washed several times with deionized water, and air dried for about 48 h. The air-dried resin was wrapped in tissue paper and kept in a desiccator for 24 h to remove traces of moisture. With a view to optimize the amount of resin required and also determine the equilibrium concentration of Cs, it was necessary to determine the selectivity of this resin for Cs ions over Na ions ($K_{Cs,Na} = m_{cs,resin} \times m_{Na,aq}/m_{Na,resin} \times m_{cs,aq}$, where m is content of ion in moles) [12]. For this, an aqueous CsCl solution (5 ml, 6.0×10^{-3} M) was added to the dry resin (0.2160 g) in Na-form, and the mixture stirred for about 12 h. The Cs ion concentration in the equilibrated solution was determined with ISE 9 (for composition see Table 1) and was found to be 1.32×10^{-4} M. From this and the cation exchange capacity of the resin as 5.6 meq/g, the $K_{Cs,Na}$ was calculated as 148. Subsequently, the inner filling solution was prepared by equilibrating dry Na-form of the resin (1.0730 g) with an aqueous CsCl solution (6.0×10^{-4} M, 25 ml) for 12 h. The Cs ion concentration in the equilibrated solution was found to be less than 10^{-7} M. After filling this solution along with the resin as an inner filling solution, the ISE was conditioned with 10^{-7} M CsCl for 24 h.

2.5. EMF measurement

All measurements were carried out at room temperature (295 ± 1 K). The potential was measured under constant stirring of the test solution with respect to double junction Orion Ag/AgCl reference electrode (cat. No. 9002), with Orion inner filling solution (cat. No. 900002) and 0.1 M lithium acetate (LiOAc) as the outer filling solution.

The cell configuration was

Ag/AgCl/Inner filling solution ($\sim$10^{-8} M CsCl with resin)//Membrane//
   Test solution//0.1 M LiOAc//Orion inner filling solution (900002)/Ag/AgCl

The activities of Cs(I) were calculated according to the Debye–Huckel procedure, using the following equation [33]

$$\log \gamma = -0.511 z^2 \left[\frac{\mu^{1/2}}{1 + 1.5 \mu^{1/2}} - 0.2 \mu \right] \tag{1}$$

where γ is the activity coefficient and μ the ionic strength of the solution and z is the valency of the ion.

2.6. Measurements at different pHs

To study the effect of pH on response of ISE for Cs(I), the EMF was measured with ISE 7. Aliquots (3.0 ml) of CsCl solution (10^{-1} M) were taken and diluted with de-ionized water (20 ml). The pH of each solution was adjusted in the range 2–12 by adding appropriate amounts of dilute aqueous HCl and NaOH solutions and made final concentration of Cs(I) as 10^{-2} M. Similar solutions of CsCl (10^{-4} M) were also made at different pH and the response was measured.

2.7. Determination of Cs(I) concentration in simulated nuclear waste solutions

For these experiments, the data of the compositions of Indian pressurized heavy water reactor (PHWR) fuel reprocessing waste, operated for 6700 MWD/ton was prepared by the waste immobilization plant (WIP), BARC, Mumbai, India. Two types of high level simulated active waste solutions designated as SIM 1 and SIM 2 were used for these experiments. Between these, only SIM 1 contained U(VI), while the compositions (Table 2) of the other metal

Table 2
Composition of the simulated high level active waste.

Element	Concentration (g/L)	Element	Concentration (g/L)
Fe	0.72	La	0.18
Cr	0.12	Pr	0.09
Ni	0.11	Nd	0.12
Na	5.5	Sm	0.086
K	0.22	Cs	0.24
Mn	0.43	Y	0.06
U	6.34	Zr	0.004
Sr	0.03	Mo	0.14
Ba	0.06	Ce	0.06

ions were same. As these solutions are highly acidic ($\sim$3 M HNO$_3$ media), their pHs were brought up between 4 and 11 prior to the measurements. For the calibration purpose, high level simulated waste solutions were also prepared with the same composition and acidity without adding the Cs-salt. The Cs(I) content in the original simulated waste solutions was determined with ISE 7 employing three different procedures.

2.7.1. Procedure 1

Eight well-cleaned 100 ml glass beakers were numbered sequentially. Aliquots (5 ml) of two sets of simulated waste solution were taken in duplicate in the beakers (nos. 1–4). Similarly, the waste solutions without Cs-salt (5 ml), prepared for calibration, were taken in another set of beakers (nos. 5–8). Aqueous CsCl solution (3 ml, 10^{-2} M) was added to the beakers 5 and 6, while CsCl solution (3 ml, 10^{-3} M) was added to the beakers 7 and 8. The solutions in all beakers were evaporated to dryness over a hot plate. After cooling to room temperature, de-ionized water (5.0 ml) was added to each of the beakers, followed by heating to dryness again. The procedure was repeated two times. Finally, de-ionized water was added to the salts left over in beakers and diluted to 30 ml. The pH was measured and found to be in the range of 4–5. The potential was measured employing ISE 7.

2.7.2. Procedure 2

Aliquots of simulated waste solutions without and with standard CsCl solutions were taken in eight beakers as mentioned in procedure 1. De-ionized water (12 ml) and two drops of phenolphthalein solution were added to all the beakers. After neutralizing the solutions with 3 M LiOH solution, the final volume was made up to 30 ml, and the potential was measured employing ISE 7.

2.7.3. Procedure 3

The Cs(I) concentration was determined by standard addition and subsequent dilution method. In this, 5.0 ml aliquots from the two test simulated waste solutions in quadruplicates were taken in eight beakers. Aqueous CsCl solution (3.0 ml, 10^{-2} M) was added to the beakers 3, 4, 7 and 8. All the solutions were neutralized with 3 M LiOH and diluted to a final volume of 30 ml. The potential in all the solutions was measured employing ISE 7. The solutions in beakers 3, 4, 7 and 8 were further diluted with de-ionized water up to 60 ml, and the responses were measured employing ISE 7.

2.8. Lifetime of ISE 7

To ascertain the lifetime of ISE 7, slope of calibration plot for Cs(I) over the concentration range of 10^{-7} to 10^{-2} M and the selectivity coefficients for all the alkali metal ions and ammonium ion were measured periodically employing ISE 7. The measurement schedule was as follows: (i) every day for the first two weeks; (ii) every alternate day during the third to fifth weeks; (iii) once a week during the sixth to fifteenth weeks; and (iv) every 15 days sixteenth week onwards till 46 weeks. The ISE 7 was left immersed in 10^{-7} M CsCl solution, when not in use.

3. Results and discussion

3.1. Responses of different ISEs for Cs ions

For these studies, six newly designed ISEs (designated as ISE 1–ISE 6) were fabricated using the ionophores L1 to L3, oNPOE or DOS as the plasticizer and KTpClPB (50 mol%) as the ion additive. Measurement of the responses of the ISEs for Cs(I) ions in the concentration range of 10^{-2} to 10^{-9} M revealed best result with ISE 5, made of L3, oNPOE and KTpClPB. For further optimization of the performance of the ISE, the composition of ISE 5 was varied by changing the KTpClPB content to 40 and 30 mol% to obtain two additional ISEs, designated as ISE7 and ISE8 respectively. The response characteristics of all the ISEs and their respective compositions are given in Table 1. Their results showed superior performance by ISE 7, amongst the chosen ISEs. Subsequently, to see the role of the resin in IFS, another ISE (ISE 9) was prepared maintaining the same composition as that of ISE 7, but changing the IFS with 10^{-3} M CsCl (without resin), and its response for Cs ions was also measured (Table 1). The results showed that the DLs and response of ISEs were improved by using low and constant activity of Cs ions along with resin as an inner filling solution.

3.2. Selectivity coefficients

The ion selectivity is one of the important characteristics of the ISEs, because it often determines the feasibility of a reliable measurement in the target samples [19]. Several methods like fixed interference method, separate solution method and matched potential method (MPM) are used to determine selectivity coefficients. IUPAC recommended the separate solution method when a low activity of the primary ion and a high activity of the interfering ion is used as IFS with the help of ion exchange resin [9]. In view of our interest in using the ISE in nuclear waste management, we followed the same protocol to determine the selectivities of all the ISEs (1–9) for Cs ions over several ions like Rb$^+$, K$^+$, Na$^+$, Li$^+$, NH$_4^+$, Sr^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+} and Hg^{2+}. The results shown in Table 3 revealed that the Cs ions selectivity was best with ISE7. Especially, its very large Cs/Na ion selectivity (log $K_{Cs,Na}$ = −4.68) would be very useful to determine Cs ions in nuclear waste solutions, where low concentration of Cs needs to be determined in the overwhelming presence of Na ions. In addition, ISE 7 also showed a low DL value (8.48 × 10^{-8} M) for the Cs ions. Hence, further studies were carried out with ISE 7 only.

3.3. pH dependence

Next, the response of ISE 7 to Cs ions was measured at different pHs using 10^{-2} M and 10^{-4} M CsCl solutions. The plots of potential versus pH (Fig. 2) revealed that the response of the ISE 7 for Cs ions is constant and stable over the pH range of 4–11 with both the concentrations of CsCl. The decrease in potential at lower pH may be due to failure of Donnan membrane equilibrium [34].

3.4. Linearity, and response time

ISE 7 showed a Nernstian response for Cs ions over the concentration range 10^{-7} to 10^{-2} M, with a slope of 56.6 mV per decade for Cs ions (Fig. 3). The response was fast with the response time less than 10 s.

3.5. Lifetime of ISE 7

Lifetime or durability of the ISEs is one of the important factors in deciding their applicability. The extent of leaching of the ionophore from the membrane is conveniently used to assess the lifetime.

Table 3
Selectivity coefficients of various ions determined by separate solution method.

Interfering element (I)	Selectivity coefficients ($-\log K_{Cs,I}$)								
	ISE 1	ISE 2	ISE 3	ISE 4	ISE 5	ISE 6	ISE 7	ISE 8	ISE 9
Rb^+	0.02	0.04	0.68	0.60	1.06	1.02	1.22	0.98	0.89
K^+	0.00	0.19	1.32	1.92	2.30	2.16	2.37	2.05	2.27
Na^+	1.89	1.79	2.30	2.47	4.52	4.32	4.68	4.60	4.35
Li^+	3.39	3.43	3.07	2.94	5.56	5.22	5.20	5.10	5.47
NH_4^+	0.68	0.59	1.31	2.06	2.17	1.98	2.14	1.85	2.02
Sr^{2+}	4.34	4.64	3.28	5.35	6.33	6.36	5.93	5.85	5.40
Ba^{2+}	4.35	4.13	2.38	5.66	6.57	6.38	6.12	6.10	6.26
Ca^{2+}	4.69	4.74	3.83	5.61	6.09	5.81	6.13	5.95	5.97
Mg^{2+}	4.37	4.57	4.14	5.52	5.92	5.63	6.02	5.78	5.58
Zn^{2+}	4.28	4.58	4.30	5.51	5.74	5.46	5.86	5.58	5.46
Cu^{2+}	4.10	4.37	3.55	5.05	5.62	5.33	5.58	5.03	6.02
Ni^{2+}	4.15	4.39	3.44	5.21	5.58	5.40	5.48	5.36	5.46
Pb^{2+}	3.21	3.59	3.33	2.11	4.68	4.31	4.58	4.28	3.86
Hg^{2+}	4.03	3.56	3.50	357	4.75	4.35	4.85	4.32	4.21

Table 4
Comparison of present cesium ion selective electrode with previously reported membrane based ISE of Cs.

Inophore	Detection limit (M Cs)	Range (M Cs)	Selectivity coefficient, $-\log K_{Cs,I}$				Life time	Ref. no.
			Rb	K	Na	NH$_4$		
2,3-Benzoquino-crown-5	2.5×10^{-5}	10^{-4}–10^{-1}	0.47	0.99	2.38	1.40	1 month	[14]
Calix[4]crown ether ester	5.0×10^{-6}	5.0×10^{-6} to 10^{-1}	–	2.0	1.30	1.50	4 months	[15]
Bis(1-propoxy) calix[4]arene dibenzocrown-6	–	10^{-6} to 10^{-1}	0.80	2.16	4.88	1.90	–	[16]
Diisopropoxy calix[4]arene-crown-6	5×10^{-7}	10^{-6} to 10^{-1}	0.89	2.18	4.46	1.98	–	[17]
Biscalix[4]arene	–	10^{-5} to 10^{-1}	–	0.90	2.20	1.3	1 month	[18]
5-(4'-Nitrophenylazo)25,27-bis(2-propyloxy)26,28-dihydroxycalix[4]arene	4.6×10^{-6}	10^{-5} to 10^{-1}	0.85	2.27	3.13	1.58	9 months	[20]
Thiacalix[4]biscrown-6,6	3.8×10^{-7}	10^{-6} to 3.2×10^{-2}	1.4	3.7	4.3	2.5	–	[21]
Thiacalix[4]crown-6	–	10^{-7} to 10^{-1}	2.20	3.50	5.10	3.10	–	[22]
Calix[4]arenetetraester	4.9×10^{-7}	10^{-06} to 10^{-01}	1.88	2.23	3.25	3.01	–	[23]
Calix[4]arenehexaethylester	–	5×10^{-5} to 10^{-1}	1.52	2.53	3.73	2.75	1 month	[24]
p-Methoxyanilino-(1,3-dioxo-2-indoxylidene)	6.3×10^{-6}	2.5×10^{-5} to 10^{-1}	0.70	1.22	2.72	1.59	18 days	[27]
25,27-Bis(1-octyloxy)calix[4]arene-crown-6 (**L3**)	8.48×10^{-8}	10^{-7} to 10^{-2}	1.22	2.37	4.68	2.14	10 months	Present work

This, in turn, depends on the properties of the plasticizer and the additive used as well as their compatibility with the ionophore. ISE 7 did not show any significant change in the slope of calibration plot for Cs(I) 56 ± 2 mV per decade concentration change in Cs(I), linearity (10^{-7} to 10^{-2} M CsCl) and selectivity coefficients up to 42 weeks ($\sim$10 months). After 44 weeks, the slope decreased to 53 mV and reduced further to 48 mV after another two weeks. Thus, the lifetime of ISE 7 was at least 10 months. This is a significant improvement over the existing Cs-ISE systems of similar design in terms of cost competitiveness.

3.6. Comparison

The characteristic features of the newly developed ISE (ISE 7) were compared with those of the other Cs-ISEs reported in the
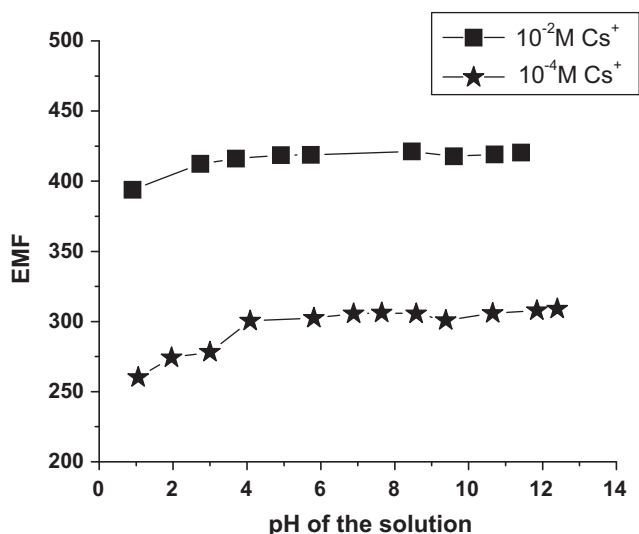

Fig. 2. Response of ISE for 10^{-2} and 10^{-4} M Cs$^+$ at different pH the solution.
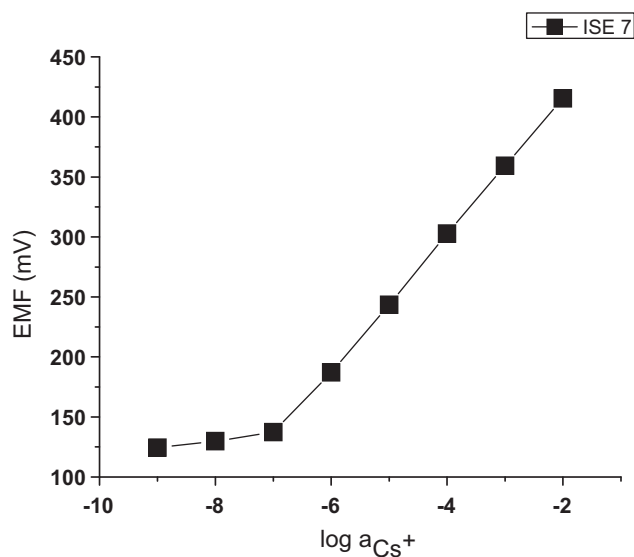

Fig. 3. Response of ISE for cesium (ISE 7, Table 1).

Table 5
Determination of cesium in simulated high level active waste solution and comparison with AAS values.

Sample ID	ISE (mg/L)			AAS (mg/L)[b]
	Method 1[a]	Method 2[a]	Method 3[a]	
SIM 1	205	210	212	212 ± 10
SIM 2	223	212	232	228 ± 11

[a] Mean of two determinations.
[b] Mean of five determinations with standard deviation.

literature. The details are given in Table 4. Selectivity and applicable range of the ISE 7 for Cs was well within the range reported in literature. However, the lifetime of the present electrode was 10 months. This is the longest lifetime for membrane-based cesium ISE so far developed or reported.

3.7. Application

3.7.1. Determination of Cs in simulated high level active waste

The ISE 7 was calibrated using the solutions in the beakers 5–8 and employing the procedures 1 and 2 given in Section 2. The procedures 1 and 2 gave the calibration slope as 53.6 ± 0.4 mV/decade and 54.2 ± 0.3 mV/decade concentration respectively. The response of the ISE to Cs ions was then measured using the solutions in beakers 1–4. Using procedure 3, the ISE 7 was calibrated from the potential response in beakers 3, 4, 7 and 8 before and after dilution. The calibration slope was found to be 52.6 ± 0.5 mV/decade concentration. From the calibration data and potential responses in beakers 1,2, 5 and 6, the Cs(I) concentration was determined in the simulated waste solutions SIM 1 and SIM 2. In all the three procedures, only the Cs ions concentration was considered for calibration. Due to the high ionic strength of the solutions (presence of large amount of salts), activity of Cs(I) got reduced, and hence the slope of calibration deviated more from the Nernstian response. Results for all the three procedures are given in Table 5. Since selectivity coefficients were not determined for several elements present in the simulated wastes, the present method was validated with AAS. Our ISE results agreed well with the AAS values (Table 5). Hence it may be concluded that there is no interference from elements like Fe, Cr, Mn, U, etc.

4. Conclusion

Ion selective electrode for cesium developed with 25,27 dioctyloxy calix[4]arene-crown-6 as ionophore has superior selectivity for Cs over other alkali, alkaline, transition elements. The ISE could be operated over wide range of pH from 4 to 11 and has been successfully employed to determine cesium content in high level simulated waste. Lifetime of the electrode is 10 months which is the highest life for any membrane based Cs-ISE so far developed.

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