Full Paper

Uranyl Selective Polymeric Membrane Sensor Based on P-Tert-Butyl-Biscalix[4]Arene

Sonika Tyagi[1], Himanshu Agarwal[1,*], Saiqa Ikram[1], Mukesh Kumar Gupta[2] and Sanjay Singh[3]

[1]*Department of Chemistry, Faculty of Natural Science Jamia Millia Islamia (Central University), New Delhi-110 025, India*

[2]*Department of Chemistry, Faculty of Science and Technology, Singhania University, Jhunjhunu- 333 515, India*

[3]*Department of Chemistry, M.M.H. College, Ghaziabad-201 001, India*

*Corresponding Author, Tel: 011-26981717 Extn 3255 (O) ;Fax: 011-26980229

E-Mail: drhimanshu.1975@gmail.com

Abstract- In recent years, the monitoring and evaluation of Uranyl (UO_2^{2+}) has received growing attention from both nutritional and toxological points of view. In this experimental study, we revealed that an electroactive material p-tert-butyl-biscalix[4]arene can be used as an ionophore in the preparation of PVC based ion selective electrode and we found that it shows ionophoric binding property for uranyl cation. This electrode shows excellent selectivity for UO_2^{2+} with respect to most of the common cations including inner transition and heavy metal ions. The proposed membrane sensor with p-tert-butyl-biscalix[4]arene based receptor exhibits wide linear range, with the slope of 29.30 ± 1.0 mV per decade over the concentration range of 8.1×10^{-8} M-1.0×10^{-1} M, and membrane sensor shows a lowest detection limit of 8.0×10^{-8} M of UO_2^{2+}. This sensor satisfactorily works in aqueous media and in non-aqueous media it works upto 40% (water-ethanol, water-methanol, water-acetone and water-acetonitrile). This electrode shows independent response within the pH range of 1.0-5.5 and its fastest response time is 10 s. The proposed membrane electrode was applied successfully for the determination of UO_2^{2+} in the presence of other cations (binary mixtures) by direct potentiometry and in tap and sea-water samples.

Keywords- P-Tert-Butyl-Biscalix[4]Arene, Ionophore, Uranyl, Poly(Vinyl Chloride) (PVC) Based Ion Selective Electrode, Binary Mixtures, Tap and Sea Waters

1. INTRODUCTION

Measurement of uranium concentration is having great importance in nuclear industry due to the application of metal as fuel in nuclear reactors. Uranium in the form of dioxide is used as in preparation of fuel pallets for nuclear power reactors. It effects the environmental safety assessment related to the nuclear industry [1-6]. So the determination of uranyl cations is important due to its toxic properties and other adverse effect on uptake of water.

There are so many analytical tools which are available at large scale (i.e. industry and highly equipped laboratory) for heavy metal and rare earth metal detection such as voltammetry, mass spectroscopy and Rutherford back-scattering techniques, higher order derivative spectrometry, ICP-MS, NAA and spectrofluorometric methods. These methods are either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories [7,8]. Ion Selective sensors are being widely used in the fields of environmental, industrial, agricultural and medicinal as they offer several advantages over other methods of analysis. The most attractive features of this technique is the speed with which samples can be analyzed, portability of the device, sample non-destruction, online monitoring, cost effectiveness and large measuring range.

The few ionophores towards the recognition of uranyl cation in the construction of ion selective electrodes are reported [9-20]. However, most of ionophores are organophosphorus based and these ionophores showed rather long response time, exhibit poor sensitivity, low stability, low selectivity, and generally short life time. So the better sensor is still required for such a toxic uranyl cations determination.

The presented experimental work explores extensive efforts to develop uranyl selective sensor by the use of innovative p-tert-butyl-biscalix[4]arene as an electroactive material in PVC matrix along with different solvent mediators.

2. EXPRIMENTAL

2.1. Reagents and chemicals

All analytical grade reagents were used as purchased. High molecular weight poly(vinyl chloride) (PVC), 1-chloronapthalene (CN), oleic acid (OA), dibutylbutylphosphonate (DBBP), dioctylphthalate (DOP), dibutylphthalate (DBP), tris(2-ethylhexyl)phosphate (TEP), Sodium tetraphenylborate (NaTPB) and tetrahydrofuran (THF), cyclohexanone were purchased from Merck. All metal nitrates were also brought from Merck. Doubled-distilled water was used to prepare the metal nitrate solutions. Stock solution of metal nitrates of 10^{-1} M concentration was obtained by dissolving weighed amounts of corresponding salt in double distilled water. Solutions of 10^{-2}-10^{-8} M concentration were obtained by diluting stock solution.

2.2. Instruments

Saturated calomel electrodes (SCE) were used as reference electrodes; a digital potentiometer ECIL, India (Model pH 5662) is used for potential measurements at 25 ± 0.1 $^{\circ}$C.

2.3. Synthesis of ionophore

Extremely selective ionophore p-tert-butyl-biscalix[4]arene was synthesized as reported in literature [21]. Ionophore is the key ingredient of ion selective membrane due to selectivity and sensitivity of membrane electrode depends on the ionophore structure and ionophore should not be dissolved in aqueous solution sample.

2.4. Membrane electrode preparation

A number of methods are available for the membrane preparation such as casting method and sol-gel method. But we prepared all membranes using casting method reported by Craggs et al. [22]. Different plasticizers such as DBP, DBBP, TEP, 1-CN, OA, DOP were used individually in same amounts along with the anion excluder NaTPB to get membrane of different composition. Membranes have been prepared by dissolving the PVC (310 mg), p-tert-butyl-biscalix[4]arene derivative (45 mg), plasticizer (470 mg), and anion excluder NaTPB (9 mg) in 15 mL THF. The mixture was shaken vigorously to obtain homogenous phase and after complete dissolution of all components it was poured in to the glass cast ring placed on a smooth glass plate and kept for 48 h for solvent evaporation. After this a membrane with uniform thickness was obtained. The membrane of 0.5 mm thickness were removed carefully from the glass cast ring and cutted it to the size of the pyrex glass tube and glued it to one end of a glass tube with the help of araldite and M-seal to avoid leakage.

2.5. Potential measurement and conditioning

Presented ionophore p-tert-butyl-biscalix[4]arene derivative was found to be more responsive to than those based on the other cations tested, showing good potential response to uranyl ions. The half cells were adjoined in the following manner for getting the potential measurement:

Internal reference electrode (SCE)	Internal reference solution (0.01 uranyl nitrate soln.)	Uranyl Selective Membrane	Test solution	External reference electrode (SCE)

Both saturated calomel electrodes were used as internal and external reference electrode. Two half cells are combined with the help of salt bridge. The potential measurements were made from low to high concentration range to avoid the memory effect. When membrane was not in used, kept in 0.1 M $UO_2(NO_3)_2$ solutions to avoid damage by cracking.

2.6. Selectivity coefficient

In present study, the selectivity coefficient has been evaluated using modified form of fixed interference method [23] at 1.0×10^{-2} M concentration of interfering ions as per IUPAC recommendation. In this method, the electromotive force (emf) was measured for solutions of constant activity of the interfering ion, a_B and varying activity of the primary ion, a_A in a cell comprising an ion-selective electrode and a reference electrode (ISE cell). The emf values obtained are plotted versus the logarithm of the activity of the primary ion. The intersection of the extrapolated linear portions of the plot indicates the value of a_A that is to be used to calculate from the following equations:

$$K_{A,B}^{Plot} = \frac{a_A}{(a_B)^{Z_A/Z_B}}$$

Where both Z_A and Z_B have the positive charges of both ions.

2.7. Analysis of tap and sea waters

Sea water samples were collected from the southern coast of India i.e. from Indian Ocean. 50 mL each of sea water and tap water samples were taken in 100 mL beaker separately. 2.5 mL of 1.0 M hexamine buffer (pH 7.0) was added to each sample and the uranyl ion content was determined by standard addition method by adding 0.5 mL of 1.0×10^{-6} M, 0.5 mL of 1.0×10^{-5} M and 0.5 mL of 1.0×10^{-4} M of uranyl ion and measuring the EMF values with the proposed uranyl ion sensor electrode .

3. RESULT AND DISCUSSION

This calixarene material will no doubt bring about great changes in the ion selective electrode field. The structure of present ionophore was found to be suitable to form metal complexes due to the presence of active sites. This ionophore underwent complexation reaction with uranyl cations in neutral medium. Ionophore for use in sensor should have adequate complex formation constants and rapid change kinetics due to conformational change between the ionophores and its metal complex in the membrane. The ionophore should be extremely soluble in the membrane matrix and also have a sufficient lipophilicity to prevent leaching from the membrane into the sample solution [24]. In actinides, the 5f-orbitals play a more active role and contribute to the chemical bond. Most applications have so far been to system with a high oxidation state of the actinide ion. A typical case is UO_2^{2+}, where the uranium ion has a formal charge of +6. As a result, three strongly covalent bonds are formed to each of the oxygen atoms. The resulting space consists of 12 electrons in 12 orbitals [25]. This active space can also be used when the uranyl ion forms complex with p-tert-butyl-biscalix[4]arene molecule.

3.1. Membrane optimization and effect of plasticizer

Out of seven membrane composition we got one optimized membrane with plasticizer DBP, PVC, p-tert-butyl-biscalix[4]-arene and NaTPB having perfect composition in ratio (470:310:45:9). Membrane electrode without plasticizer (membrane electrode No.1) exhibited a narrow working concentration range having response time of 30 s. Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore and state of ligand [26], it was expected to play a key role in determining the ion-selective characteristics. So various plasticizers (DBP, DBBP, TEP, CN, OA, and DOP) were added in changing amounts to the membranes and ion-selective characteristics were studied. The optimization of permselectivity of the membrane sensor is known to be highly dependent on the incorporation of additional membrane components, thus sodium tetra phenyl borate (NaTPB) (anionic excluder) was also added to the membrane components to increase the conductivity and minimize interference from lipophilic anions [27]. The addition of solvent mediators DBBP and CN (electrodes No. 3 and 5) improved the working concentration range but the membrane containing DOP as plasticizer (electrode No. 7), the potential remained linear in the concentration range 7.1×10^{-7}-1.0×10^{-1} M. However, the addition of the plasticizers TEP and OA (membranes No. 4 and 6) did not improve the performance of the electrodes (Table 1). The membrane having DBP as plasticizer exhibited best results (electrode No. 2). This sensor gave a Nernstian response (slope 29.30 ± 1.0 mV/ decade of activity) in the concentration range 8.1×10^{-8}-1.0×10^{-1} M of UO_2^{2+} and a response time as fast as 10 s. The results are summarized in (Table 1). Therefore electrode No. 2 with the optimum composition DBP:PVC:Ionophore:NaTPB (470:310:45:9) was chosen for all further studies. Repeated monitoring of potentials (20 measurements) on the same portion of the sample with this electrode gave a standard deviation of ± 1.0 mV. The sensing behavior of the membranes did not change when the potentials were recorded from lower to higher concentrations or vice-versa .

3.2. Calibration curve, working concentration range and slope

The working concentration range is one of the crucial parameter of Ion selective membrane electrode. Membrane electrode No. 2 gave the outstanding results. Electro-chemical cell response potential with 10^{-2} M UO_2^{2+} (as internal solution) was determined in the range of 8.1×10^{-8}-1.0×10^{-1} M UO_2^{2+} solution. A number of metal ion selective electrodes were prepared by using the given ionophore, but after extensive work it has cleared that the present ionophoric membrane electrode is extremely selective to uranyl cation (Fig. 1). Effects of the plasticizers on the calibration curve of uranyl cation have plotted (Fig. 2). It has clearly seen that the membrane consisting plasticizers DBP along with the composition of DBP:PVC:Ionophore:NaTPB in 470:310:45:9, respectively show linear response conc. range 8.1×10^{-8} M with the near Nernstian slope of 29.30 mV/decade of concentration .

**Table 1.** Membrane optimization with different plasticizers

Electrode No.	Composition of each membrane									Working Concentration Range (M)	Slope mV/decade	Response Time (sec)
	DBP (mg)	DBBP (mg)	TEP (mg)	1-CN (mg)	OA (mg)	DOP (mg)	NaTPB (mg)	*p*-tert-butyl-biscalix [4]arene derivative (mg)	PVC (mg)			
1							9	45	310	7.9×10^{-7}-1.0×10^{-1}	24.00 ± 1.0	30
2	470						9	45	310	8.1×10^{-8}-1.0×10^{-1}	29.30 ± 1.0	10
3		470					9	45	310	8.3×10^{-8}-1.0×10^{-1}	32.00 ± 1.0	25
4			470				9	45	310	8.4×10^{-8}-1.0×10^{-1}	38.00 ± 0.1	20
5				470			9	45	310	8.4×10^{-8}-1.0×10^{-1}	31.00 ± 1.0	15
6					470		9	45	310	8.1×10^{-8}-1.0×10^{-1}	35.00 ± 0.1	15
7						470	9	45	310	7.1×10^{-7}-1.0×10^{-1}	28.05 ± 0.1	25

3.3. Response and lifetime

Dynamic response time is an important factor for the evaluation of any sensor. In current study the potential response time was recorded by changing solution with different uranyl concentrations. Average time required for the membrane electrode to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of UO_2^{2+} solutions, each having a ten-fold difference in concentration, was investigated. The membrane without plasticizer (electrode No. 1) show the response time of 30 s, which was reduced by 5-15 s by the addition of different plasticizers in the presence of solvent mediator (NaTPB). The best response time was observed (electrode No. 2) having the ratio DBP:PVC:Ionophore:NaTPB (470:310:45:9) (Fig. 3). As discussed during the experiment the membrane electrode reaches its equilibrium response in a very short time of about 10 s and equilibrium potentials constant for more than 5 min, after that a very slow divergence is recorded. The reproducibility of electrode was examined with the constructed electrode under the optimum conditions. The standard deviation of ten replicate measurements is ± 0.3 mV. The long-term stability of the electrode was studied by periodically re-calibrating in standard solutions and collecting the response slope. The slope of the electrode response was reproducible over a period of at least 8 month. Thus, the proposed sensor can be used for 8 months without any considerable change in its response characteristics towards uranyl cations.
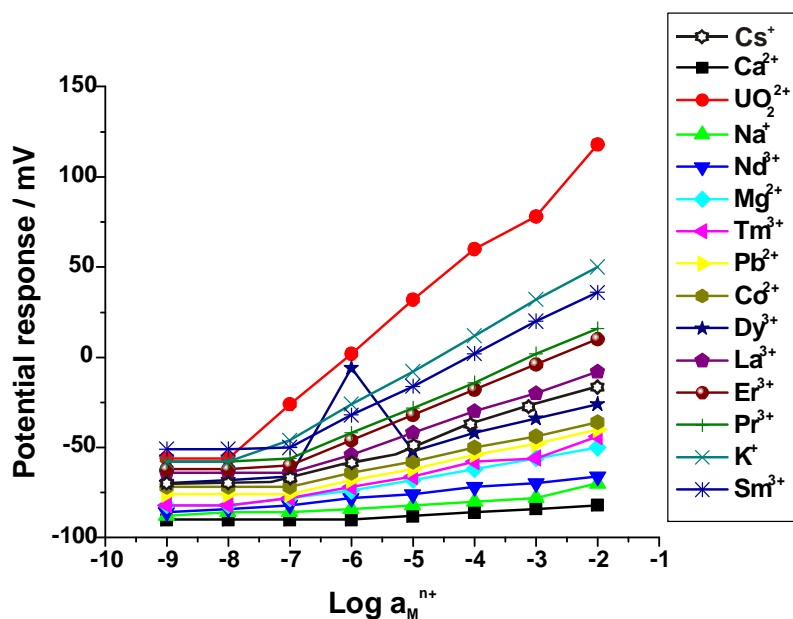
Fig. 1. Potentiometric calibration response of a PVC-based sensor using p-tert-butyl-biscalix[4]arene derivative as an ionophore towards various metal ions
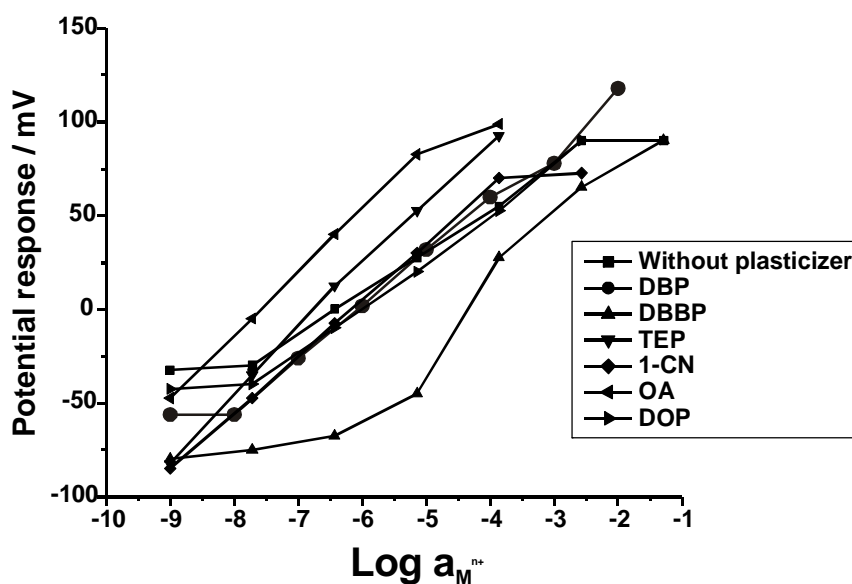
Fig. 2. Variation of potential of PVC based membrane of (I) (No. 1) without solvent mediator and (Nos. 2, 3, 4, 5, 6 and 7) with solvent mediators DBP, DBBP, TEP, 1-CN, OA, DOP respectively with UO_2^{2+} concentration

3.4. pH and non-aqueous effect

The pH dependence of the electrode potential was investigated over the pH range of 1.0 - 10.0 in 1.0×10^{-3} M and 1.0×10^{-4} M solution of UO_2^{2+} and related result is illustrated in Fig. 4. The potential was independent of pH in the range of 1.0-5.5 pH units. The pH of the test solution was adjusted either by the drop wise addition of dil. HNO_3 or hexamine. Beyond the pH range of 1.0-5.5, a gradual change in the potential was detected. The observed potential drift at higher pH value could be due to the formation of some hydroxy complexes of UO_2^{2+} in the solution. At the lower pH values the potential increased indicating that the membrane electrode responds to (H^+) hydrogen ions. The performance of electrode membrane No. 2 was also checked in partially non aqueous media using water-ethanol, water-methanol, water-acetone and water-acetonitrile mixtures. It works satisfactorily in non aqueous medium having up to 40% (v/v) content of ethanol, methanol, acetone and acetonitrile (Table 2). The working concentration range and slope remain unchanged for these mixtures but above the 40% non aqueous content working concentration range and slope were reduced and potential drift was found with time.

3.5. Selectivity coefficient

The selectivity of ISEs was highly dependent on the identity of central metal. The most important characteristics of a selective membrane electrode is its selectivity response for the primary ion over other ions present in the solutions, which is expressed in terms of selectivity coefficient values for the electrode. Thus, the selectivity studies were carried out only for sensors No. 2, which exhibit the best performance in terms of working concentration range, slope, response time and lifetime. It is seen from (Table 3) that the selectivity coefficients determined are much smaller than 1.0. Thus, both electrodes are substantially selective to uranyl ions over the all interfering ions studied. Thus, it is clear from the values of selectivity coefficients that it is possible to determine uranyl in the presence of interfering ions at a concentration level smaller or slightly higher than the uranyl concentration.
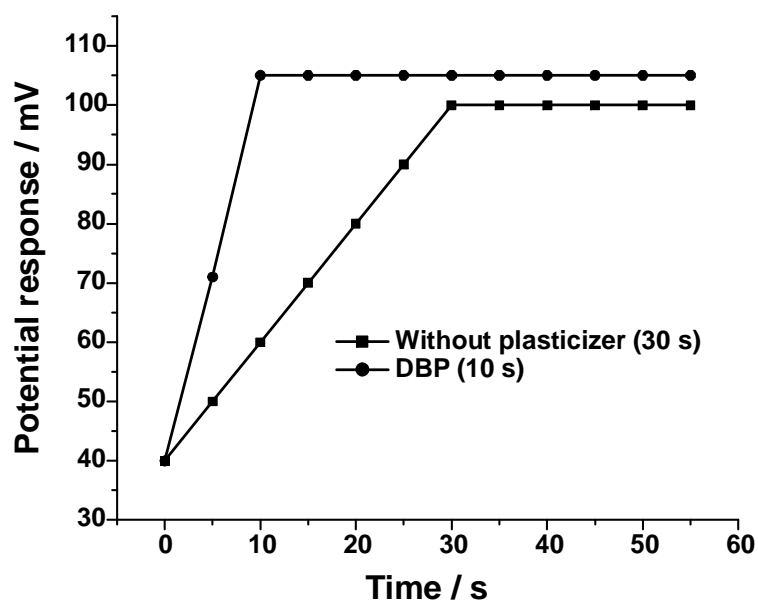
Fig. 3. Response time curve for UO_2^{2+}-ISE with plasticizer DBP
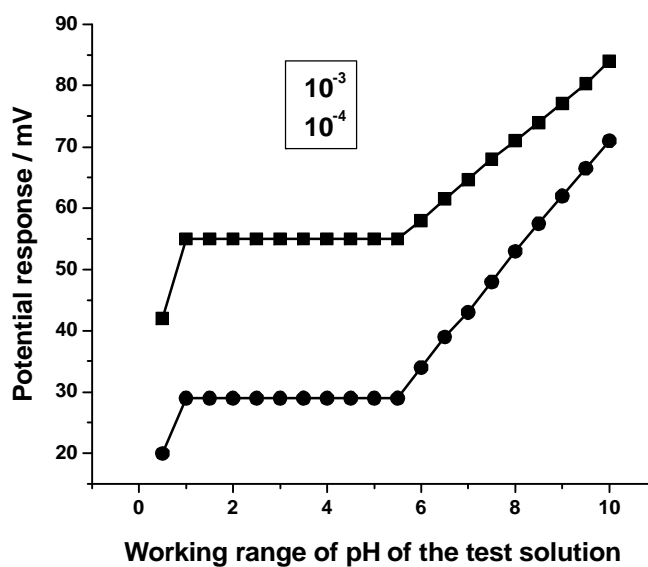
Fig. 4. Effect of pH on potential; $[UO_2^{2+}]=1.0\times10^{-3}$ M (a) and 1.0×10^{-4} M (b) for sensor No. 2

Table 2. Effect of partially non-aqueous medium on the working of UO_2^{2+} sensor (No.2)

Non-aqueous content (%v/v)	Slope (mV /decade) of activity	Working Conc. range(M)	Response time (seconds)
0	29.30±1.0	$8.1\times1\,0^{-8}$-1.0×10^{-1}	10.0
Methanol			
10	29.05±1.0	8.1×10^{-8}-1.0×10^{-1}	10.0
20	28.70±1.0	8.1×10^{-8}-1.0×10^{-1}	10.5
30	27.40±1.0	8.1×10^{-8}-1.0×10^{-1}	11.0
40	25.00±1.0	8.1×10^{-8}-1.0×10^{-1}	10.0
Ethanol			
10	29.05±1.0	8.1×10^{-8}-1.0×10^{-1}	10.5
20	28.50±1.0	8.1×10^{-8}-1.0×10^{-1}	11.0
30	27.80±1.0	7.9×10^{-8}-1.0×10^{-1}	11.0
40	25.50±1.0	7.8×10^{-8}-1.0×10^{-1}	11.0
Acetone			
10	28.00±1.0	8.1×10^{-8}–1.0×10^{-1}	10.5
20	27.03±1.0	8.1×10^{-8}–1.0×10^{-1}	11.0
30	26.99±1.0	7.9×10^{-8}–1.0×10^{-1}	11.2
40	22.50±1.0	8.1×10^{-8}–1.0×10^{-1}	11.0
Acetonitrile			
10	28.90±1.0	8.1×10^{-8}–1.0×10^{-1}	10.5
20	28.00±1.0	8.1×10^{-8}–1.0×10^{-1}	11.0
30	28.90±1.0	7.9×10^{-8}–1.0×10^{-1}	11.0
40	27.00±1.0	7.8×10^{-8}–1.0×10^{-1}	11.5

Table 3. Selectivity coefficient by Fixed Interference Method

Interfering ion (M^{n+})	Selectivity Coefficient, $K_{Uranyl\,ion,M^{n+}}^{POT}$
	Fixed Interference Method
Na^+	−1.88
K^+	−2.17
Cs^+	−2.51
Ag^+	−2.22
Ca^{2+}	−2.34
Mg^{2+}	−2.39
Pb^{2+}	−2.16
Cu^{2+}	−2.35
Co^{2+}	−2.04
Er^{3+}	−2.42
La^{3+}	−1.26
Pr^{3+}	−2.28
Sm^{3+}	−3.10
Dy^{3+}	−3.15
Tm^{3+}	−3.80
Nd^{3+}	−3.52
Gd^{3+}	−3.26
Ce^{3+}	−3.41
Yb^{3+}	−3.51
Eu^{3+}	−3.25
Lu^{3+}	−3.52

FIM: Primary ion concentration varied from 1×10^{-1} M to 1×10^{-6} M, interfering ion concentration in 1×10^{-2} M

4. ANALYTICAL APPLICATIONS

4.1. Detection of uranyl in different sample

Proposed uranyl sensor has been used for determination of the concentration of uranyl cations in tap water and sea water. The results obtained are shown in Table 5, from which it is clear that the uranyl ion content determined by the present method agree well with AAS method (Table 4).

Table 4. Uranyl ion detection in different samples

Sample	UO_2^{2+}-ISE[a] ($\mu g/L$)	AAS ($\mu g/L$)
Tap water	3.02±0.50	2.98±0.50
Sea water	1.012±0.40	1.001±0.82

4.2. Determination of uranyl ions in binary mixtures

The practical utility of the proposed membrane sensor assembly was successfully used for determination of uranyl ions in the presence of other cations (binary mixtures) by direct potentiometry. The results were found to be in good agreement with those obtained by AAS analysis (Table 5).

Table 5. Recovery of Uranyl ions from binary mixtures [UO_2^{2+}=4.0 $\mu g\ mL^{-1}$]

Added cations ($\mu g\ mL^{-1}$)	Recovery of UO_2^{2+} (%)	
	Proposed method	AAS
----	99.5±0.3	100.1±0.6
50 K^+	101.1±0.6	100.8±0.6
100 Sr^{2+}	101.1±0.7	102.1±0.6
150 Ni^{2+}	100.7±0.4	101.2±0.1
200 Co^{2+}	99.2±0.2	99.9±0.3
50 Zn^{2+}	98.7±0.6	99.3±0.3
100 Pb^{2+}	100.2±0.7	99.8±0.6
150 Fe^{3+}	101.1±0.5	99.1±0.4
200 Ca^{2+}	99.8±0.3	100.1±0.4
250 Th^{4+}	99.2±0.6	100.1±0.1

Table 6. Comparison of the reported electrodes with proposed electrode assembly

Sensor No.	Name	Working conc. range (M)	Slope (mV/decade)	pH	Response time	Life time	Reference
1	Uranyl organophosphorus complex	1.0×10^{-5}-1.0×10^{-1}	29.00 ± 1.0	1.5-3.5	-	4-8 weeks	16
2	Tri-*n*-octylphoshineoxide	1.0×10^{-6}–1.0×10^{-1}	59.00 ± 1.0	1.5-3.5	2 min	1 month	17
3	1,11-bis(-benzyloxy-5-formyl phenoxy)-3,6,9-trioxaundecane	1×10^{-4}–1.0×10^{-1}	39.40 ± 1.0	1.0-3.0	-	5 months	18
4	4-*tert*-Butylcalix[6]arene	3.9×10^{-5}-1.0×10^{-1}	29.10 ± 1.0	2.2–3.2	-	-	19
5	*o*-Methyldihexylphosphineoxide o-hexyl-2-ethylphosphoric acid uranyl complex	-	-		-		20
6	1,18-Diaza-3,4,15,16-dibenzo-5,8.11,14,21,24-hexaoxa-cyclo-hexaicosane-2,17-dione	-	-		-	-	21
7	5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,40,41,42-hexahydroxy-calix[6]arene	10^{-5}–10^{-1}	-	-	-		22
8	Benzo-substituted macrocyclic diamides	1.0×10^{-6}–1.0×10^{-1}	-	2.9–3.7	-	13 weeks	23
9	N,N'-4,5-(Propylenedioxy)-benzenebis(3,5-di-tri-butyl-salicylideneimine)L_2	1.0×10^{-6}–1.0×10^{-1}	Near nernstian	1.0–5.0	20 s	10 months	24
10	N,N'-Dibenzyl-N,N'-diphenyl-1,2-phenylenedioxy-diacetamide	1.0×10^{-6}–1.0×10^{-1}	59.2 ± 1.0	–	40 s	–	25
11	5,11,17,23-tetra-tert-butyl-25,27-bis(hydroxy)-26-(ethoxy carbonyl-methoxy)-28-(diethylcarbamoyl-methoxy) - calix[4]arene			5.5-8.5		-	25a
12	5,11,17,23-tetra-tert-butyl-25,27-bis[2-[(2-hydroxy-5-azo-benzylidene)amino]ethoxy]-26,27-dihydroxy-calix[4]arene (HAECA)	1.0×10^{-7}-1.0×10^{-1}	28.20 ± 0.2	2.2–3.6	-	-	25b
13	*p-tert*-Butyl-biscalix[4]arene derivative	8.1×10^{-8}-1.0×10^{-1}	29.30 ± 1.0	–5.5	10 s	8 months	Present work

5. CONCLISIONS

As we know that in recent years, uranyl ion has gained much attention in the field of research due to its commercial uses and its toxicological nature. That is why this paper revealed that the plasticized PVC based membrane containing p-tert-butyl-biscalix[4]arene as an ionophore, DBP as solvent mediator and NaTPB as an anion excluder in a PVC matrix in the ratio (45:310:9:470) (w/w) (Ionophore: PVC: NaTPB: DBP) could be used to determination of UO_2^{2+} within the concentration range of 8.1×10^{-8} M -1.0×10^{-1} M with the slope of 29.30 mV/decade of activity. Membrane electrode works well in a wide pH range of 1.0-5.5 with dynamic response time of 10 s. This developed electrode showed the best selectivity for UO_2^{2+} over common cations including inner transition and heavy metal ions. The assembly could be used over 8 months in aqueous and non-aqueous content medium (upto 40%) also. The proposed electrode is successfully applied in determination of UO_2^{2+} in the presence of other cations (binary mixtures) by direct potentiometry and in tap and sea-water samples. Comparable study of this sensor has been given in the (Table 6) and proved proposed electrode has the best performance in all parameters among all mentioned electrodes.

REFERENCES

[1] R. Zobel, and M. Beer, J. Biophys. Biochem. Cytol. 10 (1961) 335.

[2] H. Schröder, A. Heimers, R. Frentzel-Beyme, A. Schott, and W. Hoffman, Radiat. Prot. Dosim. 103 (2003) 211.

[3] M. Taulan, F. Paquet, C. Maubert, O. Delissen, J. Demaille, and M. C. Romey, Environmental Health Perspectives: Public Health Service, U. S. Department of Health and Human Services (2006).

[4] J. G. Hamilton, Rev. Mod. Phys. 20 (1948) 718.

[5] R. A. Bulman, Coord. Chem. Rev. 31 (1980) 221.

[6] P. Galle, Uranium. In Toxiques Nucleaires, Chapter XIII, Masson: Paris (1997) pp. 185-205.

[7] M. Shamsipur, A. R. Ghiasvand, and Y. Yamini, Anal. Chem. 71 (1999) 4892.

[8] T. E. Berma, Toxic Metals, and Their Analysis, Heyden & Sons, London (1980).

[9] D. L. Manning, J. R. Stokely, and D. W. Magouyrk, Anal. Chem. 46 (1974) 1116.

[10] C. S. Luo, F. C. Chang, and Y. C. Yeh, Anal. Chem. 54 (1982) 2333.

[11] S. Johnson, G. J. Moody, and J. D. R. Thomas, Analyst 114 (1989) 1025.

[12] V. K. Gupta, R. Mangla, U. Khurana, and P. Kumar, Electroanalysis 11 (1999) 573.

[13] A. Florido, I. Casas, J. Garcia-Raurich, R. Arad-yellin, and A. Waeshawsky, Anal. Chem. 72 (2000) 1604.

[14] M. Shamshipur, A. Soleymanpour, M. Akhond, H. Sharghi, and A. R. Massah, Talanta 58 (2002) 237.

[15] J. Ramkumar, and B. Maiti, Sens. Actuators B 96 (2003) 527.

[16] M. Shamshipur, F. Mizani, M. F. Mousavi, N. Alizadeh, K. Alizadeh, H. Esghi, and H. Karami, Anal. Chim. Acta 589 (2007) 22.

[17] D. W. Kim, K. W. Park, M. H. Yang, T. H. Kim, R. K. Mahajan, and J. S. Kim, Talanta 74 (2007) 223.

[18] J. Senkyr, D. Ammann, P. C. Meier, W. E. Morf, E. Pretsch, and W. Simon, Anal. Chem. 51 (1979) 786.

[19] D. M. Duncan, and J. S. Cockayne, Sens. Actuators B 73 (2001) 228.

[20] M. R. Ganjali, Z. Memari, R. Dinarvand, F. Faridbod, and P. Norouzi, Sens. Lett. 7 (2009) 1156.

[21] P. Schmitt, P. D. Beer, M. G. B. Drew, and P. D. Sheen, Tetrahedron Lett. 39 (1998) 6383.

[22] A. Craggs, G. J. Moody, and J. D. R. Thomas, J. Chem. Educ. 51 (1974) 541.

[23] Y. Umezawa, P. Buhlmann, K. Umezawa, K. Tohda, and S. Amemiya, Pure Appl. Chem.72 (2000) 1851.

[24] S. Chandra, C. Kumar, H. Agarwal, and R. K. Agarwal, Anal. Sci. 23 (2007) 683.

[25] Y. Kitatsuji, Z. Yoshida, H. Kudo, and S. Kihara, Anal. Sci. 17S (2001) 329.

[26] E. Bakker, P. Buhlmann, and E. Pretsch, Chem. Rev. 97 (1997) 3083.

[27] G. D. Christian, Analytical Chemistry, 1994, Chapter 4, p 331 John Wiley Pvt. Ltd., Singapore.