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Molecular octopus: octa functionalized calix[4]resorcinarene-hydroxamic acid [C4RAHA] for selective extraction, separation and preconcentration of U(VI)

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Abstract

A solvent extraction separation of uranium, in the presence of thorium, cerium and lanthanides with a new calix[4]resorcinarene bearing eight hydroxamic acid groups (C4RAHA) is described. Quantitative extraction of uranium is possible in ethyl acetate solution of C4RAHA at pH 8.0. The λ_{max} and molar absorptivity (ε) for uranium is 356 nm and 8352 L mol^{-1} cm^{-1}. The Binding ratio of uranium with C4RAHA as evaluated by Job's method is 4:1. The system obeys Beer's law over the range 0.075–6.0 μg ml^{-1} of uranium with Sandell sensitivity 0.0284 μg cm^{-2}. A preconcentration factor of 142 was achieved by directly aspirating the extract for GF-AAS measurements. The two-phase stability constant evaluated at 25 °C for uranium is 15.91. The complexation is characterized by favorable enthalpy and entropy changes. A liquid membrane transport study of uranium was carried out from source to the receiving phase under controlled conditions and a mechanism of transport is proposed. Uranium has been determined in standard and environmental samples.

Keywords: Calix[4]resorcinarene; Hydroxamic acid; Liquid–liquid extraction; Transport studies; Preconcentration

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1. Introduction

Supramolecules offer numerous and diverse possibilities; as models for biological systems, synthetic ionophores or therapeutic reagents, selective extractive agents [1,2] etc. Nowadays, the literature reports a great variety of supramolecules that have been tailor-made for specific uses.

Among the different supramolecules, calix[4]resorcinarenes [3,4] deliver a versatile molecular platform for the elaboration of more complicated host systems by virtue of its conformational flexibility, complexing properties and an easy synthetic and commercial availability. Calix[4]resorcinarenes have found applications as host molecules [5,6], components in liquid crystals [7], photoresists [8], selective membranes [9], surface reforming agents [10], HPLC stationary phase [11], as ion channel mimics [12] and metal ion extraction agents [13,14].

Uranium, not as rare as once thought, is now considered to be more plentiful than mercury, antimony, silver, or cadmium, and is about as abundant as molybdenum or arsenic. It occurs in numerous minerals such as pitchblende, uraninite, carnotite, autunite, uranophane, and tobernite. It is also found in phosphate rock, lignite, monazite sands, and can be recovered commercially from these sources [15,16]. Uranium is of great importance as a nuclear fuel in power plants. It is also used for X-ray targets for production of high-energy X-rays, and used as a photographic toner [15,16]. The selective extraction and removal of uranium from waste water coming out of nuclear reactors has drawn considerable attention as it can cause serious irreversible environmental

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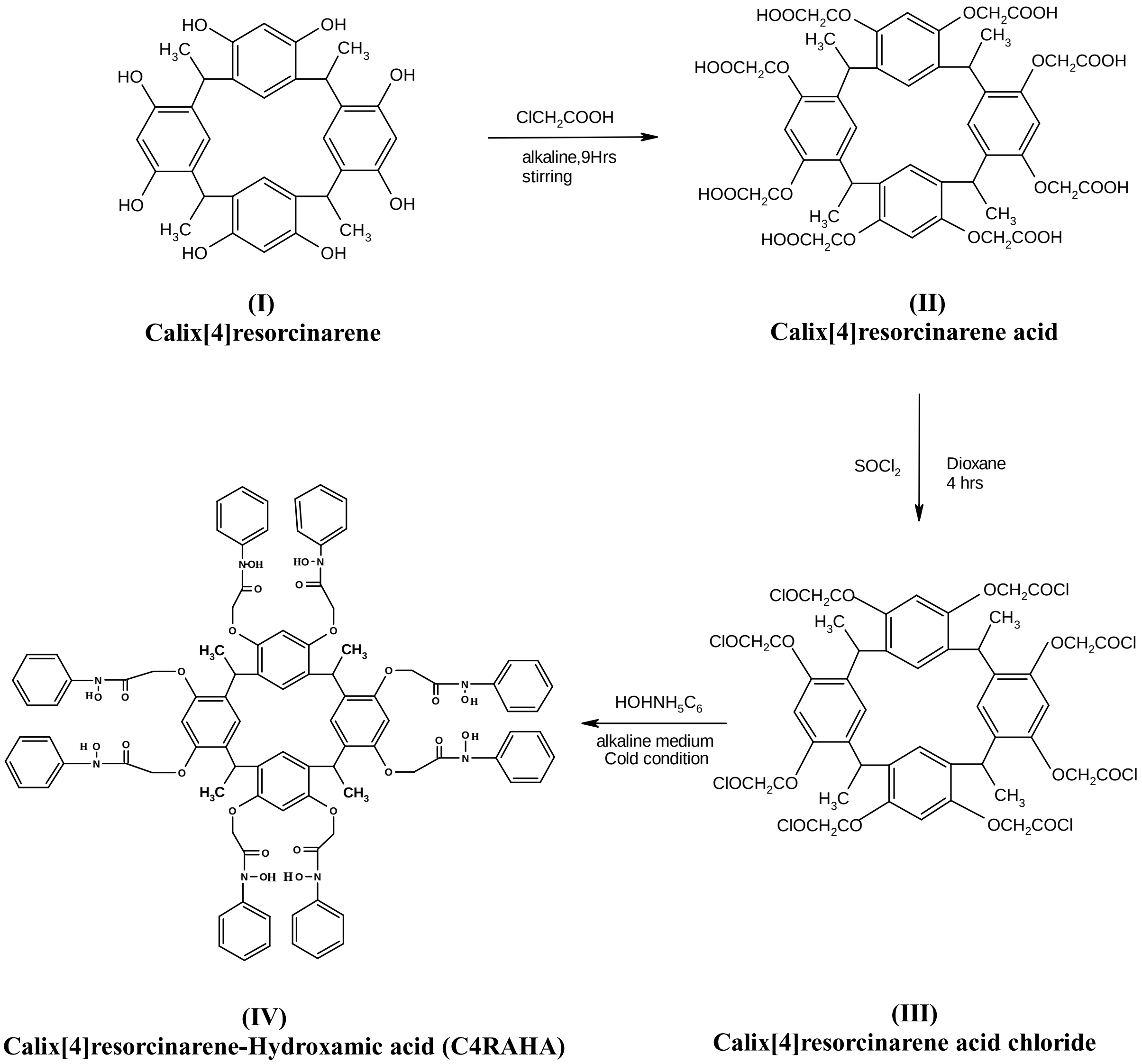


(I)
Calix[4]resorcinarene

(II)
Calix[4]resorcinarene acid

(IV)
Calix[4]resorcinarene-Hydroxamic acid (C4RAHA)

(III)
Calix[4]resorcinarene acid chloride

Fig. 1. Synthetic route for calix[4]resorcinarene-hydroxamic acid (C4RAHA).

damages. Uranium is known to cause acute toxicological effects in biological systems and mammals [17,18]. Because of these realities, the processing of nuclear waste before disposal relies most often on solvent extraction procedures, and a large number of extracting agents have been synthesized and tested with the aim of separating uranium [19–21]. ICP-AES has been used in the fields as the method of choice, for the determination of uranium, however, prior extraction is necessary [22,23]. Although, uranium has been determined by graphite furnace atomic absorption spectrophotometry, the detection limits are very poor [24]. Other techniques viz. ICP-AES and ICP-MS, using solution nebulization, are suitable for the determination of uranium. Several modifiers for electron thermal vaporization-inductively coupled plasma-mass spectrophotometry (ETV-ICP-MS) have also been reported [25,26]. The separation of uranium is done either by liquid–liquid extraction or by ion-exchange techniques. But most of the ion-exchange resins suffer from low sorption capacities and poor sensitivity towards uranyl ion [27–31].

Hydroxamic acids, the versatile metal extractants find wide applications in analytical [32], agricultural [33], and biological field [34]. Hydroxamic acids have achieved significant importance as analytical tools for the separation and determination of the large number of metal ions [35–39]. Thus there remains a need of a specific ligand that discriminate U(VI) from other metal ions present in great excess in sea water and monazite sand.

With this in view, in the present investigation we have synthesized octa functionalized-calix[4]resorcinarene (C4RAHA) and studied its analytical applications for extraction and determination of U(VI) by spectrophotometry and GF-AAS. The transportation of uranium across a liquid membrane containing C4RAHA and preconcentration in the presence of diverse ions has also been studied.

2. Experimental

2.1. Instruments and measurements

Electronic spectra were recorded on Hitachi 3210 UV–vis spectrophotometer with matching 10 mm quartz cells. AAS measurements were performed in Perkin-Elmer Model 420 with pyrolytically coated HGA-76 graphite furnace. A uranium hollow cathode lamp, 358.5 nm uranium wavelength with a spectral width of 0.2 nm was used. The argon gas with atomization temperature of 2700 °C was used.

2.2. Materials and solutions

All the chemicals were used of analytical reagent grade of E. Merck or BDH. All aqueous solutions were prepared with quartz distilled deionized water, which was further purified by a Millipore Milli-Q water purification system. Standard uranium stock solution was prepared by dissolving 2.109 g of uranyl nitrate hexahydrate in a litre of doubly deionized water in the presence of HNO_3 and was standardized spectrophotometrically [40]. A 0.02% (1.2×10^{-4} M) stock solution of C4RAHA was prepared in ethyl acetate. Working solution was subsequently prepared by appropriate dilution of the stock solution.

2.3. Synthesis of calix[4]resorcinarene-hydroxamic acid (C4RAHA)

The calix[4]resorcinarene I was synthesized by acid catalyzed condensation of resorcinol and acetaldehyde [3]. The calix[4]resorcinarene I was functionalized by chloroacetic acid in alkaline medium to form calix[4]resorcinarene acid II [41,42]. The calix[4]resorcinarene acid II (10.08 g, 0.01 mol) was refluxed with thionyl chloride (11.9 g, 0.1 mol) in dioxane medium for 4 h, excess of thionyl chloride was distilled, calix[4]resorcinarene acid chloride III was obtained.

The calix[4]resorcinarene acid chloride III, was added dropwise in a 100 ml conical flask containing ethereal solution of phenyl hydroxylamine and a saturated aqueous solution of sodium bicarbonate. The mixture was stirred continuously for 3 h at −5 °C. The reaction mixture was then brought to room temperature and solvent ether was evaporated to get the crude product IV, recrystallized from ethyl acetate–hexane medium. The yield of IV 55%, m.p. > 240 °C dec.; IR (KBr), 3184, 1622 and 900 cm^{-1}; ^1H NMR (DMSO) δ 1.65 ppm (d, $CHC\mathbf{H}_3$), δ 3.4 ppm (q, $C\mathbf{H}$), δ 4.7 ppm (s, $C\mathbf{H}_2$), δ 7–8 ppm (s, $Ar\mathbf{H}$), δ 8.8 ppm (s, $N–O\mathbf{H}$); Anal. Calcd. for $C_{96}H_{88}N_8O_{24}$: C, 66.35; H, 5.10; N, 6.45; O, 22.10. Found: C, 66.43; H, 4.83; N, 6.27, O, 22.47 (Fig. 1).

2.4. Liquid–liquid extraction procedure

An aliquot of sample solution containing 0.75–60.0 μg of uranium was transferred into a 25 ml separatory funnel. The pH of the solution was adjusted to 8.0 with the buffer solution. The mixture was shaken for 13–15 min with 3 ml of 1.05×10^{-4} M C4RAHA in ethyl acetate. The organic extract was separated, dried over anhydrous sodium sulphate and transferred into a 10 ml volumetric flask. To ensure complete recovery, the extractions were repeated with 1ml of C4RAHA. The combined extracts and washings were diluted to the mark with ethyl acetate. The absorbance of the organic phase was measured against the reagent blank at 356 nm. The total concentration of the uranyl ion $[UO_2{}^{2+}]$ species remaining in the aqueous phase $[UO_2{}^{2+}]_{(aq)}$ was measured by GF-AAS.

The concentration of uranium ion extracted into the organic phase $[UO_2{}^{2+}]_{(org)}$ as complex was estimated by $[UO_2{}^{2+}]_{(org)} = [UO_2{}^{2+}]_{(aq,initial)} - [UO_2{}^{2+}]_{(aq)}$, where $[UO_2{}^{2+}]_{(aq,initial)}$ is the initial concentration of the metal ion in the aqueous phase. The percent extraction (%E) for uranium, was calculated by:

$$\%E_U = \frac{[UO_2{}^{2+}]_{(org)}}{[UO_2{}^{2+}]_{(aq,initial)}}100$$

The extracted C4RAHA–uranium complex in ethyl acetate after appropriate dilution was also determined by GF-AAS.

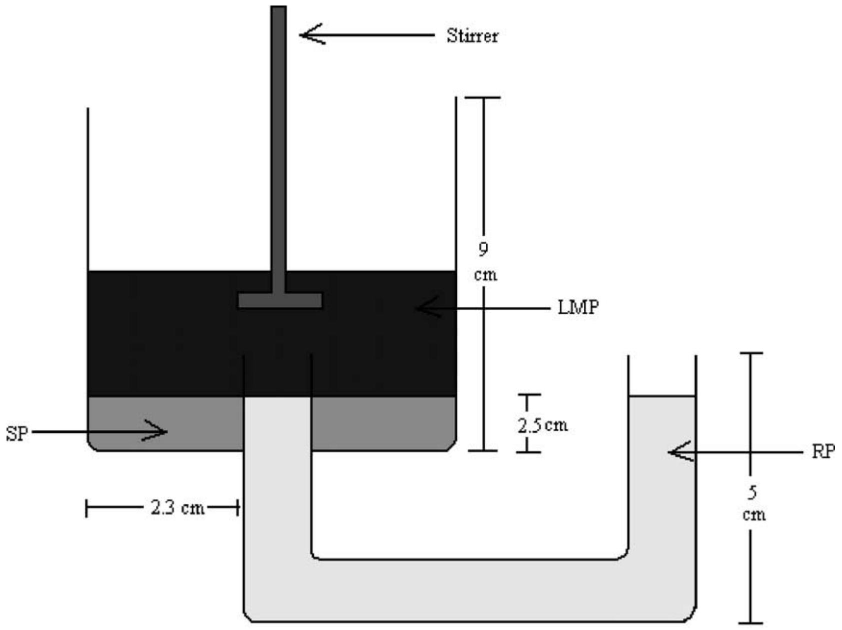
2.5. Transport of uranium

Transport of $UO_2{}^{2+}$ was carried out in a specially fabricated glass assembly as shown in Fig. 2. The reaction cell was 6.6 cm in inner diameter and 9.0 cm in height with a total capacity of 305 ml. U-tube (2.0 cm diameter, 20 cm length) was fused from the base of the cell. The height of the tube inside the cell was 4.0 cm from the basal plane. The whole assembly was kept in a thermostat maintained at 30 °C. The transport experiments were performed with 50.0 ml of 1.05×10^{-4} M uranium solution at pH 8.0 as source phase and 50.0 ml of 0.1 M HCl as receiving phase. The liquid membrane consisted of 75 ml of 1.05×10^{-4} M C4RAHA in ethyl acetate. A synchronous motor (200 rpm) provided constant reproducible stirring from the top. The amount of uranium transported from the source phase to the receiving phase was measured by GF-AAS. The transport data are the average of five runs with an experimental error of less than 1.8%.

3. Results and discussion

3.1. Spectral interpretations

Structure of **IV** was characterized by FT-IR and ^1H NMR spectroscopy and elemental analysis. The IR spectrum showed characteristic absorption at 3184 cm^{-1} due to O–H stretching vibration. It is well known that an absorption band due to O–H stretching vibrations, when free, appears around 3600 cm^{-1}; hydrogen bonding shifts this band to lower frequencies [43–45]. In hydroxamic acids, the acidic O–H group is placed in a very close proximity of the polar carbonyl group



Source Phase (SP) : 50 ml, 1.05×10^{-4} M uranium

Liquid Membrane Phase (LMP) : 75 ml, 1.05×10^{-4} M in Ethyl Acetate

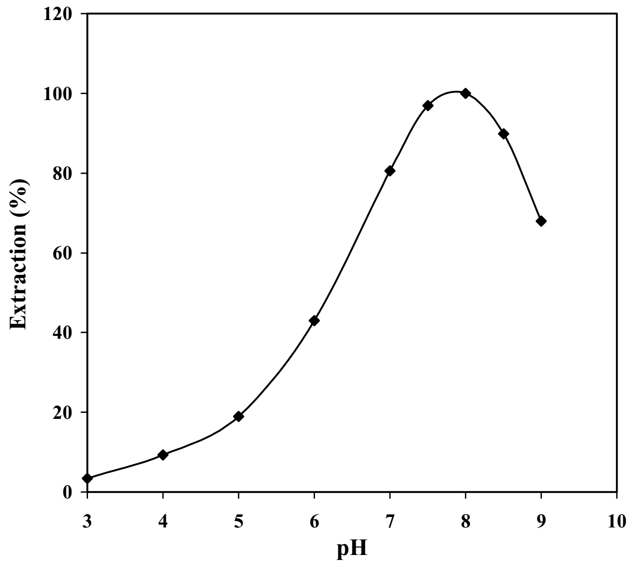
Receiving Phase (RP) : 50 ml, 0.1 M HCl

Fig. 2. Apparatus for transport studies.

C=O. The band at 1622 cm^{-1} is assigned for the C=O of hydroxamic acid group. This assignment is made with respect to the region of amide and anilide. Unsubstituted amide $RCONH_2$, this band is located between 1690 and 1650 cm^{-1}, while in substituted amides RCONHR it is observed at 1680 and 1650 cm^{-1}. The position of C=O stretching band is much influenced by molecular structure and is generally shifted to lower frequencies [46]. Thus, the hydrogen bonding lowers C=O band by 10–45 cm^{-1} [43–45]. A sharp band at 900 cm^{-1} is attributed to N–O stretching vibration in **IV** [47–49]. The ^1H NMR spectrum of **II** showed five prominent sharp peaks at 1.6, 3.2, 4.6, 7.6 and 10.2 ppm, which were assigned to methyl, methine, methene, aromatic and carboxylic groups. After phenyl hydroxylamine groups were attached to III, the ^1H NMR spectrum of **II** changed dramatically, new peak which appeared by formation of hydroxamic acid groups observed at 8.8 ppm [50] and diminished the carboxylic acid signal, of 10.2 ppm [41,42]. The results obtained from elemental analysis of **IV** confirm the presence of eight hydroxamic acid groups.

3.2. Complexation studies and statistical significance

The complexation of uranium with C4RAHA was studied under optimum conditions of pH, solvent, and reagent (C4RAHA) concentration. Fig. 3 shows that maximum extraction was possible in the pH range of 8.0–8.3, however, above and below this range the extraction of the complex



Uranium : 2 μg ml^{-1}
pH : 8.0
C4RAHA : 3 ml, 1.05×10^{-4} M
Solvent : Ethyl acetate
λ max : 356 nm

Fig. 3. Effect of pH on the extraction of C4RAHA–uranium.

Table 1
Effect of solvents on the extraction of C4RAHA–uranium(VI) complex

Solvent	Dielectric constant	Extraction (%)	Molar absorptivity ($\mathrm{L\,mol^{-1}\,cm^{-1}}$)
Benzene	2.28	14	1.09×10^3
Toluene	2.30	33	2.81×10^3
Chloroform	4.80	82	6.99×10^3
Ethyl acetate	6.40	100	8.35×10^3

Uranium: $2\,\mu\mathrm{g\,ml^{-1}}$; C4RAHA: 3.0 ml, 1.05×10^{-4} M; pH: 8.0; $\lambda_{\max}$: 356 nm.

was incomplete. It was also found that 13–15 min of shaking is sufficient for quantitative extraction of uranium. The extraction was not affected by further shaking, indicating that the equilibrium stage had been attained. The effect of solvent as shown in Table 1 on the extraction of C4RAHA–uranium complex was restricted to ethyl acetate, chloroform toluene, and benzene due its limited solubility in other organic solvents and was found that quantitative extraction is possible in ethyl acetate. The spectra of the complex of uranium showed a bathochromic shift of 33 nm respectively from that of the reagent C4RAHA in ethyl acetate as shown in Fig. 4.

Under the optimum conditions, quantitative extraction was possible with 3.0 ml, 1.04×10^{-4} M C4RAHA in ethyl acetate. The molar absorptivity measured at the wavelength of maximum absorption ($\lambda_{\max}$ 356 nm) for the extracted complex of 8352 $\mathrm{L\,mol^{-1}\,cm^{-1}}$. The system obeys Beer's law over the range was 0.075–6.0 $\mu\mathrm{g\,ml^{-1}}$. The regression analysis equation obtained from the calibrated standard solution of uranium can be represented as Abs = 0.169 × Conc. − 0.000159 with the correlation coefficient, $r = 0.997$. The Sandell's sensitivity calculated for the proposed method was 0.0284 $\mu\mathrm{g\,cm^{-2}}$. The precision of the proposed method was investigated based on the optimum condition of uranium extraction and expressed as relative standard deviation of 2.1%. The limit of detection (LOD is 2.87 ppb) was defined as that analyte concentration giving a signal equal to three times the standard deviation of blank signal [51]. The limit of quantification (LOQ is 9.58 ppb) was then set as ten times the standard deviation of the blank signal.

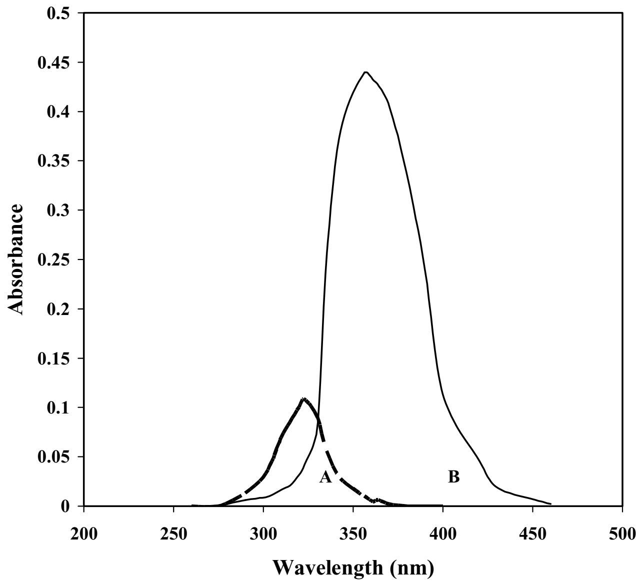
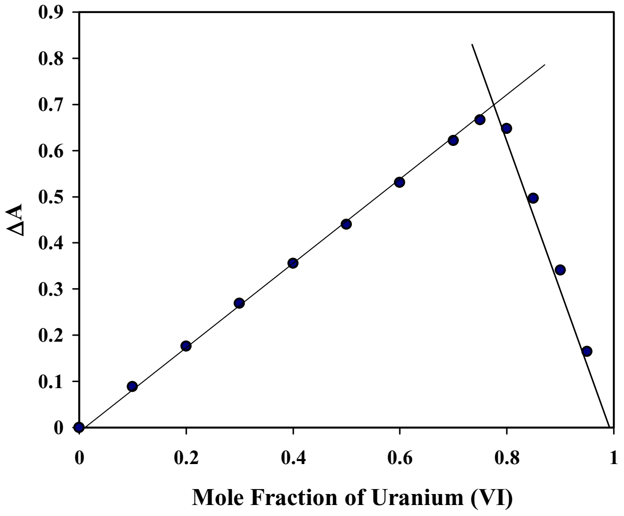


Fig. 4. Comparative spectra of reagent C4RAHA 1.05×10^{-4} M (A) and its uranium complex (B).



Uranium :$1.05\mathrm{x}10^{-4}$ M
C4RAHA : 3 ml, $1.05\mathrm{x}10^{-4}$ M
pH : 8.0
λ max : 356 nm

Fig. 5. Stoichiometry of uranium(VI)–C4RAHA complex.

3.3. Stoichiometry of the complex

The stoichiometric ratio of the uranium complex was determined by the modified Job's method of continuous variation. The absorbance of complex A_c of a series of solution containing uranyl ion (UO_2^{2+}) a and C4RAHA b at a constant total concentration a + b, but different concentration ratios was measured at 356 nm. The absorbance of b was subtracted from the observed absorbance A_c to obtain the difference absorbance ΔA.

$$\Delta A = A_c - A_b$$

ΔA values were plotted against the molar ratio of uranium(VI) ion a/(a + b) (Fig. 5). The maximum value for ΔA was clearly obtained at a/(a + b) = 0.78, indicating 4:1 stoichiometric ratio of UO_2^{2+} and C4RAHA. The accuracy of this result is possible if only a single complex is formed. To verify this, measurement were taken at different selected wavelength, which gave same value for a/(a + b) ratio.

To get more information about the nature of the extracted complex, attempts were made to isolate it from ethyl acetate extract. The extract was evaporated to dryness and subjected to elemental analysis. Further, a known weight of the dry complex was digested with perchloric and nitric acid mixture. It was centrifuged and uranium content was determined

Table 2
Stability constant and thermodynamic parameters for C4RAHA–uranium(VI) complex

Temperature (K)	$\log \beta_4$	$\log K_{\mathrm{ex}}$	ΔG (kJ mol^{-1})	ΔH* (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
298	15.90	1.0×10^{-16}	−90.64	–	98.4
303	16.25	2.24×10^{-16}	−94.19	−120.91	85.1
308	16.59	4.89×10^{-16}	−97.74	−121.39	72.2
313	16.92	1.05×10^{-15}	−101.31	−121.71	59.6
318	17.23	2.14×10^{-15}	−104.81	−118.05	47.7
323	17.53	4.26×10^{-15}	−108.32	−117.89	36.1

* Mean ΔH for uranium: −119.99 kJ mol^{-1}.

by GF-AAS. The results obtained are in conformity with the complex formulae. The experimental results obtained for elemental analysis of the uranium complex is: carbon 40.98%, nitrogen 3.87%, hydrogen 2.81% and uranium 33.83% and is comparable to their theoretical values: carbon 41.02%, nitrogen 3.99%, hydrogen 2.87% and uranium 33.90%.

3.4. Extraction studies and equlilibria

To evaluate the binding ability of C4RAHA (H_8A) with uranium, a liquid–liquid extraction (water–ethyl acetate system) was carried out and the extraction constants were determined.

The extraction equilibria for uranium(VI) can be expressed by Eq. (1):

$$4\mathrm{UO_2}^{2+}{}_{(\mathrm{a})} + \mathrm{H}_8A_{(\mathrm{o})} \rightleftarrows [(\mathrm{UO_2}^{2+})4A^{-8}]_{(\mathrm{o})} + 8[\mathrm{H}^+]_{(\mathrm{a})} \quad (1)$$

where the species in the organic and aqueous phases are denoted by the subscript (o) and (a), respectively.

The extraction constant K_{ex}, is given by Eq. (2):

$$K_{\mathrm{ex}} = \frac{[(\mathrm{UO_2}^{2+})_4A^{-8}]_{(\mathrm{o})}[\mathrm{H}^+]^8}{[\mathrm{UO_2}^{+2}]^4\,[\mathrm{H}_8A]_{(\mathrm{o})}} \quad (2)$$

Also, the distribution ratio of uranium in the two phases can be given by Eq. (3),

$$D = \frac{[(\mathrm{UO_2}^{2+})_4A^{-8}]_{(\mathrm{o})}}{[\mathrm{UO_2}^{2+}]^4} \quad (3)$$

From Eqs. (2) and (3), we obtained

$$K_{\mathrm{ex}} = \frac{D[\mathrm{H}^+]^8}{[\mathrm{H}_8A]_{(\mathrm{o})}} \quad (4)$$

Eq. (4), can be written as:

$$\log K_{\mathrm{ex}} = \log D + 8\log[\mathrm{H}^+] - \log[\mathrm{H}_0A] \quad (5)$$

The extraction constant K_{ex} may be obtained from the above Eq. (5), where

$$[\mathrm{H}_8A] = \frac{C_{\mathrm{H}_8A}P_{\mathrm{H}_8A}}{1 + P_{\mathrm{H}_8A} + (k_{\mathrm{a}}/[\mathrm{H}^+])} \quad (6)$$

In this expression C_{H_8A} is the analytical concentration of the reagent H_8A, P_{H_8A} and k_{a} are its respective distribution constant and acid dissociation constant. With the aid of Eq. (6) and the values of pk_{a} = 8.9 and $\log P_{\mathrm{H}_8A}$, the K_{ex} values were calculated by a least square procedure. Also, the two-phase stability constant ($\log \beta_4 P_{\mathrm{U-H}_8A}$) were obtained from the relation:

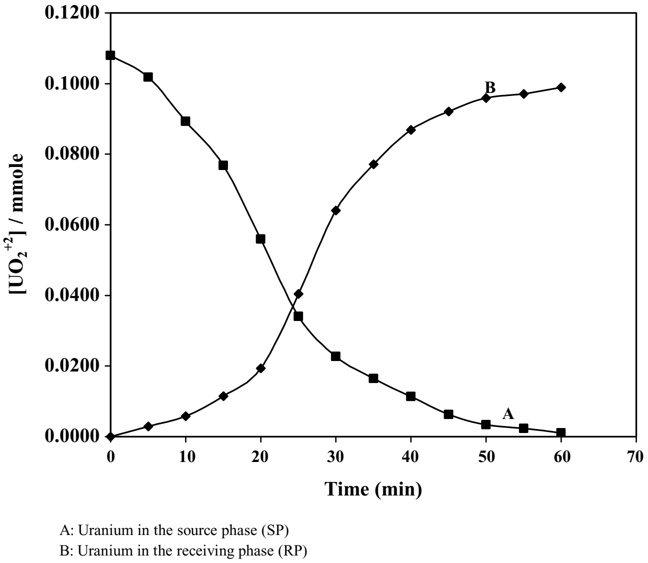
$$\log \beta_4 P_{\mathrm{U-H}_8A} = \log K_{\mathrm{ex}} + \mathrm{p}k_{\mathrm{a}} + \log P_{\mathrm{H}_8A} \quad (7)$$

where β_4 and $P_{\mathrm{U-H}_8A}$ are the respective overall formation constant and distribution constant of $[(\mathrm{UO_2}^{2+})_4{\cdot}A^{-8}]$ complex in the two phases. Table 2 summarizes the value of $\log \beta_4 P_{\mathrm{U-H}_8A}$ and $\log K_{\mathrm{ex}}$ at different temperatures.

3.5. Liquid membrane transport studies

The organic chemistry of membrane transport processes and of carrier molecules has only recently been developed, although the physico-chemical features and the biological importance of transport processes have long been recognized. The design and synthesis of receptor molecules binding selectively organic and inorganic substrates made available a range of compounds, which, if made membrane soluble, could become carrier molecules and induce selective transport by rendering membranes permeable to the bound species. Thus, transport represents one of the basic functional features of supramolecular species together with recognition and catalysis [52,53].

Considerable effort has been directed over the last two decades to the transport of metal ions across liquid membrane [54]. A liquid membrane is a liquid phase, which separates two other liquid phases with which it is immiscible. The transport of $[\mathrm{UO_2}^{2+}]$ through the membrane containing 1.05 × 10^{-4} M C4RAHA from source phase of $[\mathrm{UO_2}^{2+}]$ = 1.05 × 10^{-4} M to the receiving phase of 0.1 M HCl was carried out. As evident from Fig. 6, the concentration of $\mathrm{UO_2}^{2+}$ in the source phase started to decrease continuously and reached a concentration lower than the detection limit after 24 min (curve A), on the other hand concentration of $\mathrm{UO_2}^{2+}$ in the receiving phase increased as shown in the curve B. Therefore, it is clear that $\mathrm{UO_2}^{2+}$ moved from the source to receiving phase through the liquid membrane. Based on these facts and knowledge obtained by the extraction equilibria, the proposed mechanism of transport of uranium through the liquid membrane of C4RAHA is as shown in Fig. 7. The carrier in the membrane reacts with $\mathrm{UO_2}^{2+}$ in the source phase at the interface of these phases and forms a complex $[(\mathrm{UO_2}^{2+})_4A^{-8}]$ while releasing 8 moles of proton into the source phase. At

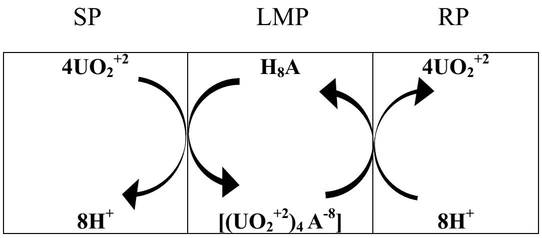


Source Phase (SP) : 50 ml, 1.05×10^{-4} M uranium

Liquid Membrane Phase (LMP) : 75 ml, 1.05×10^{-4} M C4RAHA in ethyl acetate

Receiving Phase (RP) : 50 ml, 0.1 M HCl

Fig. 6. Transport profile of uranium (UO_2^{2+}) through the liquid membrane containing C4RAHA at 30 °C.



SP : Source Phase

LMP : Liquid Membrane Phase

RP : Receiving Phase

Fig. 7. Proposed mechanism for transport of uranium through a liquid membrane containing C4RAHA.

the other interface of the membrane and the receiving phase the complex reacts with 8 moles of protons while releasing 4 moles of UO_2^{2+} in the receiving phase.

3.6. *Effect of temperature and thermodynamic parameters*

The extractions of uranium from aqueous solution were studied at different temperatures between 298 and 323 K and the results show that the extraction equilibrium constant ($\log K_{ex}$) and two-phase stability constants for uranium ($\log \beta_4 P_{U-H_8A}$) increases with increase in temperature Table 2. The change in extraction equilibrium constant ($\ln K_{ex}$) with temperature can be expressed by Van't Hoff equation:

$$\ln(K_{ex}) = \frac{\Delta H^\circ}{RT^2}$$

In order to utilize this equation for calculation, it must be integrated assuming the heat of reaction ΔH remains constant over a small range of temperature.

$$\ln(K_{ex}) = \frac{-\Delta H^\circ}{RT} + \text{constant (intercept)}$$

The plots of ($\log \beta_4 P_{U-H_8A}$) against $1/T$ yields a straight line equation $6175.6x + 36.624$ with slope (x) $-\Delta H^\circ/2.303R$ (Fig. 8). The enthalpy change accompanying the complexation was found to be $-119.99\ \text{kJ mol}^{-1}$ in the given range of temperature. The inspection of Fig. 9 (ΔH°, $-T\Delta S^\circ$, $\Delta G^\circ \rightarrow T$) reveals that the complexation is driven by favorable enthalpy and entropy changes. The negative values of free energy suggest that the reaction is exothermic and favorable for complexation.

3.7. *Effect of diverse ions*

The extraction of single metal ion under controlled condition gives an indication of potential sensitivity of the proposed method. However, the selectivity of a reagent can be more realistically determined under condition where the extraction is carried out from solution containing different metal ions. In order to examine this by the present method, the effect of various cations and anions in the separation and determination of uranium was studied. Interference studies were performed by measuring the absorbance of the extracted organic phase and the aqueous phase by GF-AAS. The tolerance limit was set as the amount of foreign ion causing a change of ±0.018 in absorbance or 2% error in the recovery of uranium.

Uranium was extracted in the presence of large number of competitive ions at optimum pH 8.0 and none of them affected the absorbance of uranium complex.

The selectivity factors for uranium ($K_{UO_2^{2+}}$) over these commonly associated metal ions (M^{n+}) may be calculated in terms of their stability constants by the equation:

$$K_{UO_2^{2+}} = \frac{\log(\beta_4 P_U)}{\log(\beta_4 P_{M-H_8A})}$$

The stability constants of complexation of competitive metal ions were determined independently at pH 8.0. As evident from Fig. 10, the proposed method has highest selectivity for uranium compared to other metal ions (Table 3).

3.8. *Preconcentration of uranium*

The concentration of uranium in natural water samples is too low for it direct determination. Therefore, preconcentration or enrichment step is necessary to bring the sample to the detectable limits of existing instrumental methods The

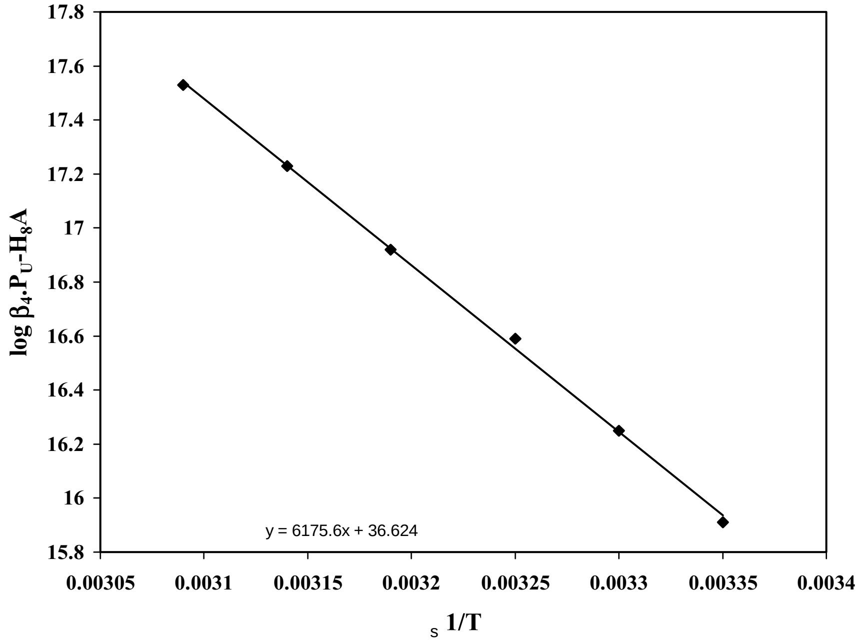


Fig. 8. Variation of two-phase stability constant with temperature (T^{-1}).

method was studied for the preconcentration of uranium in terms of its preconcentration factor (PF).

$$\mathrm{PF} = \frac{\text{concentration of metal in organic phase}}{\text{initial concentration of metal in aqueous phase}}$$

The preconcentration study was carried out by extracting 20 μg of uranium in 1000 ml aqueous phase with 7 ml of 0.005% C4RAHA in ethyl acetate. To evaluate the efficiency of preconcentration, expressed as recovery, the concentration of uranium in organic phase and the aqueous phase was

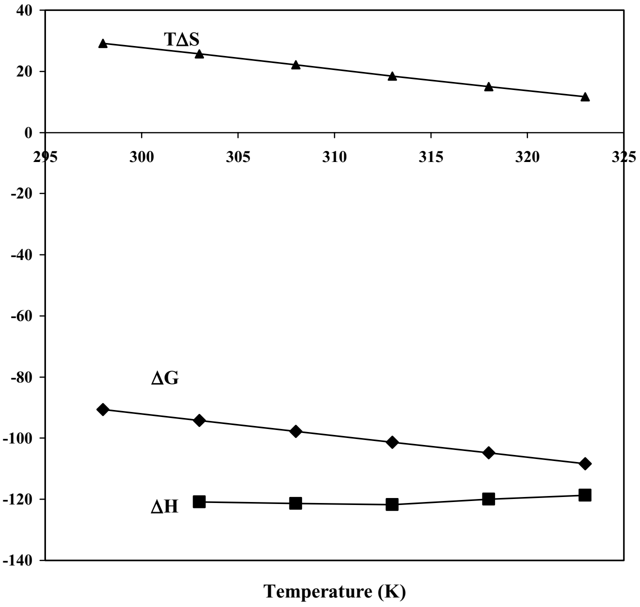


Fig. 9. Variation in thermodynamic parameter with temperature.

Table 3
Effect of diverse ions on the extraction of C4RAHA–uranium(VI) complex

Ions	Amount added (mg)	Recovery of uranium (ppm)		Selectivity factor $K_{\mathrm{UO_2}^{2+}}$
		Spectrophotometry	GF-AAS	
Al^{3+}	30	9.97	9.99	5.3
Ba^{2+}	40	9.99	9.98	6.41
Ca^{2+}	40	9.95	9.99	6.41
Cd^{2+}	40	9.94	9.99	6.38
Ce^{4+}	40	9.95	9.96	6.44
Co^{2+}	40	9.98	9.99	6.46
Ga^{+3}	40	9.97	9.99	6.41
Ga^{4+}	40	9.97	9.99	6.41
Hg^{2+}	40	9.95	9.99	8.88
$NH_4{}^{+}$	50	9.96	10.00	6.44
Mn^{2+}	40	9.97	9.99	6.44
Tl^{2+}	40	9.94	9.98	6.44
$MoO_4{}^{-2}$[a]	40	9.94	9.97	6.52
Pb^{2+}	45	9.95	9.97	7.23
Th^{4+}	30	9.98	10.01	5.37
La^{3+}	30	9.99	10.01	5.32
Pr^{3+}	30	10.00	10.02	5.30
Nd^{3+}	30	10.00	10.02	5.35
Zn^{2+}	30	9.95	9.97	5.32
Zr^{4+}	20	9.96	9.97	4.97
Nb^{5+}	40	9.99	9.99	6.41
Ta^{5+}	40	9.97	9.99	6.44
V^{5+}[b]	40	9.98	10.00	6.41

Uranium: 10 μg ml^{-1}; pH: 8.0; solvent: ethyl acetate; C4RAHA: 3 ml, 1.05 × 10^{-4} M; λ_{max}: 356 nm.

[a] Stripped with sodium oxalate.

[b] Stripped with tartaric acid.

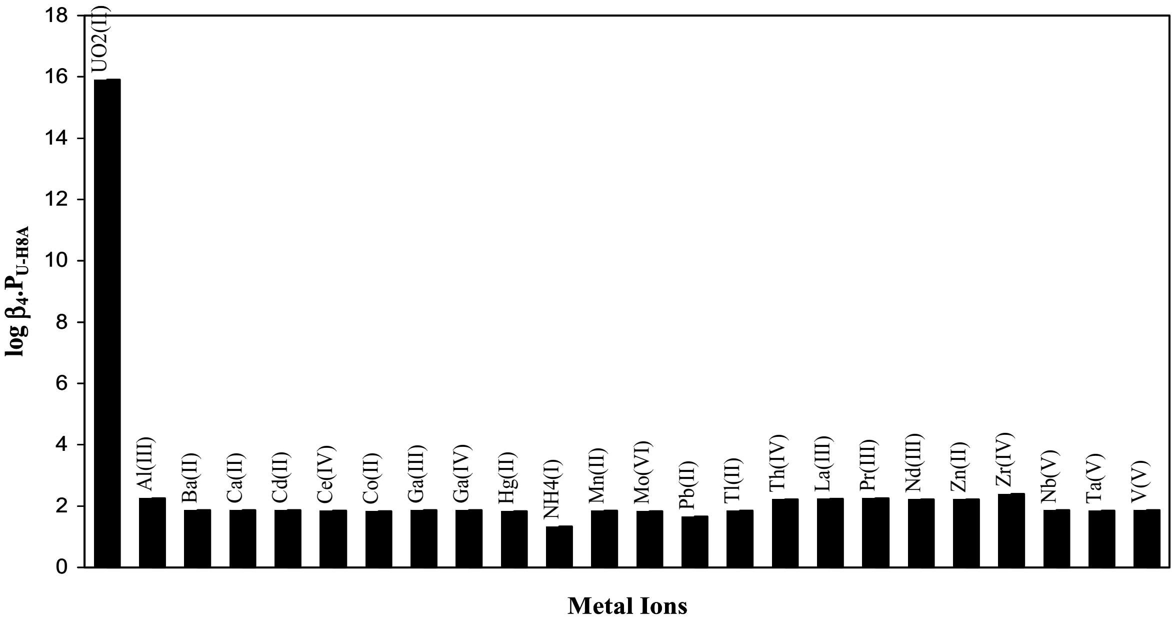


Fig. 10. Selective extraction of uranium in comparison to other competitive metal ions.

Table 4
Analysis of uranium in rocks, sea water and alloy samples

Sample	Certified value ($\mu g\,ml^{-1}$)	Present method[a] ($\mu g\,ml^{-1}$), uranium found	
		Spectrophotometry	GF-AAS
Mumbai sea water			
Belapur		0.36 ± 0.02	0.37 ± 0.01
Thane bridge		0.32 ± 0.03	0.33 ± 0.02
Mahim		0.28 ± 0.02	0.27 ± 0.02
Apollo bunder		0.20 ± 0.01	0.20 ± 0.01
Marine lines		0.25 ± 0.02	0.26 ± 0.02
Mussoori phosphate deposites	622.45	625 ± 0.8	623 ± 0.5
Rocks samples[b]	1.60	1.60 ± 0.02	1.59 ± 0.03
Monazite sand	9.79	9.8 ± 0.03	9.79 ± 0.02
Alloys (%)			
Uranium alloyed copper Cu(76), U(10)	24.22	24.30 ± 0.05	24.18 ± 0.03
Thorium uranium Th(90) and U(10)	10.01	10.02 ± 0.03	9.98 ± 0.04

[a] Average of 10 determinations.

[b] Samples from Dharwar (India) of old Kaldurga conglomerate pebbles.

determined by GF-AAS. Quantitative determination was possible with recovery up to 98% with a concentration factor of 142.

3.9. Sample analysis for uranium

The proposed method was applied for the analysis of rock and seawater samples. Matrix interferences were verified by comparison of the slopes of the calibration graphs with that using standard addition method. The results for the analysis are given in Table 4. The precision of preconcentration procedure when combined with GF-AAS was expressed as relative standard deviation of 2.1% with a recovery up to 99%.

4. Conclusion

The newly synthesized, calix[4]resorcinarene-hydroxamic acid (C4RAHA) has shown high affinity and specificity for uranium(VI) in presence of large quantities of associated metal ions. Uranium is first preconcentrated by liquid–liquid extraction technique and then subjected to GF-AAS with limit of detection 2.87 ppb and limit of quantification 9.58 ppb of uranium in the presence of complex matrix. The results obtained from the analysis of rock samples, monazite sand and seawater samples prove the reliability of the proposed method for their application towards standard and natural samples. Moreover, the molar absorptivity is 8352 L mol^{-1} cm^{-1} achieved in the present method is very high, compared to most of the analogous methods cited in the literature.

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