

## Supervanadophile: Complexation, Preconcentration and Transport Studies of Vanadium by Octa Functionalized Calix[4]resorcinarene-Hydroxamic Acid

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A new octa functionalized calix[4]resorcinarene bearing eight hydroxamic acid groups (OFCHA) has been synthesized and its analytical properties have been investigated. To elucidate the structure of the compound, elemental analysis, FT-IR and <sup>1</sup>H NMR spectral data have been used. The compound showed high affinity and selectivity for vanadium(V) in presence of large quantities of associated metal ions. The complexation of vanadium(V) with OFCHA has a 4:1 metal: ligand stoichiometry as evaluated by Job's plot. A spectrophotometric method is proposed for the extractive determination of vanadium(V) in an acidic medium in the presence of diversified matrix, and verified by ICP-AES. Under the optimum condition of acidity, solvent, interfering ions and OFCHA concentration, the molar absorptivity of the complex is 5630 l mol<sup>-1</sup> cm<sup>-1</sup> at 495 nm. The system obeys Beer's law over the range 0.125-8.75 μg ml<sup>-1</sup> of vanadium(V) with Sandell sensitivity 0.009 μg cm<sup>-2</sup>. The preconcentration factor and overall stability constant evaluated at 25 °C were 142 and 14.18, respectively. The complexation is characterized by favorable enthalpy and entropy changes. Liquid membrane transport studies of vanadium(V) were carried out from source to the receiving phase under controlled conditions and a mechanism for transport is suggested. To check the validity of the proposed method, vanadium is determined in environmental, biological samples and some standard reference materials from NIST and BCS.

**Keywords:** Calix[4]resorcinarene, Hydroxamic acid, Vanadium, Liquid-liquid extraction, Transport studies, Preconcentration

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### INTRODUCTION

Calixarenes have come a long way in offering tailor made candidates for diverse applications in the field of supramolecular chemistry [1]. They possess remarkable structural versatility, and allow an examination of co-operative interaction between the metal centers. Calix[4]resorcinarenes, a structural similar complex to calixarenes, present interesting receptor properties and can act as building blocks for large supramolecular assemblies of fascinating architecture [2,3].

Calix[4]resorcinarenes deliver a versatile molecular

platform for more elaborate systems by virtue of their conformational flexibility, complexing properties and an easy synthetic and commercial availability. These compounds are large cyclic tetramers with diverse applications as macrocyclic receptors [4], as dendrimers [5] in biological systems [6], nano-capsule [7], nanoparticles [8], optical chemosensors [9] supramolecular tectons [10], as components in liquid crystals [11], molecular switches [12] selective membranes [13], HPLC stationary phases [14], as ion channel mimics [15].

Vanadium is a trace element of highly critical role in biochemical processes and of significant importance in environmental, biological and industrial analysis due to its

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toxicity. Vanadium is an essential oxygen carrier for marine organism [16,17]. Industrial exposure of vanadium has shown to cause eye and lung irritation due to inhibition of activity of enzyme cholinesterase [18,19]. It is mainly found in teeth, bone, hairs and nails [20]. However, it becomes toxic when its concentration exceeds 0.5 ppm. The toxicity of vanadium is dependent on its oxidation state, with vanadium(V) being more toxic than vanadium(IV) [21].

Although several methods have been reported for the determination of vanadium, they suffer from several problems related with selectivity, especially with food matrixes, where the abundant presence of other ions such as iron, copper, zinc and molybdenum presents significant interferences [22,23]. Some of the recently proposed organic reagents for the spectrophotometric determination of vanadium include 5,7-dichloroxine-Rhodamine 6G [24], 6-chloro-3-hydroxy-7-methyl-2-(thienyl)-4H-chromen-4-one [25] and 1,5-diphenyl-carbazide [26]. Recently, Chiranjeevi *et al.* [27] studied novel reactions for rapid, sensitive and selective spectrophotometric determination of trace amounts of vanadium(V). Other methods for the determination of total vanadium include ICP-AES [28], ICP-MS [29], AAS [30] *etc.*, which also have some limitations in terms of high cost of instruments used in routine analysis. Till now, few reports have appeared on the use of calix[4]resorcinarenes for the extraction of metal ions. Some groups have studied the use of calix[4]resorcinarenes in the complexation of alkali metal ions especially potassium ions [31-33]. Recently, Merdivan *et al.* have reported separation and preconcentration of  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$  and  $\text{Y}^{3+}$  using calix[4]resorcinarene impregnated on polymeric support [34] and have also studied sorption of thorium and uranium on a polymeric support [35].

Hydroxamic acids are well known to be efficient extractants for Fe(III) and uranyl ion [36]. Solvent extraction by calixarenes bearing hydroxamate groups have been investigated essentially for the extraction of uranium ion and transition metal ion. Complexation of Zr, Ti, Th and Y metal ions with hydroxamic acid derivatized ligands have been reported by Agrawal *et al.* [37-40].

We have already reported the complexation studies of Th, U and Ce with calix[4]resorcinarenehydroxamic acid [41-44]. In this paper we are reporting the complexation, extraction, transport and preconcentration of vanadium with

octafunctionalized calix[4]resorcinarene-hydroxamic acid (OFCHA) (Fig. 1) from environmental samples in the presence of numerous ions.

## EXPERIMENTAL

### Instruments and Measurements

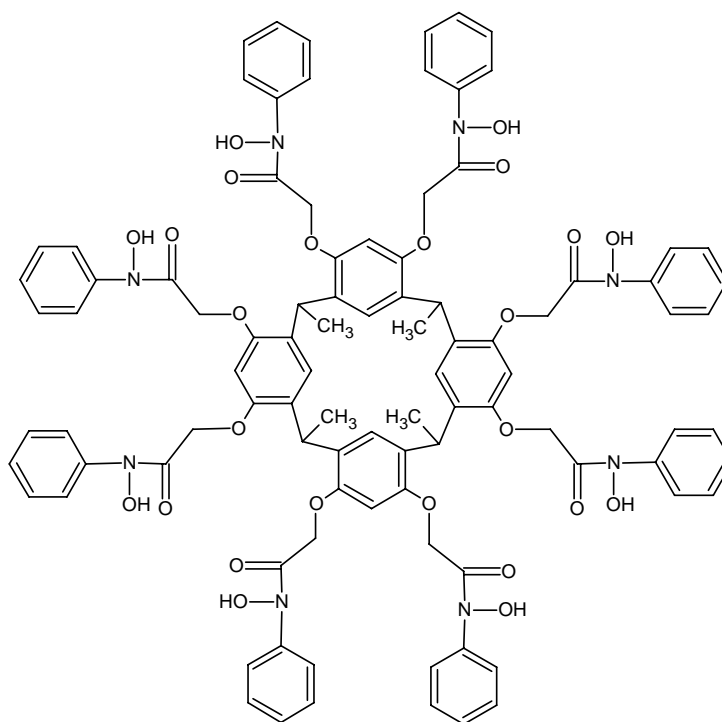
The electronic spectra were recorded on Hitachi 3210 UV-Vis spectrophotometer with matched 10 mm quartz cells. A plasma scan model 710 sequential inductively coupled plasma atomic emission spectrometer with plasma scan multitasking computer and peristaltic pump was used. The following operating conditions were set for ICP-AES: Rf, 27.12 MHz; incident power, 2000W; GMK nebulizer; sample concentration, 1 ppm; RF power, 5 W; observation height, 14 mm; argon coolant flow rate,  $9.71 \text{ min}^{-1}$ ; argon carrier flow rate,  $0.81 \text{ min}^{-1}$ ; intergraph period, 10 s; resolution, 0.004 nm; peristaltic pump flow rate,  $1 \text{ ml min}^{-1}$ ; wavelength, 309.31 nm.

### Materials and Solutions

All the chemicals used were of analytical reagent grade of E. Merck or Qualigens. The octafunctionalized calix[4]resorcinarene-hydroxamic acid (OFCHA) was synthesized and characterized as reported earlier [41]. All aqueous solutions were prepared with quartz distilled deionized water, which was further purified by a Millipore Milli-Q water purification system. The standard stock solution of vanadium ( $1.00 \times 10^{-2} \text{ M}$ ) was prepared by dissolving 0.585 g of ammonium metavanadate in 500 ml doubly deionized water and standardized spectrophotometrically [45]. A 0.05% ( $2.94 \times 10^{-4} \text{ M}$ ) stock solution of OFCHA was prepared in ethyl acetate. Working solution was subsequently prepared by appropriate dilution of the stock solution.

### Sample Preparation

The sample preparation of certified reference materials analyzed to determine the accuracy of the proposed procedure were in accordance with National Institute of Standards and Technology (NIST) and British Chemical Standard (BCS) guidelines. To a 1 g sample of the certified reference material was added, 25 ml of concentrated hydrochloric acid followed by digestion on a sand-bath for 1 h and evaporation to dryness. The residue was dissolved in 15 ml concentrated hydrochloric



**Fig. 1.** Structure of octa-functionalised calix[4]resorcinarene-hydroxamic acid (OFCHA).

acid along with 0.5 g of ammonium persulphate. The solution was diluted with distilled water, filtered and finally diluted to the mark in a 100 ml standard flask with distilled water.

### Soil Samples

A 1-2 g sample of dried soil was digested with 50 ml concentrated hydrochloric acid and 10 ml concentrated nitric acid for 1 h on a sand-bath, then the solution was evaporated to dryness. The residue was moistened with 5-10 ml of HF in a Teflon beaker, digested on a water bath and evaporated. The residue was boiled with 50 ml 0.1 M hydrochloric acid, filtered and the filtrate and washings were evaporated to dryness and the residue was taken up and diluted accurately to 100 ml with 0.1 M hydrochloric acid.

### Plant Samples

A known weight of sample (*i.e.*, 500 g) was ashed at 450 °C for 3 h. 10 g of this ash was transferred into a 200 ml Pyrex beaker and digested on a sand-bath with 100 ml concentrated hydrochloric acid and 20 ml concentrated nitric acid for about

1 h. The hot solution was centrifuged and the supernatant liquid was decanted for any siliceous matter. The residue was boiled with 50 ml of 0.1 M hydrochloric acid and filtered. The supernatant liquid and filtrates were then evaporated to dryness, and the residue was taken up and diluted accurately to 100 ml with 0.1 M hydrochloric acid.

### Blood Samples

2 ml of blood samples were digested with 20 ml of concentrated hydrochloric acid and 0.25 g of ammonium persulphate for 1 h, and then the mixture was diluted and filtered. The filtrate and washings were evaporated to dryness and residue was taken up and diluted to volume in a 25 ml standard flask with 0.1 M hydrochloric acid.

### Liquid-Liquid Extraction Procedure

An aliquot of sample solution containing 1.25-87.5 µg of vanadium was transferred into a 25 ml separatory funnel. Desired acidity of 5-8 M was adjusted with concn. hydrochloric acid and water. The mixture was shaken with 3

ml of  $2.94 \times 10^{-4}$  M OFCHA in ethyl acetate. The organic extract was separated, dried over anhydrous sodium sulfate and transferred into a 10 ml volumetric flask. To ensure complete recovery, the extraction was repeated with 1 ml of OFCHA solution. 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 495 nm. The total concentration of the vanadium ion  $[\text{VO}_2^+]$  species remaining in the aqueous phase  $[\text{VO}_2^+]_{(\text{aq})}$  was measured by ICP-AES.

The concentration of the metal ion extracted into the organic phase  $[\text{VO}_2^+]_{(\text{org})}$  as complex was estimated by  $[\text{VO}_2^+]_{(\text{org})} = [\text{VO}_2^+]_{(\text{aq, initial})} - [\text{VO}_2^+]_{(\text{aq})}$ , where  $[\text{VO}_2^+]_{(\text{aq, initial})}$  is the initial concentration of the metal ion in the aqueous phase. The extracted vanadium-OFCHA complex in ethyl acetate after appropriate dilution was also determined by ICP-AES.

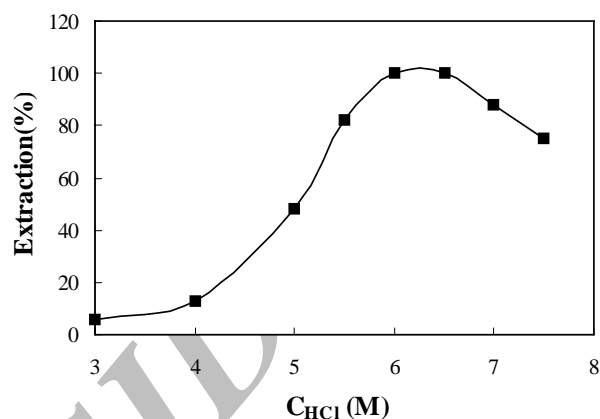
### Transport of Vanadium(V)

Transport of  $\text{VO}_2^+$  was carried out in glass assembly as already reported [41]. 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 transport experiments were performed with 50.0 ml of  $2.94 \times 10^{-4}$  M vanadium solution in 6 M HCl as source phase (B) and 50.0 ml of 0.1 M HCl as receiving phase (C). The liquid membrane (A) consisted of 75 ml of  $2.94 \times 10^{-4}$  M OFCHA in ethyl acetate. A synchronous motor (200 rpm) provided constant reproducible stirring from the top. The amount of vanadium transported from the source phase to the receiving phase was measured by ICP-AES. The transport data are the average of 5 runs with an experimental error of less than 2%.

## RESULTS AND DISCUSSION

### Complexation Studies and Figures of Merit

The complexation of vanadium with OFCHA was studied under optimum conditions of acidity (HCl), solvent and reagent (OFCHA) concentration. Vanadium is well known to exist as dioxovanadium(V) ion ( $\text{VO}_2^+$ ) in highly acidic solution. Figure 2 shows that maximum extraction of



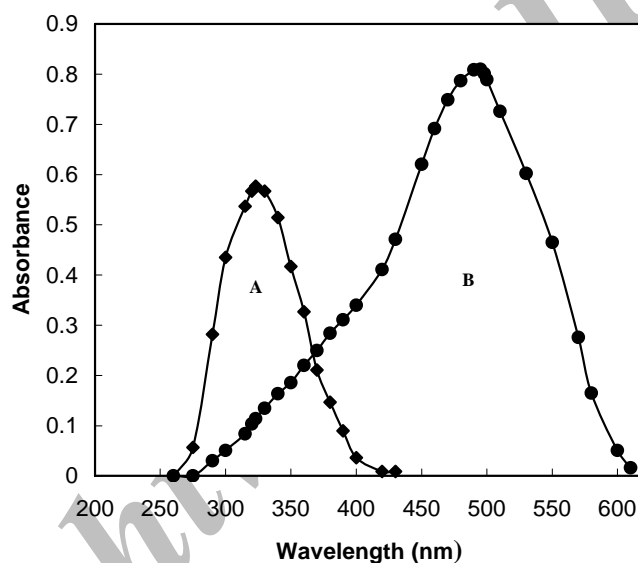
**Fig. 2.** Effect of molarity of acid on the extraction of OFCHA-vanadium complex. Condition: vanadium, 5 ml of  $2.0 \mu\text{g ml}^{-1}$ ; OFCHA, 30 ml of  $2.94 \times 10^{-4}$  M; HCl, 6 M;  $\lambda_{\text{max}}$ , 495 nm.

vanadium(V) was possible in the concentration range of 6.0-6.5 M HCl; however, above and below this concentration range the extraction of the complex was incomplete. It was also found that 5-6 min of shaking is sufficient for quantitative extraction of vanadium. Effect of solvents on the extraction of OFCHA-vanadium(V) complex was studied and the results are shown in Table 1. As seen, the extraction of the C4RAHA-vanadium complex was restricted to ethyl acetate, chloroform toluene and benzene due its limited solubility in other organic solvents. Table 1 shows that extraction efficiency is increased with increasing solvent dielectric constant, maximum being observed in ethyl acetate. The spectra of the complex showed a bathochromic shift of 172 nm from that of the reagent OFCHA in ethyl acetate, as shown in Fig. 3.

Under the optimum condition of acidity, quantitative extraction was possible with 3.0 ml,  $2.94 \times 10^{-4}$  M OFCHA in ethyl acetate. The molar absorptivity measured at the wavelength of maximum absorption (495 nm) for the extracted complex was  $5630 \text{ l mol}^{-1} \text{ cm}^{-1}$ . The system obeys Beer's law in the range of  $0.125\text{-}8.75 \mu\text{g ml}^{-1}$  of vanadium(V). The regression analysis equation obtained from the calibrated standard solution can be represented as  $\text{Abs} = 0.1105 \times \text{Conc.} - 0.00032$  with the correlation coefficient,  $r = 0.998$ . The Sandell's sensitivity calculated for the proposed method is

**Table 1.** Effect of Solvents on the Extraction of OFCHA-Vanadium(V) Complex. Conditions: Vanadium,  $2.0 \mu\text{g ml}^{-1}$ ; OFCHA,  $3.0 \text{ ml } 2.94 \times 10^{-4} \text{ M}$ ; HCl,  $6 \text{ M}$ ;  $\lambda_{\text{max}}$ ,  $495 \text{ nm}$ 

Solvent	Dielectric constant	Extraction (%)	Molar absorptivity $10^3 (\text{l mol}^{-1} \text{cm}^{-1})$
Benzene	2.30	12	0.67
Toluene	2.40	38	2.14
Chloroform	4.80	86	4.80
Ethyl acetate	6.00	100	5.63

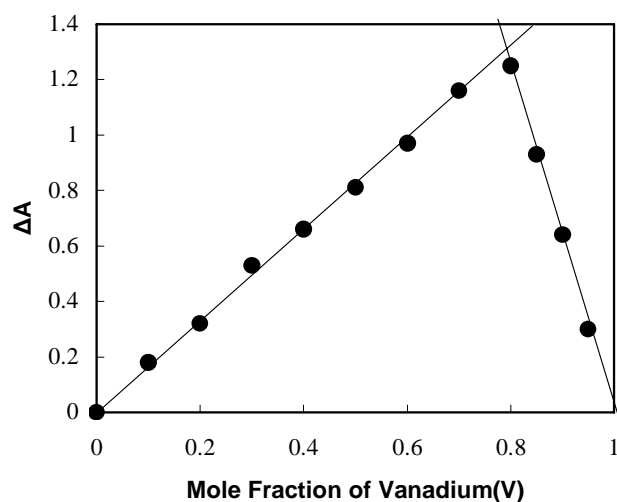
**Fig. 3.** Comparative spectra of  $2.94 \times 10^{-4} \text{ M}$  OFCHA (A) and its vanadium complex (B) in ethyl acetate solution.

$0.009 \mu\text{g cm}^{-2}$ . The precision of the proposed method was investigated based on the optimum condition of extraction and expressed as relative standard deviation of 1.8%. The limit of detection, defined as analyte concentration giving a signal equal to three times the standard deviation of blank signal [46], is  $8.84 \text{ ng ml}^{-1}$ . The limit of quantification, set as ten times the standard deviation of the blank signal, is  $29.5 \text{ ng ml}^{-1}$ . For the ICP-AES measurements a linear calibration graph was obtained from 11 to  $200 \text{ ng ml}^{-1}$  of vanadium(V) in the aqueous phase.

### Stoichiometry of the Complex

The stoichiometric ratio of the complex was determined by

the modified Job's method of continuous variation. The absorbance of complex  $A_c$  of a series of solutions containing  $\text{VO}_2^+$  ion,  $a$ , and OFCHA,  $b$ , at a constant total concentration of  $a + b$ , but with different concentration ratios were measured at  $495 \text{ nm}$ . The absorbance of  $b$  alone ( $A_b$ ) was subtracted from the observed absorbance  $A_c$  to obtain the absorbance difference  $\Delta A = A_c - A_b$ . The  $\Delta A$  values were then plotted against the molar ratio of V(V) ion,  $a/(a + b)$  (Fig. 4). As is obvious, maximum value of for  $\Delta A$  is obtained at an  $a/(a + b)$  value of 0.79, indicating a  $\text{VO}_2^+/\text{OFCHA}$  stoichiometric ratio of 4:1. 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



**Fig. 4.** Job's plot for OFCHA-V(V) complex. Conditions: Vanadium,  $2.94 \times 10^{-4}$  M; OFCHA,  $2.94 \times 10^{-4}$  M; HCl, 6 M;  $\lambda_{\max}$ , 495 nm.

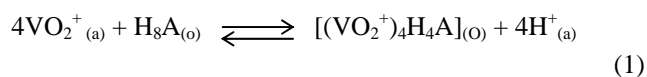
$a/(a + b)$  ratio.

To get more information about the nature of 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 in a perchloric-nitric acid mixture. This resulting solution was centrifuged and vanadium content was determined by ICP-AES. The results thus obtained supported the complex formulae. The experimental results obtained for elemental analysis of the complex are: carbon 55.70%, (cal. 55.91%) nitrogen 5.20% (cal. 5.44%), hydrogen 3.77% (cal. 3.91%) and vanadium 9.65% (cal. 9.89%).

### Extraction Studies and Equilibria

To evaluate the binding ability of OFCHA ( $H_8A$ ) with vanadium, a liquid-liquid extraction (in water-ethyl acetate system) was carried out and the extraction constants were determined.

The extraction equilibria can be expressed by the Eq. (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)

$$K_{ex} = [(VO_2^+)_4H_4A]_{(o)}[H^+]^4_{(a)} / [VO_2^+]^4_{(a)}[H_8A]_{(o)} \quad (2)$$

The distribution ratio of vanadium in the two phases can be given by the Eq. (3)

$$D = [(VO_2^+)_4H_4A]_{(o)} / [VO_2^+]^4_{(a)} \quad (3)$$

From Eq. (2) and Eq. (3), we obtain

$$K_{ex} = D[H^+]^4_{(a)} / [H_8A]_{(o)} \quad (4)$$

Equation 4, can be written as:

$$\log K_{ex} = \log D + 4\log[H^+] - \log[H_8A] \quad (5)$$

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

$$[H_8A] = (C_{H_8A} \cdot P_{H_8A}) / (1 + P_{H_8A} + (K_a / [H^+])) \quad (6)$$

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  $\log P_{H_8A}$ , the  $K_{ex}$  values were calculated by a least square procedure.

The two phase stability constant ( $\log \beta_4 \cdot P_{V-H_8A}$ ) can also be obtained from Eq. (7)

$$\log \beta_4 \cdot P_{V-H_8A} = \log K_{ex} + pK_a + \log P_{H_8A} \quad (7)$$

where  $\beta_4$  and  $P_{V-H_8A}$  are the respective overall formation constant and distribution constant of  $\{[H^+(VO_2^+)]_4A^{-8}\}$  complex in the two phases. Table 2 summarizes the values of  $\log \beta_4 \cdot P_{V-H_8A}$  and  $\log K_{ex}$  at different temperatures.

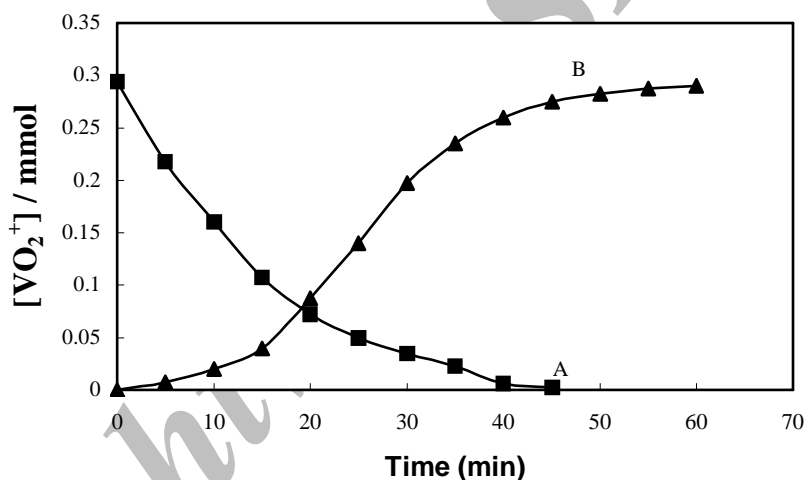
### Liquid Membrane Transport Studies

Considerable effort has been directed over the last two decades to the transport of metal ions across liquid membrane [47]. A liquid membrane is an organic liquid phase (MP), which separates two other liquid aqueous phases, source (SP)

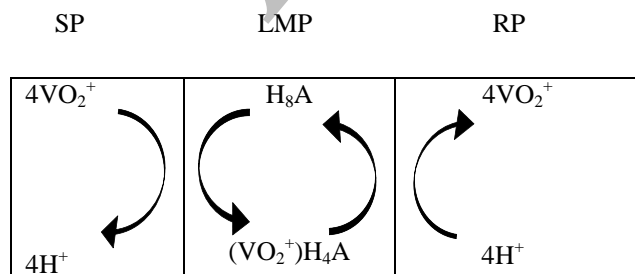
**Table 2.** Temperature Dependence of Two Phase Stability Constant ( $\log\beta_4.P_{V-H8A}$ ) and Extraction Constant for OFCHA-Vanadium(V) Complex

Temperature (K)	$\log\beta_4.P_{V-H8A}$	$K_{ex}$
298	14.18	$1.905 \times 10^{-18}$
303	14.69	$6.166 \times 10^{-18}$
308	15.19	$1.950 \times 10^{-17}$
313	15.68	$6.025 \times 10^{-17}$
318	16.16	$1.820 \times 10^{-16}$

and receiving phases (RP). These liquid membranes are of interest both for possible technological application and for fundamental studies of the transport processes. The transport of  $VO_2^+$  through the membrane containing  $2.94 \times 10^{-4}$  M, OFCHA from source phase of  $[VO_2^+] = 2.94 \times 10^{-4}$  M to the receiving phase of 0.1 M HCl was carried out, and the resulting transport profile is shown in Fig. 5. As seen, the concentration of  $VO_2^+$  in the source phase started to decrease continuously and reached a lower concentration than the detection limit after 14 min (curve A); on the other hand, the concentration of  $VO_2^+$  in the receiving phase increased as



**Fig. 5.** Transport profile of V(V) ion through a bulk liquid membrane containing OFCHA. Conditions: Source phase (SP), 50 ml aqueous  $2.94 \times 10^{-4}$  M of V(V) and 6 M HCl; Membrane phase (MP), 75 ml of  $2.94 \times 10^{-4}$  M OFCHA in ethyl acetate; Receiving phase (RP), 50 ml aqueous 0.1 M HCl; Temperature, 30 °C.



**Fig. 6.** Proposed mechanism for transport of  $VO_2^+$  ion through a liquid membrane containing OFCHA.

shown in the curve B. Therefore, it is clear that  $VO_2^+$  has transported from the source to receiving phase *via* the membrane phase.

Based on these facts and knowledge obtained by the extraction equilibria, A proposed transport mechanism is shown in Fig. 6. Here, the carrier in the membrane reacts with  $VO_2^+$  in the source phase at the interface of these phases and forms a complex  $[(H^+(VO_2^+))_4A^{8-}]$  while releasing 4 moles of proton into the source phase. At the other interface of the membrane and receiving phase, the complex reacts with 4 moles of protons while releasing 4 moles of  $VO_2^+$  into the

receiving phase.

### Effect of Temperature and Thermodynamic Parameters

The extraction of vanadium(V) from aqueous solution was studied at different temperatures between 298 K and 318 K and the results show that the extraction equilibrium constant ( $\log K_{ex}$ ) and two-phase stability constant ( $\log \beta_4 \cdot P_{V-H8A}$ ) increases with increasing temperature Table 2. The change in extraction equilibrium constant ( $\log K_{ex}$ ) with temperature can be expressed by van't Hoff equation:

$$\ln(k_{ex}) = \Delta H^\circ / RT^2 \quad (8)$$

In order to utilize this equation for calculation, it must be integrated assuming the heat of reaction  $\Delta H$  remains constant over a small range of temperature (Eq. (9)).

$$\ln(k_{ex}) = -\Delta H^\circ / RT + \text{constant (intercept)} \quad (9)$$

The plot of  $\log \beta_4 \cdot P_{V-H8A}$  against  $1/T$  yields a straight line equation  $9327.9 x + 45.458$  with slope(x) =  $-\Delta H^\circ / 2.303 R$ . The mean enthalpy change accompany the complexation is found to be  $-179.56 \text{ kJ mol}^{-1}$  for vanadium in the given range of temperature. The values of  $\Delta H^\circ$  with temperature reveal that the complexation is driven by favorable enthalpy changes.

### Effect of Diverse Ions

The extraction of a 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  $\text{VO}_2^+$  in the presence of excess amounts of diverse cationic and anionic species, under optimized experimental conditions. The interference studies were performed by measuring the absorbance of the extracted organic phase and also by carrying out the measurements of ICP-AES of both the extract and aqueous phases. The tolerance limit was set as the amount of foreign ion causing a change of  $\pm 0.02$  in absorbance or 2% error in the recovery of vanadium. The results are summarized in Table 3.

As it can be seen, except with niobium, tantalum, titanium and molybdenum, none of the cations and anions used interfere the determination of V(V). The interference due to niobium and tantalum was tolerated by their masking with 0.1% tartaric acid while the interference effect of titanium and molybdenum was removed by using 0.25 M oxalic acid as masking agent.

### Preconcentration of Vanadium

The concentration of vanadium in natural water is too low for its direct determination. Therefore, preconcentration or enrichment step is necessary to bring the sample to the detectable limits of existing instrumental methods. The method was studied for the preconcentration of vanadium in terms of its preconcentration factors  $PF = [V(V)_{(o)}] / [V(V)_{(a)}]$ , where  $[V(V)_{(o)}]$  is the concentration of metal in organic solution and  $[V(V)_{(a)}]$  is the initial concentration of metal in aqueous solution.

The preconcentration study was carried out by extracting 20  $\mu\text{g}$  of vanadium in 1000 ml aqueous phase with 7 ml of 0.015% OFCHA in ethyl acetate. To evaluate the efficiency of preconcentration, expressed as recovery, the concentration of vanadium in organic phase and the aqueous phase was determined by ICP-AES. Quantitative determination was possible with recovery up to 98% with a preconcentration factor of 142.

### Sample Analysis

In order to test the accuracy and applicability of the proposed method to the analysis of real samples, some standard reference materials of steel and natural samples of plant and rocks from the industrial area of Vatva, Ahmedabad were analyzed. The results for the analysis of standard samples of vanadium are given in Table 4 and for rock, soil, blood samples etc are reported in Table 5.

### ACKNOWLEDGEMENTS

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**Table 3.** Effect of Diverse Ions on the Extraction of C4RAHA-Vanadium(V) Complex. Conditions: Vanadium,  $1.5 \mu\text{g ml}^{-1}$ ; HCl, 6 M; Solvent, Ethyl acetate; OFCHA, 3 ml  $2.94 \times 10^{-4}$  M;  $\lambda_{\text{max}}$ , 495 nm

Ions	Added as	Amount added (mg)	Recovery of vanadium (ppm)	
			Spectrophotometry	ICP-AES
Mg <sup>2+</sup>	Mg(NO <sub>3</sub> ) <sub>2</sub>	100	1.47	1.50
Ca <sup>2+</sup>	CaCl <sub>2</sub>	100	1.50	1.49
Sr <sup>2+</sup>	Sr(NO <sub>3</sub> ) <sub>2</sub>	100	1.49	1.51
Ba <sup>2+</sup>	BaCl <sub>2</sub>	100	1.50	1.50
Cu <sup>2+</sup>	CuSO <sub>4</sub>	80	1.48	1.50
Cd <sup>2+</sup>	CdSO <sub>4</sub>	80	1.48	1.50
Zn <sup>2+</sup>	ZnCl <sub>2</sub>	80	1.50	1.51
Hg <sup>2+</sup>	HgCl <sub>2</sub>	100	1.51	1.50
Pb <sup>2+</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	100	1.47	1.49
Mn <sup>2+</sup>	MnCl <sub>2</sub>	80	1.50	1.51
Co <sup>2+</sup>	CoCl <sub>2</sub>	80	1.49	1.51
Ni <sup>2+</sup>	NiCl <sub>2</sub>	80	1.48	1.49
UO <sub>2</sub> <sup>2+</sup>	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	70	1.51	1.50
Ga <sup>3+</sup>	GaCl <sub>3</sub>	100	1.47	1.50
La <sup>3+</sup>	La(NO <sub>3</sub> ) <sub>3</sub>	100	1.48	1.50
Fe <sup>3+</sup>	FeCl <sub>3</sub>	70	1.50	1.51
Cr <sup>3+</sup>	Cr <sub>2</sub> O <sub>3</sub>	70	1.49	1.48
Sb <sup>3+</sup>	SbCl <sub>3</sub>	80	1.48	1.49
In <sup>3+</sup>	InCl <sub>3</sub>	80	1.48	1.48
Th <sup>4+</sup>	Th(NO <sub>3</sub> ) <sub>4</sub>	80	1.50	1.51
WO <sub>2</sub> <sup>2+</sup>	WO <sub>2</sub> Cl <sub>2</sub>	70	1.50	1.52
Ti <sup>4+a</sup>	TiCl <sub>4</sub>	100	1.49	1.52
Nb <sup>5+b</sup>	Nb <sub>2</sub> O <sub>5</sub>	100	1.50	1.49
Ta <sup>5+b</sup>	Ta <sub>2</sub> O <sub>5</sub>	100	1.49	1.50
Mo <sup>6+b</sup>	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> 4H <sub>2</sub> O	100	1.48	1.51

<sup>a</sup>Masked with oxalic acid. <sup>b</sup>Masked with tartaric acid.**Table 4.** Determination of Vanadium in NIST and BCS Standard Samples

No.	Sample	Certified vanadium (%)	Vanadium found (%) <sup>a</sup>
30	Cr-V steel (NIST)	0.18-0.21	0.195 ± 0.015
117	Ferrotitanium (NBS)	0.05-0.08	0.065 ± 0.005
153	Cr-V-Co-Mo-W steel (NIST)	1.63-1.86	1.745 ± 0.115
224	Cr-V steel (BCS)	0.240	0.241 ± 0.011
242/1	High speed steel (BCS)	1.570	1.569 ± 0.020

<sup>a</sup>Average ± standard deviation (10 determinations).

**Table 5.** Determination of Vanadium in Natural Materials

Sample	Vanadium found (ppm) <sup>a</sup>	No. of determinations	ICP-AES (ppm)
Rice	1.01 ± 0.05	10	0.983
Peas	0.72 ± 0.02	8	0.730
Cabbage	6.00 ± 0.02	8	5.968
Carrots	3.55 ± 0.03	9	3.565
Spinach	6.33 ± 0.02	8	6.350
Potato sample 1	5.74 ± 0.09	10	5.723
Potato sample 2	6.84 ± 0.04	10	6.820
Onion sample2	7.43 ± 0.05	10	7.450
Onion sample2	6.82 ± 0.05	10	6.830
Tomato	1.55 ± 0.03	8	1.550
Ripe mango skin	1.54 ± 0.04	8	1.550
Unripe mango skin	3.55 ± 0.03	8	3.550
Tobacco	2.18 ± 0.04	12	2.200
Sea water	0.82 ± 0.05	12	0.853
Effluent <sup>b</sup>	1.50 ± 0.05	12	1.535
Effluent <sup>b</sup>	1.80 ± 0.08	12	1.800
Lake water	1.05 ± 0.05	10	1.060
Blood sample <sup>c</sup>	0.020 ± 0.002	12	0.022
MSI <sup>d</sup>	333 ± 1.00	8	330
DVI <sup>d</sup>	320 ± 1.00	8	323
DVIII <sup>d</sup>	330 ± 1.00	8	333
Soil <sup>b</sup>	0.090 ± 0.002	8	0.088

<sup>a</sup>Mean ± standard deviation (spectrophotometrically) from 5 determinations. <sup>b</sup>Samples from industrial area of Vatva, Ahmedabad, India. <sup>c</sup>Whole blood samples from adult male. <sup>d</sup>Samples from Mussories phosphate deposits.

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