

Liquid–Liquid Extraction, Separation, Preconcentration and Spectrophotometric Determination of Vanadium(V) by Tetra Functionalized Calix[4]pyrrole Hydroxamic Acid

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A series of calix[4]pyrrole hydroxamic acids have been used for the liquid-liquid extraction, separation, preconcentration and spectrophotometric determination of vanadium(V) ions from aqueous media using ethyl acetate as a solvent. Various significant extraction parameters like pH, effect of solvents, shaking time, concentration of vanadium(V) and concentration of reagent were evaluated. The extracted complex was determined simultaneously by spectrophotometry and inductively coupled plasma atomic emission spectroscopy (ICP-AES). The wavelengths of maximum extraction (λ_{max}), molar absorptivity (ϵ), linear concentration range obeying Beers law, effect of diverse ions have been determined. The stoichiometry of complex, the regression analysis equation, relative standard deviation, limit of detection (LOD), limit of quantification (LOQ) were also evaluated. Mechanism of metal-ion transport has been proposed. The validity of proposed method was checked by determining vanadium(V) in environmental and industrial samples as well as some standard reference materials.

Keywords: Calix[4]pyrrole, hydroxamic acid, vanadium, liquid-liquid extraction, transport study.

Introduction

Calixpyrrole-chemistry is one of the most vigorous and fast growing fields in supramolecules. Calixpyrroles,^[1] the cyclic-oligomers of pyrrole(s) and ketone(s), originally named “pyrrole-acetone” and formally known as *meso*-octaalkyl-porphyrinogens are a venerable class of tetrapyrrolic macrocycle. Calix[4]pyrroles belong to the family of heterocalixarenes,^[2] which have four pyrrole units instead of phenolic ones, an easy-to-make class of neutral macrocycles, differ from the true porphyrinogens in that they can not be oxidized to their corresponding aromatic porphyrin forms.^[3] The development of calixpyrrole-based anion coordination chemistry is reflected in a number of publications appearing each year since 1996. Many new calixpyrrole-based anion receptors have been synthesized and studied by Sessler’s research group as well as by other research groups worldwide.^[1] This activity has served to establish firmly this branch of anion coordination chemistry.^[4-7] The calix[4]pyrroles having four pyrrole units give rise to non-conjugated macrocycles which possess unique supramolecular characteristic and present interesting chemical and physicochemical properties as well as wide application possibilities.^[8-11]

Till date, number of calixpyrroles derivatives containing various functional groups have been incorporated as host molecules for anions,^[4,12] neutral substrates,^[13,14] optical sensors,^[15] anion transporting agents^[16] and have been applied in many aspects, such as anion recognitions,^[17] electrochemistry,^[18] colorimetry^[19] as well as they have found novel application as catalyst in various reactions.^[20] Functionalized calix[4]pyrroles also show promise as solid supports for the separation of anionic substrates,^[21] noble

metal-cations,^[22] inorganic anions, amino acids, phenols, benzene carboxylic acids and some medicines.^[23] Recently, Ghiasvand *et al.*^[24] have proposed the method for the selective separation and preconcentration of Ag⁺ and Tl⁺ by liquid liquid extraction using tetraspirocyclohexylcalix[4]pyrrole as a suitable selective complexing ligand.

Owing to the toxic and essential nature of vanadium, a trace element of highly critical role in biochemical process and of significant importance in environmental, biological and industrial analysis, there has been considerable interest in the determination of its content in different kinds of samples. The Threshold Limit Values (TLV) for vanadium are 0.5 mg/cubic meter of air and 0.1 mg/cubic meter of fume exceeding which may cause anemia, cough, emaciation, irritation of mucous membrane, gastrointestinal disturbances and bronchopneumonia.^[25, 26]

Earlier, many spectrophotometric methods for the determination of vanadium based on the complex formation, redox reaction, ion-association, catalytic-kinetic reactions and solvent extraction have been reviewed.^[27,28] Some of the newly proposed organic reagents for the spectrophotometric determination of vanadium include 5,7-dichloroxine-Rhodamine 6G,^[29] 6-chloro-3-hydroxy-7-methyl-2-(2-thienyl)-4H-chromen-4-one,^[30] 1,5-diphenylcarbazide.^[31] In addition, several kinetic methods based on the catalytic action of vanadium(V) on the oxidation of organic reagents have been reported.^[32, 33]

Although the highly sensitive spectrophotometric determination of vanadium with pyridylazoresorcinol (PAR) is often used as a standard method,^[34] it suffers from poor selectivity and interfering effect of some metal ions. Other methods for the determination of vanadium including

ICP-AES,^[35] voltammetry^[36] and AAS^[37] have also some limitations in terms of high cost of instruments used in routine analysis and matrix effects. Thus, highly selective methods are still required for trace determination of vanadium(V) in different kinds of samples.

Hydroxamic acids are versatile metal extractants and has wide application in analytical,^[38] agriculture^[39] and biological fields.^[40] In recent years few macrocycles bearing hydroxamic acid as a functional group have been synthesized and used for complexation studies.^[41, 42]

Since we recently synthesized^[43] a series of novel calix[4]pyrrole hydroxamic acid derivatives and carried out very preliminary complexation studies with vanadium(V), we thought it worth to extend our investigations to liquid-liquid extraction, separation, preconcentration, and spectrophotometric determination of vanadium(V) in presence of several interfering ions. Various significant extraction parameters like pH, effect of solvents, extraction time, concentration of vanadium(V) and concentration of reagent were evaluated. Liquid membrane transport studies of vanadium(V) were carried out from source to the receiving phase under controlled conditions and a mechanism of transport is suggested. To check the applicability of the proposed method, vanadium(V) was determined in environmental and industrial samples as well as some standard reference materials.

Experimental

Instruments and Measurements

UV-vis absorption studies were carried out on a JASCO 570 UV/VIS/NIR spectrophotometer using 10mm quartz cells. 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, 1ppm; RF power, 5W; observation height, 14mm; argon coolant flow rate, 9.71min⁻¹; argon carrier flow rate,

0.81min⁻¹; Intergraph period, 10s; resolution, 0.004nm; peristaltic pump flow rate, 1 ml min⁻¹; wavelength, 309.31nm.

Chemicals and Reagents

All the chemicals used were of analytical reagent grade from 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 (Millipack 20, Pack name: Simpак 1, Synergy). Standard vanadium(V) stock solution (100 µg ml⁻¹) was prepared by dissolving 0.229 g of ammonium metavanadate (NH₄VO₃) in a minimum amount of concentrated HCl just to solubilize the ammonium metavanadate (NH₄VO₃) and then make up 1l with double distilled water and was standardized spectrophotometrically.^[34]

Tetra functionalized calix[4]pyrrole hydroxamic acids [C4PHAs] (Figure 1) were synthesized and characterized as earlier reported method^[43] and their stock solutions (0.1%) were prepared in ethyl acetate. Working solution was subsequently prepared by appropriate dilution of the stock solution.

Sample Treatment

Standard samples. The sample preparations of certified reference materials to determine the truthfulness of the proposed method was 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 evaporated to dryness. The residue was dissolved in 15 ml of concentrated hydrochloric 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.

Environmental and Biological Samples

Depending on the concentration of vanadium in various samples (soil, vegetables, waste water, etc.), 2-20 g of material was digested with an excess of perchloric and nitric acids. The mixture was centrifuged and filtered, and the filtrate was evaporated to

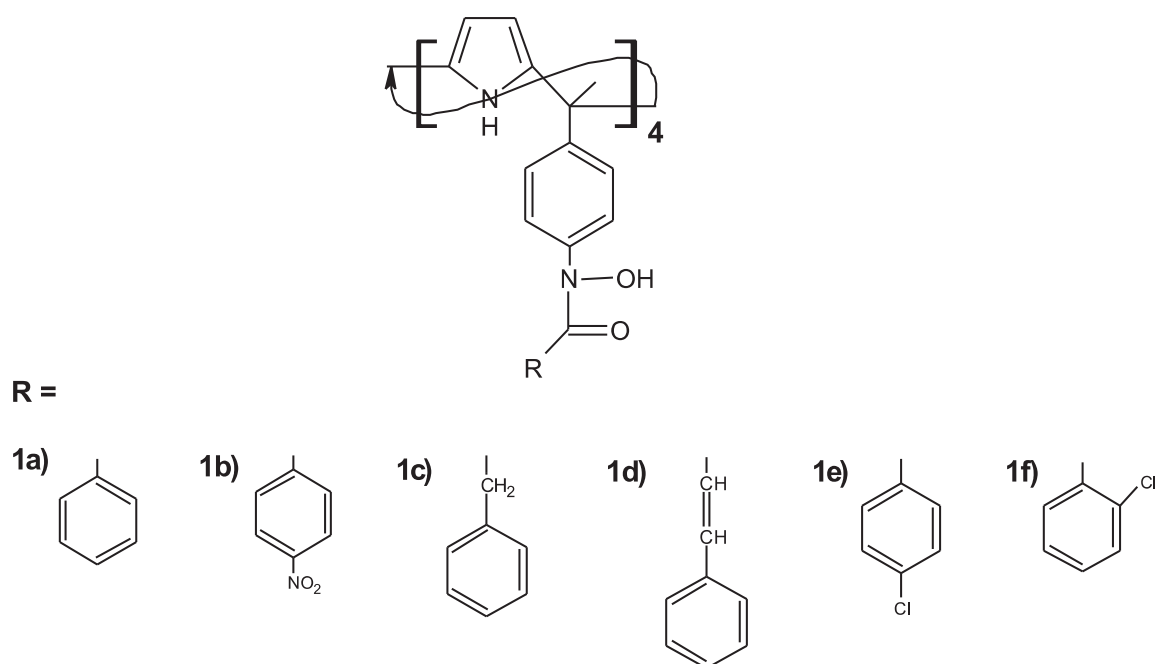


Figure 1. Tetra functionalized calix[4]pyrrole hydroxamic acids (C4PHAs).

dryness and residue was dissolved in and diluted to 100 ml with 0.1 M HCl.

General Procedure for Liquid-Liquid Extraction of Vanadium(V)

An aliquot of sample solution containing 0.4–12 µg of vanadium(V) was transferred into a 25 ml separatory funnel and optimum acidic condition of 6 M was adjusted with sufficient amounts of concentrated hydrochloric acid and water in a total aqueous phase of 10 ml. The mixture was shaken with 7 ml of 0.1% reagent (NBC4PHA) in ethyl acetate. The metal-reagent complex was extracted into the organic phase. To ensure complete recovery, the extraction was repeated with 2 ml of reagent solution; the organic extract was separated, dried over anhydrous sodium sulphate and transferred into a 10 ml volumetric flask. The combined extracts and washings were diluted to the mark (10 ml) with ethyl acetate. The absorbance of the organic phase was measured against the reagent blank at 505 nm.

The concentration of the metal ion extracted into the organic phase $[\text{VO}_2^+]_{(\text{org})}$ as complex was estimated by $[\text{VO}_2^+]_{(\text{org})} = [\text{VO}_2^+]_{(\text{aq, Init})} - [\text{VO}_2^+]_{(\text{aq})}$, where $[\text{VO}_2^+]_{(\text{aq, Init})}$ is the initial concentration of the metal ion in the aqueous phase.

The percent extraction (E, %) was calculated by

$$\% E = \frac{[\text{VO}_2^+]_{(\text{Org})}}{[\text{VO}_2^+]_{(\text{Aq, Init})}} \cdot 100$$

The concentration of vanadium ions (VO_2^+) remaining in aqueous phase and in the organic phase of extracted complex was determined by ICP-AES after appropriate dilution.

Liquid Membrane Transport Studies

Transport of vanadium(V) was carried out in a specially fabricated glass assembly (Figure 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 outer 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 ml of $3.58 \cdot 10^{-4}$ M vanadium solutions in 6M HCl as source phase

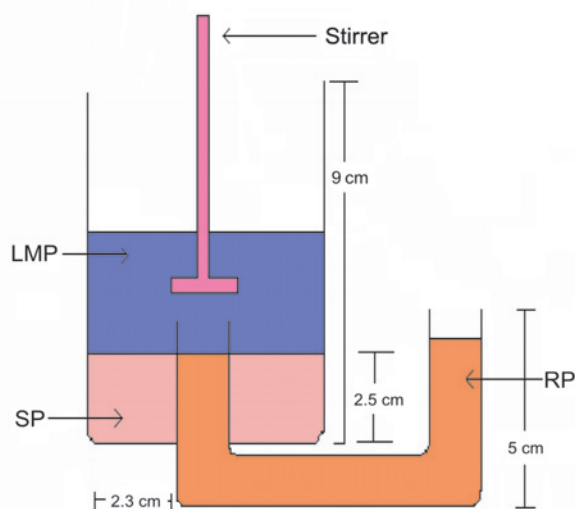


Figure 2. Apparatus for transport studies. Source phase (SP): 50 ml, $3.58 \cdot 10^{-4}$ M Vanadium solution in 6M HCl. Liquid membrane phase (LMP): 75 ml, $7.16 \cdot 10^{-4}$ M, NBC4PHA (**1b**) in ethyl acetate. Receiving phase (RP): 50 ml, 0.1M HCl.

and 50 ml, 0.1M HCl as receiving phase. The liquid membrane consisted of 75 ml of $7.16 \cdot 10^{-4}$ M, NBC4PHA (**1b**) 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 were the average of 5 runs with an experimental error of less than 2%.

For the studies simple arrangement was made which is shown in Figure 2.

Results and Discussion

Spectrophotometric Determination of Vanadium(V)

Spectral characteristics of vanadium(V) - C4PHAs complex. The synthesized calix[4]pyrrole hydroxamic acids (**1a-f**) were used for the extraction and spectrophotometric determination of vanadium(V). It has been found that among all the synthesized calix[4]pyrrole hydroxamic acids (**1a-f**), *meso*-tetra(methyl) *meso*-tetra[N-(4-nitrobenzoyl)-N-phenyl]-calix[4]pyrrole hydroxamic acid (NBC4PHA) (**1b**) was the most sensitive reagent for the vanadium(V) (Table 1). The complexation of vanadium(V) with NBC4PHA was studied under optimum acidic conditions, type of solvent and concentration of reagent (NBC4PHA).

The maximum absorbance of the pinkish violet colored complex was observed at 505 nm which showed a bathochromic shift of 282 nm from that of the reagent blank (Figure 3).

The molar absorptivity (ϵ) was found to be $4429 \text{ l} \cdot \text{mol}^{-1} \text{ cm}^{-1}$ and the system obeys Beer's law in the range of $0.4\text{--}12 \text{ } \mu\text{g} \cdot \text{ml}^{-1}$ vanadium(V). The regression analysis equation obtained from the calibrated standard solution can be represented as $\text{Abs.} = 0.0559 \times \text{concentration} + 0.0004$ with the correlation coefficient, $r = 0.997$. The limit of detection (LOD $20 \text{ } \mu\text{g l}^{-1}$) was defined as that analyte concentration giving a signal equal to three times the standard deviation of blank signal. The limit of quantification (LOQ $67 \text{ } \mu\text{g l}^{-1}$) was then set as ten times the standard deviation of the blank signal. For ICP-AES measurements, the vanadium calix[4]pyrrole hydroxamate ethyl acetate extract was inserted into plasma by means of peristaltic pump after appropriate dilution with ethyl acetate.

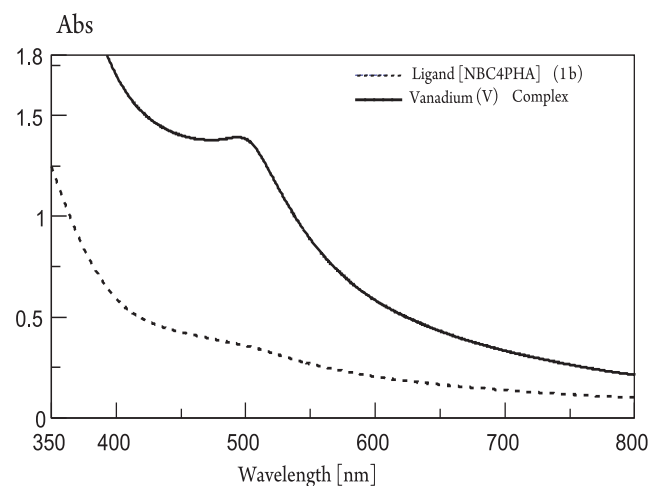


Figure 3. Comparative spectra of ligand (NBC4PHA) ($7.1 \cdot 10^{-4}$ M) and its vanadium(V) complex in ethyl acetate.

Table 1. Spectral characteristics of various tetra functionalized calix[4]pyrrole hydroxamic acids for the extraction* of vanadium(V).

No.	Calix[4]pyrrole-hydroxamic acids [C4PHAs]	$\lambda_{\max}$ (nm)	Color of the complex	Molar absorptivity (l·mol ⁻¹ ·cm ⁻¹)
1	[N-(benzoyl)-N'-phenyl] C4PHA (1a)*	495	PV	4056
2	[N-(<i>p</i> -nitrobenzoyl)-N'-phenyl] C4PHA (1b)*	505	PV	4429
3	[N-(benzoyl)-N'-phenyl] C4PHA (1c)*	494	PV	4285
4	[N-(cinnamoyl)-N'-phenyl] C4PHA (1d)*	495	PV	4209
5	[N-(<i>p</i> -chlorobenzoyl)-N'-phenyl] C4PHA (1e)*	494	PV	3852
6	[N-(<i>o</i> -chlorobenzoyl)-N'-phenyl] C4PHA (1f)*	492	PV	3622

*Extraction conditions: vanadium: 2 ml, 25 µg ml⁻¹; concentration of HCl: 6M; reagent: 0.1% C4PHAs; solvent: ethyl acetate.

Effect of Variable on Extraction

The complexation of vanadium(V) with NBC4PHA was studied under optimum conditions of the acidity, solvent and concentration of reagent (NBC4PHA).

Acidity and Shaking Time

With the increase or decrease in the concentration of acid, the percentage extraction of vanadium also decreases (Figure 4) and it was found maximum at 6M HCl, hence all the extractions were carried out at 6M HCl.

The optimum shaking time was found to be 5-10 min, which was sufficient for quantitative extraction of vanadium. The extraction were not affected by further shaking, indicating that the equilibrium state had been attained.

Solvents

The vanadium(V) - NBC4PHA complex was extracted with various solvents like ethyl acetate, chloroform, toluene, benzene, dichloromethane and carbon tetrachloride. Ethyl acetate was found to be the most suitable solvent for quantitative extraction as compared to other solvents (Table 2).

Concentration of Reagent (NBC4PHA)

The influence of varying concentration of NBC4PHA was studied by extracting a fixed amount of vanadium at 6M HCl. A 7 ml of 0.1% NBC4PHA was sufficient for the quantitative extraction of vanadium, where the extraction

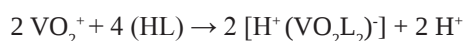
was incomplete at the lower concentration of NBC4PHA. The excess concentration of the reagent had no adverse effect on the extraction of vanadium.

Composition of Vanadium(V) - NBC4PHA Complex

The composition of vanadium(V) - NBC4PHA complex extracted into ethyl acetate was determined by slope ratio method {plotting the graph of logarithm of distribution coefficient of the metal (logD_m) against the negative logarithm of the reagent concentration -log [NBC4PHA]}. The extraction is carried out by taking a fixed concentration of vanadium solution and varying the amount of reagent.

The plot of logD_m against -log [NBC4PHA] gave a straight line with a slope of 1.86, which indicates that, the extracted species vanadium (V): NBC4PHA is in the ration of 2:1 (Figure 5).

The possible extraction mechanism of the metal species in solution, VO₂⁺ with the ligand is as follows,



One mole of reagent (NBC4PHA) consists of four hydroxamic acid groups which was represented by 4 HL in above equation and hence forms a 2:1 (M:L) complex with VO₂⁺ in the solution. The anionic complex thus formed, [VO₂L₂]⁻ takes up a proton to yield the neutral ion pair complex H⁺[VO₂L₂]⁻ which gets extracted into ethyl acetate.

To obtain 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

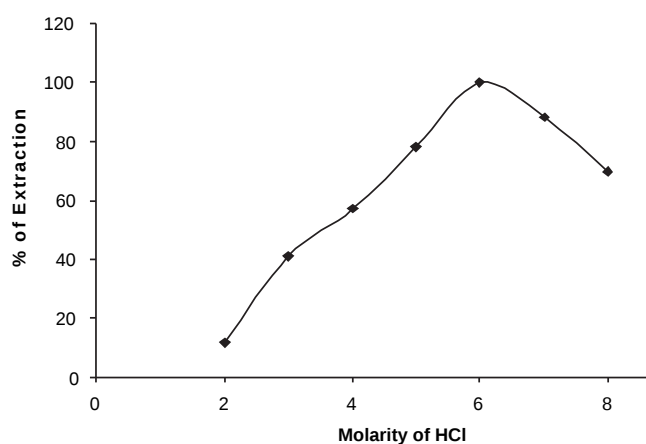


Figure 4. Effect of concentration of HCl on the extraction of vanadium(V) - NBC4PHA.

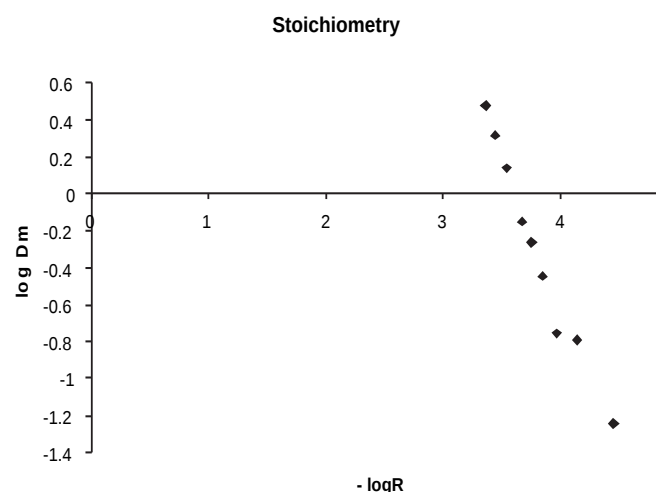


Figure 5. Plot of logD_m vs -log [NBC4PHA].

Table 2. Effect of solvents on the extraction[#] of vanadium(V) - NBC4PHA complex.

Solvent	Dielectric constant	Molar absorptivity ($L \cdot mol^{-1} \cdot cm^{-1}$)	Extraction (%)
Toluene	2.30	760	17
Carbon tetrachloride	2.20	1102	24
Benzene	2.28	1570	35
Dichloromethane	8.90	2100	48
Chloroform	4.80	3260	73
<i>Iso</i> -amyl alcohol	15.30	3764	85
Ethyl acetate	6.40	4429	100

[#]Extraction conditions: vanadium: 2 ml, 25 $\mu g \cdot ml^{-1}$; reagent: 0.1% NBC4PHA; concentration of HCl: 6M; λ_{max} : 505 nm

and a known weight of the dry complex was digested with a perchloric and nitric acid mixture. It was centrifuged and after appropriate dilution the vanadium(V) content was determined by ICP-AES, which also confirmed 2:1 (M:L) complex.

Effect of Diverse Ions

In order to assess possible analytical application of the reagent, the effect of diverse ions on the extraction of vanadium(V) was studied by adding a known amount of the metal ion in 10 ml solution containing 1.5 $\mu g \cdot ml^{-1}$ of vanadium(V) and the recommended general procedure was followed. Vanadium(V) was extracted in the presence of several other ions to determine the selectivity and utility of the method.

Table 3. Effect of diverse ions on the extraction^{*} of NBC4PHA -vanadium(V) complex.

Ions	Added as	Amount added (mg)	Recovery of vanadium ($\mu g \cdot ml^{-1}$)	
			Spectro- photometry	ICP-AES
Ca^{+2}	$CaCl_2$	100	1.47	1.50
Ag^+	$AgNO_3$	100	1.50	1.49
Cu^{+2}	$CuSO_4$	100	1.49	1.51
Co^{+2}	$CoCl_2$	70	1.50	1.50
Ba^{+2}	$BaCl_2$	100	1.48	1.50
Zn^{+2}	$ZnCl_2$	70	1.48	1.51
Mn^{+2}	$MnCl_2$	70	1.50	1.51
Pb^{+2}	$Pb(NO_3)_2$	100	1.51	1.49
Ni^{+2}	$NiCl_2$	70	1.47	1.51
Hg^{+2}	$HgCl_2$	100	1.50	1.48
Cd^{+2}	$CdSO_4$	70	1.49	1.51
UO_2^{+2}	$UO_2(NO_3)_2$	70	1.48	1.48
Ga^{+3}	$GaCl_3$	100	1.50	1.49
La^{+3}	$La(NO_3)_3$	100	1.49	1.48
Fe^{+3}	$FeCl_3$	70	1.48	1.51
Th^{+4}	$Th(NO_3)_4$	80	1.47	1.50
Sr^{+2}	$Sr(NO_3)_2$	100	1.50	1.52
Ce^{+4}	$(NH_4)_4Ce(SO_4)_4$	80	1.48	1.49

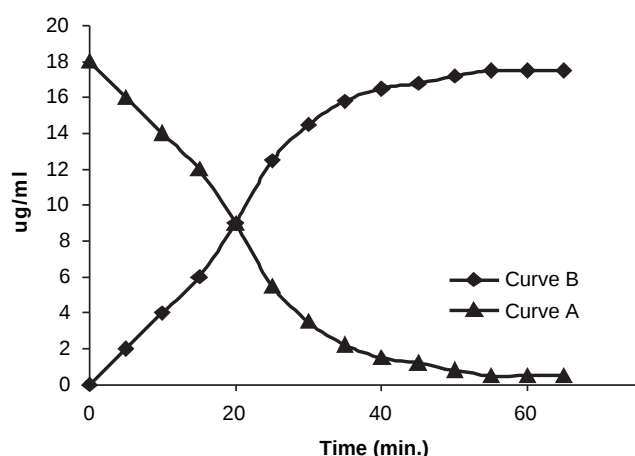
^{*}Extraction conditions: vanadium: 10 ml, 1.5 $\mu g \cdot ml^{-1}$; concentration of HCl: 6M; reagent: 0.1% NBC4PHA; solvent: ethyl acetate; λ_{max} : 505 nm

Interference studies were performed by measuring the absorbance of the extracted organic-phase and also by carrying out the measurements by ICP-AES of both the extract as well as aqueous phase. The tolerance limit was set as the amount of foreign ion causing a change of ± 0.02 in absorbance. It was observed that addition of 70-100 mg of Ca^{+2} , Ag^+ , Cu^{+2} , Co^{+2} , Ba^{+2} , Zn^{+2} , Mn^{+2} , Pb^{+2} , Ni^{+2} , Hg^{+2} , Cd^{+2} , UO_2^{+2} , Fe^{+3} , Ga^{+3} , La^{+3} , Th^{+4} , Ce^{+4} and Sr^{+2} do not interfere in the determination of vanadium(V). The results are shown in Table 3.

Liquid Membrane Transport Studies

A liquid membrane is a liquid phase, which separates two other liquid phases with which it is immiscible. These liquid membranes are of interest both for possible technological application and for fundamental studies of the transport process. The transport of VO_2^+ through the membrane containing $7.16 \cdot 10^{-4}$ M, NBC4PHA from source phase of $[VO_2^+] = 3.58 \cdot 10^{-4}$ M to the receiving phase of 0.1M HCl was carried out. As evident from Figure 6, the concentration of VO_2^+ in the source phase started decreasing continuously and it took about 20 min to transport half of the VO_2^+ from source phase to receiving phase (curve A). On the other hand concentration of VO_2^+ in the receiving phase starts increasing as shown in the curve B.

Therefore, it is clear that VO_2^+ moved from the source to receiving phase through the liquid membrane. Based

**Figure 6** Transport profile of vanadium(V) through the liquid membrane containing NBC4PHA at 30°C.

on these facts and knowledge obtained by the extraction equilibria, the proposed mechanism of transport of vanadium through the liquid membrane of NBC4PHA is as shown in Figure 7.

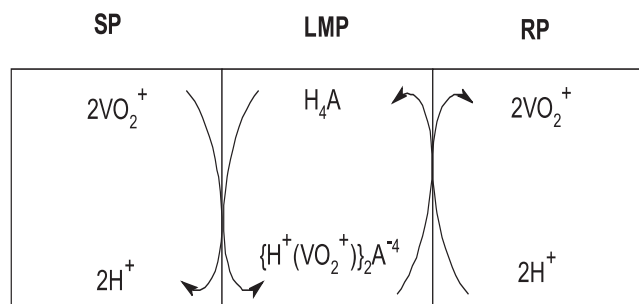


Figure 7. Proposed mechanism for transport of vanadium(V) through a liquid membrane containing NBC4PHA. SP : Source phase. LMP: Liquid membrane phase. RP : Receiving phase

The carrier in the membrane reacts with VO_2^+ in the source phase at the interface of these phases and forms a complex $[\{\text{H}^+(\text{VO}_2^+)\}_2\text{A}^{-4}]$ while releasing 2 moles of proton into the source phase. At the other interface of the membrane and the receiving phase the complex reacts with 2 moles of protons while releasing 2 moles of VO_2^+ in the receiving phase.

Preconcentration of Vanadium(V)

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.

$$\text{PF} = \frac{\text{Concentration of metal in organic solution}}{\text{Initial concentration of metal in aqueous solution}}$$

The preconcentration study was carried out by extracting 20 μg of vanadium in 1000 ml aqueous phase with 7 ml of 0.1% NBC4PHA 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 concentration factor of 118.

Table 5. Analysis of vanadium(V) in NBS and BCS standard samples.

No.	Sample	Certified vanadium (%)	Vanadium found with present method ^a (%)	Vanadium found by ICP-AES (%)
242/1	High speed steel (BCS)	1.570	1.569 $\pm$ 0.02	1.568
153	Cr-V-Co-Mo-W steel (NIST)	1.63 - 1.86	1.75 $\pm$ 0.02	1.695
117	Ferrotitanium (NBS)	0.05 - 0.08	0.06 $\pm$ 0.01	0.065
224	Cr-V steel (BCS)	0.240	0.239 $\pm$ 0.02	0.239
30	Cr-V steel (NIST)	0.18 - 0.21	0.201 $\pm$ 0.02	0.210

^a Average of 10 determinations.

Applications

The vanadium contents in alloy, steels, soil, water, plant materials *etc.* samples were analyzed by the proposed method and the results are summarized in Tables 4, 5. In all cases, the results were compared with the ICP-AES determination.

Table 4. Determination of vanadium(V) in various samples.

Samples	Vanadium(V) found ($\mu\text{g}\cdot\text{ml}^{-1}$)	
	Spectrophotometric ^a	ICP-AES
Rice	1.01 $\pm$ 0.05	0.983
Peas	0.72 $\pm$ 0.02	0.730
Cabbage	6.00 $\pm$ 0.02	5.968
Carrots	3.55 $\pm$ 0.03	3.565
Spinach	5.08 $\pm$ 0.02	5.080
Potato sample	5.74 $\pm$ 0.09	5.723
Bottle guard	3.99 $\pm$ 0.07	3.979
Onion sample	7.43 $\pm$ 0.05	7.450
Coriander	2.72 $\pm$ 0.05	2.719
Tomato	1.55 $\pm$ 0.03	1.550
Neem leaves ^b	2.54 $\pm$ 0.05	2.539
Soil sample ^b	1.63 $\pm$ 0.03	1.628
Tobacco	2.18 $\pm$ 0.04	2.200
Sabarmati water	0.82 $\pm$ 0.05	0.853
Effluent ^b	1.50 $\pm$ 0.05	1.535
Ceramic Color 1 ^b	8.23 $\pm$ 0.06	8.229
Ceramic Color 2 ^b	5.49 $\pm$ 0.02	5.486
Pond water ^b	1.05 $\pm$ 0.05	1.060

^aMean $\pm$ standard deviation (spectrophotometrically) from 5 determinations.

^bSamples from industrial area of Kadi, Mahesana, India.

Conclusion

Newly synthesized calix[4]pyrrole hydroxamic acids have been used for the liquid-liquid extraction, separation, membrane transportation, preconcentration and spectrophotometric determination of vanadium(V). All the important results presented in this article will add to a series of buoyant novel host compound in the field of pyrrole-based hetero-calixarene. The proposed method with low detection limit, is selective and specific for the determination of vanadium ion in presence of large quantities of associated metal ions by calix[4]pyrrole hydroxamic acid. The present

method describes a new, simple, sensitive, precise, reliable and reproducible spectrophotometric method for determination of vanadium(V) in environmental and industrial samples as well as certified standard materials.

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