Scientific paper

Design, Synthesis, Characterization and Complexation Studies of Novel Vanadophiles: Calix[4]pyrrole Hydroxamic Acids

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Abstract

New four armed calix[4]pyrrole bearing four hydroxamic acid groups (C4PHA) have been synthesized by reacting partially reduced mesotetramethyl-mesotetra (p-nitrophenyl) calix[4]pyrrole with different aromatic acid chlorides (benzoyl chloride, p-nitrobenzoyl chloride, cinnamoyl chloride, phenyl acetyl chloride and p-chlorobenzoyl chloride) at low temperature. Synthesized compounds were characterized by elemental analysis, FT-IR, NMR and Mass data. Extraction studies showed that synthesized ligands exhibit high affinity and selectivity for vanadium(V), especially **3e**. Thus, various significant extraction parameters like pH, concentration of vanadium(V), reagent (ligand) concentration and solvent effects were optimized for **3e**. The results of extraction studies with **3e**, (using optimized procedure) were very encouraging, hence, the extraction experiments were further extended to natural and industrial samples in presence of diverse ions. The stoichiometry of vanadium-C4PHA (**3e**) complex was determined by slope-ratio method using UV-Visible spectrophotometry and the results were validated by ICP-OES analysis. Transportation studies of vanadium(V) across a liquid membrane containing C4PHA (**3e**) in a three-phase system were carried out in a specially fabricated glass assembly under controlled conditions and the mechanism of metal-ion transport has been explained.

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

1. Introduction

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 toxicity.[1,2] Several methods have been proposed for the determination of vanadium, mainly based on the liquid-liquid extraction technique followed by spectrophotometry.[3–6] These methods although sensitive, are not selective especially for real sample analysis. Thus, highly sensitive and selective methods are still required for trace analysis of vanadium in different kinds of samples, especially environmental samples.

Calixpyrroles, have been extensively studied as powerful building blocks to furnish functional receptors for ionic and molecular recognition.[7–9] Calix[4]pyrroles possess four pyrrole units assembled in a calixarene like manner, replacing phenolic units, and display conformational behavior similar to that of the calix[4]arenes. Easy construction of calixpyrroles with pre-designated core size and ligand location widens the scope of their applicability for design of ion-selective receptors.[10–13] Hydroxamic acids, on the other hand, are versatile extractants and they

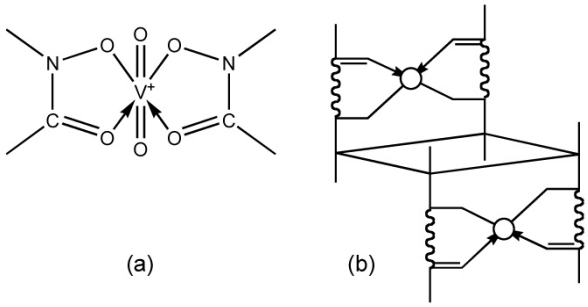


Figure 1: (a) Schematic complexation of vanadium with a pair of hydroxamic acids (b) Metal complexation by a pair of ligands pre-organized on a 1,2-alternate scaffold

have achieved significant importance as analytical tools for the separation and determination of a large number of metal-ions; especially as a selective/specific reagent for the determination of vanadium(V) metal-ion.[14,15] In recent years, calixarene with hydroxamic acid as a functional group have been synthesized and used for the complexation studies.[16–18]

With this in view, we have designed, synthesized and characterized novel calix[4]pyrrole derivatives containing hydroxamic-acid chelating sites attached to all four meso-positions. The basis of the design process is a well known fact[19] that in ca. 6N acid solution vanadium exists as VO_2^+ species which is readily co-ordinated by a pair of hydroxamic acid functionality as $[VO_2^+\{C(=O)N(-O)^-\}_2]^+$ (Figure 1a). The calix[4]pyrrole derivative **1** chosen as the platform exists in 1,2-alternate conformation (i.e. the phenyl residues on meso position are in 1,2-alternate conformation). This means if the phenyl rings can be manipulated to accommodate hydroxamic acid moiety, two pairs of hydroxamic acid chains on each side of the molecular plane can be achieved, which can simultaneously complex two vanadyl ions (Figure 1b). The proposed pre-organization of the ligands was manifested by first partially reducing the nitro functionality on each phenyl ring (anchored to meso positions) to hydroxylamine and coupling it with suitable acylchloride. The hydroxamic acid derivatives prepared in this way were examined for vanadium complexation and were found to be excellent reagents for detection, determination and separation under optimized conditions.

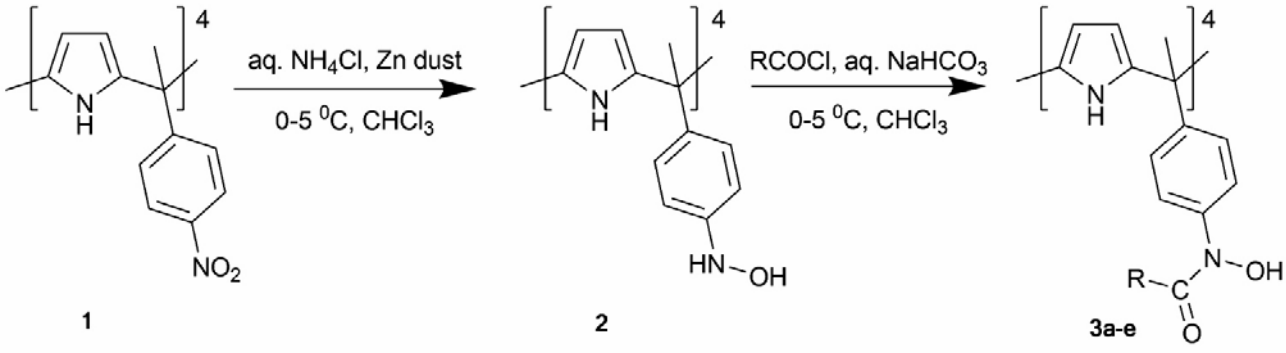
2. Experimental

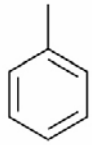
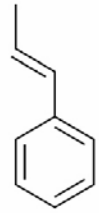
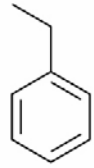
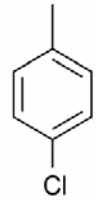
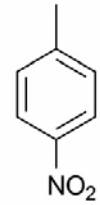
2. 1. General

Melting points were taken in a single capillary tube using a Toshniwal (India) melting point apparatus and were uncorrected. Elemental analysis was done on Heraeus CarloEbra 1108 elemental analyzer. IR spectra were recorded on FTIR-410 ratio recording Jasco Infrared spectrophotometer as KBr pellets and expressed in cm^{-1}. ^1H NMR spectra were recorded on DRX 300 operating at 300 MHz for proton in DMSO-d6 with tetramethylsilane as internal standard. Mass Spectra were recorded on JEOL SX 102/DA 6000 mass spectrometer using xenon/argon (6KV/10KV, 10mA) as the FAB-gas. UV-Visible spectrometric studies were carried out on a JASCO 570 UV/VIS/NIR Spectrophotometer.

2. 2. Synthesis

Synthesis of meso-tetramethyl-meso-tetra-(p-nitrophenyl)-calix[4]pyrrole **1** was carried out with previously reported procedure.[20] Further proceedings were done according to Scheme 1.



Hydroxamic acid derivative	3a	3b	3c	3d	3e
R					

Scheme 1: Synthetic route for **3a–e**

2. 2. 1. Procedure for partial reduction of 1

1 (5 g, ca. 10 mM) was dissolved in chloroform:THF (1:1, 100 mL), added with a solution of NH_4Cl (5 g) in water (100 mL) and stirred for 10 min with aid of magnetic stirrer. Zn powder (7 g) was then added in small portions (0.3–0.5 g) after every 5 min until the reduction was complete. After additional stirring of 15min the contents were allowed to cool to ambient temperature. Organic layer was collected, dried with $MgSO_4$ and concentrated under vacuum until pale yellow crystals of hydroxylamine were observed. The concentrate along with crystals was cooled to –10 °C and filtered instantaneously over a glass frit with aid of vacuum. Yield was 58%. As aromatic hydroxylamines are very unstable in air, the product **2** was re-dissolved in dry chloroform and kept at low (0–4 °C) temperature until coupled with acylchlorides.

2. 2. 2. General Procedure for Coupling

The partially reduced nitro derivative **2** (ca. 10 mM in 100 mL chloroform) was covered with saturated solution of $NaHCO_3$ and cold acylchloride of choice (ca. 45 mM in dry chloroform) was added drop wise directly into lower layer with slow stirring. After the addition was complete (ca. 30 min), the stirring was continued faster for another 30min. The organic layer was collected and washed with water, concentrated to $1/5^{th}$ with flash evaporator and acetone was added drop wise until precipitation of brown powder was complete. The brown powder (products **3a–e**, depending upon acylchloride employed) was collected and purified by re-crystallization from ethyl acetate. Yield 70–74%.

2. 3. Characterization Data

3a: Yield 70%, mp 180 °C, IR (KBr): ν 3402 cm^{-1} (–OH), 859 cm^{-1} (N–O), ^1H NMR (500 MHz, DMSO-d6) : δ 1.96 (s, 12H, CH_3), 7.62–7.82 (d, 16H, C4P ArH), 7.29 (s, 4H, Pyrrole NH), 5.84–5.89 (s, 8H, Pyrrole aromatic), 8.80 (s, 4H, N–OH), 7.42–7.50 (m, 30H, ArH), FAB MS m/z 1215 (M-1), Anal. calcd for $C_{76}H_{64}N_8O_8$: C 75.0, H 5.26, N 9.21. Found: C 74.98, H 5.30, N 9.41.

3b: Yield 72%, mp 166 °C, IR (KBr): ν 3395 cm^{-1} (–OH), 860 cm^{-1} (N–O), ^1H NMR (500 MHz, DMSO-d6) : δ 1.96 (s, 12H, CH_3), 7.60–7.72 (d, 16H, C4P ArH), 7.30 (s, 4H, Pyrrole NH), 5.84–5.89 (s, 8H, Pyrrole aromatic), 8.80 (s, 4H, N–OH), 4.68–4.76 (d, 8H, CH=CH), 7.82–7.91 (m, 30H, ArH), FAB MS m/z 1320 (M-1), Anal. calcd for $C_{84}H_{72}N_8O_8$: C 76.36, H 5.45, N 8.48. Found: C 75.98, H 5.30, N 8.41.

3c: Yield 70%, mp 183 °C, IR (KBr): ν 3409 cm^{-1} (–OH), 866 cm^{-1} (N–O), ^1H NMR (500 MHz, DMSO-d6) : δ 1.99 (s, 12H, CH_3), 7.42–7.50 (d, 16H, C4P ArH), 7.29 (s, 4H, Pyrrole NH), 5.84–5.89 (s, 8H, Pyrrole aromatic), 8.82 (s, 4H, N–OH), 3.75 (s, 8H, $COCH_2$), 7.66–7.72 (m, 30H ArH), FAB MS m/z 1272 (M-1), Anal. calcd for $C_{80}H_{72}N_8O_8$: C 75.47, H 5.66, N 8.80. Found: C 75.58, H 5.60, N 8.81.

3d: Yield 73%, mp 160 °C, IR (KBr): ν 3400 cm^{-1} (–OH), 854 cm^{-1} (N–O), ^1H NMR (500 MHz, DMSO-d6) : δ 1.96 (s, 12H, CH_3), 7.62–7.82 (d, 16H, C4P ArH), 7.29(s, 4H, Pyrrole NH), 5.84–5.89 (s, 8H, Pyrrole aromatic), 8.80 (s, 4H, N–OH), 7.50–7.59 (m, 30H, ArH), FAB MS m/z 1354 (M-1), Anal. calcd for $C_{76}H_{60}N_8O_8Cl_4$: C 67.35, H 4.43, N 8.27. Found: C 67.30, H 4.40, N 8.20.

3e: Yield 74%, mp 180 °C, IR (KBr): ν 3401 cm^{-1} (–OH), 863 cm^{-1} (N–O), ^1H NMR (500 MHz, DMSO-d6) : δ 1.97 (s, 12H, CH_3), 7.61–7.76 (d, 16H, C4P ArH), 7.29 (s, 4H, Pyrrole NH), 5.84–5.89 (s, 8H, Pyrrole aromatic), 8.81 (s, 4H, N–OH), 7.26–7.62 (m, 30H ArH), FAB MS m/z 1396 (M–1), Anal. calcd for $C_{76}H_{60}N_{12}O_{16}$: C 65.33, H 4.29, N 8.02. Found: C 65.29, H 4.21, N 8.0.

2. 4. Analytical Studies

For complexation studies, stock solutions of ligands **3a–e** (7.1×10^{-2} M) were prepared by separately dissolving appropriate amounts of each in 1L of ethyl acetate. The vanadium stock solution (4.9×10^{-2}M) was prepared by dissolving requisite amount of ammonium metavanadate in 5 mL conc. HCl and diluting to 1 L with 6 M HCl. The stock solutions were further diluted 100 folds to obtain working solutions of (7.1×10^{-4} M) and (4.9×10^{-4} M) for ligands and vanadium respectively. For extraction studies, appropriate volumes of ligand and metal solutions were mixed (as per requirement of the experiment, 1–10 mL), shaken for 10 min and separated through a separatory funnel. The organic layer was then dried with $MgSO_4$ and diluted to 100 mL with appropriate solvent. Solutions thus prepared were examined for UV-Vis absorptions at suitable wavelengths. The quantitative results were validated by ICP-OES measurements at 309.31 nm emission line for vanadium. Natural and industrial test samples were prepared according to following procedure : 1 g sample was suspended in acid mixture ($HCl:HNO_3$, 1:3 v/v) and evaporated to dryness thrice, dissolved in 15 mL concentrated hydrochloric acid along with 0.5 g of ammonium persulphate and diluted with distilled water to 100 mL. The natural samples were burnt on red-hot flame after first evaporation. Results of the study represent average values of 10 determinations.

3. Results and Discussion

All the synthesized calix[4]pyrrole hydroxamic acids **3a–e** were tested for the extraction and spectrophotometric determination of vanadium(V). Analytical studies were carried out by extraction of vanadium at acidic pH from aqueous to organic layer. It was found that among all the synthesized calix[4]pyrrole hydroxamic acids, **3e** is the most sensitive reagent (Table 1). The maxi-

mum absorption for the pinkish violet vanadium:**3e** complex was measured at 498 nm and showed a bathochromic shift of 238 nm from the reagent blank (260nm). Further, **3e** being the most sensitive reagent, extraction studies and efforts for optimization of significant parameters were directed towards **3e**.

Table 1: Comparative extraction ability of **3a–e** (Experimental Details – Vanadium: 2 mL, 4.9×10^{-4} M; **3a–e**: 10 mL, 7.1×10^{-4} M; HCl: 6 M; Solvent: Ethyl acetate)

Calix[4]pyrrole Hydroxamic acids	λ_{max} (nm)	Molar absoptivity (l mol^{-1} cm^{-1})
3a	499	7.3×10^3
3b	499	9.4×10^3
3c	485	8.9×10^3
3d	497	1.3×10^4
3e	498	1.9×10^4

3. 1. Effect of Variables on the Extraction

3. 1. 1. Acidity

Maximum extractability of vanadium-**3e** complex was obtained with 6M HCl, but as the concentration of acid solution decreases, the percentage extraction of vanadium also decreased (Figure 2), hence all the extractions were carried out at 6M HCl.

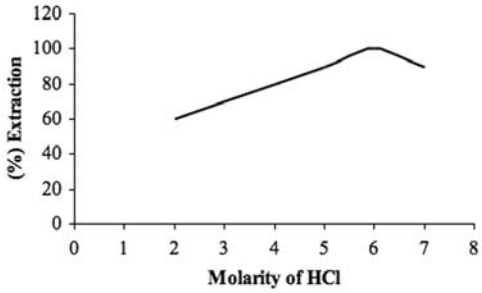


Figure 2: Effect of HCl concentration on the Vanadium-**3e** Complexation. (Experimental Details – Vanadium: 2 mL, 4.9×10^{-4} M; **3e**: 10 mL, 7.1×10^{-4} M; Solvent : Ethyl acetate)

3. 1. 2. Solvent

The vanadium-**3e** complex was extracted with various solvents like ethyl acetate, chloroform, toluene, benzene, dichloromethane and carbon tetrachloride (Table 2). Highest extractability of the complex was observed with ethyl acetate and thus it was deemed to be the most suitable solvent for quantitative extraction in the entire study.

Table 2: Effect of Solvents on the extraction of Vanadium-**3e** complex (Experimental Details – Vanadium: 2 mL, 4.9×10^{-4} M; **3e**: 10 mL, 7.1×10^{-4} M; HCl: 6 M; λ_{max} : 498nm)

Solvent	Extraction (%)
Toluene	17
$CHCl_3$	28
Benzene	31
CH_2Cl_2	68
$CHCl_3$	73
Ethyl acetate	100

3. 1. 3. Reagent Concentration

Extraction with various concentration of reagent showed that 7 mL of 0.1% **3e** was sufficient for the quantitative extraction of vanadium (Table 3). Lower concentration resulted in incomplete extraction whereas higher concentration has no adverse effect on the extraction of vanadium.

Table 3: Effect of reagent (**3e**) concentration on extraction of vanadium (Experimental Details – Vanadium: 5 mL, 4.9×10^{-4} M; HCl: 6 M; Solvent: Ethyl acetate; λ_{max}: 498nm)

mL of reagent (0.1% 3e)	Molar absorptivity ε_m (L mol^{-1} cm^{-1})
10	1.91×10^4
9	1.90×10^4
8	1.91×10^4
7	1.91×10^4
6	1.62×10^4
5	1.31×10^4
4	0.97×10^4
3	0.72×10^4
2	0.55×10^4
1	0.27×10^4

3. 1. 4. Shaking Time

The optimum shaking time was found to be 5–6 min, which was sufficient for quantitative extraction of vanadium. The extraction was not affected by further shaking, indicating the equilibrium state for complexation.

3. 2. Stoichiometry of the Complex

The composition of vanadium-**3e** complex extracted into ethyl-acetate was studied by 'Slope Ratio Method'. The absorbance (at λ_{max}) values were plotted against corresponding concentration for two set of observations. For the first set, the extraction was carried out by taking a fixed (excess) concentration of vanadium solution with varying amounts of **3e**. For second set, the vanadium concentration was varied keeping **3e** concentration fixed (in excess). The plot gave two straight lines defined by linear equations *y=0.2731x-0.2513* (set I) and *y=0.1365x-0.1257* (set II) (Figure 3). The ratio of the slopes found was 2.00, indicating that 1 mole of **3e** co-ordinates with 2 moles of vanadium, i.e. the extracted species is $[(VO_2^+)_2(\mathbf{3e})^{-4}]^{+2}$.

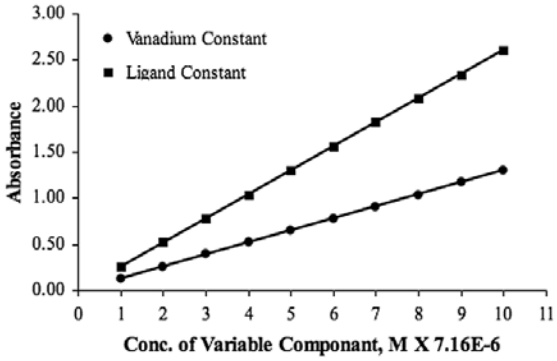


Figure 3: Slope ratio plot for stoichiometry (Experimental details – Fixed Concentration: 1.96×10^{-4} M (3e); HCl: 6 M; Solvent: Ethyl acetate; λ_{max}: 498 nm)

3. 3. Effect of Diverse Ions

Extraction of a single metal ion from a sample containing a variety of other ions gives an indication of potential sensitivity and selectivity of the ligand. Thus, an interference study was performed by extracting vanadium with **3e** from a matrix containing controlled amount of potential interferences. The tolerance limit was set as the amount of foreign ion causing 2% change in quantification (recovery) of vanadium. The quantification was carried out with ICP-OES analysis of organic phase containing extracted complex. Table 4 summarizes results of 'diverse ion effect' studies.

Table 4: Tolerance limit for various ions in extraction of vanadium with **3e** (Experimental Details – Vanadium: 5 mL, 1.96×10^{-3} M; HCl: 6 M; Solvent: Ethyl acetate; λ_{max}: 498 nm; various ions were added in increments of 5mg at a time)

Ion	Added as	Tolerance limit (mg)
Ag^{+}	$AgNO_3$	40
Pb^{+2}	$Pb(NO_3)_2$	45
Mn^{+2}	$MnCl_2$	40
Cu^{+2}	$CuCl_2$	50
Al^{+3}	$AlCl_3$	50
Cr^{+3}	Cr_2O_3	40
La^{+3}	La_2O_3	70
Ce^{+4}	$Ce(SO_4)_2$	50
Mo^{+6}	$(NH_4)_6Mo_7O_{24}$	25
UO_2^{+2}	$UO_2(NO_3)_2$	50

3. 4. Analysis of Real Samples

In addition to diverse ion effect, some natural and industrial samples collected from 'Vatva Industrial Area' (GIDC, Ahmedabad, Gujarat, India) were also tested to determine vanadium content with aid of **3e**. The test samples were prepared as described in experimental section. Vanadium was extracted with **3e** from the test samples and quantified by UV-Visible absorption analysis. The results obtained were compared with results of ICP-OES analysis for same samples. The summary is tabulated in Table 5.

Table 5: Vanadium found in natural and industrial samples

Sample	Concentration in ppm	
	Spectrophotometer	ICP-OES
Tobacco[a]	2.18 ± 0.03	2.198
Lake water	1.05 ± 0.01	1.060
Industrial effluent	1.80 ± 0.02	1.802
Blood sample[b]	0.02 ± 0.01	0.021
Soil	0.09 ± 0.01	0.088

[a] Tobacco sample was collected from a farm in vicinity of the said industrial area
[b] Blood sample was generously provided by a volunteer working in the said industrial area

3. 5. Liquid Membrane Transport Studies

Considerable effort has been directed for over two decades towards the transport of metal ions across liquid

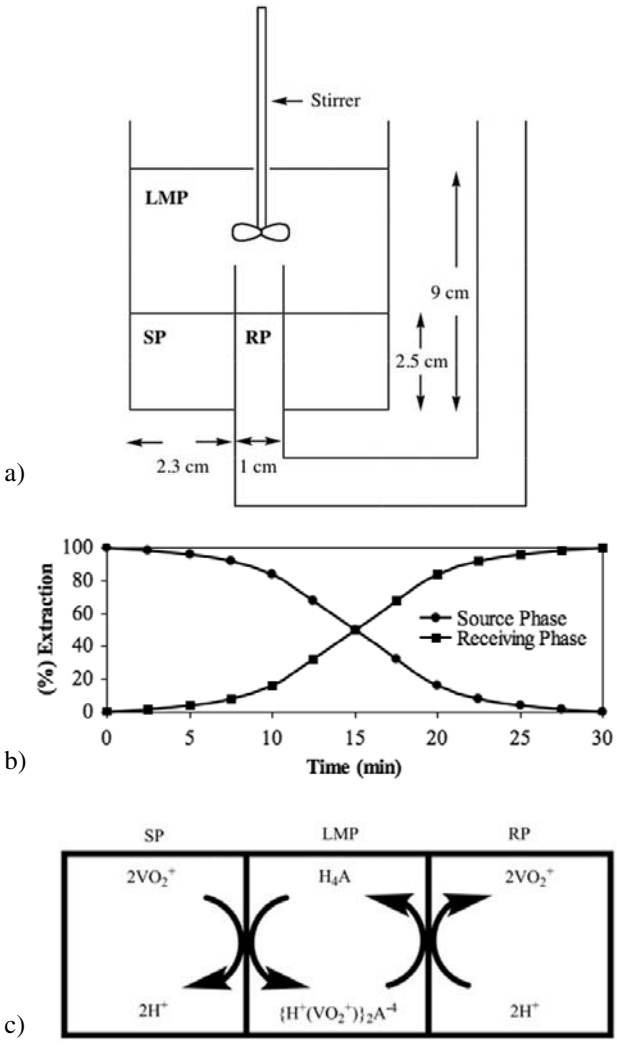


Figure 4: (a) Apparatus for transport studies (b) Transport Profile of vanadium across Liquid Membrane – ethyl acetate solution of **3e** (c) Pictorial representation of transportation mechanism through liquid membrane

membrane. These liquid membranes are of interest for both, possible technological application and fundamental studies of the transport process. Transport of vanadium ion was carried out in a specially fabricated glass assembly as shown in the Figure 4a. The experimental setup was : Source Phase (SP): 14 mL, 7.16×10^{-4} M vanadium in 6M HCl; Liquid Membrane Phase (LMP):40 mL, 7.16×10^{-4}M **3e** in Ethyl Acetate; Receiving Phase (RP): 14 mL, 0.1 M HCl; Temp. 30 °C. The transport studies indicated very encouraging results especially $t_{½}$ which is 15 min. indicating very fast transport of metal through the liquid membrane (Figure 4b).

Among the synthesized derivatives, **3e** was found to be very much promising candidate for the purpose of complexation and thus can be used for pre-concentration and separation from diverse matrix. Figure 4c depicts the mechanism for transport of vanadium through a liquid membrane containing H_4A (i.e. C4PHA).

4. Conclusion

In conclusion, calix[4]pyrrole based hydroxamic acids were synthesized and characterized. Their abilities for extraction of vanadium(V) were extensively studied and they were found to be very good extractants, in particular compound **3e** (ε_m: 1.9×10^4), for which, the extraction parameters were optimized with very encouraging results. Further, **3e** was tested for sensitivity and selectivity in presence of various foreign ions (diverse ion effect/interference) and the extraction studies were further extended to real samples as well with very high accuracy, as compared (validated) with ICP-OES analysis. Liquid membrane transport studies were also carried out using ethyl acetate solution of **3e** as liquid membrane. The transport studies indicated very encouraging results with very short transportation half-time ($t_{½}$: 15 min) indicating rapid transport of metal through the liquid membrane. The mechanism for the transport phenomena is explained.

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Povzetek

Pripravili smo nove kaliks[4]pirole s štirimi hidroksamskimi kislinami (C4PHA) in jih karakterizirali z elementno analizo, FT-IR, NMR in masno spektrometrijo. Spojine imajo visoko afiniteto in selektivnost kot ligandi pri ekstrakciji vanadija(V). Ekstrakcijo smo testirali tudi na kompleksnih vzorcih, ki vsebujejo različne ione. Stehiometrijo kompleksa vanadija s **3e** smo določili s UV-vidno spektroskopijo in ICP-OES analizo. [tudirali smo tudi transport vanadija(V) skozi tekočo membrano, ki je vsebovala **3e**.