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Synthesis of Calix[4]pyrogallolarene and its Application in Spectrophotometric Determination of V(V) Metal

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Calix[4]pyrogallolarene was synthesized and its characterization was carried out using elemental analysis, FTIR, NMR technique. The reagent was then used for the development of a new method for the extractive spectrophotometric determination of V(V) metal. The reagent forms complex with the metal to produce blue coloured complex which was then extracted into *n*-butanol at pH 4.2 having maxima at 600 nm. The effect of diverse anions and cations was also studied. The developed method was employed to determine V(V) metal from synthetic mixtures.

Key Words: Calix[4]pyrogallolarene, Determination of V(V).

INTRODUCTION

Literature survey[1] reveals that a number of organic reagents are used for the spectrophotometric determination of V(V).

In supramolecular chemistry, calixarenes[2] play an important role in cation selective electrodes, optical sensors, selective extraction of alkali and alkaline earth metals. The first success in demonstrating complex abilities of calixarene was achieved by Izatt and his colleagues[3, 4]. An extensive work was carried out by Chang and Cho[5] who prepared carboalkoxy methyl ethers of *p*-tertbutyl-calix[4]arene, *p*-tertbutyl-calix[6]arene, *p*-tertbutyl-calix(8)arene and measured their abilities to extract cations from the aqueous phase into non-aqueous phase. A number of vanadium(III) complexes of calix[4]arene have also been reported[6]. The paper describes a simple and sensitive spectrophotometric determination of micro amounts of vanadium using calix[4]pyrogallolarene.

EXPERIMENTAL

Synthesis of calix[4]pyrogallolarene: Recrystallized pyrogallol (50 mmol) was taken in a 100 mL round-bottom flask having ethanol : water : HCl (2 : 2 : 1) as a solvent system at room temperature. The homogeneous solution was then refluxed at 80°C and 4-chloro benzaldehyde (50 mmol) was slowly added. The solution was gently refluxed for 48 h on a water bath with stirring. During the reaction, after 3 h the solid cyclic oligomer was separated out. The reaction was cooled on an ice-bath and the solid was separated by filtration and the filtrate was added to ice to obtain the second fraction of the precipitate. Both the precipitates were washed with sufficient amount of water to neutralize the acidity. After the characterization studies, both the products were found to be same and were mixed. The crude product was recrystallized from ethyl acetate. The product was solid and dark pinkish brown in colour. The cyclic oligomer was characterized by FTIR, ^{1}H NMR and elemental analysis. Elemental analysis (%) for $C_{52}H_{36}Cl_4O_{12}$: Found (Calcd.): C, 62.88 (62.78); H, 3.65 (3.62); Cl, 14.05 (14.26).

The pyrogallol derivative had good solubility in DMSO for NMR spectroscopy. ^{1}H NMR displayed single singlet at δ 5.638 for methylene bridging, singlet for aromatic hydrogen at δ 6.338 and double doublet of hydrogen present in 4-chloro benzaldehyde at δ 6.591 and δ 6.959; for OH three singlets at δ 7.654, δ 7.739 and δ 7.780.

The presence of intramolecular hydrogen bonding between the OH groups on adjacent pyrogallol rings was confirmed by IR spectroscopy. In DMSO, the hydrogen bonded ν(OH) was at 3480 cm^{-1}. It was noted that the hydrogen bonding in the calix[n]pyrogallolarene is much weaker than that in the calix[n]arene system. A band near 400 cm^{-1} is staged to be useful in differentiating cyclic tetramer from cyclic hexamer and cyclic octamer. The presence of a sharp band at 440 cm^{-1} confirming the formation of tetramer oligomer.

RESULTS AND DISCUSSION

Calix[4]pyrogallaolarene forms blue coloured complex with V(V), which can be extracted into organic phase. The extraction of V(V) from an aqueous phase by calix[4]pyrogallolarene in *n*-butanol is studied over a wide range of experimental conditions. The results of various studies are discussed below:

Effect of pH on the extraction of V(V): The extraction of vanadium with calix[4]pyrogallolarene has been studied over the pH range 1–10. It was observed that the percentage of V(V) with calix[4]pyrogallolarene was maximum between the pH range 3.8 to 4.6 and further, the extraction of the complex decreases.

Absorption Spectrum: The absorption spectrum of vanadium(V) : calix[4]-pyrogallaolarene in *n*-butanol shows the maximum absorption at 600 nm. The absorption due to the reagent at this wavelength is nearly negligible. Hence 600 nm was selected for the absorbance measurement in spectrophotometric determination of vanadium against the reagent blank.

Extraction of V(V) : Calix[4]pyrogallolarene into different media: Many organic solvents have been employed to determine vanadium using solvent extraction technique. The organic solvents can be arranged in the order with calix[4]pyrogallolarene as *n*-butanol > MIBK > ethyl methyl ketone > ethyl acetate > $CHCl_3$ > diethyl ether = toulene = CCl_4 = hexane = nitrobenzene.

Effect of salting out agents: The presence of 0.1 M nitrate salts of alkali and alkaline metals does not show any effect over the absorbance value of V(V) : calix[4]pyrogallolarene complex extract. Hence, these salts were not added in the aqueous phase before further studies.

Effect of reagent concentration: The study of change in colour intensity of vanadium extract with varying concentration of calix[4]pyrogallolarene in aqueous phase was studied. The experimental data shows that 2 mL of 0.1% calix[4]pyrogallolarene in aqueous solution is required for quantitative extraction of vanadium and full colour development due to 80 μg of vanadium solution in aqueous phase. Hence, 2.0 mL of methanolic solution of calix[4]pyrogallolarene (0.1%) has been employed for further studies.

Effect of equilibration time: The study change in absorbance with variation in equilibrium time for extraction of V(V) shows that equilibrium time of 30 s is sufficient for quantitative extraction of vanadium.

Stability of the complex with time: The study of stability of colour of the V(V) : calix[4]pyrogallolarene complex with respect to time shows that the absorbance due to extracted species is stable up to 72.0 h after which slight decrease in absorbance is observed. Throughout the experimental work, for the reason of practical convenience, the measurements have been carried out within 1 h of extraction of vanadium.

Calibration plot: A calibration plot of absorbance against concentration of V(V) gives linear and reproducible graph in the concentration range 1–12 ppm of vanadium indicating that the Beer's law is obeyed in this range. The molar absorptivity and Sandell sensitivity is found to be 0.356×10^3 L mol^{-1} cm^{-1} and 0.357 μg cm^{-2}, respectively (Fig. 1).

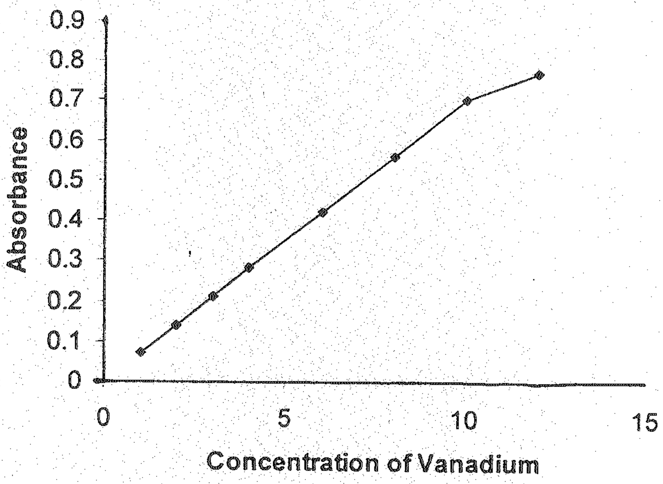

Fig. 1. Calibration plot of V(V) with calix[4]pyrogallolarene

Nature of extracted species

The composition of extracted species has been determined by Job's continuous variation method, Slope ratio method and Mole ratio method. It is seen that the composition of V(V) : calix[4]pyrogallaolarene complex is 1 : 1 (Fig. 2).

Effect of divalent ions and foreign ions: Varying amounts of foreign ions like Cl^-, Br^-, I^-, F^-, ClO_3^-, BrO_3^-, IO_3^-, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, NO_2^-, NO_3^-, PO_4^{3-}, $P_2O_7^{2-}$, CN^-, CNS^-, ClO_4^-, thiourea, oxalate, Li^+, Na^+, K^+, Mg^{2+}, Ca^{3+}, Sr^{2+}, Ag^+ Be^{2+}, Pb^{2+}, Hg^{2+}, Ba^{2+}, Bi^{3+}, Cu^{2+}, Cr^{3+}, Sn^{3+}, Fe^{3+}, Zn^{2+}, Sb^{2+}, Pd^{2+} were added to a fixed amount of vanadium (200 μg) to study the interference in the recommended extraction and subsequent determination procedure. The tolerance limit was set at the amount of foreign ion required to cause ±1.0% error in the recommended procedure.

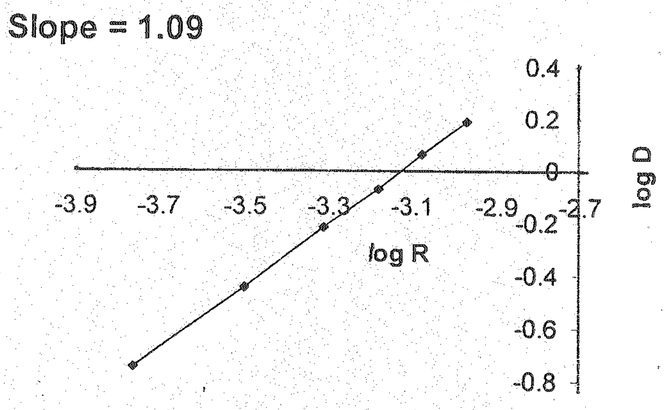

Fig. 2. Stoichiometric ratio of metal to reagent complex of V(V) with calix[4]pyrogallolarene in *n*-butanol from aqueous media

Precision and accuracy: The precision and accuracy of the spectrophotometric method have been studied by analyzing five solutions each containing 100 μg of vanadium.

Percentage recovery: Recovery of the vanadium from different acid media was carried out by using standard PAN method, containing 80 μg of vanadium and 2.0 mL of 0.1% reagent solution (Table-1). H_3PO_4 is used, but in this acid organic and aqueous phases are miscible and could not be separated.

TABLE-1
PERCENTAGE RECOVERY

Amount ofvanadium: 200 μg; Aqueous phase: 10.0 mL containing 1.0 mL of calix[4]pyrogallolarene in methanol; Organic phase: 10.0 mL (2 × 5) of *n*-butanol.

S.No.	Stripping agent	Recovery (%)			
		1 M	2 M	3 M	4 M
1.	HCl	98.5	72.0	52.0	51.50
2.	$HClO_4$	28.0	24.0	23.0	21.0
3.	HNO_3	25.0	77.0	95.0	25.0
4.	H_2SO_4	15.0	23.0	—	—

Applications

Procedure for determination of vanadium in synthetic mixtures and high speed steel samples: Several synthetic, technical samples and high speed steel samples were analyzed using this newly developed method with satisfactory results.

Synthetic mixtures were prepared by mixing solutions of V(V) and other metal ions in suitable proportions. High speed steel super rapid extra 500 (0.1 g) was dissolved by boiling with minimum amount of aqua regia. Iron was then precipited as $Fe(OH)_3$ by adding 1.2 g of ammonium chloride followed by aqueous ammonia. The precipitate was filtered off and washed with 1% ammonia solution. The filtrate along with the washings was heated to remove excess of ammonia, cooled and adjusted to 100 mL final volume. An aliquot (1 mL) was taken for determination of V(V) by the proposed procedure (Table-2).

TABLE-2
DETERMINATION OF VANADIUM IN SYNTHETIC MIXTURES AND STEEL ALLOY

Composition of sample (μg)	V(V) (μg)	
	Added	Found*
Mn (5), Co (7), Ni (2)	5	5.2
U (0.4), Se (0.7), Re (0.1), Os (0.05)	10	9.7
Cd (95), Hg (4), Ag (0.05)	15	14.8
Sr (3), Ru (0.02), Pb (2)	25	24.8
Au (0.04), W (0.1), Th (0.05)	10	10.1
Cr (0.5), Pd (0.005), Pt (0.002)	30	29.6
High speed steel super rapid extra 500	1%#	0.955%

*Average of three analyses. # Certified value.

Conclusion

The results obtained show that calix[4]pyrogallolarene in *n*-butanol can be effectively used for quantitative extraction of V(V) from aqueous media. The extraction requires little amount of solvent, reaches equilibrium in 30 s. The method is sensitive, precise and was effectively applied for commercial samples and synthetic binary samples.

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