Molecular Dynamics, Biological Study and Extractive Spectrophotometric Determination of Vanadium (V) - 2-methyl-8-quinolinol Complex

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ABSTRACT: *An extractive spectrophotometric method is developed for the trace determination of vanadium (V). 2-Methyl-8-quinolinol(MQ) reacts with vanadium(V) to form a 1:2 (V : MQ) light brown complex in an aqueous medium at 0.05 M CH_3COOH concentration which is quantitatively extractable into chloroform exhibiting maximum absorbance in the range 397- 405 nm..The complex is synthesized in 1:2 ratio and the structure of the formed complex is elucidated on the basis of IR, NMR, and TGA techniques aided with computational studies. The formed V (V)-MQ complex is also screened for its in vitro antimicrobial activity. The method obeys Beer's law up to 6.2 µg V/mL with molar absorptivity and Sandell's sensitivity of 2.449 × 10^3 L/mol.cm and 0.0208 µg V/cm^2, respectively, at 400 nm. The method is simple, rapid, and has good reproducibility with a standard deviation of ± 0.0027 absorbance units.*

KEYWORDS:*Vanadium (V); 2-methyl-8-quinolinol; Extraction; Spectrophotometric determination; Structural elucidation; Antimicrobial activity*.

INTRODUCTION

Vanadium is one of the abundant elements in earth's crust [1] and is one of the essential elements for animals and plants [2]. Among the plant products that contain vanadium include rice, beans, potatoes, barley, green salad etc. Vanadium is found in trace levels in microorganisms and is involved in the regulation of cardiovascular activities, stimulates growth and cell production. Vanadium and its compounds are toxic at excessive entry into the body causing disorders such as respiratory irritation, nervous disorders and change in blood counts [1].

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Vanadium affects favourably the diuretic kidney function, the cardiac muscle and cell growth. Antidiabetic function of vanadium is a subject of intense studies [3]. It has been established that drink water containing 25-75 ppb vanadium normalises the sugar level of rats suffering from diabetes [4]. Traces of vanadium in drinking water are suggested to affect favourably the human health, while higher level of vanadium content causes toxification. There are cases of vanadium poisoning, the symptoms of which are nervous depression, coughing, vomiting, diarrhoea, anaemia and increasing risk of lung cancer; such afflictions are sometimes fatal [5]. Vanadium has also been reported as the index element in urban environmental pollution, especially air pollution [6]. The toxicity of vanadium is determined by its oxidation state which ranges from -1 to +5 [7], +2 to +5 being the most stable in solution. However vanadium in +5 oxidation state is even more toxic than any other oxidation state [8]. This toxic effect necessitates the development of a rapid method for the determination of metal in trace quantities. 8-Hydroxyquinoline and its derivatives [9, 10] are very well known for complexation tendency with metals, the principle used in analysis. This chelating characteristic is further enhanced in presence of an electron releasing group at 2-position as is employed in the proposed studies using 2-methyl-8-quinolinol (MQ) as a chelating/complexing agent.

In the proposed investigation, vanadium (V)-MQ complex has been synthesized and characterized by the physicochemical studies followed by its antibacterial activities.

EXPERIMENTAL SECTION

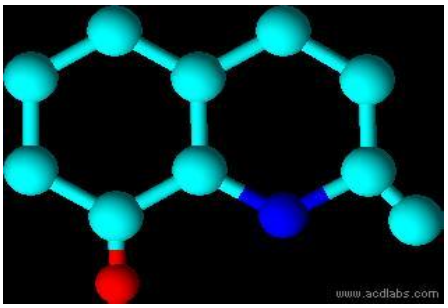
Materials

The metal salt, sodium metavanadate ($NaVO_3$;sd fine chem) is used for the spectrophotometric, synthetic and antimicrobial studies. A standard stock solution (1 mg/mL, 100 mL) is prepared by dissolution of 0.239 g of $NaVO_3$ in deionized water and suitably diluted to give working solutions of 100 and 50 µg/mLstrength.

2-Methyl-8-quinolinol (MQ; HiMedia Laboratories) and dissolved in ethanol to give 1.0% (w/v) solution for spectrophotometric determination.

Acetic acid (1M; CDH; 'AR') is prepared by suitable dilution of glacial acetic acid (17.4M).

Chloroform (CDH; 'AR') is distilled and fraction distilling at 60-61° C is used for extraction of the V(V)-MQ complex.



[2-METHYL-8-QUINOLINOL(MQ)]

Test microorganisms for antimicrobial activity

Total four microbial strains are selected on the basis of their clinical importance in causing diseases in human beings. Two Gram-positive bacteria (*Staphylococcus aureus* MTCC 96 and *Bacillus subtilis* MTCC 121) and two Gram-negative bacteria (*Escherichia coli* MTCC 1652 and *Pseudomonas aeruginosa* MTCC 741) are screened for evaluation of antibacterial activity of the chemical compounds. All the microbial cultures are procured from Microbial Type Culture Collection (MTCC), IMTECH, Chandigarh. The bacteria are subcultured on Nutrient agar plates and slants.

Instrumentation

Spectrophotometric studies are carried out by using a UV-VIS spectrophotometer (2375; Electronics India) with 1cm matched quartz cells. Infrared spectra for the complexes were recorded on FTIR spectrophotometer (Agilent Technologies) from 4000-400 cm^{-1}.

Recommended Procedure

Extraction and spectrophotometric determination of vanadium(V)

An aliquot of the sample solution containing vanadium (V) up to 62 µg is mixed with 1M acetic acid (0.5 mL), 1.0 % ethanolic solution of MQ (1.0 mL) and enough deionized water to make the final aqueous volume 10 mL. The aqueous phase is then equilibrated once for 10 s with equal volume (10 mL) of chloroform. The light brown organic phase is allowed to separate and filtered into a 10 mL volumetric flask through a Whatman filter paper (No.41, 9 cm diameter, pretreated with chloroform) to remove water droplets if any and absorbance of the extract is measured at 400 nm against the similarly prepared reagent blank.

The vanadium content is determined from the calibration plot between absorbance and variable concentration of vanadium(V) prepared under identical conditions of the procedure.

Synthesis of V(V) - MQ complex

An ethanolic solution (20 mL) of 2-methyl-8-quinolinol (MQ, 1.592 g,10 mmol) is added to an aqueous solution (1mL ethanol and 9 ml of deionized water) of sodium matavanadate (0.609 g, 5 mmol). The mixture is stirred at room temperature and refluxed for 2-3 hours. The obtained solid yellow product is collected by vacuum filtration, washed with ethanol and subjected to spectroscopic and microbial studies. The formed complex is found to be stable for more than one weak with melting point=110˚C

Antimicrobial activity of chemical compounds

The antimicrobial activity of the V(V)-MQ (03) complex is evaluated by the agar well diffusion method. All the microbial cultures are adjusted to 0.5 McFarland standards, which is visually comparable to a microbial suspension of approximately 1.5 $\times 10^8$cfu/mL. 20 mL of agar medium is poured into each Petri plate and plates are swabbed with 100 µl inocula of the test microorganisms and kept for adsorption for 15 min. Using sterile cork borer of 8 mm diameter, wells are bored into the seeded agar plates and these are loaded with a 100 µl volume with concentration of 4.0 mg ml^{-1} of each compound reconstituted in dimethylsulphoxide (DMSO). All the plates are incubated at 37^0C for 24 hrs. Antimicrobial activity of each compound is evaluated by measuring the zone of growth inhibition against the test organisms with zone reader (HiAntibiotic zone scale). DMSO is used as a negative control whereas Ciprofloxacin as the positive control for bacteria. This procedure is performed in three replicate plates for each organism [11].

Determination of Minimum Inhibitory Concentration (MIC) of chemical compounds

MIC is the lowest concentration of an antimicrobial compounds that inhibits the visible growth of microorganisms after overnight incubation**.** MIC of the various compounds against bacterial strains is tested through a modified agar well diffusion method [11, 12]. In this method, a two fold serial dilution of each chemically synthesized compound is prepared by first reconstituting the compound in DMSO followed by dilution in sterile deionized water to achieve a decreasing concentration range of 2000 to 62.5 µg ml^{-1}. A 100 µl volume of each dilution is introduced into wells (in triplicate) in the agar plates already seeded with 100 µl of standardized inoculum (10^6 cfu ml^{-1}) of the test microbial strain. All test plates are incubated aerobically at 37°C for 24 hrs and observed for the inhibition zones. MIC, taken as the lowest concentration of the chemical compound that completely inhibited growth of the microbe, shown by a clear zone of inhibition, was recorded for each test organism. Ciprofloxacin is used as positive control while DMSO as negative control.

RESULTS AND DISCUSSION

It has been observed that vanadium (V) reacts with MQ in weakly acetic acid medium to give an extractable light brown coloured complex. With a single contact, the metal complex is quantitatively transferred to chloroform, remains stable for more than 1hr and exhibits maximum absorbance at 397-405 nm (Fig. 1). At this wavelength, the reagent blank also shows small absorbance. Therefore, all observations are noted against the reagent blank. In strong acids likeH_2SO_4, H_3PO_4, HCl and $HClO_4$ colouris not stable and the colour intensity is observed to decrease in the order: CH_3COOH > H_3PO_4 > $HClO_4$ > H_2SO_4 > HCl.

Maximum extraction with stable and maximum absorbance value of the complex is found in chloroform whereas complex is also extracted by a large number of organic, water immiscible solvents. The absorbance decreases in the order: chloroform > amyl alcohol > dichloromethane >isobutylmethylketone> ethyl acetate > 1, 2-dichloroethane > amyl acetate > benzene > n-butyl acetate > toluene > carbon tetrachloride > cyclohexane. A single extraction with equal volume (10 mL) of the solvent is sufficient to give quantitative (100%) extraction of the complex.

Other operative parameters having optimum values found for attaining maximum and constant absorbance are: 0.04-0.11M CH_3COOH, 0.8-1.3 ml of 1.0% (w/v) ethanolic solution of MQ and 5 - 60 s equilibration time for ≤ 62 µg of vanadium in 10 ml of aqueous solution (Table1).

Optical characteristics and Correlation data

The V (V)-MQ obeys linearity over the concentration range 0.0-6.2 µg V/mL(Fig/ 2). However, the optimum

Table 1: Effect of various parameters on the absorbance of V (V) - MQ complex.

CH_3COOH^a/M Absorbance	0.010 0.134	0.020 0.152	0.030 0.155	0.040 - 0.110 0.165	0.120 0.155	0.150 0.140		
HMQ[b]/ml Absorbance	0.050 0.055	0.350 0.125	0.750 0.188	0.800 -1.300 0.200	1.350 0.191	1.500 0.182	1.750 0.175	
Equilibration time[c]/sec Absorbance	0 0.150	2 0.200	5-60 0.240	80 0.230	120 0.180	180 0.160	120 0.210	180 0.218

conditions:

a) V(V) = 50 µg ; CH_3COOH(1M) = variable ; MQ [0.5%(w/v) in ethanol] =1 mL; aqueous volume = solvent volume =10 mL; solvent = chloroform; equilibration time = 1 min; λ_{max}= 400 nm.

b) CH_3COOH(1M) = 0.5 mL; other conditions are the same as in (i) excepting variation in MQ (1M) concentration.

c) MQ[1%(w/v) in ethanol]=1 mL; other conditions are the same as in (ii) excepting variation in equilibration time.

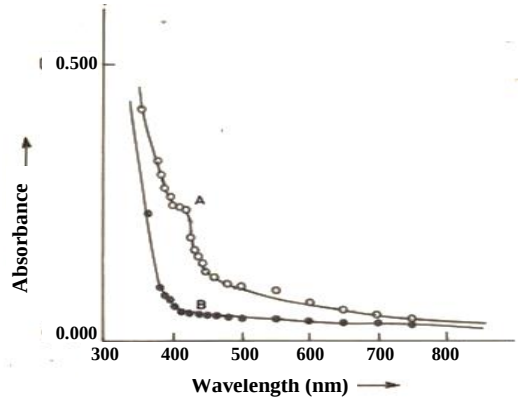


Fig. 1: Absorption spectrum of V (V)-HMQ complex. A) Complex against reagent blank. B) Reagent blank against pure chloroform 5.0 µg/ml V(V); other conditions same as in the procedure.

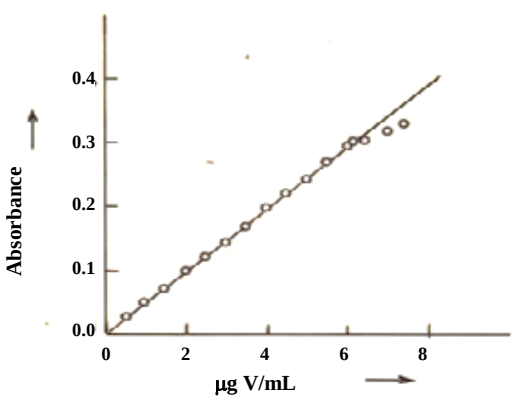


Fig. 2: Beer's law range for V (V)-HMQ complex

range for accurate determination of vanadium as obtained from Ringbomcurve[13] at 400 nm is 2.88-6.16 µg V/mL.The molar absorptivity and Sandell's sensitivity are calculated to be 2.449×10^3 L/mol.cm and 0.0208 µg V/cm^2, respectively at 400 nm. Reproducibility of the method is tested by performing ten sets of experiments taking 5 µg V/mL each time. The results obtained are highly reproducible with a standard deviation of ± 0.0027 absorbance unit. The linear regression equation of the method is Y=0.048 X + 0.003 with regression coefficient of 0.9998 and limit of detection 0.168 µg/mL (Table 2).

Stoichiometry of V (V) - MQ complex

Stoichiometry of the formed complex is determined by Job's method of continuous variations as modified by *Vosburgh* and *Cooper* [14, 15] for two phase system. The M: L composition is further confirmed by mole ratio method [16].

Job's continuous variations method

Equimolar solutions (9.8×10^{-3}) of metal ion and MQ are mixed so that mole fraction of V (V) varies from 0 to1.After adjusting other experimental conditions, the absorbance is measured at two different wavelengths namely 400 nm and 430 nm. The plot of absorbance versus mole fraction indicates that the metal and reagent are present in the ratio 1:2 in the proposed complex.

Mole-ratio method

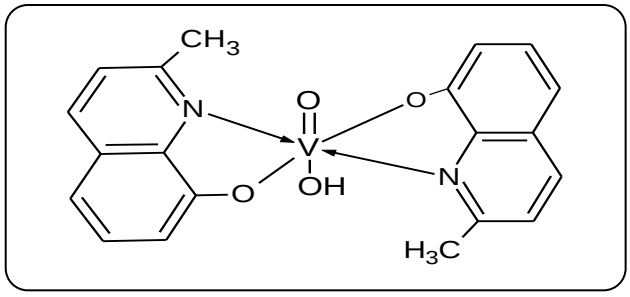
In the mole-ratio method, concentration of one of the components is fixed while that of the other is varied. In the present investigation, the concentration of vanadium (V) is fixed at 9.8×10^{-3}M and concentration of MQ is varied. The absorbance is again noted at two different wavelengths namely 400 nm and 430 nm. The plot of absorbance versus mole ratio of the two components shows a clear break at 1:2 V (V)-MQ ratio.

On the basis of this study, the probable structure of V (V)-MQ complex may be assigned as:

Table 2: Optical characteristics and correlation data.

S. No.	Parameter	Value
1	λ_{max} (nm)	397 – 405 nm
2	Beer's law limits (µg/mL)	0.0 – 6.2 µg V/mL
3	Optimum range from Ringbom plot	2.88-6.16 µg V/mL
4	Molar absorptivity (l/mol.cm)	2.449×10^3 l/mol.cm
5	Sandell's sensitivity (µg/cm^2)	0.0208 µg V/cm^2
6	Correlation coefficient (r)	0.9998
7	Regression equation (Y)*	Y=0.048 X + 0.003
8	Slope (b)	0.048
9	Intercept (a)	0.003
10	Standard deviation	± 0.0027
11	Limit of detection (µg/mL)	0.168 µg/mL

**Y= bX + a; where Y = absorbance and X = Concentration of V (V) in µg/mL*



[PROPOSED STRUCTURE OF V (V) - MQ COMPLEX]

STRUCTURAL ELUCIDATION

IR Spectrum

The band present in the spectrum of complex at ~3200 cm^{-1} related to hydroxyl group bonded to vanadium metal. The absence of any peak, in the range 3550-3700 cm^{-1}, due to free quinolinic hydroxyl group indicates the formation of complex [17]. Moreover, presence of characteristic M-O band at 570 cm^{-1} confirms the coordination of hydroxyl oxygen with vanadium metal [18]. A weak intensity band near 460-470 cm^{-1} can be ascribed to the *v* (V-N) band indicating that complex have been formed [18]. The peaks at 1450-1600cm^{-1} are due to aromatic skeleton vibrations (Supplementary material).

NMR Spectrum

The ^{1}H NMR spectra of complex was recorded in DMSO-d6. The chemical shifts (δ) are expressed in ppm downfield from TMS [19]. The NMR spectrum was studied in deuterated DMSO. NMR spectrum of complex shows mainly two peaks. Three methyl protons present in the metal-ligand complex are indicated by the singlet observed at δ 1.63 ppm whereas the ring protons resonate at 7.34 ppm. Absence of any peak around δ 4.89 ppm due to quinolic hydroxyl proton [9] further confirms the coordination of oxygen atom of hydroxyl group with the central metal atom [19] (Supplementary material).

Thermogravimetric Analysis

The complex is stable and do not melt even up to 300° C but prolonged heating changes the colour of the complex. Therefore to confirm the final decomposition thermogram of the complex was recorded from ambient to 800° C. The complex decomposed above 800°C (Fig. 3). The absenceof any decomposition step from 150-250° C may be indicative of absence of lattice water which is further confirmed by the absence of any corresponding signal in the IR spectra around 3400 cm^{-1} due to water molecule. The complex decomposes in three steps. The steep curve in the range 250-300° C indicates the sudden decomposition of complex and may corresponds to the decomposition of the organic part along with metal ion i.e., VO(OH) (Obs.= 22.21%, calc. = 22.69%). The second decomposition step corresponds to the decomposition of two methyl groups of the ligand (Obs. = 7.95%,

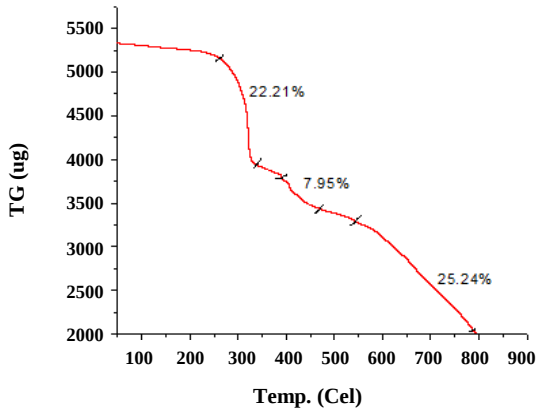


Fig. 3: Thermogravimetric Analysis of V (V)-MQ complex.

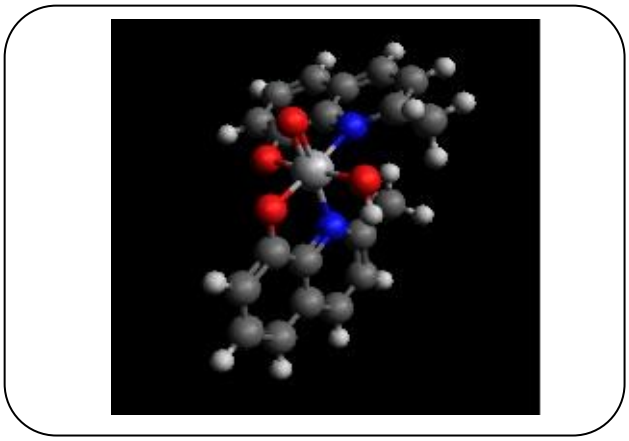


Fig. 4: Energy optimized structure of V (V)-MQ complex.

Calc. = 8.10%). The final step corresponds to the decomposition of C_6H_4N moiety (Obs. = 25.24%, Calc. = 24.86%).

Computational Studies

The ligand-M complex was modelled by Avogadro 1.01 program. Ligand containing metal ion was optimized using molecular mechanic methods. Several cycles of energy minimization had to be carried out for the complex. The root mean square gradient for the complex was less than one [20-23].

The energy optimized structure of V (V)-MQ complex (Fig. 4) was found to have distorted octahedral geometry with auto optimized energy 441.426 KJ/mol. The two quinolinol rings are perpendicular to each other. The equitorial M-O distance being 1.918 Å. The axial position is being occupied by one of the oxygen atom with M=O distance of 1.75 Å and nitrogen atom with M-N distance of 2.10Å. These values are close to the ideal distance of 1.75 Å and 2.05 Å, respectively. The N-V-O bond angles are 85.2°.

Results of antimicrobial activity

Ligand, metal and complex were screened for their antibacterial activity. All the tested chemical compounds possessed variable antibacterial activity against both the Gram-positive (*Staphylococcus aureus* and *Bacillus subtilis*) bacteria and Gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*). Positive controls produced significantly sized inhibition zones against the tested bacteria. However, negative control produced no observable inhibitory effect against any of the test organism. On the basis of maximum inhibitory activity shown against bacteria, complex was found to be most effective against both Gram negative and positive bacteria with zone of inhibition ranging between 21 mm to 35 mm. However, highest effectiveness was observed in case of Gram positive bacteria i.e. (*Staphylococcus aureus* and *Bacillus subtilis*). So, it is found to be best in inhibiting the growth of Gram positive bacteria (Table 3). Although ligand and metal have also shown some zone of inhibition against bacteria but results are not very much significant.

MIC of various tested chemical compounds ranged between 200 and 62.5µg/ml were checked against bacteria with significant zone of inhibition. Metal-complex was found to be best as they exhibit the lowest MIC of 62.5µg/ml against *S. aureus* and 250µg/ml against *B. subtilis.* Similarly,MIC of 125µg/mL and 250µg/mL were observed in case of *E.coli* and *P.aeruginosa* (Table 4).

Amongall the tested chemical compounds, metal-complex shown good activity against the tested bacterial, thus this compound can be further used as an antimicrobial agent in pharmaceutical industry, after testing its toxicity.

CONCLUSIONS

A new extractive spectrophotometric method has been developed for the micro determination of vanadium (V) using 2-Methyl-8-quinolinol(MQ) as a complexing agent. MQ reacts with vanadium(V) to form a 1:2 (V: MQ) light brown complex extractable into chloroform exhibiting maximum absorbance at 400 nm. The method is simple, rapid and has good reproducibility with a standard deviation of ± 0.0027 absorbance units. Further the complex has been synthesized and tested for antimicrobial activity in comparison to that of the metal and ligand alone.

Table 3: In vitro antimicrobial activity of chemical compounds through agar well diffusion method.

Compound No.	Diameter of growth of inhibition zone (mm)[a]			
	Staphylococcus aureus	Bacillus subtilis	Escherichia coli	Pseudomonas aeruginosa
1	09	14	12	13
2	13	18	09	10
3	35	21	23	22
Ciprofloxacin	26.6	24.0	25.0	22.0

-No activity; [a]Values, including diameter of the well (8mm), are means of three replicates

.Table 4: Minimum inhibitory concentration (MIC) (in µg/ml) of compounds by using modified agar well diffusion method

Compound No.	Diameter of growth of inhibition zone (mm)[a]			
	Staphylococcus aureus	Bacillus subtilis	Escherichia coli	Pseudomonas aeruginosa
1	Nt	Nt	Nt	Nt
2	Nt	500	Nt	Nt
3	62.5	250	125	250
Ciprofloxacin	62.5	62.5	62.5	125

On the basis of maximum inhibitory activity shown against bacteria, out of metal, ligand and complex, the complex has been found to be most effective against both Gram negative and positive bacteria with zone of inhibition ranging between 21-35 mm. Though some zone of inhibition has also been shown by the metal and ligand against bacteria but not very much significant. The metal complex has been found to be most effective against tested pathogens, may be due to interference with the metabolic activity of microorganisms via chelation therapy [24]. In case of *S. Aureus*, the MIC of complex was found to be comparable with that of standard drug. Therefore, the complex can be used as potent pharmaceutical agent after testing its cytotoxicity.

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