VANADOPHILIC HETEROCYCLIC β-DIKETONES: SYNTHESIS, CHARACTERIZATION AND COMPLEXATION

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BY
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DECLARATION

I hereby declare that the matter embodied in the thesis entitled **"VANADOPHILIC HETEROCYCLIC β-DIKETONES: SYNTHESIS, CHARACTERIZATION AND COMPLEXATION"** is the result of investigations carried out by me in the Chemical Sciences and Technology Division of National Institute for Interdisciplinary Science and Technology (Formerly Regional Research Laboratory), CSIR, Thiruvananthapuram-695 019, under the supervision of Dr.M.L.P.Reddy, ScientistF, NIIST, Thiruvananthapuram and the same has not been submitted elsewhere for any other degree.

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Thiruvananthapuram
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CERTIFICATE

This is to certify that the work embodied in the thesis entitled **"VANADOPHILIC HETEROCYCLIC β-DIKETONES: SYNTHESIS, CHARACTERIZATION AND COMPLEXATION”** is the result of investigations carried out by Mrs. Remya, P.N. under my supervision in the Chemical Sciences and Technology Division of National Institute for Interdisciplinary Science and Technology (Formerly Regional Research Laboratory), CSIR, Thiruvananthapuram, and the same has not been submitted elsewhere for any other degree.

Dr. M.L.P. Reddy
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LIST OF PUBLICATIONS

1. Reduction of vanadium(V) by 1-phenyl-3-methyl-4-toluoyl-5-pyrazolone at acidic and neutral pH: spectroscopic characterization and structure modeling. **P.N. Remya**, C.H. Suresh and M.L.P. Reddy. *Polyhedron*, 26, xx-xx, (2007).

2. Para-substituted 1-Phenyl-3-methyl-4-aroyl-5-pyrazolones as selective extractants for vanadium(V). **P.N. Remya**, D.B. Ambili Raj, M.L.P. Reddy. *Solvent Extr. Ion Exch.*, 24(6), 877-892 (2006).

3. 4-Acylbis(1-phenyl-3-methyl-5-pyrazolones) as highly selective extractants for vanadium(V) from titania waste chloride liquors. **P.N. Remya**, Rani Pavithran, M.L.P. Reddy. *Solvent Extr. Ion Exch.*, 23(4), 1-18, (2005).

4. Extraction and separation of vanadium(V) from multimetal chloride solutions using bis-(2,4,4-trimethylpentyl)phosphinic acid. **P.N. Remya**, J. Saji and M.L.P. Reddy. *Solvent Extr. Res. Develop.,* 11, 173-185 (2004).

5. Solvent extraction of titanium(IV), vanadium(V) and iron(III) from simulated waste chloride liquors of titanium minerals processing industry by the trialkylphosphine oxide Cyanex 923. **P.N. Remya**, and M.L.P. Reddy. *J. Chem. Technol. Biotechnol.*, 79(7), 734-741 (2004).

6. 3-phenyl-4-acyl-5-isoxazolones as reagents for the solvent extraction separation of titanium(IV) and iron(III) from multivalent metal chloride solutions. **P.N. Remya**, Rani Pavithran and M.L.P. Reddy. *Solvent Extr. Ion Exch.*, 22(3), 473-490 (2004).

7. Solvent extraction and separation of vanadium(V) from multivalent metal chloride solutions by Cyanex 923. **P.N. Remya**, J. Saji and M.L.P. Reddy. *Solvent Extr. Ion Exch.*, 21(4), 573-589 (2003).

CONTENTS

PREFACE

The thesis entitled **"VANADOPHILIC HETEROCYCLIC β-DIKETONES: SYNTHESIS, CHARACTERIZATION AND COMPLEXATION"** embodies the results of the investigations carried out on the synthesis and characterization of various substituted 4-acyl-5-pyrazolones and their complexation behavior with vanadium. The objective of the present work is to generate the knowledge base to achieve the recovery of vanadium from multi-metal waste chloride liquors originating from the illmenite beneficiation industries by employing liquid-liquid extraction as a separation technique. The thesis is comprised of four chapters.

The introductory chapter highlights the significance of the design and development of selective ligands for the recovery of vanadium from waste chloride liquors. A comprehensive review of literature on the recent developments in the extraction and separation of vanadium(V) from acidic aqueous solutions by employing various commercially available solvent extraction reagents has also been presented in this chapter.

The second Chapter describes the synthesis and characterization of various 4-aroyl-5-pyrazolones. Para-substituted 4-aroyl derivatives of 1-phenyl-3-methyl-5-pyrazolones (HX), namely, 1-phenyl-3-methyl-4-(4-fluorobenzoyl)-5-pyrazolone (Hpmfbp) and 1-phenyl-3-methyl-4-(4-toluoyl)-5-pyrazolone (Hpmtp) were examined with regard to the extraction behavior of vanadium(V) along with multivalent metal ions, such as magnesium(II), aluminium(III), titanium(IV), chromium(III), manganese(II), iron(II), and iron(III) that are present in the titania waste chloride liquors. Further, in order to have a better understanding of the complexation behavior of oxovanadium with various 4-aroyl-5-pyrazolones, solid complexes have been isolated and characterized by cyclicvoltammetry, electron paramagnetic resonance spectroscopy, magnetic susceptibility, FT-IR, electronic spectroscopy, high-resolution mass spectroscopy and elemental analyses.

4-Acylbis(pyrazolones) of varying polymethylene chain length have been synthesized and utilized for studying the extraction behavior of multivalent metal ions that are present in the titania waste chloride liquors, in the presence and absence of neutral organophosphorus extractants and the results are given in chapter 3. The results demonstrate that vanadium(V) is selectively extracted into chloroform with 4-acylbis(1-phenyl-3-methyl-5-pyrazolones). The extraction efficiency of vanadium(V) has been correlated with the donor ability of phosphoryl oxygen of the neutral organophosphorus extractants in terms of their ^{31}P NMR chemical shifts and their basicity values. In order to have a better understanding of the complexation behavior of vanadium with various bis-4-acyl-5-pyrazolones, solid complexes have been isolated and characterized by various spectroscopic techniques. These results have been incorporated as part II in this chapter. The complexes were characterized using cyclicvoltammetry, electron para magnetic resonance spectroscopy, magnetic susceptibility, FT-IR, electronic spectroscopy, high-resolution mass spectroscopy and elemental analyses.

The contributions to the new knowledge arising out of this thesis have been highlighted in the concluding chapter. The relevant references used in this work have been cited towards the end of the thesis.

ABBREVIATIONS

acac	acetylacetone
CMPO	octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide
Cyanex 272	bis(2,4,4-trimethylpentyl)phosphinic acid
DEHPA	di-(2-ethylhexyl)phosphoric acid
EHEHPA	2-ethylhexylphosphonic acid mono-2-ethylhexyl ester
Hpmbp	1-phenyl-3-methyl-4-benzoyl-5-pyrazolone
Hpmfp	1-phenyl-3-methyl-4-(4-fluorobenzoyl)-5-pyrazolone
Hpmtp	1-phenyl-3-methyl-4-(4-toluoyl)-5-pyrazolone
H_2AdBP	4-adipoylbis(1-phenyl-3-methyl-5-pyrazolone)
H_2DdBP	4-dodecandioylbis(1-phenyl-3-methyl-5-pyrazolone)
H_2SbBP	4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone)
TBP	tri-*n*-butylphosphate
TOPO	trioctylphosphine oxide
TRPO	trialkylphosphine oxide

Chapter I

Introduction

Vanadium was named after the Norse goddess *Vanadis* which represented beauty and fertility. The appellation was selected since the element's beautiful colors are used as a dye for the manufacture of pottery and ceramics [Vanadium 2003]. The element was first discovered in 1801 within a lead vanadate ore by a Mexican, Andres Manuel del Rio, but was mistaken as a form of chromium [Habashi 2002]. It was rediscovered in 1830 within converter slags from certain iron ores by the Swedish Chemist Nils Gabriel Seftstrom, who then named it. The nearly pure element, which is number 23 in the Mendeleyev's periodic table, was isolated in 1867 by Sir Henry Roscoe.

Uses of Vanadium

Vanadium is an extremely versatile and biologically essential element. It is used

- in the preparation of Vanadium-Steel alloys, where the resulting decrease in the grain size results in increased tensile strength,
- in the preparation of catalysts for the chemical industry for the preparation of sulphuric acid and for the oxidation of naphthalene,
- in the form of its salts as accelerators in the drying of paints, and
- in the manufacture of glass.

It is becoming increasingly apparent that the chemistry of vanadium is of great importance to a wide variety of biological and industrial systems. Its oxo-ions vanadium(IV) and vanadium(V) are potential inhibitors of phosphate-metabolizing enzymes as well as activators. It is also important in nitrogenase, haloperoxidase, as insulin enhancing agents and antitumour agents. Most of the vanadium biochemistry is intrinsically related to the oxidation-reduction and the coordination chemistry of this element. Vanadium(IV and V) ions experience extensive redox chemistry under physiological conditions. Vanadium also acts as a co-factor for enzymes involved in blood sugar metabolism, lipid and cholesterol metabolism, bone and tooth development, fertility, thyroid function, hormone production and neurotransmitter metabolism.

Sources of Vanadium

Vanadium is found in approximately 54 different minerals as well as phosphate rocks, certain iron ores, some crude oils (in the form of complexes) and meteorites. As these deposits are being consumed fast and the vanadium needs are continuously increasing, the metal began to be extracted from other minerals, such as patronite, carnotite (Colorado, Arizona, New Mexico) and some titaniferrous magnetite. Other vanadium minerals, although of smaller importance, are the bravoite (Mina Ragra, Peru), the sulvanite (Australia), the roscoelite (Colorado and Utah, EUA), the davidite (Australia), the uvanite (Utah, USA) and the vanadinite (Mexico and Argentina) [Perron 2001].

- Carnotite [$U_2O_3.V_2O_5.K_2O.3H_2O$]
- Patronite [V_2S_5]
- Vanadinite [$Pb_5(VO_4)Cl_3$]

Nowadays vanadium is mostly recovered as a co-product from secondary sources or from industrial waste streams such as titaniferrous magnetite, vanadium-bearing ferrophosphorus slag, fly ash, spent catalysts and Bayer's sludge [Vanadium profile, 2003]. The solid wastes from titanium minerals processing industry represent another potential source of vanadium. The manufacture of the versatile white pigment TiO_2 through the 'chloride process' generates large amounts of acidic waste chloride liquors containing multivalent metal ions such as magnesium(II), aluminium(III), titanium(IV), vanadium(V), chromium(III), manganese(II) and iron(III). The typical composition of titania waste chloride liquors obtained from Kerala Minerals and Metals Limited, Kollam, Kerala is given in Table 1.1 [Remya and Reddy 2004]. Further, the management of the waste chloride liquors represents a major environmental issue, affecting every industrialized country. Pyrohydrolysis of the spent acid for the recovery of hydrochloric acid generates impure iron oxide containing several other metal ions with no marketable outlets, resulting in a solid waste. The more our economy recovers and recycles useful metals from its wastes, the less mining will be needed and less environmental damage will result from waste disposal.

Solvent extraction is one of the techniques being increasingly used for the recovery of vanadium values from industrial waste streams [Toyabe et al. 1995; Gupta 1984].

Table 1.1. Composition of waste chloride liquors of titanium minerals processing industry.

Constituent	g dm^{-3}
$FeCl_2$	215.66
$FeCl_3$	48.67
$MgCl_2$	13.41
$MnCl_2$	5.96
$AlCl_3$	13.36
$TiOCl_2$	0.22
$CrCl_3$	0.78
$VOCl_3$	1.16
HCl	33.32

Solvent Extraction Separation of Vanadium(V)

In our laboratory, various acidic and neutral organophosphorous extractants such as 2-ethylhexylphosphonic acid mono-2-ethylhexylester [Saji and Reddy

2002], bis(2,4,4-trimethylpentyl)phosphinic acid [Remya et al. 2004] and tributylphosphate [Thomas et al. 2003] have been employed as extractants for the extraction and separation of vanadium(V) from titania waste chloride liquors. Poor selectivity has been noticed with the above organophosphorus extractants for vanadium(V) from the other associated multivalent metal ions, *viz.* Fe(III), Fe(II), Mn(II), Al(III), Zn(II) and Cr(III) when extracted from acidic liquors. This has prompted us to explore Cyanex 923 (TRPO) as an extractant for the extraction and separation of vanadium(V) from titania waste chloride liquors. Cyanex 923 is a mixture of four trialkylphosphine oxides ($R_3P = O$, $R'_3P = O$, $R_2R'P = O$, $R'_2RP = O$; where R = octyl and R′ = hexyl) and is commercially available from Cytec, Canada. Further, the above solvent mixture has the advantage of being a liquid and is completely miscible with all commonly used hydrocarbons.

Thus in the beginning of the present work, the solvent extraction behavior of vanadium(V) and other associated metal ions that are present in the titania waste chloride liquors has been investigated as a function of hydrochloric acid concentration using trialkylphosphine oxide in kerosene as the extractant [Remya et al. 2003; Remya and Reddy 2004]. The results demonstrated that titanium(IV), vanadium(V) and iron(III) are extracted (Figure 1.1) into kerosene as:

$$TiO^{2+}_{aq} + 2Cl^{-}_{aq} + 2TRPO_{org} \xrightleftharpoons{K_{ex,\,Ti(IV)}} TiOCl_2 \cdot 2TRPO_{org}$$

$$VO_2^{+}{}_{aq} + Cl^{-}_{aq} + TRPO_{org} \xrightleftharpoons{K_{ex,\,V(V)}} VOCl_2 \cdot TRPO_{org}$$

$$Fe^{3+}_{aq} + H^{+}_{aq} + Cl^{-}_{aq} + TRPO_{org} \xrightleftharpoons{K_{ex,\,Fe(III)}} HFeCl_4 \cdot 2TRPO_{org}$$

where $K_{ex,Ti(IV)}$, $K_{ex,V(V)}$ and $K_{ex,Fe(III)}$ denote the equilibrium constants for titanium(IV) vanadium(V) and iron(III), respectively. On the other hand, magnesium(II), aluminium(III), chromium(III) and manganese(II) are not extracted with TRPO from waste chloride liquor solutions. Thus this study clearly highlights that by employing Cyanex 923, selectivity for vanadium(V) over other associated metal ions cannot be achieved. This stimulated us to design and development of new vanadophilic ligands. The main objective of the present investigations is to synthesize novel ligands for the selective separation of vanadium(V) from acidic chloride solutions. Another objective of the present study is to generate a knowledge base on the coordination chemistry of oxovanadium species with the synthesized heterocyclic β-diketones.

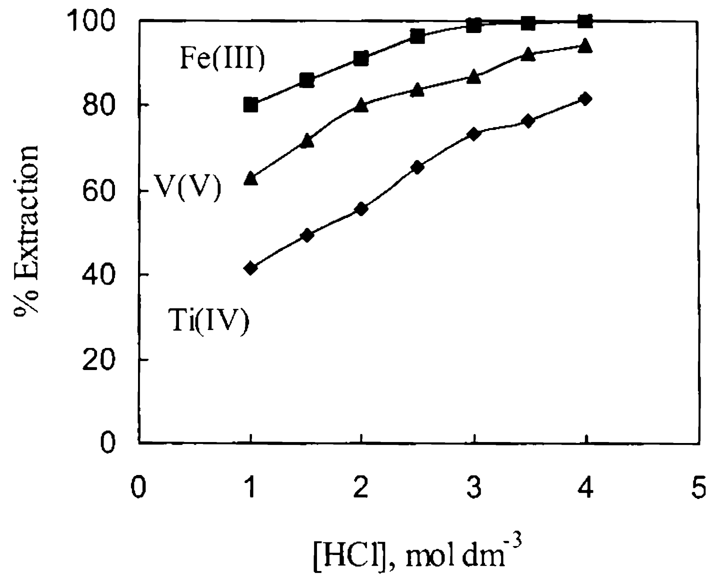
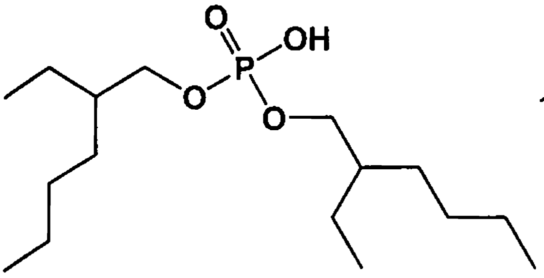


Figure 1.1. Extraction behavior of magnesium(II), aluminium(III), titanium(IV), vanadium(V), chromium(III), manganese(II) and iron(III) from hydrochloric acid solutions using TRPO (0.5 mol dm^{-3}) in kerosene.

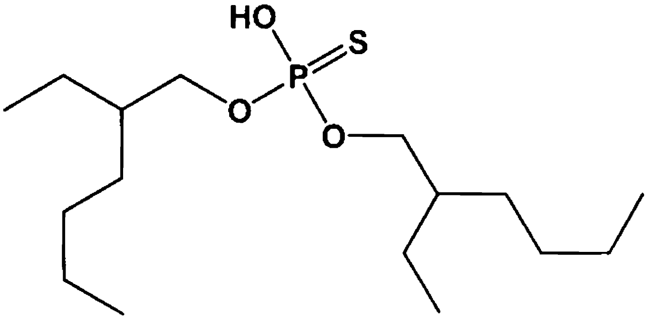
Literature Review:Solvent Ex traction of Vanadium(V)

A. Extraction by acidic extractants

Acidic organophosphorus extractants: Among acidic organophosphorus extractants, di-(2-ethylhexyl) phosphoric acid (DEHPA) has been extensively used for the extraction of vanadium from acidic aqueous solutions [Hirai et al. 1995; Ho et al. 1994; Tebbe 1982]. The solvent extraction of vanadium(V) from acidic sulphate and chloride solutions has been investigated with DEHPA (HX) as an extractant and reported the extracted complexes as $VO_2X{\cdot}HX$ [Hirai et al. 1995]. Further, these authors also examined the extraction behavior of vanadium(V) using bis(2-ethylhexyl)monothiophosphoric acid (DEHTPA ≡ HL) and found that VO_3^- in the aqueous phase was getting reduced to VO^{2-} in the presence of DEHTPA, there by oxidizing the extractant to disulfide. The extracted complex has been found to be VOL_2.



B(2-ethylhexyl)phosphoric acid

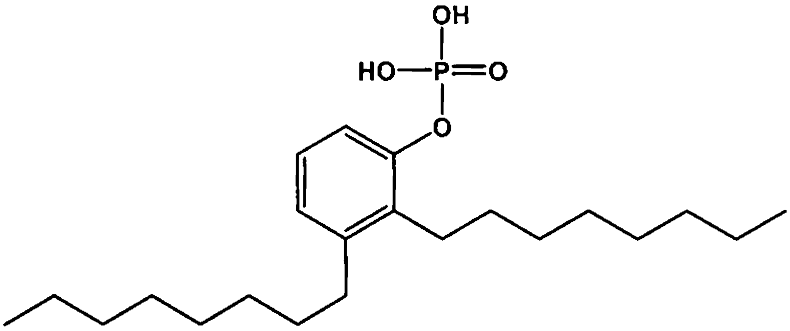


B(2-ethylhexyl)monothiophosphoric acid

Extractions of vanadium(V) from diluted and concentrated nitric acid solutions by bis(2-ethylhexyl)phosphoric acid in various solvents has been studied [Brunette et al. 1979]. From dilute nitric acid solutions, vanadium(V) is extracted as dimer in non polar solvents such as kerosene and as monomer in polar solvents such as *n*-butanol. From concentrated nitric acid solutions the extracted complexes of vanadium involves nitrate group participation. Further, these authors have noticed poor selectivity for vanadium(V) over iron(III).

Commercial process for the recovery of vanadium focus either on the extraction of vanadium(V) as any one of its anionic species using tertiary or quaternary amines or the extraction of vanadium(IV) as VO^{2+} using DEHPA from acidic solutions [Ho et al. 1994]. In the commercial recovery of vanadium from uranium circuits, iron powder is added to the feed solution to convert iron to ferrous state and vanadium to the tetravalent form [Rosenbaum 1971]. This is followed by either sequential extraction of uranium at pH < 1.8 and vanadium(IV) at pH 2.0 or by simultaneous extraction at pH 2.0 using DEHPA followed by selective stripping of vanadium with sodium carbonate.

A solvent extraction process has been described for the simultaneous oxidation and extraction of vanadium from wet process phosphoric acid using DEHPA or dioctylphenylphosphoric acid (DOPPA) in combination with trioctylphosphine oxide (TOPO) as the extractant system [Tebbe 1982]. US patent 4,594,235 describes a process for the extraction of vanadium as VO^{2+} from acidic sulphate or chloride solutions using DEHPA followed by precipitation stripping using ammonium hydroxide [Gardner 1986]. The resulting vanadyl hydrate is reacted with carbon to produce vanadium carbide.

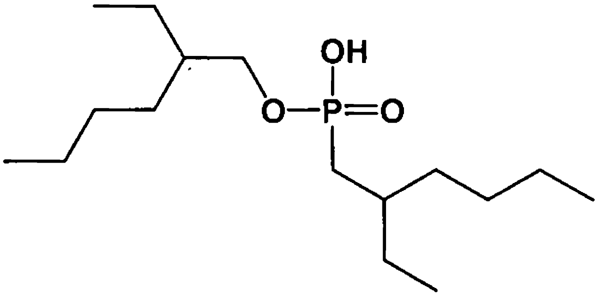


Dioctylphenylphosphoric acid

The extraction behavior of vanadium(V) from hydrochloric acid solutions has been investigated using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) in kerosene as an extractant [Saji and Reddy 2002] and reported the extraction equilibrium as:

$$VO_2{}^{+}{}_{aq} + (HX)_{2\,org} \xrightleftharpoons{K_{ex}} VO_2X \cdot HX_{org} + H^{+}{}_{aq}$$

where $(HX)_2$ refers to the dimeric form of EHEHPA and $K_{ex,V(V)}$ denotes the equilibrium constant. The equilibrium constant of the above extracted complex has been calculated and found to be $K_{exV(V)} = 3.14$. The extracted complex has been confirmed with the aid of IR spectral data. In the IR spectra of the vanadium(V)-EHEHPA complex, the P=O stretching frequency at 1195 cm^{-1} shifts towards lower frequency by 30 cm^{-1}; the P-OH stretching band at 986 cm^{-1} becomes significantly weaker; and a new absorption band which is ascribed to the V=O stretching frequency appears at 935 cm^{-1}. These results showed that when the dimeric EHEHPA forms a complex with vanadium(V), the hydrogen atom of P-OH is substituted by vanadium(V) and simultaneously, the oxygen atom in the P=O group takes part in the coordination with the metal ion. These spectral changes were in good agreement with the cation exchange mechanism reported. The potential of the EHEHPA has also been assessed for the recovery of vanadium(V) from titania waste chloride liquors. However, poor selectivity has been noticed for vanadium(V) over the other associated metal ions are present in the waste chloride liquors of titanium minerals processing industry.



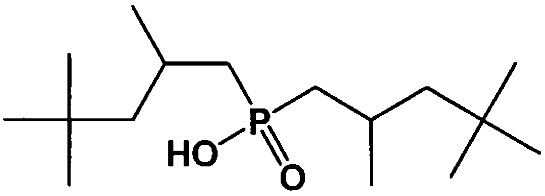
2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester

A solvent extraction process for the separation of vanadium(V) from spent catalyst has been described by employing EHEHPA as an extractant [Shimauchi et al. 1994]. The process involves the extraction of vanadium(V) with EHEHPA from a feed solution containing molybdenum and aluminium in the pH range 1.0-4.0 by EHEHPA and back extracting the metal into the aqueous phase with 0.05-2.0 mol dm^{-3} mineral acid solution as the stripping agent.

A solvent extraction based process for the recovery of vanadium and molybdenum from sulphate leach liquors of spent catalysts containing iron, aluminium, nickel and cobalt has also been reported [Toyabe et al. 1995]. The process involves roasting of the waste catalyst followed by reduction, dissolution in sulphuric acid and recovery of aluminium as ammonium aluminium sulphate.

Molybdenum was then removed by solvent extraction using N-lauryl(trialkylmethyl)amine in xylene as an extractant followed by a second solvent extraction step for the recovery of vanadium using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester in xylene as an extractant and subsequent stripping using sulphuric acid.

By employing phosphinic acid compounds, a solvent extraction process has been proposed for the selective recovery of vanadium(V) from the aqueous feed solutions containing vanadium(V) and iron(III) [Inoe et al. 1994].

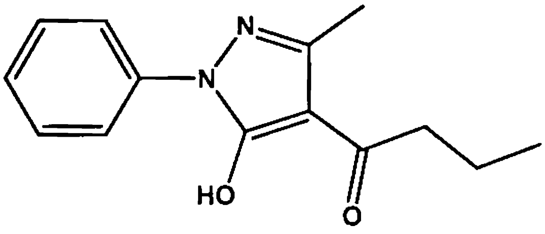


Bis(2,4,4-trimethylpentyl)phosphinic acid

The solvent extraction behavior of vanadium(V) from hydrochloric acid solutions has been investigated using bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272 ≡ BTMPPA) in kerosene as the extractant and reported the extracted complex as $VO_2X{\cdot}HX$ (HX ≡ BTMPPA) [Remya et al. 2004]. The separation and recovery possibilities of vanadium(V) from other associated metal ions *viz.*, magnesium(II), aluminium(III), titanium(IV), chromium(III), manganese(II) and iron(III), present in the waste chloride liquors of the titanium minerals processing industry has also been explored and found poor selectivity for vanadium(V) over the other associated metal ions.

Extraction by chelating ligands: The extraction of vanadium(V) and iron(III) from aqueous medium using 1-phenyl-3-methyl-4-butyrylpyrazolone (HBuP) in chloroform-butanol and MIBK-butanol mixtures has been investigated [Uzoukwu and Etesin 1995]. The study shows that iron(III) is extracted as $Fe(BuP)_3$ and vanadium is extracted as $VO_2(BuP)(HBuP)$.

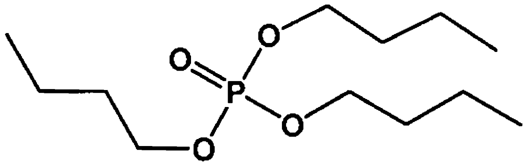
The extraction equilibrium of vanadium(III, IV, V) with acetyl acetone in non polar organic solvents such as heptane, benzene, and chloroform has been investigated at pH 1.0 - 7.0 under nitrogen atmosphere [Imura and Suzuki 1986]. Vanadium(V) is found to be extracted as vanadium(IV) chelate after reduction.



1-Phenyl-3-methyl-4-butyrylpyrazolone

B. Extraction by solvating extractants

Neutral organophosphorus extractants: Among neutral organophosphorus extractants, tributylphosphate (TBP) has been widely employed for the extraction of vanadium [Tedesco and Rumi 1980; Thomas et al. 2003].



Tributylphosphate

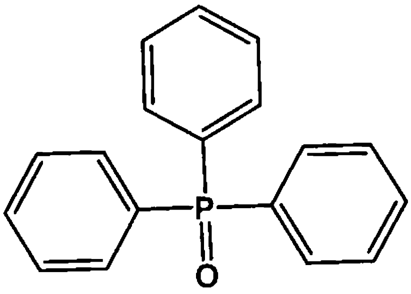
The extraction of vanadium(V) from hydrochloric acid solutions using TBP in carbon tetrachloride as an extractant has been studied and reported the extraction equilibrium as [Tedesco and Rumi 1980]:

$$VO_2Cl_{aq} + n\,TBP_{org} \rightleftharpoons VO_2Cl \cdot n\,TBP_{org}$$

where $n = 2$ or 3. Further, these authors have also studied the reduction of vanadium(V) to vanadium(IV) in hydrochloric acid solutions and reported that the extent of reduction depends on the acid concentration and time.

Solvent extraction of vanadium(V) from hydrochloric acid solutions using tributylphosphate in kerosene as an extractant has been studied and reported the extracted complexes as $VO_2Cl \cdot 2HCl \cdot 2TBP$ [Thomas et al. 2003]. Further, these authors also investigated the separation possibility of vanadium(V) from other associated metal ions, such as magnesium(II), aluminium(III), titanium(IV), chromium(III), manganese(II) and iron(III), present in the waste chloride liquors of titanium minerals processing industry and found poor selectivity.

A simple and rapid method for extracting vanadium(V), niobium(V) and tantalum(V) from halide media using triphenylphosphine oxide (TPPO) in xylene as an extractant has been reported [Kakade and Shinde 1994]. Further, these authors have reported the extracted complexes as VOX_3. 2TPPO, where X = Cl^- or Br^-. Tris(2-ethylhexyl)phosphate in toluene has also been proposed as a solvent extraction reagent for the extraction of vanadium(V) [Gaudh and Shinde 1995].



Triphenylphosphine oxide

The solvent extraction behavior of vanadium(V) has been investigated by using Cyanex 923 (TRPO) in kerosene as an extractant [Remya et al. 2003]. For comparison, extraction studies have also been carried out with vanadium(IV). The results demonstrate that vanadium(V) is extracted into the organic phase as $VO_2Cl \cdot TRPO$. On the other hand, vanadium(IV) is extracted into the organic phase as $VOCl_2 \cdot TRPO$. The equilibrium constants of the extracted complexes were found to be $K_{ex,V(V)} = 3.13$ and $K_{ex,V(IV)} = 0.14$ for vanadium(V) and vanadium(IV), respectively. IR spectral studies of the extracted complex were used to further clarify the nature of the extracted complex. Later the authors

[Remya and Reddy 2004] examined the solvent extraction behavior of magnesium(II), aluminium(III), titanium(IV), vanadium(V), chromium(III), manganese(II) and iron(III) from hydrochloric acid solutions using trialkylphosphine oxide in kerosene as an extractant. The results showed that titanium(IV), vanadium(V) and iron(III) are extracted together into kerosene as $TiOCl_2 \cdot 2TRPO$, $VO_2Cl \cdot TRPO$ and $HFeCl_4 \cdot 2TRPO$, respectively. On the other hand, magnesium(II), aluminium(III), chromium(III) and manganese(II) were found to be not extracted with TRPO from hydrochloric acid solutions (1.0 to 4.0 mol dm^{-3}) under the experimental conditions. The potential of the TRPO system for the separation and recovery of titanium(IV), vanadium(V) and iron(III) from the simulated waste chloride liquors of the titanium minerals processing industry has also been assessed.

C. Extraction by anion exchangers

Amines have been widely applied as extractants for vanadium(V) to recover the metal from several leach liquors [Lozano and Juan 2001; Lozano and Godinez 2003; Tangri et al. 1998; Sadanandam et al. 1996; Hirai and Komasawa 1991].

A solvent extraction process for the recovery of vanadium(V) from spent sulphuric acid catalyst using PRIMENE 81R in kerosene as an extractant [Lozano and Juan 2001] has been reported. The authors reported the extraction equilibrium in the pH range 2.0 - 2.5 as:

$$5RNH_{2\,org} + 5H^{+}{}_{aq} + HV_{10}O_{28\,aq}^{5-} \rightleftharpoons [(RNH_3)_5 + HV_{10}\,O_{28}^{5-}]_{org}$$

The extraction of vanadium(V) from acidic sulphate solutions using PRIMENE JMT has been investigated and found that the extraction efficiency was higher in the pH range in which polymeric anionic species of vanadium(V) are present [Nekovar and Schrotterova 2000].

The US Bureau of Mines developed a process for the extraction of vanadium resulting from sulphuric acid leaching of dolomitic shale [Brooks and Potter 1974]. Best results were obtained according to the following order of the extractants: ADOGEN 363 > AMBERLITELA-2 > Tri-isoaoctylamine > PRIMENE JMT. Thus primary amines show the worst extraction yield under these conditions.

Commercial tertiary amines such as ALAMINE 336 [Wilkomirsky et al. 1985; Tangri et al. 1998] and ADOGEN 364 [Ho et al. 1994; Chatterjee and Basu 1991] have been employed for the extraction of vanadium(V). Ternary amines were found to be better extractants for vanadium in the pH range 1.5-4.0. On the other hand, quaternary amines were found to be effective extractants for vanadium in the pH range 1.5-12, reaching optimum values between pH 6 - 9 [Wilkomirsky et al. 1985].

Tricarpylmethyl ammonium chloride (ALIQUAT 336), a liquid anion exchanger has been used for the commercial recovery of vanadium and chromium from alkaline leach liquors obtained from titaniferrous magnetite ore [Ritcey and Lucas 1977]. The separation was based on the preferential extraction of vanadium at pH 9.0 and chromium at pH 13.5. Chromium was first extracted and stripped with NaCl. The raffinate is then used for vanadium extraction using ALIQUAT 336 followed by stripping with NH_4Cl solution.

ALAMINE 336 has also been used commercially for the recovery of vanadium from uranium circuits involving sulphuric acid leach liquors of the carnotite ores [Brooks and Potter 1971]. The separation method involved simultaneous extraction of uranium and vanadium at pH 2.0 followed by selective stripping of vanadium by H_2SO_4 and that of uranium by 1.0 mol dm^{-3} Na_2CO_3.

A process for the recovery of high purity V_2O_5 (>99.9%) from spent catalyst obtained from the manufacture of sulphuric acid by contact process using

ALAMINE 336 as an extractant has been reported [Tangri et al. 1998]. The extraction equilibrium of vanadium at pH 2.0-6.5 reported was:

$$4R_3NHHSO_{4org} + H_2V_{10}O^{4-}_{28aq} \rightleftharpoons (R_3NH)_4 \cdot H_2V_{10}O_{28org} + 4HSO^{-}_{4aq}$$

The extraction of vanadium from hydrochloric acid using tri-n-octylmethyl ammonium chloride as an extractant has been studied and reported the extracted species as $VO_2Cl \cdot 2R$ and $(VO_2)_2Cl_2 \cdot 2R$, where R denotes monomeric species of the extractant in benzene diluent [Hirai and Komasawa 1991]. Further, these authors have also reported that the extracted species as $VO_2Cl \cdot R$ and $VO_2Cl \cdot 2R$ when chloroform was used as the diluent.

A process has been reported for the recovery of vanadium from acidic sulphate solutions containing iron by solvent extraction using mixed solvent systems containing tricarpyl amine and tributylphosphate [Brown et al. 1982]. The extraction stage is preceded by an oxidation step using hydrogen peroxide to convert tetravalent vanadium to pentavalent state.

ALIQUAT 336 has been employed by some researchers for the separation of vanadium from leach liquors generated from fly ash. [Hubred and Leirsburg 1985; Lakshmanan et al. 1990].

Complexation of Oxovanadium with *O,O*-donor Ligands

The advances in vanadium chemistry over the past fifteen years are discussed in the areas of solution chemistry, coordination chemistry and bioinorganic chemistry in a recent review article entitled "Fifteen years of dancing with vanadium" [Crans 2005]. Some of the developments of the coordination chemistry of oxovanadium, especially, using oxo-donor ligands have also been covered in another review entitled "Development of coordination chemistry of vanadium through bis(acetylacetonato)oxovanadium(IV): synthesis, reactivity and structural aspects" [Maurya 2003].

Among the oxovanadium(IV) complexes, the vanadyl acetylacetonate [$VO(acac)_2$] is certainly the most representative species. $VO(acac)_2$ has been the subject of many experimental investigations devoted to its interesting paramagnetic and physicochemical properties, mainly associated with the $3d^1$ electronic configuration [Selbin 1965; Chasteen 1981; Gregson and Mitra 1980; Selbin and Ortolano 1964; Tantrawong et al. 1993]. $VO(acac)_2$ possesses a square-pyramidal arrangement of the five coordinated oxygen atoms, with the vanadium atom close to the center of gravity of the pyramid. Early X-ray crystal structure determinations and a more recent gas-phase electron diffraction study have pointed to a monomeric structure of C_{2V} symmetry, with the V=O bond along the 2-fold axis [Dodge et al. 1961; Forsyth et al. 1990]. Magnetic susceptibility and ESR data have indicated a magnetic moment and paramagnetic resonance factors both consistent with a single unpaired electron.

The electronic structure of $VO(acac)_2$ complex has been investigated using effective core potential configuration interaction *ab initio* calculations, UV-photoelectron spectroscopy, and electronic spectroscopy [Di Bella et al. 1996]. The metal-ligand bonding with the equatorial $acac^-$ ligands is dominated by σ interactions involving the filled ligand orbitals and the empty orbitals of the d^1 vanadium(IV) ion. The oxovanadium interactions involve a larger metal-d participation thus resulting in a strong V-O bonding having partial triple-bond character. Additional three-orbital-four-electron stabilizing interactions involving the filled $acac^-$ MOs and the oxovanadium orbitals further reinforce both the axial and equatorial bonds. The unpaired metal-d electron is completely localized in the nonbonding d_{x2-y2} orbital.

The syntheses and the solid state structural and spectroscopic solution characterizations of $VO(Me\text{-}acac)_2$ and $VO(Et\text{-}acac)_2$ (where Me-acac is 3-methyl-

2,4-pentanedionato and Et-acac is 3-ethyl-2,4-pentanedionato) have been conducted since both of these have long-term *in vivo* insulin mimetic-effects [Amin et al. 2000]. X-ray structural characterizations of $VO(Me\text{-}acac)_2$ and $VO(Et\text{-}acac)_2$ show that both contain five-coordinate vanadium similar to the parent $VO(acac)_2$. The unit cells for $VO(Et\text{-}acac)_2$ and $VO(Me\text{-}acac)_2$ are both triclinic. The single crystal X-ray structures revealed that both $VO(Et\text{-}acac)_2$ and $VO(Me\text{-}acac)_2$ exist in the solid state as discrete mononuclear complexes, with the vanadium atoms in distorted square pyramidal coordination environments. Three species were observed from the EPR simulations and were assigned as the *trans*-$VO(acac)_2H_2O$ (A) adduct, *cis*-$VO\text{-}(acac)_2H_2O$ (B) adduct, and a hydrolysis product containing one vanadium atom and one R-acac- group (C) (Figure 1.2).

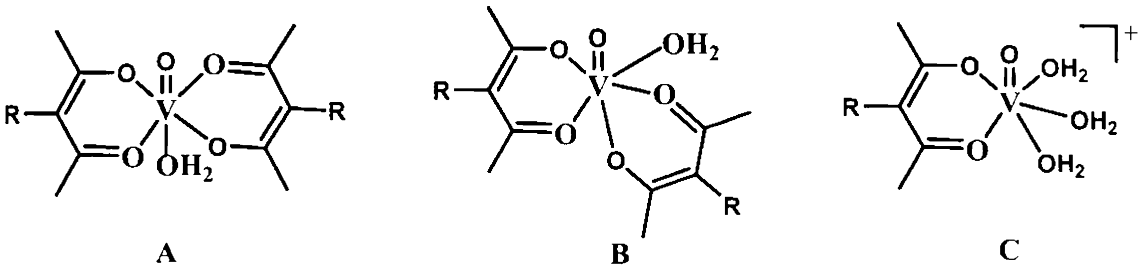


Figure 1.2. The three species observed from the EPR simulations.

The electronic structure of derivatives of $VO(acac)_2$ is probed using gas-phase UV-photoelectron spectroscopy [Gruhn et al. 2002]. The effect on the metal center of electron-donating and -withdrawing groups on the acac ligands (Figure 1.3) is examined. Ionizations from metal-based, acac-based, and V=O based orbitals are clearly observed. The authors found that changes at the ligand periphery lead to equivalent changes in the energies of the metal-based and ligand-based ionizations. Additionally, the authors have also noticed the existence of linear correlation between the ionization energies of the metalated complexes and the p*K*a values of the free ligands, indicating that the pK_a is a good indication of the overall electron-donating abilities of acac ligands.

Bis(acetylamido)oxovanadium(IV) complexes have been synthesized and characterized by various spectroscopic techniques [Crans et al. 2001]. In VO(acac-$NMe_2)_2$, the vanadium ion is in a distorted square pyramidal coordination environment. These complexes are found to be less stable than $VO(acaca)_2$.

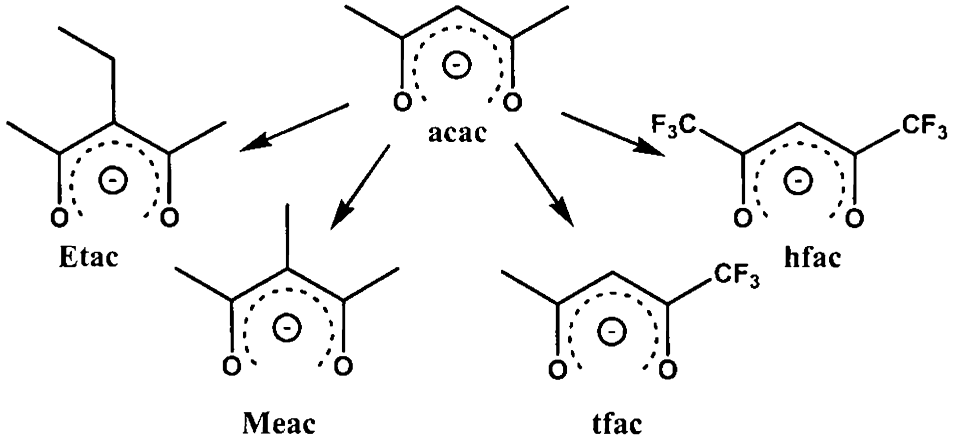
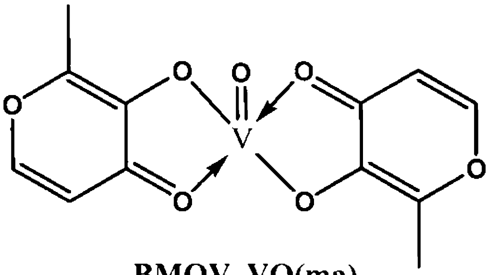


Figure 1.3. Structures of the ligands.

Bis(maltolato)oxovanadium(IV) (abbreviated BMOV or $VO(ma)_2$) has been characterized by electron paramagnetic resonance (EPR) spectroscopy in CH_2Cl_2, H_2O, MeOH, and pyridine at both room-temperature and lower temperatures [Hanson et al. 1996]. Configurations of solvated vanadyl/maltol complexes, $VO(ma)_2S$, in solution (S-solvent) are proposed on the basis of a comparison of their hyperfine coupling constants with those obtained for related vanadium(IV) compounds in the literature. Whereas at room-temperature pyridine coordinates to $VO(ma)_2$ in a position *cis* to the oxo ligand (*cis* isomer), in H_2O or in MeOH solvated and unsolvated *cis* and *trans* adducts of $VO(ma)_2$ are all formed, with the *cis* isomer being the dominant one. As expected, the coordinating ability was found to be in the order py > H_2O > MeOH > CH_2Cl_2. In aqueous solutions at room temperature and neutral pH, *cis*- and *trans*-$VO(ma)_2(H_2O)$ complexes are present as major and minor components, respectively.

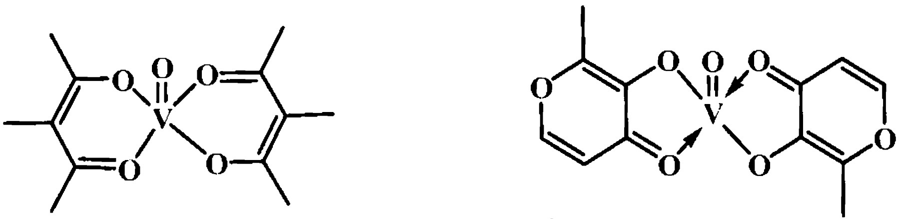
The structure and conformation of bis(acetylacetonato)oxovanadium(IV) [$VO(acac)_2$] and bis(maltolato)oxovanadium(IV) [$VO(malto)_2$] in frozen methanol have been determined by the application of electron nuclear double resonance



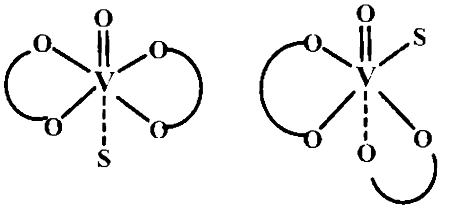
BMOV, $VO(ma)_2$

(ENDOR) spectroscopy [Mustafi and Makinen 2005]. The positions of inner- and outer-sphere-coordinated solvents were assigned by ENDOR through use of selectively deuterated analogues of methanol (Figure 1.4). Similarly, the methyl and methylinyl proton resonance features of $VO(acac)_2$ were identified by site-selective deuteration. For $VO(acac)_2$, the ENDOR-determined metal-proton distances were best accounted for by a complex of tetragonal-pyramidal geometry, but with an inner sphere solvent molecule coordinated *trans* to the vanadyl oxygen and an axially positioned solvent molecule hydrogen bonded to the vanadyl oxygen. The $VO(malto)_2$ complex was found in a *cis* conformation whereby the donor oxygen atoms of one maltolato ligand occupied equatorial coordination sites. One of the donor oxygen atoms of the second maltolato ligand occupied the axial coordination site opposite to the vanadyl oxygen atom, and the other an equatorial position. An inner-sphere-coordinated methanol molecule in the equatorial plane and solvent molecule hydrogen bonded to the vanadyl oxygen were also identified. No evidence for the *trans* isomer was observed in $VO(malto)_2$.

Various 1-phenyl-3-methyl-4-acyl-5-pyrazolone complexes with oxovanadium(IV) were synthesized and characterized by UV-vis and IR spectral studies and reported the molecular formulae of the complexes as VOA_2 where A is the acylpyrazolone anion [Uzoukwu 1992]. The $\nu(V=O)$ appeared near 895 cm^{-1} in the FT-IR spectra and the low absorption band is attributed to the possible presence of bridging vanadyl group in the complexes.



Bis(acetylacetonato)oxovanadium(IV) **Bis(maltato)oxovanadium(IV)**



trans **cis**

Figure 1.4. Illustration of chemical bonding structures of bis(acetylacetonato) oxovanadium(IV) and bis(maltolato)oxovanadium(IV).

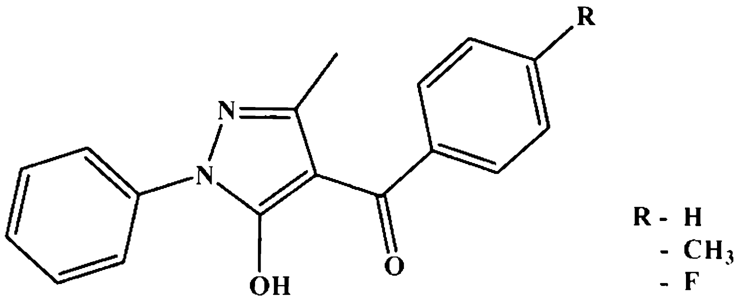
Chapter II

Synthesis and Characterization of Para-Substituted 1-Phenyl-3- methyl-4-aroyl-5-pyrazolones: Complexation of Vanadium

It is clear from the literature review that various organophosphorus extractants, di-(2-ethylhexyl)phosphoric acid [Brunette et al. 1979], 2-ethylhexylphosphonic acid mono-2-ethylhexylester [Saji and Reddy 2002; Saji and Reddy 2003], bis(2,4,4-trimethylpentyl) phosphinic acid [Remya et al. 2004; Zhang et al. 1996], tributylphosphate [Thomas et al. 2003; Moskalyk and Alfantazi 2003; Tedesco and de Rumi 1980] and trialkylphosphine oxide [Remya et al. 2003; Remya and Reddy 2004] have been employed for the extraction and separation of vanadium(V) from acidic chloride solutions, and poor selectivity has been reported over other associated multivalent metal ions present in the waste chloride liquors of titanium. The above factors have prompted us to design and develop new vanadium selective solvent extraction reagents for the recovery of vanadium from titania waste chloride liquors.

4-Acyl-5-pyrazolones are an interesting class of β-diketones containing a pyrazolone ring fused to a chelating arm [Marchetti et al. 2005; Umetani et al. 2000], capable of extracting metal ions from strong acidic solutions compared to conventional β-diketones such as acetylacetone (pK_a = 9.0) and thenoyltrifluoroacetone (pK_a = 6.25) due to their low pK_a values (2.56-4.02) [Meera and Reddy 2004]. The nature of the substituent in the fourth position of the pyrazolone ring causes significant variations in the electronic, steric, and solubility parameters of the ligand, thereby affecting complexation and extraction of metal ions. To the best our knowledge, no reports have appeared in the literature on the extraction of vanadium(V) and associated metal ions from hydrochloric acid solutions with para-substituted 4-aroyl derivatives of 1-phenyl-3-methyl-5-pyrazolones (**A**).

These factors prompted us to synthesize such ligands namely, 1-phenyl-3-methyl-4-(4-fluorobenzoyl)-5-pyrazolone (Hpmfbp) and 1-phenyl-3-methyl-4-(4-toluoyl)-5-pyrazolone (Hpmtp), by introducing both electron-withdrawing (–F) and electron-donating (-CH_3) groups and, then examine their effects on the extraction of vanadium(V) and other associated multivalent metal ions that are present in the titania waste chloride liquors. For comparison, studies have also been performed with 1-phenyl-3-methyl-4-(4-benzoyl)-5-pyrazolone (Hpmbp). Chloroform was chosen as a diluent, even though it is not a practical diluent because of the solubility limitations of the reagents in kerosene based solvent systems. Moreover chloroform provides simpler behavior and this enables interpretation of the extraction data.



4-Aroyl-5-pyrazolones

A

EXPERIMENTAL

Instrumentation

Absorbance was measured using a Shimadzu UV-2450 Spectrophotometer. Deconvolution of UV spectra was carried out by employing Peak Fit 4.12 software. An Orion (USA) 720A Ion Analyzer was used for the pH measurements. A Perkin Elmer A Analyst 100 atomic absorption spectrophotometer was used for the analysis of metal ions in multi-component mixtures. Elemental analyses were performed with a Perkin-Elmer Series 2 Elemental Analyser 2400. The mass of the complexes were determined by fast atom bombardment high-resolution mass spectrometry (FAB-HRMS; JEOL JSM600). A Nicolet FT-IR 560 Magna Spectrometer using KBr (neat) was used to obtain IR spectral data and a Bruker 300 MHz NMR spectrometer was used to obtain ^1H NMR and ^{13}C NMR spectra of the compounds in $CDCl_3$. The EPR spectra were recorded on Varion E-112 spectrometer at liquid nitrogen as well as room-temperature. The magnetic moments were measured using a model 155 vibrating sample magnetometer system.

Cyclic voltammetric experiments were conducted using a Cypress Systems Model CS-1090 computer-controlled voltammetric analyzer, (BAS 100 electrochemical analyzer Graphtec WX 1200 recorder). All the experiments were done under nitrogen atmosphere at ambient temperature in solutions with 0.1 M tetrabutylammonium hexa-flurophosphate as the supporting electrolyte. Cyclic voltammograms (CV) were obtained using a three-electrode system consisting of glassy-carbon working, Pt wire auxiliary, and SCE reference electrodes. The ferrocenium/ferrocene couple was used to monitor the reference electrode and was observed at 0.450V with $\Delta Ep = 0.120$ V and $ip_c/ip_a \approx 1.0$ in acetonitrile under these conditions.

X-ray Crystallography Data Collection and Processing

X-ray single crystal data were recorded at room-temperature on a Bruker Smart 6000 diffractometer equipped with a CCD detector and a copper tube source. Data were processed using SAINTPLUS (SAINTPLUS, program suite for data processing, Bruker AXS, Inc., Madison, Wisconsin, USA). Structures were solved and refined using SHELXL97 [SHELX97 - Program package for Crystal Structure Analysis. G. M. Sheldrick, Institüt für Anorganische Chemie der Universität, Göttingen, Germany, 1998]. Non-hydrogen atoms were refined anisotropically and a riding model was used for C-H hydrogen atoms.

DFT Calculation

The electronic structure of the ligands and complexes were calculated using the unrestricted density functional theory (DFT) method using the B3LYP functional [Becke 1993; Lee et al. 1988] as implemented in the Gaussian03 suite of programs. For vanadium atom, the LANL2DZ basis set was selected together with the effective core potential of Hay and Wadt [Hay and Wadt 1985a; Hay and Wadt 1985b]. For the other elements, the 6-31G* basis sets were selected [Hariharan and Pople 1974]. The geometry of the ligand system Hpmtp was also optimized at the B3LYP/6-31G* level of theory.

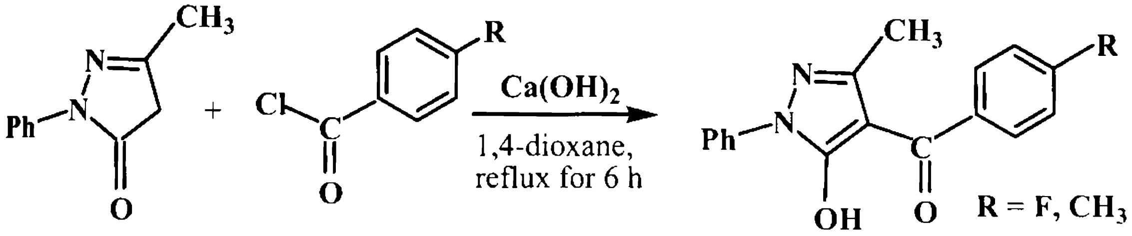
Materials

The acid chlorides (para-toluoyl chloride: 98% purity; 4-flurobenzoyl chloride: 98% purity) and 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (Hpmbp) were purchased from Aldrich Chemical Company USA. Chloroform of analytical reagent quality supplied by Merck, India was used as the diluent. All other chemicals used were of analytical reagent grade.

Vanadium(V) stock solution was prepared by dissolving 5.85 g of ammonium monovanadate in hydrochloric acid and diluting to 1.0 dm^3 with distilled water. Freshly prepared solutions of vanadium(V) were used in all the experimental studies to prevent the partial reduction to tetravalent vanadium in HCl solutions with respect to time [Tedesco and De Rumi 1978]. Titanium(IV) solutions were prepared from $TiCl_4$ (99.0%) solution by diluting to the required concentration with hydrochloric acid. Stock solutions of magnesium(II), aluminium(III), chromium(III), manganese(II), iron(II), and iron(III) were prepared by dissolving 12.32 g of $MgSO_4 \cdot 7H_2O$, 18.76 g of $Al(NO_3)_3 \cdot 9H_2O$, 24.97 g of $CrK(SO_4)_2 \cdot 12H_2O$, 8.45 g of $MnSO_4 \cdot H_2O$, 162.75 g of $FeCl_2 \cdot 2H_2O$, and 162.21 g of $FeCl_3$ each in 1.0 dm^3 of distilled water, respectively. Suitably diluted stock solutions of the above-mentioned metal ions were used in the extraction and analytical studies. All organic phase solutions were prepared by dissolving weighed amounts 1-phenyl-3-methyl-4-aroyl-5-pyrazolone in chloroform and then diluting to the required concentration.

Syntheses of Various Para-substituted 4-Aroyl-5-pyrazolones

4-Aroyl derivatives of 1-phenyl-3-methyl-5-pyrazolone, Hpmfbp and Hpmtp, were synthesized from 1-phenyl-3-methyl-5-pyrazolone and the corresponding acid chloride following the method described elsewhere (Scheme 2.1) [Meera and Reddy 2004]. The synthesized 4-aroyl-5-pyrazolones were identified by elemental analyses, FT-IR and ^{1}H NMR spectral data.



Scheme 2.1

1-phenyl-3-methyl-4-(4-toluoyl)-5-pyrazolone (Hpmtp): m.p. 105-106°C; ^{1}H NMR ($CDCl_3$) data: δ (ppm) 7.26-7.98 (m, 9H, phenyl); 2.14 (s, 3H, CH_3 of pyrazole ring); 2.45 (s, 3H, CH_3 of the aromatic ring) (Figure 2.1); FT-IR (KBr) data ν (cm^{-1}): 1600 (C=O), 1537, 753; Elemental analysis: Calculated for $C_{18}H_{16}N_2O_2$, C 73.97; H 5.48; N 9.59%; Found: C 74.64; H 5.66; N 9.57%. In the ^{1}H NMR spectrum of Hpmtp, no peak corresponding to the enolic -OH has been vobserved. However, the absence of a peak at δ 3.4 ppm, corresponding to the methylene proton at the fourth position of the pyrazolone ring, confirms the existence of Hpmtp in the enolic form.

The crystallographic data for Hpmtp are listed in Table 2.1. An ORTEP diagram for the common repeating unit is shown in Figure 2.2. The molecular structure reveals a planar arrangement of non hydrogen atoms (O2, C11, C8, C9, O1).

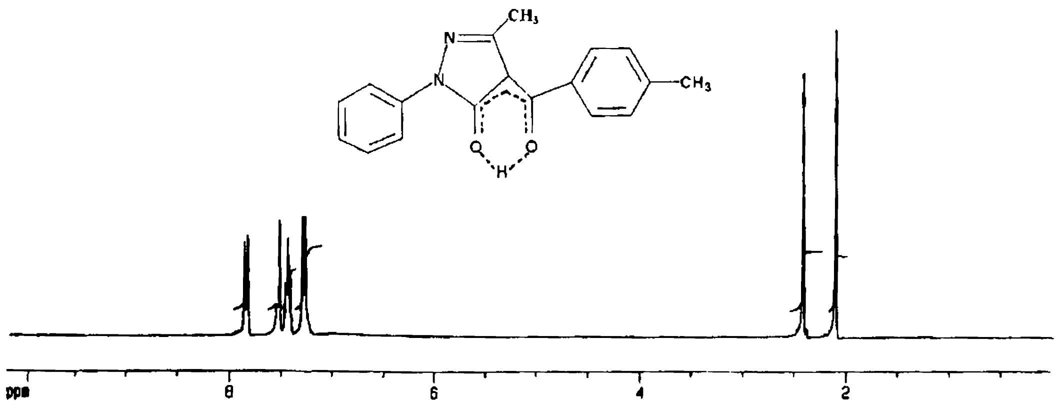


Figure 2.1. ^{1}H NMR spectrum of 1-phenyl-3-methyl-4-(4-toluoyl)-5-pyrazolone.

Table 2.1. Crystal data, collection, and structure refinement parameters for 1-phenyl-3-methyl-4-(4-toluoyl)-5-pyrazolone (Hpmtp).

Parameters	Hpmtp
empirical formula	$C_{18}H_{16}N_2O_2$
Fw	292.32
crystal system	monoclinic
space group	P21/n
cryst size (mm^3)	0.30 × 0.30 × 0.20
temperature (K)	293(2)
a/Å	15.3610(7)
b/Å	5.1971(2)
c/Å	18.2056(8)
α (deg)	90
β (deg)	90.9250(6)
γ (deg)	90
V / Å^3	1453.21(11)
Z	4
ρ_{calcd}/g cm^{-3}	1.332
μ/mm^{-1}	0.088
F(000)	612
R1 [$I > 2\sigma(I)$]	0.0429
wR2 [$I > 2\sigma(I)$]	0.1345
R1 (all data)	0.0628
wR2 (all data)	0.1345
GOF	1.077

The carbonyl bond lengths C9-O1 and C11-O2 are 1.307 and 1.268 Å, respectively. There is an intra molecular hydrogen bond between the atoms O1 and O2 (O1-H····O2, 2.257 Å, 116.32°). These data suggest that, in the ring consisting of O1/O2, the enolic proton is not shared symmetrically with the carbonyl oxygens; that is Hpmtp exists in the enol form in the solid state.

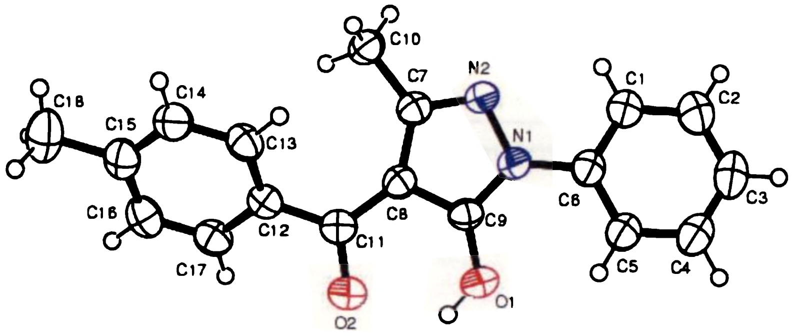


Figure 2.2. ORTEP diagram of 1-phenyl-3-methyl-4-(4-toluoyl)-5-pyrazolone.

1-phenyl-3-methyl-4-(4-fluorobenzoyl)-5-pyrazolone (Hpmfbp): m.p.: 132-133°C; ^{1}H NMR ($CDCl_3$) data: δ (ppm) 7.17-7.87 (m, 9H, phenyl); 2.12 (s, 3H, CH_3 of the pyrazole ring) (Figure 2.3); FT-IR (KBr) data ν (cm^{-1}): 2800, 1620 (C=O), 1590, 1500, 1356, 1214, 752; Elemental analysis: Calculated for $C_{17}H_{13}N_2O_2F$, C 68.92; H 4.39; N 9.46%; Found: C 69.06; H 4.26; N 9.48%. In the ^{1}H NMR spectrum of Hpmfbp, no peak corresponding to the enolic -OH has been observed. However, the absence of a peak at δ 3.4 ppm, corresponding to the methylene proton at the fourth position of the pyrazolone ring, confirms the existence of Hpmfbp in the enolic form. The structure of 1-phenyl-3-methyl-4-(4-fluorobenzoyl)-5-pyrazolone was then modeled using DFT molecular modeling calculations and the minimum energy structure obtained is shown in Figure 2.4.

The existence of Hpmbp in the enolic form was confirmed from its single crystal X-ray structure (Figure 2.5). The crystallographic data for Hpmbp are listed in Table 2.2. The carbonyl bond lengths C9-O1 and C11-O2 are 1.296 and 1.255 Å, respectively. There is an intra molecular hydrogen bond between the atoms O1 and O2 (O1-H····O2, 2.622 Å, 137.78°).

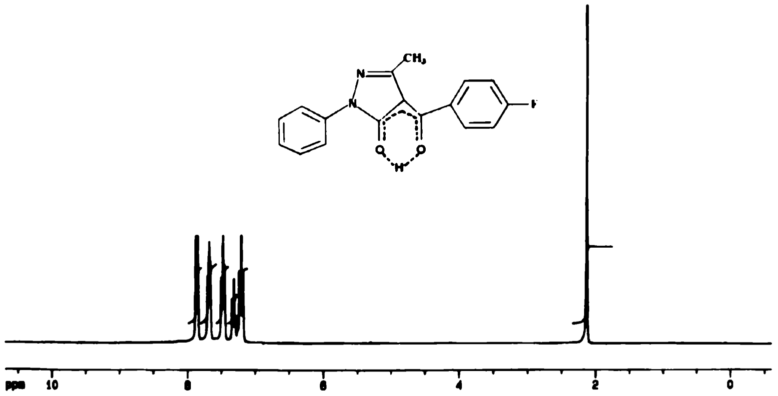


Figure 2.3. ^{1}H NMR Spectrum of 1-phenyl-3-methyl-4-(4-fluorobenzoyl)-5-pyrazolone.

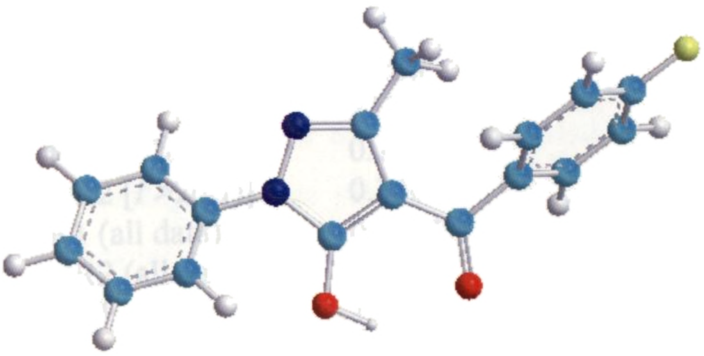


Figure 2.4. The optimized structure of 1-phenyl-3-methyl-4-(4-fluorobenzoyl)-5-pyrazolone at the B3LYP/6-31G* level of DFT.

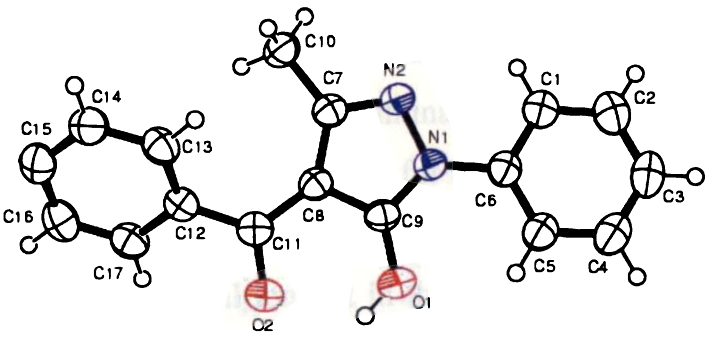


Figure 2.5. ORTEP diagram of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone.

Table 2.2. Crystal data, collection, and structure refinement parameters for 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (Hpmbp).

Parameters	Hpmbp
empirical formula	$C_{17} H_{14} N_2 O_2$
fw	278.30
crystal system	monoclinic
space group	$C2/c$
cryst size (mm^3)	0.30 × 0.30 × 0.20
temperature (K)	293(2)
a/Å	14.3075(10)
b/Å	14.3942(10)
c/Å	27.1840(18)
α (deg)	90
β (deg)	91.099(6)
γ (deg)	90
V / Å^3	5597.4(7)
Z	16
ρ_{calcd}/g cm^{-3}	1.321
μ/mm^{-1}	0.088
F(000)	2336
R1 [$I > 2\sigma(I)$]	0.1269
wR2 [$I > 2\sigma(I)$]	0.3404
R1 (all data)	0.1624
wR2 (all data)	0.3765
GOF	1.156

Liquid-Liquid Extraction and Analytical Procedure

Solvent extraction and stripping experiments were carried out by shaking equal volumes of aqueous and organic phases in glass-stoppered vials using a mechanical shaker at 303 ± 1K for 2 h. Preliminary experiments showed that the extraction equilibrium was attained within 2 h for both vanadium(V) and iron(III). The solutions were then allowed to settle, the phases were separated and the concentration of a particular metal ion left in the aqueous phase was determined using standard procedures. Thus, vanadium(V) (detection limit 0.1 mg cm^{-3}) and titanium(IV) (detection limit 0.5 mg cm^{-3}) were analyzed spectrophotometrically using hydrogen peroxide method [Vogel 1989a]. Magnesium(II), aluminium(III), chromium(III), iron(II) and iron(III) were analyzed spectrophotometrically using Eriochrome Black-T (detection limit <100 μg Mg(II)) [Vogel 1989a], Eriochrome Cyanine-R (detection limit 2-70 μg Al(III)) [Vogel 1989a], 1,5-diphenylcarbazide (detection limit 0.5mg Cr(III) in 100 cm^3) [Clesceri 1998], and 1,10-Phenanthroline (detection limit 0.1 - 0.5 mg) [Vogel 1989a], respectively. Manganese(II) was analyzed titrimetrically using EDTA (detection limit 0.01 mol dm^{-3}) [Vogel 1989b]. The concentration of the metal ion in the organic phase was then obtained by mass balance. The distribution ratio, *D*, was taken as the ratio of the concentration of metal ion in the organic phase to that present in the aqueous phase. All the experiments were performed in duplicate and the general agreement between the distribution ratio values obtained was within ± 5%.

Preparation of Vanadium Complexes

To a well stirred ethanol solution of para-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolone (2.0 mM), aqueous solution of NaOH (2.0 mM) was added. After the complete dissolution of 1-phenyl-3-methyl-4-aroyl-5-pyrazolone, 1.0 mM of ammonium monovanadate was added, the pH was adjusted to 7 and 1 and the reaction mixture was stirred for 8 h. The precipitate formed was filtered, washed with ethanol, then with distilled water, and recrystallized using dichloromethane/hexane mixture. Efforts to grow crystals of these complexes in various solvents were not fruitful.

Polymerization

In order to identify the formation of free-radical in the process of preparation of the solid complexes, the polymerization reaction of 5% (v/v) acrylonitrile has been carried out at room-temperature in inert atmosphere in presence of oxovanadium(V) (0.001 mol dm^{-3}) and para-substituted 1-phenyl-3-methyl-4-

aroyl-5-pyrazolone (0.01 mol dm^{-3}). A cloudy suspension was observed within a few minutes after the addition of metal solution. The reaction was then kept under stirring for 2 h. The polymer formed was then precipitated by adding methanol to the reaction mixture. On the other hand, in the absence of either para-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolone or oxovanadium(V) no detectable polymerization was noticed. These experiments can be considered as indirect evidence to the free radicals during complexation of oxovanadium(V) by para-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolone, since such species are instrumental in initiating the polymerization of acrylonitrile.

Part I

Para-substituted 1-Phenyl-3-methyl-4-aroyl-5-pyrazolones as Selective Extractants for Vanadium(V) from Acidic Chloride Solutions

RESULTS AND DISCUSSION

Effect of Hydrochloric Acid Concentration on the Extraction of Multivalent Metal Ions Present in the Titania Waste Chloride Liquors

The extraction behavior of magnesium(II) (0.005 mol dm^{-3}), aluminium(III) (0.005 mol dm^{-3}), titanium(IV) (0.005 mol dm^{-3}), vanadium(V) (0.005 mol dm^{-3}), chromium(III) (0.005 mol dm^{-3}), manganese(II) (0.005 mol dm^{-3}), iron(II) (0.005 mol dm^{-3}) and iron(III) (0.005 mol dm^{-3}) that are present in the waste chloride liquors of titanium minerals processing industry has been investigated as a function of hydrochloric acid concentration using 0.1 mol dm^{-3} of 4-aroyl-5-pyrazolone in chloroform as an extractant and the results are depicted in Figure 2.6. It is clear from the results that vanadium(V) and iron(III) are extracted into the organic phase. On the other hand, magnesium(II), aluminium(III), titanium(IV), chromium(III), iron(II) and manganese(II) were not extracted into the organic phase under the present experimental conditions. Further, the selectivity between vanadium(V) and iron(III) increases with increase in hydrochloric acid concentration (Table 2.3) and the extraction of iron(III) is almost negligible at and above 1.5 mol dm^{-3} HCl. Thus, it can be concluded from these results that vanadium(V) can be selectively extracted and separated from the above associated metal ions by controlling the hydrochloric acid concentration in the aqueous phase.

The stripping behavior of vanadium(V) has been investigated using HCl as the stripping agent from a loaded phase (0.1 mol dm^{-3} HX) containing 0.005 mol dm^{-3} vanadium(V) and the results are given in Figure 2.7. The percentage recovery of vanadium(V) increases with increase in HCl concentration in the aqueous phase and was found to be almost quantitative above 6.0 mol dm^{-3} HCl. In the present study, above 4.0 mol dm^{-3} HCl, a slight reduction of vanadium(V) to vanadium(IV) (10%) was noticed, as reported elsewhere [Tedesco and De Rumi 1978].

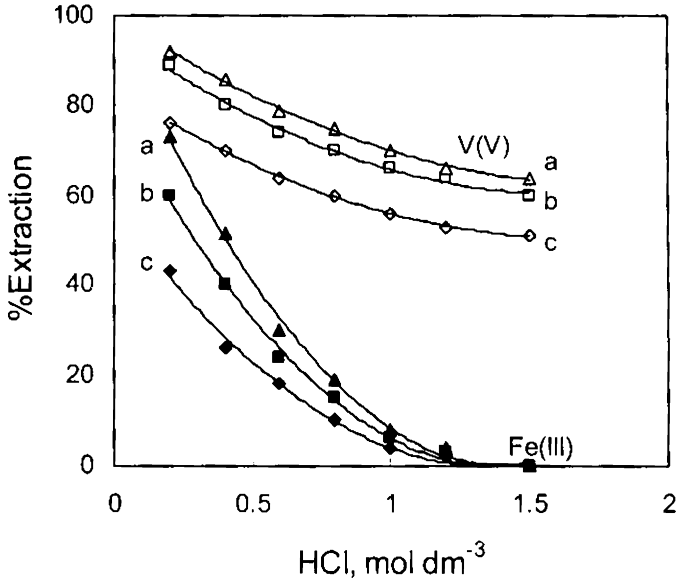


Figure 2.6. Effect of HCl concentration on the extraction of vanadium(V) and iron(III) using para-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolones. a = Hpmfbp, b = Hpmbp, c = Hpmtp = 0.1 mol dm^{-3}.

Table 2.3. Separation factors between vanadium(V) and iron(III) with various 4-aroyl-5-pyrazolones (HX = 0.1 mol dm^{-3}) as a function of HCl concentration.

HCl mol dm^{-3}	Separation Factor (S.F = $D_{V(V)}/D_{Fe(III)}$)		
	Hpmfbp	Hpmbp	Hpmtp
0.2	4.25	5.39	5.78
0.4	5.76	6.06	8.53
0.6	8.77	9.01	10.20
0.8	12.77	13.24	15.60
1.0	26.78	30.81	36.67
1.2	47.32	59.0	168.33

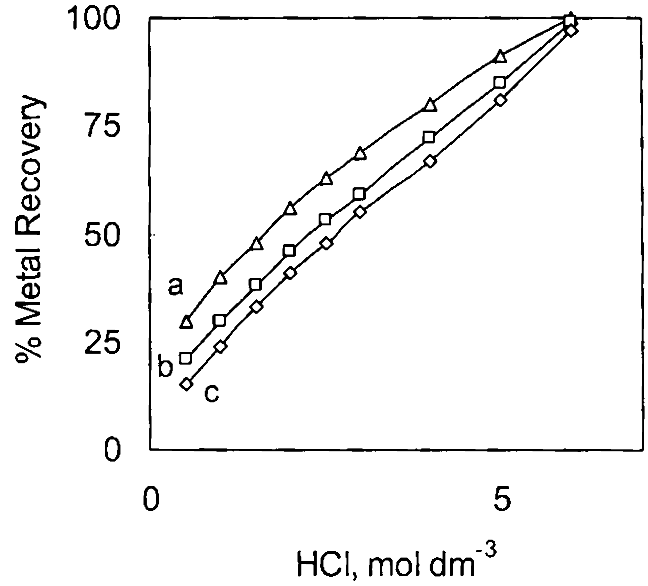


Figure 2.7. Stripping behavior of vanadium(V) from loaded 4-aroyl-5-pyrazolones using HCl. a = Hpmfbp, b = Hpmbp, c = Hpmtp.

Extraction Equilibria of Vanadium(V) and Iron(III) with Various Para-substituted 4-Aroyl-5-pyrazolones

The effect of ligand concentration on the extraction of vanadium(V) and iron(III) has been studied by keeping metal ion (5×10^{-3} mol dm^{-3}) and hydrochloric acid concentrations (0.2 mol dm^{-3}) constant and the results are shown in Figure 2.8. It is clear from the results that the extraction of both vanadium(V) and iron(III) increases with increase in concentration of various 1-phenyl-3-methyl-4-aroyl-5-pyrazolones (HX). The log-log plots gave slopes of 2.0 ± 0.1 and 3.0 ± 0.1 for vanadium(V) and iron(III), respectively.

The extraction of vanadium(V) and iron(III) with various 1-phenyl-3-methyl-4-aroyl-5-pyrazolones (5×10^{-2} mol dm^{-3} for vanadium(V) and 0.1 mol dm^{-3} for iron(III)) in chloroform as a function of hydrogen ion concentration at constant chloride ion concentration (1.0 mol dm^{-3}) has been investigated using HCl + NaCl mixtures. In both cases, the extraction behavior showed an inverse dependence on the acidity. The log-log plots (Figure 2.9) gave slopes of -1.0 ± 0.1 and -3.0 ± 0.1, indicating the release of one and three hydrogen ions to the aqueous phase in the extraction of vanadium(V) and iron(III), respectively. The effect of chloride ion concentration (0.1 - 2.0 mol dm^{-3}) on the extraction of vanadium(V) and iron(III) by various 4-aroyl-1-phenyl-3-methyl-5-pyrazolones (0.05 mol dm^{-3} for vanadium(V) and 0.1 mol dm^{-3} for iron(III)) in chloroform at constant metal (5 × 10^{-3} mol dm^{-3}) and hydrogen ion (0.1 mol dm^{-3}) concentrations, shows that the extraction of both metal ions are independent of chloride ion concentration in the investigated range.

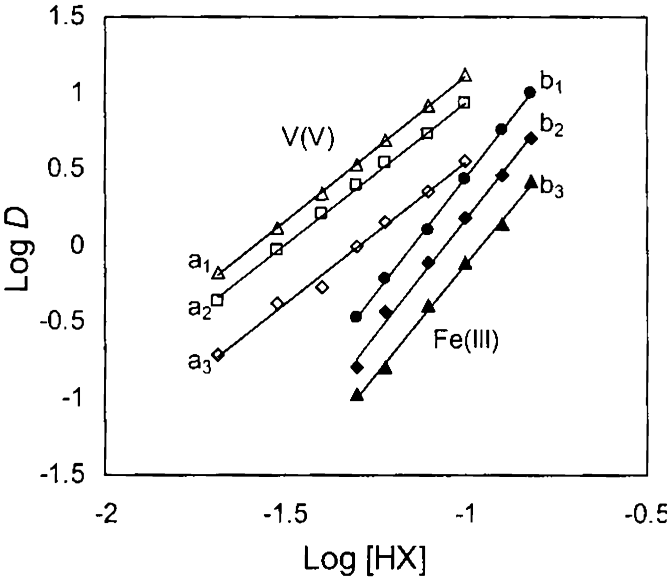


Figure 2.8. Effect of 1-phenyl-3-methyl-4-aroyl-5-pyrazolone (HX) concentration on the extraction of vanadium(V) and iron(III) from 0.2 mol dm^{-3} HCl solutions. [V(V)] = [Fe(III)] = 5 × 10^{-3} mol dm^{-3}. Slope of the line for V(V) = 2.00 $\pm$ 0.01; Fe(III) = 3.0 $\pm$ 0.1. a_1 = Hpmfbp, a_2 = Hpmbp, a_3 = Hpmtp for V(V); b_1 = Hpmfbp, b_2 = Hpmbp, b_3 = Hpmtp for Fe(III).

The effect of metal ion concentration on the extraction of vanadium(V) and iron(III) (3 × 10^{-3} – 9 × 10^{-3} mol dm^{-3}) from 0.2 mol dm^{-3} HCl solutions (0.2 mol dm^{-3}) by various 1-phenyl-3-methyl-4-aroyl-5-pyrazolones (5 × 10^{-2} mol dm^{-3} for vanadium(V) and 0.1 mol dm^{-3} for iron(III)) in chloroform showed that the extraction is independent of metal ion concentration in the investigated range. The log-log plots of equilibrium organic phase metal concentration to the aqueous phase metal concentrations are linear with slopes of unity, indicating the extraction of mono- nuclear species into the organic phase (Figure 2.10).

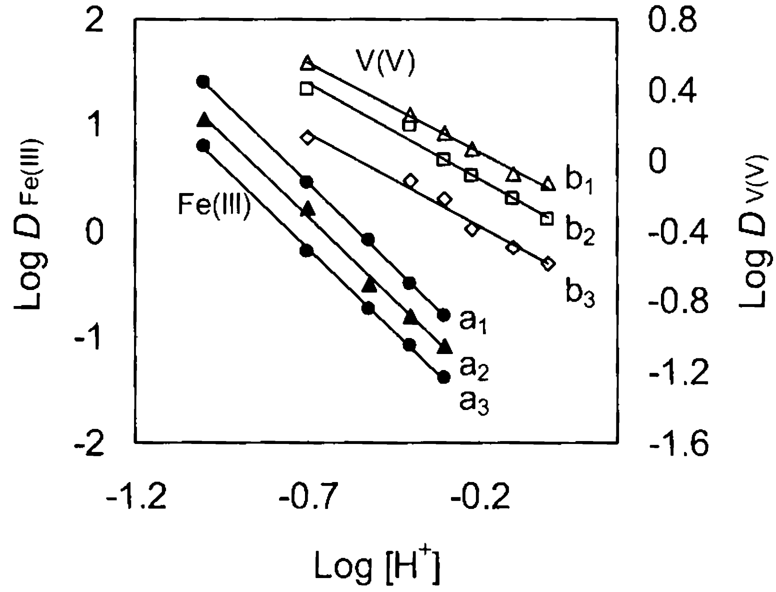


Figure 2.9. Effect of hydrogen ion concentration on the extraction of vanadium(V) and iron(III). HX = 5×10^{-2} mol dm^{-3} for vanadium(V) and 0.1 mol dm^{-3} for iron(III). [V(V)] = [Fe(III)] = 5×10^{-3} mol dm^{-3}. Slope of the line for V(V) = - 1.0 ± 0.1; Fe(III) = - 3.0 ± 0.1. a_1 = Hpmfbp, a_2 = Hpmbp, a_3 = Hpmtp for V(V); b_1 = Hpmfbp, b_2 = Hpmbp, b_3 = Hpmtp for Fe(III).

Based on the preceding results, the extraction equilibria of vanadium(V) and iron(III) from hydrochloric acid solutions with 1-phenyl-3-methyl-4-aroyl-5-pyrazolone (HX) may be represented as:

$$VO_{2\,aq}^{+} + 2\,HX_{org} \overset{K_{ex,V(V)}}{\rightleftharpoons} VO_2X\cdot HX_{org} + H^{+}_{aq} \qquad (1)$$

$$Fe^{3+}_{aq} + 3\,HX_{org} \overset{K_{ex,Fe(III)}}{\rightleftharpoons} FeX_{3\,org} + H^{+}_{aq} \qquad (2)$$

where $K_{ex,V(V)}$ and $K_{ex,Fe(III)}$ denote the equilibrium constants for vanadium(V) and iron(III), respectively and are given by,

$$K_{ex,V(V)} = \frac{[VO_2X \cdot HX]\,[H^+]}{[VO_2^+]\,[HX]^2} \qquad K_{ex,Fe(III)} = \frac{[FeX_3]\,[H^+]^3}{[Fe^{3+}]\,[HX]^3}$$

The K_{ex} values thus calculated refer only to concentration quotients, calculated on the assumption that the activity coefficients of the species involved do not change significantly under the present experimental conditions.

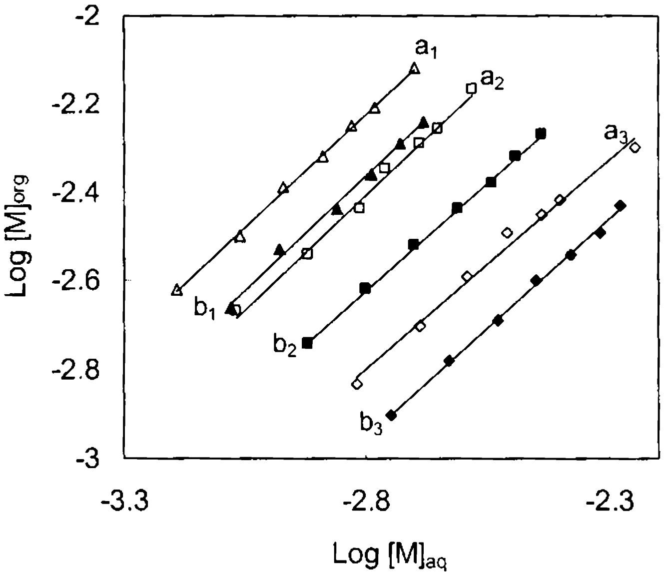


Figure 2.10. Effect of metal ion concentration on the extraction of vanadium(V) and iron(III) from 0.2 mol dm^{-3} hydrochloric acid solutions. HX = 5 × 10^{-2} mol dm^{-3} for vanadium(V) and 0.1 mol dm^{-3} for iron(III). a_1 = Hpmfbp, a_2 = Hpmbp, a_3 = Hpmtp for V(V); b_1 = Hpmfbp, b_2 = Hpmbp, b_3 = Hpmtp for Fe(III).

In the present experiments, the concentration of vanadium(V) (0.005 mol dm^{-3}) and iron(III) (0.005 mol dm^{-3}) in the aqueous phase is lower as compared to the concentration of 4-aroyl-5-pyrazolone in the organic phase (0.05 - 0.1 mol dm^{-3}) and H^+ (0.2 - 1.5 mol dm^{-3}) and Cl^- (0.2 - 1.5 mol dm^{-3}) in the aqueous phase. Hence the activities of all the species present in the aqueous and organic phases have been considered as equal to their equilibrium concentrations. Similar extracted complexes have been reported in the extraction of iron(III) and vanadium(V) from hydrochloric acid solutions by employing 1-phenyl-3-methyl-

4-butyryl-5-pyrazolone in mixed solvent media [Uzokwu and Etesim 1995]. But the extraction efficiency of vanadium(V) with 4-aroyl-5-pyrazolone was found to be higher in hydrochloric acid solutions Than that reported for 1-phenyl-3-methyl-4-butyryl-5-pyrazolone. On the other hand, the extraction of iron(III) was found to be significantly lower for 4-aroyl-5-pyrazolones as compared to 1-phenyl-3-methyl-4-butyryl-5-pyrazolone [Uzokwu and Etesim 1995].

The log $K_{ex,V(V)}$ of vanadium(V) and log $K_{ex,Fe(III)}$ of iron(III) with various 4-aroyl-5-pyrazolones follows the order Hpmfbp > Hpmbp > Hpmtp. In order to evaluate the influence of the acidity of the various para-substituted pyrazolones on the extraction efficiency of these metal ions, the correlation between log K_{ex} and pK_a value was investigated. The pK_a values of these pyrazolones were obtained from the literature [Meera and Reddy 2004; Umetani and Matsui 1983]. Figure 2.11 shows a linear correlation between log K_{ex} and pK_a for both vanadium(V) and iron(III) and this indicating that there is no obvious steric hindrance due to the para-substituents in the chelate formation reaction.

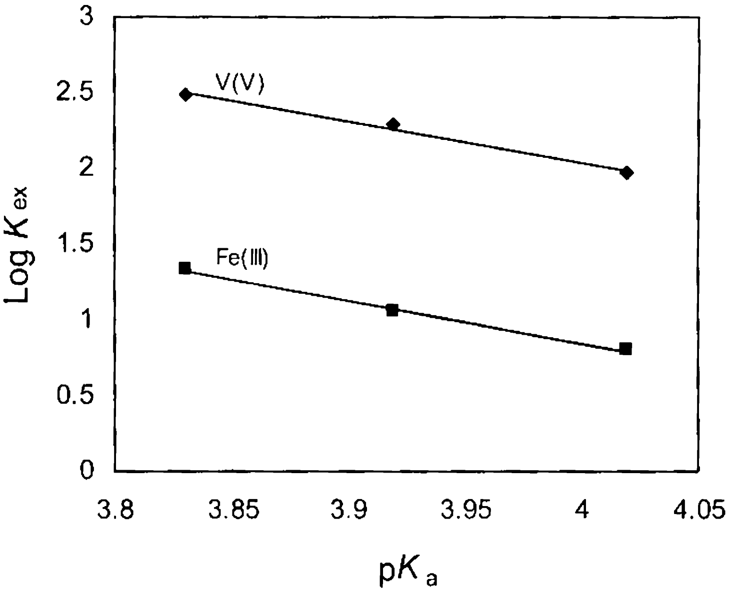


Figure 2.11. Log K_{ex} vs pK_a for the extraction of vanadium(V) and iron(III) with various para-substituted 4-aroyl-5-pyrazolones.

It is evident from the present results that the extraction efficiency of these metal ions with various para-substituted 4-aroyl-5-pyrazolones varies in accordance with their pK_a values (Table 2.4). Further, it is also clear from the study that the log K_{ex} values for both vanadium(V) and iron(III) with various para-substituted 4-aroyl-5-pyrazolones vary in accordance with the nature of the substituent, electron-withdrawing (-F) or electron-donating ($-CH_3$) group, on the benzoyl moiety of the pyrazolone.

Table 2.4. Log equilibrium constants for the extraction of vandium(V) and iron(III) with various 1-phenyl-3-methyl-4-aroyl-5-pyrazolones.

Extractant	pK_a	Log $K_{ex,0}$	
		V(V)	Fe(III)
Hpmfbp	3.83	2.48 ± 0.03	1.33 ± 0.03
Hpmbp	3.92	2.27 ± 0.04	1.04 ± 0.04
Hpmtp	4.02	1.97 ± 0.04	0.76 ± 0.04

UV Absorption Spectra of the Extracted Complexes

The electronic spectra (Figure 2.12) of Hpmfbp in chloroform showed two absorption maxima at 290 nm and 255 nm. The absorption peak at 290 nm corresponds to the n-π* transition of the carbonyl of the ligand and that at 255 nm correspond to the π-π* absorption of the phenyl ring [Zhou et al. 1997]. The UV absorption spectra of vanadium loaded Hpmfbp showed a red shift to 305 nm and 260 nm, indicating the involvement of the carbonyl group in bond formation. While in the iron loaded Hpmfbp, these absorptions undergo a blue shift and can be due to the back donation, possible by the presence of d-electrons to the ligand [Huhey et al. 1999].

FT-IR Spectra of the Extracted Complexes

The Hpmfbp dissolved in chloroform exhibits two types of strong C=O stretching vibrations in FT-IR spectrum (Table 2.5, Figure 2.13a). The peak around 1620 cm^{-1} is assigned to the stretching frequency of the carbonyl at the 5th position of the pyrazolone ring, and the one at 1590 cm^{-1} corresponds to the aroyl carbonyl in the 4th position of the pyrazolone ring [Zhou et al. 1997]. In the extracted complexes of vanadium(V) (Figure 2.13b) and iron(III) (Figure 2.13c), these carbonyl stretching frequencies have been shifted to lower wave numbers suggesting the involvement of carbonyl oxygens of Hpmfbp in bond formation with the metal ions. Further, in the IR spectrum of the vanadium(V) complex, a peak at 1620 cm^{-1} (b_1) which corresponds to the free C=O also has been noticed, which indicates the existence of one free carbonyl group in one of the Hpmfbp molecules. The new absorption bands occurring at 962 and 920 cm^{-1} in the vanadium complex corresponds to the O=V=O stretching frequencies [Mahroof-Tahir et al. 1997]. It can be concluded from this study that there is a strong interaction between the carbonyl group oxygen of Hpmfbp and vanadium(V) and iron(III), which is also evident from their respective equilibrium constants (Table 2.4).

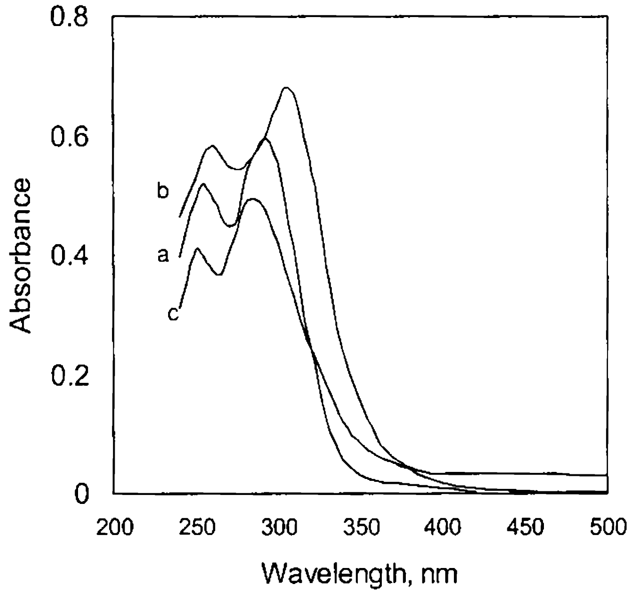


Figure 2.12. UV absorption spectra for Hpmfbp (a), $VO_2(pmfbp)\cdot Hpmfbp$ (b) and $Fe(pmfbp)_3$ (c).

Table 2.5. The major absorption peaks in the FT-IR spectra of Hpmfbp, VO_2(pmfbp)·Hpmfbp and Fe(pmfbp)$_3$.

Stretching frequencies in FT-IR spectra				
Complex	C = O cm^{-1}		M = O cm^{-1}	
Hpmfbp	1620 (a_1)	1590 (a_2)		
VO_2(pmfbp)·Hpmfbp	1598 (b_2)	1568 (b_3)	962 (b_4)	920 (b_5)
Fe(pmfbp)$_3$	1604 (c_1)	1562 (c_2)		

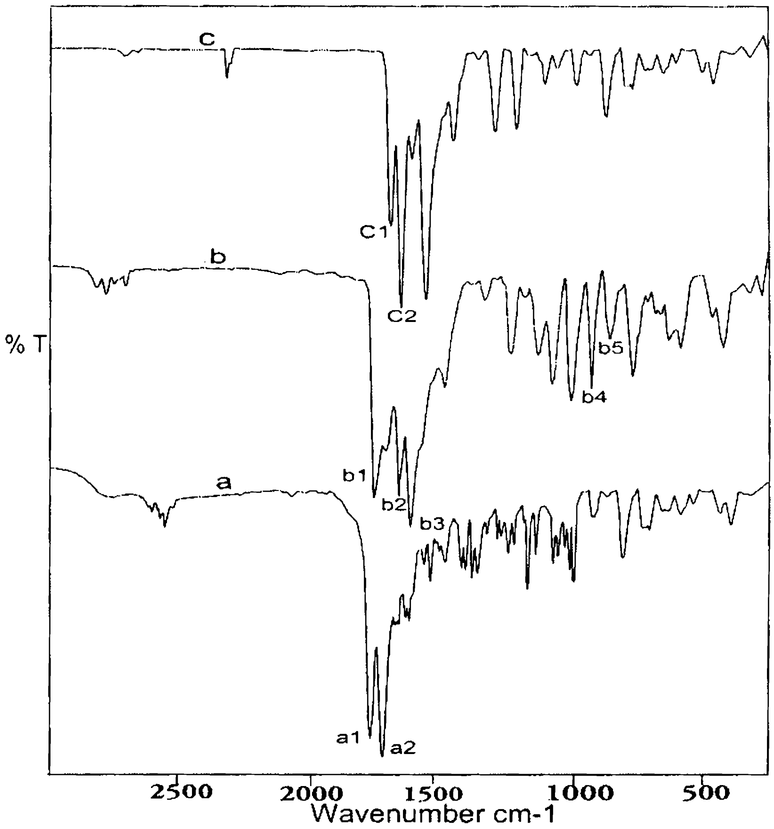


Figure 2.13. IR spectra for Hpmfbp (a); VO_2(pmfbp)·Hpmfbp (b) and Fe(pmfbp)$_3$ (c).

It is worth mentioning here that the vanadium(V) loaded chloroform phase gently reduces to vanadium(IV) in the presence of excess ligand (above ten fold to the metal) over a period of time (after 3 h), which has been ascertained by FT-IR study. After a period of 3 h, the FT-IR spectrum of the metal loaded solvent phase shows only one V=O stretching frequency (984 cm^{-1}) corresponding to oxovanadium(IV) complex. Further the color of the vanadium(V) loaded organic phase also gently changes from wine red to green.

Extraction and Separation of Vanadium(V) from Simulated Titania Waste Chloride Liquors using Hpmfbp

Based on the above results, a synthetic waste chloride liquor (half diluted concentration of actual waste chloride liquor, Table 1.1) in 2.0 mol dm^{-3} hydrochloric acid was prepared and subjected to two stages of batch extractions (Aq. : Org. = 1 : 1) using 0.2 mol dm^{-3} Hpmfbp in chloroform as the extractant. Vanadium was then quantitatively recovered from the organic phase using 3.5 mol dm^{-3} HCl as the stripping agent. The typical results are shown in Table 2.6. It is clear from the results that vanadium was selectively extracted into the organic phase leaving behind all the other associated metal ions in the raffinate. Thus, these results clearly highlight that vanadium can be selectively recovered from the waste chloride liquors of titanium minerals process industry using 1-phenyl-3-methyl-4-aroyl-5-pyrazolone in chloroform as the extractant.

Table 2.6. Extraction and separation of vanadium(V) from synthetic titania waste chloride liquor.

Metal ion	Feed mol dm^{-3}	Raffinate mol dm^{-3}	Strip liquor mol dm^{-3}
Mg(II)	0.08	0.08	N. D.
Al(III)	0.015	0.015	N. D.
Ti(IV)	0.01	0.01	N. D.
V(V)	0.01	N. D.	0.01
Cr(III)	0.015	0.015	N. D.
Mn(II)	0.03	0.03	N. D.
Fe(II)	0.20	0.20	N. D.
Fe(III)	0.15	0.15	N. D.

N. D. = Not detectable (< 1.0 × 10^{-5} mol dm^{-3})

Part II

Preparation and Characterization of Solid Complexes of Oxovanadium with Para-substituted 1-Phenyl-3-methyl-4-aroyl-5-pyrazolones

In order to understand the complexation behavior of oxovanadium(V) with 4-aroyl-5-pyrazolones, corresponding solid complexes have been prepared and characterized by various spectroscopic techniques. However, in the course of preparation of the oxovanadium(V) complexes with various 4-aroyl-5-pyrazolones, reduction of oxovanadium(V) to oxovanadium(IV) has been noticed in the presence of 4-aroyl-5-pyrazolones. The use of vanadium coordination complexes as therapeutic agents for diabetes underlines the importance of this element's redox chemistry under physiological conditions [Crans et al. 2004; Levina et al. 2000]. The first kinetic study of the reduction of oxovanadium(V) with ascorbic acid was reported in 1973 [Kustin and Toppen 1973]. Recently, the reduction of oxovanadium(V) by ascorbic acid in the pH range 0.4-7.0 has been investigated and reported both inner- and outer-sphere electron-transfer pathways for the formation of oxovanadium(IV) complexes with ascorbate or dehydroascorbate, respectively [Wilkins et al. 2006]. The stoichiometry and kinetics of oxovanadium(V) reduction by pinacol [Littler and Waters 1959a], cyclopentanone [Littler and Waters 1959b], and cyclohexanone [Littler and Waters 1959b] were also studied. In all cases indirect evidence to free-radical formation was observed and the one-electron reduction of oxovanadium(V) to oxovanadium(IV) was demonstrated. Wells and Kuritsyn, 1970 had suggested that the reduction of oxovanadium(V) by hydroquinone may proceed via inner-sphere mechanism, giving the products oxovanadium(IV) and p-benzoquinone. The significance of these reports arise when we consider the fact that oxovanadium(IV) compounds with O,O-donor ligands are very effective insulin-mimics [Thompson et al. 1999; Thompson and Orvig 2000]. Bis(2,4-pentanedionato-O,O′) oxovanadium(IV) [$(VO(acac)_2)$] was found to have insulin-mimetic properties superior to those of $VOSO_4$ in cell culture studies [Amin et al. 2000; Li et al. 1996].

Almost all vanadium ligands investigated for their reducing behavior are monofunctional or 1, 2 bifunctional. Interestingly 1, 3 functional reducing ligands for vanadium are reported rarely which will have implications in complexation. 4-Toropchina et al. 2003, has studied the electron transfer process in a series of pyrazolones and their thioanalogues both experimentally and theoretically. The reduction of oxovanadium(V) by 1-phenyl-3-methyl-4-aroyl-5-pyrazolone over the pH range of 1.0-7.0 has been assessed by cyclicvoltammetry, electron paramagnetic resonance spectroscopy, magnetic susceptibility, FT-IR, electronic spectroscopy, high-resolution mass spectroscopy and elemental analyses.

RESULTS AND DISCUSSION

Characterization of Solid Complexes of Oxovanadium with 1-Phenyl-3-methyl-4-aroyl-5-pyrazolone

$VO(pmtp)_2$ (pH 7): m.p.: 259.8 °C. FT-IR (KBr) data ν (cm^{-1}): 1566, 1519, 962, 752. Mass spectrum: (m + 1) peak 650.53, 291.43, 119.15 (Figure 2.14). Elemental analysis: Calc. for $C_{36}H_{30}N_4O_5V$: C 66.56, H 4.65, N 8.62%. Found: C 66.45, H 4.75, N 8.71%.

$VO(pmtp)_2$ (pH 1): m.p.: 260.1 °C. FT-IR (KBr) data ν (cm^{-1}): 1566, 1519, 962, 752. Mass spectrum: (m + 1) peak 650.42, 291.31, 119.15 (Figure 2.15). Elemental analysis: Calc. for $C_{36}H_{30}N_4O_5V$: C 66.56, H 4.65, N 8.62%. Found: C 66.05, H 4.75, N 8.71%

$VO(pmbp)_2$ (pH 7): m.p.: 256.4 °C. FT-IR (KBr) data ν (cm^{-1}): 1576, 1519, 982, 752. Mass spectrum: (m + 1) peak 621.6, 296.21, 154.0 (Figure 2.16). Elemental analysis: Calc. for $C_{34}H_{26}N_4O_5V$: C 65.70, H 4.22, N 9.06%. Found: C 65.45, H 4.15, N 9.41%.

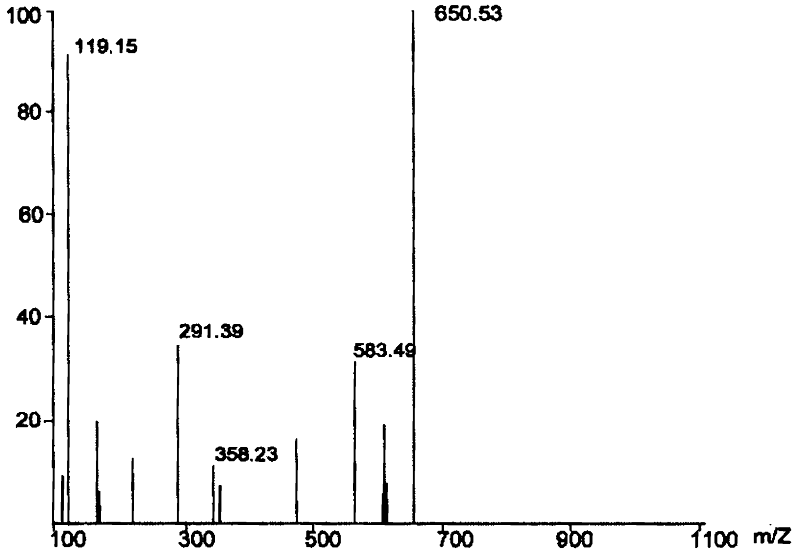


Figure 2.14. Mass spectrum of VO(pmtp)$_2$ prepared at pH 7.

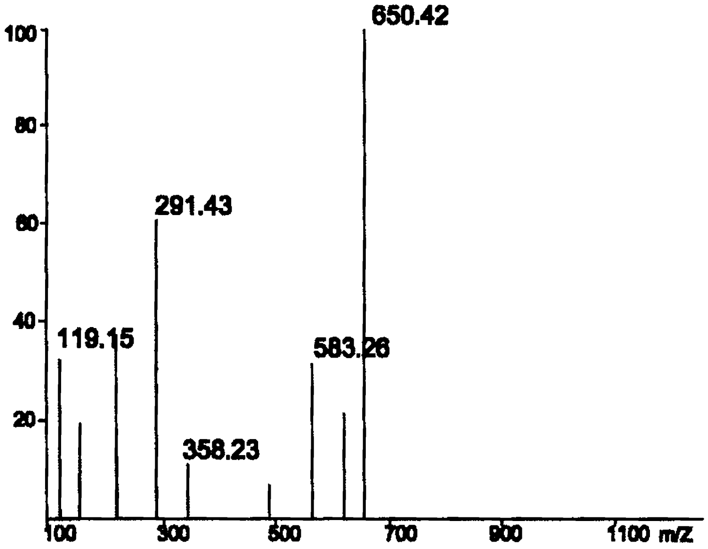


Figure 2.15. Mass spectrum VO(pmtp)$_2$ prepared at pH 1.

VO(pmbp)$_2$ (pH 1): m.p.: 255.8 °C. FT-IR (KBr) data ν (cm^{-1}): 1566, 1519, 982, 752. Mass spectrum: (m + 1) peak 621.18, 296.72, 154.37 (Figure 2.17). Elemental analysis: Calc. for $C_{34}H_{26}N_4O_5V$: C 65.70, H 4.22, N 9.06%. Found: C 65.75, H 4.55, N 9.22%.

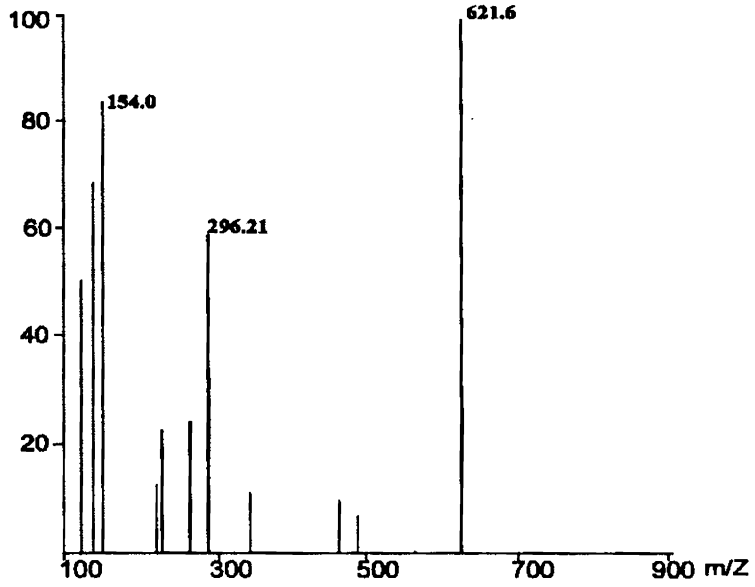


Figure 2.16. Mass spectrum of VO(pmbp)$_2$ prepared at pH 7.

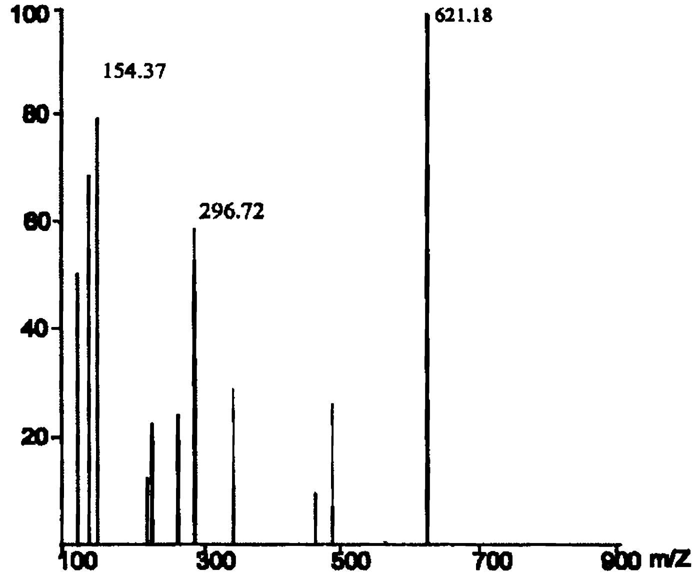


Figure 2.17. Mass spectrum of VO(pmbp)$_2$ prepared at pH 1.

VO(pmfbp)$_2$ (pH 7): m.p.: 257.2 °C. FT-IR (KBr) data ν (cm^{-1}): 1566, 1519, 996, 752. Mass spectrum: (m + 1) peak 658.03, 297.17, 122.63 (Figure 2.18). Elemental analysis: Calc. for $C_{34}H_{24}N_4O_5F_2V$: C 62.11, H 3.68, N 8.52%. Found: C 62.45, H 3.75, N 8.71%.

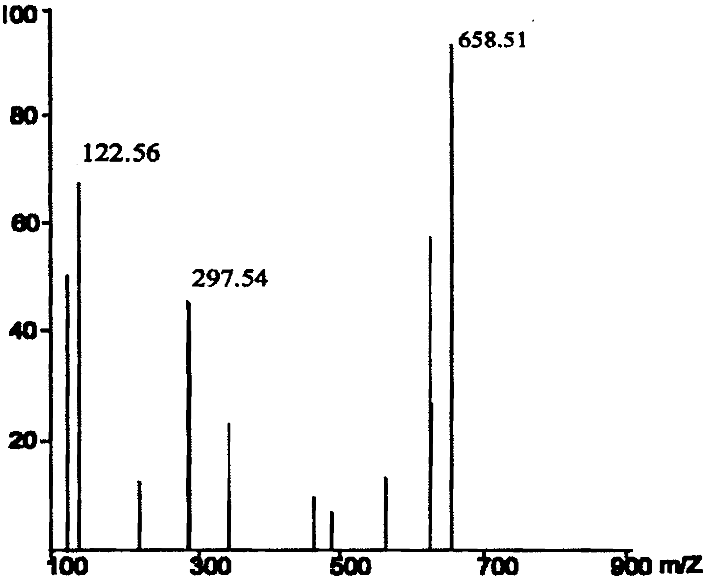


Figure 2.18. Mass spectrum of VO(pmfbp)$_2$ prepared at pH 7.

VO(pmfbp)$_2$ (pH 1): m.p.: 257.2 °C. FT-IR (KBr) data ν (cm^{-1}): 1566, 1519, 996, 752. Mass spectrum: (m + 1) peak 658.51, 297.54, 122.56 (Figure 2.19). Elemental analysis: Calc. for $C_{34}H_{24}N_4O_5F_2V$: C 62.11, H 3.68, N 8.52%. Found: C 62.42, H 3.25, N 8.11%.

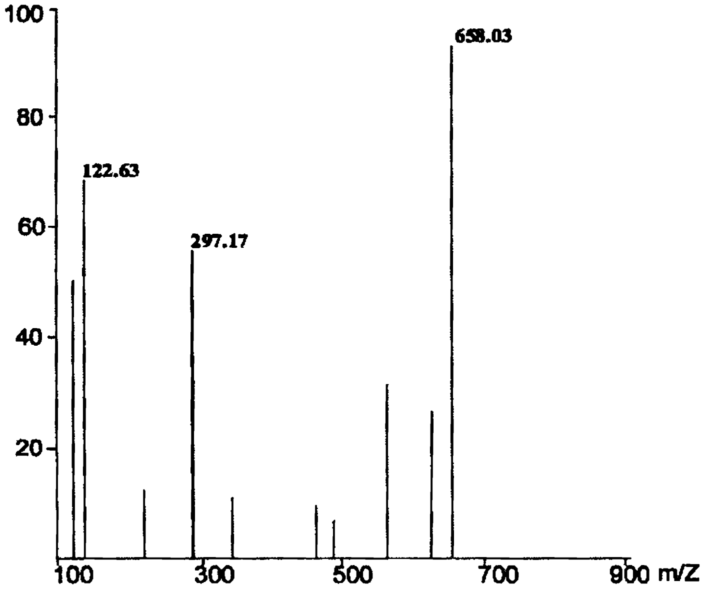


Figure 2.19. Mass spectrum of VO(pmfbp)$_2$ prepared at pH 1.

Electrochemistry of 4-Aroyl-5-pyrazolones

In order to understand the redox chemistry of various substituted 4-aroyl-5-pyrazolones in the presence and absence of oxovanadium(V), cyclicvoltametric studies have been conducted in the range 2.0 to -2.0 V. The voltammogram of the Hpmtp in acetonitrile solution (25 mM) has an irreversible oxidation peak around 1.37 V (Figure 2.20), which indicates the formation of a stable oxidized species of Hpmtp. Existence of a similar stable oxidized species of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone has been well documented elsewhere [Toropchina et al. 2003]. As can be seen from the voltammogram of Hpmtp in acetonitrile solution in the presence of 25 mM of oxovanadium(V), the peak current corresponding to the oxidation of the ligand decreases and a new peak corresponding to the oxidation of oxovanadium(IV) to oxovanadium(V) appears at ~ 0.57 V. Since the reduction of oxovanadium(V) to oxovanadium(IV) occurs at a potential (~1 V) [Huhey et al. 1999] lower than the oxidation potential of the ligands, the transfer of one electron is possible from the ligand to oxovanadium(V). Derivatives with electron-acceptor benzoyl substituents in the 4th position of heterocyclic system undergo oxidation at potentials that are less positive than that for the unsubstituted one [Toropchina et al. 2003]. In Hpmfbp, bearing an electron-withdrawing substituent (-F) in the 4th position of the benzoyl moiety undergoes oxidation at a potential less than that of Hpmbp (Table 2.7). On the other hand, presence of the electron-donating group (-CH_3) in Hpmbp, results in oxidation occuring at a potential higher than that of Hpmbp. Thus it can be concluded from this study that the nature of the substituent on the benzoyl moiety in the 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone causes variations in the oxidation potentials. The energies of the highest occupied molecular orbitals (HOMO) ε_{HOMO}, of these ligands were calculated from molecular modeling, which also suggests the order as Hpmtp > Hpmbp > Hpmfbp (Table 2.7) as observed for oxidation potentials.

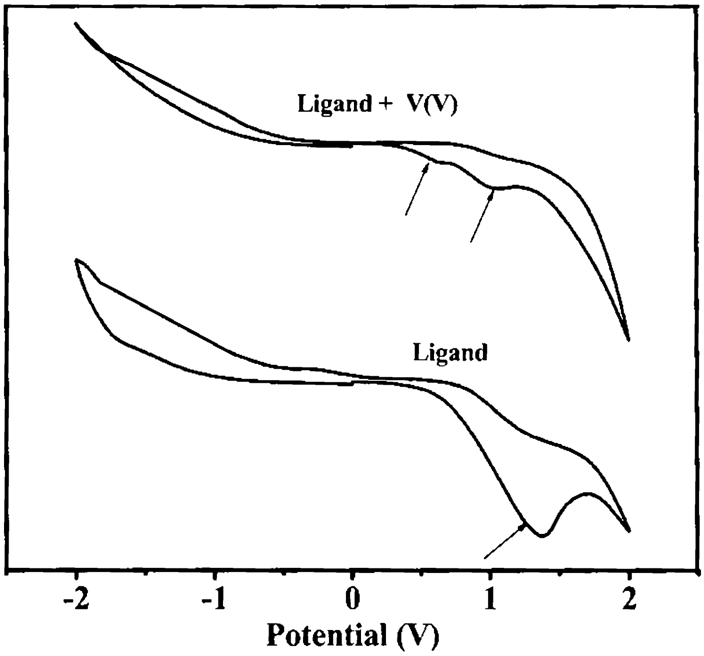


Figure 2.20. Cyclicvoltammograms recorded in acetonitrile a: Hpmtp; b: Hpmtp in presence of oxovanadium(V); scan rate 50 mV s^{-1}. SCE was used as the reference electrode.

Table 2.7. Oxidation potentials of 1-phenyl-3-methyl-4-aroyl-5-pyrazolones (E_p^{ox} eV) and energies ε_{HOMO} as obtained by molecular modeling calculations.

Ligand	E_p^{ox} eV	ε_{HOMO} eV
Hpmtp	1.37	9.046
Hpmbp	1.29	9.068
Hpmfbp	1.22	9.149

Formation of Free-radical Intermediates of 4-Aroyl-5-pyrazolones

It is clear from the cyclic voltammetric studies that 4-aroyl-5-pyrazolones transfer one electron to oxovanadium(V) and form free radical intermediates. A typical example (Hpmtp) is shown in Scheme 2.2. An indirect evidence for the formation of a free radical intermediate has been obtained by observing the polymerization of acrylonitrile in the presence of oxovanadium(V) and 1-phenyl-

3-methyl-4-aroyl-5-pyrazolone. In the absence of either 1-phenyl-3-methyl-4-aroyl-5-pyrazolone or oxovanadium(V), no polymerization was detected. This clearly suggests the formation of a free radical intermediate, which initiates the polymerization of acrylonitrile. Thus from the present study, it can be concluded that the reaction proceeds *via* a free-radical mechanism wherein oxovanadium(V) undergoes a one-electron reduction as in accordance with the cyclic voltammetric studies. The free-radical thus generated finally couples with another free radical and forms a stable dimer. The dimeric species of the ligands have been isolated from the filtrate of the complexing medium and characterized by IR, ^{1}H NMR (Figures 2.21 - 2.23) and ^{13}C NMR spectra (Figures 2.24 - 2.26). In the ^{1}H NMR spectrum of the dimer, the δ values showed considerable shift from that of 1-phenyl-3-methyl-4-aroyl-5-pyrazolones, which indicates the formation of new species. The IR spectrum of the dimers showed two strong absorptions in the region 1668-1610 cm^{-1} and also shows the presence of two C=O groups. Upon dimerization, the sp^2 hybridized (δ 110-140 ppm) carbon in the pyrazole ring (C$_4$) becomes a sp^3 hybridized one (δ 0-80 ppm), which can be clearly seen from the ^{13}C NMR spectra of dimers of various 1-phenyl-3-methyl-4-aroyl-5-pyrazolones isolated.

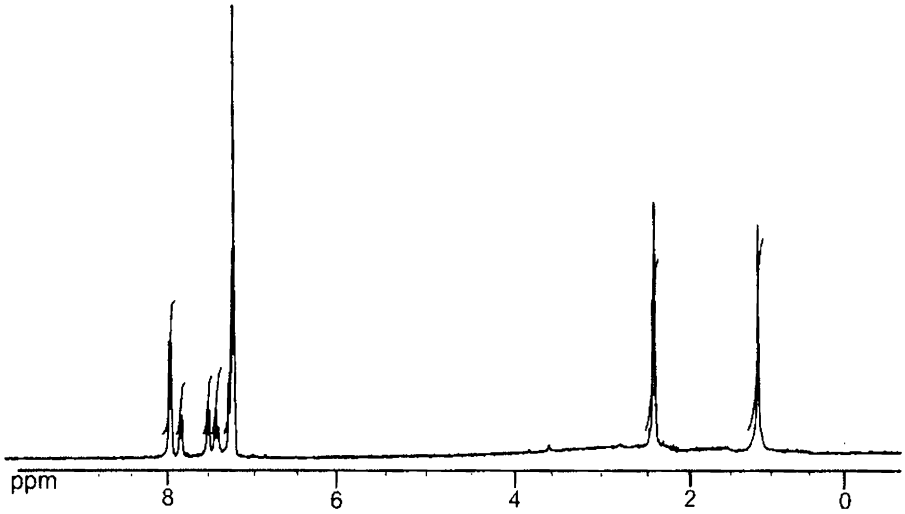


Figure 2.21. ^{1}H NMR spectrum of the dimer of 1-phenyl-3-methyl-4-toluoyl-5-pyrazolone.

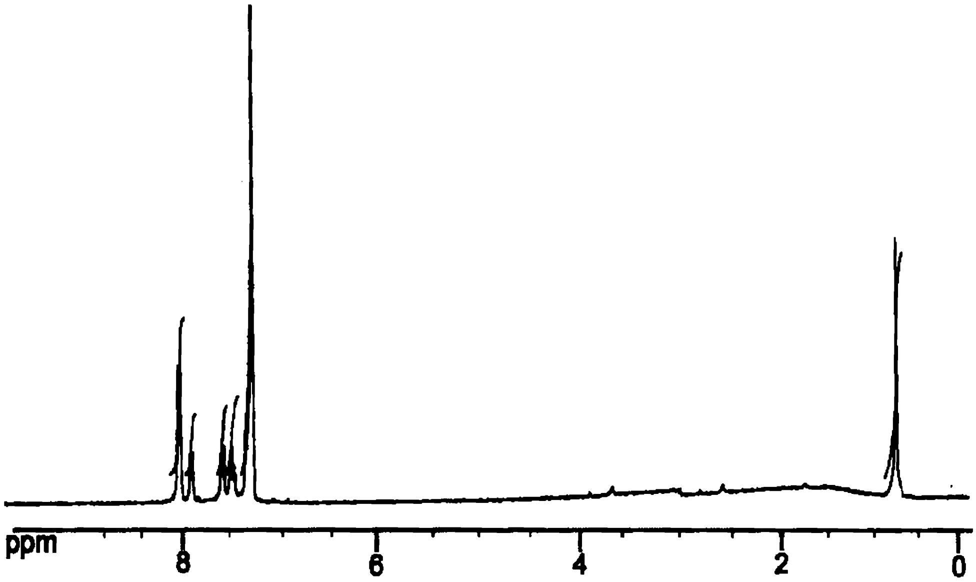


Figure 2.22. ^{1}H NMR spectrum of the dimer of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone.

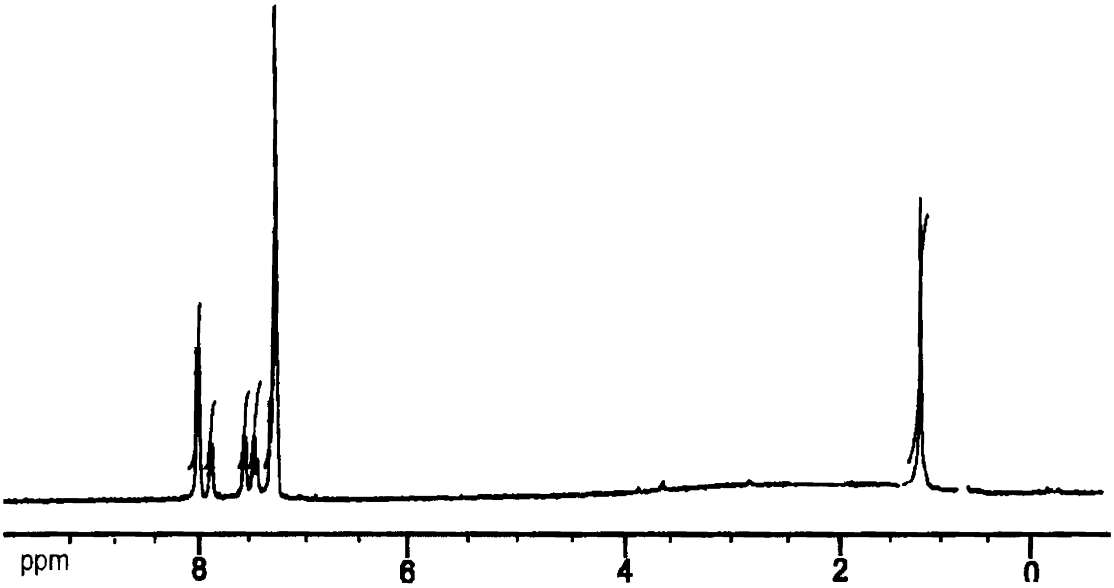


Figure 2.23. ^{1}H NMR spectrum of the dimer of 1-phenyl-3-methyl-4-fluorobenzoyl-5-pyrazolone.

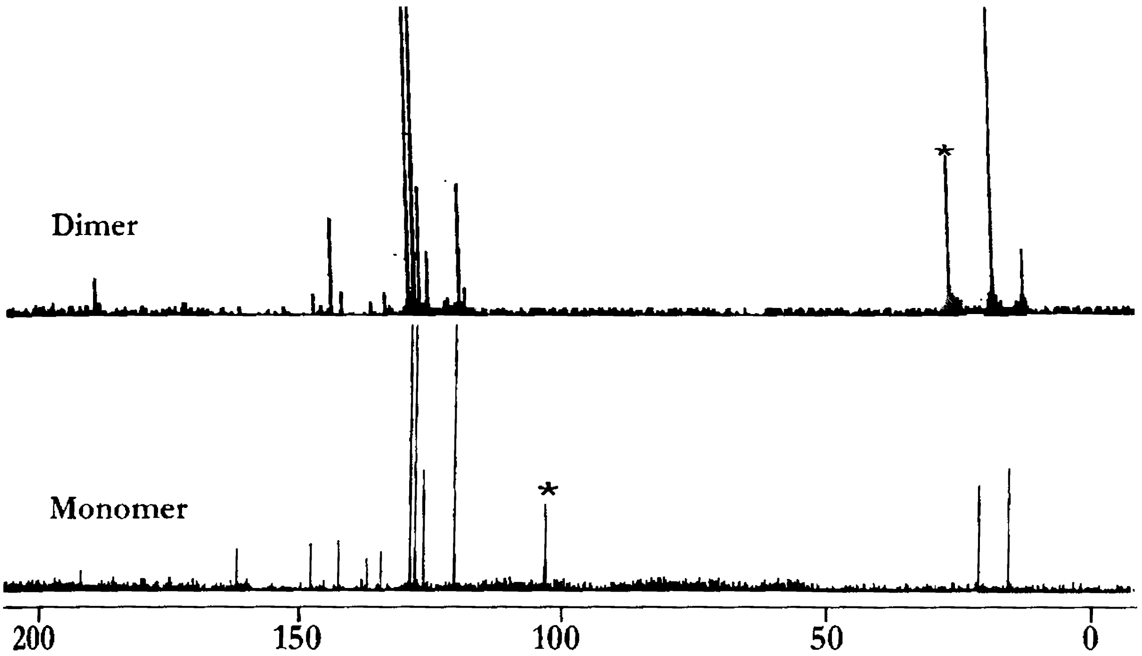


Figure 2.24. ^{13}C NMR spectrum of 1-phenyl-3-methyl-4-toluoyl-5-pyrazolone and its dimer.

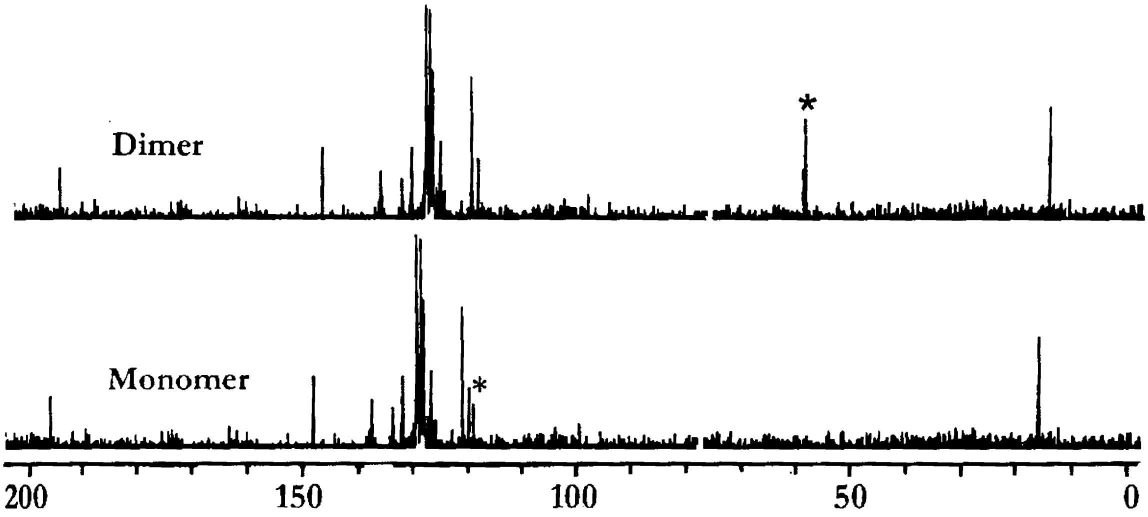


Figure 2.25. ^{13}C NMR spectrum of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and its dimer.

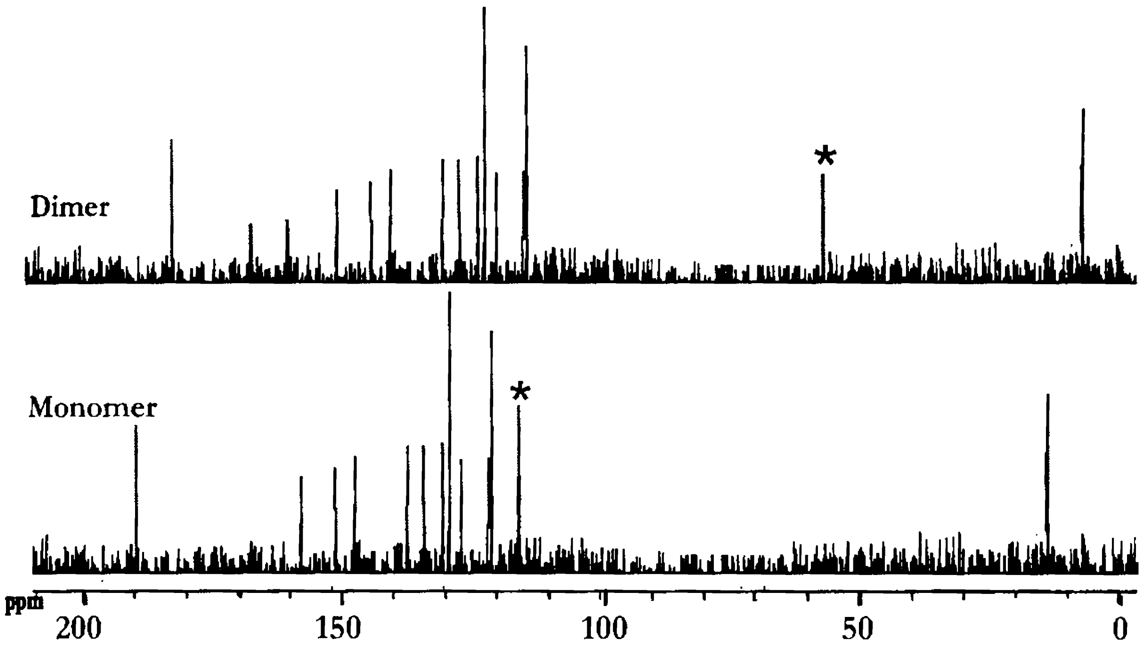


Figure 2.26. ^{13}C NMR spectrum of 1-phenyl-3-methyl-4-(4-flourobenzoyl)-5-pyrazolone and its dimer.

Stoichiometry

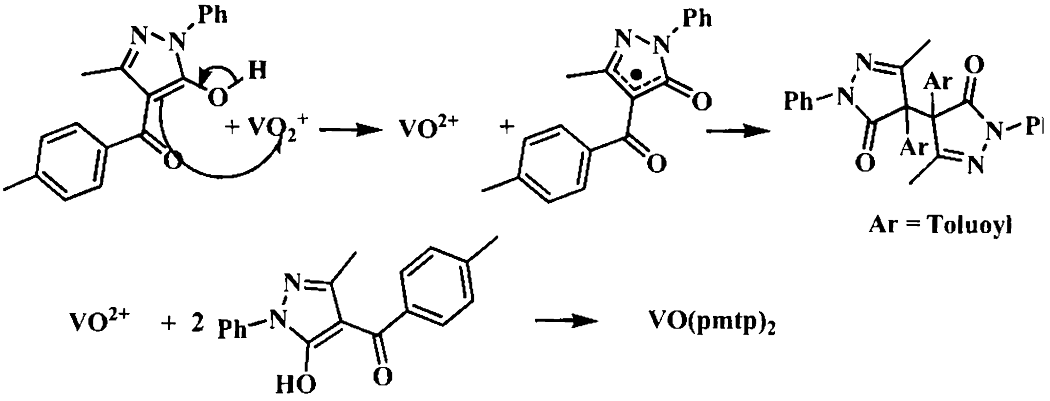
1-Phenyl-3-methyl-4-aroyl-5-pyrazolone reduces aqueous oxovanadium(V) in both acidic and neutral media according to the following equation:

$$2VO_2^+ + 6HL \longrightarrow 2VOL_2 + \text{Dimer} + 2H_2O + 2H^+$$

The 1:3 stoichiometry of metal to ligand was confirmed at pH 1 and 7 by analyzing both the filtrate of the complexing media and the resultant complex formed.

Mechanism of Reduction of Oxovanadium(V) to Oxovanadium(IV) and Subsequent Complexation by 1-Phenyl-3-methyl-4-aroyl-5-pyrazolone

Based on the above studies the detailed scheme for the reduction of oxovanadium(V) to oxovanadium(IV) and subsequent complexation can be expressed as:



Scheme 2.2. Reduction and complexation of oxovanadium(V) with 1-phenyl-3-methyl-4-toluoyl-5-pyrazolone

Spectroscopic Characterization of Oxovanadium(IV) Complexes

The elemental analyses and mass spectral studies of the complexes prepared at both acidic and neutral pH conditions show a metal-to-ligand ratio of 1:2. Further, these values correspond to oxovanadium(IV) species rather than oxovanadium(V) species.

Fourier-Transform Infrared Spectroscopy

In the FT-IR spectra of VO(pmtp)$_2$, VO(pmbp)$_2$ and VO(pmfbp)$_2$ there are strong absorption bands at 1570-1515 cm^{-1} assigned to the stretching ν(C=O), ν(C=C) and ν(C=N) modes of the acylpyrazolone ring coordinated to the metal centre. Further, the ν(V=O) stretch is observed at 960 cm^{-1}, 984 cm^{-1} and 996 cm^{-1} in VO(pmtp)$_2$, VO(pmbp)$_2$ and VO(pmfbp)$_2$, respectively. Usually, the ν(V=O) of most vanadium(IV) complexes are observed in the region 930-1010 cm^{-1} [Maurya 2003; Cornman et al. 1997]. It is reported that the v(V=O) absorption band is sensitive to the substituents on the ligand and donors that increase the electron density on the metal, thereby reducing its acceptor properties towards oxygen, lower the V=O multiple bond character and stretching frequency [Vigee and

Selbin 1968; Popp et al. 1969]. The absence of broad absorption in the region 3000 – 3500 cm^{-1} is absent suggesting that there is no coordinated H_2O in the complex, which is consistent with the thermo-gravimetric analysis of the complexes where no weight loss was observed in the range 50 – 350 °C.

Magnetic and EPR Measurements

The room-temperature magnetic susceptibility data for the complexes show essentially paramagnetic behavior attributed to the d^1 system. The effective magnetic moments obtained for the prepared complexes (1.69 – 1.71 B.M) were in the normal range (1.57 - 2.1 B.M) [Pessoa et al. 1992; Selbin 1965] typical of an oxovanadium(IV) complex (Table 2.8).

The X-band EPR spectra of the vanadium complexes, $VO(pmtp)_2$, $VO(pmbp)_2$ and $VO(pmfbp)_2$, prepared at various conditions exhibit a set of eight line hyperfine spectra arising from the interaction of the unpaired electron of vanadium(IV) with the nuclear spin (7/2) (Figures 2.27-2.29). Further, the eight lines in the spectra of the complexes are also an indication of their monomeric structure [Selbin 1965]. The symmetry reduction due to geometry distortion produces significant changes in EPR spectrum. For square pyramidal complexes with C_{4v} symmetry, the V=O bond is along the Z axis and the four donor atoms are along the X and Y axes, an anisotropic EPR spectrum is expected, exhibiting two g ($g_z = g_{\parallel} < g_{\perp} = g_x = g_y$) and two A ($A_z = A_{\parallel} > A_{\perp} = A_x = A_y$) values. A distortion from square pyramidal geometry can give rise to three g and three A values. It is clear from the EPR parameters of the complexes listed in Table 2.9 that all the complexes have a slightly distorted square pyramidal geometry. The g-values lie in the 1.9-1.99 range and agree with the fact that when d-shell is less than half filled, the spin-orbit effect reduces g value from that of a free electron (2.0023) [Klich et al. 1996; Pessoa et al. 1992]. The order and magnitude of resonance parameters are typical of the spectra displayed by a slightly distorted square pyramidal oxovanadium(IV) complex with the unpaired electron in an orbital of mostly d_{xy} character. It can be concluded from the EPR spectral data that all the complexes are typical mononuclear vanadium(IV) species, which in turn confirms that 1-phenyl-3-methyl-4-aroyl-5-pyrazolone interacts with aqueous vanadium(V) over the pH range of 1.0 - 7.0 and form oxovanadium(IV) complexes.

Table 2.8. Magnetic moments of oxovanadium(IV) complexes of 1-phenyl-3-methyl-4-aroyl-5-pyrazolone.

Complex	Magnetic moment B.M
$VO(pmtp)_2$ (pH 7)	1.783
$VO(pmtp)_2$ (pH 1)	1.786
$VO(pmbp)_2$ (pH 7)	1.815
$VO(pmbp)_2$ (pH 1)	1.811
$VO(pmfbp)_2$ (pH 7)	1.864
$VO(pmfbp)_2$ (pH 1)	1.866

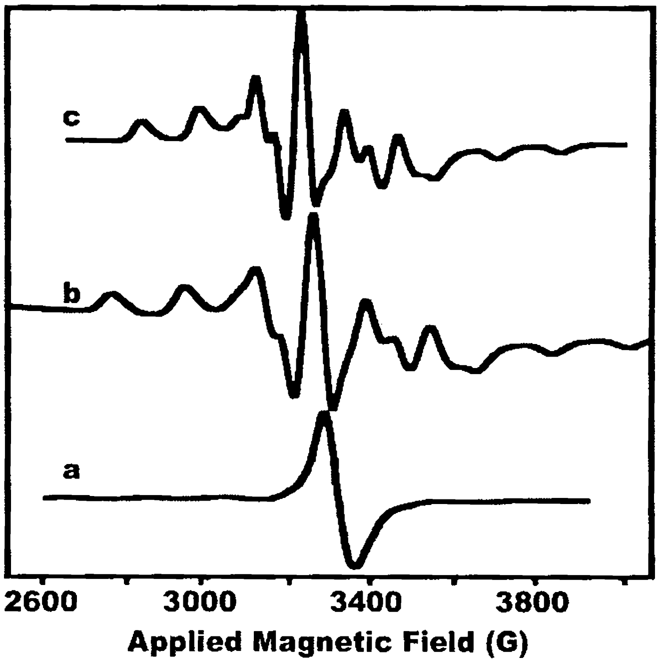


Figure 2.27. ESR spectra of $VO(pmtp)_2$. a. At room-temperature; b. Solid state at 77 K; c. Dissolved in acetonitrile at 77 K.

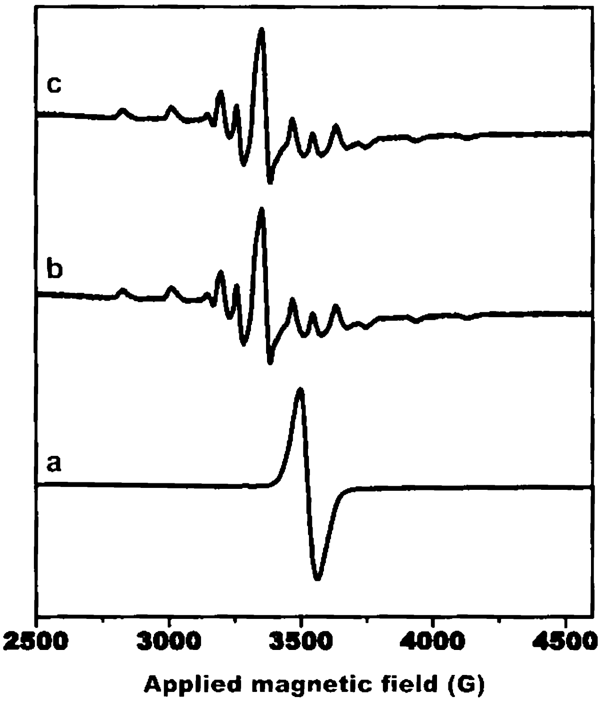


Figure 2.28. ESR spectra of VO(pmbp)$_2$. a. At room-temperature; b. Solid state at 77 K; c. Dissolved in acetonitrile at 77 K.

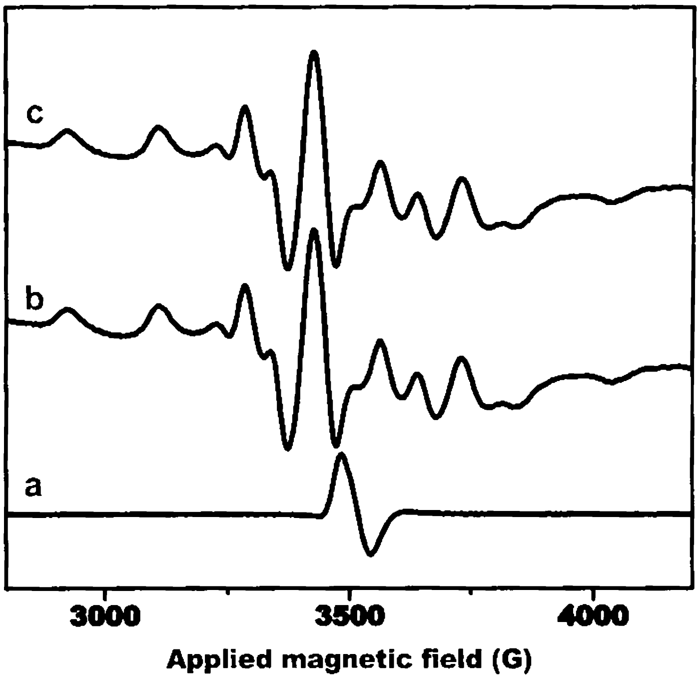


Figure 2.29. ESR spectra of VO(pmfbp)$_2$. a. At room-temperature; b. Solid state at 77 K; c. Dissolved in acetonitrile at 77 K.

Table 2.9. ESR parameters of oxovanadium(IV) complexes of 1-phenyl-3-methyl-4-aroyl-5-pyrazolones.

Complexes	T	g_x	g_y	g_z	A_x	A_y	A_z
	RT (S)	1.936			109.28		
$VO(pmtp)_2$	77 K (S)	1.949	1.938	1.904	67.14	74.28	192.86
	77 K (L)	1.949	1.932	1.907	67.78	74.28	192.14
	RT (S)	1.959			113.44		
$VO(pmbp)_2$	77 K (S)	1.977	1.970	1.929	62.18	77.87	195.34
	77 K (L)	1.974	1.969	1.923	62.15	77.86	195.34
	RT (S)	1.962			116.54		
$VO(pmfbp)_2$	77 K (S)	1.981	1.976	1.935	52.48	81.95	198.34
	77 K (L)	1.981	1.972	1.937	52.58	81.95	198.74

RT – Room temperature S – Solid L – Dissolved in acetonitrile

Electronic Absorption Spectra

In the electronic spectra of 1-phenyl-3-methyl-4-aroyl-5-pyrazolone in acetonitrile solution, the n-π* transition of the carbonyl group and the π-π* transitions of the phenyl group were observed and both transitions had ε values of the order 10^5 mol^{-1} cm^{-1}. In the complexes these absorption bands are red shifted indicating the involvement of the carbonyl group in complex formation with the metal ion (Table 2.10).

The UV-vis spectra of the complexes have overlapping peaks in the 400-800 cm^{-1} region. Hence curve fitting of the spectrum was carried out using Peak fit 4.12 software. In the curve fitting procedure, the peaks were assumed to be a number of Gaussian peaks, but no physical significance was attached to these peaks apart from the fact that their presence results in satisfactory curve fitting. The deconvoluted spectrum of $VO(pmtp)_2$ (Figure 2.30), $VO(pmbp)_2$ and

$VO(pmfbp)_2$ prepared at acidic conditions has four transitions in the visible region. The observed absorption peaks correspond to the transitions from the d_{xy} orbital to d_{xz}, d_{yz}, $d_{x^2-y^2}$ and d_{z^2} in accordance with the reports on the transitions of oxovanadium(IV) complexes having distorted square pyramidal geometry. The d-d absorption spectra of square pyramidal oxovanadium(IV) complexes (Table 2.11) are generally interpreted by the scheme proposed by Ballhausen and Gray [Ballhausen and Gray 1992]. The V=O bond defines the Z axis and X and Y axes are in the equatorial plane. The energy levels predicted for 3d orbitals in this scheme follows the order: d_{xy} (b_2) < d_{xz}, d_{yz} (e) < $d_{x^2-y^2}$ (b_1) < d_{z^2} (a_1). The three transitions, $b_2 \rightarrow e$, $b_2 \rightarrow b_1$ and $b_2 \rightarrow a_1$, are typical of a square pyramidal complex. A distortion from square pyramidal geometry removes the degeneracy between d_{xz} and d_{yz}. The 'e' level will then be split into $b_1(d_{xy})$ and $b_2(d_{yz})$ and accordingly four transitions will be observed in the case of a complex with distorted square pyramidal geometry [Maurya 2003; Cornman et al. 1997]. These type of d-d transitions are reported elsewhere [Fukuda et al. 1996; Klich et al. 1996]. It can be concluded from the above spectral data that, the oxovanadium(IV) ion with two coordinating ligands will be present in a slightly distorted square pyramidal geometry.

Table 2.10. Electronic absorptions of 1-phenyl-3-methyl-4-aroyl-5-pyrazolones and their oxovanadium(IV) complexes.

Ligand/Complex	n-π* nm	π-π* nm
Hpmtp	285	245
$VO(pmtp)_2$	305	250
Hpmbp	292	257
$VO(pmbp)_2$	308	263
Hpmfbp	305	276
$VO(pmfp)_2$	315	282

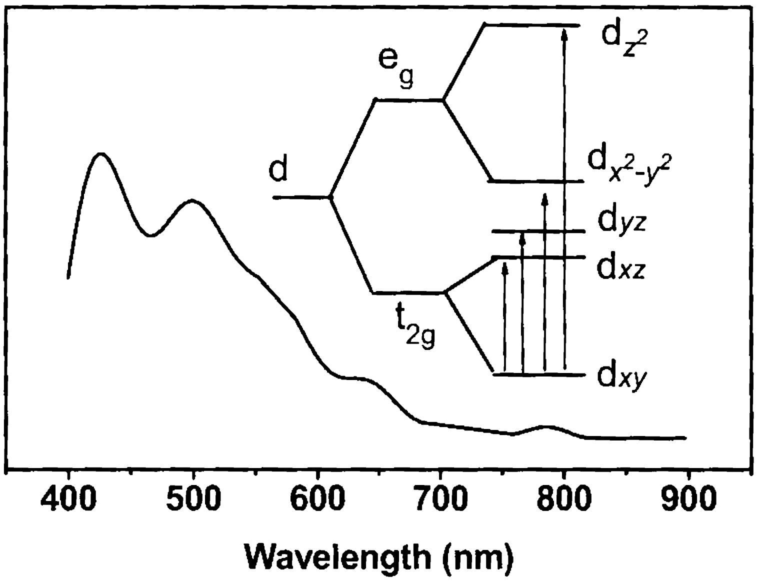


Figure 2.30. Deconvoluted UV spectrum of VO(pmtp)$_2$.

Table 2.11. d-d transitions in the oxovanadium(IV) complexes of various 1-phenyl-3-methyl-4-aroyl-5-pyrazolones.

Complex	d_{xy} - d_{xz} nm	d_{xy} - d_{yz} nm	d_{xy} - $d_{x^2-y^2}$ nm	d_{xy} - d_{z^2} nm
VO(pmtp)$_2$	794	643	501	424
VO(pmbp)$_2$	805	657	511	433
VO(pmfbp)$_2$	820	669	521	442

Optimized Geometry of Distorted Square Pyramidal Oxovanadium(IV) Complex

The presence of the labile hydrogen atom in Hpmtp ligand is the main reason for its versatile coordination property towards metal centers. The removal of this hydrogen atom as proton would lead to the formation of the highly electron rich anion pmtp (Figure 2.31). The toluoyl carbonyl group of pmtp$^-$ showed a twist angle of 21.7^o with respect to the pyrazolone ring, meaning that the two carbonyl groups are nearly in the same plane and pointing toward at the same direction. Further, the carbonyl oxygen atoms are separated by a distance of 3.071Å.

The electron distribution in the pmtp$^-$ anion is examined in terms of the molecular electrostatic potential (MESP) calculated at the B3LYP/6-31G* level [Politizer and Truhlar 1981; Gadre and Shirsat 2000; Suresh and Gadre 1998; Suresh and Gadre 1999; Suresh and Koga 2002]. The MESP analysis as summarized in Figure 2.32 suggests that the carbonyl oxygen atoms are the most electron rich centers of the anionic ligand. Between the two oxygen atoms, the pyrazolone oxygen showed a slightly higher negative MESP value (-157.6 kcal mol^{-1}) than the toluoyl oxygen (-156.1 kcal mol^{-1}). Thus we can see that the structural and electronic feature of pmtp at the OC-C-CO region is fit for a bidentate binding mode of this ligand with metal centers.

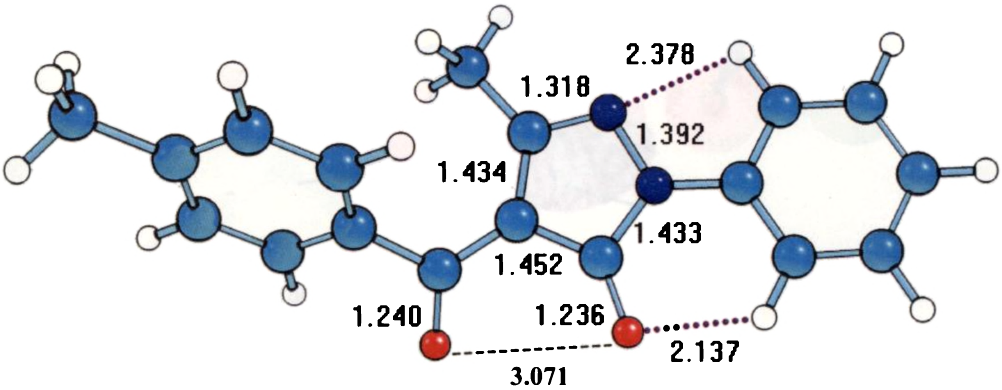


Figure 2.31. The optimized geometry of pmtp$^-$ at B3LYP/6-31G* level. All bond lengths in Å.

A square pyramidal geometry containing two ligand moieties is considered as the most probable oxovanadium(IV) complex. The optimized geometries of the oxovanadium(IV) complexes at the B3LYP/6-31G* level of DFT are depicted in Figures 2.33-2.35. It can be seen from Figure 2.34 that the four oxygen atoms from the two ligands are at the base and a VO double bond of length 1.584 Å is pointing towards the apex of the pyramid. Two different V-O single bonds can be seen, a short one of length 1.963 Å with pyrazolone oxygen and a long one of 1.994 Å with the toluoyl oxygen. The high coordination power of the pyrazolone oxygen is reflected in its short V-O bond, in accordance with the highest negative MESP of -157.6 kcal/mol observed for this oxygen in the pmtp$^-$ system. The molecular orbital and the spin density analysis of the complex showed that the unpaired electron of the vanadium atom is mainly localized on the d_{xy} orbital, further supporting the earlier mentioned electronic transitions originating from this orbital.

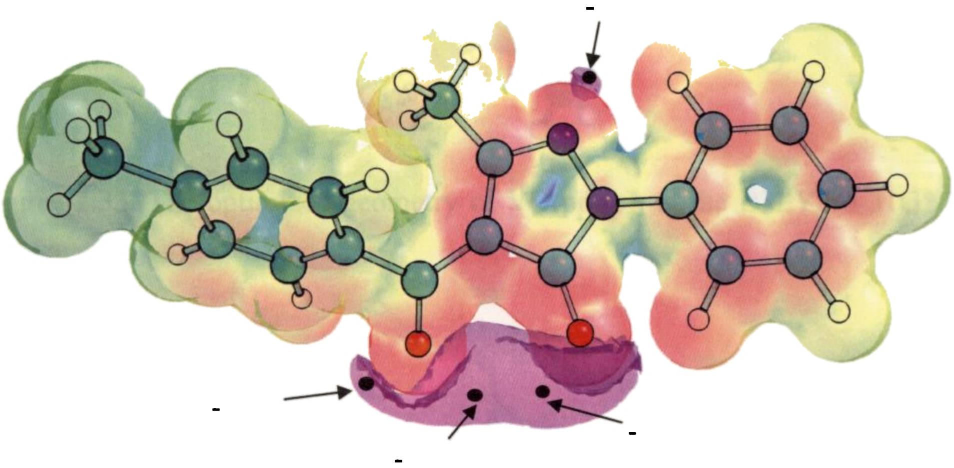


Figure 2.32. The surface engulfing the whole molecule is the MESP-painted Van der Waals surface of pmtp$^-$(the red regions are the most electron rich). An MESP isosurface of -125.5 kcal mol^{-1}(violet) and the MESP minima (in kcal mol^{-1}) around the CO oxygen and the pyrazolone nitrogen are also plotted.

The bond distances of V-O of ligands are significantly longer than VO double bond, as observed in the X-ray crystal structure of VO(acac)$_2$ (acac = acetylacetone) [Ballhausen and Gray, 1962] and VO(acac-NMe$_2$)$_2$ (acac-NMe$_2$ = *N,N*-dimethoxyacetylacetamido) [Dodge et al. 1961]. Further, VO double bond of length in VO(pmtp)$_2$ (1.584 Å) deduced by DFT is in the same range as observed in the VO(acac)$_2$ (1.592 Å).

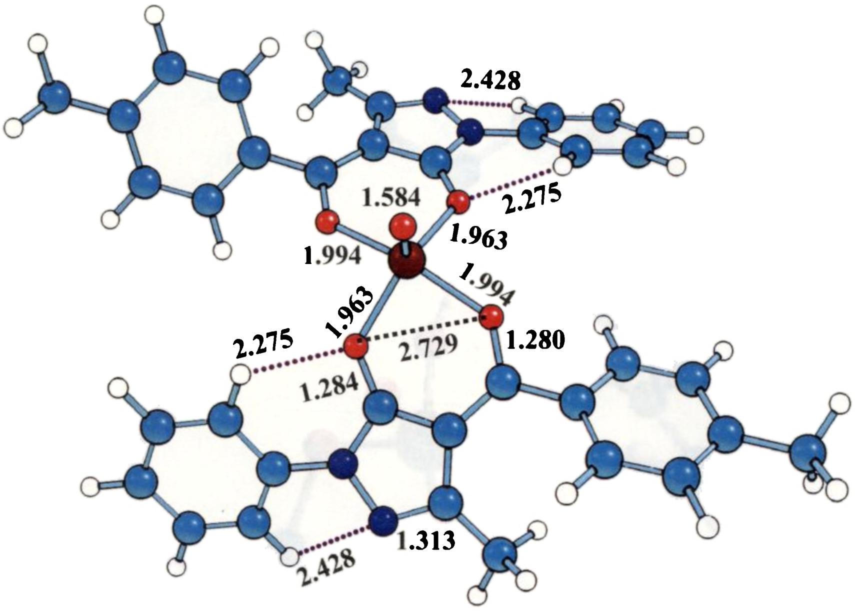


Figure 2.33. The optimized geometry of VO(pmtp)$_2$ at the B3LYP/6-31G* level of DFT.

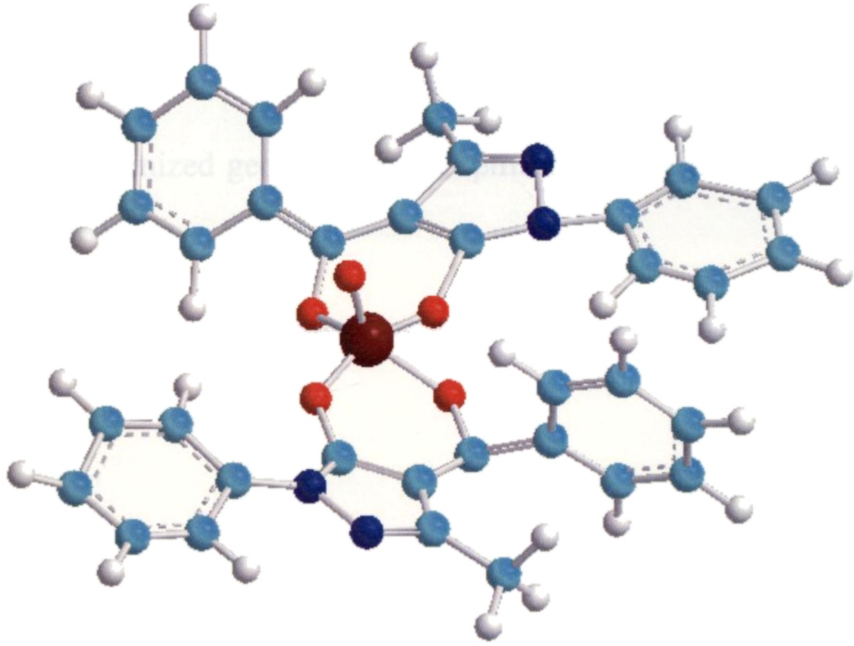
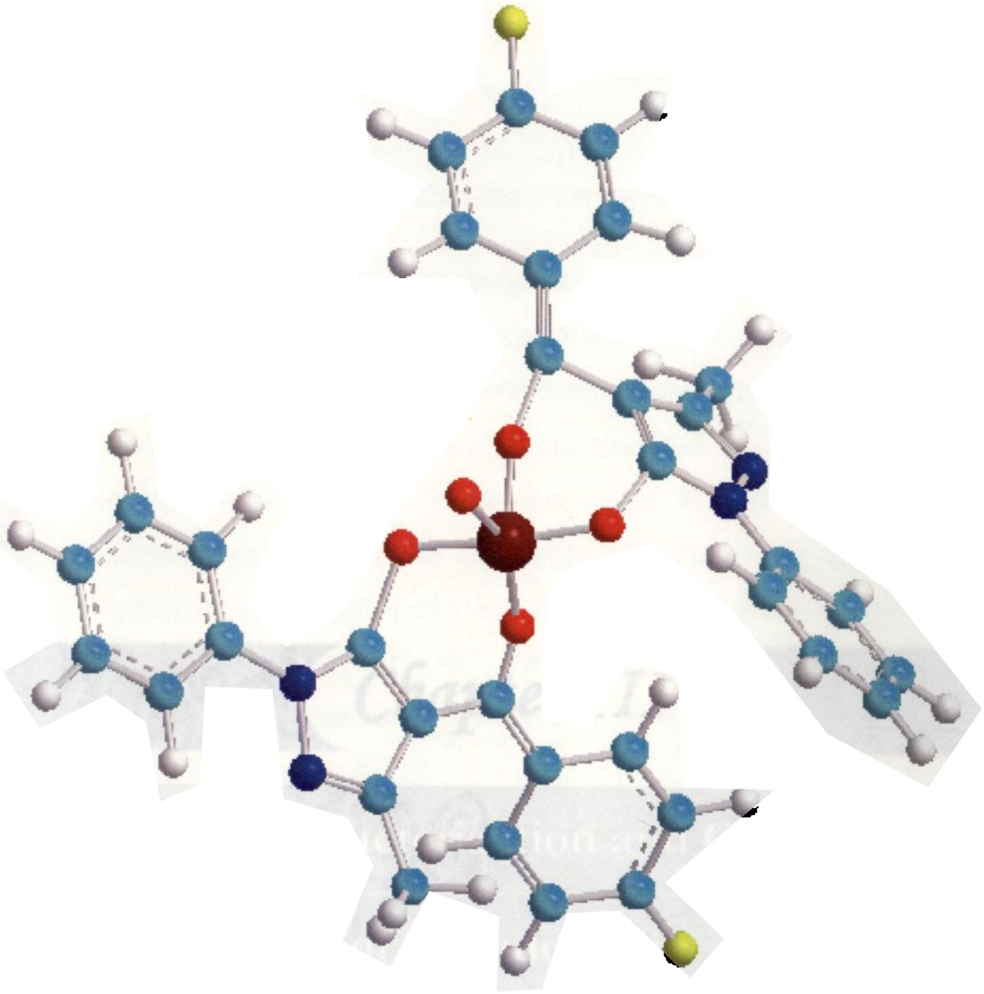


Figure 2.34. The optimized geometry of VO(pmbp)$_2$ at the B3LYP/6-31G* level of DFT.

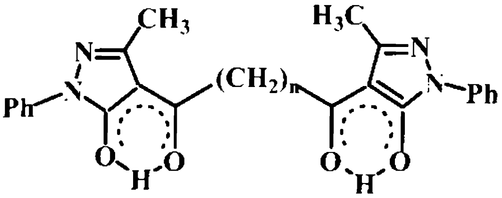


igure 2.35. The optimized geometry of VO(pmfbp)$_2$ at the B3LYP/6-31G* level fDFT.

Chapter III

Synthesis, Characterization and Complexation of Vanadophilic 4- Acylbis(1-phenyl-3-methyl-5-pyrazolones)

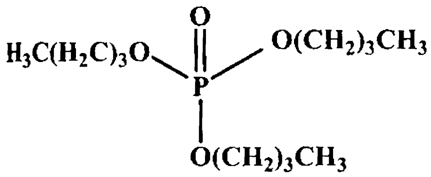
The 4-acylbis(pyrazolone) (**A**) designed by combining two 1-phenyl-3-methyl-4-acyl-5-pyrazolone subunits linked by a polymethylene chain of varying lengths -$(CH_2)_n$- (n = 0-8, 10, 20) exhibit several unique properties such as larger partition coefficients than the parent 4-acyl-5-pyrazolone and has two β-diketone donor sites on both sides of the polymethylene chain, is expected to give specific complexation towards metal ions depending on the polymethylene chain length. The dependence of the polymethylene chain length of 4-acylbis(pyrazolone) on the extraction behavior of Cu^{2+}, Ni^{2+}, Zn^{2+}, Am^{3+}, Cm^{3+}, Cf^{3+}, UO_2^{2+}, Th^{4+}, Np^{4+} and Pu^{4+} has been documented [Miyazaki et al. 1989; Miyazaki et al. 1991; Reddy et al. 2000; Takeishi et al. 2001].



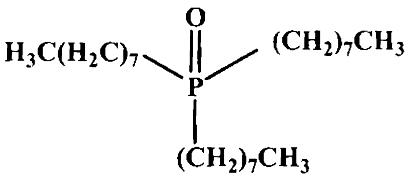
4-Acylbis(pyrazolones)

A

A synergistic effect is often set to bring about enhanced extraction but poorer separation among the metal ions. However, interestingly, in the extraction of Zn^{2+} and Ni^{2+} with 4-acylbis(pyrazolones), an enhanced extraction and an improved separation have been reported in the presence of TOPO as a synergist [Miyazaki et al. 1991]. The above factors stimulated us to synthesize various derivatives of 4-acylbis(pyrazolones) of varying polymethylene chain length and investigate their extraction behavior with the multivalent metal ions present in the waste liquors of titania industry. The effect of addition of various mono- (TOPO, TRPO and TBP) and bifunctional (CMPO) organophosphorus extractants on the extraction of the multivalent metal ions with 4-acylbis(pyrazolone) has also been evaluated.



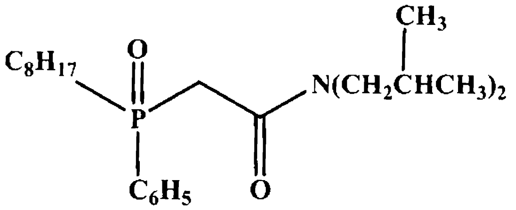
TBP



TOPO

$R_3P=O$
$R_2R'P=O$
$R'_2RP=O$

TRPO (where R = octyl and R' = hexyl)



CMPO

EXPERIMENTAL

Instrumentation

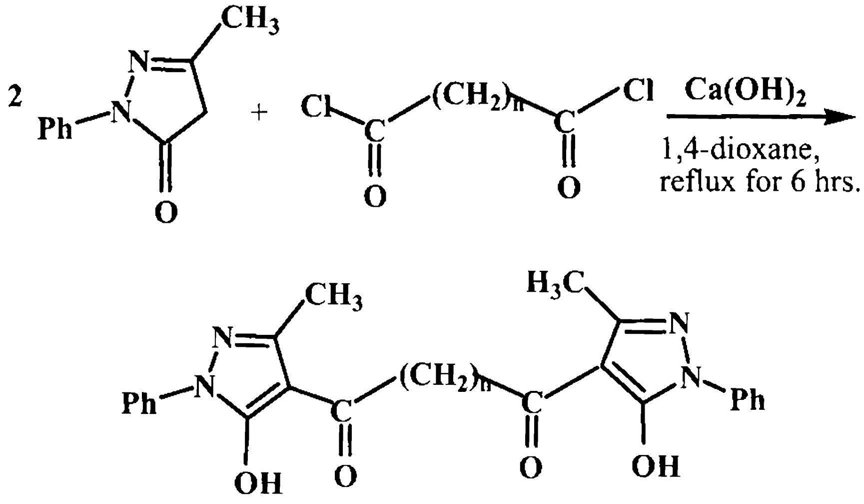
^{31}P NMR spectra of the synergistic complexes (in $CDCl_3$ and 85% H_3PO_4 as an external standard) were recorded using a Bruker 121.47 MHz NMR spectrometer. The methods for the preparation of stock solutions of metal ions and other instruments employed in this chapter are the same as described in Chapter 2.

Materials

TBP, TOPO and the starting materials (1-phenyl-3-methyl-5-pyrazolone and various acid dichlorides) for the syntheses of ligands were obtained from Sigma-Aldrich. TRPO (Cyanex 923) is a mixture of four trialkyl phosphine oxides ($R_3P=O$, $R_2R'P=O$, $R'_2RP=O$; where R = octyl and R' = hexyl), has been commercially available from Cytec, Canada was used after purification (purity > 99%; average molecular weight = 348 g) [Jun et al. 1998]. CMPO was synthesized and purified by standard procedures [Mathur et al. 1992; Gatrone et al. 1987]. All other chemicals used were of analytical reagent grade.

Syntheses of Various 4-Acylbis(1-phenyl-3-methyl-5-pyrazolones)

Various 4-acylbis(1-phenyl-3-methyl-5-pyrazolones) were synthesized by the acylation of 1-phenyl-3-methyl-5-pyrazolone with the corresponding acid dichlorides (Scheme 3.1). The synthesized compounds were characterized by elemental analyses, IR and ^1H NMR spectral data. Recrystallization of the ligands was carried out using chloroform-hexane mixtures.



n = 4 (adipoyl), n = 8 (sebacoyl), n = 10 (dodecandioyl)

Scheme 3.1

4-Adipoylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2AdBP): m.p.: 199°C; Elemental analysis: calculated for $C_{26}H_{26}O_4N_4$: C, 68.12; H, 5.68; N, 12.23%; Found C, 68.27; H, 6.19; N, 12.04%; ^1H NMR data ($CDCl_3$/TMS) (figure 3.: δ 7.80-7.83, 7.42-7.47, 7.27-7.31 (m, 10H, Ph); 2.80-2.83 (t, 4H, $(CH_2)_2$); 2.49 (s, 6H, CH_3); 1.85-1.92 (m, 4H, $(CH_2)_2$) (Figure 3. 1); IR (KBr) data (ν cm^{-1}): 3409 (br, OH); 1627 (s, C=O); 1593 (s, phenyl C=C); 1554 (s, pyrazolone ring).

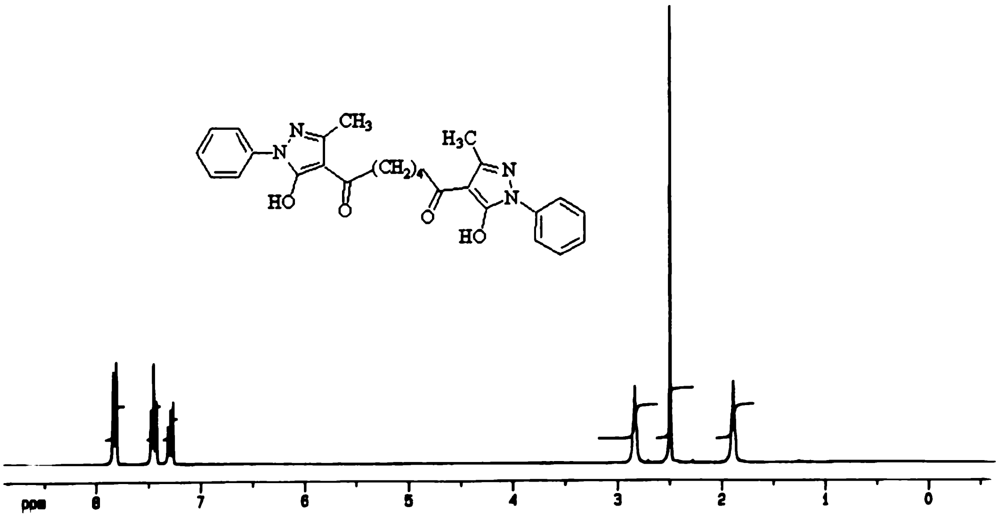


Figure 3.1. ^{1}H NMR spectrum of 4-adipoylbis(1-phenyl-3-methyl-5-pyrazolone).

The crystallographic data for H_2AdBP are listed in Table 3.1. An ORTEP diagram for the common repeating unit is shown in Figure 3.2. The molecular structure reveals a planar arrangement of non hydrogen atoms (O2, C11, C8, C9, O1). The carbonyl bond lengths C9-O1 and C11-O2 are 1.315 and 1.235 Å, respectively. There is an intramolecular hydrogen bond between the atoms O1 and O2 (O2-H····O1, 2.2678 Å, 138.2°). These data suggest that, in the ring consisting of O1/O2, the enolic proton is not shared symmetrically with the carbonyl oxygens; that is H_2AdBP exists in the enol form.

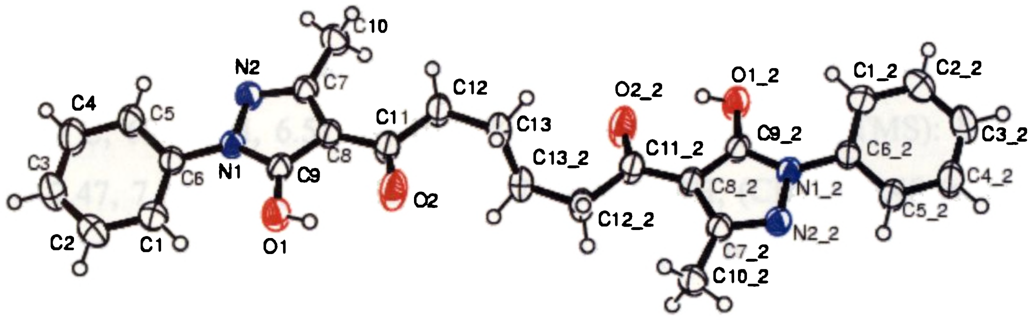


Figure 3.2. ORTEP diagram of 4-adipoylbis(1-phenyl-3-methyl-5-pyrazolone).

Table 3.1. Crystal data, collection, and structure refinement parameters for 4-adipoylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2AdBP).

Parameters	H_2AdBP
empirical formula	$C_{26}H_{26}N_4O_4$
fw	458.51
crystal system	triclinic
space group	P1
cryst size (mm^3)	0.30 × 0.20 × 0.20
temperature (K)	293(2)
a/Å	5.2585(2)
b/Å	8.1371(4)
c/Å	13.9088(6)
α (deg)	91.393(3)
β (deg)	100.811(2)
γ (deg)	106.602(2)
V / Å^3	555.29(4)
Z	1
ρ_{calcd}/g cm^{-3}	1.364
μ/mm^{-1}	0.094
F(000)	242
R1 [$I > 2\sigma(I)$]	0.0486
wR2 [$I > 2\sigma(I)$]	0.1468
R1 (all data)	0.0656
wR2 (all data)	0.1685
GOF	1.103

4-Sebacoylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2SbBP): m.p.: 136°C; Elemental analysis: calculated for $C_{30}H_{34}O_4N_4$: C, 70.03; H, 6.61; N, 10.89%; Found C, 69.48; H, 6.51; N, 10.67%; ^{1}H NMR data($CDCl_3$/TMS): δ 7.81-7.84, 7.42-7.47, 7.28-7.30 (m, 10H, Ph); 2.71-2.76 (t, 4H, $(CH_2)_2$); 2.48 (s, 6H, CH_3); 1.73-1.77 (m, 4H, $(CH_2)_2$); 1.39 (m, 8H, $(CH_2)_4$) (Figure 3.3); IR (KBr) data (ν cm^{-1}): 3430 (br, OH); 1620 (s, C=O); 1593 (s, phenyl C=C); 1553 (s, pyrazolone ring). Efforts to grow the single crystals of H_2SbBP were failed and hence DFT molecular modeling calculations have been performed to optimize the molecular structure (Figure 3.4).

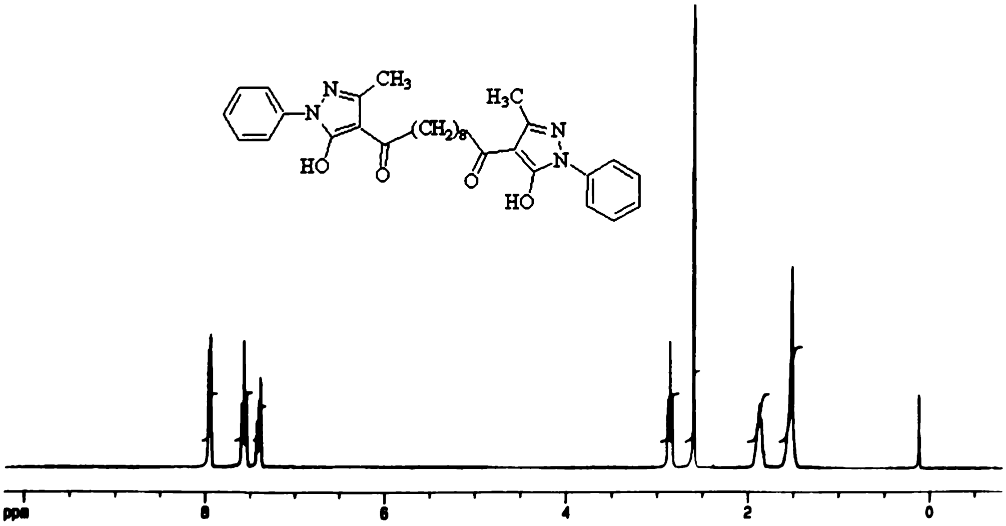


Figure 3.3. ^{1}H NMR spectrum of 4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone.

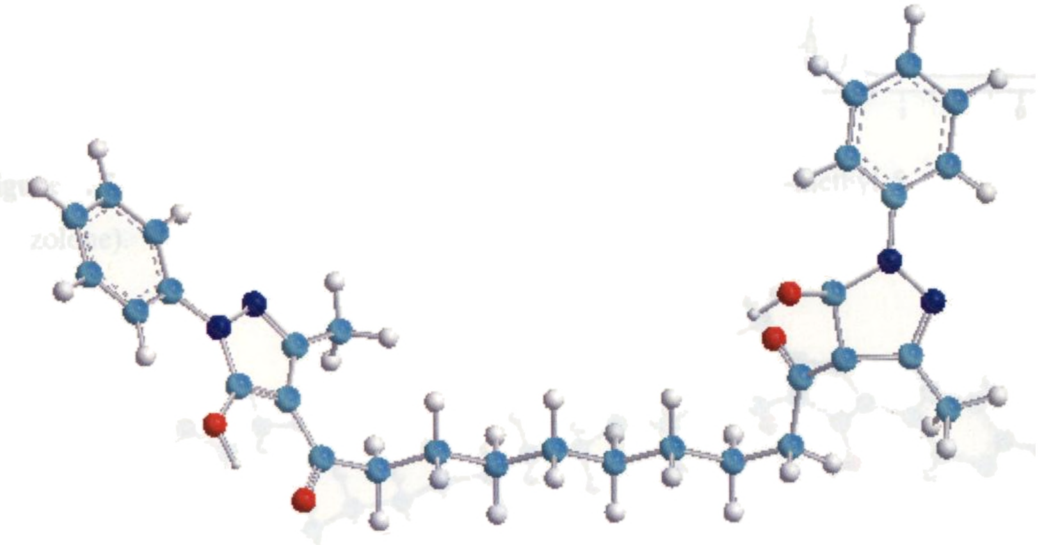


Figure 3.4. The optimized structure of 4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone at the B3LYP/6-31G* level of DFT.

4-Dodecandioylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2DdBP): m.p.: 152°C; Elemental analysis: calculated for $C_{32}H_{38}O_4N_4$: C, 70.84; H, 7.01; N, 10.33%; Found C, 71.32; H, 7.45; N, 10.35%; ^{1}H NMR data ($CDCl_3$/TMS): δ 7.81-7.84, 7.42-7.47, 7.28-7.30 (m, 10H, Ph); 2.71-2.76 (t, 4H, $(CH_2)_2$); 2.48 (s, 6H, CH_3);

1.69-1.77 (m, 4H, $(CH_2)_2$) (Figure 3.5); 1.33 (m, 12H, $(CH_2)_6$); IR (KBr) data (ν cm^{-1}): 3436 (br, OH); 1618 (s, C=O); 1591 (s, phenyl C=C); 1552 (s, pyrazolone ring). The enolic form of H_2DdBP was modeled using DFT molecular modeling (Figure 3.6).

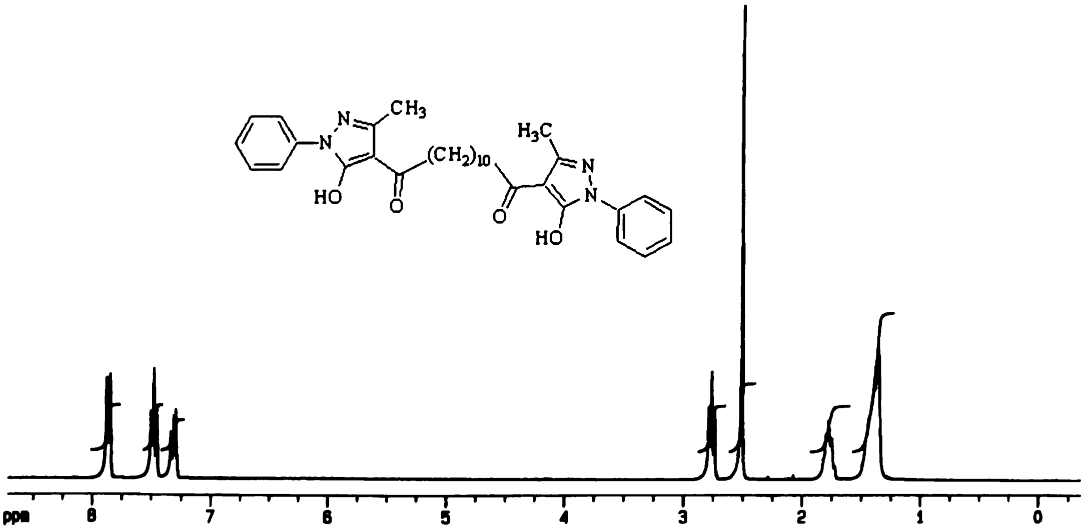


Figure 3. 5. ^1H NMR spectrum of 4-dodecandioylbis(1-phenyl-3-methyl-5-pyrazolone).

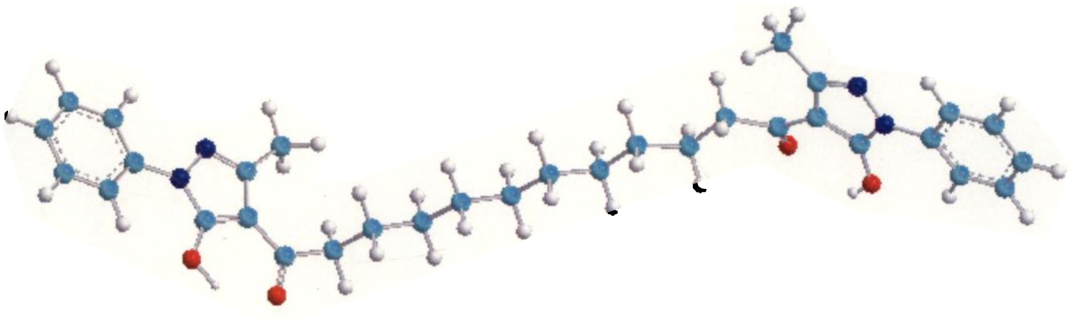


Figure 3.6. The optimized structure of 4-dodecandioylbis(1-phenyl-3-methyl-5-pyrazolone) at the B3LYP/6-31G* level of DFT.

In general, heterocyclic β-diketones exhibit keto-enol tautomerism. In the present work, in the ^1H NMR spectra of various 4-acylbis(1-phenyl-3-methyl-5-pyrazolones), peaks corresponding to the enolic OH have not been observed.

However, the absence of a peak corresponding to the methyne proton at the 4th position of the pyrazolone ring, confirms the existence of various 4-acylbis(1-phenyl-3-methyl-5-pyrazolones) quantitatively in the enolic form.

Liquid-Liquid Extraction and Analytical Procedure

The solvent extraction and analytical procedure used for the determination of metal ions are the same as described in Chapter 2. Preliminary experiments showed that the equilibrium was attained within 1 h for vanadium(V).

Preparation of Oxovanadium Complexes

To a well stirred ethanol solution of 1.0 mM 4-acylbis(1-phenyl-3-methyl-5-pyrazolone), aqueous solution of NaOH (0.4 g) was added. After the complete dissolution of 4-acylbis(1-phenyl-3-methyl-5-pyrazolone), 0.117 g ammonium monovanadate was added, the pH was adjusted to 7 and 1, and the reaction mixture was stirred for 10 h. The precipitate formed was filtered, washed with ethanol, then with distilled water and dried in a desiccator over fused calcium chloride.

Part I

4-Acylbis(1-phenyl-3-methyl-5-pyrazolones) as Highly Selective Extractants for Vanadium(V): Synergistic Effect with Neutral Organophosphorus Extractants

Effect of Hydrochloric Acid Concentration on the Extraction of Multivalent Metal Ions Present in the Titania Waste Chloride Liquors

The extraction behavior of vanadium(V) (0.02 mol dm^{-3}), and other associated metal ions, *viz.*, magnesium(II) (0.06 mol dm^{-3}), aluminium(III) (0.03 mol dm^{-3}), titanium(IV) (0.02 mol dm^{-3}), chromium(III) (0.03 mol dm^{-3}), manganese(II) (0.16 mol dm^{-3}), iron(II) (0.45 mol dm^{-3}) and iron(III) (0.3 mol dm^{-3}) present in the waste chloride liquors of titanium minerals processing industry, has been investigated as a function of HCl concentration using 0.03 mol dm^{-3} 4-acylbis-5-pyrazolone in chloroform as the extractant (Figure 3.7). It is clear from the results that vanadium(V) is selectively extracted into the organic phase. On the other hand, magnesium(II), aluminium(III), titanium(IV), chromium(III), manganese(II), iron(II) and iron(III) were not extracted into the organic phase under the present experimental conditions.

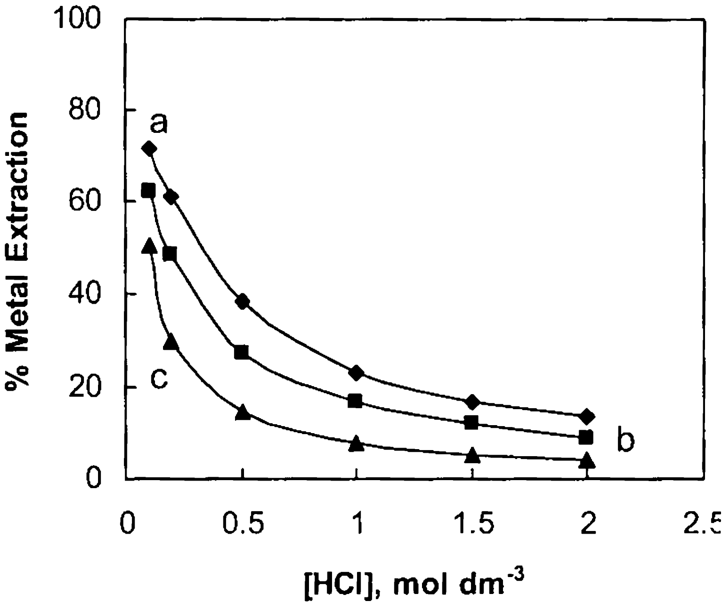


Figure 3.7. Percentage extraction of vanadium(V) as a function of HCl concentration. H_2SbBP (a) = H_2DdBP (b) = H_2AdBP (c) = 0.03 mol dm^{-3} in chloroform.

The stripping behavior of vanadium(V) has been investigated using hydrochloric acid as the stripping agent from a loaded organic phase (0.03 mol dm^{-3} H_2SbBP) containing 1.0 g dm^{-3} vanadium(V) and the results are given in Figure 3.8. The percentage recovery of vanadium increases with increasing HCl concentrations in the aqueous phase and was found to be almost quantitative (>99.9%) at about 6.0 mol dm^{-3} HCl. In the present study, at a concentration of HCl greater than or equal to 4.0 mol dm^{-3}, a slight reduction of vanadium(V) to vanadium(IV) (10%) has been noticed, as reported by Tedesco and Rumi [Tedesco and Rumi, 1978].

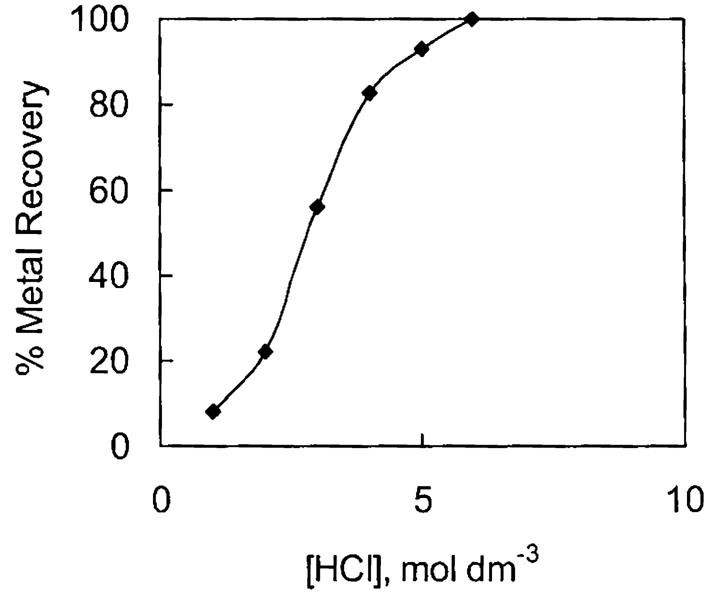


Figure 3.8. Stripping behavior of vanadium(V) from loaded H_2SbBP using HCl.

Extraction of Vanadium(V) with Various 4-Acylbis(1-phenyl-3-methyl-5-pyrazolones)

The effect of H_2AdBP, H_2SbBP, and H_2DdBP concentrations (0.009-0.02 mol dm^{-3}) on the extraction of vanadium(V) has been investigated at constant metal (1×10^{-3} mol dm^{-3}) and hydrochloric acid (0.1 mol dm^{-3}) concentrations, and the results are depicted in Figure 3.9. It is clear from the results that the extraction of vanadium(V) increases linearly with increasing concentration of 4-acylbis(1-phenyl-3-methyl-5-pyrazolones) (H_2X). The log-log plots were linear with slopes of unity, indicating the involvement of one molecule of the extractant in the complex formation.

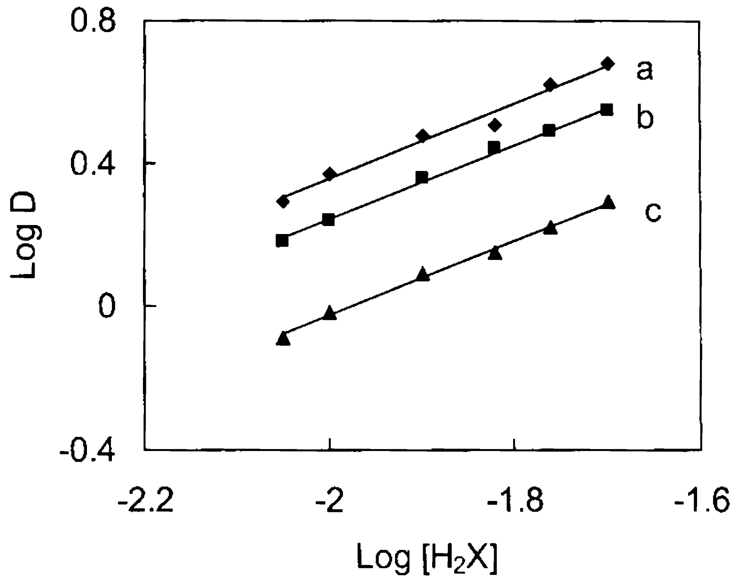


Figure 3.9. Effect of 4-acylbis-(1-phenyl-3-methyl-5-pyrazolone) (H_2X) concentration on the extraction of vanadium(V) (1×10^{-3} mol dm^{-3}) from 0.1 mol dm^{-3} hydrochloric acid solutions. Slope of the line (a) H_2SbBP = 1.0 ± 0.06, (b) H_2DdBP = 1.0 ± 0.05, (c) H_2AdBP = 1.0 ± 0.05.

The extraction of vanadium(V) with various 4-acylbis(1-phenyl-3-methyl-5-pyrazolones) (0.01 mol dm^{-3}) in chloroform as a function of hydrogen ion concentration at constant metal (1×10^{-3} mol dm^{-3}) and chloride ion (2.0 mol dm^{-3}) concentrations has been studied using HCl + NaCl mixtures. The extraction behaviour showed an inverse dependence on the acidity. The log-log plots (Figure 3.10) gave slopes of -1.0, indicating the involvement of one of the β-diketone sites of H_2X in complex formation with vanadium(V) releasing one molecule of H^+ ion from the reagent.

The effect of chloride ion concentration (0.1 - 2.0 mol dm^{-3}) on the extraction efficiency of vanadium(V) has also been investigated at constant metal ion (1×10^{-3} mol dm^{-3}), hydrogen ion (0.1 mol dm^{-3}), and 4-acylbis(1-phenyl-3-methyl-5-

pyrazolone) (0.01 mol dm^{-3}) concentrations. The extraction of vanadium(V) was found to be independent of the chloride ion concentration under the present experimental conditions.

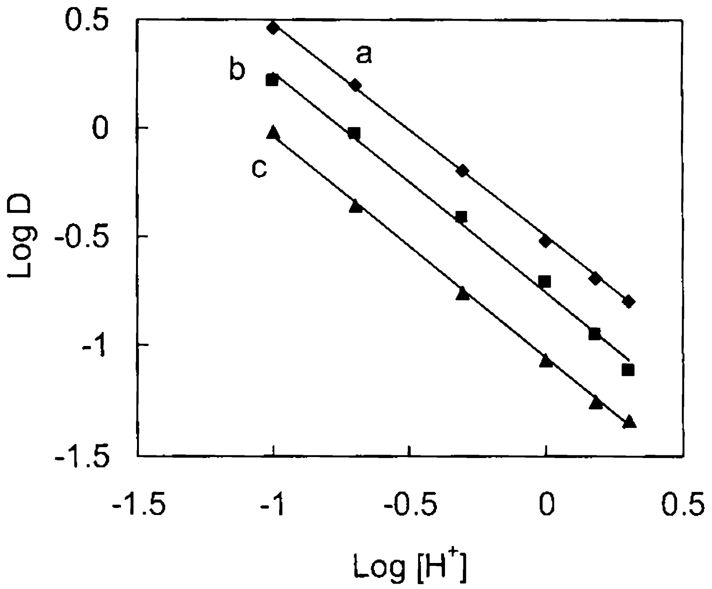


Figure 3.10. Effect of hydrogen ion concentration on the extraction of vanadium(V) (1 × 10^{-3} mol dm^{-3}). [H_2AdBP] = [H_2DdBP] = [H_2SbBP] = 0.01 mol dm^{-3}, [Cl^-] = 2.0 mol dm^{-3}. Slope of the line (a) H_2SbBP = -1.0, (b) H_2DdBP = -1.0 ± 0.05, (c) H_2AdBP = -1.0 ± 0.05.

The effect of metal ion concentration (8 × 10^{-4}- 3 × 10^{-3} mol dm^{-3}) on the extraction process of vanadium(V) from 0.1 mol dm^{-3} hydrochloric acid solutions has been studied by employing various 4-acylbis(1-phenyl-3-methyl-5-pyrazolones) (0.01 mol dm^{-3}) in chloroform. It has been observed that the extraction of vanadium is independent of the metal ion concentration in the investigated range. The log-log plots (Figure 3.11) of equilibrium organic phase metal concentrations against aqueous phase metal concentration were linear with slopes of unity, indicating the extraction of mononuclear species into the organic phase.

Based on the preceding results, the extraction equilibrium of vanadium(V) from hydrochloric acid solutions with 4-acylbis(1-phenyl-3-methyl-5-pyrazolone)

(H_2X) may be represented as:

$$VO_{2\,aq}^{+} + H_2X_{org} \overset{K_{ex,\,V(V)}}{\rightleftharpoons} VO_2X\cdot(HX)_{org} + H_{aq}^{+} \qquad (1)$$

where $K_{ex,V(V)}$ denotes the equilibrium constant and is given by,

$$K_{ex,\,V(V)} = \frac{[VO_2\,X\cdot(HX)]\,[H^+]}{[VO_2^+]\,[H_2X]} \qquad (2)$$

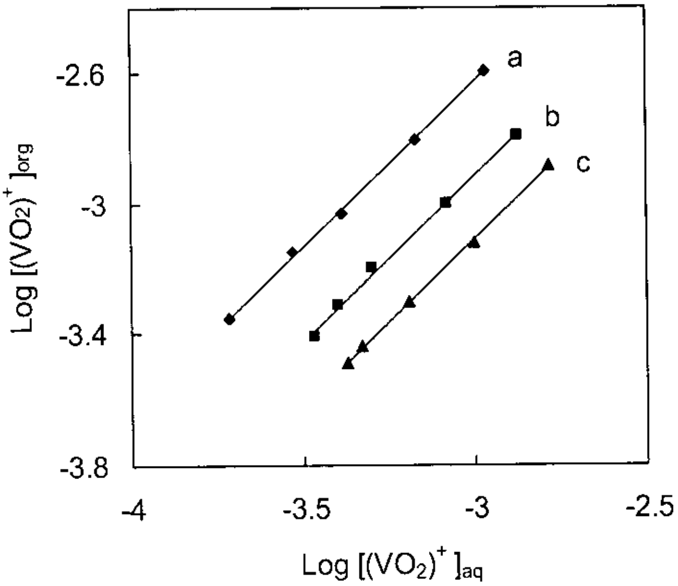


Figure 3.11. Effect of metal ion concentration on the extraction (8 × 10^{-4}- 3 × 10^{-3} mol dm^{-3}). [H_2AdBP] = [H_2SbBP] = [H_2DdBP] = 0.01 mol dm^{-3}, [HCl] = 0.1 mol dm^{-3}. Slope of the line (a) H_2SbBP = 1.0 ± 0.05, (b) H_2DdBP = 1.0 ± 0.05, (c) H_2AdBP = 1.0 ± 0.05.

The $K_{ex,V(V)}$ values of the extracted complexes were determined by nonlinear regression analysis as described in our earlier publication [Francis and Reddy, 2003] and are given in Table 3.2. The $K_{ex,V(V)}$ values thus calculated refer only to concentration quotients, calculated on the assumption that the activity coefficients of the species involved do not change significantly under the present experimental conditions. In the present experiments, the concentration of vanadium(V) in the aqueous phase (0.001 mol dm^{-3}) is low as compared to the concentration of 4-acylbis(pyrazolones) in the organic phase (0.009 - 0.02 mol dm^{-3}), and H^+ (0.1-2.0 mol dm^{-3}) and Cl^- (0.1- 2.0 mol dm^{-3}) concentrations in the aqueous phase. Hence the activities of all the species present in the aqueous and organic phases have been considered as equal to their equilibrium concentrations.

Table 3.2. Two phase equilibrium constants ($K_{ex,V(V)}$) of vanadium(V) with various 4-acylbis(1-phenyl-3-methyl-5-pyrazolone)-chloroform systems.

Extractant	Number of Methylene groups (n)	Log $K_{ex,V(V)}$
H_2AdBP	4	0.96 ± 0.03
H_2SbBP	8	1.42 ± 0.02
H_2DdBP	10	1.27 ± 0.03

The log $K_{ex,V(V)}$ value of vanadium(V) with various 4-acylbis(pyrazolones) follows the order $H_2SbBP > H_2DdBP > H_2AdBP$. The decrease in the extraction efficiency for polymethylene chain length, $n = 10$ can be attributed to the increasing steric effects caused by increasing polymethylene chain length. A similar trend has also been observed by many investigators in the extraction of trivalent lanthanides, [Reddy et al. 2000] actinides [Takeishi et al. 2001, Uzoukwu et al. 1998], nickel(II), and zinc(II) [Miyazaki et al. 1991; Diantouba et al. 1994].

IR spectra of the Extracted Complexes

In the 1500-1630 cm^{-1} region, strong bands due to ν (C=O), ν (C=N) and ν (C=C) of the aromatic rings have been observed in the IR spectra of the complexes, where the carbonyl band (1627 cm^{-1} in H_2AdBP, 1620 cm^{-1} in H_2SbBP and 1618 cm^{-1} in H_2DdBP) was shifted to lower frequencies (1600 cm^{-1} in VO_2HAdBP, 1600 cm^{-1} in VO_2HSbBP and 1597 cm^{-1} in VO_2HDdBP) upon coordination with vanadium(V). This suggests that the carbonyl group in the 4-acylbis(1-phenyl-3-methyl-5-pyrazolone) is involved in the complex formation with the metal ion. Further, new absorption bands corresponding to the O=V=O stretching of vanadium(V) were appeared around 964, 906 (VO_2HAdBP), 965, 911 (VO_2HSbBP) and 970, 915 cm^{-1} (VO_2HDdBP) [Clark 1973]. This clearly indicates that vanadium exists as oxovanadium(V) species in the extracted complexes in the chloroform phase. However, with respect to time (> 3h) the color of the organic phase changes from wine red to green, suggesting the reduction of the oxovanadium(V) to oxovanadium(IV). This has been ascertained by IR spectral data of the extracted complex, where only one V=O stretch was observed at 984 cm^{-1} for the H_2SbBP complex. Similar behavior was observed in the case of 4-acylbis(1-phenyl-3-methyl-5-pyrazolone) complexes also.

Loading Capacity

Aliquots of 10 cm^3 of 0.03 mol dm^{-3} H_2SbBP were repeatedly extracted at 303 $\pm$ 1 K for 120 min with equal volumes of aqueous phase containing 1.0 g dm^{-3} of vanadium(V) and 1.0 mol dm^{-3} of HCl. The aqueous phases were analyzed after each stage of extraction and the cumulative vanadium content transferred into the organic phases were calculated. The cumulative vanadium content in the organic phase / 100 g of H_2SbBP is plotted against the number of stages of contact and is presented in Figure 3.12. It is clear that the loading capacity of H_2SbBP in chloroform for the extraction of vanadium(V) from hydrochloric acid solutions is 8.92 g of vanadium(V) / 100 g of H_2SbBP.

Extraction of Vanadium(V) with H_2SbBP in the Presence of Mono- and Bifunctional Neutral Organophosphorus Extractants

In view of its better extraction efficiency, H_2SbBP has been chosen for further investigations , especially , in the synergistic extraction experiments.

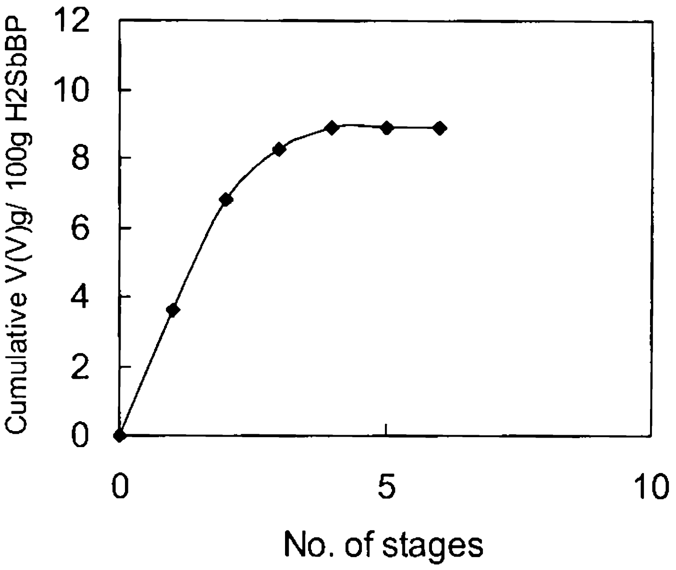


Figure 3.12. Loading capacity of 4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone by vanadium(V).

The synergistic extraction of vanadium(V) from 0.2 mol dm^{-3} hydrochloric acid solutions with mixtures of H_2SbBP (0.005 - 0.012 mol dm^{-3}), and TOPO (0.005 - 0.012 mol dm^{-3}), TRPO (0.005 - 0.012 mol dm^{-3}), CMPO (0.005 - 0.012 mol dm^{-3}), or TBP (0.05 - 0.2 mol dm^{-3}) into chloroform has been investigated and the results are shown in Table 3.3. It was found that the extraction of vanadium(V) with the above neutral organophosphorus extractants was negligible under the present experimental conditions. However, with mixtures of H_2SbBP and neutral organophosphorus extractants, a considerable synergistic enhancement (synergistic enhancement factor (S.E.F) = D_{mix} / ($D_{\text{H}_2\text{SbBP}}$ + D_{S}), where D_{mix} = distribution ratio with H_2SbBP + S; D_{H2SbBP} = distribution ratio with H_2SbBP alone; D_s = distribution ratio with S alone) in the extraction of vanadium(V) has been observed. Further, it is clear from Table 3.3 that the synergistic enhancement factor increases with the increase in concentration of the neutral organophosphorus extractants. Antisynergism was also noticed, especially with H_2SbBP (0.01 mol dm^{-3}) in the presence of low concentrations of TBP (0.05 mol dm^{-3}) and CMPO (0.005 mol dm^{-3}).

Table 3.3. Synergistic enhancement factors (S.E.F) of vanadium(V) with H_2SbBP in the presence of mono- and bifunctional neutral organophosphorus extractants. Aqueous phase = 0.2 mol dm^{-3} HCl containing 0.001 mol dm^{-3} vanadium(V).

S	[H_2SbBP] mol dm^{-3}	[S] mol dm^{-3}	D_{H_2SbBP}	D_S	$D_{H_2SbBP+S}$	S.E.F
TOPO	0.01	0.007	1.58	<0.01	10.47	6.63
	0.01	0.01	1.58	0.02	14.79	9.36
	0.01	0.015	1.58	0.05	21.88	13.85
TRPO	0.01	0.007	1.58	<0.01	3.55	2.25
	0.01	0.01	1.58	0.01	4.57	2.89
	0.01	0.015	1.58	0.03	7.24	4.58
CMPO	0.01	0.007	1.58	<0.01	1.78	1.13
	0.01	0.009	1.58	<0.01	2.41	1.52
	0.01	0.015	1.58	<0.01	3.39	2.15
TBP	0.01	0.07	1.58	<0.01	1.66	1.05
	0.01	0.15	1.58	0.01	3.23	2.04
	0.01	0.2	1.58	0.02	4.27	2.70

It is clear from the plot (Figure 3.13) of log *D* *vs* log [H_2SbBP] that at constant neutral organophosphorus extractant concentration (0.01 mol dm^{-3} in the case of TOPO, TRPO, and CMPO and 0.1 mol dm^{-3} in the case of TBP), one molecule of H_2SbBP is involved in the synergistically extracted complex.

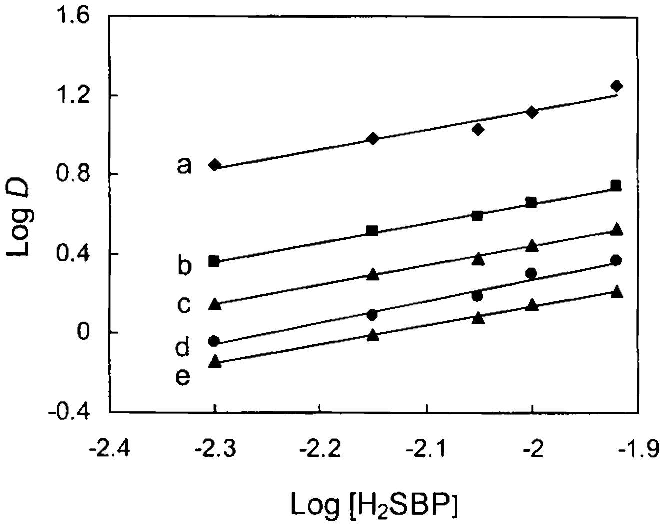


Figure 3.13. Effect of H_2SbBP concentration on the extraction of vanadium(V) at constant S concentration. Aqueous phase = 0.01 mol dm^{-3} vanadium(V) + 0.2 mol dm^{-3} HCl. TOPO (a) = TRPO (b) = CMPO (c) = 0.01 mol dm^{-3}, TBP (d) = 0.1 mol dm^{-3}. Slope of the line (a) = 1.0 ± 0.05, (b) =1.0, (c) = 1.0, (d) = 1.0 ± 0.1, (e) = H_2SbBP alone.

The effect of concentration of various organophosphorus extractants on the extraction of vanadium(V) at constant H_2SbBP concentration (0.01 mol dm^{-3}) has been examined from 0.2 mol dm^{-3} hydrochloric acid solutions (Figure 3.14). The extraction of vanadium(V) was found to increase linearly with the increase in concentration of S. From the log-log plots, it is clear that one molecule of S is involved in the synergistically extracted complex.

The extraction of vanadium(V) with H_2SbBP (0.01 mol dm^{-3}) in the presence of various neutral organophosphorus extractants (0.01 mol dm^{-3} of TOPO or TRPO or CMPO and 0.1 mol dm^{-3} TBP) in chloroform at constant chloride ion concentration (2.0 mol dm^{-3}) as a function of hydrogen ion concentration has been studied using HCl + NaCl mixtures. The extraction behavior shows an inverse dependence on the acidity. The log-log plots (Figure 3.15) gave a slope of –1.0, indicating the release of one hydrogen ion to the aqueous phase by reacting with one of the β-diketone sites of H_2SbBP molecule.

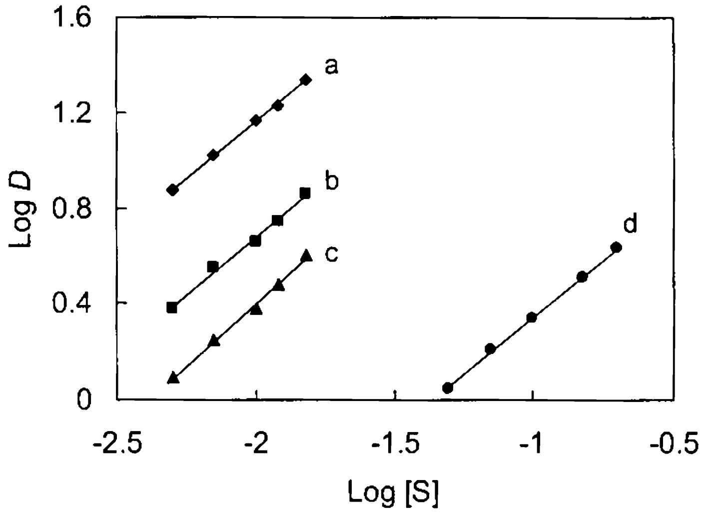


Figure 3.14. Effect of concentration of the neutral organophosphorus extractant (S) on the extraction of vanadium(V) at constant H_2SbBP concentration. Aq. phase = 0.01 mol dm^{-3} vanadium(V) + 0.2 mol dm^{-3} HCl; H_2SbBP = 0.01 mol dm^{-3}. Slope of the line TOPO (a) = 1.0 ± 0.05, TRPO (b) =1.0, CMPO (c) = 1.0, TBP (d) = 1.0 ± 0.1.

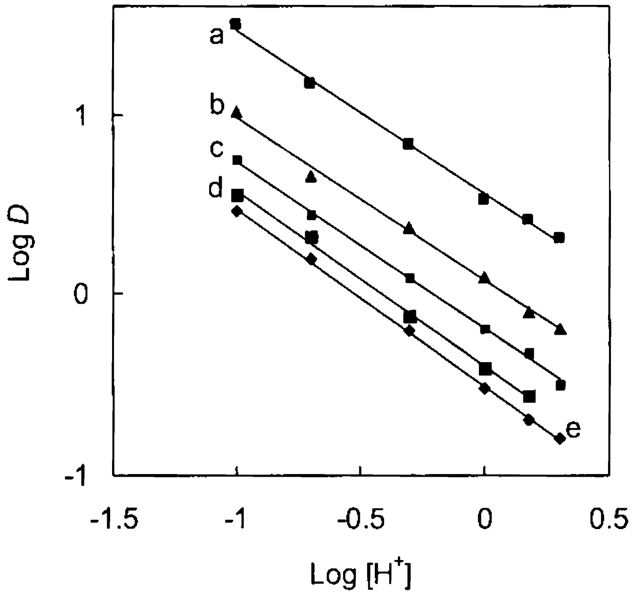


Figure 3.15. Effect of hydrogen ion concentration on the extraction of vanadium(V) at constant Cl^- concentration. Aqueous phase = 0.01 mol dm^{-3} vanadium(V) + 2.0 mol dm^{-3} Cl^-. H_2SbBP = 0.01 mol dm^{-3}. Slope of the line

TOPO (a) = -1.0 ± 0.05, TRPO (b) =-1.0, CMPO (c) = -1.0, TBP (d) = -1.0 ± 0.1, with out synergist (e) = -1.0 ± 0.1.

The effect of metal ion concentration ($8 \times 10^{-4} - 3 \times 10^{-3}$) on the extraction of vanadium(V) from 0.2 mol dm^{-3} hydrochloric acid solutions has been studied with H_2SbBP (0.01 mol dm^{-3}) in the presence of various neutral organophosphorus extractants (0.01 mol dm^{-3} TOPO, TRPO, and CMPO, 0.1 mol dm^{-3} TBP). It has been observed that the extraction of vanadium(V) was independent of metal ion concentration in the investigated range. The log-log plot of equilibrium organic phase metal concentration against aqueous phase metal concentration is linear with a slope of unity indicating the extraction of mononuclear species into the organic phase. Based on the above results, the extraction equilibrium of vanadium(V) from hydrochloric acid solutions with H_2SbBP (H_2X) in the presence of neutral organophosphorus extractants may be represented as:

$$VO_{2\,aq}^{+} + H_2X_{org} + S_{org} \xrightleftharpoons{K_{syn,1}} VO_2X \cdot (HX) \cdot S_{org} \quad + H^{+}_{aq} \qquad (3)$$

where $K_{syn,1}$ represents the synergistic equilibrium constant and is given by,

$$K_{syn,1} = \frac{[VO_2X(HX) \cdot S]_{org} \, [H^+]_{aq}}{[VO_2^+]_{aq} \, [H_2X]_{org} \, [S]_{org}} \qquad (4)$$

The interactions between a *β*-diketone and a neutral oxo-donor in chloroform are, in general, weaker when the diluent itself has strong interaction with the neutral oxygen donor [Sekine 1983]. Hence, it is assumed to have negligible interaction between H_2SbBP and S in chloroform. The adduct formation reaction in the organic phase and the stability constant, K_s is given by,

$$VO_2X \cdot (HX)_{org} + S_{org} \xrightleftharpoons{K_s} VO_2X \cdot HX \cdot S_{org} \qquad (5)$$

$$K_s = K_{syn,1} \,/\, K_{ex,V(V)} \qquad (6)$$

The equilibrium constants of synergistic complexes ($K_{syn,1}$ of vanadium(V) were calculated from the extraction data and are given in Table 3.4. The stability constants, K_s, for the organic phase synergistic reaction of vanadium(V)–H_2SbBP chelate with S were also calculated according to Eqn. (6) and are given in Table 3.4. The complexation strength of vanadium(V) with various neutral organophosphorus extractants follows the order: TOPO > TRPO > CMPO > TBP, which is in accordance with their oxygen basicity values, K_H [Sahu et al. 2000] (where K_H is the equilibrium constant for the HNO_3 uptake by neutral organophosphorus extractant (S) expressed as:

$$H^{+}_{aq} + NO^{-}_{3\,aq} + S_{org} \xrightleftharpoons{K_{HH}} HNO_3 \cdot S_{org}$$

Table 3.4. Two phase equilibrium constants of vanadium(V)-H_2SbBP-S-Chloroform systems.

Extraction System	K_H	Log Synergistic Constant (Log $K_{syn,1}$)	Log Stability Constant (Log K_s)
H_2SbBP+TOPO	8.9	4.41±0.02	3.00±0.02
H_2SbBP+TRPO	8.6	3.87±0.04	2.46±0.04
H_2SbBP+CMPO	2.9	3.41±0.02	2.00±0.02
H_2SbBP+TBP	0.2	2.52±0.03	1.10±0.03

The ^{31}P NMR spectral data may help to study the influence of neutral organophosphorus extractant in the synergistic extraction systems, as there exists a strong correlation between the electron density of the oxygen of the P=O group in the neutral organophosphorus extractant and extraction efficiency [Inova et al. 2001]. Figure 3.16 shows that log $K_{syn,1}$ value of vanadium(V) increases linearly with increase in δ (^{31}P) NMR chemical shift of the neutral oxygen bearing organophosphorus extractant (TOPO > TRPO > TBP). Thus, the donor ability of the phosphoryl oxygen, which is correlated with the δ(^{31}P) NMR chemical shift [i.e., a high electron density on the oxygen atom induces a low electron density on the phosphorus atom and thus a high value of the δ (^{31}P) NMR chemical shift] is the key parameter for the increase in the extraction efficiency of vanadium(V) with H_2SbBP in the presence of neutral organophosphorus extractants.

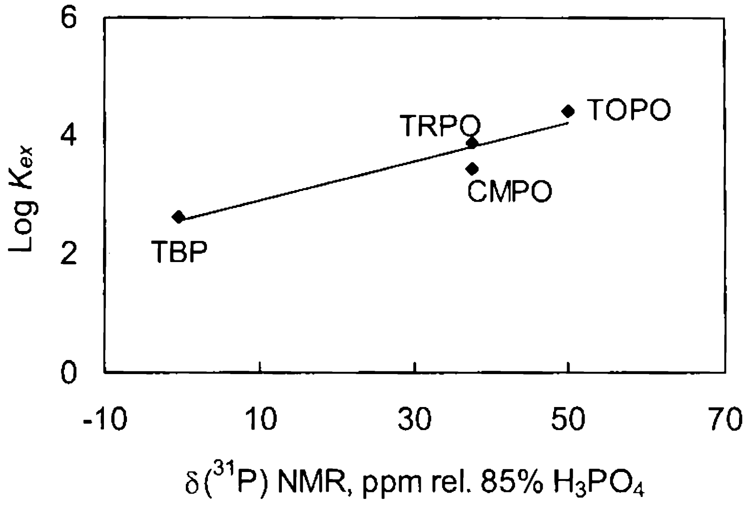


Figure 3.16. Variation of synergistic equilibrium constant ($K_{syn,1}$) of vanadium(V) with δ (^{31}P) NMR chemical shift values of neutral organophosphorus extractants.

Extraction and Separation of Vanadium(V) from Multivalent Metal Chloride Solutions with H_2SbBP in the Presence and Absence of TOPO

A McCabe-Thiele plot (Figure 3.17) was generated for a typical feed solution containing 1.0 g dm^{-3} of vanadium(V) and 1.0 mol dm^{-3} HCl using 0.03 mol dm^{-3} H_2SbBP in chloroform as the extractant. The McCabe-Thiele plot showed that the quantitative extraction of vanadium(V) was possible in four counter-current stages at an A : O (Aq. : Org.) ratio of 1 : 2.

Based on the above results, a synthetic waste chloride liquor consisting of magnesium(II) (0.06 mol dm^{-3}), aluminium(III) (0.03 mol dm^{-3}), titanium(IV) (0.02 mol dm^{-3}), vanadium(V) (0.02 mol dm^{-3}), chromium(III) (0.03 mol dm^{-3}), manganese(II) (0.16 mol dm^{-3}), iron(II) (0.45 mol dm^{-3}) and iron(III)

(0.3 mol dm^{-3}) in 1.0 mol dm^{-3} hydrochloric acid was prepared and subjected to four stages of batch extractions (Aq. : Org. = 1 : 2) using 0.03 mol dm^{-3} H_2SbBP in chloroform as the extractant. Vanadium was then quantitatively recovered from the organic phase using 6.0 mol dm^{-3} HCl as the stripping agent. The typical results are shown in Table 3.5. It is clear from the results that vanadium was selectively extracted into the organic phase leaving behind all the other associated metal ions in the raffinate. Vanadium was then quantitatively recovered from the loaded organic phase using 6.0 mol dm^{-3} HCl as the stripping agent. Thus, these results clearly highlights that vanadium can be selectively recovered from the waste chloride liquors of titanium minerals process industry using H_2SbBP in chloroform as an extractant.

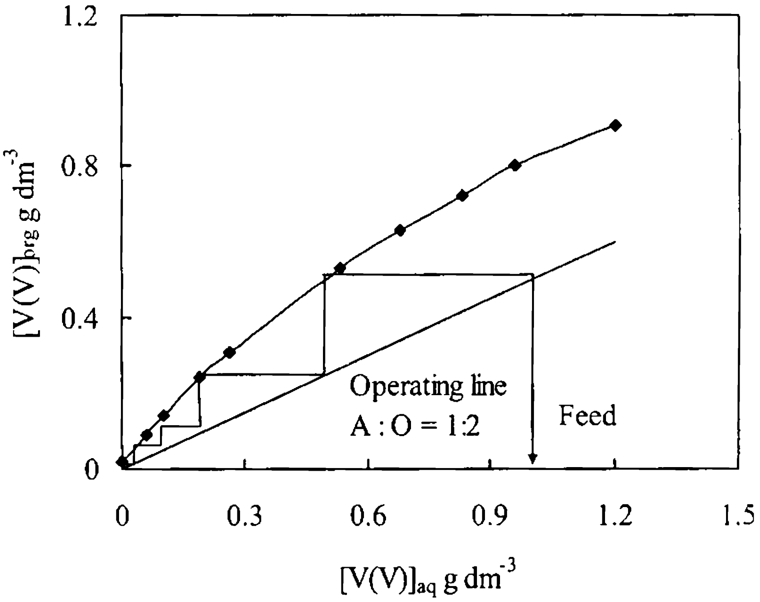


Figure 3.17. McCabe-Thiele plot for vanadium(V) extraction. Vanadium(V) = 1 g dm^{-3}, 1.0 mol dm^{-3} HCl, 0.03 mol dm^{-3} H_2SbBP.

The extraction behavior of vanadium(V) and other associated metal ions present in the waste chloride liquors of titanium minerals processing industry has been investigated as a function of HCl concentration using H_2SbBP (0.01 mol dm^{-3}) + TOPO (0.01 mol dm^{-3}) in chloroform as the extractant. It is clear from the results that the extraction of vanadium(V) moderately decreases with increase in HCl concentration from 0.2 to 2 mol dm^{-3} (Figure 3.18). The extraction of iron(III) also decreases with increase in HCl concentration and is negligible at about 2 mol dm^{-3} HCl concentration. Further, magnesium(II) aluminium(III), titanium(IV), chromium(III), manganese(II) and iron(III) were found to be not extracted under the present experimental conditions. It can be concluded from these results that by controlling the HCl concentration in the aqueous phase vanadium(V) can be selectively extracted and can be recovered from the titania waste chloride liquors by employing the mixed solvent system consisting of H_2SbBP and TOPO.

Table 3.5. Extraction and separation of vanadium(V) from synthetic titania waste chloride liquor

Metal ion	Feed (mol dm^{-3})	Raffinate (mol dm^{-3})	Strip liquor (mol dm^{-3})
Mg(II)	0.13	0.13	N. D.
Al(III)	0.03	0.03.	N. D.
Ti(IV)	0.02	0.02	N. D.
V(V)	0.02	N. D.	0.01
Cr(III)	0.03	0..03	N. D.
Mn(II)	0.07	0.07	N. D.
Fe(II)	0.45	0.45	N. D.
Fe(III)	0.35	0.35	N. D.

N. D. = Not detectable

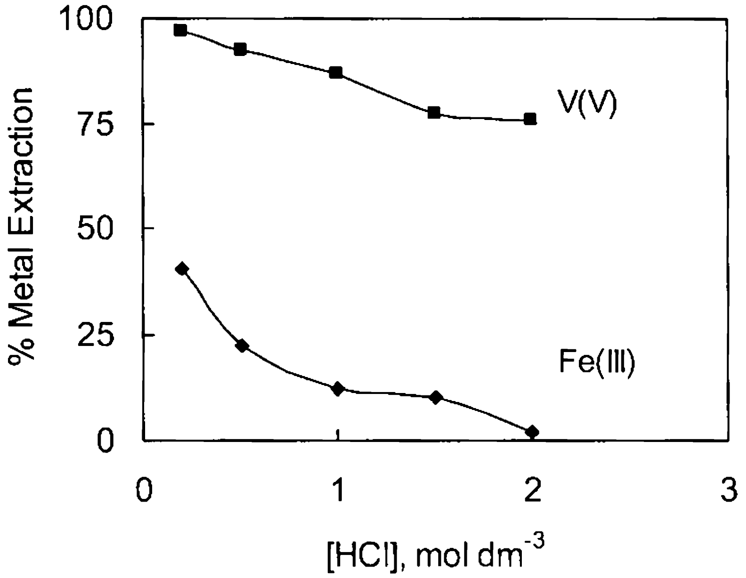


Figure 3.18. Percentage extraction of metal ions as a function of HCl concentration. Organic phase = H_2SbBP (0.01 mol dm^{-3}) + TOPO (0.01 mol dm^{-3}) in chloroform.

Part II

Preparation and Characterization of Solid Complexes of Oxovanadium with 4-Acylbis(1-phenyl-3-methyl-5-pyrazolones)

Characterization of Solid Complexes of Oxovanadium with 4-Acylbis(1-phenyl-3-methyl-5-pyrazolones)

VO(AdBP) (pH 7): m.p.: 257.8 °C; FT-IR (KBr) data ν (cm^{-1}): 1598, 1509, 968, 757; Mass spectrum: (m + 1) peak 523.12, 458.56, 328.88, 153.96 (Figure 3.19); Elemental analysis: Calc. for $C_{26}H_{24}N_4O_5V$: C 59.66, H 4.62, N 10.70%; Found: C 59.78, H 4.63, N 10.63%.

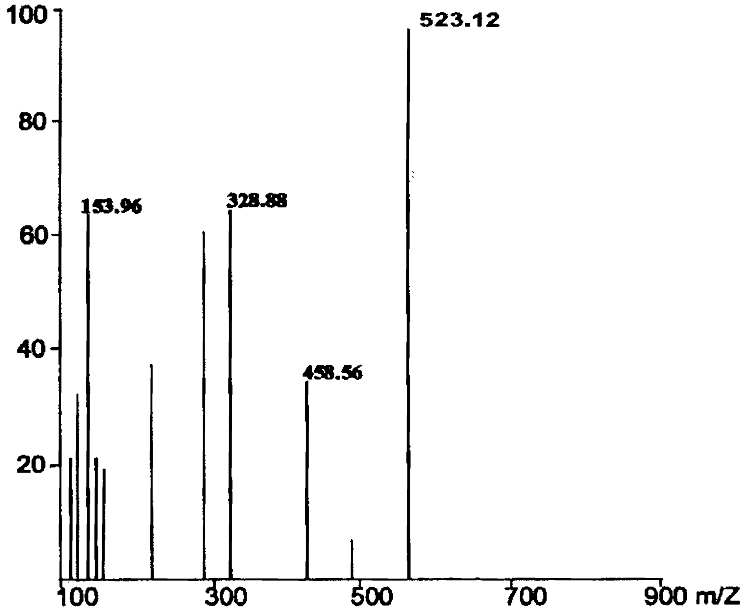


Figure 3.19. FAB-Mass spectrum of VO(AdBP) prepared at pH 7.

VO(AdBP) (pH 1): m.p.: 257.2 °C; FT-IR (KBr) data ν (cm^{-1}): 1598, 1509, 968, 757; Mass spectrum: (m + 1) peak 521.72, 291.43, 119.15 (Figure 3.20); Elemental analysis: Calc. for $C_{26}H_{24}N_4O_5V$: C 59.66, H 4.62, N 10.70%; Found: C 59.18, H 4.43, N 10.83%.

VO(SbBP) (pH 7): m.p.: 261.9 °C; FT-IR (KBr) data ν (cm^{-1}): 1603, 1511, 984, 761; Mass spectrum: (m + 1) peak 579.93, 515.15, 229.01, 201.03, 136.02 (Figure 3.21); Elemental analysis: Calc. for $C_{30}H_{32}N_4O_5V$: C 62.17, H 5.57, N 9.67%; Found: C 62.27, H 5.13, N 9.52%.

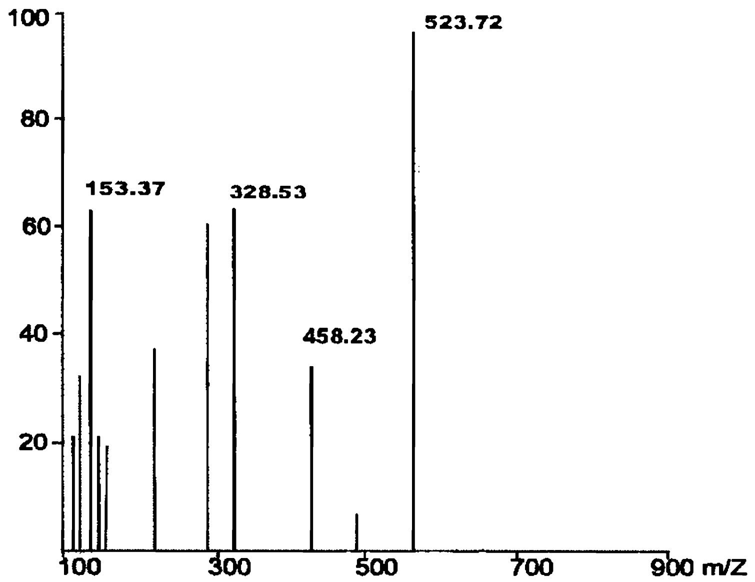


Figure 3.20. FAB-Mass spectrum of VO(AdBP) prepared at pH 1.

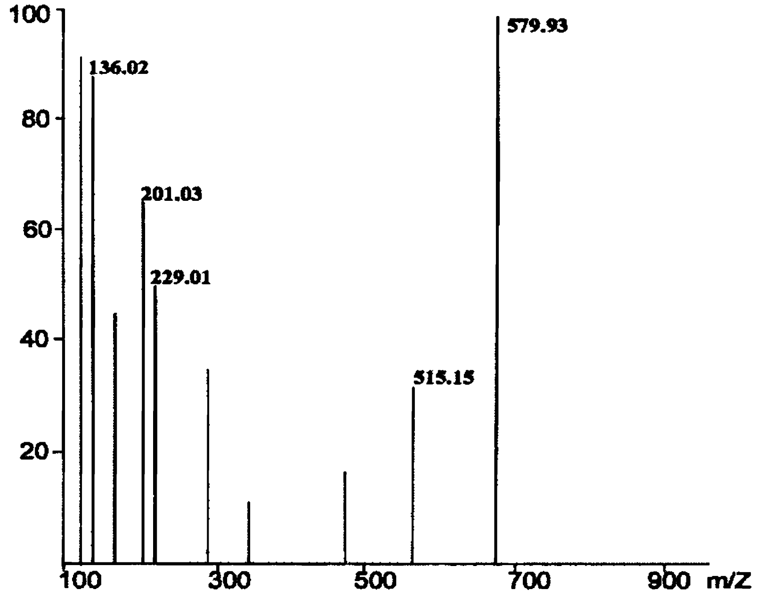


Figure 3.21. FAB-Mass spectrum of VO(SbBP) prepared at pH 7.

VO(SbBP) (pH 1): m.p.: 261.8 °C; FT-IR (KBr) data ν (cm^{-1}): 1603, 1511, 984, 761; Mass spectrum: (m + 1) peak 579.23, 515.47, 229.18, 201.64, 136.02 (Figure 3.22); Elemental analysis: Calc. for $C_{30}H_{32}N_4O_5V$: C 62.17, H 5.57, N 9.67%; Found: C 62.40, H 5.53, N 9.40%.

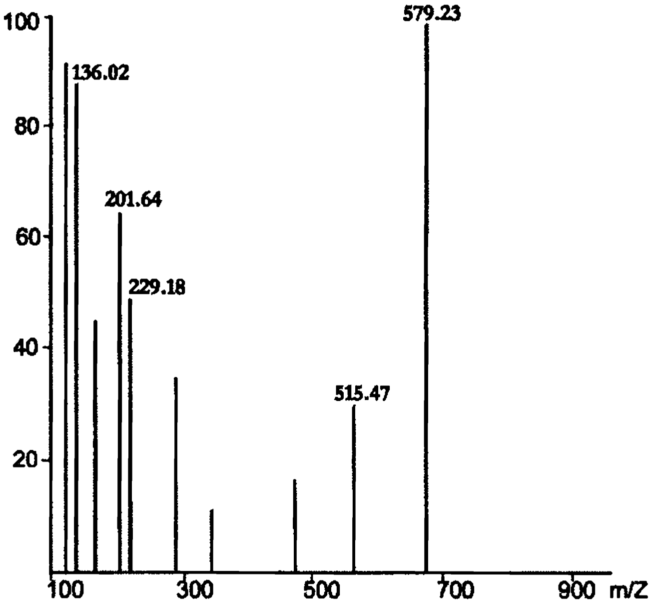


Figure 3.22. FAB-Mass spectrum of VO(SbBP) prepared at pH 1.

VO(DdBP) (pH 7): m.p.: 263.5 °C; FT-IR (KBr) data ν (cm^{-1}): 1608, 1519, 996, 763; Mass spectrum: (m + 1) peak 607.89, 542.96, 288.97, 135.99 (Figure 3.23); Elemental analysis: Calc. for $C_{36}H_{30}N_4O_5V$: C 61.74, H 5.96, N 8.75%; Found: C 61.34, H 5.91, N 8.95%.

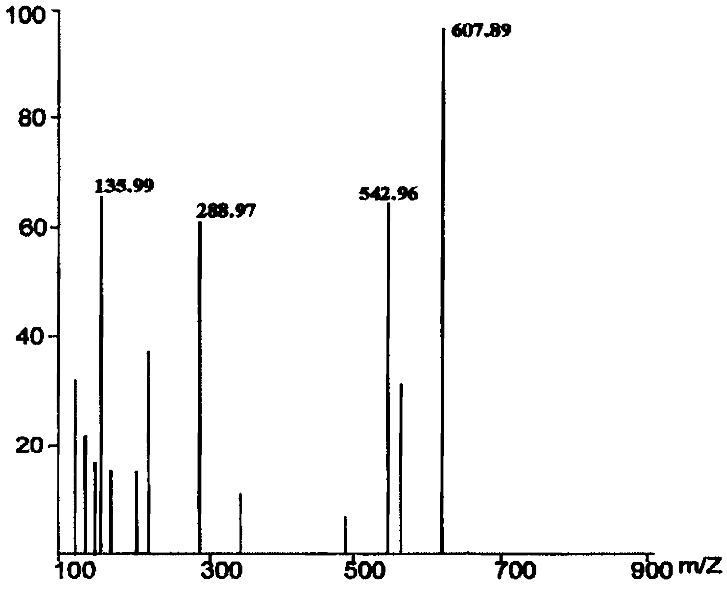


Figure 3.23. FAB-Mass spectrum of VO(DdBP) prepared at pH 7.

VO(DdBP) (pH 1): m.p.: 263.3 °C; FT-IR (KBr) data ν (cm^{-1}): 1608, 1519, 996, 763; Mass spectrum: (m + 1) peak 607.59,542.78, 288.61, 135.99 (Figure 3.24); Elemental analysis: Calc. for $C_{36}H_{30}N_4O_5V$: C 61.74, H 5.96, N 8.75%; Found: C 61.17, H 5.77, N 8.35%.

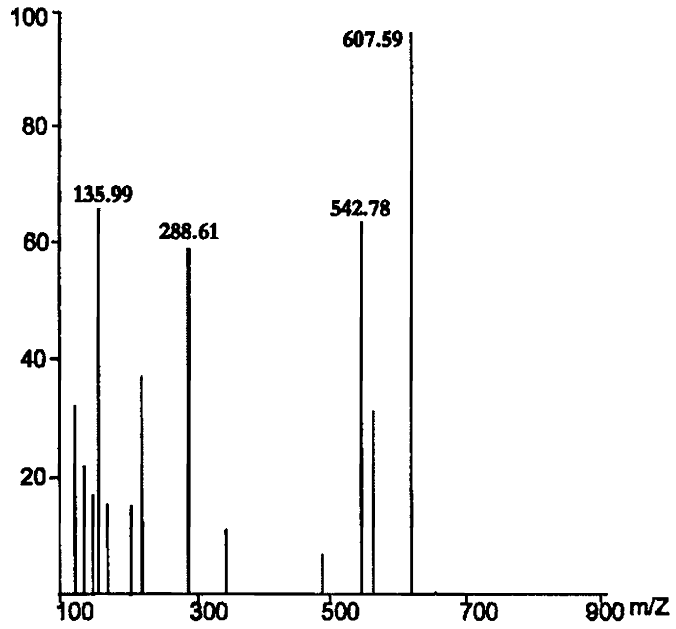


Figure 3.24. FAB-Mass spectrum of VO(DdBP) prepared at pH 1.

RESULTS AND DISCUSSION

Electrochemistry of 4-Acylbis(1-phenyl-3-methyl-5-pyrazolone)

In order to understand the redox chemistry of 4-acylbis(1-phenyl-3-methyl-5-pyrazolone), the electrochemical responses were recorded by cyclic voltammetry using platinum as working and SCE as reference electrodes. All the three ligands showed irreversible oxidation peaks, showing the formation of stable oxidized species of the respective ligands. The oxidation potentials are given in Table 3.6. All the ligands undergo oxidation at potential higher than that for the reduction of oxovanadium(V) to oxovanadium(IV) (~1 V) [Huhey et al. 1999], and thus the transfer of one electron is possible from the ligand to oxovanadium(V). The oxidation potentials of 4-acylbis(1-phenyl-3-methyl-5-pyrazolones) increases with increasing poly methylene chain length ($H_2DdBP > H_2SbBP > H_2AdBP$), due to the increase of electron density on the pyrazole moiety. The energies of the highest occupied molecular orbitals (HOMO) ε_{HOMO}, of these ligands were calculated from molecular modeling, which also suggests the order as $H_2DdBP > H_2SbBP > H_2AdBP$ (Table 3.6).

Table 3.6. Oxidation potentials of 4-acylbis(1-phenyl-3-methyl-5-pyrazolones) (E_p^{ox}) and energies ε_{HOMO} as obtained by molecular modeling calculations.

Ligand	E_p^{ox} eV	ε_{HOMO} eV
H_2AdBP	1.265	9.165
H_2SbBP	1.326	9.141
H_2DdBP	1.475	8.589

Formation of Free-radical Intermediates of 4-Acylbis(1-phenyl-3-methyl-5-pyrazolones)

From the cyclic voltammetric studies it is clear that 4-acylbis(1-phenyl-3-methyl-5-pyrazolones) transfer one electron to oxovanadium(V) and form a stable oxidized species. This is consistent with the earlier reports for 1-phenyl-3-methyl-4-aroyl-5-pyrazolones [Toropchina et al. 2003, Remya et al. 2007], where the formation of a stable oxidized species has been noticed. The formation of a free radical intermediate during the complexation process has been assessed by investigating the polymerization of acrylonitrile in the presence of oxovanadium(V) and 4-acylbis(1-phenyl-3-methyl-5-pyrazolones). As observed in the case of 1-phenyl-3-methyl-4-aroyl-5-pyrazolone no detectable polymerization was occurring in the absence of either 4-acylbis(1-phenyl-3-methyl-5-pyrazolones) or oxovanadium(V). This is an indirect evidence for the formation of a free radical intermediate during the complexation process of oxovanadium species with 4-acylbis(1-phenyl-3-methyl-5-pyrazolones). Thus, the reaction proceeds *via* the formation of a free radical intermediate by the transfer of an electron to oxovanadium(V) which undergoes a one-electron reduction as is evident from the electrochemical studies. The free-radical thus generated finally couples with the other end of the free radical from the same ligand and forms a stable dimeric species. The stable oxidized species formed from the ligands have been isolated from the filtrate of the complexing medium and characterized by IR, ^{1}H NMR (Figures 3.25-3.27) and ^{13}C NMR spectra (Figures 3.28 -3.30). In the ^{1}H NMR spectrum of the dimer, the δ values showed considerable shift from that of 4-acylbis(1-phenyl-3-methyl-5-pyrazolones), which indicates the formation of new species. Upon dimerization, the sp^2 hybridized (δ 110-140 ppm) carbons on the pyrazole moieties become an sp^3 hybridized one (δ 0-80 ppm), which can be clearly seen from the ^{13}C NMR spectra of dimers of various 4-acylbis(1-phenyl-3-methyl-5-pyrazolones). The FT-IR spectrum of the dimers showed two strong absorptions in the region 1670-1600 cm^{-1}, indicating the presence of two types of C=O groups.

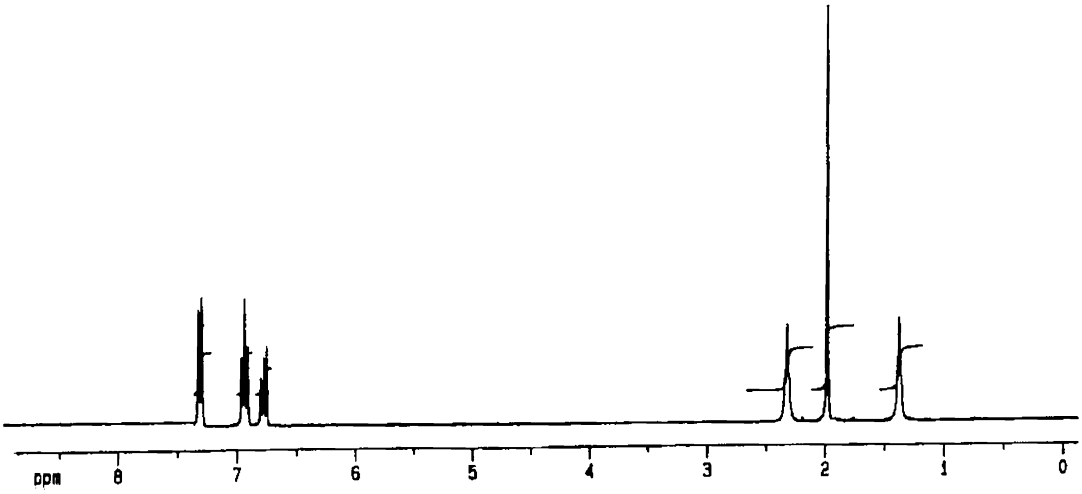


Figure 3.25. ^{1}H NMR spectrum of the dimer of 4-adipoylbis(1-phenyl-3-methyl-5-pyrazolone).

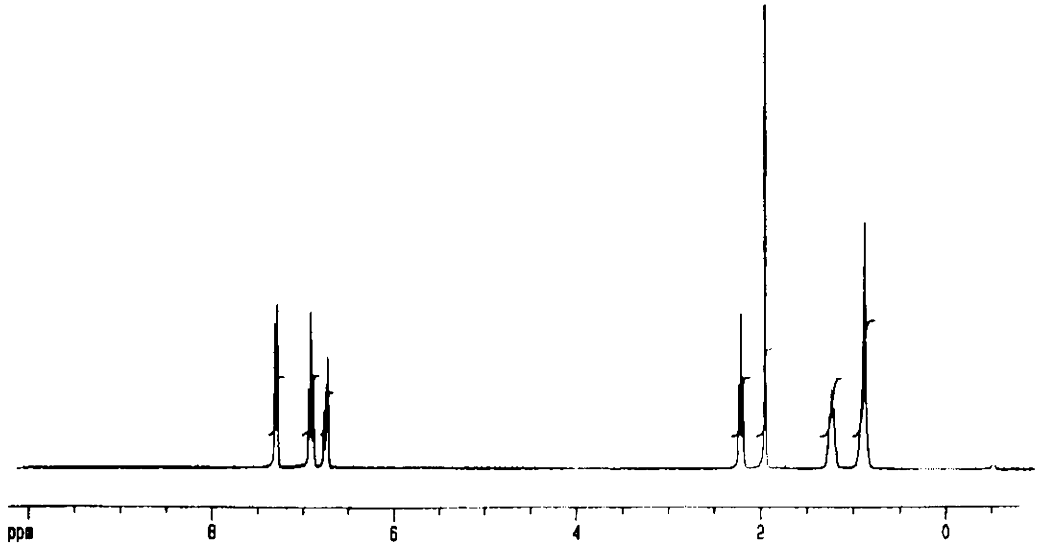


Figure 3.26. ^{1}H NMR spectrum of the dimer of 4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone).

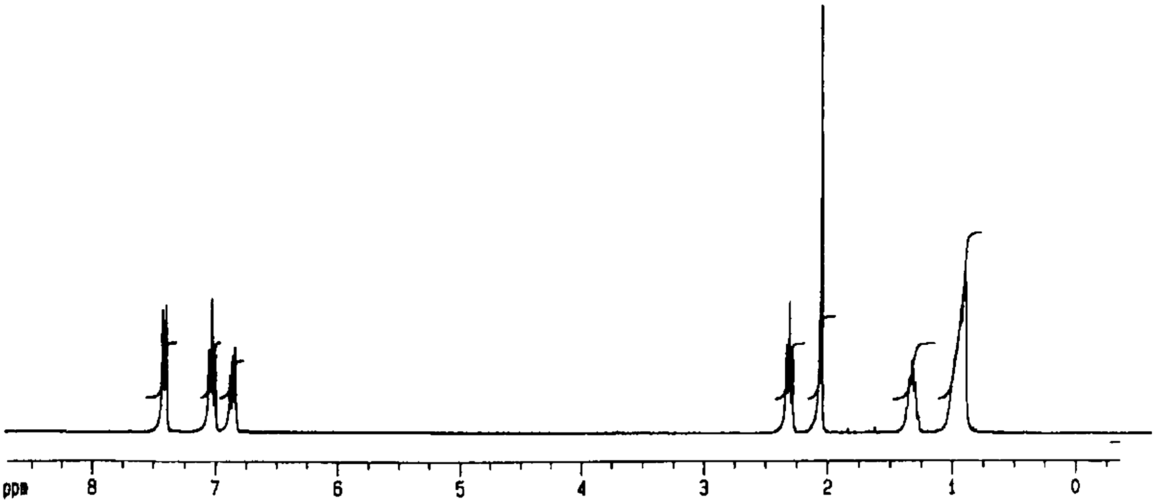


Figure 3.27. ^{1}H NMR spectrum of the dimer of 4-dodecandioylbis(1-phenyl-3-methyl-5-pyrazolone).

Stoichiometry

The metal to ligand stoichiometry, 2:3 was confirmed at pH 1 and 7 by analyzing both the filtrate of the complexing media and the resultant complexes formed.

4-acylbis(1-phenyl-3-methyl-5-pyrazolone) reduces aqueous oxovanadium(V) in both acidic and neutral media according to the following equation:

$$2VO_2^+ + 3H_2L \longrightarrow 2VOL + \text{Dimer} + 2H_2O + 2H^+$$

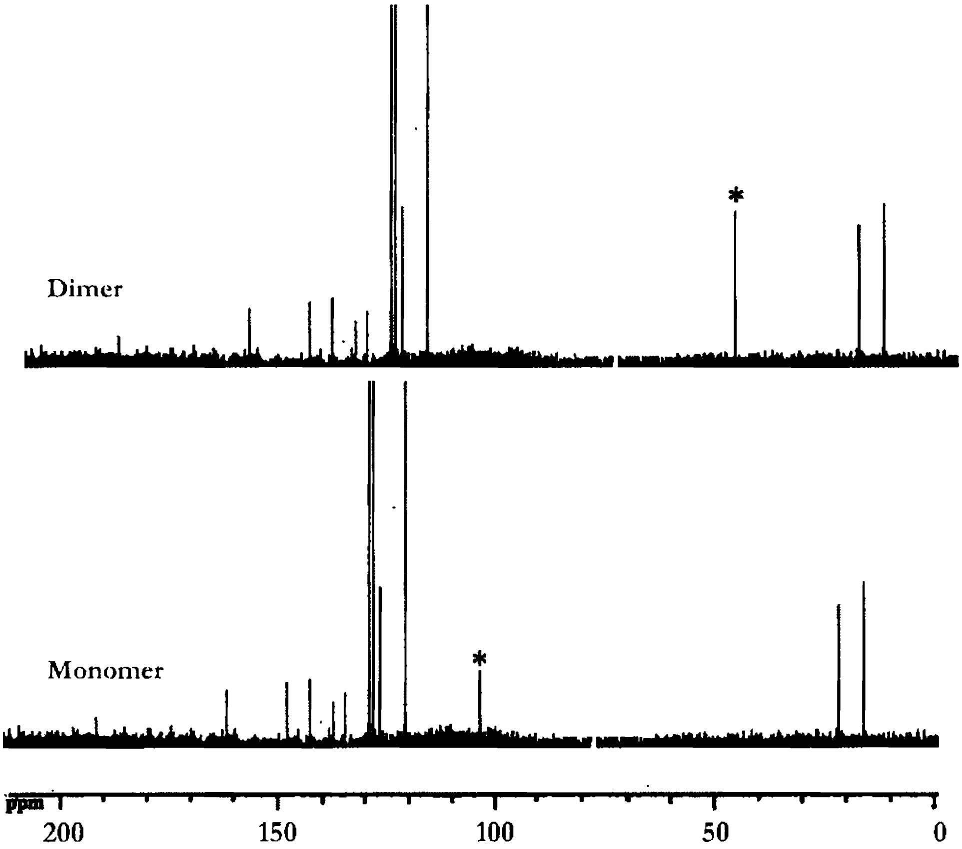


Figure 3.28. ^{13}C NMR spectrum of 4-adipoylbis(1-phenyl-3-methyl-5-pyrazolone) and its dimer.

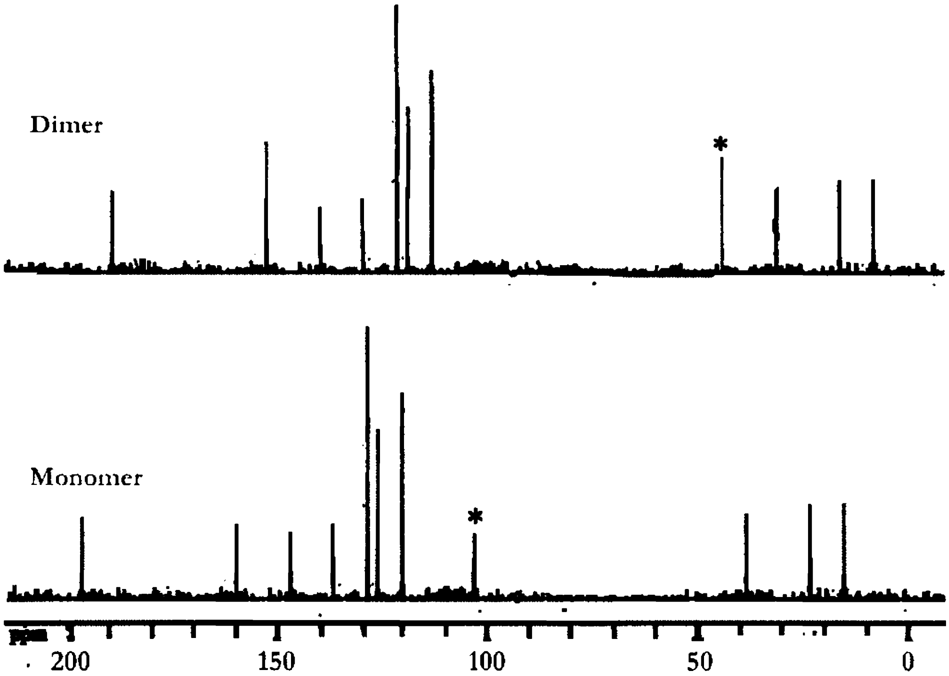


Figure 3.29. ^{13}C NMR spectrum of 4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone) and its dimer.

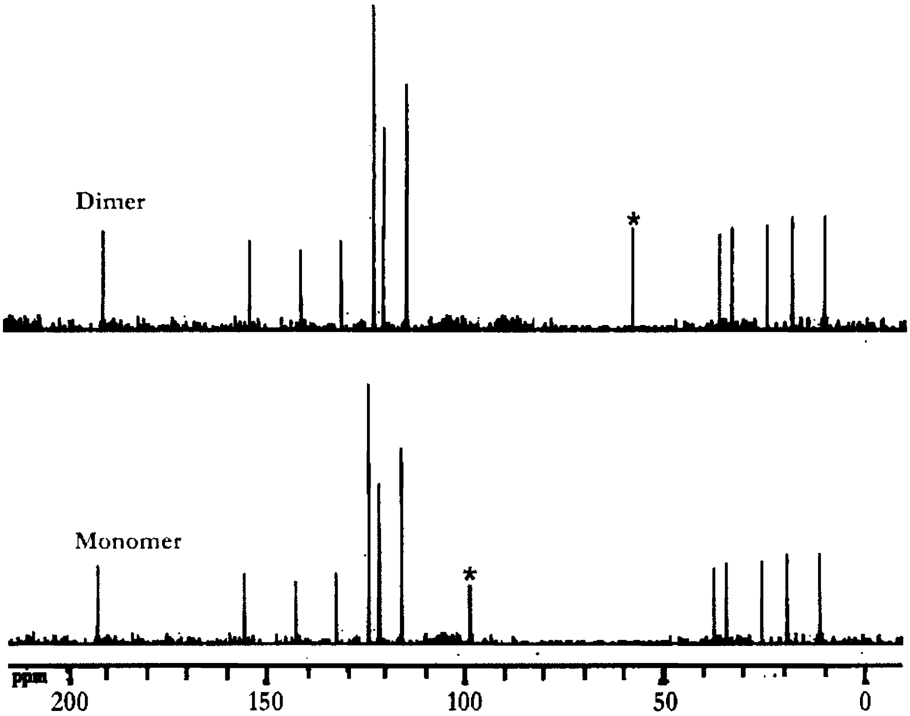
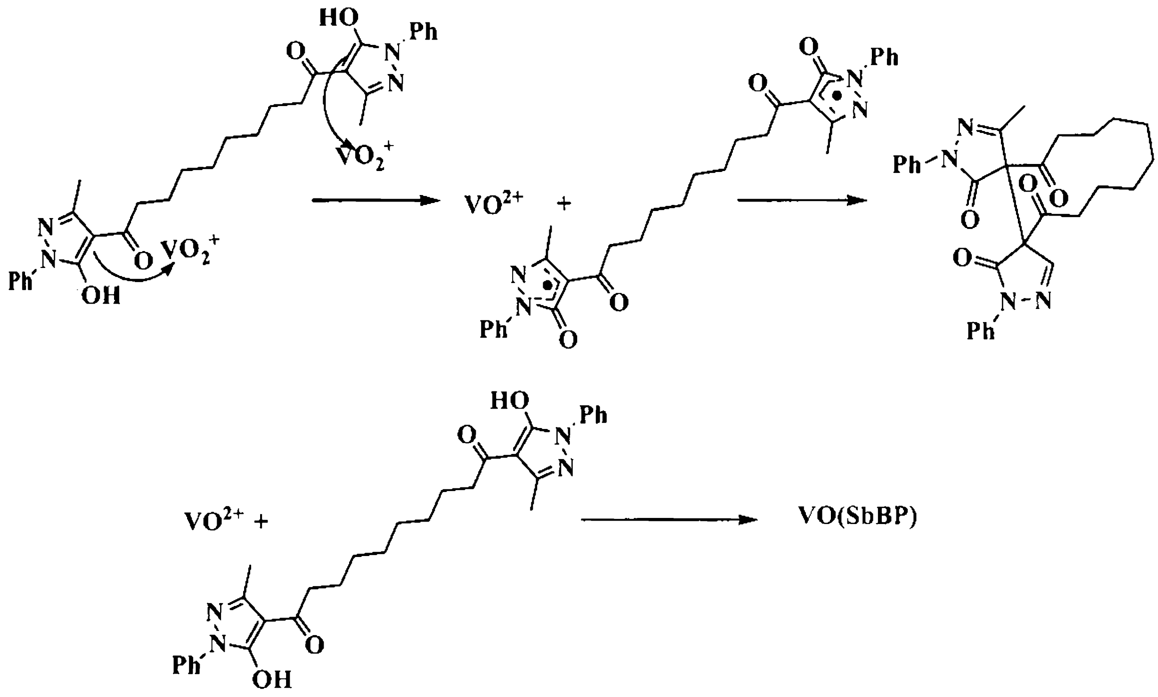


Figure 3.30. ^{13}C NMR spectrum of 4-dodecandioylbis(1-phenyl-3-methyl-5-pyrazolone) and its dimer.

Mechanism of Reduction of Oxovanadium(V) to Oxovanadium(IV) and Subsequent Complexation by 4-Acylbis(1-phenyl-3-methyl-5-pyrazolone)

Based on the above studies a detailed scheme for the reduction of oxovanadium(V) to oxovanadium(IV) and subsequent complexation can be expressed as:



Scheme 3.2. Reduction and complexation of oxovanadium(V) with 4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone).

Spectroscopic Characterization of Oxovanadium(IV) Complexes

The 1:1 metal-to-ligand ratio was obtained from elemental analyses and mass spectral studies of the complexes prepared at both acidic and neutral pH conditions. Further, these values correspond to oxovanadium(IV) species rather than oxovanadium(V) species.

Fourier-Transform Infrared Spectroscopy

The characteristic absorptions of acylpyrazolone ring, due to the stretching ν(C=O), ν(C=C) and ν(C=N) modes were observed at 1610-1590 cm^{-1} in the FT-IR spectra of VO(AdBP), VO(SbBP) and VO(DdBP). Further, these spectra displayed the stretching frequency attributable to ν(V=O) stretch at 968 cm^{-1}, 984 cm^{-1} and 996 cm^{-1}, respectively in VO(AdBP), VO(SbBP) and VO(DdBP). The broad absorptions due to coordinated H_2O in the complex, in the region 3000 – 3500 cm^{-1} were absent suggesting that no H_2O is present in the complexes.

Magnetic and EPR Measurements

The room temperature magnetic moments of the complexes, VO(AdBP), VO(SbBP) and VO(DdBP), prepared at both acidic and neutral conditions are given in Table 3.7. All the complexes show essentially paramagnetic behavior attributed to the d^1 species.

The X-band ESR spectra of these compounds at liquid nitrogen temperature, both solid state and dissolved in acetonitrile, showed the expected characteristic octet structure due to hyperfine interaction between the vanadium nucleus (^{51}V; I = 7/2) and the unpaired electron (Figure 3.31-3.33). It is clear from the EPR parameters of the complexes listed in Table 3.8 that the complexes have a slightly distorted square pyramidal geometry. The g-values lie in the 1.9-1.99 range and agree with the fact that when d-shell is less than half filled, the spin-orbit effect reduces g value from that of a free electron (2.0023). It can be concluded from the EPR spectral data all the complexes are typical mononuclear oxovanadium(IV) species.

Table 3.7. Magnetic moments of oxovanadium(IV) complexes of 4-acylbis(1-phenyl-3-methyl-5-pyrazolone).

Complex	Magnetic moment (B.M)
VO(AdBP) (pH 7)	1.841
VO(AdBP) (pH 1)	1.846
VO(SbBP) (pH 7)	1.821
VO(SbBP) (pH 1)	1.827
VO(DdBP) (pH 7)	1.791
VO(DdBP) (pH 1)	1.797

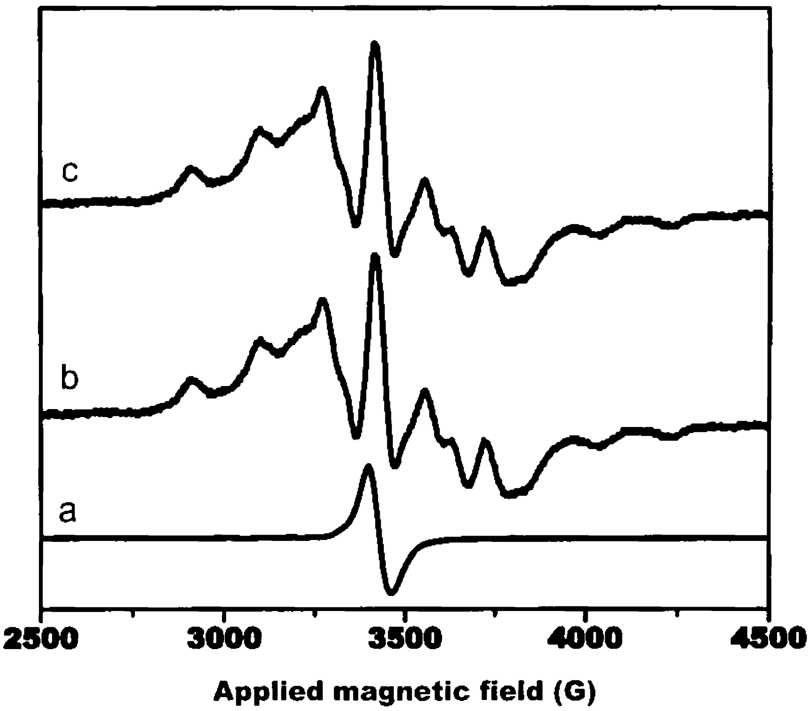


Figure 3.31. ESR spectra of VO(AdBP). a. At room temperature; b. Solid state at 77 K; c. Dissolved in acetonitrile at 77 K.

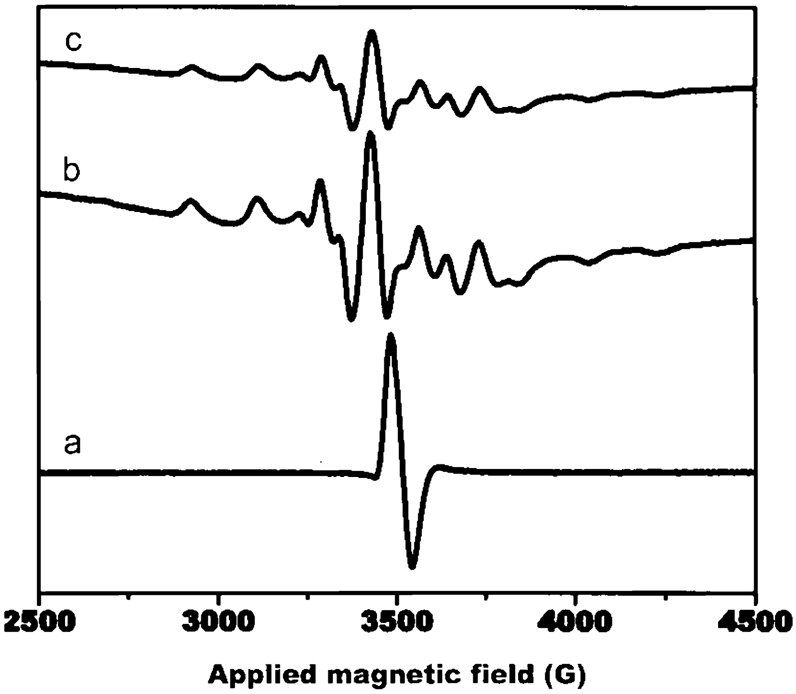


Figure 3.32. ESR spectra of VO(SbBP). a. At room temperature; b. Solid state at 77 K; c. Dissolved in acetonitrile at 77 K.

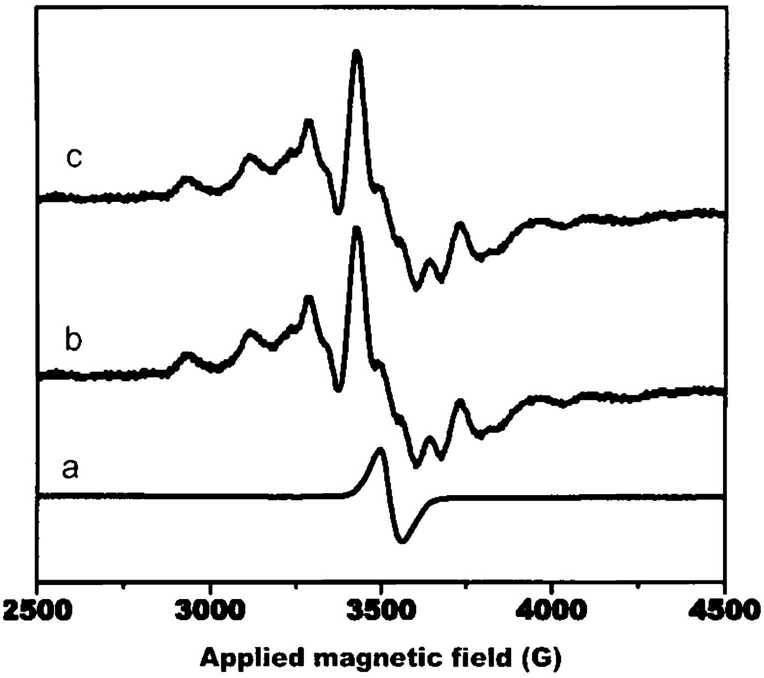


Figure 3.33. ESR spectra of VO(DdBP). a. At room temperature; b. Solid state at 77 K; c. Dissolved in acetonitrile at 77 K.

Table 3.8. ESR parameters of oxovanadium(IV) complexes of 4-acylbis(1-phenyl-3-methyl-5-pyrazolones).

Complex	T	g_x	g_y	g_z	A_x	A_y	A_z
VO(AdBP)	RT (S)	1.915			141.45		
	77 K (S)	1.931	1.923	1.892	105.75	128.81	189.83
	77 K (L)	1.933	1.924	1.897	105.78	128.28	189.14
VO(SbBP)	RT (S)	1.935			146.38		
	77 K (S)	1.951	1.946	1.912	109.42	139.73	190.01
	77 K (L)	1.949	1.942	1.917	109.78	139.78	190.14
VO(DdBP)	RT (S)	1.953			155.21		
	77 K (S)	1.968	1.961	1.931	118.68	154.51	192.43
	77 K (L)	1.964	1.959	1.932	118.15	154.86	192.44

RT – Room temperature S – Solid L – Dissolved in acetonitrile

Electronic Spectra

The electronic spectra of 4-acylbis(1-phenyl-3-methyl-5-pyrazolone) in acetonitrile solution, displayed the n-π* transition of the carbonyl group having an extinction coefficient (ε) of the order 10^5 mol^{-1} cm^{-1}. After complexation, these absorption bands are red shifted showing the involvement of the carbonyl group in complex formation with the metal ion (Table 3.9).

The UV-vis spectra of the complexes, VO(AdBP), VO(SbBP) and VO(DdBP), displayed four d-d transitions typical of an oxovanadium(IV) complex with a slightly distorted square pyramidal geometry (Figure 3.34). The four bands are weak, with extinction coefficients in the range 21-56 dm^3 mol^{-1} cm^{-1}, consistent with d-d origin of the transitions (Table 3.10). The coordination geometry of the complexes, which is a slightly distorted square pyramidal one, has significant effects on the absorption spectra. The slight distortion of geometry from the square pyramid, lowers the symmetry from C_{4v} and removes the degeneracy between the d_{xz} and d_{yz} orbitals. The observed absorption peaks correspond to the transitions from the d_{xy} orbital to d_{xz}, d_{yz}, $d_{x^2-y^2}$ and d_{z^2} in accordance with the reports on the transitions of oxovanadium(IV) complexes having distorted square pyramidal geometry.

Table 3.9. Electronic absorptions of 4-acylbis(1-phenyl-3-methyl-5-pyrazolones) and their oxovanadium(IV) complexes.

Ligand/Complex	n-π* nm
H_2AdBP	285
VO(AdBP)	290
H_2SbBP	286
VO(SbBP)	292
H_2DdBP	287
VO(DdBP)	294

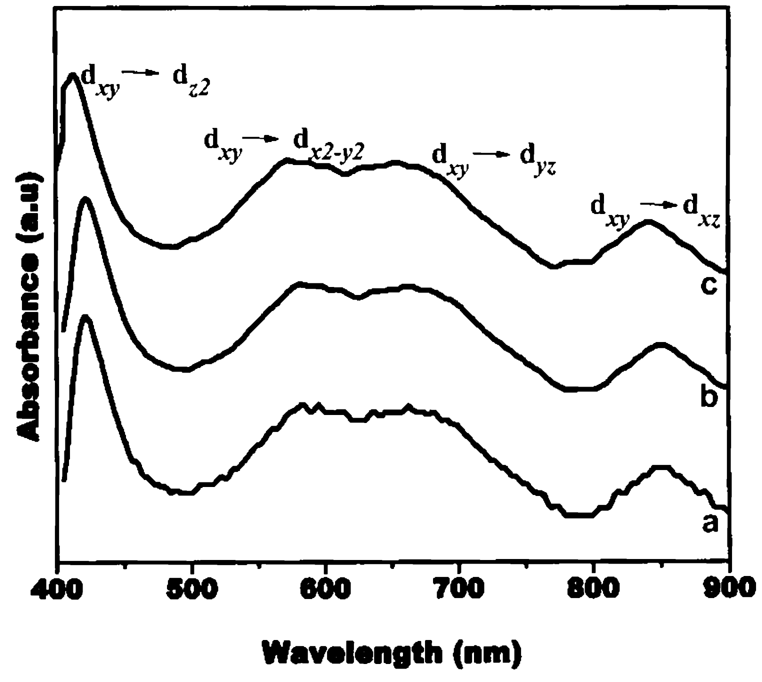


Figure 3.34. UV spectrum of VO(AdBP) (a), VO(SbBP) (b) and VO(DdBP) (c).

Table 3.10. d-d transitions in the oxovanadium(IV) complexes of various 4-acylbis(1-phenyl-3-methyl-5-pyrazolones).

Complex	d_{xy} - d_{xz} nm	d_{xy} - d_{yz} nm	d_{xy} - $d_{x^2-y^2}$ nm	d_{xy} - d_{z^2} nm
VO(AdBP)	854	673	594	424
VO(SbBP)	850	668	585	421
VO(DdBP)	841	656	572	410

Optimized Geometry of Distorted Square Pyramidal Oxovanadium(IV) Complex

The geometries of the oxovanadium(IV) complexes optimized at the B3LYP/6-31G* level of DFT are depicted in Figures 3.35-3.37. The most probable oxovanadium(IV) complex is considered as a square pyramidal geometry containing one ligand moiety. The four oxygen atoms from the two sides of the 4-acylbis(1-phenyl-3-methyl-5-pyrazolone) form the base and a VO double bond (1.580 Å in VO(AdBP), 1.577 Å in VO(SbBP) and 1.555 Å in VO(DdBP)) is pointing towards the apex of the pyramid. Two different V-O single bonds can be seen, a short one with pyrazolone oxygen (1.884 Å in VO(AdBP), 1.881 Å in VO(SbBP) and 1.878 Å in VO(DdBP)) and a long one with the acyl oxygen (1.923 Å in VO(AdBP), 1.917 Å in VO(SbBP) and 1.915 Å in VO(DdBP)).

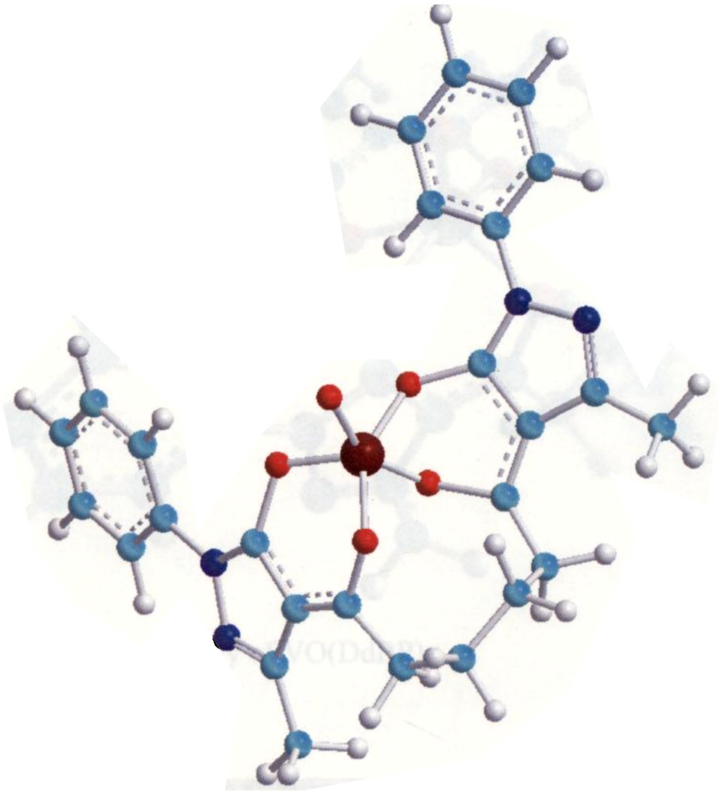


Figure 3.35. Optimized geometry of VO(AdBP).

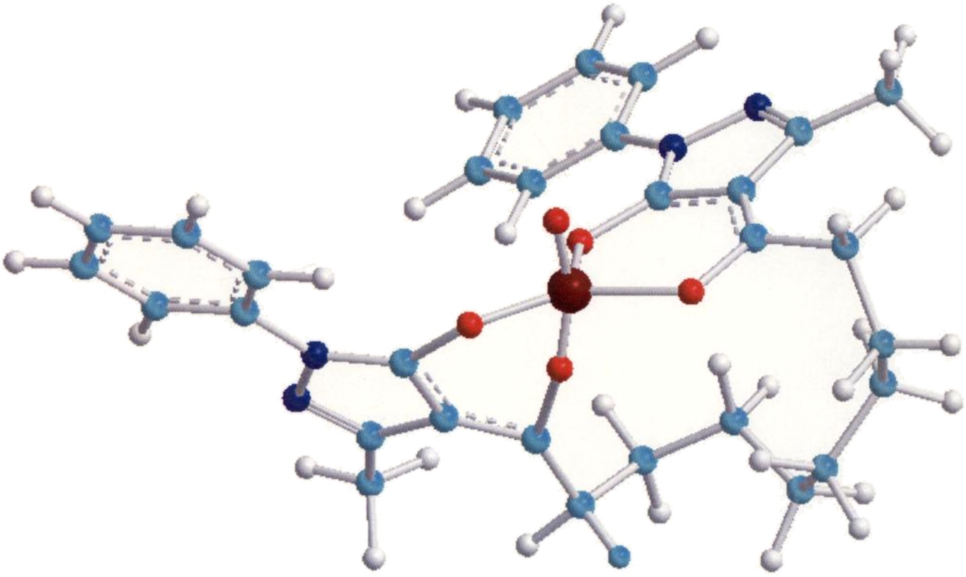


Figure 3.36. Optimized geometry of VO(SbBP).

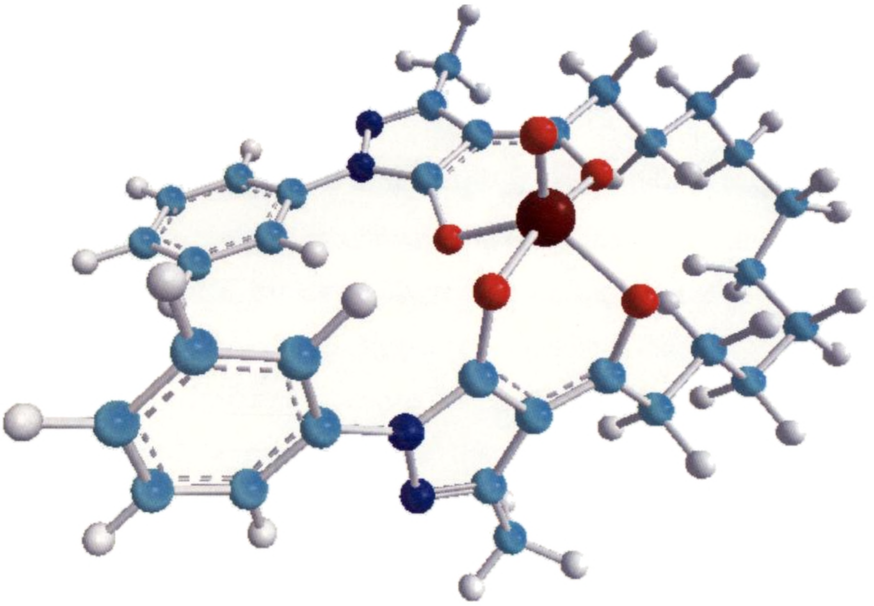


Figure 3.37. Optimized geometry of VO(DdBP).

Chapter IV

Summary and Conclusions

Vanadium is employed in a wide range of alloys in combination with iron, titanium, nickel, aluminium, chromium, and other metals for a diverse range of commercial applications extending from train rails, tool steels, catalysts, to the aerospace industry. The global supply of vanadium originates from primary sources such as ore feed stocks, concentrates, metallurgical slags, and petroleum residues. The solid wastes from the titanium minerals processing industry represent another potential source of vanadium. The more our economy recovers and recycles useful metals from its wastes, the less mining will be needed, and less environmental damage will result from waste disposal. Solvent extraction is one of the techniques being increasingly used for the recovery of vanadium from industrial waste streams.

It is clear from the literature review that various organophosphorus extractants, di-(2-ethylhexyl)phosphoric acid, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, bis(2,4,4-trimethylpentyl) phosphinic acid and tributyl phosphate have been used for the extraction of vanadium(V) from waste chloride liquors of titanium minerals processing industry. However, the major disadvantage with these reagents is poor selectivity for vanadium(V) over other associated multivalent metal ions. This prompted us to search for alternative solvent extraction reagents for the selective recovery of vanadium(V) from waste chloride liquors. Thus a commercially available reagent Cyanex 923 has been examined for the recovery of vanadium(V) from the titania waste chloride liquors. The extraction behavior of vanadium(V) and other multivalent metal ions present in the waste chloride liquors has been investigated using Cyanex 923 in kerosene as an extractant [Remya et al., 2003; Remya and Reddy 2004]. The results demonstrate that vanadium(V), titanium(IV) and iron(III) are extracted into the organic phase, leaving behind other metal ions in the raffinate. Thus this study clearly highlights that the selective extraction of vanadium(V) from the waste chloride liquors by employing Cyanex 923 is not feasible. This forms the basis for the synthesis of new heterocyclic ligands in the present work.

Para-substituted 4-aroyl derivatives of 1-phenyl-3-methyl-4-aroyl-5-pyrazolones, namely, 1-phenyl-3-methyl-4-(4-fluorobenzoyl)-5-pyrazolone (Hpmfbp) and 1-phenyl-3-methyl-4-(4-toluoyl)-5-pyrazolone (Hpmtp), by introducing both electron-withdrawing (-F) and electron-donating ($-CH_3$) groups, have been synthesized and characterized by various spectroscopic techniques. The synthesized ligands have been examined with regard to the extraction behavior of multivalent metal ions such as magnesium(II), aluminium(III), titanium(IV), vanadium(V), chromium(III), manganese(II), iron(II), and iron(III) that are present in the titania waste chloride liquors. For comparison, studies have also been carried out with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (Hpmbp). The extraction data has been analyzed by graphical methods. The equilibrium constant of the extracted complex has been calculated from the extraction data and correlated with their p*K*a values. Solid complexes of oxovanadium with 1-phenyl-3-methyl-4-aroyl-5-pyrazolones have been isolated and characterized by various spectroscopic techniques. The potential of these reagents for the selective extraction and separation of vanadium(V) from titania waste chloride liquors has also been assessed. The conclusions drawn from the above investigations are listed below:

(i) The results demonstrate that vanadium(V) and iron(III) are getting extracted into the organic phase from hydrochloric acid solutions. On the other hand, magnesium(II), aluminium(III), titanium(IV), chromium(III), manganese(II), and iron(II) were not extracted in to the organic phase when extracted with 4-aroyl-5-pyrazolones. However, the extraction of iron(III) is negligible at and above 1.5 mol dm^{-3} of HCl. Thus by controlling the hydrochloric acid concentration in the aqueous phase, vanadium(V) can be selectively extracted and separated from multivalent metal ions that are present in the titania wastes.

(ii) However, the solubility limitations of these ligands in industrially used diluents hinder the practical utility of these reagents. The impregnation of these ligands in suitable ion exchange resin particles could possibly address this problem, leading to some practical applications of these ligands for the recovery of vanadium(V) from waste chloride liquors.

(iii) The extraction efficiency of vanadium(V) and iron(III) with various 4-aroyl-5-pyrazolones follows the order: Hpmfbp > Hpmbp > Hpmtp. The substitution of an electron-withdrawing fluorine atom in the fourth position of the benzoyl moiety in Hpmbp molecule improves the extraction efficiency of these metal ions as compared to Hpmbp. On the other hand, the substitution of an electron-releasing group ($-CH_3$) diminishes the extraction efficiency as compared to Hpmbp.

(iv) Vanadium(V) and iron(III) were extracted into chloroform with 4-aroyl-5-pyrazolones (HX) as $VO_2X{\cdot}HX$ and FeX_3, respectively.

(v) Comparing the equilibrium constants of various 1-phenyl-3-methyl-4-aroyl-5-pyrazolones for the extraction of vanadium(V) and iron(III) with their pK_a values, it can be concluded that log equilibrium constant value increases as pK_a value decreases.

(vi) In FT-IR spectrum of the extracted complexes of vanadium(V) and iron(III) the carbonyl stretching frequencies have been shifted to lower wave numbers suggesting the involvement of carbonyl oxygens of Hpmfbp in bond formation with the metal ions.

(vii) Further, in the FT-IR spectrum of the loaded 1-phenyl-3-methyl-4-aroyl-5-pyrazolone (chloroform phase) with vanadium(V), a peak at 1620 cm^{-1} which corresponds to the free C=O also has been noticed, which indicates the existence of one free carbonyl group in one of the Hpmfbp molecules. The new absorption bands occurring at 962 and 920

cm^{-1} in the vanadium complex corresponds to the O=V=O stretching frequencies.

(viii) It is interesting to note that after a period of 3 h, the color of the vanadium(V) loaded organic phase gently changes from wine red to green. Further, the FT-IR spectrum of the vanadium loaded solvent phase shows only one V=O stretching frequency (984 cm^{-1}) corresponding to oxovanadium(IV) complex after 3h. This clearly indicates that oxovanadium(V) reduces to oxovanadium(IV) species with respect to time (after a period of 3 h).

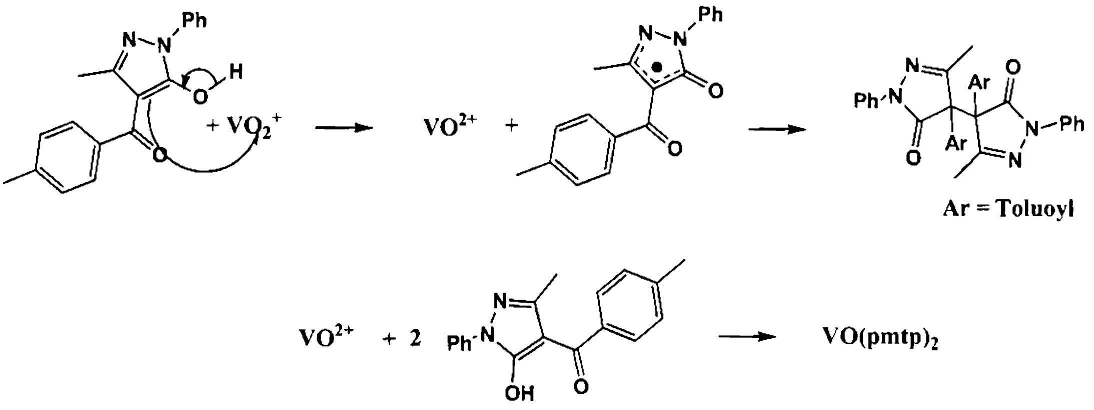
(ix) In order to understand more about the redox chemistry of oxovanadium(V) with 4-aroyl-5-pyrazolones, corresponding solid complexes have been isolated and characterized by various spectroscopic techniques. The reduction of oxovanadium(V) by 1-phenyl-3-methyl-4-aroyl-5-pyrazolone over the pH range of 1.0-7.0 has been assessed by cyclicvoltammetry, electron paramagnetic resonance spectroscopy, magnetic susceptibility, FT-IR, electronic spectroscopy, high-resolution mass spectroscopy and elemental analyses.

(x) The voltammogram of the 1-phenyl-3-methyl-4-aroyl-5-pyrazolones in acetonitrile solution (25 mM) have irreversible oxidation peaks at 1.37 (Hpmtp), 1.29 (Hpmbp) and 1.22 V (Hpmfbp), which indicates the formation of a stable oxidized species. Since the reduction of oxovanadium(V) to oxovanadium(IV) occurs at a potential (~1 V) lower than the oxidation potential of the ligands, the transfer of one electron is possible from the ligand to oxovanadium(V).

(xi) The reduction reaction proceeds by the transfer of one electron by 4-aroyl-5-pyrazolone to oxovanadium(V) *via* the formation of a free-radical intermediate, and subsequently the reduced oxovanadium(IV) species rapidly complexes with the available free ligand.

(xii) An indirect evidence for the generation of the free radical intermediate in the process of reduction has been confirmed by acrylonitrile polymerization. The free radical intermediates thus generated in the process couples to form a dimer, which also has been confirmed by various spectroscopic techniques.

(xiii) The reduction of oxovanadium(V) to oxovanadium(IV) and subsequent complexation can be expressed as:



(xiv) In the FT-IR spectra of $\mathrm{VO(pmtp)_2}$, $\mathrm{VO(pmbp)_2}$ and $\mathrm{VO(pmfbp)_2}$ there are strong absorption bands at 1570-1515 cm^{-1} assigned to the stretching ν(C=O), ν(C=C) and ν(C=N) modes of the acylpyrazolone ring coordinated to the metal centre. Further, the ν(V=O) stretch is observed at 960 cm^{-1}, 984 cm^{-1} and 996 cm^{-1} in $\mathrm{VO(pmtp)_2}$, $\mathrm{VO(pmbp)_2}$ and $\mathrm{VO(pmfbp)_2}$, respectively suggests the presence of oxovanadium(IV) in these complexes

(xv) The effective magnetic moments obtained for the prepared complexes (1.69 – 1.71 B.M) were in the normal range (1.57 - 2.1 B.M), typical of an oxovanadium(IV) complex.

(xvi) The X-band ESR spectra of the vanadium complexes, $\mathrm{VO(pmtp)_2}$, $\mathrm{VO(pmbp)_2}$ and $\mathrm{VO(pmfbp)_2}$, prepared at various conditions exhibit a set of eight line hyperfine spectra arising from the interaction of the unpaired electron of vanadium(IV) with the nuclear spin (7/2) which is also an indication of their monomeric structure. The order and magnitude of resonance parameters of the ESR spectra are typical of the spectra displayed by a slightly distorted square pyramidal oxovanadium(IV) complex with the unpaired electron in an orbital of mostly d_{xy} character.

(xvii) The electronic spectrum of $VO(pmtp)_2$ displays characteristic absorption peaks corresponding to the transitions from the d_{xy} orbital to d_{xz}, d_{yz}, d_{x2-y2} and $d_z{}^2$ of oxovanadium(IV) complexes with a distorted square pyramidal geometry.

(xviii) The slightly distorted square pyramidal geometry was obtained from the DFT calculation with the four oxygen atoms from the two pmtp$^-$ at the base and a VO double bond of length 1.584 Å pointing towards the apex of the pyramid.

(xix) It can be concluded from the spectral characterizations that all the complexes are typical mononuclear vanadium(IV) species, which in turn confirms that 1-phenyl-3-methyl-4-aroyl-5-pyrazolone interacts with aqueous vanadium(V) over the pH range of 1.0-7.0 and form oxovanadium(IV) complexes.

(xx) These reductions occur under physiological conditions and thus could be important for the reduction of vanadium(V)-containing coordination compounds used as insulin-enhancing agents for treatment of diabetics.

Various 4-acylbis(pyrazolones), namely, 4-adipoylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2AdBP, $n = 4$), 4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2SbBP, $n = 8$) and 4-dodecandioylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2DdBP, $n = 10$) have been synthesized and characterized by elemental analyses, IR and ^{1}H NMR spectral data. These ligands have been utilized in the investigations on the extraction behavior of the multivalent metal ions present in the waste liquors of titanium minerals processing industry in the presence and absence of neutral organophosphorus extractants (TOPO, TRPO, TBP and CMPO). The equilibrium constants of the extracted complexes have been deduced by non-linear regression analysis. The synergistic equilibrium constants have been correlated with the donor ability of the phosphoryl oxygen of the neutral organophosphorus extractants in terms of their ^{31}P NMR chemical shifts and their nitric acid uptake constant (K_H) values. The extracted complexes have been characterized by IR and ^{31}P NMR spectral data to understand the interactions of neutral organophosphorus extractants with metal chelates. The potential of these reagents as extractants for the separation and recovery of vanadium(V) from the waste chloride liquors of the titanium mineral processing industry has also been assessed. The conclusions from the above investigations are as follows:

(i) Vanadium(V) is selectively extracted into chloroform with 4-acylbis(1-phenyl-3-methyl-5-pyrazolone) as $VO_2(HX)$, where H_2X refers to the 4-acylbis(1-phenyl-3-methyl-5-pyrazolone). On the other hand, magnesium(II), aluminium(III), titanium(IV), chromium(III), manganese(II), iron(II), and iron(III), were not found to be extracted into the organic phase. Thus, these results clearly highlight that vanadium can be selectively recovered from the waste chloride liquors of titanium minerals process industry using 4-acylbis(1-phenyl-3-methyl-5-pyrazolone in chloroform as an extractant.

(ii) 4-Acylbis(pyrazolones) showed an initial increase in the extraction efficiency of vanadium(V) with increasing polymethylene chain length, $-(CH_2)_n-$, from $n = 4$ to 8 and thereafter a decreasing trend, for $n = 10$ due to steric effects. The $K_{ex,V(V)}$ values of various 4-acylbispyrazolone derivatives follow the order: $H_2SbBP > H_2DdBP > H_2AdBP$. The extraction efficiency of 4-acylbispyrazolones is determined by the hydrophobicity of the complex formed and the pK_a of the ligand

($pK_{aH2AdBP} = 4.41$; $pK_{aH2SbBP} = 4.78$; $pK_{aH2DdBP} = 4.9$) ie., K_{ex} increases with increase in hydrophobicity and decrease in pK_a value. Hydrophobicity of the complexes and pK_a increase as chain length increases. Hence the most favorable chain length for the formation of a stable complex is $n = 8$.

(iii) The addition of a neutral organophosphorus extractant to the vanadium(V)-chelate system improves the extraction efficiency.

(iv) The complexation strength of vanadium(V) with neutral organophosphorus extractants follows the order: TOPO > TRPO > CMPO > TBP.

(v) The Log $K_{syn,1}$ values of vanadium(V) increase linearly with increase in $\delta(^{31}P)$ NMR chemical shift of the neutral O-bearing organophosphorus extractant. However, CMPO was found to deviate from linearity. It may be due to the bidentate nature of CMPO in the complex formation with VO_2^- ion as is also evident from the IR spectral data, where both P=O and C=O stretching frequencies of CMPO have shifted to lower wave numbers, indicating the involvement of oxygen atoms of both carbonyl and phosphoryl groups in complexation.

(vi) In the FT-IR spectra of the vanadium(V) complexes extracted in to chloroform phase, the carbonyl stretching frequencies (1627 cm^{-1} in H_2AdBP, 1620 cm^{-1} in H_2SbBP and 1618 cm^{-1} in H_2DdBP) were shifted to lower frequencies (1600 cm^{-1} in VO_2HAdBP, 1600 cm^{-1} in VO_2HSbBP and 1597 cm^{-1} in VO_2HDdBP). This suggests that the carbonyl group in the 4-acylbis(1-phenyl-3-methyl-5-pyrazolone) is involved in the complex formation with the metal ion.

(vii) Further, new absorption bands corresponding to the O=V=O stretching of vanadium(V) were appeared around 964, 906 (VO_2HAdBP), 965, 911 (VO_2HSbBP) and 970, 915 cm^{-1} (VO_2HDdBP), indicating that the vanadium exists as oxovanadium(V) species in the extracted complexes in the chloroform phase.

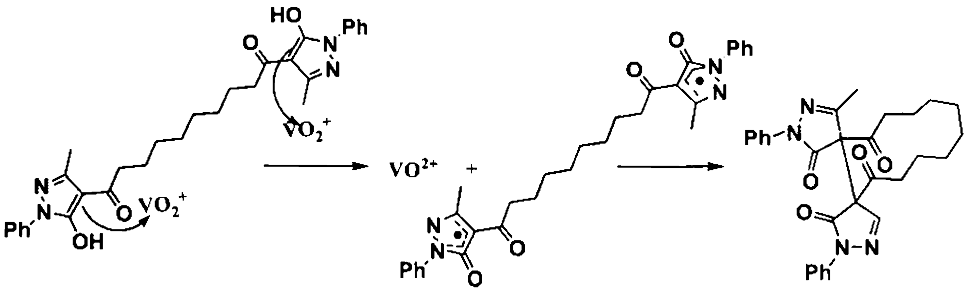
(viii) With respect to time (> 3h) the color of the oxovanadium(V) loaded organic phase has changed from wine red to green, suggesting the reduction of the oxovanadium(V) to oxovanadium(IV). This has been ascertained by IR spectral data of the extracted complex, where only one V=O stretch was observed.

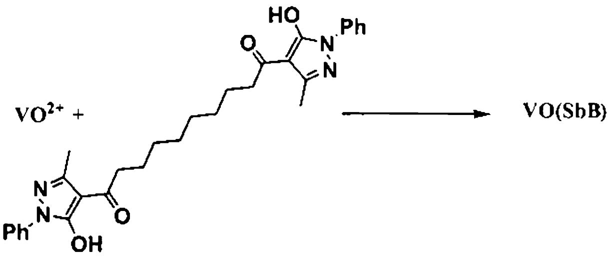
(ix) In order to understand more about coordination chemistry of oxovanadium complex with 4-acylbis(pyrazolones), solid complexes of vanadium with various 4-acylbis(pyrazolones) have been prepared at both acidic and neutral pH conditions characterized using various spectroscopic techniques.

(x) In order to understand the redox chemistry of 4-acylbis(1-phenyl-3-methyl-5-pyrazolone), the electrochemical responses were recorded by cyclic voltammetry. All the three ligands showed irreversible oxidation peaks, showing the formation of stable oxidized species of the respective ligands. Further, the ligands undergo oxidation at potentials higher than that for the reduction of oxovanadium(V) to oxovanadium(IV) (~1 V), the transfer of one electron is possible from the ligand to oxovanadium(V).

(xi) The formation of a free radical intermediate during the complexation process has been assessed by investigating the polymerization of acrylonitrile in the presence of oxovanadium(V) and 4-acylbis(1-phenyl-3-methyl-5-pyrazolones). The free radical intermediates thus generated in the process couples to form a dimer, which also has been confirmed by various spectroscopic techniques.

(xii) The reduction of oxovanadium(V) to oxovanadium(IV) and subsequent complexation can be expressed as:





(xiii) In the FT-IR spectra of VO(AdBP), VO(SbBP) and VO(DdBP), the stretching frequency attributable to v(V=O) stretch have been observed at 968 cm^{-1}, 984 cm^{-1} and 996 cm^{-1}, respectively.

(xiv) The room-temperature magnetic moments of the complexes, VO(AdBP), VO(SbBP) and VO(DdBP), prepared at both acidic and neutral conditions show paramagnetic behaviour attributed to the d^{1} species.

(xv) The EPR parameters of the complexes VO(AdBP), VO(SbBP) and VO(DdBP) suggest a slightly distorted square pyramidal geometry.

(xvi) The UV-vis spectra of the complexes, VO(AdBP), VO(SbBP) and VO(DdBP), displayed four d-d transitions typical of an oxovanadium(IV) complex with a slightly distorted square pyramidal geometry.

(xvii) The geometries of the oxovanadium(IV) complexes of 4-acylbis(pyrazolones) have been optimized at the B3LYP/6-31G* level of DFT.

(xviii) All the spectral data obtained confirms that the complex formed is an oxovanadium(IV) complex, 4-acylbis(1-phenyl-3-methyl-5-pyrazolones) reduces oxovanadium(V) to oxovanadium(IV) at both acidic and neutral pH conditions and rapidly forms an oxovanadium(IV) complex.

(xix) Thus synthesized oxovandium(IV) complexes with various 4-acylbis(1-phenyl-3-methyl-5-pyrazolones) may also find potential applications as therapeutic agents for diabetes.

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