http://www.e-journals.in
DOI:10.7598/cst2014.684

Chemical Science Transactions
2014, **3(1),** 181-186

RESEARCH ARTICLE

Characterization and Effects of the pH on the Oxidation Potentials of Oxovanadium(IV)-Citrate Complex

VED PRAKASH

Shriram Institute for Industrial Research, Delhi-110007, India
ved.chem@gmail.com

Received 16 July 2013 / Accepted 30 August 2013

Abstract: The electrochemical behavior of binuclear oxovanadium complex with citric acid has been studied at a glassy carbon working electrode (GCE) in aqueous 0.1 M $NaClO_4$ as a supporting electrolyte at pH 5.9 and 8.0. It was found that $[VO(Cit.)]_2.6H_2O$ complex is irreversibly oxidized ($VO^{2+/3+}$) with anodic peak potential, Epa=+899 mV to +1260 mV *vs.* Ag/AgCl for scan rate 10 to 500 mVs^{-1}. It should be mentioned that dependence of Ipa on $\nu^{1/2}$ is linear without any intercept, suggesting that the anodic process is diffusion controlled. It is observed that the oxidation of the complex, $[VO(Cit.)]_2.6H_2O$ becomes more difficult with increasing pH. IR bands at 934 cm^{-1} indicating the presence of oxovanadium(IV)complex. The title complex shows two absorption peaks, one in UV region at 300 nm and second peak at 567 nm in visible region in their electronic absorption spectra.

Keywords: Citric acid, Binuclear oxovanadium(IV)complex, Cyclic voltammetery, IR spectroscopy, UV-Visible spectroscopy

Introduction

In the form of two predominant oxidation states, V(IV) and V(V), vanadium is thought to exert its influence by interacting with a plethora of molecules in biological fluids. Such molecules include both high molecular mass (*e.g.* proteins) as well as low molecular mass (*e.g.* organic acids, amino acid *etc*.) ligands. Among the potential low molecular mass binders found in biological fluids such as human plasma, the tricarboxylic acid, citric acid, is prevalent[1a,1b]. Its abundance in blood plasma, at concentrations reaching 0.1 mM, enables it to promote aqueous chemistries with different metal ions, including vanadium, thereby increasing their solubility and potential bioavailability. Furthermore, depending on the redox conditions prevailing at various intracellular and extracellular sites in human fluids, citric acid has the potential to develop its interactive chemistry with vanadium at either oxidation state (IV or V). Therefore, a rich vanadium-citric acid chemistry is expected to arise in biologically relevant media, numerous aspects of which remain unexplored[2].

Citric acid is an important compound in biological processes. For example, citrates occur at 0.3 wt% in teeth and bone. They regulate some fundamental physiological processes and are intermediates in carbohydrate metabolism, *e.g.* in the "Krebs cycle"[3a]. Vanadium complexes are used as restriction enzymes to break the simple nucleotides and their polymers *i.e.*, DNA and RNA and also used as anticancer drugs[3b]. Citric acid, acting as a tetradentate ligand, readily forms polynuclear complexes with numerous metal ions. Citric acid under different experimental conditions directs the metal atoms to different oxidation states[3c].

Despite the fact, though, the synthetically isolated V(IV,V) complexes with various ligands are known, detailed investigation in to the possible inter-relationships among vanadium(IV,V)-citrate synthetic examples, through the study of their systematic pH-dependent synthesis and exploration of their chemical properties in solution and solid state, were limited[4].

This ionic complex $[VO(Cit.)]_2^{4-}$ is first example of an edge-sharing octahedral oxovanadium(IV) dimer that exhibits a ferromagnetic interaction between the metal centers and has anti-coplanar configuration[6]. The structure of citric acid ligand is given in Figure 1.

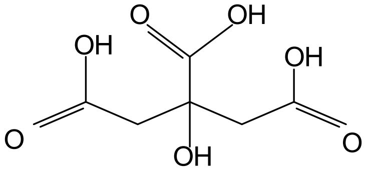

Figure 1.Structure of citric acid

In this paper we report the cyclic voltammetric and spectral behaviour of title complex.

Experimental

The cyclic voltammetric investigation was carried out with a BAS Electrochemical System Model EPSILON instrument having an electrochemical cell with a three electrode system. The working electrode was glassy carbon, platinum wire as an auxiliary electrode and Ag/AgCl as reference electrode. All the cyclic voltammetry experiments were done in an inert atmosphere of nitrogen achieved by purging the cell solution with pure nitrogen gas (99.99%) for about 20 min. An inert atmosphere of nitrogen gas was also maintained over the cell solution during recording of the voltammograms. Double distilled water was used as a solvent.

Citric acid, $VOSO_4.H_2O$ and $NaClO_4$ are received from Sigma-Aldrich Chemicals Pvt. Ltd., $NaClO_4$ was used as a supporting electrolyte. The pH of solution is raised by aqueous solution of NaOH. The pH of solution was measured by ICON INDIA DIGITAL pH METER. All the experiments were performed at 25±0.1 °C. The IR spectra of dioxovanadium complex were carried out in IR spectrophotometer model FTLA-2000 by preparing palates with potassium bromide, between 4000-400 cm^{-1} ranges. Electronic absorption spectra of the complexes have been recorded in water at room temperature by Perkin-Elmer UV-Visible spectrophotometer Model Lambda-35.

Preparation of complex

The oxovanadium(IV) complex, $[VO(cit.)]_2.6H_2O$ was synthesized based on the previously published procedure[6].

Results and Discussion

Electrochemical investigation

The cyclic voltammetric behavior of 2 mM binuclear oxovandium(IV) complex, $[VO(cit.)]_2.6H_2O$ has been investigated at pH 5.9 and 8.0 at a glassy carbon working electrode (GCE) in aqueous medium containing 0.1 M $NaClO_4$ as a supporting electrolyte. A positive scan initiated at 0.0V in the potential range from -1000mV to +1300mV *vs.* Ag/AgCl reveals a totally irreversible oxidation peak, at $Ep_{a} =$ 953 mV at scan rate 50 mVs^{-1} (Figure 2) and in the reverse scan no cathodic peak is observed up to -1000 mV. Similar behavior is also observed at pH 8.0. The oxidation peak potential shifts positively with increasing scan rate, showing that the oxidation of complex becomes more difficult with increasing scan rate (Figure 3 and 4) and also with increasing pH (Figure 5). A plot of Ipa *vs.*, square root of the scan rate ($\nu^{1/2}$) gives a straight line passing through origin, suggesting that the anodic process is diffusion-controlled[5] (Figure 6).

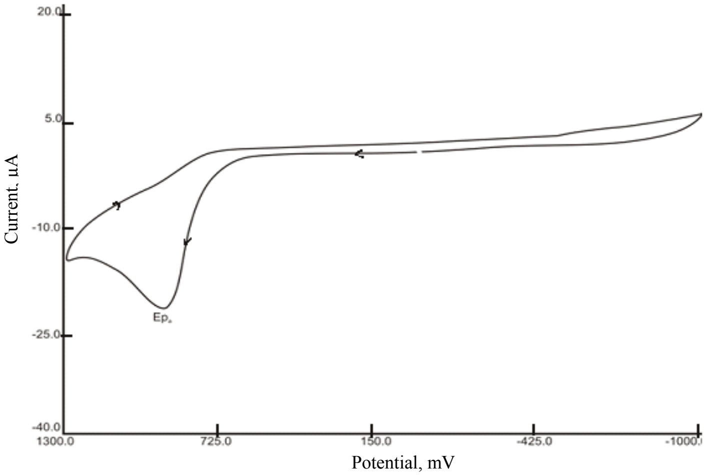

Figure 2. Cyclic voltammogram of 2 mM $K_4[VO(Cit.]_2.6H_2O$ in aqueous 0.1 M $NaClO_4$ at pH 5.9 (ν = 50 mVs-1).

Table 1. CV data for 4 mM $[VO(cit.)]_2.6H_2O$ in aqueous 0.1 M $NaClO_4$

	pH			
	5.9		8.0	
Scan rate mVs^{-1}	Epa/mV	Ipa/µA	Epa/mV	Ipa/µA
10	899	4.0	1141	9.4
25	934	10.8	1210	14.4
50	953	18.0	1260	20.6
100	992	24.4	-	-
200	1020	31.0	-	-
300	1045	38.0	-	-
400	1070	43.7	-	-
500	1090	48.6	-	-

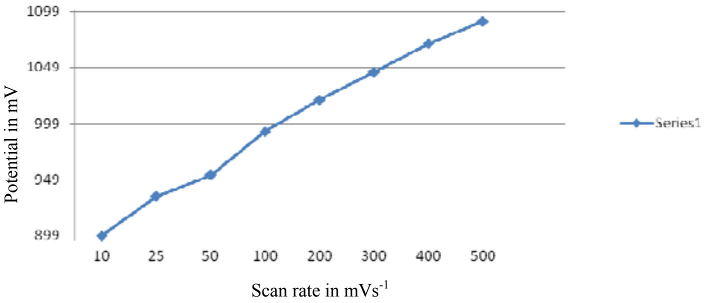

Figure 3. Positive shifts of potentials with respect to scan rate at pH 5.9

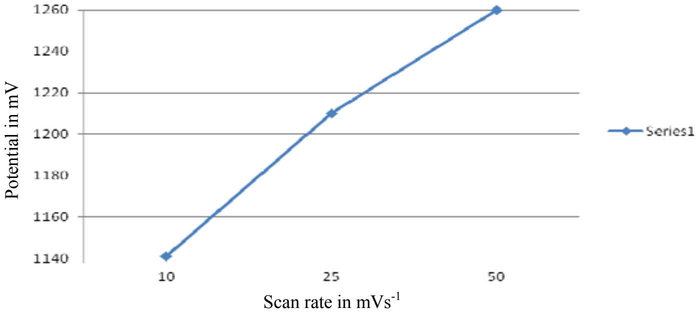

Figure 4. Postive shifts of potentials with respect to scan rates at pH 8.0

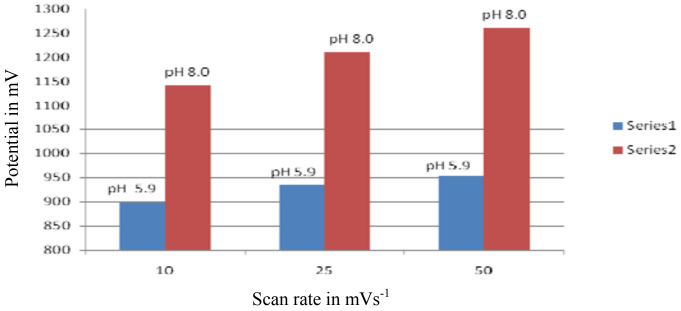

Figure 5. Effect of the pH on the oxidation potentials

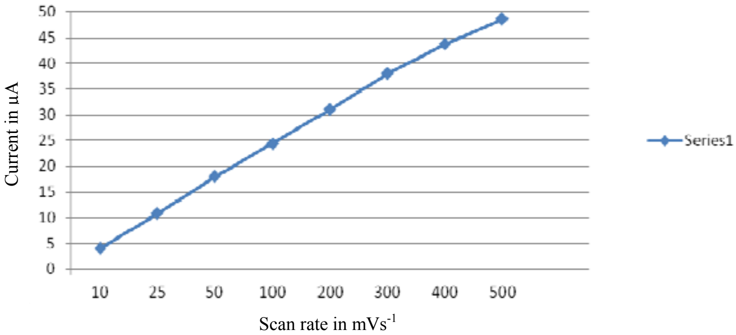

Figure 6. Plot of current *vs.* square root of the scan rate (**$v^{1/2}$**) at pH 5.9

IR spectral studies

Solid state properties of the oxo-vanadium(IV) complex were examined by infrared spectroscopy. For complex [VO(Citrate)]$_2$.6H$_2$O the characteristic υ(V=O) stretching at 934 cm^{-1} was observed, as reported for other oxovanadium(IV) derivatives[7].

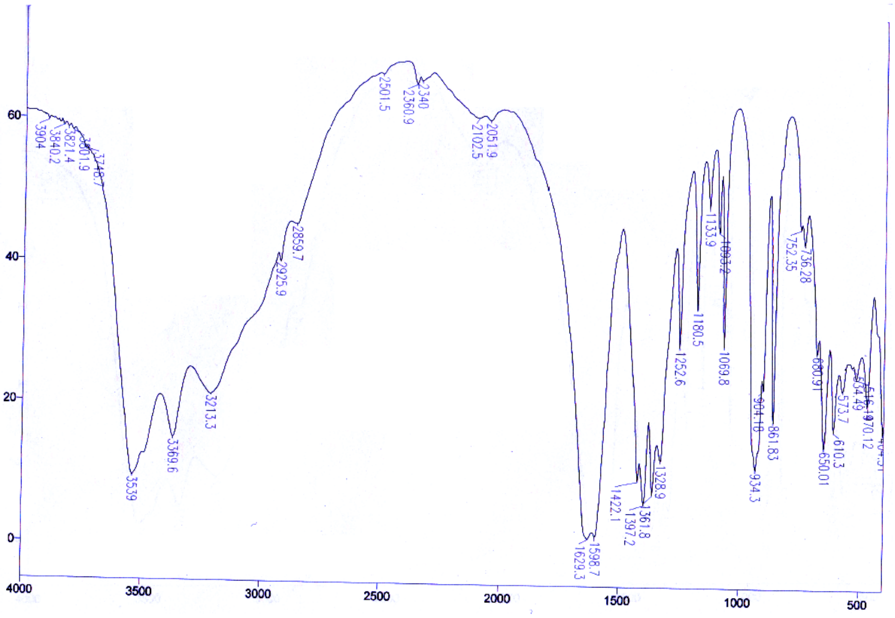

Figure 7. FITR spectra of dioxovanadium-citrate complex

UV-Visible spectral behaviour

The electronic absorption spectra of title complex was studied in aqueous medium from 250 nm to 1000 nm range (Figure 8). The color of complex was light blue. There are two peaks observed, one peak in visible region at 567 nm due to d-d transition, and other second peak in UV region at 300 nm may also be considered to be charge transfer.

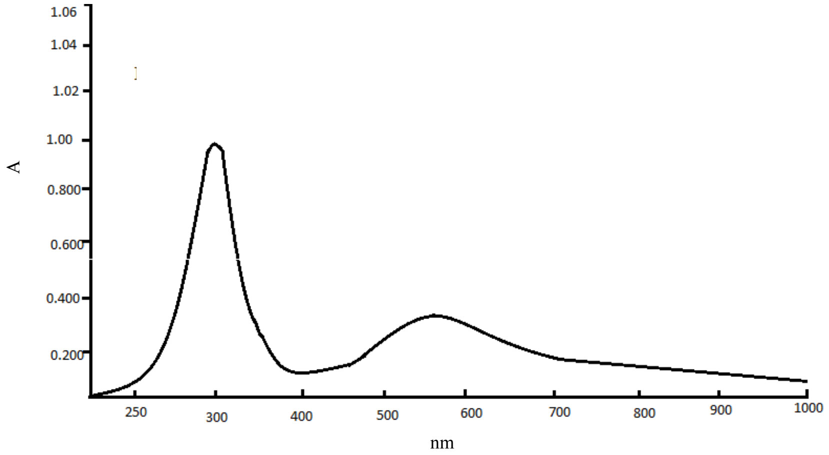

Figure 8. UV-Visible spectra of dioxovanadium-citrate complex

Conclusion

In cyclic voltammetric behavior of binuclear oxovanadium(IV)- citrate complex exhibit only one oxidation peak in positive potential region and no any reduction peak are appear between +1.3 to -1.0 V, compound have shows stability towards reduction. On increasing the pH of the complex solution, oxidation will be more difficult. The IR band at 934 cm^{-1} confirm the presence of V=O stretching. The electronic absorption spectra shows two peaks one in UV region and other is in visible region which is close to characteristics of V(IV)O metal complex.

References

1. (a) Crans D C, In Metal Ions in Biological Systems : Vanadium and its Role in Life; Sigel H and Sigel A, Eds., Marcel Dekker, New York, 1995, **31**, Chapter 5, 147; (b) Martin R B, *J Inorg Biochem*., 1986, **28(2-3)**, 181-187; http://dx.doi.org/10.1016/0162-0134(86)80081-2
2. Kaliva M, Giannadaki T, Salifoglou A, Raptopoulou C P and Terzis A, *Inorg Chem*., 2002, **41(15)**, 3850-3858; DOI:10.1021/ic010971v
3. (a) Djordjevic C, Lee M and Sinn E, *Inorg Chem.,* 1989, **28(4)**, 719-723; DOI:10.1021/ic00303a022 (b) Dean N S, Mokry M L, Bond M R, CO’Conor C J and Carrano C G, *Inorg Chem*., 1996, **35(10)**, 2818-2825; DOI:10.1021/ic9514556 (c) Wright D W, Humiston P A, Orme-Johnson W H and Davis W M, *Inorg Chem.,* 1995, **34(16)**, 4194-4194; DOI:10.1021/ic00120a026
4. Tsaramyrsi M, Kaliva M, Salifoglou A, Raptopoulou C P, Terzis A, Tangoulis V and Giapintzakis J, *Inorg Chem.,* 2001, **40(23)**, 5772-5779; DOI:10.1021/ic010276n
5. Prasad J, Yadav P, Prakash V, Srivastava K and Pandeya K B, *J Indian Chem Soc*., 2008, **85(2)**, 153-158.
6. Velayutham M, Varghese B and Subramanian S, *Inorg Chem*., 1998, **37(6)**, 1336-1340; DOI:10.1021/ic9707467
7. Asadi M, Ghatee M H, Torabi S, Mohammadi K and Moosavi F, *J Chem Sci*., 2010, **122(4)**, 539-548; DOI:10.1007/s12039-010-0088-6