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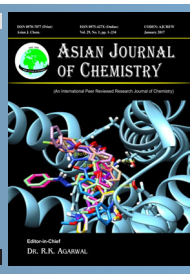

Oxidation of Vanadium(III) to Vanadium(IV) by Thioredoxin and L-Serine Contemplating the *in vitro* Redox Behavior of Vanadium in the Vanadocyte of Ascidians

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Ascidians are known to accumulate high levels of vanadium from sea water, in their blood cells, called vanadocytes. To evaluate the fact whether the total accumulation process of vanadium by ascidians are redox or not, and to justify the subsistence of trace extent of vanadium(IV) with large extent of vanadium(III) in the vanadocyte of ascidians. The oxidation behaviour of vanadium(III) to vanadium(IV) followed by series of amino acids and thioredoxin were investigated. UV-visible and electron spin resonance (ESR) spectroscopy revealed that thioredoxin and only serine (L-Ser) assist very fast oxidation having adoption the physiological pH (4.0-5.5) region relevant to vanadocyte. Specially, amino acids favour the oxidation of vanadium(III) which have the low stability constant with vanadium(III) and larger stability constant with vanadium(IV), *i.e.*, log K_1 and log K_2 >10.

Keywords: Vanadium, Ascidian, Thioredoxin, L-Serine, Oxidation behaviour.

INTRODUCTION

Vanadium, a multivalent transition metal is characterized by oxidation states from -2 to +5, although it is generally present in the environment as +5, +4 and +3 oxidation states [1-3]. The most interesting biological occurrence of vanadium (which exist as +5 oxidation state in sea water) is the incorporation to the certain ascidian's (which belong to suborder *Phlebobranchia*; also known as sea squirts or tunicates) blood cells, which is known as vanadocyte *via* +4 oxidation state and store in the vanadocyte vacuoles as +3 oxidation state [4-10]. In a remarkable case, the ascidians can approach up to 300 mM blood concentration of vanadium, which represents more than 10 million times of its concentration with respect to the sea-water in which it lives [11]. The serendipitous discovery of the noninvasive ESR measurements revealed that, most of the vanadium (97.6 %) in vanadocytes is in the +3 oxidation state, which is the most reduced state of vanadium in the biological systems, while 2.4 % of the vanadium is in the +4 oxidation state [6,7,12-15]. Nonetheless, the existence of the extremely acidic homogenate of the blood cells of ascidians [4,16-18] is contrary to the recent investigation that suggested that the physiological pH of the vanadocyte could also adopt moderate acidic environment (up to pH 5.0) [11].

Ever since, this unusual physiological phenomenon, never before reported in other organisms, have attracted the interdisciplinary attention of chemists, physiologists, biologists and biochemists because the ascidians have key chordate features in common with the vertebrates [8,9,19,20]. Although, many *in vitro* experiments have been conducted so far to elucidate the reduction behaviour of vanadium in ascidians [21-25], a very limited works have been proposed to explain the existence of small amount of vanadium(IV) in the vanadocytes of ascidians [26].

Many vanadium binding proteins (known as vanabins), which have been recently isolated from vanadium-rich ascidians can transport vanadium into vanadocytes [8,27-31]. All vanabins are rich in cysteine residues, but these cysteine residues exist entirely in the oxidized form with disulfide bonds in the structurally identified compounds [32]. Interestingly, it was found in our earlier work that, the oxidized matrix in vanabins or very rarely the intracellular proteins [33-35] with disulfide bonds, *viz.*, cystine and glutathione (oxidized form) can oxidize vanadium(III) to vanadium(IV) potentially [26]. So, it can be logically presumable that, the amino acid residues in vanabin proteins may provide the functionalities that promote the oxidation of vanadium(III) [26]. On the other hand, some vanadium(IV) species can also be intact during the reduction process from V(V) → V(IV) → V(III). Nervertheless, as vanadium(III) oxidation state is fairly unstable in solution and the redox potential is rather very low for V^{4+}/V^{3+}: 0.337 V [36], and vanadium(III) is very sensitive to oxidation [37], it may

be possible the oxidation of vanadium from +3 oxidation state to +4 oxidation state to some extent by thioredoxin and other amino acid residues exist in vanabins.

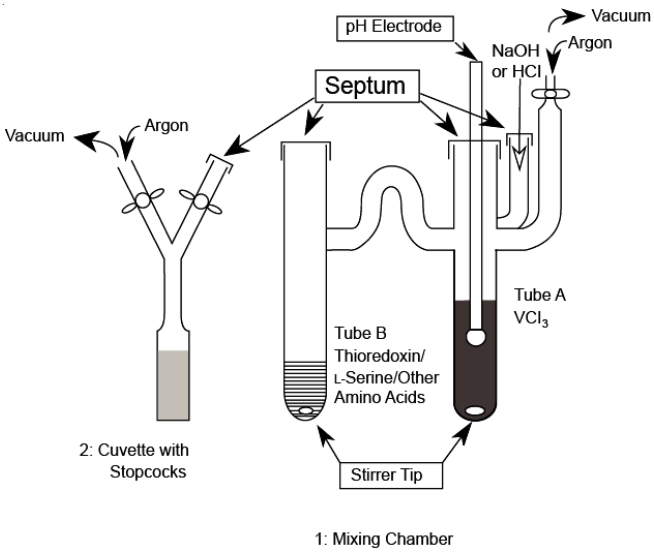
Since less work have been conducted to resolve this underlying redox mechanism, a continued research is developed with the relevant biogenic oxidants namely thioredoxin and a series of amino acids in which only L-Ser is proved to be able to oxidize the vanadium(III) state to vanadium(IV) state in this report.

EXPERIMENTAL

Vanadium trichloride (VCl_3) was purchased from Santa Cruz Biotechnology, U.S.A. Acetic acid, sodium hydroxide, thioredoxin and all amino acids (L-Gly, L-Ala, L-Val, L-Leu, L-Ile, L-Phe, L-Ser, L-Met, L-Thr, L-Asp, L-Asn, L-Glu, L-Gln, L-His, L-Tyr, L-Trp, L-Lys, L-Arg, L-Pro) were purchased from Sigma-Aldrich, Munich, Germany. All chemicals were used without further purification.

UV-visible absorption spectra were recorded on a Perkin Elmer Lambda-25 spectrophotometer under anaerobic condition. During successive spectral measurements, reaction solution was not stirred and reaction temperature was not controlled (ambient temperature). ESR studies were carried out on a JEOL JES-RE1X spectrometer at X-band frequencies under anaerobic condition flowing argon gas continuously through the solution. ESR spectrometer operated at 1 mW microwave power, 9.40 GHz microwave frequency and 1 G at 100 kHz modulation amplitude.

Sample preparation for spectroscopic measurements: Sample preparation for oxidation of vanadium(III) by thioredoxin and amino acids (L-Gly, L-Ala, L-Val, L-Leu, L-Ile, L-Phe, L-Ser, L-Met, L-Thr, L-Asp, L-Asn, L-Glu, L-Gln, L-His, L-Tyr, L-Trp, L-Lys, L-Arg, L-Pro): In a mixing chamber (**Scheme-I**), three equivalents (w/w) amount of vanadium trichloride (VCl_3) (0.100 g) and one equivalent (w/w) amount of thioredoxin (0.033 g) were put in the tube A and tube B, respectively. Deaerated CH_3COOH-CH_3COONa buffer (30 cm^3, 100 mM, pH 4.45) was added to vanadium trichloride of the tube A by syringe technique to get a vanadium(III) solution of 21.19 mol/dm^3. The mixing chamber was then deaerated and saturated with argon. At this stage, the colour of the vanadium(III) solution was reddish brown. Thioredoxin was then dissolved in the vanadium(III) solution. The resulting mixture was then put back to tube A and the pH of the solution was adjusted to 4.45 by adding 0.5 mol/dm^3 HCl. After the addition of thioredoxin to the vanadium(III) solution, the colour of the reaction mixture changed to light green and the solution was put back to tube B after adjusting the pH and the required volume of the solution was transferred to a cuvette equipped with stopcocks using syringe technique for UV-visible measurements.



Scheme-I: Mixing chamber for UV-visible measurements

The subsequent procedure was performed according to above manner as thioredoxin for the series of amino acids (L-Gly, L-Ala, L-Val, L-Leu, L-Ile, L-Phe, L-Ser, L-Met, L-Thr, L-Asp, L-Asn, L-Glu, L-Gln, L-His, L-Tyr, L-Trp, L-Lys, L-Arg, L-Pro) systems where the three equivalents amount of vanadium trichloride (VCl_3) were reacted with one equivalent amount of subsequent amino acid in millimolar basis and the colour of the reaction mixture changed to light green after addition of respective amino acids to the vanadium(III) solution except it was bright blue in case of L-Ser.

RESULTS AND DISCUSSION

To rationalize whether the oxidation of vanadium(III) to vanadium(IV) by the biogenic oxidants occurred or not, UV-visible as well as ESR spectroscopic measurements were studied, since both the vanadium(III) and vanadium(IV) species were coloured and thus UV-visible spectral change was not considered to be a concrete evidence for the oxidation of vanadium(IV).

Oxidation of vanadium(III) to vanadium(IV) by thioredoxin: Though, vanadium(III) (d^2 configuration, reddish brown or light green colour) and vanadium(IV) (d^1 configuration, typical blue or green colour), both species are coloured, the successive time-dependent absorption spectra could be a useful tool to monitor the oxidation in the course of the reaction. Just after addition of one equivalent (w/w) amount of thioredoxin to the vanadium(III) solution, the successive time dependent UV-visible spectral measurements had been started in an anaerobic condition. The initial colour of the reaction mixture was reddish brown which had been turned to deep green after 30 h. Fig. 1 shows the spectral change observed for vanadium(III)/thioredoxin system over time as a typical example. The absorbance in the UV-visible region increased over time with development of the bands at 600 and 795 nm which are characteristic of the oxovanadium(IV) species [38-40]. This observation clearly indicates that vanadium(III) species was oxidized to vanadium(IV) species. The change of absorbance at 795 nm became constant after 65 h as indicated in the inset of Fig. 1.

The mononuclear vanadyl complexes exhibit typical eight widely-spaced ESR lines due to the coupling of the unpaired electron with the large moment of the nearly 100 % abundant ^{51}V nucleus (I = 7/2), adopting the number (n) of hyperfine signal of vanadyl state; n = 2I + 1 [41,42]. So, ESR is proved to be an excellent tool to detect the oxidation of vanadium(III) to vanadium(IV) because the former species is ESR silent though the later is ESR active.

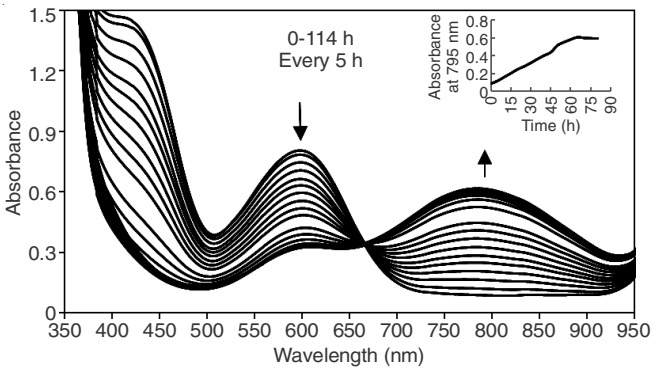


Fig. 1. Successive absorption spectra observed at 5 h intervals: $3VCl_3$/thioredoxin in CH_3COOH-CH_3COONa (100 mM, pH 4.45), [V] = 21.19 mM

X-band ESR spectrum was observed for the initial and final reaction solutions for the vanadium(III)/thioredoxin system. Although the initial solution yielded no ESR signal, the final solution exhibited an eight-line ESR pattern typical of oxovanadium(IV) species which is shown in Fig. 2. Since no chemical species of vanadium with +3 oxidation state have ever been reported in neutral or alkaline solution [20], and raising pH up to 7 generate several oligomeric and polymeric spin paired vanadyl (VO^{2+}) species that are ESR silent [41,43-45]. Present ESR studies along with the UV-visible results are well-resembled in indicating the oxidation of vanadium(III) to vanadium(IV) by thioredoxin having adoption the pH precisely between 4.0-5.5.

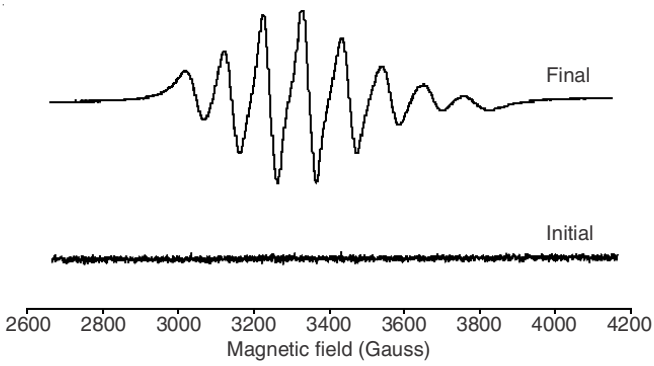


Fig. 2. ESR spectra of the initial aqueous reaction solution (30 cm^3) containing VCl_3 (0.100 g) and the final aqueous reaction solution (30 cm^3) containing VCl_3 (0.100 g) in which thioredoxin (0.033 g) was added and pH was adjusted to 4.45

Oxidation of vanadium(III) to vanadium(IV) by amino acids: It is notable that the amino acids have only two coordination functionalities (bidentate ligand), namely, the amino and carboxylate groups and are classified as the moderately weak chelators. The successive time dependent UV-visible spectral measurements have been carried out for a series of vanadium(III)/amino acids of this group (L-Gly, L-Ala, L-Val, L-Leu, L-Ile, L-Phe, L-Pro) systems. The visible absorption spectra yielded no evidence of vanadium(IV) species for these amino acids. Interestingly, L-Pro was found to promote the oxidation of vanadium(III) albeit ineffectively. In addition to that, L-Ser, L-Met, L-Thr, L-Asp, L-Asn, L-Glu, L-Gln, L-His, L-Tyr, L-Trp, L-Lys and L-Arg have an additional functionality in their side chains. Thus, these amino acids can be considered as the potential tridentate ligands. Among the amino acids of this group and vanadium(III) systems, only in case of vanadium(III)/L-Ser, the absorbance in the UV-visible region increased over time with development of the bands around 600 nm and 795 nm which are characteristic of the oxovanadium(IV) species. This observation clearly indicates that vanadium(III) was fully oxidized to vanadium(IV) in this system. The absorbance at 795 nm became constant after 90 h as indicated in the inset of Fig. 3.

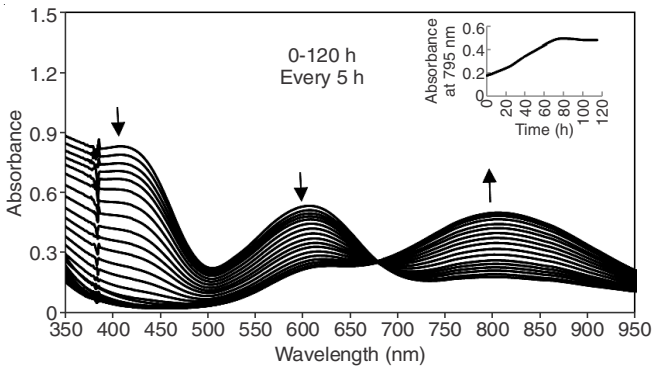


Fig. 3. Successive absorption spectra observed at 5 h intervals: $3VCl_3$/L-Ser (7.073 mM) in CH_3COOH-CH_3COONa (100 mM, pH 4.45), [V] = 21.19 mM

X-band ESR spectra were observed for the initial and final reaction solutions for the vanadium(III)/L-Ser system. The similar ESR patterns were also obtained in this case as like vanadium(III)/thioredoxin system, strongly supports the successive time dependent UV-visible spectral measurements in indicating the oxidation of vanadium(III) to vanadium(IV) by L-Ser having adoption of the pH precisely between 4.0-5.5.

A comparative UV-visible spectral feature of authentic vanadium(III) solution of VCl_3, the final reaction solution of VCl_3 with thioredoxin, L-Ser, L-Val and L-Pro is shown in Fig. 4. The final spectrum obtained from the $3VCl_3$/thioredoxin (Fig. 4B) and $3VCl_3$/L-Ser (Fig. 4C) systems in the visible region showed two distinct bands around 600 and 795 nm, which are aversely resemble to the oxovanadium(IV) species, were almost dissimilar to those of an authentic vanadium(III) solution of VCl_3 (Fig. 4A). Though $3VCl_3$/L-Pro (Fig. 4E) system showed oxidation insufficiently, the $3VCl_3$/L-Val (Fig. 5D) system was incapable to oxidize vanadium(III) completely.

Stability constant: A concern for the ligands promoting the oxidation of vanadium(III) by amino acids: It is noteworthy that the ligand that has the greater ability to stabilize the vanadium(IV) complex [in other words, a larger stability constant with vanadium(IV)] will have a greater ability to promote oxidation of vanadium(III). Amino acids form very weak complexes with vanadium(III) rather than vanadium(IV). Furthermore, a very few binary complexes of vanadium(III) with amino acids have been found in the literatures due to geometrical restrictions and therefore form very weak complexes with vanadium(III). The stability constants of V(III) complexes with salicylic acid and various amino acids are shown in Table-1. The species largely predominant between $4 < pH < 5$ taken into consideration because all the reactions carried out in this work are between pH 4.4-4.5. It is interestingly seen that, all

TABLE-1
STABILITY CONSTANT OF VANADIUM(III) AND VANADIUM(IV) COMPLEXES WITH VARIOUS BIOGENIC LIGANDS

Metal	Ligand	Stability constant (log value)	Method	References
V(III) complexes with salicylic acid and various amino acids				
V(III)	HSerine	1.64	Potentiometry	[46]
	HThr	1.25	Potentiometry	[46]
	HMet	1.6	Potentiometry	[46]
	HPhe	0.5	Potentiometry	[46]
	HGly	1.6-1.9	Potentiometry	[46]
	HαAla	3.0	Potentiometry	[46]
	HβAla	4.34	Potentiometry	[46]
	HPro	2.9	Potentiometry	[46]
V(III) complexes with 8-hydroxyquinoline and various amino acids				
V(III)	H_2Glu	7.29	Potentiometry	[47]
	H_2Asp	10.0	Potentiometry	[47]
	HHis	15.7	Potentiometry	[47]
	HGly	9.72	Potentiometry	[48]
	HαAla	8.5	Potentiometry	[48]
	HβAla	10.28	Potentiometry	[48]
	HPro	8.9	Potentiometry	[48]
V(IV) complexes with various amino acids				
V(IV)	Gly	6.51 (K_1), 5.31 (K_2); 8.24 (K_1), 7.42 (K_2)	Potentiometry	[47,49]
	L-Ala	6.87 (K_1), 5.53 (K_2); 8.34 (K_1), 7.29 (K_2)	Potentiometry	[50,51]
	L-Serine	10.37(K_1), 10.37 (K_2)	Potentiometry & Spectroscopy	[52]
	L-Val	6.37 (K_1), 5.05 (K_2)	NMR	[53]
	L-Thr	6.41 (K_1), 5.52 (K_2)	Potentiometry	[54]
	L-Asn	7.50 (K_1), 7.10 (K_2); 6.52 (K_1), 929 (K_2)	Potentiometry & Spectroscopy	[52,55]
	L-Gln	7.40 (K_1), 7.00 (K_2)	Potentiometry	[56]
	L-Pro	7.28 (K_1), 5.84 (K_2)	NMR	[53]
	L-Glu	8.06 (K_1), 5.45 (K_2); 7.73 (K_1), 6.37 (K_2)	Potentiometry & NMR	[53,56]
	L-Asp	7.23 (K_1), 5.41 (K_2); 8.98 (K_1), 6.49 (K_2)	Potentiometry & NMR	[53,56]
	L-His	9.04 (K_1), 6.44 (K_2)	Potentiometry	[57]

Here, K_1 = [VL]/[V][L], K_2 = [VL_2]/[VL][L], L = deprotonated form of ligands.

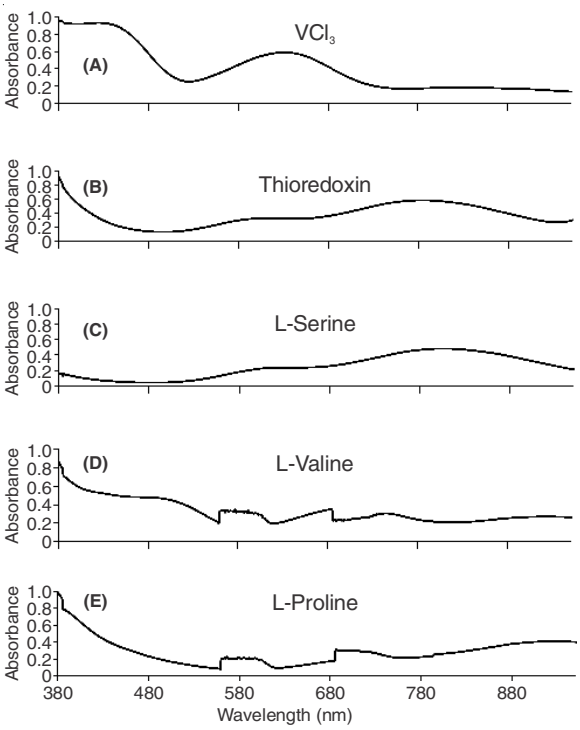


Fig. 4. Absorption spectra of: (A) The initial aqueous reaction solution (30 cm^3) containing VCl_3 (0.100 g, 21.19 mM, pH 4.45); The final aqueous reaction solution (30 cm^3) containing VCl_3 (21.19 mM) in which (B) Thioredoxin (0.033 g), (C) L-Ser (0.0223 g, 7.073 mM), (D) L-Val (0.0248 g, 7.056 mM) and (E) L-Pro (0.0244 g, 7.0645 mM) has added individually and pH was adjusted to 4.45

the amino acids taken into account adopt very low stability constant values with vanadium(III) species. In addition, stability constants of vanadium(III) complexes with 8-hydroxyquinoline and various amino acids are shown in Table-1, where the species taken into account are in good agreement with the pH range in this study. All the amino acids with vanadium(III) and 8-hydroxyquinoline shown here form stronger complexes comparing that of the complexes of salicylic acid.

On the other hand, available stability constants of vanadium(IV) complexes with the ligands studied here are also summarized in Table-1. In case of L-Ser, the stability constants have been calculated with two different methods having two different models where MLH and ML species were abundant in our considerable pH range. It is notable that, the ligands do not promote the oxidation of vanadium(III), namely, Gly, L-Ala, L-Val, L-Thr, L-Asn, L-Gln, L-Pro, L-Glu, L-Asp, L-His have formation constant values (log K_1 and log K_2) <10. In contrast, the ligand, namely L-Ser is only found to promote the oxidation of vanadium(III) have, in general, log K_1 and log K_2 >10 indicating the stronger complex formation with vanadium(IV) which also shown a very low stability constant value with vanadium(III) and salicylic acid. This observation clearly indicates that, L-Ser favours the oxidation of vanadium(III) to vanadium(IV) due to high stability constant value with vanadium(IV) than vanadium(III) and in agreement with the criterion, *i.e.*, log K_1 and log K_2 >10 with vanadium(IV). It is also presumable that, L-Glu, L-Asp, L-His, L-Gly, L-Ala

and L-Pro do not favour the oxidation of vanadium(III) due to adoption of high stability constant value with vanadium(III) (Table-1) than that of vanadium(IV) (Table-1).

Conclusion

Proteins or amino acids may bind to metal ions in a specific or no-specific manner. The specific coordination sites are generally provided by the donor groups of amino acid residues of the proteins specially arranged by the tertiary structure of the proteins. Although vanadium-protein interactions have been rigorously studied including vanabin proteins [31], crystal structures of vanadium-protein complexes are rarely found in literature. At present we believe that, the oxidation of vanadium(III) to vanadium(IV) presumably proceed by the functioning by ligated matrix of vanabin (like L-Ser) or intracellular protein (like thioredoxin) as chelators to prevent the precipitation of free vanadium(IV) in moderately acidic environment [31]. In any event, from our present study it is inferable that the direct coordination of thinyl anion (in case of thioredoxin) and hydrogen bonding with the side arm of amino acid (in case of L-Ser) to the vanadium(IV) center could be geometrically preferential that would perform the oxidations. The similar argument has been advanced in our earlier work concerning oxidized glutathione and cysteine [26].

In particular, the significant present findings lead to a more clear picture about oxidation of vanadium(III) by the biogenic oxidants such as thioredoxin and an amino acid L-Ser which favour the oxidation of vanadium(III) to vanadium(IV) due to high stability constant value with vanadium(IV), *i.e.*, log K_1 and log K_2 >10 than vanadium(III). So, it can be clearly assumed that, amino acids favour the oxidation of vanadium(III) which have the low stability constant with vanadium(III) and larger stability constant with vanadium(IV), *i.e.*, log K_1 and log K_2 > 10. Both the reactions assist very fast oxidation having adoption of the physiological pH (4.0-5.5) region relevant to vanadocyte.

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