Biological aspects kinetic analysis of the vanadium (V) to vanadium (IV) by (EDTA) in sulphuric acid medium

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Abstract

Catalytic oxidative behavior of ethylenediamminetetraacetic acid (EDTA) in the context of reduction of vanadium(V) to vanadium(IV), has been investigated The reaction was followed spectrophotometrically in the acidic medium by measuring the decrease in absorbance of the pale yellow complex $[VOSO_4 H_2O]^+$ at 365 nm Spectrophotometrically evidence has been obtained for a complex formation between the respective reactive species of vanadium(V) and EDTA prior to electron transfer The reaction is first-order with respect to each [EDTA] and [vanadium(V)] catalysed by H_2SO_4 The reaction does not involve one-step two-electron transfer as vanadium(III) could not be detected under the experimental conditions The activation parameters Ea = 65 kJ mol^{-1}, ΔH# = 63 kJ mol^{-1}, ΔS# = −212 J K^{-1} mol^{-1}, and ΔG# = 131 kJ mol^{-1} are calculated and discussed Reaction products are also examined, the formation of vanadium(IV) aqua ion was observed confirming the single-electron sequence

Keywords: *Kinetics, Reduction, Vanadium(V), Oxidation, EDTA and Mechanism*

The reduction of vanadium(V) to vanadium(IV) by different inorganic and biologically relevant reducing agents has been the subject of investigation by a large number of workers [1-3]. The biologically important reducing agents which reduce vanadium(V) are cysteine [4], ascorbic acid [5], glutathione [6], blood pigments (tunichroms), NADPH and norepinephrine [7] It has been established that vanadium compounds are accumulated in the blood cells of certain ascidians (tunicates). Ethylenediamineteraacetic acid is a synthetic amino-acid and was first used for treatment of heavy metal poisoning [8]. It is also used for the emergency treatment of hypercalcemia and control of ventricular arrhythmias associated with digitalis toxicity. The $-OH^-$ group of ascorbic acid and EDTA has a profound effect on the zeta potential of blood and are able to bring deposits in the cardiovascular system back into solution [9]. It is also used as an antioxidant in foods, as a chelating agent in many pharmaceuticals, cosmeceuticals, and plant food and also as an anticoagulant for blood taken for hematological investigations [10]. In addition, the EDTA susceptibility to biodegradation is an important criterion for assessing their environmental impact and toxicology The biodegradation of aminopolycarboxylic acids (DTPA, NTA, HEDTA and EDTA) was described in the literature [11]. A method reported by Nortemann [12] for the isolation of EDTA-degrading bacteria suggested that the chemical speciation did not influence the biodegradation of EDTA. Different types of behavior of EDTA such as inhibition[13-14], catalytic[9,15] and vanadate stimulating [16-17] in the redox chemistry of vanadium has been reported in the literature but no report is available in which EDTA acts as reductant in the vanadium reactions. In this article, we propose the results of an experimental study of the kinetics of vanadium(V) reduction by EDTA.

The chemicals, ethylenediaminetetraacetic acid disodium salt (98%, BDH), ammonium monovanadate (99%, Merck Germany), H2SO4 (d =1.84, Merck India) and acrylonitrile (Merck India) were used without additional purification. The solvent, H_2O, was doubleddistilled in an all-glass apparatus (first time from

an alkaline $KMnO_4$ solution) Solution of vanadium(V) and the reaction mixture containing the requisite amount of EDTA, H_2SO_4 and other necessary chemicals were separately thermostatted (± 0.1 °C) in a three-necked reaction vessel fitted with a doubled walled spiral condenser (to arrest evaporation). The reaction was initiated by adding the requisite [vanadium(V)] to the reaction mixture and zero time was recorded when half of the solution had been added. A spectronic 21-D spectrophotometer was used for the measurement of the progress of the reaction using a cell of 1 cm path length. Vanadium(V) reduction was carried out in the presence of excess [vanadium(V)] at 760 nm (characteristic of vanadium(IV)). The pseudo first-order rate constants (k_{obs}, s^{-1}) were determined from the plots of log $(A_\infty-A_0)$ /$(A_\infty-A_t)$ versus time(t) (Fig 1a) Throughout the experiment, no other species except vanadium(IV) absorbed at 760 nm. Reproducible results giving good first-order plots were obtained for each reaction run (correlation coefficient, $r \geq 0.998$).

In order to confirm the reduction product of vanadium(V), solution of Vanadium(V) (60.0×10^{-3} mol dm^{-3}), [H_2SO_4] (1 78 mol dm^{-3}) and EDTA (5.0×10^{-3} mol dm^{-3}) were mixed at 50 °C. Spectra of reaction mixture were recorded under different conditions (Fig 1b).

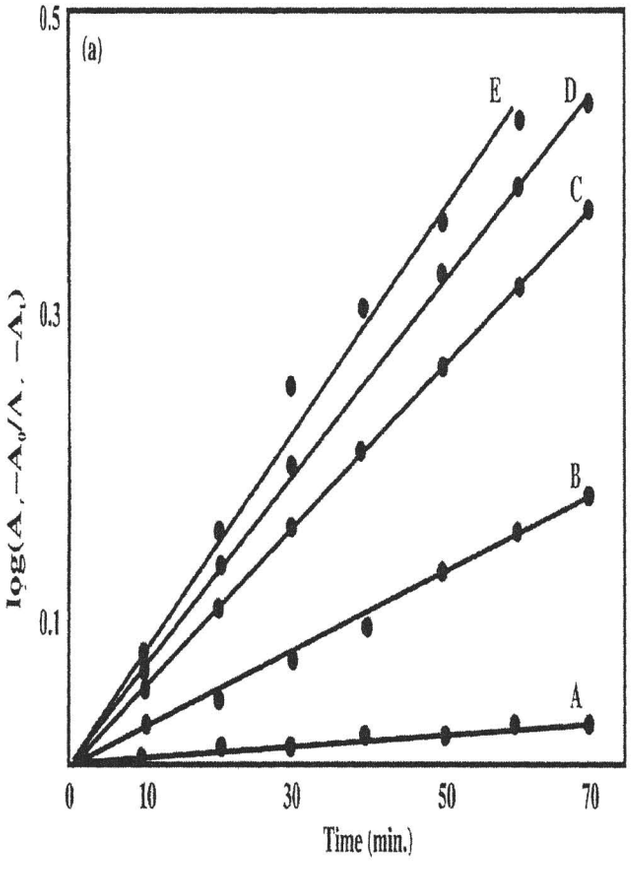

Fig. 1– (a). Plots of $\log(A_\infty-A_0 / A_\infty-A_t)$ *versus* time for the oxidation of EDTA (5.0×10^{-3} mol dm^{-3}) by vanadium(V) (60.0×10^{-3} mol dm^{-3}) at 50 °C as a function of [H_2SO_4] (0.30 (A); 0.67 (B), 1.04(C); 1 41 (D) and 1.78(E) mol dm^{-3})

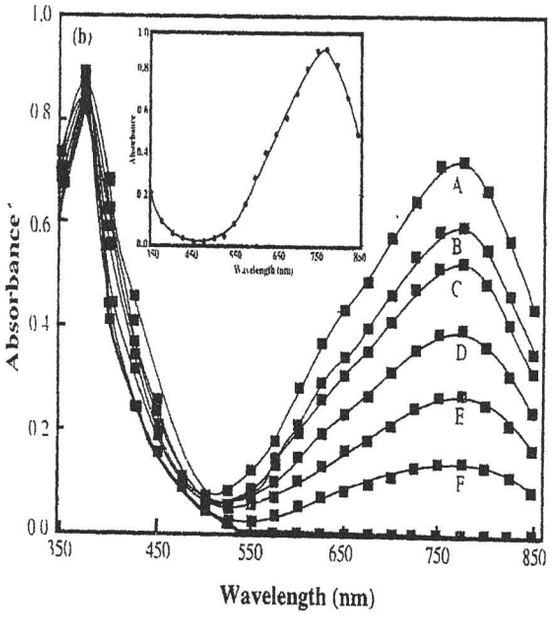

Fig.1 (b)– UV-Vis spectra of the reaction mixture under different experimental conditions· vanadium(V) and H_2SO_4 (•); vanadium(V) + H_2SO_4 + EDTA (■) *Reaction conditions*· [EDTA] = 1.0×10^{-3} (F), 2.0×10^{-3} (E); 3.0×10^{-3} (D), 4.0×10^{-3} (C), 5.0×10^{-3} (B), 6.0×10^{-3} (A) mol dm^{-3}. [Vanadium)V)] 60.0×10^{-3} mol dm^{-3} and [H_2SO_4] 1 78 mol dm^{-3} in each spectrum *Inset*· Spectrum of the reaction mixture containing [vanadium (V)] 20.0×10^{-3}mol dm^{-3}, [EDTA] 50×10^{-3} mol dm^{-3} and [H_2SO_4] 1 78 mol dm^{-3} at 50 °C after the completion of the reaction.

As the reaction proceeds, a peak at 760 nm appears Taking into account the nature of vanadium(IV) species, interestingly, it is to be noted that the two peaks

Table 1–Values of pseudo-first-order rate constants for EDTA-vanadium(V) reaction at 50 °C

10^3[EDTA] (mol dm^{-3})	10^3[V(V)] (mol dm^{-3})	[H_2SO_4] (mol dm^{-3})	k_{obs} x10^4 (s^{-1})
1 0	60 0	1 78	2 8
2 0			2 8
3 0			2 9
40			2 8
5 0			2 8
6 0			2 9
5 0	50 0	1 78	2 4
	55 0		2 5
	60.0		2.8
	65 0		3 2
	70 0		3 4
	75 0		3 6
	80 0		3.9
5 0	60 0	0 30	0.1
		0 67	0 9
		1 04	2.0
		1 41	2 3
		1 78	2 8
		2 15	3 3
		2.51	3 6

(777nm, dxy → dxz, yz and 585 nm dxy →. dx^2-y^2) are the characteristics of the oxovanadium(IV) complexes with various aminocarboxylate ligands [18]. The position of the λ_{max} depends upon pH of the reaction mixture. At the end of the reaction the one sharp peak observed at 760 nm (Fig 1b Inset) was assigned to the Vanadium(IV) ion. The experimental finding is that the yellow (λ_{max} = 365 nm) reaction mixture becomes blue (λ_{max}= 760 nm) after the completion of the reaction The most characteristic part of vanadium(IV) spectrum is the one d-d transition observable in the visible region [19-20] Our spectra consist of one band with λ_{max}= 760 nm Thus, vanadium(IV) ion is confirmed as the product under the experimental conditions used in this work. Carbon dioxide and formaldehyde were identified by the reported methods as the other reaction products.

The observed rate constant values for varying concentrations of vanadium(V) (50.0×10^{-3} –$80\ 0\times10^{-3}$ mol dm^{-3}) and fixed concentration of EDTA (5.0×10^{-3} mol dm^{-3}) at constant H_2SO_4 (1 78 mol dm^{-3}) have been recorded The values of k_{obs} at 50 °C are summarized in Table 1. The plot of log k_{obs} *versus* log [H_2SO_4] resulted in two straight line portions with slopes 2.29 and 0.72 indicating the order with respect to [H_2SO_4] to be more than two at lower and fractional at higher acid concentrations. The k_{obs} values, summarized in Table 1, initially increase, and then tend toward a limiting value with increasing [H_2SO_4] Further, the plot yields a curve concave in nature (facing down).

Vanadium compounds are biologically important where physiological and microbiological activities depend largely in their redox properties, and this behavior of vanadium has been attributed to the accumulation of vanadium(III) in ascidian's blood cells. The major fraction of vanadium in ascidians is found as vanadium(III) with in the vanadocytes. Reduction of vanadium(III) by a number of biologically important reductants has been studied. Their reductions yield only vanadium (IV) as the product. It has been accepted that the low molecular weight blood pigments that have the catechol like functional groups are responsible for the redox behavior of vanadium species in seawater. As reported, an adequate coordination sphere around vanadium may stabilize the vanadium(III) as the reaction product. It is interesting, that EDTA (a hexadentate ligand) is not in a position to reduce vanadium(V) to vanadium (III) in the present case. Again, the reducing nature of EDTA may be explained by the inner-sphere complexation between EDTA and vanadium(V); this type of behavior is rare in the redox reactions involving intramolecular electron transfer from the chelated reductant to the oxidant. It is well established that complex formation results in considerable increase in the oxidation potential of a metal ion. This is good reason to believe that the influence of –COOH groups in the oxidation potential of vanadium(V) may have a profound effect on the

oxidizing tendency of vanadium(V) in aqueous solutions.

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