Kinetic studies on effects of EDTA and surfactants on reduction of vanadium(V) to vanadium(IV) in sulphuric acid medium

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Reduction kinetics of vanadium(V) to vanadium(IV) by EDTA and effects of surfactant have been studied using thiourea as a reductant at $40\pm1°C$ in acidic medium at 350 nm. UV-vis and ESR spectral techniques have been used to confirm the reduction product of vanadium(V). Electronic absorption spectra of the reaction products suggest the formation of aqua vanadium(IV) and vanadium(IV)-EDTA complex in the absence and presence of EDTA, respectively. The oxidation of thiourea by vanadium(V) has also been studied in the presence of surfactants. The anionic sodium dodecyl sulphate and non-ionic TX-100 surfactants catalyze the reaction whereas the cationic surfactant, cetyltrimethylammonium bromide, has no effect. The single electron sequence is confirmed by the formation of vanadium(IV) aqua ion. The experimentally determined intermediate complex formation constant, K_{es} is 34 mol^{-1} dm^3.

Keywords: Kinetics, Reaction mechanisms, Surfactants, Reductions, EDTA

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Inclusion of vanadium in enzymes such as bromoperoxidase[1] and nitrogenase[2] reveals the importance of its redox chemistry. A number of model complex systems have been investigated in order to elucidate vanadium's redox mechanisms[3-5]. The metabolism, physiological role and pharmacological effects of biologically active vanadium complexes have been reviewed[6-7].

The reduction of vanadium(V) to vanadium(IV) by different inorganic and biologically relevant reducing agents has been the subject of investigation by several researchers[8-10]. Ethylenediaminetetraacetic acid (EDTA) is used as an antioxidant in foods, as a chelating agent in pharmaceuticals, cosmeceuticals and plant food and also as an anticoagulant[11]. In addition, the EDTA susceptibility to biodegradation is an important criterion for assessing its environmental impact and toxicology. The inhibitory[12-14], catalytic[15] and vanadate-stimulating[16,17] behavior of EDTA in the redox chemistry of vanadium has been reported in the

literature but there is no report on the reduction of vanadium by EDTA.

We report herein the results of kinetic studies on vanadium(V) reduction by EDTA. The oxidation of thiourea has also been studied in order to find out how thiourea differs in its kinetic features from EDTA. In addition, the effects of anionic, cationic and non-ionic surfactants have also been reported.

Materials and Methods

Ethylenediaminetetraacetic acid disodium salt (SD Fine India, 98%), ammonium monovanadate (99%, Merck Germany), H_2SO_4 (Merck, India, 98%), thiourea (Merck, India, 99%) and acrylonitrile (Merck India) were used without additional purification. Triton X-100 (SD Fine India, 99%), sodium dodecyl sulphate (Merck India, 99%) and cetyltrimethyl-ammonium bromide (BDH England, 99%) were used without further purification. Doubly distilled, deionized and CO_2-free water was used as the solvent. The vanadium(V) solutions were prepared by dissolving ammonium monovanadate in the calculated amounts in H_2SO_4 solution as required with

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vigorous shaking. The vanadium(V) solutions were quite stable.

Solutions of vanadium(V) and the reaction mixture containing the requisite amounts of EDTA, H_2SO_4 were separately thermostatted ($\pm 0.1°C$) in a three-necked reaction vessel fitted with a double walled spiral condenser (to arrest evaporation). The reaction was initiated by adding the required amount of vanadium(V) to the reaction mixture and zero time was recorded when half of the solution had been added.

A spectronic 21-D spectrophotometer (Bauch & Lomb) was employed 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 of vanadium(V) at 760 nm. 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. 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 ($r \geq$ 0.998).

The presence of free radical in the reaction mixture was evaluated by using acrylonitrile monomer. When the reaction mixture containing vanadium(V) $(60.0\times10^{-3}$ mol dm$^{-3})$, EDTA $(5.0\times10^{-3}$ mol dm$^{-3})$, acrylonitrile (20% *v/v*) and H_2SO_4 $(1.78$ mol dm$^{-3})$ was allowed to stand for 24 h, the reaction mixture became a thick white precipitate, indicating *in situ* generation of free radical during the oxidation of EDTA by vanadium(V). Controlled experiments without EDTA or vanadium(V) did not give such polymerization with acrylonitrile.

In order to confirm the reduction product of vanadium(V), solution of vanadium(V) $(60.0\times10^{-3}$ mol dm$^{-3})$, H_2SO_4 $(1.78$ mol dm$^{-3})$ and EDTA $(5.0\times10^{-3}$ mol dm$^{-3})$ were mixed at 50°C and UV-vis spectra of reaction mixture was recorded. At the end of the reaction a sharp peak was observed at 760 nm, characteristics of the vanadium(IV) ion (*d-d* transition). The yellow (λ_{max} = 365 nm) reaction mixture became blue (λ_{max} = 760 nm) after completion of the reaction. Thus, vanadium(IV) ion was confirmed as the product under the experimental conditions. Carbon dioxide and formaldehyde were identified by the standard methods as the other reaction products.

Results and Discussion

The observed rate constant values for varying concentrations of vanadium(V) $(50.0\times10^{-3}$-80.0×10^{-3} mol dm$^{-3})$ and fixed concentration of EDTA $(5.0\times10^{-3}$ mol dm$^{-3})$ at constant H_2SO_4 $(1.78$ mol dm$^{-3})$ have been recorded. A plot of k_{obs} versus [vanadium(V)] was linear passing through the origin, (Fig. 1) indicating first order with respect to [vanadium(V)]. On the other hand, the invariance of rate constants over a variation of initial [EDTA] $(1.0\times10^{-3}$-6.0×10^{-3} mol dm$^{-3})$ at fixed [vanadium (V)] $(60\times10^{-3}$ mol dm$^{-3})$, [H_2SO_4] $(1.78$ mol dm$^{-3})$ and temperature (50°C) is indicative of pseudo-first-order dependence of the reaction in [EDTA], leading to Eq. (1),

$$-\frac{d[V(V)]}{dt} = k_{obs}[EDTA]_T[V(V)]_T \qquad …(1)$$

where T is the total concentration.

The reaction rate is found to increase with increase in [H_2SO_4] at constant [oxidant] and [reductant]. 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 respectively. The k_{obs} values, initially increased and then tend toward a limiting value with increasing [H_2SO_4] (Fig. 1). Further, the plot yields a curve concave in nature.
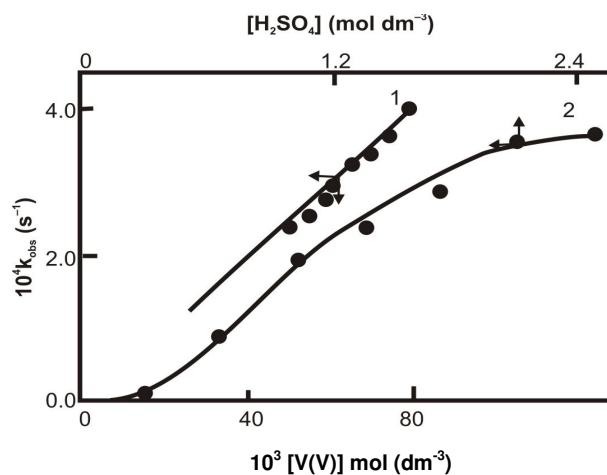

Fig. 1—Plots of pseudo first order rate constants (*k*obs) versus [vanadium(V)] and [H_2SO_4] for the oxidation of EDTA by vanadium(V). [React. cond.: [EDTA] = 5.0×10^{-3} mol dm^{-3}; temp. = 50°C. 1, Variation of [vanadium(V)]; 2, Variation of concentration of [H_2SO_4].

The plot of $1/k_{obs}$ versus $1/[H_2SO_4]$ is also linear ($[H_2SO_4]$=1.04-2.51 mol dm^{-3}) with a positive intercept and slope, indicative of Michaelis-Menten behavior and complex formation between the reactants and H_2SO_4. Due to the existence of so many proton-dependent equilibria among EDTA and vanadium(V) species, the exact dependence on [H$^+$] is complicated. The observation is in agreement with the fact that the vanadium-EDTA reaction in aqueous H_2SO_4 medium is catalyzed by [H$^+$]. On protonation, the positive charge on the vanadium(V)-sulphate species increases, and facilitates the electron transfer towards the vanadium(V) center.

Effect of thiourea in absence of EDTA

Kinetics of the reduction of vanadium(V) by thiourea in H_2SO_4 aqueous medium was investigated. The invariance of k_{obs1}, over varying initial [V(V)], $(1.0\times10^{-3}$-6.0×10^{-3} mol dm$^{-3})$ at fixed [thiourea]$_T$ = 60.0×0^{-3} mol dm^{-3}, $[H_2SO_4]$ = 0.39 mol dm^{-3} and temperature = 40°C is indicative of first order dependence of the reaction in [V(V)]$_T$ (Table 1). k_{obs1} increases with increase in [thiourea]$_T$ and the plot between k_{obs1} versus [thiourea]$_T$ shows that the reaction is second-order with respect to [thiourea]$_T$ (a double logarithmic plot with a slope of 1.85 with average linear regression coefficient, γ = 0.998).

Effect of temperature was also studied within the range 35-60°C at constant [V(V)]$_T$, [thiourea]$_T$ and $[H_2SO_4]$. Activation parameters were calculated from Arrhenius and Erying equations and are given in Table 2.

Effect of $[H_2SO_4]$ on k_{obs1} at constant [V(V)]$_T$ $(5.0\times10^{-3}$ mol dm$^{-3})$, [thiourea]$_T$ $(60.0\times10^{-3}$ mol dm$^{-3})$ and temperature (40°C) (Table 1) was studied. The k_{obs1} increases from 0.5×10^{-4} to 11.3×10^{-4} s^{-1} when $[H_2SO_4]$ is increased from 0.02 to 0.58 mol dm^{-3} and the order is one with respect to $[H_2SO_4]$. This is in agreement with the fact that the vanadium-thiourea reaction in aqueous H_2SO_4 medium is catalyzed by [H$^+$]. Protonation leads to the generation of more reactive species of reactants, thiourea and vanadium(V), which enhances the rate of the reaction. Also, the positive charge on the vanadium (V)-sulphate species increases with decrease in pH and facilitates the electron transfer towards the vanadium (V) center. Again, the vanadium (III) state becomes more favorable as a result of pH dependence of the reaction: $VO_2^+ + 4H^+ + 2e^- \rightarrow V^{3+} + 2H_2O$.

In order to further confirm the formation of aqua vanadium(IV) ion, the EPR spectrum of the reaction mixture was recorded after completion of the reaction. The room temperature (303 K) spectrum shows a distinct eight-line pattern indicating that a single vanadium (I = 7/2) is present in the molecule, i.e., it is a monomer of vanadium(IV) aqua ion. Our results are in good agreement with the observations of other investigators[12]. The above reaction mixture was allowed to cool down. On cooling, the yellow crystals of CC′-dithiobis (formamidinium) were obtained. The

Table 1—Pseudo-firstorder rate constants for thiourea-vanadium(V) reaction at 40°C

10^3[V(V)] (mol dm^{-3})	10^3[thiourea] (mol dm^{-3})	10[H$_2$SO$_4$] (mol dm^{-3})	$10^4 k_{obs1}$ (s^{-1})
1.0	60.0	3.9	6.8
2.0			6.9
3.0			6.8
4.0			7.0
5.0			6.9
6.0			6.9
5.0	50.0	3.9	4.8
	55.0		5.7
	60.0		6.9
	65.0		8.0
	70.0		9.2
	75.0		10.2
	80.0		11.5
5.0	60.0	0.2	0.5
		1.2	1.5
		2.1	3.4
		3.0	4.6
		3.9	6.9
		4.9	8.4
		5.8	11.3

Table 2—Pseudo-firstorder rate constants (k_{obs1}) and activation parameters for thiourea-vanadium(V) reaction. [[V(V)] = 5.0×10^{-3} mol dm^{-3}; [thiourea] = 60.0×10^{-3} mol dm^{-3}; $[H_2SO_4]$ = 0.39 mol dm^{-3}]

Temp. (°C)	$k_{obs1} \times 10^4$ (s^{-1})
35	4.6
40	6.9
45	7.5
50	9.9
55	12.1
60	15.9
Activation parameters	
E_a (kJ mol^{-1})	42.0±1
$\Delta H^{\#}$ (kJ mol^{-1})	42.0±1
$\Delta S^{\#}$ (JK^{-1} mol^{-1})	-168.0±1
$\Delta G^{\#}$ (kJ mol^{-1})	95.0±1