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Redox behaviour of cysteine in the presence of ammonium trioxovanadate(V)

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Abstract

The interaction of ammonium trioxovanadate(V) with cysteine in aqueous solution was studied by cyclic voltammetry and absorption spectroscopy techniques. In the absence of cysteine, the cyclic voltammogram (CV) of ammonium trioxovanadate(V) solution in 0.1 M phosphate buffer (pH 7) gave two peaks at −0.130 V (reversible) and −0.400 V (irreversible). These peaks (−0.130 V, −0.400 V) can be attributed to V(V)/V(IV) and V(IV)/V(III) redox processes, respectively. In the presence of cysteine at low scan rate (40 mV/s), the peak at −0.780 V, which is assigned to the irreversible reduction of free cystine, was observed. In addition, the reduction peak of the disulfidic anion S_2^{2-} was seen at −0.650 V. Under aerobic conditions, the peaks of the disulfidic anion S_2^{2-} and free cystine are well separated. From electronic spectra of ammonium trioxovanadate(V) and cysteine mixtures, LMCT transition associated with V(V)–cyteine complex was obtained at 743 nm. The stoichiometry (ML_2) and stability constant ($\log \beta_{1:2} = 6.67$) of V(V)–cysteine complex were determined by means of mole ratio method.

Keywords: Ammonium trioxovanadate(V)–cysteine, voltammetry; Electronic spectra

1. Introduction

Vanadium is an essential element in biological systems. Therefore, the interest in vanadium chemistry from a biological and pharmacological perspective has exploded over the past years. Vanadium takes over the role of a cofactor in redox enzymes. The use of (oxo)vanadium complexes in oxidation and oxo transfer catalysis [1] has been noted. The potential medicinal application the treatment of insulin deficiency and insulin resistance [2] has further stimulated research into vanadium coordination compounds. To understand the biological role of vanadium, many model complexes have been synthesized in recent years [3–5]. In particular vanadium complexes with ligands, thiol functions have been paid great attention [3,6,7]. The reaction of vanadium (V) or (IV) with thiol-containing molecules usually results in the reduction of vanadium and in the concomitant oxidation of thiol-containing molecules to disulfide [8]. A vanadium compound once administered and absorbed will encounter thioloate (cysteine, cystine, methionine, glutathione) and its oxidised form in the intracellular medium. Vanadium(V) is stable under aerobic conditions, and vanadium(IV) under anaerobic conditions, i.e., in the cytoplasma. At pH 7 and a V(V)/V(IV) ratio equal to 10^3, the redox potential (for $VO^{2+} 3H_2O \rightleftarrows H_2VO_4^- + e^- + 4H^+$) is −0.17 V [4] in a range where redox chemistry under physiological conditions occurs.

In this study, the interaction of ammonium trioxovanadate(V) with cysteine in aqueous solution reported by using by cyclic voltammetry and absorption spectroscopy techniques. Redox interaction of cysteine with vanadium(V) is therefore of interest and has been included this study. Also, this voltammetric study seemed to provide a better understanding of redox chemistry of vanadium.

2. Experimental

2.1. Reagents

Commercially available L-cysteine and NH_4VO_3 from Merck were used. Phosphate buffer were prepared from chemicals of analytical purity grade.

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2.2. Spectroscopy

The electronic absorption spectra in the 900–200 nm range were recorded on Unicam V2-100 UV/Vis spectrophotometer, using 1-cm quartz cells.

The electronic spectra of mixtures with ambient mole ratio of both NH_4VO_3 and cysteine aqueous solutions were recorded, following the changes in the absorbance value at 743 nm.

2.3. Electrochemical measurements

Voltammetric experiments were performed with an EG&G PAR Model 384B polarographic analyzer. A standard three-electrode cell (EG&G PARC Model 303A polarographic stand (Princeton, NJ, USA)) was used with a hanging mercury drop electrode (HMDE), a Pt counter electrode and a $Ag|AgCl|KCl_{sat}$ reference electrode.

All solutions were prepared in deionized and triply distilled water. Also, the experiments were performed in 0.1 M phosphate buffer (pH 7) as supporting electrolyte.

Prior to each experiment, a voltammogram of the solution containing only the supporting electrolyte was measured. Solutions of NH_4VO_3 and/or cysteine in water were added to the cell containing the supporting electrolyte and their voltammograms were recorded.

Oxygen in the solutions was removed by purging the solutions with pure nitrogen gas.

3. Results and discussion

3.1. Electrochemical measurements

In the absence of cysteine, the cyclic voltammogram (CV) of 1.77×10^{-5} M NH_4VO_3 solution in 0.1 M phosphate buffer (pH 7) gave two cathodic peaks at -0.130 and -0.400 V in the potential range from 0.0 to -1.0 V (Fig. 1). As can be seen in Fig. 1, the cathodic peak at -0.130 V has an anodic counterpart, while other cathodic peak is not given a peak in the anodic branch. For the peak couple at -0.130 V, the difference between the currents of cathodic and anodic peaks shows that this electrode process is affected by adsorption. Since I_{pa} is higher than I_{pc}, this situation is verified that the product is probable adsorbed on the mercury electrode surface. As regards the presented results, it can be said that the nature of electrode process of the peak at -0.400 V is irreversible. It was reported that vanadium(V) characteristically gives two cathodic waves in acidic, neutral and some complex-forming media, but only a single cathodic wave in strongly alkaline media. In the former, the first wave represents reduction to V(IV), while the second wave has properties identical with those of the cathodic wave of vanadium(IV) [9]. We can suggest that the electrode reactions for the observed peaks take place as follows:

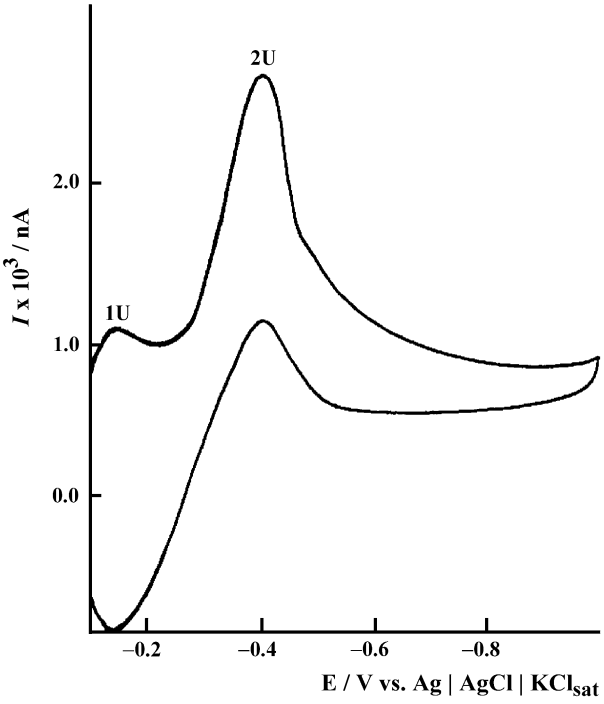

Fig. 1. Cyclic voltammograms of 1.77×10^{-5} M NH_4VO_3 solution. (1U) The reduction of V(V) to V(IV); (2U) the reduction of V(IV) to V(III). Experimental conditions: scan rate, 500 mV s^{-1}; scan increment, 2 mV; equilibrium time, 5 s; drop size, medium.

$$V(V) + e^- \rightleftarrows V(IV)_{ads} \quad (-0.130\ V)\ (\Delta E_p \approx 0) \tag{1}$$

$$V(IV)_{ads} + e^- \rightarrow V(III) \quad (-0.400\ V) \tag{2}$$

Under the same experimental conditions, CV of 7.70×10^{-5} M cysteine solution in the absence of NH_4VO_3 produces two reversible peaks at -0.110 and -0.542 V (Fig. 2). When mercury electrode is polarized, cysteine reacts with Hg in an ionic reaction and produces mercuric cysteine thiolate ($Hg(SR)_2$), which adsorbs at the Hg surface. These peaks (-0.110 and -0.542 V) are attributed to the reduction of mercuric cysteine thiolate to mercurous cysteine thiolate ($Hg_2(SR)_2$) and of mercurous cysteine thiolate to metallic mercury and free thiolate ions, respectively [10].

$$2[Hg(SR)_2]_{ads} + 2e^- + 2H^+ \rightleftarrows [Hg_2(SR)_2]_{ads} + 2RSH$$

$$(-0.110\ V) \tag{3}$$

$$[Hg_2(SR)_2]_{ads} + 2e^- + 2H^+ \rightleftarrows 2Hg + 2RSH$$

$$(-0.542\ V) \tag{4}$$

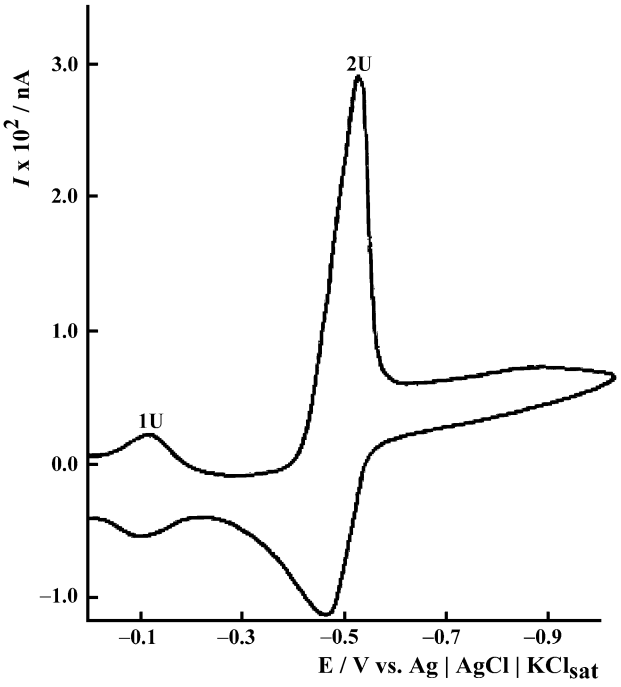

Fig. 2. Cyclic voltammogram of 7.70×10^{-5} M cysteine solution. Other conditions as in Fig. 1. (1U) The reduction of mercuric cysteine thiolate to mercurous cysteine thiolate; (2U) the reduction of mercurous cysteine thiolate to metallic mercury and free thiolate ions.

When cysteine was added to the cell that is including NH_4VO_3 solution, the cyclic voltammogram of NH_4VO_3 considerably changed. Fig. 3 shows an indication of changing voltammogram of vanadium(V) species after cysteine is added. At low scan rate (40 mV/s), and in the presence of 3.86×10^{-5} M cysteine, 1.74×10^{-5} M NH_4VO_3 gives the well-defined and separated CV peaks. The peaks of V(V)/V(IV) (-0.130 V) and V(IV)/V(III) (-0.400 V) shift to more positive potentials (-0.020 V (1U) and -0.304 V (3U)) and new peaks at -0.126 V (2U), -0.650 V (4U) and -0.780 V (5U) were observed (Fig. 3). The shift in the peak potentials is probably due to the reactions coupled with electron transfer. It can be said that the reductions of V(V) to V(IV), and of V(IV) to V(III), are very easy in the presence of cysteine. The V(IV) is also probable to interact with cystine, formed by oxidation of cysteine in the presence of V(V). The peak at -0.126 V can be attributed to V(V)/V(IV) redox couples for distinct vanadium sites. The similar case was observed for calcinated vanadium molecular sieve, VAPO-5 [11]. Under unaerobic conditions, the cathodic and anodic peaks ($\Delta E_p \approx 30$ mV) for electrode process at -0.650 V are well seen at low cysteine concentration (Fig. 3). It has been observed that the currents of V(IV) and new peaks at -0.650 and -0.780 V increase with time and reach a plato region.

From all of the identified decomposition products of cystine photolysis [12], the only species which is polarographically reducible and can be transformed into *S*-sulfocysteine ($RSSO_3^-$) is the disulfidic anion S_2^{2-} [13]. In our previous paper [14], square-wave adsorptive stripping voltammetric behaviour of fresh and aged cystine solutions at physiological pH (7.4) was reported. Fresh solutions of cystine exhibited three reduction peak at -0.29 V (reduction of mercuric cysteine thiolate), -0.64 V (reduction of mercurous cysteine thiolate) and -0.75 V (reduction for disulphide bond of free cystine, $RSSR + 2e^- \rightarrow 2RS^-$). The reduction of the disulfidic anion S_2^{2-}, the decomposition product of cystine at physiological pH (7.4), was seen at -0.68 V ($S_2^{2-} + 2e^- + 2H_2O \rightleftarrows 2SH^- + 2OH^-$) [14] for aged cystine solution (a few hours) in the presence of sunlight and air. The peak of the disulfidic anion became clear with longer times (2 weeks or more). The peak intensity of the disulfidic anion S_2^{2-} increased gradually with time while those of the peaks of mercuric and mercurous cysteine thiolates decreased.

In Fig. 3, the irreversible peak at -0.780 V may be assigned to the reduction of free cystine. An increasing amount of cysteine increases the cathodic peak currents of V(IV), and new peaks at -0.650 and -0.780 V increases reach a maximum and then decrease. Also, the current of peak at -0.650 V shifts to more negative potentials (-0.692 V) with increasing cysteine concentration (Fig. 4). The peak at -0.692 V can be attributed to the reduction of the disulfidic anion S_2^{2-}.

On the cyclic voltammogram of 2.26×10^{-5} M NH_4VO_3 in the presence of excess cysteine (5.33×10^{-4} M), a new

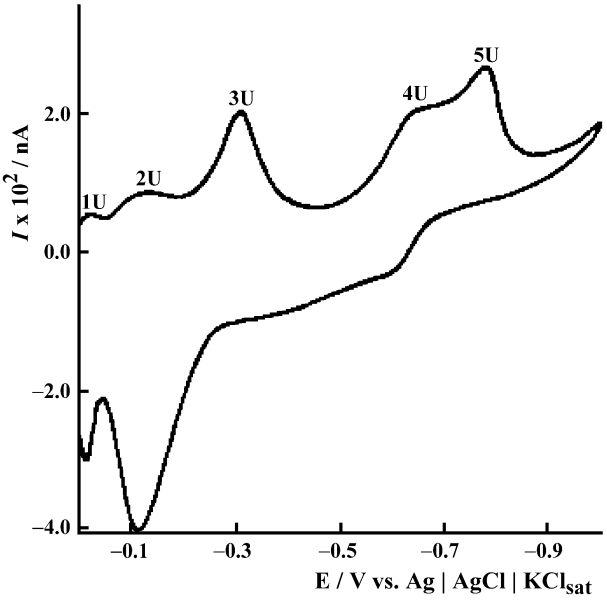

Fig. 3. Cyclic voltammogram of 1.74×10^{-4} M NH_4VO_3 solution in the presence of 3.86×10^{-5} M cysteine (scan rate = 40 mV/s and other conditions as in Fig. 1). (1U) The reduction of V(V) to V(IV); (2U) the reduction of V(V)/V(IV) redox couple for distinct vanadium sites; (3U) the reduction of V(IV) to V(III); (4U) the reduction of the disulfidic anion S_2^{2-}; (5U) the reduction of free cystine.

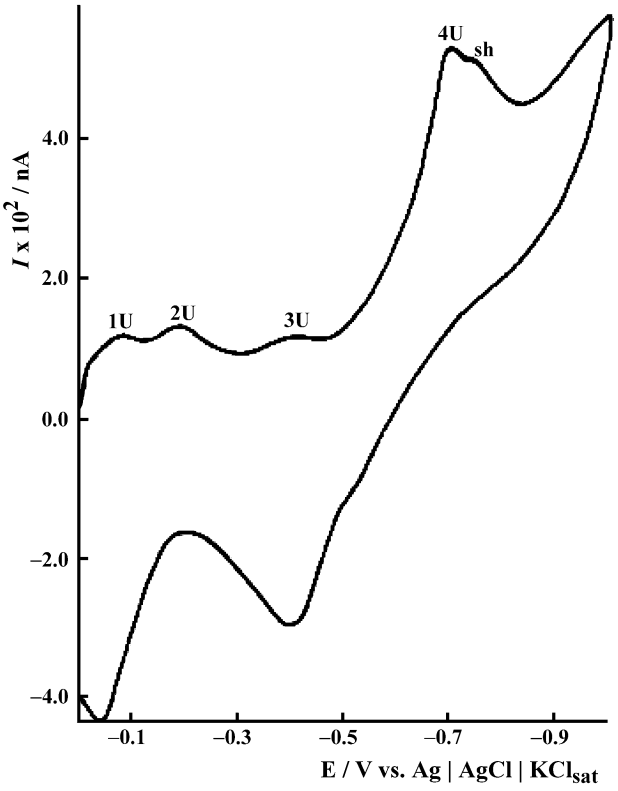

Fig. 4. Cyclic voltammograms of 2.26×10^{-5} M NH_4VO_3 solution in the presence of 5.33×10^{-4} M cysteine (scan rate = 50 mV/s and other conditions as in Fig. 1. (1U) The reduction of V(V) to V(IV); (2U) the reduction of non-complexed V(IV) to V(III); (3U) the reduction of V(IV)–cysteine complex; (4U) the reduction of the disulfidic anion S_2^{2-}; (shoulder (sh)) the reduction of free cystine.

reversible peak clearly also appeared at more positive potential (-0.412 V) than the (-0.542 V) second peak of cysteine in the absence of vanadium(V) species (Fig. 4). Similarly, the reversible reduction wave for oxo-vanadium(IV) complex of 2-amino-1-cyclopentene-1-dithiocarboxylate was observed at -0.610 V (vs. Ag/AgCl electrode) on HMDE [15]. The reversible peak at -0.412 V can be assigned to the reduction of vanadium(IV) complex to vanadium(III). In the presence of excess cysteine, the reduction peaks of V(V) and non-complexed V(IV) are observed at more positive potentials (Fig. 4).

The oxidation of several biologically related thiols by vanadium(V) generates the corresponding thiyl radicals (RS·) [16]. In addition, thiyl radicals might react with another thiol molecule to generate the superoxide ($O_2{\cdot}^-$) radical as follows [17,18]:

$$RS\cdot + RSH \rightarrow RSSR\cdot^- + H^+ \quad (5)$$

$$RSSR\cdot^- + O_2 \rightarrow RSSR + O_2{\cdot}^- \quad (6)$$

The generation of the $O_2{\cdot}^-$ radical might lead to the formation of H_2O_2 and other reactive oxygenated species [17,19].

The interaction of vanadium(V) by cysteine was studied in neutral aqueous solution under aerobic conditions. In the presence of oxygen (Fig. 5), the cathodic and anodic peaks of disulfidic anion S_2^{2-} are well defined. In addition, the peaks of disulfidic anion S_2^{2-} and free cystine are well separated. Although the peaks of V(V)/V(IV) and V(IV)/V(III) are seen, the peak of V(III)/V(II) is not observed (Fig. 5). The concentration of O_2 in water solution is less or near 1 mM, and in large excess to other components. Therefore, the free O_2 peak could be seen. The diffusion coefficient of O_2 is larger that that of common reagents so its signal generally is height. As can be seen in Fig. 5, in the presence of oxygen a new peak is also seen at -0.262 V. The potential of new peak is different from that of the non-complexed V(IV), and its current is suppressed by increasing amounts of other components. The peak at -0.262 V can be probably inferred from the reduction of O_2. Although cysteine concentration under the aerobic conditions (Fig. 5) is lower than that of unaerobic conditions (Fig. 4), the peak currents of disulfidic anion and free cystine under the aerobic conditions is higher than those of unaerobic conditions. It has been observed that the peak currents of V(IV)–cysteine complex, disulfidic anion and free cystine under the aerobic conditions increase gradually with time or

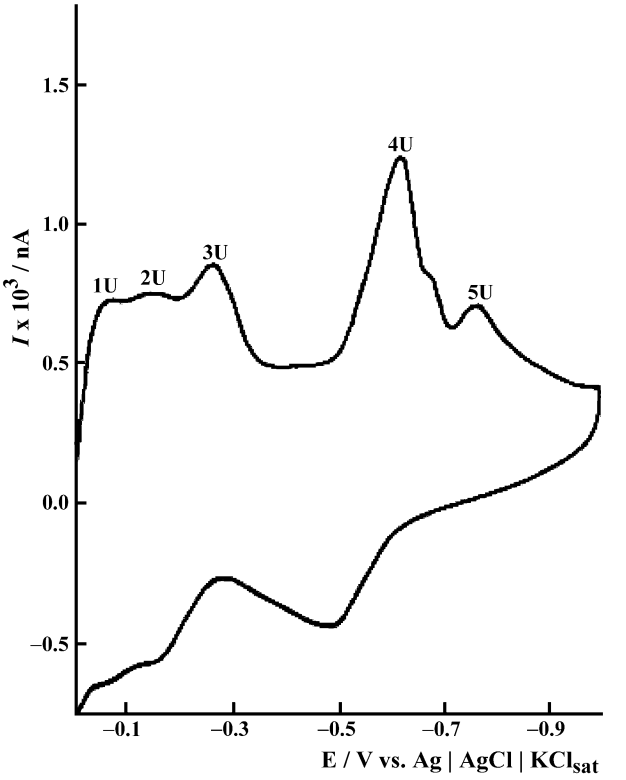

Fig. 5. Cyclic voltammogram of 7.62×10^{-5} M cysteine in the presence of 3.81×10^{-5} M NH_4VO_3 under aerobic conditions (scan rate = 500 mV/s and other conditions as in Fig. 1). (1U) The reduction of V(V) to V(IV); (2U) the reduction of non-complexed V(IV) to V(III); (3U) the reduction peak of oxygen; (4U) the reduction of the disulfidic anion S_2^{2-}; (5U) the reduction of free cystine.

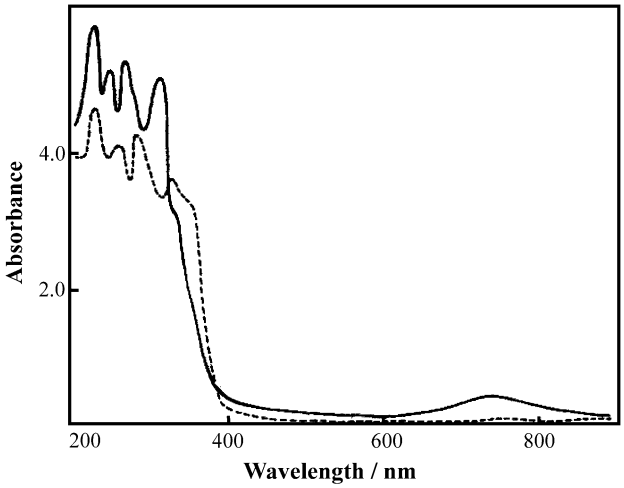

Fig. 6. Electronic spectra of 2×10^{-2} M NH_4VO_3 solution (---). Electronic spectra of 0.6×10^{-2} M NH_4VO_3 in the presence of 1.4×10^{-2} M cysteine (—).

increasing cysteine concentration, reach a maximum and then decrease slowly. With increasing cysteine concentration, the amount of V(IV) increases and but the peak current of V(IV) reaches the maximum at longer times.

Similarly, the reduction of vanadium(V) complex of lactic acid by cysteine was reported by Biagioli et al. [20]. With elapsing time, vanadium(V) is reduced to EPR-active oxovanadium(IV) in neutral aqueous solution under aerobic conditions. With elapsing time, cysteine is oxidized to cystine and the VO(IV) ions remain bound to the α-hydroxycarboxylate ligand beside cysteine or cystine [20].

According to the presented data above, it can be said that the formation of both cystine and its decomposition product is accelerated under aerobic conditions.

3.2. Electronic spectra

It was already mentioned that vanadium oxidation states change and a redox reaction forms in the mixing solutions of NH_4VO_3 and cysteine during the electrochemical measurements. In order to clarify the nature of the transformations of this redox and the vanadium complex, the electronic spectra of these solutions were also investigated. The electronic spectra of the NH_4VO_3 in water gave the maximum absorption bands at 231, 266, 283, 330 and 749 nm (Fig. 6). After addition of cysteine, the spectrum of NH_4VO_3 solution was also recorded, some shifts in the band positions were observed (Table 1). The absorbance value at 743 nm agrees with the continuous various [cysteine]/[NH_4VO_3] ratio. Bosque-Sendra et al. [21] reported the separation and preconcentration of V(IV) and V(V) using Sephadex DEAE A-25 with Eriochrome Cyanine R. The absorbance was measured at 563 nm for V(IV), at 585 nm for V(V) and at 750 nm for both. Vanadium(V) is a d^0 species and therefore no d–d transitions are observed On the other hand, complexes with VO^{3+} or bare V^{5+} bound to phenolic or catecholate groups all show intense absorption bands in the visible region from 550 to 800 nm, and these can be assigned to LMCT transitions from the phenolate oxygens to empty d orbitals on the vanadium [22]. Hence, the band at 743 nm can be attributed to LMCT transitions associated with the V(V)–cyteine complex, formed by redox reaction between V(V) species and cysteine. The stability constant and stoichiometry of the V(V)–cysteine complex were determined by mole ratio method (Fig. 7). As can be seen in Fig. 7, the complex absorbs more than the reactants, a maximum occurs at a mole ratio, corresponding to the combining ratio NH_4VO_3 and cysteine in the complex. At the plot in Fig. 7, this maximum suggests the formation of V(V)–cysteine complex of the formula ML_2. Also, the logarithm of the complex stability constant was calculated as 6.67. The electronic spectrum of NH_4VO_3 and cysteine mixture under anaerobic conditions agrees with that (740, 615 and 540 nm) reported by Ferrer et al. [23].

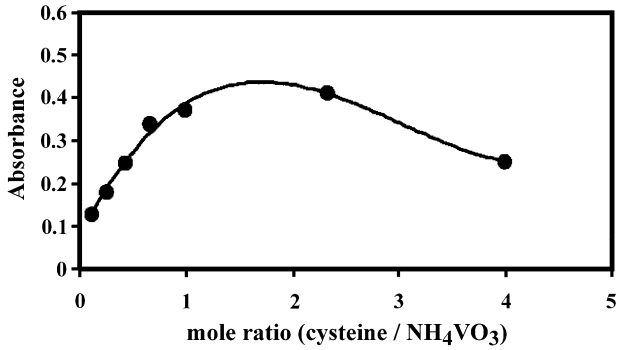

Fig. 7. Plot of absorbance (at $\lambda = 743$ nm) vs. the mole ratio (cysteine/NH_4VO_3).

Table 1
Absorption maxima (in nm) data of NH_4VO_3 and NH_4VO_3 + cysteine in aqueous solution

2×10^{-2} M NH_4VO_3	0.6×10^{-2} M NH_4VO_3 + 1.4×10^{-2} M cysteine
231	235
266	256
283	275
330	319
749	743

4. Conclusions

Finally, this work demonstrates the cystine formation and redox behaviour of cysteine in the presence of vanadium(V) at neutral pH(7). In addition, the present results show that for the NH_4VO_3 and cysteine system under aerobic and anaerobic conditions, the various vanadium species formed in the solution are strongly dependent on the metal-to-ligand ratio and the presence of oxygen. For V(V) system in the presence of cysteine under anaerobic and anaerobic conditions, the appearance of the reduction of disulfidic anion

S_2^{2-} explains the formation of redox process between cysteine and vanadium(V), and also the decomposition of cystine. In the presence of oxygen, the reactions of formation and decomposition of cystine were accelerated.

Acknowledgements

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