Reduction of Vanadium(IV) to Vanadium(III) by Cysteine Methyl Ester in Water in the Presence of Amino Polycarboxylates

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The reduction behavior of vanadium(IV) by several thiolate compounds in water was investigated in the presence of amino polycarboxylates. Vanadium(IV) can be reduced by cysteine methyl ester in the presence of edta or cydta to yield [V^{III}(edta or cydta)(H$_2$O)]$^-$, respectively.

The specific accumulation of vanadium by certain ascidians, known as sea squirts or tunicates, has been of long-standing interest.[1,2] Since vanadium is in the +5 oxidation state in sea water [3] but in the +3 state in ascidian blood cells,[1] some reducing agent must participate in the accumulation process. Tunichromes, which were isolated from some ascidian species[4] and identified to be a class of hydroxy-dopa containing tripeptides,[5] have been significantly studied as a candidate of the reducing agent in ascidians.[4,6] However, direct evidence for the reduction to the +3 state by tunichromes has not yet been obtained,[2b] though Ryan *et al.* explained their EPR results as indicating that tunichromes would reduce vanadium(V) and (IV) to the +3 oxidation sate in water.[6] (In tetrahydrofuran, an excess of pyrogallol, a model compound of tunichromes, has been shown to reduce [VO(acac)$_2$] to yield vanadium(III) compounds.)[7] Furthermore, the finding that vanadium and tunichrome are located in separate blood cells has raised further questions as to the participation of tunichromes in the vanadium reduction process.[8]

Frank *et al.* have shown that ascidian blood cells contain several kinds of sulfur-containing compounds, such as an aliphatic sulfonic acid and a disulfide together with vanadium(III) ions.[9] Since these sulfur compounds are formed by the oxidation of thiols, Frank's observation indicates that a thiol would be another candidate as a reducing agent in ascidians. However, in simple inorganic systems, thiols such as cysteine are only able to reduce V^{5+} to V^{4+} and not further to V^{3+}.[10] In fact, a stable vanadyl(IV) complex, [VO(L-cysme)$_2$], has been obtained.[11] Therefore, some chelating agent should be required to stabilize the +3 oxidation state and as a result allow easier access to the +3 oxidation state. Several vanadium(III) complexes containing an amino polycarboxylate have been prepared and well characterized.[12-15] These complexes resist air oxidation to some extent. We, therefore, investigated if thiols can reduce vanadium(IV) to (III) in water in the presence of amino polycarboxylates.

When Na$_2$H$_2$edta·2H$_2$O (0.26 g, 0.7 mmol) and 0.22 g (1.0 mmol) of VOSO$_4$·3H$_2$O were dissolved in 15 cm^3 of water, a deep blue solution was obtained. The visible absorption spectrum (Figure 1-A) was of a typical vanadyl species. To the solution was added an aqueous solution (15 cm^3) of L-cysteine methyl ester (L-cysme) hydrochloride (0.34 g, 2.0 mmol). The solution was immediately deaerated and filled with argon. The pH of the solution was adjusted to 6.5 by adding 1 mol/dm^3 of NaOH. The color of the solution turned dark blue, then to dark green in a few minutes. Later the color slowly changed to a dark reddish brown.

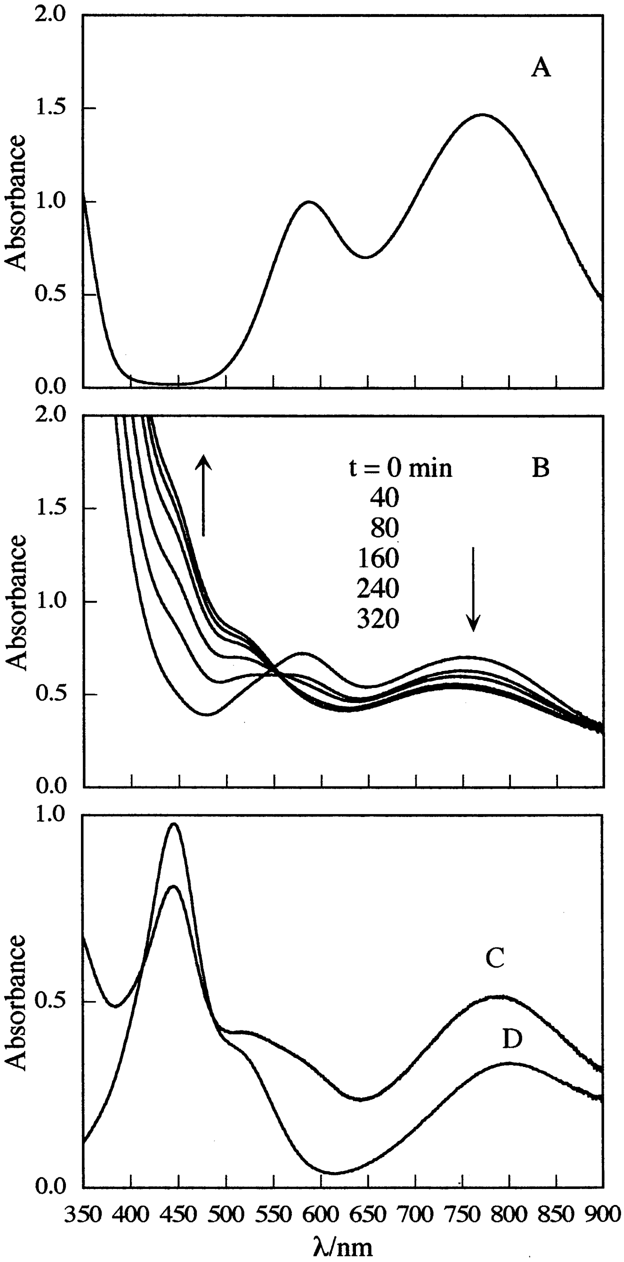

Figure 1. Visible absorption spectra of reaction solution: A, aqueous solution (15 cm^3) containing 0.7 mmol of Na$_2$H$_2$edta and 1.0 mmol of VOSO$_4$ (pH 1.59); B, time-dependence when aqueous solution (15 cm^3) of L-cysme (2.0 mmol) was added to A and pH was adjusted to 6.5; C, another portion of Na$_2$H$_2$edta (0.3 mmol) was added to B; D, Na[V^{III}(edta)(H$_2$O)] (30.5 mmol/dm^3)

In the course of this reaction, the visible absorption bands at 580 and 770 nm became weak and new bands appeared around 450 and 530 nm (Figure 1-B). After about 4 h, the change in the visible spectrum became slight. At this stage, another portion of Na_2H_2edta (0.11 g, 0.3 mmol) was added to the reaction mixture, then the color of the solution became bright reddish-brown. A small amount of fine insoluble material was noticed in this solution. The resulting solution exhibited spectral features (Figure 1-C) very similar to those of the authentic sample of Na[V^{III}(edta)(H_2O)][11] (Figure 1-D).

The above solution was evaporated to dryness and 15 cm^3 of water was added to the residue. After the insoluble material was filtered off, the filtrate was evaporated to *ca.* 2 cm^3 and ethanol (0.5 cm^3) was added. Purple crystals were obtained by cooling the solution overnight in a refrigerator. The elemental analysis, and the visible and infrared absorption spectra confirm that these crystals are Na[V^{III}(edta)(H_2O)]. Thus, it was finally concluded that L-cysme can reduce vanadium(IV) to vanadium(III) in water in the presence of edta.

When an equimolar amount of edta was added to the VO^{2+} solution during the initial stage of the reaction, the reduction did not occur. The reduction also did not proceed in acidic solutions. These facts indicate that the direct coordination of the thiolate group of L-cysme to a free coordination site of V(IV) is necessary in the reduction; thus the reduction likely proceeded through an inner-sphere electron transfer mechanism. When a half equivalent of edta was used during the initial stage, a purple powder, which was identified to be [VO(L-cysme)$_2$],[11] was deposited upon adding L-cysme. We, therefore, performed the reaction using 0.7 equivalent of edta. Under this condition the reduction proceeded and little precipitation occurred.

When L-cysteine, D-penicillamine, or glutathione was used instead of L-cysme, the reaction solution remained dark blue and the reduction to the vanadium(III) state was not observed. For these reducing agents, a free carboxylate group would preferentially coordinate to a hard vanadium(IV) center and a thiolate group would be left free from coordination. On the other hand, when aminoethanethiol (aet) was used, a brown precipitate, which was formed above pH 4, prevented the reduction of vanadium(IV). This precipitation was not able to be avoided even with a smaller amount of aet. In summary, among the thiolate compounds used, only L-cysme could yield a soluble vanadyl complex coordinated by a thiolato group in aqueous edta solution, followed by the reduction of V(IV). The reduction also occurred when trans-1,2-cyclohexanediamine-*N,N,N',N'*-tetraacetate (cydta) was used instead of edta. Interestingly, the reduction did not proceed with 1,3-propanediamine-*N,N,N',N'*-tetraacetate (1,3-pdta) and ethylenediamine-*N,N'*-diacetate-*N,N'*-dipropionate (eddda). This difference in the reduction behavior may relate to the structures of the vanadium(III) complexes containing these amino polycarboxylates. 1,3-pdta and eddda yield normal hexacoordinate vanadium(III) complexes.[14,15] These complexes undergo base hydrolysis in a neutral pH region to give an oxo-bridged dinuclear complex.[15] On the other hand, edta and cydta yield a heptacoordinate vanadium(III) complex with a water molecule as the seventh ligand.[12,13] These complexes undergo a deprotonation of the coordinated water molecule, but retain their monomeric structure even in basic solution.[15] Namely, in the edta or cydta system, only a protonation to a vanadyl oxygen, not an elimination of the vanadyl oxygen, would be required for the structural change accompanied by the reduction from V(IV) to the V(III) state. This situation should be energetically more favorable than in the eddda or 1,3-pdta system that needs a considerable structural change during the reduction. The similar argument has been advanced concerning the importance of the aqua ligand in the electron-transfer reaction between [V(hedtra)(H_2O)] and [CoX(NH_3)$_5$]$^{2+}$.[16]

Cystine was isolated as an oxidized product from the reaction mixture of the VO^{2+} – L-cysme – edta or – cydta system. Since the ester moiety in L-cysme is not likely to participate in the reduction of vanadium(IV), the cleavage of the ester bond would be due to a subsidiary reaction such as a metal-promoted hydrolysis of the ester bond.

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