Voltammetric Determination of Vanadium(V) and Vanadium(IV) through the Formation of a 12-Molybdovanadate(V) Complex

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A simple voltammetric method has been developed for the determination of V(V) and V(IV). When a mixture of V(V) and V(IV) is added last of all to a 50 mM Mo(VI)-0.3 M HCl-70% (v/v) CH₃CN system, only V(V) reacts with Mo(VI) to form a 12-molybdovanadate(V) complex which undergoes a two-step reduction at the glassy carbon (GC) electrode; the reduction current is directly proportional to the V(V) concentration in the mixture. On the other hand, when HCl is added last after heating the Mo(VI)-CH₃CN system containing a mixture of V(V) and V(IV) at 60°C for 10 min, V(IV) is completely oxidized to V(V), and the total concentration of vanadium is determined. The V(IV) concentration is determined by subtracting the V(V) concentration before oxidation from the total concentration of vanadium. Interferences from foreign ions are also discussed.

Keywords 12-Molybdovanadate(V), voltammetric determination, vanadium(V), vanadium(IV)

The formation of the so-called Keggin-type heteropoly-complex has been the basis for a widely utilized determination of oxoanions.¹ However, most studies have been limited to the determination of several oxoanions such as phosphate, arsenate, silicate and germanate. Increasing attention has been paid to the development of new methods based on the formation of heteropoly-complexes incorporating various types of oxoanions. Recently, we found that a water-soluble [CrMo₆O₂₄H₆]³⁻ anion was readily formed by the reaction of Mo(VI) with Cr(III) in an aqueous solution of pH 2–3; this reaction was applied to the simultaneous determination of Cr(III) and Cr(VI) with capillary electrophoresis.²

The use of water-miscible organic solvents, such as CH₃CN and CH₃COCH₃, as auxiliary solvents made it possible to develop several methods for the direct determination of oxoanions. In acidic media containing CH₃CN, PHO₃²⁻ reacts directly with Mo(VI) to form a heteropolyanion which undergoes two-step reduction at the GC electrode; this reaction was utilized as the basis of a voltammetric determination of PHO₃²⁻.³ In the presence of CH₃COCH₃, the so-called heteropoly-blue species are obtained by the reaction of SO₄²⁻, PHO₃²⁻ and P₂O₇⁴⁻ with the Mo(VI)-Mo(V) reagent. The color-forming reaction was used in the spectrophotometric determination of these three oxoanions.^{4,5} This behavior was also applied to the voltammetric determination of SO₄²⁻.⁶

During the course of studies on the complex-forma-

tion between Mo(VI) and various oxoanions in such aqueous organic media, we found that V(V) reacted with an acidic Mo(VI) solution to give a Keggin-type 12-molybdovanadate(V) complex, [VMo₁₂O₄₀]³⁻, which exhibited a two-step reduction wave at the GC electrode.⁷ Since the amount of the [VMo₁₂O₄₀]³⁻ complex formed is proportional to the V(V) concentration, the voltammetric reduction current can be used to determine V(V). For the determination of V(IV), heating of the Mo(VI)-V(IV) system containing CH₃CN leads to the complete oxidation of V(IV) to V(V). This pretreatment makes it possible to determine V(IV).

Teshima *et al.* developed a flow injection method for the determination of V(V) and V(IV).⁸ Recently, capillary electrophoresis was also applied to the separation of V(V) and V(IV) after complexation with diethylenetriaminepentaacetic acid (DTPA).⁹ However, the voltammetric determinations of V(V) and V(IV) are quite few.

Experimental

The absorption spectra were obtained with a Hitachi Model U-3000 spectrophotometer. Voltammetric measurements were made with a microcomputer-controlled system. A Tokai GC rod (GC-30S) with a surface area of 0.071 cm² was used as a working electrode. A platinum wire served as the counter electrode and an Ag/AgCl electrode as the reference. Prior to each measurement, the GC electrode was polished manually with 0.25 μm diamond slurry, and washed with distilled

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water in an ultrasonic bath. Unless otherwise noted, the voltage scan rate was set at 100 mV/s. The voltammetric measurements were made at 25°C.

A 40 mM V(V) stock solution was prepared by dissolving NH_4VO_3 in water. A stock solution of V(IV) was prepared by dissolving appropriate amount of $\text{VOSO}_4 \cdot n\text{H}_2\text{O}$ in 0.1 M HCl; the vanadium content was determined with a Shimadzu Model ICPS-5000 inductively coupled argon plasma emission spectrometer. Sodium molybdate, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ was used to prepare Mo(VI) stock solutions. All other reagents were of analytical grade and were used as received.

Results and Discussion

Reaction between Mo(VI) and V(V) or V(IV) in aqueous solution

With the addition of V(V) to a 50 mM Mo(VI) solution (pH 3.0), as shown in Fig. 1(a), the solution turned to yellow, due to the formation of the monovanadium derivative of $[\text{Mo}_6\text{O}_{19}]^{2-}$; *i.e.*, $[\text{VMo}_5\text{O}_{19}]^{3-}$.¹⁰ In contrast to the Mo(VI)–V(IV) system, as discussed below, only the $[\text{VMo}_5\text{O}_{19}]^{3-}$ complex is isolated even in the presence of excess of V(V) with respect to Mo(VI). Wallace and Mellon applied this reaction to the spectrophotometric determination of V(V).¹¹

On the other hand, a dark-purple solution was obtained upon the addition of a blue V(IV) solution to the 50 mM Mo(VI) solution around pH 6. As shown in Fig. 1(b), the solution exhibited an absorption maximum at 570 nm, indicating the formation of some mixed molybdovanadate(IV) complexes. However, the compositional ratio of Mo/V in the tetraalkylammonium salts of the dark-purple complexes depended on the V(IV) concentration added. Despite various attempts, the dark-purple molybdovanadate(IV) complex was not successfully prepared as a discrete polyanion. Besides,

this color-forming reaction is not applied to the direct determination of V(IV) because the molar absorptivity of the dark-purple molybdovanadate(IV) complex is too low.

In order to compare their formation conditions, the absorbance values were plotted against the pH for the 50 mM Mo(VI)–5 mM V(V) or V(IV) systems, and are shown in Fig. 2. The yellow $[\text{VMo}_5\text{O}_{19}]^{3-}$ complex occurs predominantly around pH 2.5 (Fig. 2(a)), while the dark-purple molybdovanadate(IV) complexes are formed in the pH range of 4–7 (Fig. 2(b)).

Oxidation of V(IV) to V(V) through the formation of the dark-purple molybdovanadate(IV) complex

Preliminary experiments showed that the dark-purple molybdovanadate(IV) complexes were easily oxidized to Mo(VI) and V(V), compared to the blue V(IV) species. Figure 3(a,b) compares the absorbance values as a function of the reaction time for 2 mM V(IV)–0.2 M carbonate buffer solutions (pH 6) in the presence and absence of 50 mM Mo(VI). The absorbance values at 570 nm were measured after heating a solution for some period at 60°C; the period is denoted as the reaction time. As shown in Fig. 3(a), the blue V(IV) species are rather stable against air-oxidation, even in neutral solutions. On the other hand, the dark-purple molybdovanadate(IV) species, which is readily formed by the reaction of Mo(VI) and V(IV), are easily oxidized to Mo(VI) and V(V). Accordingly, the absorbance values at 570 nm decreased abruptly (Fig. 3(b)). Furthermore, the presence of CH_3CN at concentrations >30% (v/v) accelerated the oxidation reaction of the dark-purple species (Fig. 3(c)), whereas the stability of the free V(IV) species was practically unchanged by the presence of CH_3CN . The oxidation reaction became faster by the increase of the CH_3CN concentration. It was also found that as a result of the reaction between Mo(VI) and V(V), the yellow $[\text{VMo}_5\text{O}_{19}]^{3-}$

Fig. 1 UV-visible spectra for a 50 mM Mo(VI) solution containing (a) 5 mM V(V) (pH 3); (b) 5 mM V(IV) (pH 6). Path length, 1 cm.

Fig. 2 Relationship between the absorbance values and pH for a 50 mM Mo(VI) solution containing (a) 5 mM V(V) (at 400 nm); (b) 5 mM V(IV) (at 570 nm). Path length, 1 cm.

Fig. 3 Absorbance change (at 570 nm) with time for (a) a 2 mM V(IV) solution (pH 6); (b) a 50 mM Mo(VI)–2 mM V(IV) solution (pH 6); (c) a 50 mM Mo(VI)–2 mM V(IV)–30%(v/v) CH₃CN solution. Absorbance values were measured after heating the solution at 60°C. Path length, 1 cm.

complex was subsequently formed in both aqueous and aqueous-CH₃CN media.

Optimization for the formation conditions of the Keggin-type 12-molybdovanadate(V) complex in aqueous organic solution

As described above, the presence of water-miscible organic solvents leads to the formation of the yellow [VMo₅O₁₉]³⁻ complex at weaker acidities. On the other hand, a Keggin-type [VMo₁₂O₄₀]³⁻ complex is formed at stronger acidities in the presence of organic solvents, probably due to a lower relative permittivity. Figure 4 shows cyclic voltammograms for a 50 mM Mo(VI)–0.3 M HCl–50%(v/v) CH₃CN system. In the absence of V(V), no reduction waves were observed until the current rise due to the reduction of [Mo₆O₁₉]²⁻ (Fig. 4(a)).¹² With the addition of 0.1 mM V(V), as shown in Fig. 4(b), a well-defined two-step reduction wave with an equal height appeared with peak-potentials at 0.34 and 0.24 V. The reduction current was unchanged, after attaining a constant value within a few minutes at ambient temperature. As already described⁷, each of the two-step wave corresponds to a two-electron reduction of the molybdenum atoms in the peripheral position of the [VMo₁₂O₄₀]³⁻ complex; the first reduction current is denoted as *i*₁. This behavior is the basis for the determination of V(V) because the reduction current increased linearly with an increase of the V(V) concentration up to 1 mM. With further addition of V(V), a new reduction current, denoted as *i*₂, appeared at more positive potentials than the first wave for the [VMo₁₂O₄₀]³⁻ complex (Fig. 4(c)), indicating the formation of vanadium-substituted mixed complexes, [H_{x-1}V(V_xMo_{12-x})O₄₀]⁴⁻ (*x*=1–3).¹⁰ The current, *i*₂ is due to a reduction of the peripheral vanadium atoms in

Fig. 4 Cyclic voltammograms for a 50 mM Mo(VI)–0.3 M HCl–50%(v/v) CH₃CN system with (a) none; (b) 0.1 mM V(V); (c) 2 mM V(V).

the mixed complexes. The linear plot of *i*₁ against the V(V) concentration curved downwards at V(V) concentrations >1 mM, owing to the formation of the mixed complexes. The increase in the Mo(VI) concentration caused the linear range to expand to higher V(V) concentrations.

In order to compare the formation conditions of the [VMo₁₂O₄₀]³⁻ and [H_{x-1}V(V_xMo_{12-x})O₄₀]⁴⁻ complexes, a series of cyclic voltammograms were recorded for 50 mM Mo(VI)–50%(v/v) CH₃CN systems containing various concentrations of HCl, and *i*₁ and *i*₂ were measured at V(V) concentrations of 0.1 and 5 mM, respectively; the results are shown in Fig. 5. The formation of the [VMo₁₂O₄₀]³⁻ complex became maximal around a HCl concentration of 0.3 M (Fig. 5(a)), while the [H_{x-1}V(V_xMo_{12-x})O₄₀]⁴⁻ complexes were favored at weaker acidities (Fig. 5(b)).

Fig. 5 Reduction currents as a function of the HCl concentration for 50 mM Mo(VI)–50%(v/v) CH₃CN system with (a) 0.1 mM V(V) (*i*₁); (b) 5 mM V(V) (*i*₂).

Fig. 6 Reduction currents (i_1) for a 50 mM Mo(VI)–1 mM V(V)–0.3 M HCl system containing various concentrations of (a) CH_3CN ; (b) CH_3COCH_3 ; (c) C_2H_5OH .

The presence of water-miscible organic solvents is essential for the formation of the $[VMO_{12}O_{40}]^{3-}$ complex. As far as the choice of organic solvents was concerned, i_1 was measured for a 50 mM Mo(VI)–1.0 mM V(V)–0.3 M HCl system containing various concentrations of CH_3CN , CH_3COCH_3 or C_2H_5OH . As shown in Fig. 6, the i_1 value was increased monotonously as the concentration of the organic solvent was increased. Of the three organic solvents, CH_3CN was preferable because the biggest i_1 value was obtained; a concentration of 70%(v/v) was chosen as a compromise.

On the basis of these findings, the 50 mM Mo(VI)–0.3 M HCl–70%(v/v) CH_3CN system was chosen as being optimum for the determination of V(V), because two separate phases resulted at Mo(VI) concentrations >60 mM. Cyclic voltammograms were recorded for this system containing V(V), and the i_1 values are directly proportional to the V(V) concentrations in the range of 0.05 – 1 mM. An advantage of this method is that removal of dissolved oxygen is not required because the $[VMO_{12}O_{40}]^{3-}$ complex is reduced at potentials more positive than that of dissolved oxygen. Since V(IV) does not react with Mo(VI) in such strongly acidified aqueous– CH_3CN media, this procedure gives only the V(V) concentration in the mixture of V(V) and V(IV).

On the other hand, the V(IV) concentration can be determined after oxidation to the $[VMO_5O_{19}]^{3-}$ complex by heating the aqueous Mo(VI)–V(IV) system (pH 6) containing CH_3CN . The $[VMO_5O_{19}]^{3-}$ complex transforms spontaneously into the Keggin-type $[VMO_{12}O_{40}]^{3-}$ complex in strongly acidified aqueous-organic media.¹⁰

Recommended procedure for the determination of V(V)

In a 20 ml volumetric flask are placed 2 ml of 500 mM Mo(VI) and 0.6 ml of 10 M HCl, followed by the

addition of 14 ml of CH_3CN . After an appropriate amount of a V(V) sample solution is added to the mixture, the solution is diluted to the mark with distilled water. After standing the solution for a few minutes at ambient temperature, a cyclic voltammogram is recorded. After making sure that i_2 is not observed at this time, the V(V) concentration is determined by a comparison with the calibration curve. When the sample solution comprises V(V) and V(IV), this procedure gives only the V(V) concentration, because V(IV) does not react with Mo(VI) under these conditions. Actually, the presence of V(IV) in concentrations of up to 10 mM did not interfere with the determination of 0.5 mM V(V).

Recommended procedure for the determination of V(IV) and total V (V(V)+V(IV))

After the pH of a solution containing 2 ml of 500 mM Mo(VI) and an appropriate amount of a V(IV) sample solution is adjusted to 6, 14 ml of CH_3CN is added. In order to oxidize V(IV), the solution is heated at 60°C for 10 min. By this procedure, V(IV) is completely oxidized to V(V), which subsequently forms the $[VMO_5O_{19}]^{3-}$ complex. Upon the addition of 0.6 ml of 10 M HCl, the $[VMO_5O_{19}]^{3-}$ complex transforms spontaneously into the $[VMO_{12}O_{40}]^{3-}$ complex. The solution is transferred to a 20 ml volumetric flask and is diluted to the mark with distilled water. When the sample solution contains both V(V) and V(IV), this procedure gives the total concentration of vanadium. Then, the V(IV) concentration is estimated by subtracting the V(V) concentration before oxidation from the total concentration of vanadium.

Interferences from foreign ions

The effects of foreign ions on the determination of vanadium were investigated for a 50 mM Mo(VI)–0.3 M HCl–70%(v/v) CH_3CN system containing 0.5 mM V(V)+0.5 mM V(IV). Table 1 summarizes relative errors for the determination of V(V) and of the total concentration of vanadium, based on two procedures described above, respectively. The presence of NaCl at concentrations <10⁻² M caused no significant interference. Nitrate ions did not interfere with the determination of the total concentrations of V(V) and V(IV), but caused positive errors for the determination of V(V), due to the oxidation of V(IV) to V(V). Oxoanions such as PO_4^{3-} , AsO_4^{3-} , SiO_4^{4-} and GeO_4^{4-} also produce the corresponding Keggin-type heteropoly-complexes under the recommended conditions. Since the Keggin complexes undergo a two-electron reduction at nearly the same potentials as the $[VMO_{12}O_{40}]^{3-}$ complex, the presence of such oxoanions caused serious positive errors. The presence of SO_4^{2-} caused a slight positive error, owing to the formation of the Dawson-type $[S_2Mo_{18}O_{62}]^{4-}$ complex.^{13,14}

Table 1 Effect of foreign ions on the determination of ① V(V) and ② V(V)+V(IV)

Ion added as	Concentration/M	Relative error, %	
		①	②
NaCl	10 ⁻²	+3	+3
	10 ⁻³	+2	+1
NaNO ₃	10 ⁻¹	+8	0
	10 ⁻²	+6	0
Na ₂ SiO ₃	10 ⁻⁴	+26	+11
	10 ⁻⁵	+11	+3
Na ₂ GeO ₃	10 ⁻⁴	+20	+9
	10 ⁻⁵	+11	+4
NaH ₂ PO ₄	10 ⁻⁴	+9	+6
	10 ⁻⁵	+8	+2
Na ₂ HAsO ₄	10 ⁻⁴	+26	+13
	10 ⁻⁵	+10	+5
NaHSO ₄	10 ⁻⁴	+5	+6
	10 ⁻⁵	+3	+4

A 50 mM Mo(VI)-0.3 M HCl-70%(v/v)CH₃CN system containing 0.5 mM V(V)+5 mM V(IV).

Measured after heating at 60°C for 10 min.

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