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Preparation and Properties of Heteropoly Molybdovanadate(V) Complexes

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Tetrabutylammonium salts of the mixed heteropoly molybdovanadate(V) anions, $[H_{x-1}V(V_xMo_{12-x})O_{40}]^{4-}$ (x=1—3) were prepared from a Mo(VI)–V(V)–CH_3CN system at room temperature. These mixed heteropoly anions were distinguished by their voltammetric behavior; the anions with x=1, 2, and 3 were electroreduced by one-, two-, and three-electrons due to the peripheral V atoms at a glassy carbon electrode. The spectroscopic properties were also reported. Their formation conditions were compared with those of 12-molybdovanadate (V), $[VMo_{12}O_{40}]^{3-}$, especially regarding the concentrations of Mo(VI), V(V), acid, and organic solvents, the nature of organic solvents, and the ionic strength of the system. It should be emphasized that the 12-molybdovanadate(V) and mixed molybdovanadate(V) complexes are not formed in the absence of organic solvents.

We have prepared several heteropolymolybdate complexes, which are formed only in the presence of water-miscible organc solvents such as acetonitrile.[1] In the course of the preparative studies from aqueous–organic media, we have recently isolated tetrabutylammonium (n-Bu_4N^+) salts of 12-molybdovanadate(V), which is considered to be a Keggin anion with a central VO_4 tetrahedron, from an acidic Mo(VI)–V(V) solution admixed with acetonitrile.[2] In the present study, the existence of several vanadium-substituted mixed molybdovanadate(V) complexes was ascertained in the solid state and in aqueous–organic solution.

Fortuitously, a mixed-valence reduced crystal of a mixed molybdovanadate(V) complex, $K_6V(V^{IV}V^{V}Mo_{10})O_{40}\cdot 13H_2O$ has been obtained upon slow crystallization of $K_8V_8Mo_4O_{36}\cdot 12H_2O$, and it has been shown by X-ray diffraction analysis that the mixed complex possesses a Keggin-type structure.[3] According to recent ^{51}V NMR studies,[4] heteropoly molybdovanadate(V) complexes are only supposed to be formed in an aqueous Mo(VI)–V(V) system. On the basis of our results, however, it should be stressed that the presence of organic solvents in concentrations greater than 30% (v/v) is essential for the formation of heteropoly molybdovanadate(V) complexes.

The present study was undertaken to characterize the mixed molybdovanadate(V) complexes and to elucidate their formation conditions in relation to those of 12-molybdovanadate(V). This paper also reports voltammetric evidence for the spontaneous conversion of $[VMo_5O_{19}]^{3-}$ into heteropoly molydovanadate(V) anions in acidified aqueous–organic system.

Experimental

UV-visible absorption spectra were recorded on a Hitachi Model 220-A spectrophotometer using a quartz cell with path length of 1.0 cm. Voltammetric measurements were made with a PARC Model 174-A polarographic analyzer equipped with a Yokogawa Model 3023 X-Y recorder. A working electrode was a glassy carbon (Tokai Carbon, GC-30S) with a surface area of 0.071 cm^2. A platinum wire was used as the counter electrode and a saturated calomel electrode (SCE) as the reference. Unless stated otherwise, voltage scan rate was set at 100 mV s^{-1}. UV-visible spectrophotometric and voltammetric measurements were made at 25±0.1 °C. Controlled potential electrolysis was carried out with a Hokuto Denko Model HA-501 potentiostat. TG-DTA was carried out with a Rigaku Denki 8002-SD thermal analyzer. A Hitachi Model 270-30 spectrophotometer was used to record IR spectra using KBr pellets.

Results and Discussion

Preparation of Molybdovanadate(V) Complexes. **(n-$Bu_4N)_3VMo_{12}O_{40}$:** This complex was prepared and purified as described.[2]

(n-$Bu_4N)_4V(VMo_{11})O_{40}$: A solution of 1.17 g (10.0 mmol) NH_4VO_3 in 125 ml of 2 M HCl (1 M=1 mol dm^{-3}) was added to a solution of 6.05 g (25.0 mmol) of $Na_2MoO_4\cdot 2H_2O$ in 75 ml of water. Then, 300 ml of acetonitrile was added with stirring to the mixture. This resulted in a rapid color change from pale-yellow due to vanadate(V) to orange-yellow. After the solution was stirred for 1 h at room temperature, 10 g of n-Bu_4NBr was added to precipitate an orange-yellow salt. The salt was isolated by filtration, and washed with water and ethanol (Yield 5.4 g). The salt was purified by recrystallization from 350 ml of acetonitrile.

Anal. Calcd for (n-$Bu_4N)_4V(VMo_{11})O_{40}$: Mo, 38.14; V, 3.68; C, 27.78; H, 5.25; N, 2.02%. Found: Mo, 37.70; V, 3.82; C, 27.71; H, 5.42; N, 2.08%.

(n-$Bu_4N)_4HV(V_2Mo_{10})O_{40}$: This preparation is similar to that of the preceding salt. A solution of 2.05 g (17.5 mmol) of NH_4VO_3 in 100 ml of 2 M HCl was added to a solution of 6.05 g (25.0 mmol) of $Na_2MoO_4\cdot 2H_2O$ in 100 ml of water. After the addition of 300 ml of acetonitrile, the solution was stirred for 1 h at room temperature. The addition of 10 g of n-Bu_4NBr led to immediate precipitation of an orange salt (Yield 6.3 g), which was subsequently recrystallized from 300 ml of acetonitrile.

Anal. Calcd for (n-$Bu_4N)_4HV(V_2Mo_{10})O_{40}$: Mo, 35.25; V, 5.61; C, 28.24; H, 5.37; N, 2.06%. Found: Mo, 34.89; V, 5.63; C, 27.94; H, 5.20; N, 2.06%.

$(n\text{-Bu}_4\text{N})_4\text{H}_2\text{V}(\text{V}_3\text{Mo}_9)\text{O}_{40}$: This compound was prepared with the use of the procedure described for $(n\text{-Bu}_4\text{N})_4\text{HV}(\text{V}_2\text{Mo}_{10})\text{O}_{40}$ by substituting 2.98 g (25.0 mmol) of NH_4VO_3 for 2.05 g (Yield 6.8 g).

Anal. Calcd for $(n\text{-Bu}_4\text{N})_4\text{H}_2\text{V}(\text{V}_3\text{Mo}_9)\text{O}_{40}$: Mo, 32.23; V, 7.61; C, 28.69; H, 5.49; N, 2.09%. Found: Mo, 32.58; V, 7.57; C, 28.29; H, 5.50; N, 2.13%.

In the TG-DTA, the evolution of water was not observed up to about 260 °C for the mixed heteropoly molybdovanadate(V) complexes.

The mixed molybdovanadate(V) complexes are not distinguished by their IR spectra because they show the strong absorption bands of the same pattern at 946, 880, and 774 cm^{-1}; the 12-molybdovanadate(V) complex gives the corresponding bands at 958, 887, and 776 cm^{-1}.[2] Despite various attempts , complexes with higher vanadium contents were not successfully prepared.

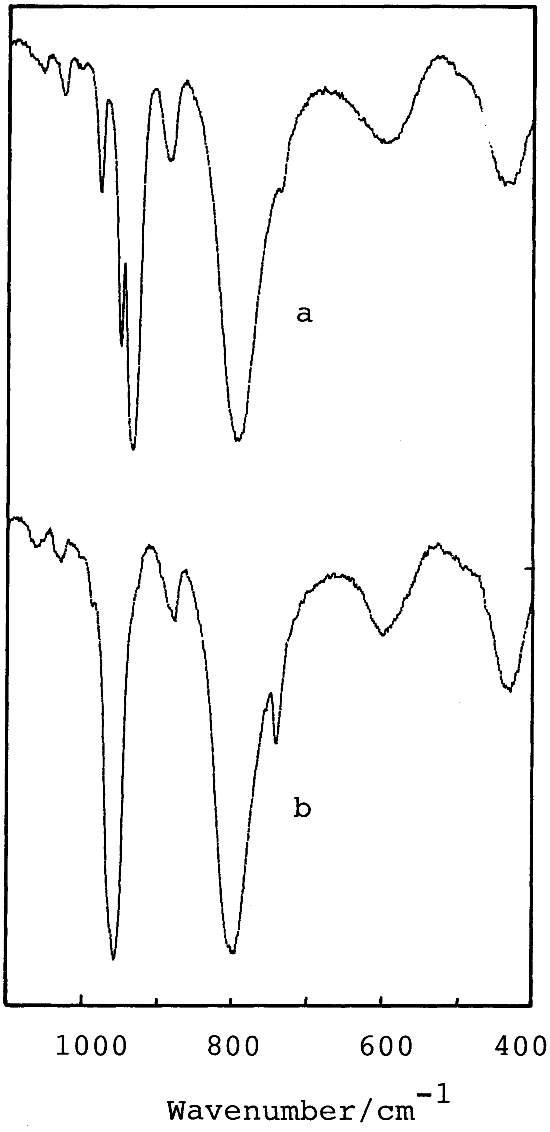

Fig. 1. IR spectra of (a) $(n\text{-Bu}_4\text{N})_3\text{VMo}_5\text{O}_{19}$ and (b) $(n\text{-Bu}_4\text{N})_2\text{Mo}_6\text{O}_{19}$ in the KBr pellets. Numerical data are given in the Text.

In addition, the $[\text{VMo}_5\text{O}_{19}]^{3-}$ anion was prepared with a view to investigating the possibility of its transformation reaction into hereropoly molybdovanadate(V) anions.[5] According to Flynn, Jr. and Pope,[6] mixed tungstovanadate(V) anions such as $[\text{V}(\text{V}_2\text{W}_{10})\text{O}_{40}]^{5-}$ and $[\text{V}(\text{V}_3\text{W}_9)\text{O}_{40}]^{6-}$ have been prepared by acidifying the aqueous solution of the mixed Lindqvist anion, $[\text{V}_2\text{W}_4\text{O}_{19}]^{4-}$, although 12-tungstovanadate(V) is still unknown.

$(n\text{-Bu}_4\text{N})_3\text{VMo}_5\text{O}_{19}$: A solution of 0.234 g (2.0 mmol) NH_4VO_3 in 20 ml of 0.15 M NaOH was added to a solution of 2.42 g (10.0 mmol) of $Na_2MoO_4 \cdot 2H_2O$ in 480 ml of water, and the pH of the solution was adjusted to pH 3.2 with HCl.[7] The resulting yellow solution was stirred for 1 h at room temperature. A yellow salt was precipitated by the addition of 5 g of n-Bu_4NBr, being filtered off, washed with water and ethanol, and dried at 40 °C (Yield 2.9 g). The yellow salt was recrystallized from 100 ml of acetonitrile.

Anal. Calcd for $(n\text{-Bu}_4\text{N})_3\text{VMo}_5\text{O}_{19}$; Mo, 30.71; V, 3.26; C, 36.91; H, 6.97; N, 2.69%. Found: Mo, 30.76; V, 3.27; C, 36.76; H, 7.11; N, 2.75%. IR (400—1000 cm^{-1}): 978, 950, 934, 796, 596, 436 cm^{-1} (Fig. 1(a)). For comparison, Fig. 1(b) shows an IR spectrum of $(n\text{-Bu}_4\text{N})_2\text{Mo}_6\text{O}_{19}$ prepared according to the previous procedure.[8] IR (400—1000 cm^{-1}): 956, 798, 598, 436 cm^{-1}.

UV-Visible Spectra. The $n\text{-Bu}_4\text{N}^+$ salts of the mixed heteropoly molybdovanadate(V) anions are reasonably soluble in polar aprotic solvents such as

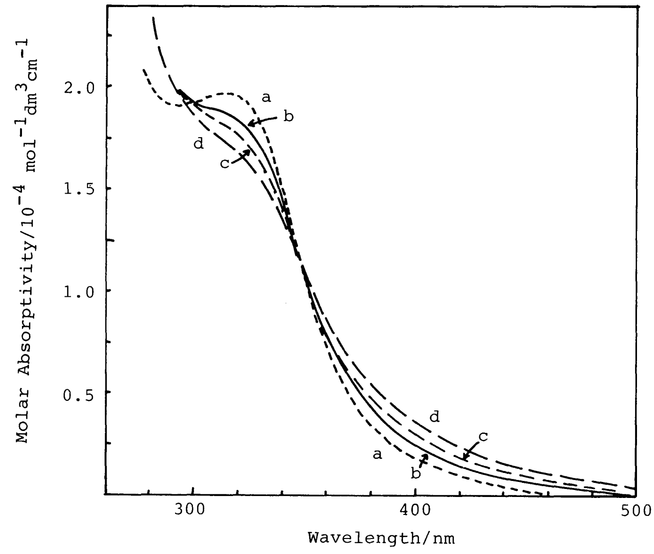

Fig. 2. UV-visible spectra of 0.04 mM $[\text{H}_{x-1}\text{V}(\text{V}_x\text{Mo}_{12-x})\text{O}_{40}]^{4-}$ in neat acetonitrile. (b), x=1; (c), x=2; (d), x=3. The spectrum of 0.04 mM $[\text{VMo}_{12}\text{O}_{40}]^{3-}$ is included for comparison (curve (a)).

acetonitrile and acetone, and insoluble in water, ethanol, and 1,4-dioxane. Figure 2 shows UV-visible absorption spectra of 0.04 mM (M=mol dm^{-3}) solutions of the $[H_{x-1}V(V_xMo_{12-x})O_{40}]^{4-}$ anions in neat acetonitrile. The solutions obeyed Beer's law in the spectral region studied. As the substituted vanadium content increased, the spectrum appeared like a shoulder and there was a decrease in molar absorptivities at 310 nm (1.90×10^4, 1.82×10^4, and 1.75×10^4 mol^{-1} dm^3 cm^{-1} for the $[H_{x-1}V(V_xMo_{12-x})O_{40}]^{4-}$ anions with x=1, 2, and 3, respectively). These behaviors are similar to those of a series of mixed molybdovanadophosphate(V) complexes with the Keggin-type structure.[9,10]

Voltammetric Characterization of the Heteropoly Molybdovanadate(V) Anions. Figures 3 and 4 show cyclic and normal pulse voltammograms, respectively, of 0.2 mM solutions of the heteropoly molybdovanadate(V) complexes in 95% (v/v) CH_3CN containing 0.1 M $HClO_4$.

The $[VMo_{12}O_{40}]^{3-}$ Anion: Reproducible voltammograms were obtained (curve (a)). As already described,[2] the first reduction wave corresponds to a reversible two-electron transfer. The separation of the cathodic and anodic peaks averages 27—30 mV. The peak-potential (E_p) showed positive shift as the $HClO_4$ concentration was increased in the range of −log

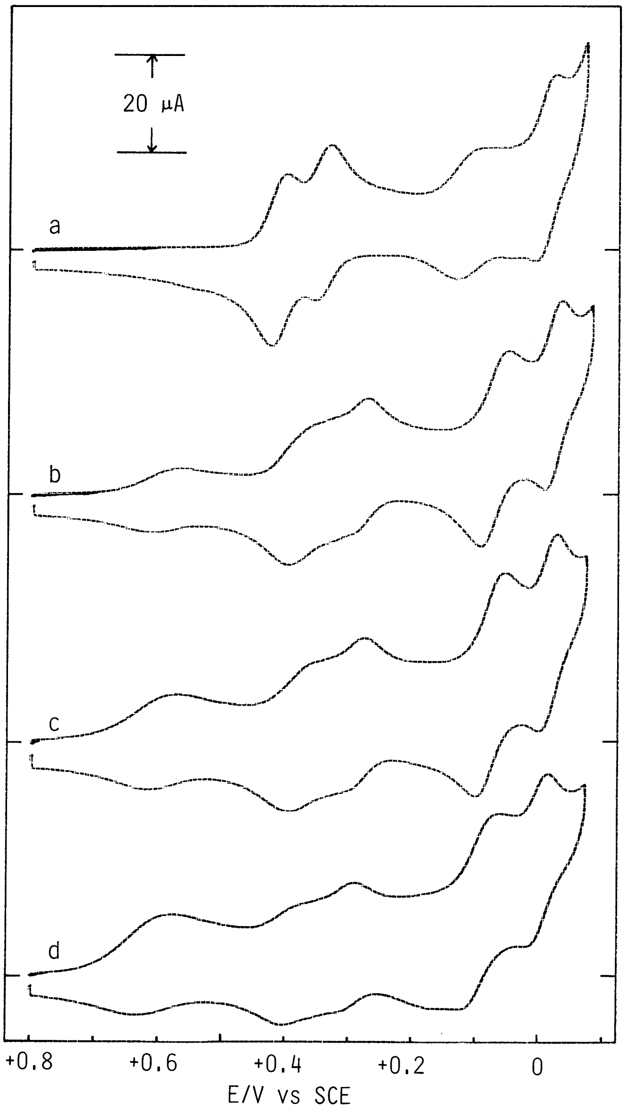

Fig. 3. Cyclic voltammograms of 0.2 mM $[H_{x-1}V(V_xMo_{12-x})O_{40}]^{4-}$ in 95%(v/v) CH_3CN-water containing 0.1 M $HClO_4$. (b) x=1; (c), x=2; (d), x=3. The voltammogram of 0.2 mM $[VMo_{12}O_{40}]^{3-}$ is included for comparison (curve (a)).

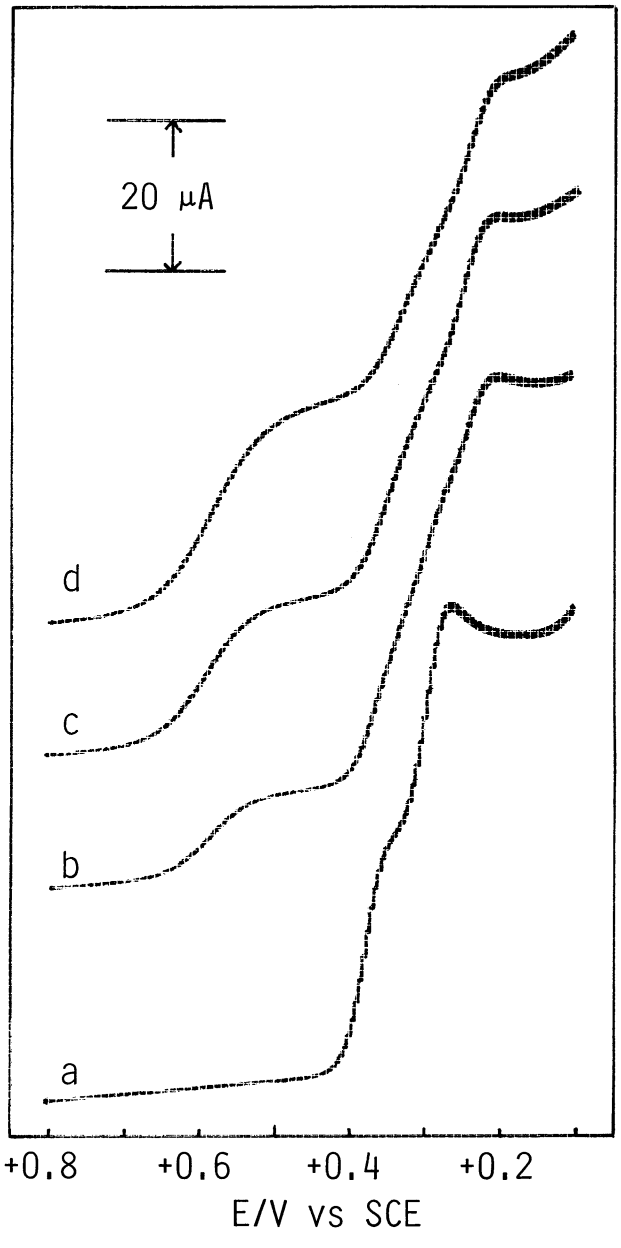

Fig. 4. Normal pulse voltammograms of 0.2 mM $[H_{x-1}V(V_xMo_{12-x})O_{40}]^{4-}$ in 95%(v/v) CH_3CN-water containing 0.1 M $HClO_4$. (b), x=1; (c), x=2; (d), x=3. The voltammogram of 0.2 mM $[VMo_{12}O_{40}]^{3-}$ is included for comparison (curve (a)).

$[H^+]=2.6—1.0$ ($I=0.1$ M ($NaClO_4$)), where I=ionic strength. The slope of $E_p/-\log[H^+]$ was estimated to be 65 mV, indicating that two protons are consumed in the reduction process:

$$[VMo_{12}O_{40}]^{3-} + 2e + 2H^+ = [H_2V(Mo^{V}_2Mo_{10})O_{40}]^{3-}$$

The $[H_{x-1}V(V_xMo_{12-x})O_{40}]^{3-}$ Anions: The voltammograms recorded 1 h later remained identical under these conditions; however, the solutions examined after 24 h standing gave decayed or distorted voltammograms, indicating the decomposition of the complexes. Therefore, curves (b)—(d) of Figs. 3 and 4 were recorded for freshly prepared solutions.

The voltammograms for the $[H_{x-1}V(V_xMo_{12-x})O_{40}]^{4-}$ anions gave additional reduction waves at about 0.2 V more positive than the first reduction wave of $[VMo_{12}O_{40}]^{3-}$. The currents were dependent on the square root of the voltage scan rate (20—200 mV s^{-1}), indicating that the electrode processes are diffusion-controlled. The additional waves can be ascribed to the reduction of the peripheral V atoms, because the reduction currents are dependent on the vanadium content. This is in line with the previous observations that the V atoms in the peripheral structure are more easily reduced than the Mo or W atoms in vanadium-substituted mixed complexes with P as the central heteroatom, i.e., $[P(V_xMo_{12-x})O_{40}]^{(3+x)-}$ and $[P(V_xW_{12-x})O_{40}]^{(3+x)-}$.[11—14]

As long as the $[V(VMo_{11})O_{40}]^{4-}$ anion is concerned, the voltammetric wave corresponds to a reversible one-electron transfer, because the separation of the cathodic and anodic peaks are 60 mV, being independent of the voltage scan rate (20—200 mV s^{-1}) in cyclic voltammetry. The E_p's for the reduction and oxidation waves were shifted to more positive potentials as the $HClO_4$ concentration was increased in the range of $-\log[H^+]=2.6—1.0$ ($I=0.1$ M ($NaClO_4$)), and the slope was estimated to be 65 mV, which indicates that the electrode process corresponds to the reaction:

$$[V(V^{V}Mo_{11})O_{40}]^{4-} + e + H^+ = [HV(V^{IV}Mo_{11})O_{40}]^{4-}$$

Both cyclic and normal pulse voltammetric reduction currents for the $[HV(V_2Mo_{10})O_{40}]^{4-}$ and $[H_2V(V_3Mo_9)O_{40}]^{4-}$ anions were approximately 2 and 3 times that for the one-electron reduction current of the $[V(VMo_{11})O_{40}]^{4-}$ anion. These results indicate that both reduction processes involve a sequence of 2 and 3 one-electron steps with different standard potentials, E^0, rather than single two- and three-electron reductions, respectively:[15—17] In the case of the reduction of the $[HV(V_2Mo_{10})O_{40}]^{4-}$ anion, for example,

$$[HV(V_2^{V}Mo_{10})O_{40}]^{4-} \underset{E_1^0}{\overset{e}{\rightleftharpoons}} [HV(V^{IV}V^{V}Mo_{10})O_{40}]^{5-}$$

$$\underset{E_2^0}{\overset{e}{\rightleftharpoons}} [HV(V_2^{IV}Mo_{10})O_{40}]^{6-}$$

When $-90\text{ mV}<\Delta E^0(=E_2^0-E_1^0)<0$ mV, the individual waves merge into one broad wave.[17] This is further substantiated by the fact that in cyclic voltammetry, the E_p values for the cathodic and anodic waves were not affected by the voltage scan rate (20—200 mV s^{-1}) (the separation averaged 60—70 mV). These reduction behaviors suggest that the V atoms are not in the adjacent position in the peripheral structure.[15] It has been shown by X-ray crystallographic structural analysis that the Mo and V atoms are randomly distributed in the peripheral structures of $[V(V^{IV}V^{V}Mo_{10})O_{40}]^{6-}$ and $[P(V_xMo_{12-x})O_{40}]^{(3+x)-}$ (x=2 and 3).[3,18] It was found that the E_p values shifted to more positive potentials with an increase of the $HClO_4$ concentration. However, quantitative treatment could not be made owing to the complicated electrode processes.

As shown in curves (b)—(d) of Fig. 3, the voltammetric waves due to the reduction of molybdenum appeared at potentials more negative than +0.4 V, being distorted similar to irreversible waves. However, the distorted waves remained unchanged in position on the potential axis as a function of the voltage scan rate (20—200 mV s^{-1}), which indicates the reversible nature of their electrode processes. At present we are unable to account quantitatively for this electrode behavior; however, a possible explanation can be given in terms of the existence of several isomers in oxidized and/or reduced forms with slightly different E^0.[17]

The distorted waves due to the reduction of molybdenum decreased in height with an increase of the vanadium content in the complexes. These results can be accounted for in terms of the decomposition of the vanadium-substituted complexes as a result of the reduction of the peripheral V atoms. This is confirmed by the following observations: For the $[H_{x-1}V(V_xMo_{12-x})O_{40}]^{4-}$ anions, the solutions changed from orange to blue by controlled potential electrolysis at a reduction potential of the peripheral V atoms; however, colorless solutions resulted at the end of controlled potential electrolysis because of the decomposition of the blue species.

Formation of the Heteropoly Molybdovanadate(V) Anions. Figure 5 shows cyclic voltammograms of a 10 mM Mo(VI)-0.2 M HCl-50%(v/v) CH_3CN system. In the absence of V(V), as shown in curve (a), no voltammetric waves were obtained until a current rise due to the reduction of $[Mo_6O_{19}]^{2-}$ around +0.1 V.[8,19] On the addition of 0.2 mM V(V), a two-step voltammetric wave with an equal height was obtained (curve (b)). The currents were diffusion-controlled. As shown in curve (a) of Fig. 6, the voltammetric currents attained to a constant value around one min

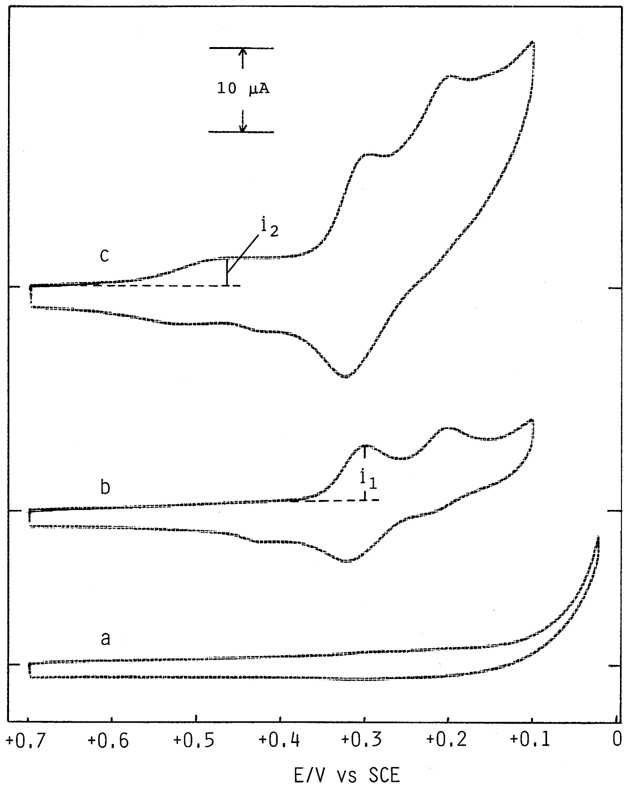

Fig. 5. Cyclic voltammograms of 10 mM Mo(VI)–0.2 M HCl–50%(v/v) CH_3CN systems. [V(V)]/mM, (a) none; (b) 0.2; (c) 1.0.

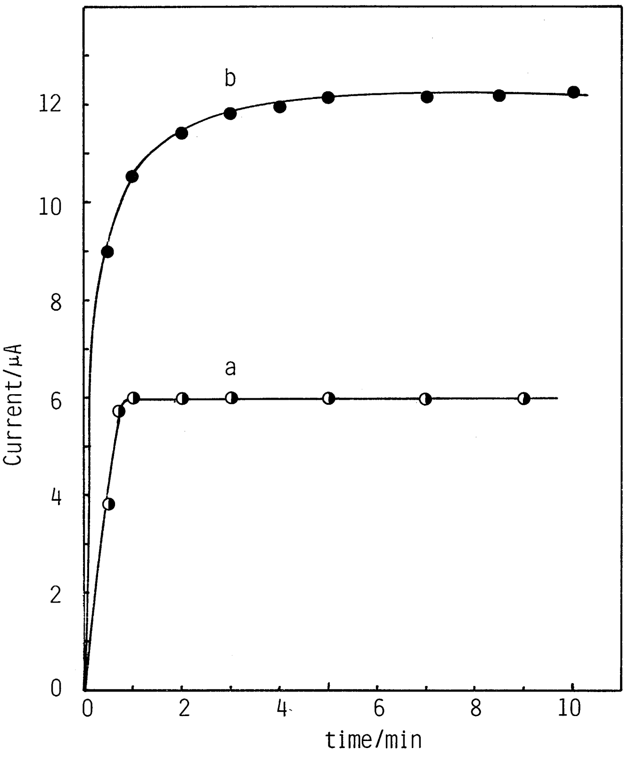

Fig. 6. Current-time profiles for 30 mM Mo(VI)–0.1 M $HClO_4$–50%(v/v) CH_3CN systems. [V(V)]/mM, (a), 0.2 (i_1); (b), 2.0 (i_2).

after the addition of V(V). The $[VMo_{12}O_{40}]^{3-}$ anion is responsible for the voltammetric waves shown in curve (b) of Fig. 5. The first peak current is represented by i_1 in the following.

The increase of the V(V) concentration caused the voltammetric behavior to change significantly. With an increase of the V(V) concentration while other conditions were kept unchanged, the solution turned from yellow to orange. Simultaneously, a new voltammetric wave appeared at more positive potentials than those for the voltammetric wave of $[VMo_{12}O_{40}]^{3-}$ (curve (c) of Fig. 5). The new voltammetric current corresponding to the reduction of the peripheral V atoms attained to a constant value around 5 min after the addition of V(V) as shown in curve (b) of Fig. 6, being denoted as i_2 in the following. This behavior can be ascribed to the formation of vanadium-substituted derivatives of the $[VMo_{12}O_{40}]^{3-}$ anion. After the current-increase periods, both 12-molybdovanadate(V) and vanadium-substituted derivatives are stable under these conditions, as judged by no change of i_1 and i_2.

Figure 7 shows the dependence of i_1 and i_2 on the concentration of V(V) in 10 mM Mo(VI)–0.2 M HCl–50%(v/v) CH_3CN systems. For V(V) concentrations< 0.5 mM, i_2 was hardly detected, which indicates that $[VMo_{12}O_{40}]^{3-}$ is predominant. Both i_1 and i_2 increased as the V(V) concentration was increased from 0.5 to 1 mM. Above 1 mM V(V), i_2 increased further at the expense of i_1.

The formation conditions of 12-molybdovanadate (V) and vanadium-substituted derivatives were inves-

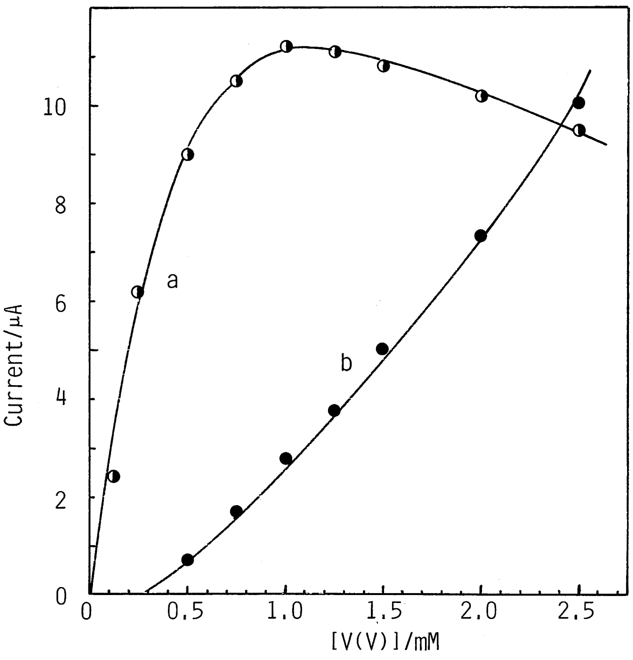

Fig. 7. Dependence of (a) i_1 and (b) i_2 on the concentration of V(V) for 10 mM Mo(VI)–0.2 M HCl–50%(v/v) CH_3CN systems.

tigated by monitoring i_1 and i_2, respectively. Curves (a) and (b) of Fig. 8 show i_1 and i_2 as a function of the $HClO_4$ concentration for 30 mM Mo(VI)–50%(v/v) CH_3CN systems containing 0.1 and 0.5 mM V(V), respectively. The ionic strength was adjusted to be 0.5 M with $NaClO_4$. The 12-molybdovanadate(V) anion is formed in the $HClO_4$ concentration range 0.06—0.6 M while the vanadium-substituted derivative anions are formed in 0.04—0.4 M $HClO_4$. Curve (c) shows absorbance values at 400 nm for 30 mM Mo(VI)–50%(v/v) CH_3CN systems in the absence of V(V) to illustrate the formation conditions of $[Mo_6O_{19}]^{2-}$. The $[VMo_5O_{19}]^{3-}$ ion was not detected in these aqueous-organic solutions; the anion is formed in aqueous solutions of about pH 3,[4,7] or in nonaqueous media.[5]

Figure 9 shows the dependence of i_1 and i_2 on the ionic strength for 30 mM Mo(VI)–0.1 M $HClO_4$–50%(v/v) CH_3CN systems containing various concentrations of $NaClO_4$ (0—0.4 M). It was found that i_1 decreased while i_2 increased with an increase of the ionic strength from 0.1 to 0.5 M, which means that the increase of the ionic strength of the solution favors the formation of the tetravalent anions rather than the trivalent anion.

The effects of the nature and concentration of organic solvents on the formation of 12-molybdovanadate(V) and vanadium-substituted derivatives were also investigated by measuring i_1 and i_2 in solutions of 30 mM Mo(VI) containing 0.2 and 2.0 mM V(V), respectively. Figures 10 and 11 show the results. It can be concluded that neither of 12-molybdovanadate(V) and vanadium-substituted derivatives is formed in the absence of organic solvents, and the increase of the concentration of organic solvents favors the formation of the heteropoly molybdovanadate(V) complexes.

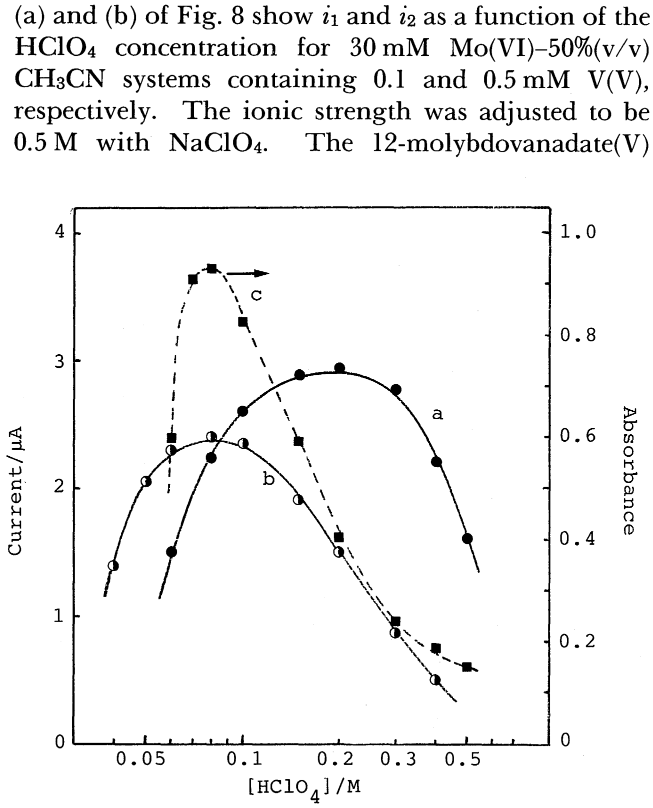

Fig. 8. Formation ranges of (a) $[VMo_{12}O_{40}]^{3-}$, (b), $[H_{x-1}V(V_xMo_{12-x})O_{40}]^{4-}$, and (c) $[Mo_6O_{19}]^{2-}$ for 30 mM Mo(VI)–50%(v/v) CH_3CN systems as a function of the $HClO_4$ concentration (I=0.5 M ($NaClO_4$)). (a), i_1 for [V(V)]=0.1 mM; (b) i_2 for [V(V)]=0.5 mM; (c) absorbances at 400 nm in the absence of V(V).

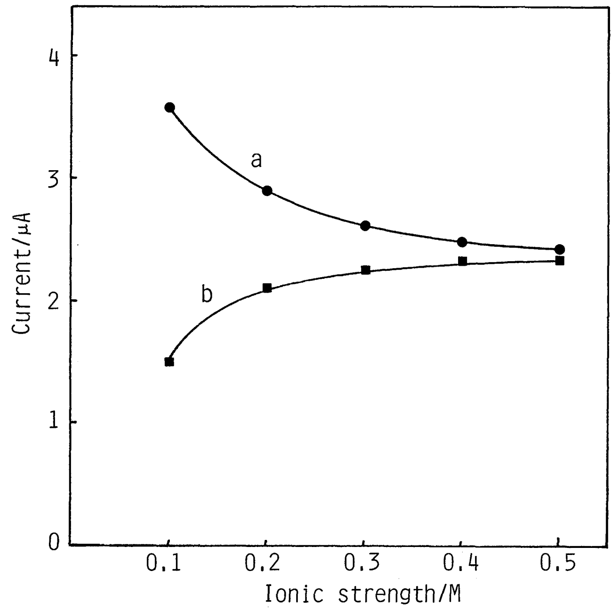

Fig. 9. Effect of ionic strength on (a) i_1 and (b) i_2 for 30 mM Mo(VI)–0.1 M $HClO_4$–50%(v/v) CH_3CN systems containing various concentrations of $NaClO_4$ (0—0.4 M).

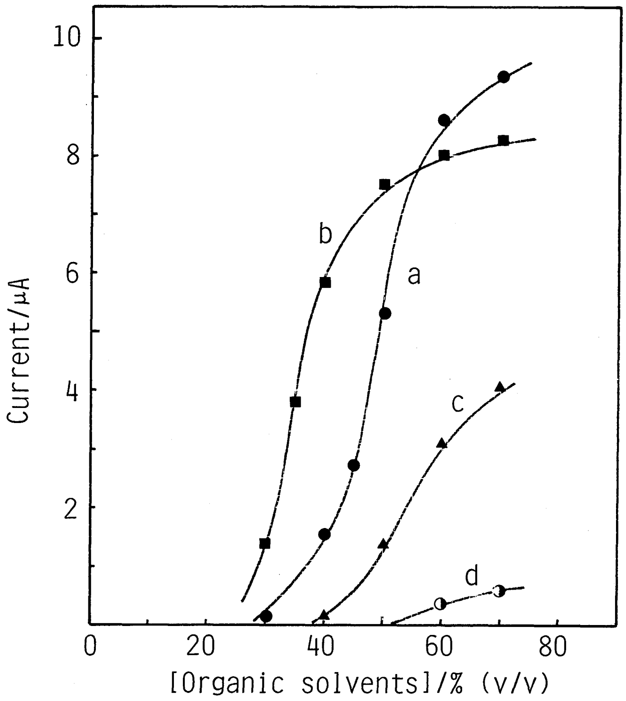

Fig. 10. Effect of concentrations of organic solvents on i_1 for 30 mM Mo(VI)–0.2 mM V(V)–0.3 M $HClO_4$ systems containing (a) acetonitrile; (b), acetone; (c), ethanol; (d), 1,4-dioxane.

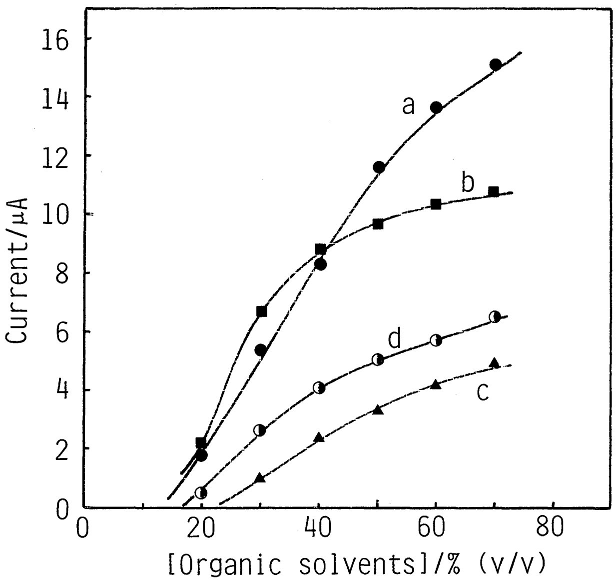

Fig. 11. Effect of concentrations of organic solvents on i_2 for 30 mM Mo(VI)-2.0 mM V(V)-0.05 M $HClO_4$ systems (I=0.1 M ($NaClO_4$)) containing (a), acetonitrile; (b), acetone; (c), ethanol; (d), 1,4-dioxane.

Conversion of $[VMo_5O_{19}]^{3-}$ into Mixed Heteropoly Molybdovanadate(V) Anions. As shown in curve (a) of Fig. 12, a cyclic voltammogram of 0.32 mM $[VMo_5O_{19}]^{3-}$ showed a couple of reduction and oxidation waves in 90%(v/v) CH_3CN-water containing 0.001 M $HClO_4$ (I=0.1 M ($NaClO_4$)). The waves were diffusion-controlled. The peak-separation for the reduction-oxidation couple was found to be 70 mV, and the E_p values were almost independent of the voltage scan rate (20—100 mV s^{-1}), which indicates that the wave corresponds to the reversible reduction of $[VMo_5O_{19}]^{3-}$ to $[V^{IV}Mo_5O_{19}]^{4-}$. In addition to the reversible wave, an irreversible reduction wave appeared at potentials more negative than −0.1 V. The irreversible wave can be ascribed to the reduction of molybdenum because the four-electron reduction wave of $[Mo_6O_{19}]^{2-}$ appears around the same potentials under these conditions.[19]

As time elapsed, a new reduction wave appeared with an E_p value of +0.37 V; the current increased with time until a constant value was attained in ca. 60 min. The ultimate voltammogram is shown in curve (b). Orange salts were obtained by the addition of tetraethylammonium bromide to the solution, being identified as mixed heteropoly molybdovanadate(V) complexes by the IR spectroscopic measurement. These results clearly show that the $[VMo_5O_{19}]^{3-}$ anion transforms spontaneously into mixed heteropoly molybdovanadate(V) anions under these conditions. Comparison of the reduction currents due to the peripheral V atoms in Fig. 12 with those in Fig. 3 leads to the conclusion that a mixture of $[V(VMo_{11})O_{40}]^{4-}$ and $[HV(V_2Mo_{10})O_{40}]^{4-}$ is formed as a result of the transformation. This conversion reaction was observed for 90%(v/v) CH_3CN-water solutions containing 0.001—0.1 M $HClO_4$ (I=0.1 M); however, it did not occur in the absence of acid. Similar conversion reaction was also observed in acidic solutions containing >60%(v/v) acetone. Flynn, Jr. and Pope have reported similar conversion of $[V_2W_4O_{19}]^{4-}$ into mixed heteropoly tungstovanadate(V) anions in acidified aqueous solutions.[6]

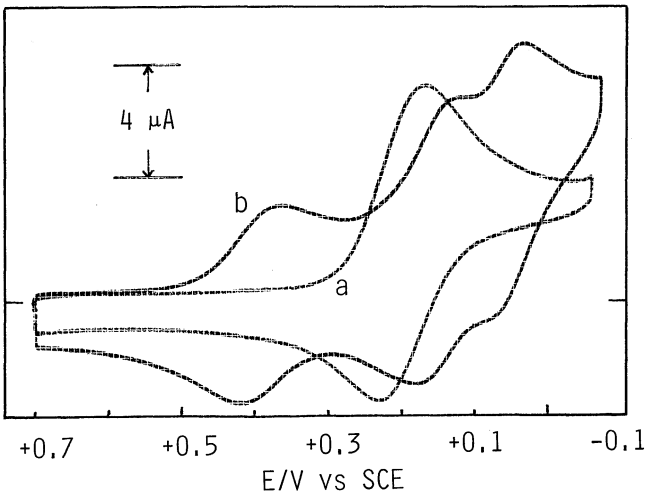

Fig. 12. Cyclic voltammograms of 0.32 mM $[VMo_5O_{19}]^{3-}$ in 90%(v/v) CH_3CN-water containing 0.001 M $HClO_4$ (I=0.1 M ($NaClO_4$)). Recorded (a) immediately after the addition of $[VMo_5O_{19}]^{3-}$; (b) after 60 min.

References

1) T. Hori and S. Himeno, *Chem. Lett.*, **1987**, 53; S. Himeno, T. Hori, and A. Saito, *Bull. Chem. Soc. Jpn.*, **62**, 2184 (1989); T. Hori, O. Tamada, and S. Himeno, *J. Chem. Soc., Dalton Trans.*, **1989**, 1491; S. Himeno, A. Saito, and T. Hori, *Bull. Chem. Soc. Jpn.*, **63**, 1602 (1990); S. Himeno, T. Osakai, A. Saito, and T. Hori, *Talanta*, **37**, 1071 (1990).

2) S. Himeno and A. Saito, *Inorg. Chim. Acta*, **171**, 135 (1990).

3) A. Bjornberg and B. Hedman, *Acta Crystallogr., Sect. B*, **36**, 1018 (1980).

4) R. I. Maksimovskaya and N. N. Chumachenko, *Polyhedron*, 6, 1813 (1987).

5) M. Filowitz, R. K. C. Ho, W. G. Klemperer, and W. Shum, *Inorg. Chem.*, **18**, 93 (1979).

6) C. M. Flynn, Jr. and M. T. Pope, *Inorg. Chem.*, **10**, 2745 (1971); **11**, 1950 (1972).

7) G. W. Wallace and M. G. Mellon, *Anal. Chim. Acta*, **23**, 355 (1960).

8) S. Himeno, N. Ishii, M. Hasegawa, A. Saito, and T. Hori, *Inorg. Chim. Acta*, **131**, 11 (1987).

9) P. Courtin, F. Chauveau, and P. Souchay, *C. R. Acad. Sci. (Paris)*, **258**, 1247 (1964).

10) P. Courtin, *Rev. Chim. Miner.*, **8**, 75 (1971).

11) M. P. Courtin, *Bull. Soc. Chim. Fr.*, **1968**, 4799.

12) G. A. Tsigdinos and C. J. Hallada, *J. Less-Common*

Met., **36**, 79 (1974).

13) D. P. Smith and M. T. Pope, *Inorg. Chem.*, **12**, 331 (1973).

14) G. A. Tsigdinos, "Electrochemical Properties of Heteropoly Molybdates," Climax Molybdenum Company Bulletin Cdb-15, 1971.

15) W. F. Sokol, D. H. Evans, K. Niki, and T. Yagi, *J. Electroanal. Chem. Interfacial Electrochem.*, **108**, 107 (1980).

16) A. J. Bard and L. R. Faulkner, "Electrochemical Methods," John Wiley and Sons, New York (1980), Chap. 6.

17) D. S. Polcyn and I. Shain, *Anal. Chem.*, **38**, 370 (1966).

18) V. S. Sergienko, M. A. Porai-Koshits, and E. N. Yurchenko, *J. Struct. Chem. (Eng. Transl.)*, **21**, 87 (1980).

19) T. Osakai, S. Himeno, A. Saito, and T. Hori, *J. Electroanal. Chem. Interfacial Electrochem.*, **258**, 209 (1990).