Preparation and Characterization of 11-Molybdoarsenite(III) Complex

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A green 11-molybdoarsenite(III) complex, which was formed in an Mo(VI)–AsO_3^{3-}–HCl–CH_3CN system at room temperature, was isolated as the tetrabutylammonium (n-Bu_4N^+) salt, being characterized by its voltammetric behavior and its IR and UV-visible spectra. The heteropolyanion undergoes two-step one-electron reductions in CH_3CN and three-step two-electron reductions in acidified CH_3CN. The electrochemical reduction produces mixed-valence blue species at the glassy carbon (GC) electrode. The formation conditions and chemical properties were compared with those of 12-molybdoarsenate(V) with the Keggin structure. The presence of water-miscible organic solvents like CH_3CN and CH_3COCH_3 is absolutely necessary for the formation of the green heteropolyanion.

Heteropolymolybdate anions have attracted a great interest as redox catalysts, and extensive investigations have been directed mainly at correlating their structures with electrochemical properties.[1] However, most of the studies has been conducted on limited types of heteropoly complexes incorporating an XO_4 tetrahedron, i.e., Keggin- and Dawson-complexes.

The structure of heteropoly complexes may depend on the configuration of oxoanions capable of acting as a central hetero-ion. Knowledge of such dependences will provide information on the geometrical requirements for heteropoly complexes with electrochemically active properties. In view of these considerations, we have tried to prepare heteropolymolybdate complexes based on an X_2O_7-type oxoanion instead of the XO_4 tetrahedron. In an Mo(VI)–$P_2O_7^{4-}$–HCl–CH_3CN system, we have demonstrated the existence of a yellow 18-molybdopyrophosphate anion, $[P_2Mo_{18}O_{61}]^{4-}$ which is electrochemically reduced to heteropoly blue species.[2] Unlike the Dawson-type $[P_2Mo_{18}O_{62}]^{6-}$ anion which contains A-type PMo_9 units, the $[P_2Mo_{18}O_{61}]^{4-}$ anion may be based on two B-type PMo_9 units; the crystallographic structure is now under investigation.

Subsequently, we have investigated the possibility of preparing electrochemically active heteropolyanions incorporating an XO_3-type oxoanion. As a result, a yellow 12-molybdodiphosphonate(III) complex has been isolated as the n-Bu_4N^+ salt from an Mo(VI)–HPO_3^{2-}–HCl–CH_3CN system.[3] The yellow heteropolyanion undergoes apparent two-step reduction to blue species.

However, no comprehensive studies have been reported concerning electrochemically active heteropolyanions incorporating the XO_3-type oxoanion. Heteropolyanions based on these types of oxoanions such as HXO_3 and XO_3 must take structures which can adapt an H atom and an unshared electron pair occupying the tetrahedral vertices, respectively. In order to shed more light on this problem, we have continued the preparative studies of electrochemically active heteropolyanions based on the XO_3-type oxoanion, with the use of AsO_3^{3-}. The present study has revealed that a green molybdoarsenite(III) complex is formed in an Mo(VI)–AsO_3^{3-}–HCl–CH_3CN system at room temperature. Unlike the yellow 12-molybdodiphosphonate-(III) complex, the molybdoarsenite(III) complex has a compositional ratio of Mo/As=11/1. The green heteropolyanion is electrochemically reduced to heteropoly blues in CH_3CN.

As far as heteropoly complexes with such XO_3-type oxoanions are concerned, pentamolybdo-complexes like $[S_2Mo_5O_{21}]^{4-}$, $[Se_2Mo_5O_{21}]^{4-}$, and $[(HP)_2Mo_5O_{21}]^{4-}$ have been well established.[4—8] However, these colorless complexes, being isomorphous with $[P_2Mo_5O_{23}]^{6-}$ whose structure has been determined by Strandberg,[9] are not voltammetrically reducible.

Experimental

A Hitachi Model 270-30 spectrophotometer was used to record IR spectra as KBr pellets. UV-visible absorption spectra were recorded on a Hitachi Model 220-A spectrophotometer. Cyclic voltammograms were acquired with a microcomputer-controlled system.[10] A Tokai glassy carbon rod (GC-30S) with a surface area of 0.20 cm^2 was used as a working electrode and a platinum wire served as the counter. The reference electrode was either an Ag/AgCl electrode for the CH_3CN–water mixed media or an Ag/Ag^+ (0.01 M; CH_3CN) electrode for the CH_3CN media. Unless stated otherwise, the voltage scan rate was set at 100 $mV\,s^{-1}$. The voltammetric measurements were made at 25±0.1°C. Coulometric analysis was made using a Hokuto Denko Model HF-202D coulometer. Powder X-ray diffraction patterns were obtained with a Rigaku Denki Model RINT 1200 M X-ray diffractometer with Cu Kα radiation. The TG-DTA measurements were performed with a Rigaku Denki Model 8002-SD thermal analyzer.

All reagents were of analytical grade and were used as received. Solutions of Mo(VI) and As(V) were prepared by direct weighing of $Na_2MoO_4 \cdot 2H_2O$ and $Na_2HAsO_4 \cdot 7H_2O$, respectively. A solution of As(III) was prepared by dissolving As_2O_3 in a minimum quantity of sodium hydroxide. A stock solution of 0.10 M (M=mol dm^{-3}) CF_3SO_3H was prepared by dissolving the 1.50 g quantity in 100 ml of CH_3CN.

Preparation of 11-Molybdoarsenite(III). A solution of 3.0 g of $Na_2MoO_4 \cdot 2H_2O$ in 100 ml of water was treated with a solution of 0.50 g of As_2O_3 in 25 ml of 0.5 M NaOH, followed by the addition of 18.5 ml of concd HCl. Then 100 ml of CH_3CN was added. The resultant solution was stirred for 30 min at room temperature. After the addition of 2 g of *n*-Bu_4NBr, the solution was allowed to stand until precipitation was complete. After 30 min, a green precipitate was collected by filtration, washed with water and ethanol, and dried over Drierite in a desiccator (yield 1.5 g). In order to purify further the precipitate, a 1.0 g quantity was dissolved in 50 ml of acetone, and a crystalline material was obtained by the step-wise addition of 20 ml of *n*-pentane; the yield is 0.7 g.

Anal. Calcd for $(n\text{-}Bu_4N)_3H_6AsMo_{11}O_{39}$: Mo, 42.42; As, 3.01; C, 23.18; H, 4.62; N, 1.69%. Found: Mo, 42.55; As, 3.06; C, 22.75; H, 4.41; N, 1.68%. The TG-DTA results showed an endothermal transformation around 160 °C, and an exothermal decomposition commenced around 320 °C.

Molybdenum was determined with a Shimadzu Model ICPS-5000 inductively coupled argon plasma emission spectrometer. After oxidation of arsenite(III) to arsenate(V) with H_2O_2, arsenic was determined with a Hitachi high-performance liquid chromatograph (a Model L-6000 pump, a Model L-3720 conductivity detector, and a Model D-2500 data processor); the separation was performed with a Tosoh TSKgel IC-Anion-PW_{XL} column. The eluent was comprised of 1.2 mM potassium gluconate, 3.0 mM borax, and 15.0 mM boric acid. It must be emphasized that arsenate(V) is not detected in the blank test, indicating that the present heteropolyanion contains As(III) as a hetero-atom.

As shown in Fig. 1a, an IR spectrum of $(n\text{-}Bu_4N)_3H_6AsMo_{11}O_{39}$ was characterized by three strong bands at 955, 884, and 808 cm^{-1}. For comparison studies, α-$(n\text{-}Bu_4N)_3AsMo_{12}O_{40}$ was prepared by the method of Rocchiccioli-Deltcheff et al.[11] IR (400—1000 cm^{-1}): 964, 895, 858, 794 cm^{-1} (Fig. 1b). Comparison of both IR spectra can allow us to distinguish between the *n*-Bu_4N^+ salts of 11-molybdoarsenite(III) and 12-molybdoarsenate(V). Besides, powder X-ray diffraction patterns can be used to distinguish them in the solid states. The 2θ values in degrees for $(n\text{-}Bu_4N)_3H_6AsMo_{11}O_{39}$ are: 7.12 (40); 7.46 (100); 7.82 (17); 8.62 (47); 18.98 (6); 24.68 (7); 25.92 (6), while the corresponding values for α-$(n\text{-}Bu_4N)_3AsMo_{12}O_{40}$ are: 6.44 (22); 7.18 (37); 7.34 (71); 7.72 (100); 8.08 (18); 23.12 (13); 24.34 (11), where numerals in parentheses are the relative intensities, I/I_0.

Results and Discussion

UV-visible Absorption Sectra. The *n*-Bu_4N^+ salt of 11-molybdoarsenite(III) is soluble in polar aprotic solvents like CH_3CN, giving rise to green solutions, but insoluble in water or ethanol. A UV-visible spectrum of 11-molybdoarsenite(III) shows an absorption maximum at 306 nm in CH_3CN (Fig. 2a). The spectrum, which conforms to Beer's law ($\varepsilon = 1.95 \times 10^4$ $mol^{-1}\,dm^3\,cm^{-1}$ at 306 nm), resembles to those of the Keggin-type heteropolymolybdate anions characterized by absorption maxima around 310 nm.[12—16] This is in marked contrast to the behavior of 11-molybdophosphate(V) which shows only a shoulder around 295 nm in CH_3CN.[17] For comparison, Fig. 2b shows a UV-visible spectrum of 12-molybdoarsenate(V), which has an absorption maximum at 312 nm ($\varepsilon = 2.21 \times 10^4$ $mol^{-1}\,dm^3\,cm^{-1}$).

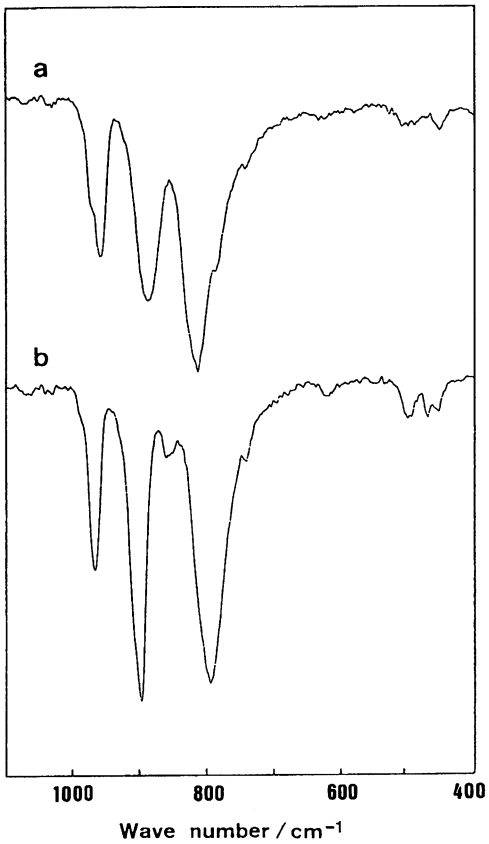

Fig. 1. IR spectra of (a) $(n\text{-}Bu_4N)_3H_6AsMo_{11}O_{39}$; (b) α-$(n\text{-}Bu_4N)_3AsMo_{12}O_{40}$ in the KBr pellets.

Cyclic Voltammograms. One-Electron Redox Waves: A cyclic voltammogram of 0.5 mM 11-molybdoarsenite(III) in CH_3CN containing 0.05 M *n*-Bu_4NClO_4 is shown in Fig. 3a. Two successive redox waves were obtained with midpoint potentials (E_{mid}) of −0.143 and −0.536 V, where $E_{mid} = (E_{pc} + E_{pa})/2$; E_{pc} and E_{pa} are cathodic and anodic peak-potentials. These waves were diffusion-controlled, and their reversible nature was ascertained by the results that the E_{pc} and E_{pa} values were independent of the voltage scan rate (20—200 mV s^{-1}). Coulometric analysis confirmed that each wave involved a one-electron transfer. On the other hand, 12-molybdoarsenate(V) underwent three one-electron reductions with the E_{mid} values of −0.146, −0.563, and −1.287 V in CH_3CN containing 0.05 M *n*-Bu_4NClO_4 (Fig. 3b). It should be noted that the E_{mid} value of the first wave for 11-molybdoarsenite(III) agrees practically with the corresponding value for 12-molybdoarsenate(V).

According to Combs-Walker and Hill,[17] 11-molybdophosphate(V) is electrochemically reduced irreversibly at more negative potentials than 12-molybdoposphate-

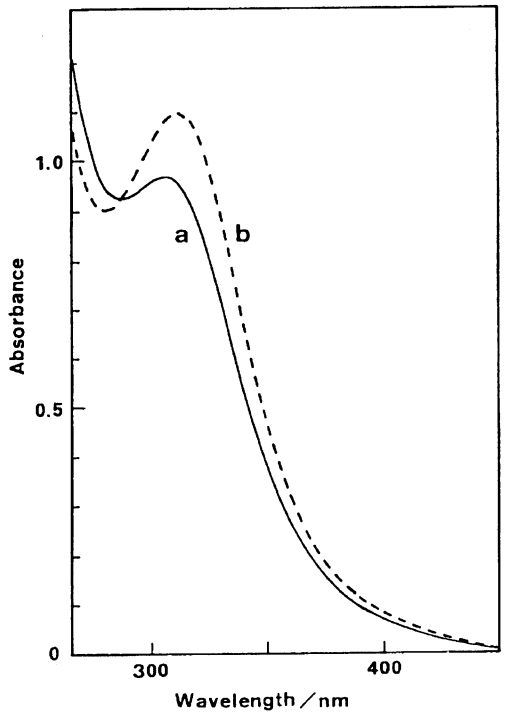

Fig. 2. UV-visible spectra of 0.05 mM solutions of (a) 11-molybdoarsenite(III); (b) 12-molybdoarsenate(V) in CH_3CN.

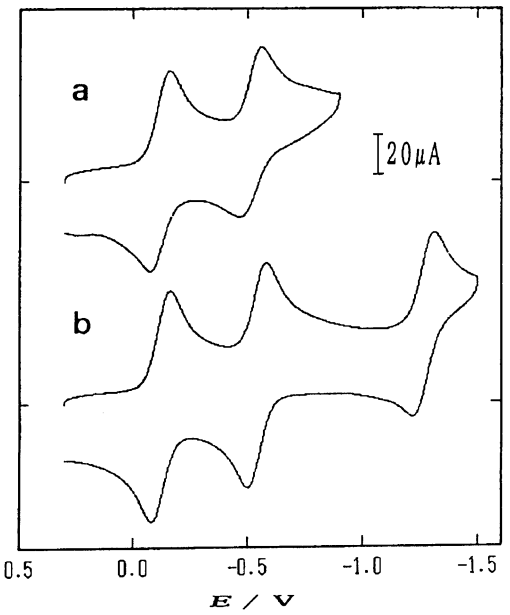

Fig. 3. Cyclic voltammograms of 0.5 mM solutions of (a) 11-molybdoarsenite(III); (b) 12-molybdoarsenate(V) in CH_3CN containing 0.05 M n-Bu_4NClO_4. Scan rate; 200 $mV\,s^{-1}$.

(V) in CH_3CN containing 0.1 M n-Bu_4NPF_6. Unlike the molybdophosphate(V) complexes, the voltammetric and UV-visible spectroscopic properties of 11-molybdoarsenite(III) are similar to those of 12-molybdoarsenate(V) (Figs. 2 and 3).

The controlled potential electrolysis at each reduction wave in Fig. 3a produced a mixed-valence blue species. The green heteropolyanion was regenerated by reoxidation of the one-electron reduction species at +0.30 V, indicating that the heteropoly skeleton is retained in the blue species. However, it was not identified that the two-electron reduction species was reoxidized to the green heteropoly species, because the cyclic voltammogram for the reoxidized anion did not trace the orginal one.

Two-Electron Redox Waves: Figure 4 shows a cyclic voltammogram of 0.2 mM 11-molybdoarsenite(III) in CH_3CN containing 0.05 M n-Bu_4NClO_4 and 2 mM CF_3SO_3H. Three well-defined reduction waves were obtained with the E_{pc} values of +0.246, +0.134, and −0.124 V. According to the coulometric analysis and the ratios of the normal pulse voltammetric currents for the three reduction waves, each wave consumes two electrons. Controlled potential electrolysis at each wave gave a blue species, which could be reoxidized to the original green species.

As the CF_3SO_3H concentration was increased, the E_{pc} values shifted to more positive potentials, indicating that protonation accompanies the reduction. Simultaneously, the third wave decreased in height (Fig. 5a). The voltammetric waves show slight irreversible characters under these conditions, but they become reversible by the presence of water; since the second and third waves disappear with the addition of water, only the first wave is used for the following treatment. For example, the slopes of the logarithmic analyses for the normal pulse voltammetric first waves are 65 mV in CH_3CN and 33 mV in 95% (v/v) CH_3CN–water, each solution containing 0.2 mM 11-molybdoarsenite(III), 0.05 M n-Bu_4NClO_4, and 10 mM CF_3SO_3H. The latter value is close to the theoretical value for a reversible two-electron reduction.

On the basis of these results, the number of proton participating in the reduction process of 11-molybdoarsenite(III) was determined from plots of

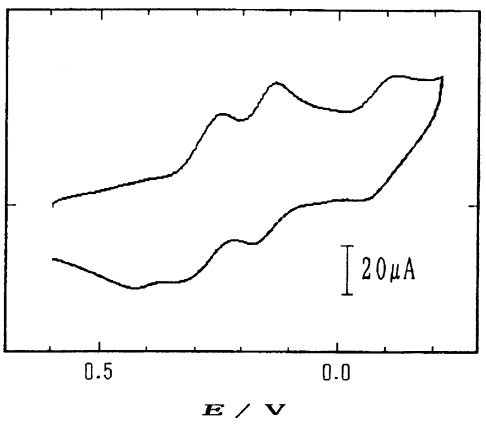

Fig. 4. A cyclic voltammogram of 0.2 mM 11-molybdoarsenite(III) in CH_3CN containing 0.05 M n-Bu_4NClO_4 and 2 mM CF_3SO_3H.

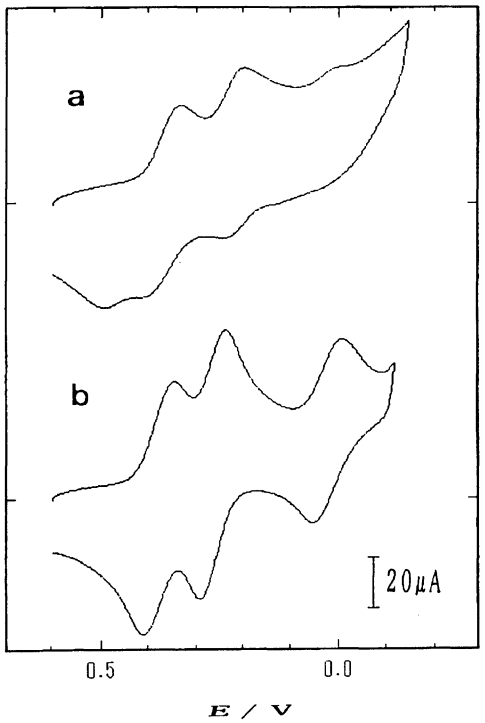

Fig. 5. Cyclic voltammograms of 0.2 mM solutions of (a) 11-molybdoarsenite(III); (b) 12-molybdoarsenate(V) in CH_3CN containing 0.05 M n-Bu_4NClO_4 and 10 mM CF_3SO_3H.

the E_{pc} value vs. $\log[H^+]$ for a series of 95% (v/v) CH_3CN–water solutions with various concentrations of CF_3SO_3H (2.0—25 mM) (I=0.05 M (n-Bu_4NClO_4)). The conclusion is reached that two protons are consumed for the first reduction wave, since a straight line with a slope of 65 mV is obtained. This result is in line with those for Keggin- and Dawson-type heteropolymolybdates. Figure 5b shows two-electron redox waves for 12-molybdoarsenate(V) under the same conditions as in Fig. 5a. It is found that the E_{pc} values of both first waves are close together.

Further study is being undertaken to elucidate the effect of acid and/or water on the second and third waves of 11-molybdoarsenite(III).

The Conversion Process of One-Electron Waves to Two-Election Waves: Figure 6 shows the conversion process of the one-electron waves into the two-electron waves as a function of the CF_3SO_3H concentration. These behaviors are very similar to those for the Dawson- and Keggin-type heteropolymolybdates in CH_3CN.[18,19]

Though the voltammetric behavior of 11-molybdoarsenite(III) is very sensitive to the presence of traces of acid, the one-electron waves are obtained (Fig. 3a), which indicates that the proton in the salt of $(n\text{-}Bu_4N)_3H_6AsMo_{11}O_{39}$ is not acidic; in other words, 11-molybdoarsenite(III) can be written as $[H_6AsMo_{11}O_{39}]^{3-}$. As for the Keggin-type heteropolyanions, the E_{mid} value of the first one-electron

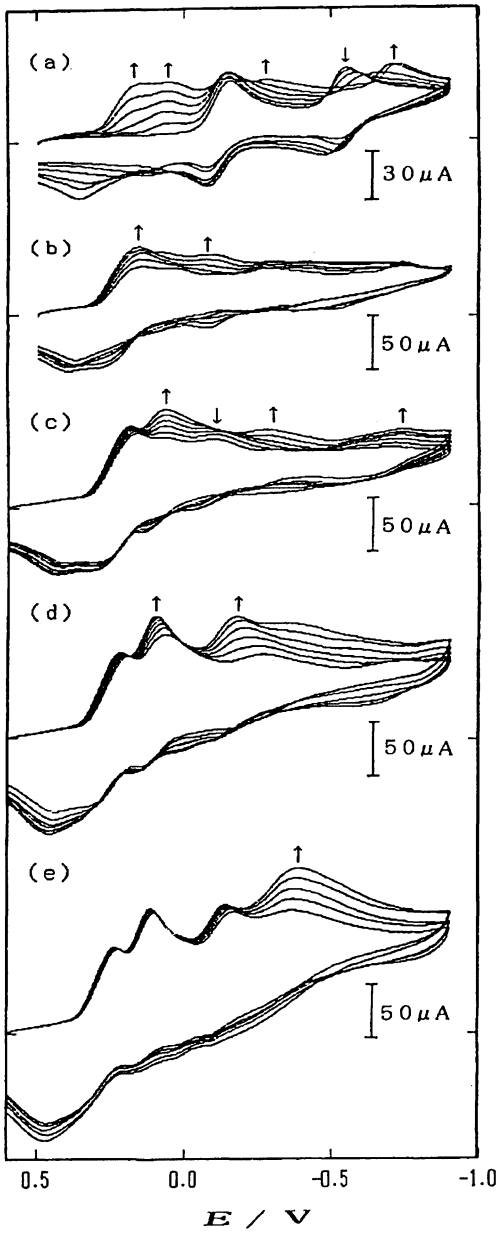

Fig. 6. Cyclic voltammograms of 0.5 mM 11-molybdoarsenite(III) in CH_3CN containing 0.05 M n-Bu_4NClO_4. [CF_3SO_3H]/mM: (a) 0—0.5; (b) 0.6—1.0; (c) 1.1—1.6; (d) 1.7—2.2; (e) 2.4—3.2.

redox wave depends on the ionic charge.[19] The coincidence of the E_{mid} values for the first waves in Figs. 3a and 3b supports that 11-molybdoarsenite(III) and 12-molybdoarsenate(V) possess the common ionic charge of −3 in CH_3CN.

Formation of the 11-Molybdoarsenite(III) Anion. Fig. 7a shows a cyclic voltammogram of a 50 mM Mo(VI)–0.3 M HCl–50% (v/v) CH_3CN system. No reduction waves were observed until the current rise due to the reduction of $Mo_6O_{19}^{2-}$ at +0.2 V.[20] Upon the addition of 1 mM AsO_3^{3-}, a single-step reduction wave appeared with the E_{pc} value of ca. +0.32 V (Fig. 7b).

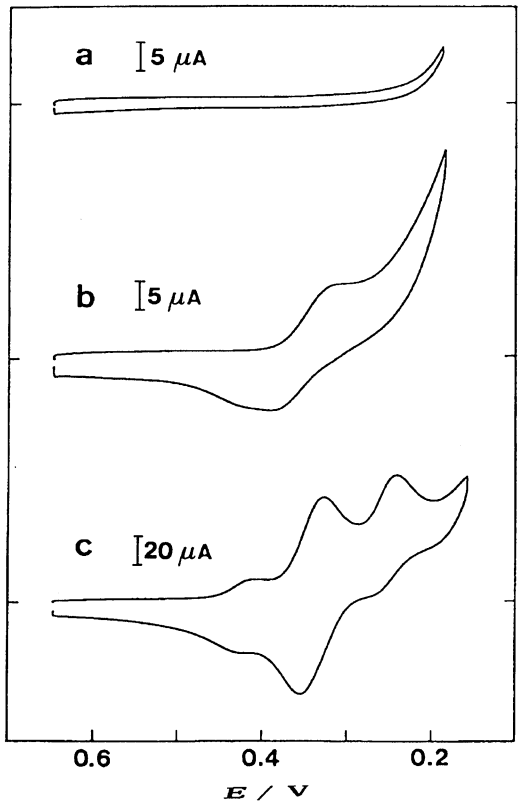

Fig. 7. Cyclic voltammograms for 50 mM Mo(VI)–0.3 M HCl–50% (v/v) CH_3CN systems. (a) Without AsO_3^{3-} or AsO_4^{3-}; (b) with 1.0 mM AsO_3^{3-}; (c) with 1.0 mM AsO_4^{3-}.

The reduction current was diffusion-controlled, indicating that a heteropolyanion with As(III) as a heteroatom is formed in the bulk of the solution. The heteropolyanion was stable in the solution, as judged by no current change with time.

In order to confirm that the 11-molybdoarsenite(III) anion was actually formed in the system, a cyclic voltammogram was taken for the 50 mM Mo(VI)–0.3 M HCl–50% (v/v) CH_3CN system containing 1 mM AsO_4^{3-} instead of AsO_3^{3-}, and shown in Fig. 7c. Three reduction waves with different height were obtained with the E_{pc} values of +0.411, +0.326, and +0.237 V. As time elapsed, the first wave decreased in height with a simultaneous increase of the third wave while the second wave was unchanged. This behavior has been interpreted in terms of the formation of a mixture of α- and β-$[XMo_{12}O_{40}]^{n-}$ and the subsequent transformation of the β-isomer to the stable α-isomer.[13,21—23] Thus, the voltammetric behavior of the As(V)–Mo(VI) system is entirely different from that of the As(III)–Mo(VI) system, indicating that 11-molybdoarsenite(III) is responsible for the voltammogram shown in Fig. 7b. The E_{pc} value for the first wave of the α-isomer is close to the corresponding value for 11-molybdoarsenite(III), which is in agreement with the result shown in Fig. 5.

In order to obtain the formation conditions for

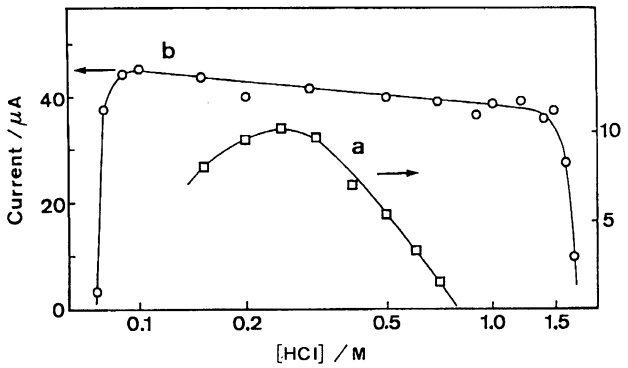

Fig. 8. Normal pulse voltammetric currents for 50 mM Mo(VI)–50% (v/v) CH_3CN systems as a function of the HCl concentration. (a) With 1.0 mM AsO_3^{3-}; (b) with 1.0 mM AsO_4^{3-}.

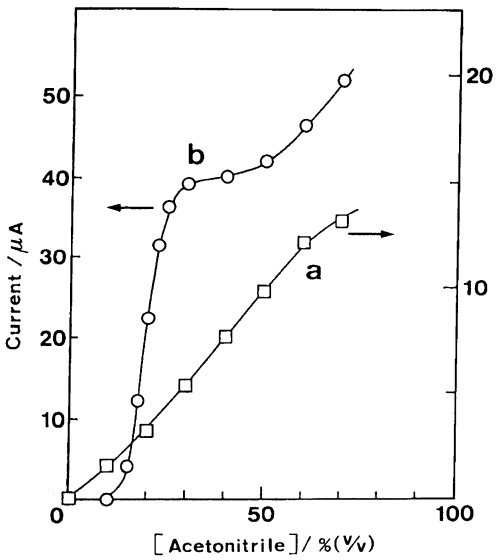

Fig. 9. Normal pulse voltammetric currents for 50 mM Mo(VI)–0.3 M HCl systems as a function of the CH_3CN concentration. (a) With 1.0 mM AsO_3^{3-}; (b) with 1.0 mM AsO_4^{3-}.

11-molybdoarsenite(III), normal pulse voltammetric measurements were performed for a series of 50 mM Mo(VI)–1.0 mM AsO_3^{3-}–50% (v/v) CH_3CN systems with various concentrations of HCl. Figure 8a shows the limiting currents of the first wave as a function of the HCl concentration. The green heteropolyanion was formed in the HCl concentration range 0.15—0.7 M, the range being close to that for the formation of the 12-molybdodiphosphonate(III) complex.[3] In the HCl concentration range<0.15 M, the formation of $Mo_6O_{19}^{2-}$ became predominant, and the reduction current for 11-molybdoarsenite(III) merged into the current rise due to the yellow isopolyanion. In order to compare the formation conditions with those of 12-molybdoarsenate(V), similar measurements were made for the systems containing 1.0 mM AsO_4^{3-} instead of AsO_3^{3-}, and the results are shown in Fig. 8b; the currents are for the

first wave of the α-isomer. 11-molybdoarsenite(III) was formed in narrower HCl concentration ranges and in smaller amounts than 12-molybdoarsenate(V) under the same conditions.

The effect of the CH_3CN concentration on the formation of 11-molybdoarsenite(III) was investigated for 50 mM Mo(VI)–1.0 mM AsO_3^{3-}–0.3 M HCl systems. As shown in Fig. 9a, the reduction current was increased monotonously as the CH_3CN concentration was increased. Similar behavior was observed for the systems containing CH_3COCH_3. It must be stressed that 11-molbdoarsenite(III) is not formed in the absence of such water–miscible organic solvents. For comparison, Fig. 9b shows the first reduction currents for α-12-molybdoarsenate(V) as a function of the CH_3CN concentration.

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