

traligand bond distances are sizable orientational changes in the anionic ligand with respect to the OC–W–CO angular arrangement due to the presence of the bulky triethylphosphine ligand. The interrelationship, if any, of these structural differences attendant upon CO substitution by phosphine in the coordination sphere of the metal are not apparent at this time.

In addition, the solution property of the acetate ligand to labilize cis CO ligands in  $W(CO)_5O_2CCH_3^-$  was markedly diminished upon CO replacement by  $PR_3$ .

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**Registry No.** 1, 36515-92-1; 2, 80327-42-0; [PNP][ $W(CO)_4(PMe_3)_2O_2CCH_3$ ], 80327-40-8; [PNP][ $W(CO)_4(PMe_2Ph)_2O_2CCH_3$ ], 80327-38-4; [PNP][ $W(CO)_4[P(OMe)_3]_2O_2CCH_3$ ], 80327-36-2; [PNP][ $W(CO)_5Cl$ ], 39048-34-5.

**Supplementary Material Available:** Listings of observed and calculated structure factors for both complexes, final thermal parameters for all atoms, hydrogen atom positions for 1, and bond distances and bond angles for the [PNP]<sup>+</sup> cations (54 pages). Ordering information is given on any current masthead page.

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## Voltammetric and Spectroelectrochemical Studies of 12-Molybdophosphoric Acid in Aqueous and Water–Dioxane Solutions at a Gold-Minigrad Optically Transparent Thin-Layer Electrode

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The redox behavior of 12-molybdophosphoric acid (12-MPA) in aqueous and water–dioxane media has been studied at a gold-minigrad optically transparent thin-layer electrode cell. The thin-layer cyclic voltammogram of 12-MPA in 50% (v/v) water–dioxane solutions containing 0.2 M  $H_2SO_4$  exhibits three two-electron reversible waves. On the other hand, the thin-layer cyclic voltammogram of 12-MPA in aqueous solutions containing 0.2 M  $H_2SO_4$  is relatively complicated. It is clarified by spectroelectrochemical experiments that each of the first two reduction processes is a reversible two-electron transfer even in aqueous solutions containing 0.2 M  $H_2SO_4$ . The six-electron reduction product in aqueous solutions seems to change quickly to other heteropolyanions, which are reoxidized to the two-electron reduction product of 12-MPA at about +0.2 V vs. SCE.

### Introduction

Traces of phosphorus can be determined colorimetrically by reducing 12-molybdophosphoric acid (12-MPA) to produce a very deep blue color. It is well-known that this deep blue is due to the formation of a so-called class II mixed-valence complex<sup>1</sup> with Keggin structure.<sup>2</sup>

Electrochemical studies of 12-MPA have been made by conventional polarography.<sup>3,4</sup> Tsigdinos<sup>4</sup> has clarified by direct- and alternating-current polarography and cyclic voltammetry in 1:1 water–dioxane solutions that the reduction of 12-MPA in this medium proceeds in three two-electron reversible steps and that the products formed at each step are stable. However, such reliable results had been restricted to electrochemical investigations of 12-MPA in such mixed solutions because 12-MPA in aqueous solutions is subject to hydrolytic degradation even in acid solutions.<sup>5–7</sup> In addition to the electrochemical properties of 12-MPA, absorption spectra of reduced compounds of 12-MPA in solutions have been reported<sup>8</sup> that show charge-transfer bands with large molar extinction coefficients in the visible region.

**Table I.** Voltammetric and Spectroelectrometric Results for 12-Molybdophosphoric Acid in 50% Water–Dioxane Mixed Solution Containing 0.2 M  $H_2SO_4$

process	voltammetry	coulometry		spectroelectrometry	
	$E^\circ/V$ vs. SCE	$Q/mC$	$n$	$E^\circ/V$ vs. SCE	$n$
I	+0.31 (+0.31) <sup>a</sup>	7.85	2.02 (2)	+0.310 (+0.310)	1.87 (2)
II	+0.17 (+0.18)	7.92	2.04 (2)	+0.178 (+0.18)	1.87 (2)
III	–0.06 (–0.065)	7.97	2.05 (2)		

<sup>a</sup> Tsigdinos, G. A., Hallada, C. J. *J. Less-Common Met.* 1974, 36, 79.

In this study, 12-MPA has been investigated by thin-layer voltammetry and spectroelectrochemistry in water–dioxane solutions as well as in aqueous solutions in order to clarify the oxidation–reduction properties of 12-MPA and its reduction products.

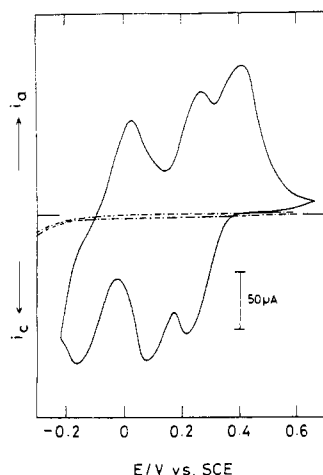
### Experimental Section

An optically transparent thin-layer electrode (OTTLE) was constructed by sandwiching a gold-minigrad electrode (500 mesh, 60% transmittance; Buckbee-Mears Co.) between two glass or two quartz slides that were slightly separated (ca. 0.2 mm) by Teflon tape spacers along the edges.<sup>9</sup> The spectroelectrochemical cell used in this study was an OTTLE constructed with two quartz slides. The calibration of an OTTLE used for voltammetric investigations was carried out

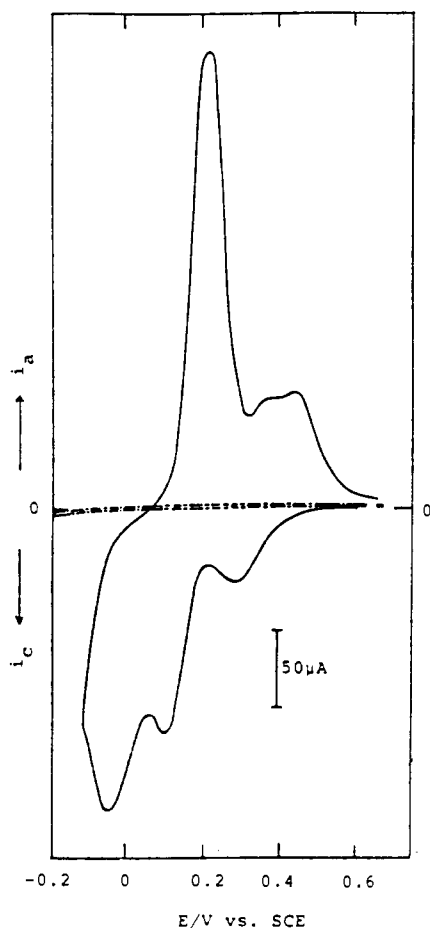
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**Figure 1.** Thin-layer cyclic voltammogram of  $10^{-3}$  M 12-molybdophosphoric acid in 50% water-dioxane mixed solution containing 0.2 M  $\text{H}_2\text{SO}_4$ ; scan rate  $2 \text{ mV s}^{-1}$ ; initial potential  $+0.60 \text{ V vs. SCE}$ ; initial scan direction cathodic. Dashed line is of the supporting electrolyte alone, 0.2 M  $\text{H}_2\text{SO}_4$ .

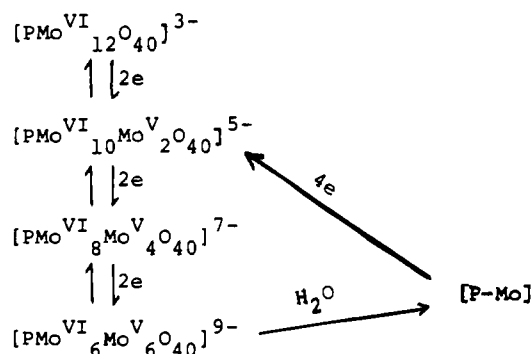


**Figure 2.** Thin-layer cyclic voltammogram of  $10^{-3}$  M 12-molybdophosphoric acid in aqueous solution containing 0.2 M  $\text{H}_2\text{SO}_4$ ; scan rate  $2 \text{ mV s}^{-1}$ ; initial potential  $+0.60 \text{ V vs. SCE}$ ; initial scan direction cathodic. Dashed line is of the supporting electrolyte alone, 0.2 M  $\text{H}_2\text{SO}_4$ .

by controlled-potential coulometry with a standard potassium ferrocyanide solution. The electrochemical cell volume was  $40.2 \mu\text{L}$ . The reference and the auxiliary electrodes were a saturated sodium chloride calomel electrode (H cell) and a platinum wire, respectively.

Voltammetric experiments were carried out with a potentiostat (Fuso Co., Model 311) an X-Y recorder (Riken Denshi Co., Model D72B), and a digital coulometer (Fuso Co., Model 343) in a room thermostated at  $22 \pm 1^\circ\text{C}$ . Spectropotentiostatic measurements were carried out with a potentiostat of conventional operational amplifier

#### Scheme I



design and a digital voltmeter. A spectrophotometer (Hitachi Co., Model EPS-3) with a cell compartment modified to permit positioning of OTTLE cells and introducing electrical leads was used for the spectroelectrochemical experiments.

12-Molybdophosphoric acid ( $\alpha$  isomer<sup>10</sup>) was obtained from Alpha Products Co. Other chemicals used in this study were of reagent grade and were used without further purification. The preparation of all solutions was made with doubly distilled water. For a water-dioxane mixed solvent, the ratio of the volume of dioxane to that of water is represented with the volume percentage of dioxane. The sample solution deoxygenated by bubbling nitrogen gas was transferred into the OTTLE by capillary action.

Standard procedures were used for the thin-layer spectropotentiostatic experiment and thin-layer coulometry.<sup>11</sup>

#### Results and Discussion

**Voltammetry.** The results of the voltammetric investigations of 12-MPA in 50% water-dioxane solutions containing 0.2 M  $\text{H}_2\text{SO}_4$  as a supporting electrolyte are given in Table I, and typical thin-layer cyclic voltammograms of 12-MPA and the supporting electrolyte are shown in Figure 1.

According to the previous polarographic results,<sup>3,4</sup> the voltammogram given by solid line in Figure 1 should show three two-electron reversible reductions. The two-electron transfer was verified for each three steps by controlled-potential coulometry at the OTTLE cell (Table I). As for the reversibility, however, the voltammogram was skewed to a great extent by large solution resistance in thin-layer cell, especially in nonaqueous solutions.

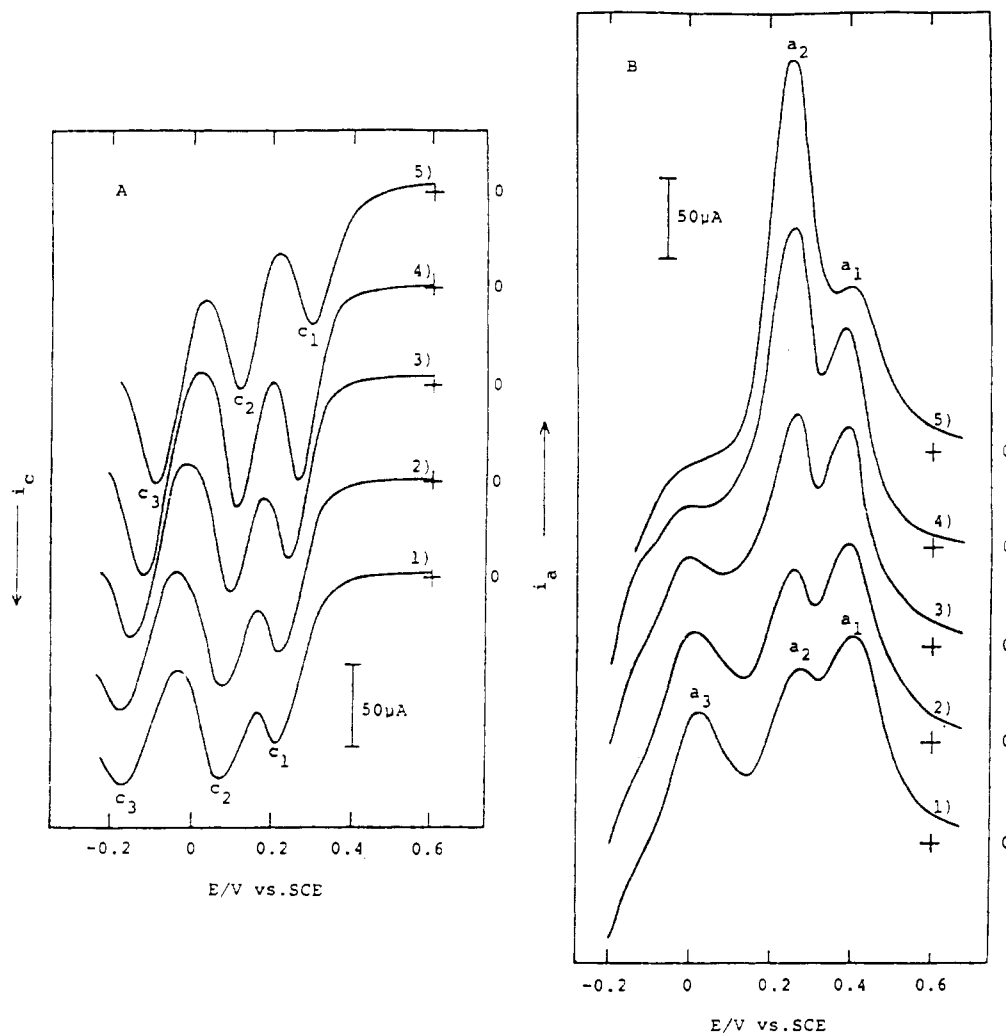
Typical thin-layer cyclic voltammograms of 12-MPA and of the supporting electrolyte, 0.2 M  $\text{H}_2\text{SO}_4$ , in water are presented in Figure 2. It is interesting that the voltammogram of 12-MPA obtained in aqueous solutions is remarkably different, especially in terms of the shape of the anodic reoxidation waves, from that obtained in 50% water-dioxane solutions. This suggests the need for further clarification of the electrochemical processes of 12-MPA in aqueous solutions, especially of the reoxidation processes.

Thin-layer cyclic voltammograms of 12-MPA obtained at various ratios of dioxane are given in Figure 3. The reoxidation processes are apparently dependent on the ratio of dioxane (Figure 3B) while the reduction processes are not (Figure 3A). As the ratio of dioxane decreases, the anodic peak  $a_3$  becomes smaller and simultaneously the anodic peak  $a_2$  becomes larger. So that such an influence of the ratio of dioxane on the thin-layer cyclic voltammograms could be explained, the reaction mechanisms given in Scheme I were proposed.

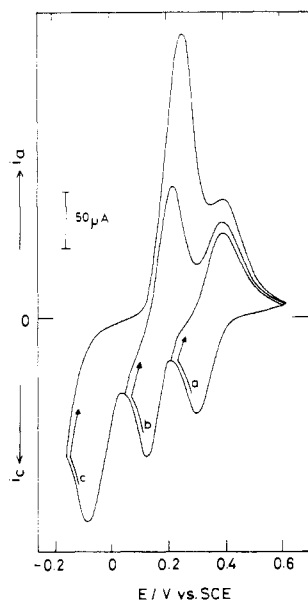
Both the first and the second reduction processes of 12-MPA are reversible two-electron transfer regardless of the ratio of dioxane. This was ascertained by reversing scan direction at the potentials right after the first cathodic peak and right after the second one. The voltammograms obtained in 10% dioxane

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**Figure 3.** Thin-layer cyclic voltammograms of  $10^{-3}$  M 12-molybdophosphoric acid in water-dioxane mixed solutions containing 0.2 M  $\text{H}_2\text{SO}_4$  (scan rate  $2 \text{ mV s}^{-1}$ ; initial potential  $+0.60 \text{ V vs. SCE}$ ; initial scan direction cathodic): A, cathodic waves; B, anodic waves. Dioxane ratio: (1) 50%; (2) 40%; (3) 30%; (4) 20%; (5) 10%.



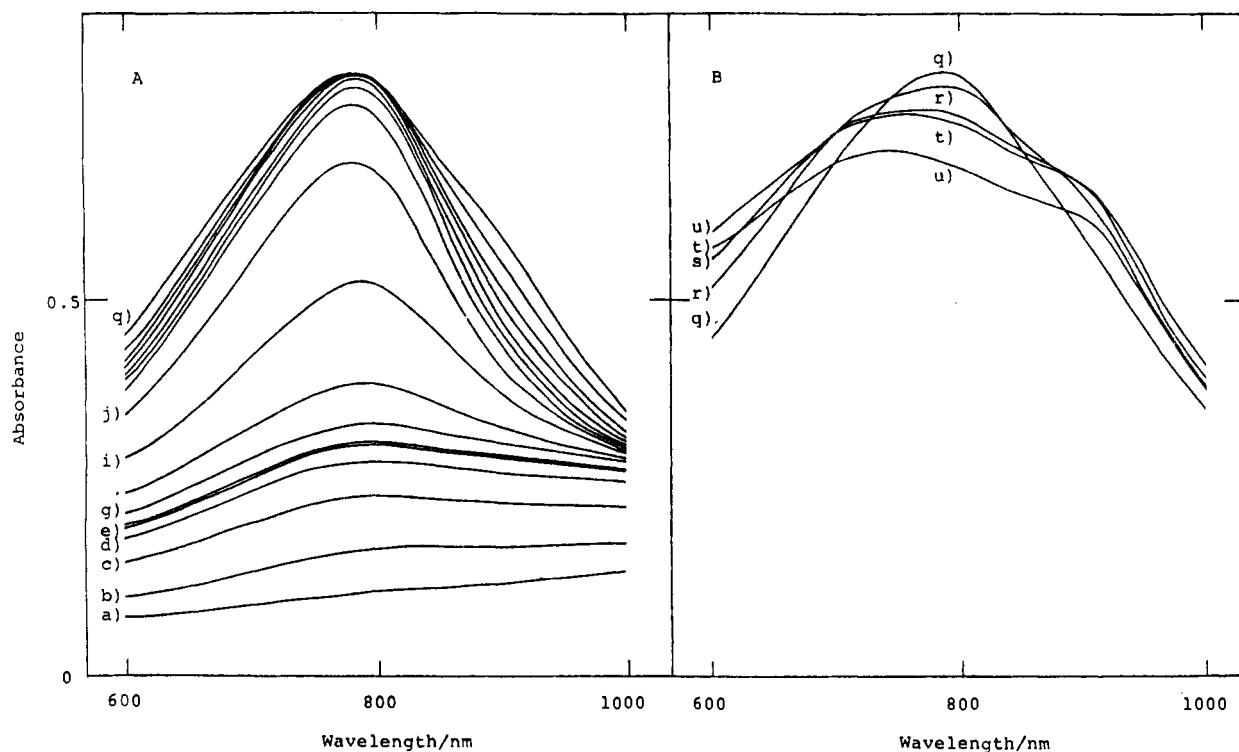
**Figure 4.** Thin-layer cyclic voltammograms of  $10^{-3}$  M 12-molybdophosphoric acid in 10% dioxane mixed solution containing 0.2 M  $\text{H}_2\text{SO}_4$ ; scan rate  $2 \text{ mV s}^{-1}$ ; initial potential  $+0.60 \text{ V vs. SCE}$ ; initial scan direction cathodic. Points of reversing scan: (a) after the first cathodic peak; (b) after the second cathodic peak; (c) after the third cathodic peak.

mixed solutions, for example, were shown in Figure 4. The six-electron reduction product of 12-MPA formed at the third reduction step seems to become less stable with decreasing ratio of dioxane. The six-electron reduction product may undergo some homogeneous reaction in a thin-layer solution to change rapidly to some heteropoly compound [P-Mo] at a low ratio of dioxane. It is not clear what this heteropoly compound is, although it is oxidized to the two-electron reduction product of 12-MPA at the peak potential  $a_2$ .

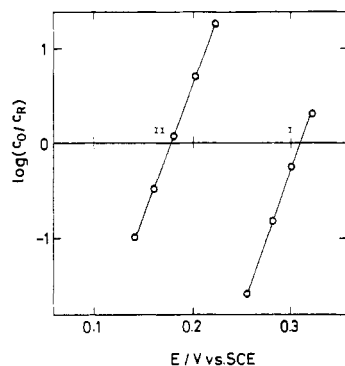
In aqueous solutions, the six-electron reduction product of 12-MPA changes to [P-Mo] almost quantitatively. This apparently explains the cyclic voltammogram given in Figure 2, in which the anodic peak  $a_3$  was not observed but  $a_2$  was very large.

**Spectroelectrochemistry.** Absorption spectra which were obtained with 12-MPA in 50% water-dioxane solutions containing 0.2 M  $\text{H}_2\text{SO}_4$  during a sequence of applied potentials are shown in Figure 5. Curve a corresponds to the unreduced form of 12-MPA, which shows no absorption in the 700–900-nm region. Curve e corresponds to the completely reduced form of the first reduction, which shows absorption in some degree at 780 nm. Curve q corresponds to the completely reduced form of the second reduction, which shows a strong absorption at 780 nm.

Nernst plots of applied potentials  $E_{\text{appl}}$  vs.  $\log(c_{\text{O}}/c_{\text{R}})$  at 780 nm for the first two steps are shown in Figure 6, where  $c_{\text{O}}$  and  $c_{\text{R}}$  represent the concentration of the oxidized and the



**Figure 5.** Spectra of  $2 \times 10^{-3}$  M 12-molybdophosphoric acid in 50% water-dioxane mixed solution containing 0.2 M  $\text{H}_2\text{SO}_4$  from spectropotentiostatic experiment.  $E_{\text{app}}$ : (a) +0.600; (b) +0.352; (c) +0.322; (d) +0.303; (e) +0.283; (f) +0.259; (g) +0.240; (h) +0.220; (i) +0.200; (j) +0.181; (k) +0.161; (l) +0.137; (m) +0.118; (n) +0.097; (o) +0.073; (p) +0.054; (q) +0.024; (r) -0.024; (s) -0.048; (t) -0.068; (u) -0.092 V vs. SCE.



**Figure 6.** Plots of  $E_{\text{app}}$  vs.  $\log(c_{\text{O}}/c_{\text{R}})$  for 12-molybdophosphoric acid in 50% water-dioxane solution containing 0.2 M  $\text{H}_2\text{SO}_4$ : I, first reduction step; II, second reduction step.

reduced forms, respectively. The value of  $c_{\text{O}}/c_{\text{R}}$  at each potential is calculated from the spectra by eq 1 where  $A_{\text{R}}$  is the

$$c_{\text{O}}/c_{\text{R}} = (A_{\text{R}} - A)/(A - A_{\text{O}}) \quad (1)$$

absorbance of the completely reduced form,  $A_{\text{O}}$  is that of the oxidized form, and  $A$  is that of the mixture of the oxidized and the reduced form.

A linear Nernst plot (I in Figure 6) corresponding to the first reduction process of 12-MPA in 50% water-dioxane solution gave a value for  $E^{\circ'}$  of +0.310 V vs. SCE from the potential-axis intercept and an  $n$  value of 1.87 from the slope, when the values of  $A_{\text{O}}$  and  $A_{\text{R}}$  were obtained from curves a and e in Figure 4, respectively. A linear Nernst plot (II in Figure 6), corresponding to the second reduction process, gave a value for  $E^{\circ'}$  of +0.178 V vs. SCE and an  $n$  value of 1.87 when the values of  $A_{\text{O}}$  and  $A_{\text{R}}$  were obtained from curves e and q in Figure 5, respectively. These results strongly suggest that both the first and the second reduction processes of 12-MPA in 50% water-dioxane solutions containing 0.2 M  $\text{H}_2\text{SO}_4$  are of a reversible two-electron transfer.

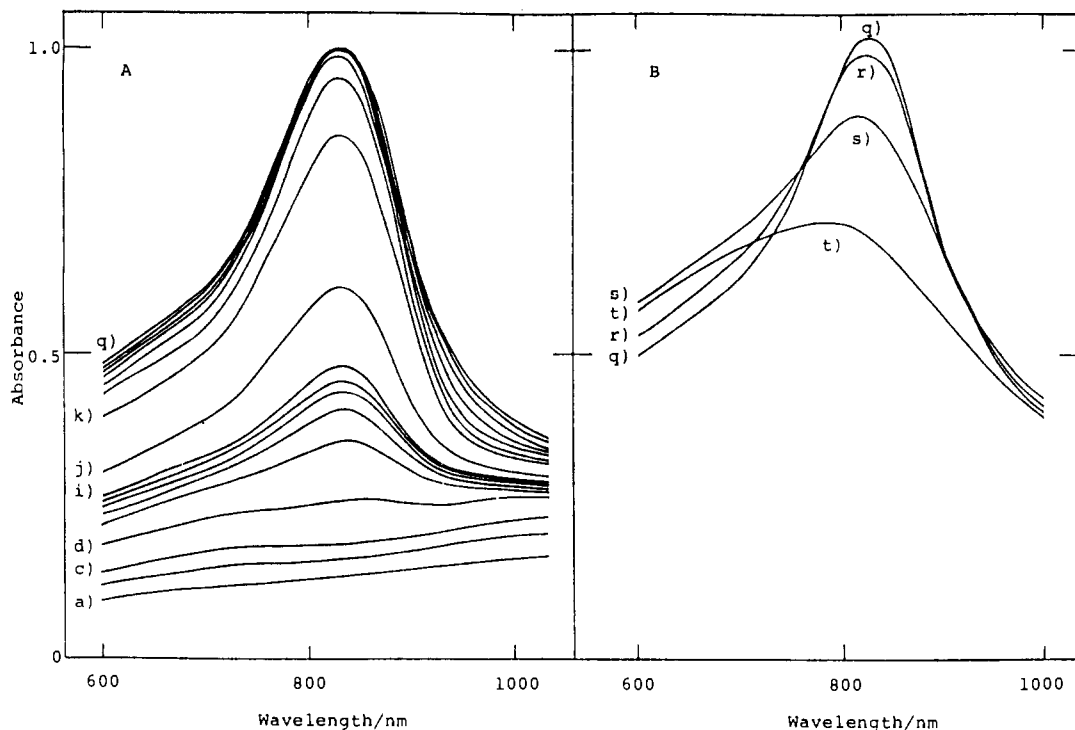
The spectral changes accompanying the third reduction of 12-MPA are shown by curves r-u in Figure 5B. These spectra have no isosbestic point, which may indicate that the six-electron reduction product of 12-MPA undergoes some slow homogeneous reaction of 12-MPA, even in 50% water-dioxane solutions. This seems to be in agreement with the reaction mechanisms in Scheme I proposed from the voltammetric results.

Absorption spectra which were obtained for 12-MPA in aqueous solutions containing 0.2 M  $\text{H}_2\text{SO}_4$  during a sequence of applied potentials are shown in Figure 7. These spectral changes are due to the formation of the reduction products of 12-MPA in water because the spectral changes shown in Figure 7 are similar to those shown in Figure 5. A difference in the absorption maximum for the reduction products between 50% water-dioxane solutions and aqueous solutions may be ascribed to the solvent effect.

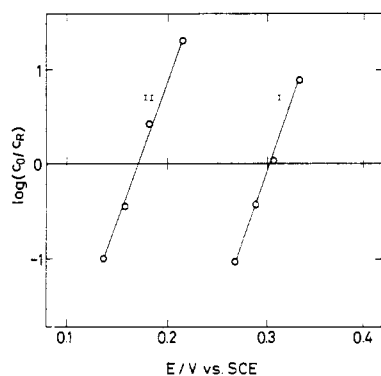
Nernst plots with the absorbance at 830 nm are given in Figure 8. The values of  $A_{\text{O}}$  and  $A_{\text{R}}$  of the first reduction process were obtained from curves a and g in Figure 7, respectively, and those of the second reduction process from curves g and q in Figure 7, respectively.

A linear plot (I in Figure 8) corresponding to the first reduction process of 12-MPA in aqueous solution gave a value for  $E^{\circ'}$  of +0.306 V vs. SCE and an  $n$  value of 1.85. A linear plot (II in Figure 8) corresponding to the second reduction process gave a value for  $E^{\circ'}$  of +0.170 V vs. SCE and an  $n$  value of 1.95. These results are in agreement with those obtained by the spectropotentiostatic method in 50% water-dioxane solutions. Namely, both the first and the second reduction processes of 12-MPA in aqueous solutions are of a reversible two-electron transfer as well as those in 50% water-dioxane solutions.

The spectral changes accompanying the third reduction of 12-MPA in aqueous solutions are shown in Figure 7B. These spectra also have no isosbestic point, which can not be explained by the mechanisms in Scheme I. This suggests that



**Figure 7.** Spectra of  $2 \times 10^{-3}$  M 12-molybdophosphoric acid in aqueous solution containing 0.2 M  $\text{H}_2\text{SO}_4$  from spectropotentiostatic experiment.  $E_{\text{appl}}$ : (a) +0.600; (b) +0.502; (c) +0.370; (d) +0.330; (e) +0.307; (f) +0.280; (g) +0.268; (h) +0.239; (i) +0.209; (j) +0.180; (k) +0.161; (l) +0.137; (m) +0.108; (n) +0.089; (o) +0.065; (p) +0.041; (q) +0.001; (r) -0.038; (s) -0.083; (t) -0.118 V vs. SCE.



**Figure 8.** Plots of  $E_{\text{appl}}$  vs.  $\log(c_{\text{O}}/c_{\text{R}})$  for 12-molybdophosphoric acid in aqueous solution containing 0.2 M  $\text{H}_2\text{SO}_4$ : I, first reduction step; II, second reduction step.

[P-Mo] gradually changes further to other heteropoly compounds.

In conclusion, each of the first two reduction processes of 12-MPA is of a reversible two-electron transfer, and both the two-electron and the four-electron reduction products are stable in aqueous solutions as well as in water-dioxane solutions. The six-electron reduction product of 12-MPA in aqueous solutions is unstable and changes to some heteropoly compound. This heteropoly compound may be a structural isomer or a degradation compound of 12-MPA such as 11-MPA because it is oxidized at about +0.2 V vs. SCE to the two-electron reduction product of 12-MPA.

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