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Medium Effects on the Redox Properties of 12-Molybdophosphate and 12-Molybdosilicate

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The formal redox potentials of 12-molybdophosphate and 12-molybdosilicate up to the twelve-electron reduction per heteropolymolybdate ion were determined by cyclic voltammetry at a glassy carbon electrode in 50% (v/v) water-organic media containing some inorganic acids. These heteropolymolybdates in the presence of 1,4-dioxane (DO) or tetrahydrofuran (THF) display five two-electron reversible cathodic waves, followed by an irreversible two-electron wave, whereas the same heteropolymolybdates in the presence of 1,2-dimethoxyethane, *N*,*N*-dimethylformamide, acetonitrile, ethanol, or acetone yield five successive redox couples of 2, 2, 2, 4, and $2e^-$ (electrons) each. The eight-electron reduction species of 12-heteropolymolybdates are stabilized by cyclic ethers such as DO or THF. The stabilization of the eight-electron reduction species by the addition of a cyclic ether has been explained by taking into account the adduct formation between the molecules of the cyclic ether and 12-heteropolymolybdate.

Many electrochemical studies of 12-molybdophophoric acid (12-MPA) and related 12-heteropolymolybdates have been carried out in order to make clear the redox properties of a series of mixed valence Mo(V, VI) complexes known as a Kiggin structure. The previous voltammetric and polarographic investigations have shown that 12-MPA as well as 12-molybdosilicic acid (12-MSA) in acidic solutions containing some organic solvents undergoes a series of consecutive two-electron reduction to yield various mixed valence Mo(V, VI) complexes.[1] It seems likely that the first three two-electron redox couples of 12-heteropolymolybdates in acidic solutions containing dioxane (DO) or ethanol (EtOH) are remarkably fast and reversible.[2-6] On further reduction above six electrons, however, different results have been reported concerning the fourth and subsequent redox reactions of 12-heteropolymolybdates in acidic solutions containing DO or EtOH.[2,3]

Tsigdinos and Hallada[2] have shown that 12-MSA in 50% (v/v) water-dioxane solutions containing hydrochloric acid exhibited five two-electron reduction waves. Recently, an identical result was reported on the reduction processes of both 12-MPA and 12-MSA in aqueous dioxane media containing sulfuric acid.[5] On the other hand, Souchay and his colleagues[3] have reported that the reduction processes of both 12-MPA and 12-MSA in 50% (v/v) water-ethanol media containing hydrochloric acid displayed three two-electron waves, and 12-heteropoly acids were not further reduced above six electrons in acidic media containing ethanol.

These results suggest that the redox processes of 12-heteropolymolybdates in acidic solutions are influenced by the nature of organic solvent.

This paper presents some unusual solvent effects on the gradual reduction processes of 12-heteropolymolybdates in acidic solutions containing some organic solvents at a glassy carbon electrode.

Experimental

All electrochemical measurements were carried out with a potentiostat (Fuso Co., Model 311) equipped with a function generator (Fuso Co., Model 321) and a recorder (Riken Denshi Co., Model F-43P). A Tokai glassy carbon disc electrode (GCE) with a geometric surface area of 0.071 cm^2 was employed as a working electrode. The counter electrode was a platinum spiral. The potential of the working electrode was measured against a saturated calomel electrode (SCE).

12-Molybdophosphoric acid was purchased from Alfa Chemical Products Co., and was used as received. 12-molybdosilicic acid was obtained from High Purity Chemical Institute (Saitama). Data reported here for both 12-MPA and 12-MSA refer to the stable α-form.[1] All other chemicals were of analytical reagent grade and were used without further purification. All solutions were made up with twice-distilled water and were deaerated with water-pumped nitrogen. All measurements were performed at 25 °C.

Results and Discussion

12-Molybdophosphoric Acid. Figure 1 shows typical cyclic voltammograms of 12-MPA in 50% (v/v) water-dioxane medium containing 0.5 mol dm^{-3} H_2SO_4. The cathodic sweep up to -0.8 V displays six peaks and one flat wave. The first four cathodic waves are reversible. Each step of these waves shows the following characteristics. The cathodic and anodic peak potentials (E_{pc} and E_{pa}) are invariant with scan rate (v) for v between 10 and 200 mV s^{-1}, and the potential difference $\Delta E_p (=E_{pc}-E_{pa})$ is $-(29\pm2)$ mV. This corresponds closely to the theoretical value of -29 mV for a Nernstian two-electron wave at 25 °C. The fifth cathodic peak is also invariant with scan rate, however, ΔE_p is $-(40\pm2)$ mV, and the peak height is approximately half of the first cathodic peak. The potential separation between the fifth cathodic peak and the rising potential of the irreversible wave near -0.45 V is about 50 mV. This result suggests that the potential separation on the successive reductions is so small that the fifth peak is distorted by the following wave. It has been pointed out by Polcyn and Shain[7] that the indi-

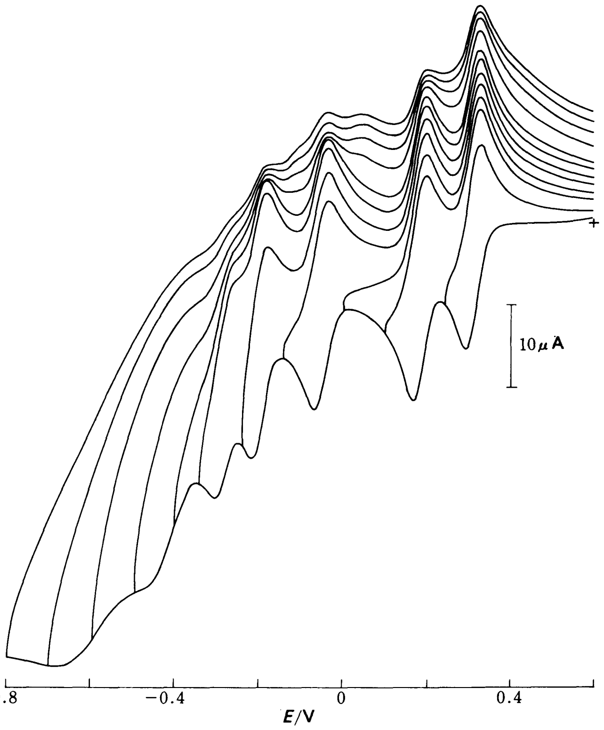

Fig. 1. Cyclic voltammograms of 1×10^{-3} mol dm^{-3} 12-molybdophosphoric acid in 50%(v/v) water-dioxane solution containing 0.5 mol dm^{-3} H_2SO_4 at sweep rate 0.05 V s^{-1}.

vidual waves of the stepwise reductions merge into one broad distorted wave whose peak height and shape is no longer characteristic of a reversible wave, as the potential separation between the successive reductions becomes less than about 100 mV n^{-1}, where n is the number of electrons involved in the electrode process. In order that the cyclic voltammograms on the successive reductions behave as independent reversible waves, a certain minimum potential separation of about 118 mV n^{-1} is required.

The first five cathodic waves have been previously assigned to the addition of two electrons for each step.[2,5]

The flat wave near −0.45 V is irreversible. The flat wave increased in height with increase in scan rate, however, it shifted toward more negative potentials, and merged into the broad wave near −0.65 V at scan rates above 200 mV s^{-1}. The height of the flat wave is nearly equal to the first cathodic peak. It is reasonable to infer that the flat wave corresponds to a two-electron process. The broad wave near −0.65 V is also irreversible, and exhibits a plateau current rather than a peak at scan rates above 100 mV s^{-1}. The plot of the current function $i_{pc}v^{-1/2}$ vs. v decreased with increasing scan rate, where i_{pc} was measured from the base current observed in acidic dioxane solution in the absence of 12-MPA. The variation of the current function (i_{pc} $v^{-1/2}$) with scan rate would indicate that the total current function of the broad wave is made up of charge transfer coupled to homogeneous chemical reactions.[8]

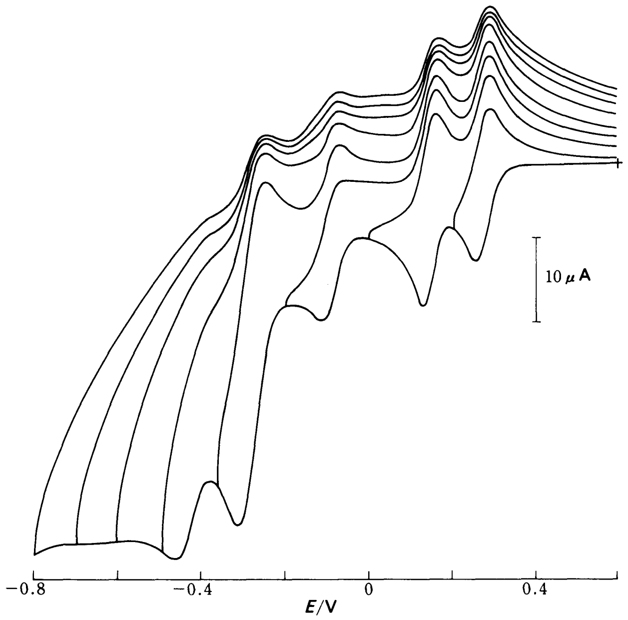

Fig. 2. Cyclic voltammograms of 1×10^{-3} mol dm^{-3} 12-molybdophosphoric acid in 50%(v/v) water-DMF solution containing 0.5 mol dm^{-3} H_2SO_4 at sweep rate 0.05 V s^{-1}.

A similar cyclic voltammogram with six cathodic peaks and one flat wave was also observed in acidic solutions containing tetrahydrofuran (THF).

On the other hand, 12-MPA in acidic solution containing *N,N*-dimethylformamide (DMF) gives five well-defined cathodic peaks, as shown in Fig. 2. The first three cathodic waves correspond to a two-electron process for each step.[2,5] The fourth step is also reversible, but its peak height is approximately 2.65 times the height of the first cathodic peak. The peak current on the stationary electrode voltammetry is proportional to $n^{3/2}$, where n is the number of electrons involved in the electrode process.[8] If the fourth step corresponds to a four-electron process, the height of the fourth step is $2^{3/2}$ times the height of the first two-electron reversible wave. Accordingly, the fourth step is attributable to a four-electron process. Although the fifth cathodic wave is less reversible than the first cathodic one, the first and fifth cathodic steps have nearly equal height. It is reasonable to assign that the fifth cathodic step slso corresponds to a two-electron process. Similar cyclic voltammograms with five cathodic steps up to −0.80 V were observed in acidified mixed solvents containing 1,2-dimethoxyethane (DME), acetonitrile (MeCN), EtOH, or acetone. A four-electron transfer process on the one-step has been considered to be a phenomenon that appears only rarely, however, the four-electron transfer has been found for the reduction processes of $[X_2Mo_{18}O_{62}]^{6-}$ in acidic solutions, where X is P or As.[1]

The formal redox potential $E_f^{\circ\prime}$ was determined by using the equation $E_f^{\circ\prime}=(E_{pc}+E_{pa})/2$. These data are summarized in Table 1.

Table 1. Voltammetric Characteristics of 12-Molybdophosphoric Acid[a]

No.	Medium	$E_f^{\circ\prime}$ vs. SCE/V					
		$n^{b)}=2$	4	6	8	10	12
1.	0.5 mol dm^{-3} H_2SO_4, 50%[c] DO[d]	+0.315	+0.187	−0.042	−0.189	−0.266	(−0.45s)
2.	0.5 mol dm^{-3} $HClO_4$, 50% DO	+0.317	+0.187	−0.042	−0.191	−0.268	(−0.45s)
3.	0.5 mol dm^{-3} HNO_3, 50% DO	+0.317	+0.187	−0.042	−0.191	−0.267	(−0.46s)
4.	0.5 mol dm^{-3} HCl, 50% DO	+0.304	+0.171	−0.054	−0.200	−0.275	(−0.45s)
5.	0.5 mol dm^{-3} H_2SO_4, 50% THF[e]	+0.251	+0.173	−0.097	−0.239	−0.285	(−0.44s)
6.	0.5 mol dm^{-3} H_2SO_4, 50% DME[f]	+0.248	+0.151	−0.096		−0.276	(−0.44)
7.	0.5 mol dm^{-3} H_2SO_4, 50% DMF[g]	+0.271	+0.144	−0.092		−0.282	(−0.46)
8.	0.5 mol dm^{-3} H_2SO_4, 50% MeCN[h]	+0.280	+0.168	−0.066		−0.259	(−0.39)
9.	0.5 mol dm^{-3} H_2SO_4, 50% EtOH[i]	+0.280	+0.174	−0.070		−0.247	(−0.40)
10.	0.5 mol dm^{-3} H_2SO_4, 50% acetone	+0.256	+0.160	−0.082		−0.263	(−0.43)

a) The concentration of 12-MPA was 1×10^{-3} mol dm^{-3}. b) Number of electrons. c) Vol%. d) 1,4-Dioxane. e) Tetrahydrofuran. f) 1,2-Dimethoxyethane. g) *N,N*-Dimethylformamide. h) Acetonitrile. i) Ethanol. s) Flat cathodic wave. Parentheses indicate the cathodic peak potentials.

Table 2. Voltammetric Characteristics of 12-Molybdosilicic Acid[a]

No.	Medium	$E_f^{\circ\prime}$ vs. SCE/V					
		$n=2$	4	6	8	10	12
1.	0.5 mol dm^{-3} H_2SO_4, 50% DO	+0.292	+0.175	−0.047	−0.196	−0.272	−0.48
2.	0.5 mol dm^{-3} $HClO_4$, 50% DO	+0.284	+0.176	−0.043	−0.197	−0.270	−0.42
3.	0.5 mol dm^{-3} HNO_3, 50% DO	+0.286	+0.180	−0.041	−0.195	−0.272	−0.43
4.	0.5 mol dm^{-3} HCl, 50% DO	+0.302	+0.187	−0.035	−0.185	−0.266	−0.39
5.	0.5 mol dm^{-3} H_2SO_4, 50% THF	+0.288	+0.175	−0.091	−0.220	−0.288	−0.38
6.	0.5 mol dm^{-3} H_2SO_4, 50% DME	+0.242	+0.155	−0.086		−0.271	−0.41
7.	0.5 mol dm^{-3} H_2SO_4, 50% DMF	+0.198	+0.138	−0.072		−0.301	−0.52
8.	0.5 mol dm^{-3} H_2SO_4, 50% MeCN	+0.240	+0.171	−0.041		−0.249	−0.34
9.	0.5 mol dm^{-3} H_2SO_4, 50% EtOH	+0.235	+0.157	−0.061		−0.245	−0.34
10.	0.5 mol dm^{-3} H_2SO_4, 50% acetone	+0.235	+0.163	−0.067		−0.274	−0.38
11.	0.5 mol dm^{-3} H_2SO_4	+0.271	+0.156	−0.018		−0.215	−0.38
12.	0.5 mol dm^{-3} $HClO_4$	+0.275	+0.159	−0.015		−0.217	−0.41
13.	0.5 mol dm^{-3} HNO_3	+0.268	+0.155	−0.017		−0.227	−0.47
14.	0.5 mol dm^{-3} HCl	+0.275	+0.162	−0.013		−0.219	−0.47

a) The concentration of 12-MSA was 1×10^{-3} mol dm^{-3}. The abbreviation of the organic solvent is the same as that of Table 1.

12-Molybdosilicic Acid. The same set of experiments was performed for 12-MSA. 12-MSA in acidic solutions containing DO or THF is reduced in six steps. Each step appears to correspond to the addition of $2e^-$ (electrons). Whereas, the same heteropoly acids with DME, DMF, MeCN, EtOH, or acetone present give five cathodic peaks of 2, 2, 2, 4, and $2e^-$ each.

12-MSA is moderately stable for the hydrolytic degradation in acidic solutions even though organic solvent is not present in the solution. Some experiments were carried out in acidic solutions in the absence of organic solvent. 12-MSA in aqueous solutions containing H_2SO_4, HNO_3, or HCl is reduced in five steps of 2, 2, 2, 4, and $2e^-$ each, up to −0.80 V. The formal redox potentials of 12-MSA in acidic solutions with and without organic solvent present are listed in Table 2.

Solvent Effect. In acidic solution alone, 12-MPA undergoes hydrolytic degradation, however, it is stabilized by addition of comparatively large amounts of organic solvent. On the other hand, 12-MSA is stable in acidic media with and without organic solvent present. The most striking aspect of the present work is that the eight-electron reduction species of both 12-MPA and 12-MSA are stabilized by cyclic ethers such as DO or THF, however, they are unstable in the presence of DME, DMF, MeCN, EtOH, or acetone. It seems likely that the dielectric constant of the organic solvent plays an important role in the stabilization of the eight-electron reduction species of heteropolymolybdates. A decrease in dielectric constant of the solvent should be accompanied by a decrease in the dissociation of ionic aggregates such as 12-heteropolymolybdates.

Pure DMF, MeCN, EtOH, and acetone have high dielectric constants, ranging from 20 to 50.[9] For ethers such as DO, THF, and DME, the range of the dielectric constants is about 2—8. Consequently, extensive ionic aggregation and a suppression of reorganization are expected for 12-heteropolymolybdates in acidic mixed solvents containing ethers. In spite of the fact that DME and DO have nearly the same dielectric constants, DO rather than DME in acidic mixed solvents is better suited for stabilizing the eight-reduction species of 12-heteropolymolybdates. This finding raises the question whether the dielectric constant of the solvent serves to any significant extent for stabilizing heteropoly molybdenum blues in acidic solvents. Ethers employed in the present work have low dipole moments, ranging from 0.5 to 1.7.[9)] However, the eight-electron reduction species of 12-heteropolymolybdates is not stabilized in acidic solutions containing DME. The possibility can be ruled out that the dipole moment of the organic solvents plays an important role in the stabilization of the eight-electron reduction species of heteropolymolybdates.

12-MSA in sulfuric acid solutions containing DO or THF is reduced at more positive potentials than that in the same electrolyte solution without organic additive present, as is shown in Table 2. The opposite effect was observed in the presence of DME, DMF, MeCN, EtOH, or acetone. The voltammetric behavior of 12-MSA in sulfuric acid solution containing DME is almost identical to that in the same electrolyte solution containing DMF, MeCN, EtOH, or acetone.

The fact that 12-MSA in acidic solutions containing cyclic ethers is reduced at potentials more positive than the hydrated 12-MSA in acidic solutions in the absence of organic solvents suggests that the cyclic ether stimulates the electroreduction of 12-MSA, and that a specific interaction is involved between 12-MSA and the cyclic ether. Such an interaction should be regarded as the coordination of the cyclic ether to the Mo atoms, or the formation of Lewis acid-base adducts between 12-MSA and cyclic ether. It has been shown that the formal redox potentials of the first three redox couples of 12-MPA in sulfuric acid solutions containing DO shift toward more positive potentials with increase in concentration of DO over the concentration range from 10 to 50% in volume.[4)] A solid 12-MSA containing 1,4-dioxane molecules instead of water as a crystallization solvent molecule has been prepared.[2)] These results further indicate that a strong solvation force is involved between 12-heteropoly acids and 1,4-dioxane. It seems reasonable to suppose that the cyclic ether acts as a Lewis base even in acidic solutions, since large amounts of ether are present in the electrolyte solutions.

The redox behavior of 12-heteropolymolybdates in acidic media is little influenced by the kind of inorganic acid. It has been shown from the conductivity measurements that hydrochloric acid in water-dioxane mixtures behaves as a strong electrolyte, even up to 70% dioxane.[10)] Accordingly, it seems likely that various inorganic acids remain unassociated at the concentration employed in the present work.

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