Electrochemical Formation of 11-Molybdophosphate Anion at the Nitrobenzene/Water Interface and Its Applicability to the Determination of Orthophosphate Ion

Toshiyuki Osakai,* Sadayuki Himeno, and Atsuyoshi Saito
Department of Chemistry, College of Liberal Arts, Kobe University, Nada-ku, Kobe 657

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Transfer of the hexamolybdate ion, $Mo_6O_{19}^{2-}$, at the nitrobenzene(NB)/water(W) interface was studied by ion-transfer voltammetry. The $Mo_6O_{19}^{2-}$ ion decomposed immediately after being transfered from NB to W. In the presence of orthophosphate ions in the weakly acidic W phase (pH 3.1), molybdophosphate anions, i.e. $[H_3PMo_{11}O_{39}]^{4-}$, were formed at the interface. A well-defined voltammetric wave due to the transfer of complex anions from W to NB was observed; the peak current was proportional to the bulk concentration of orthophosphate ions. Thus, the NB/W interface containing $Mo_6O_{19}^{2-}$ in NB can function as an ion-selective electrode surface for a voltammetric determination of orthophosphate ions.

Much attention is presently being paid to a new voltammetric method for the determination of ions with a polarizable oil/water interface.[1–4] Previously, one of the authors (T.O.) and co-workers developed oil/water interfaces which function as voltammetric (or amperometric) ion-selective electrode (ISE)-surfaces for several cations, including: Na^+, K^+, and NH_4^+.[5] Some of these ISE's were further applied to the design of amperometric chemical sensors for ammonia,[6] urea,[7] and volatile amines.[8] Most of the ISE's and sensors, however, are based upon the cation selectivity of crown ethers.

In our recent studies,[9,10] the transfer of heteropolyanions at the NB/W interface was investigated by ion-transfer voltammetry.[1–4] As already described,[9,10] such voltammetric studies shed light on the mechanisms of extraction processes of heteropolyacids. Still, it should be noted that another important objective of the studies is to develop oil/water interfaces which serve as ISE-surfaces for a voltammetric determination of such oxoanions as orthophosphate and silicate ions.

In parallel with the above-mentioned studies concerning the phase transfer of heteropolyanions, we have investigated electrode reactions of heteropoly- and isopolymolybdate anions.[11–13] In a previous study[13] we elucidated that the hexamolybdate ion, $Mo_6O_{19}^{2-}$, is partially electroreduced to decompose rapidly to Mo(V) and Mo(VI) in acidic aqueous-organic media. On the basis of this electrode reaction, the formation of a certain blue (reduced) heteropoly complex(es) can be electrochemically controlled. As an example of the application, we reported on a voltammetric method for the determination of the sulfate ion as the blue molybdosulfate complex.[12]

In this study, it has been found that when $Mo_6O_{19}^{2-}$ transfers across a nitrobenzene(NB)/water(W) interface from NB to W, it decomposes rapidly to some Mo(VI) species. In the presence of orthophosphate ions in W, a yellow (oxidized) heteropoly complex is formed at the interface. The present paper describes the principle of a new method for the voltammetric determination of orthophosphate ions based on such an electrochemical formation of this yellow complex at the NB/W interface.

Experimental

Electrochemical Measurements. Since a large current due to the transfer of $Mo_6O_{19}^{2-}$ flows through the interface, a three-electrode cell (Fig. 1) was used instead of the two-electrode cell previously used.[9] The cell system was supplemented with an Ag/AgCl electrode (F) as the reference

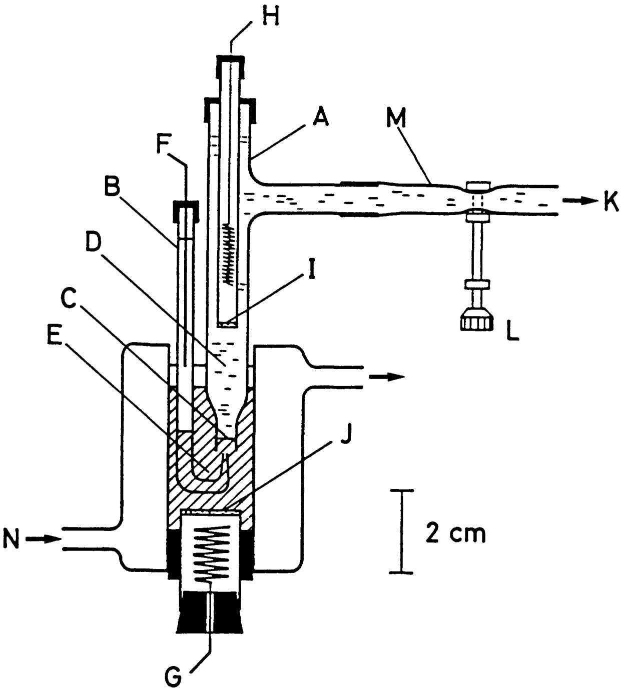

Fig. 1. Diagram of the three-electrode cell. A, glass tube; B, Luggin capillary; C, test interface (0.127 cm²); D, water phase; E, oil phase; F, G, and H, Ag/AgCl electrodes; I and J, glass sinters; K, to solution reservoir; L, screw cock for the interface adjustment; M, silicone tube; N, thermostated water (25±0.1 °C).

electrode, which was connected to the NB phase close to the test interface (C) through a Luggin capillary (B). The Ag/AgCl electrodes (F and G) were immersed in 0.1 M (1 M=1 mol dm^{-3}) tetrabutylammonium chloride (TBACl) aqueous solutions, while the Ag/AgCl electrode (H) was immersed in a 0.5 M $MgCl_2$ aqueous solution separated from the W phase by means of a glass sinter (I). Accordingly, the electrochemical cell can be expressed as

$$\begin{array}{c|c|c|}
 & \text{I} & \text{II} \\
 & 0.1\ \text{M} & 0.1\ \text{M TBATPB} \\
\text{Ag/AgCl} & \text{TBACl} & a\ \text{mM (TBA)}_2\text{Mo}_6\text{O}_{19} \\
\text{(F or G)} & \text{(W)} & \text{(NB)}
\end{array}$$

$$\begin{array}{c\vdots c|cc}
\text{III} & \text{IV} & & \\
0.5\ \text{M MgCl}_2\text{+buffer} & 0.5\ \text{M} & & \\
(+b\ \text{mM KH}_2\text{PO}_4) & \text{MgCl}_2 & \text{AgCl/Ag.} & \text{(A)} \\
\text{(W)} & \text{(W)} & \text{(H)} &
\end{array}$$

Here, TBATPB stands for tetrabutylammonium tetraphenylborate. The pH of phase-III was adjusted with a CH_3COOH-$(CH_3COO)_2Mg$ buffer ($[CH_3COO^-]$=0.1 M) or HCl (at pH<3). The potential difference (E) between the metal phases of electrodes F and H was controlled by a programmable function generator (Hokuto Denko Model HB-105) through a laboratory-made potentiostat. The solution resistance between the tip of the Luggin capillary and electrode H was compensated for by positive feedback. The current flowing through the test interface was detected by means of Ag/AgCl electrodes G and H with large surface areas (ca. 15 and ca. 10 cm^2, respectively), and the cyclic voltammograms were recorded with an X-Y pen recorder (Yokogawa Model 3023), unless otherwise noted.

Chemicals. The $(TBA)_2Mo_6O_{19}$ salt was prepared as described previously.[13,14] Other chemicals, except for $(TBA)_4[H_3PMo_{11}O_{39}]$ (see below), were described in the previous paper.[9]

The $(TBA)_4[H_3PMo_{11}O_{39}]$ salt was prepared according to the following procedure: To a stirred aqueous solution containing 120 mM $Na_2MoO_4\cdot 2H_2O$ and 10 mM $Na_2HPO_4\cdot 12H_2O$, concd HCl was added dropwise until the pH became 3.1. The addition of solid TBABr produced yellow precipitates. These precipitates were collected by filtration, washed several times with acetone to remove any TBA$^+$-salt of the Keggin anion $(TBA)_3[PMo_{12}O_{40}]$ (yellow) formed simultaneously, and then dried at 50 °C. The results of an elemental analysis for the resulting pale-yellow salt are as follows. Found: Mo, 39.12; P, 1.14; C, 28.75; H, 5.50; N, 2.09%. Calcd for $(TBA)_4[H_3PMo_{11}O_{39}]$: Mo, 39.33; P, 1.15; C, 28.65; H, 5.52; N, 2.08%. In the TG-DTA, the evolution of water was not observed up to 120 °C.

Figure 2(a) shows the IR spectrum of $(TBA)_4[H_3PMo_{11}O_{39}]$, which was recorded with a Hitachi Model 270-30 spectrophotometer. The spectrum is characterized by absorption bands at 1081, 1041, 936, 863, 821, and 762 cm^{-1}. For a comparison, Fig. 2(b) shows the IR spectrum of the TBA$^+$-salt of the Keggin anion, $(TBA)_3[PMo_{12}O_{40}]$, prepared according to a reported method.[15] The strong band at 1062 cm^{-1} for the Keggin anion, which can be assigned to the asymmetric stretch of the PO_4 group, splits into two bands at 1081 and 1041 cm^{-1} for $[H_3PMo_{11}O_{39}]^{4-}$. A similar splitting has been reported for the 11-tungstophosphate anion.[16-18] Rocchiccioli-Deltcheff and Thouvenot[18] reported corresponding bands at 1060 and 1010 cm^{-1} for the NH_4^+-salt of the 11-molybdophosphate anion. However, it should be noted that the crystal $Na_3H_6Mo_9PO_{34}(H_2O)_x$ prepared according to Strandberg's method[19] gave the same two bands at 1061 and 1009 cm^{-1}.

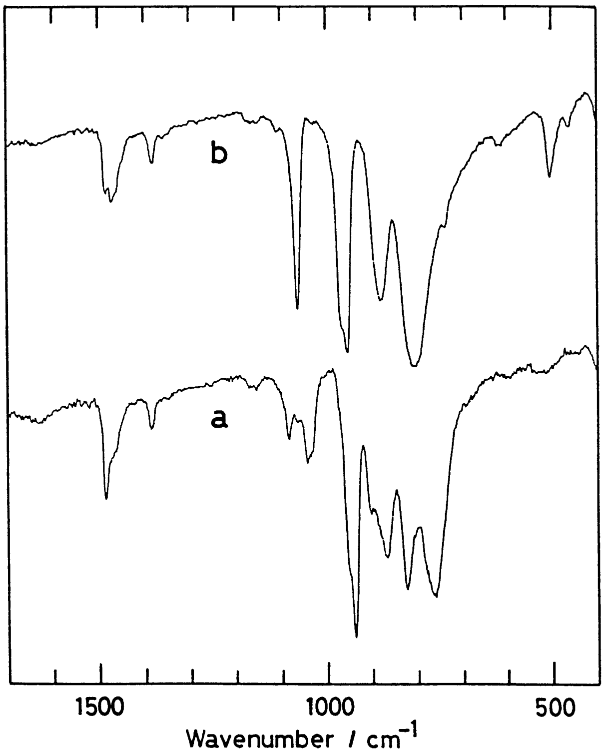

Fig. 2. IR spectra of (a) $(TBA)_4[H_3PMo_{11}O_{39}]$ and (b) $(TBA)_3[PMo_{12}O_{40}]$ in the KBr pellets.

From the above results it may be concluded that the $[H_3PMo_{11}O_{39}]^{4-}$ anion is a so-called "lacunary" derivative of the Keggin structure.[20]

Results and Discussion

Phase Transfer of $Mo_6O_{19}^{2-}$. Figure 3 shows cyclic voltammograms recorded at various scan rates when the NB phase contained 0.2 mM $Mo_6O_{19}^{2-}$ (note that orthophosphate ion was absent in this case).

At high scan rates (1.0—5.0 V s^{-1}), a typical wave with a pair of anodic (positive-current) and cathodic (negative-current) peaks was obtained, as represented by voltammogram (1). The anodic and cathodic peaks correspond, respectively, to the transfer of $Mo_6O_{19}^{2-}$ from NB to W and its transfer back to NB. Both the anodic and cathodic peak potentials, E_{pa} and E_{pc}, were almost independent of the pH of the W phase in the range 1.5 to 5.0. The midpoint potential, E_{mid} ($\equiv(E_{pa}+E_{pc})/2=0.387\pm0.002$ V), may be taken as a reversible half-wave potential, $E^r_{1/2}$, from which the standard potential difference, $\Delta^{W}_{NB}\phi^{\ominus}$, and the standard Gibbs energy, $\Delta G^{\ominus,NB\rightarrow W}_{tr}$, for the $Mo_6O_{19}^{2-}$ transfer were determined to be 0.164 V and 32 kJ mol^{-1}, in a similar manner as described previously.[9]

At lower scan rates ($\leq$0.2 V s^{-1}), the cyclic voltammogram showed an irreversible behavior. As can be

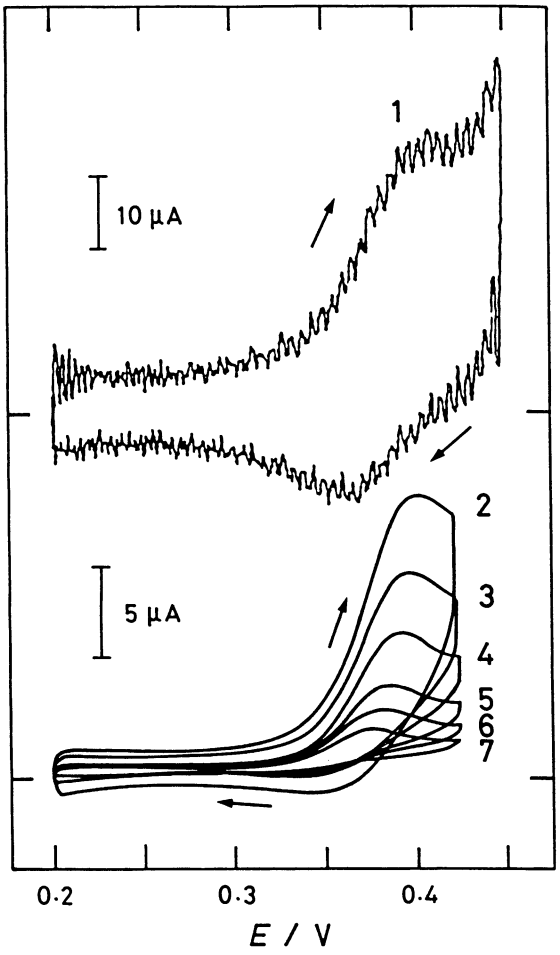

Fig. 3. Cyclic voltammograms of the transfer of $Mo_6O_{19}^{2-}$ at the NB/W (pH 3.1) interface. The NB phase contained 0.2 mM $(TBA)_2Mo_6O_{19}$. Scan rate: (1) 1.0; (2) 0.2; (3) 0.1; (4) 0.05; (5) 0.02; (6) 0.01; (7) 0.005 V s^{-1}. Voltammogram (1) was recorded with a transient recorder (Yokogawa Model 3655) instead of an X-Y pen recorder.

seen in voltammograms (2)—(7) in Fig. 3, no distinct cathodic peak due to the transfer of $Mo_6O_{19}^{2-}$ back to NB was observed, clearly showing that the anion decomposed rapidly in the W phase. This result is in line with the previous observations, that $Mo_6O_{19}^{2-}$ could be hardly detected in aqueous solutions; the anion was stabilized by the addition of certain water-miscible organic solvents.[13,14] Thus, the present ion-transfer process can be represented by

$$Mo_6O_{19}^{2-}(NB) \rightleftarrows Mo_6O_{19}^{2-}(W) \qquad (1)$$

and

$$Mo_6O_{19}^{2-}(W) \xrightarrow{k_d} Mo(VI)(W). \qquad (2)$$

To this system we can apply the theory of stationary electrode voltammetry[21] for a reversible charge transfer followed by an irreversible chemical reaction. According to the theory, it follows that E_{pa} is given by

$$E_{pa} = E^{r}_{1/2} - 0.780\,(RT/zF) + (RT/2zF)\ln[k_d(RT/|z|F)/v], \qquad (3)$$

where k_d is the first-order rate constant of the decomposition reaction (Eq. 2), v the scan rate, and z the ionic valence (here, $z=-2$). R, T, and F have their usual meanings. In accord with Eq. 3, E_{pa} shifted toward positive potentials by about 18 mV for a tenfold increase in v. The value of 18 mV is close to the theoretical value of 15 mV ($=-2.303(RT/2zF)$) at 25 °C. Using Eq. 3 and the $E^{r}_{1/2}$-value of 0.387 V, k_d was estimated to be 12±3 s^{-1} (at pH 3.1).

Electrochemical Formation of a Molybdophosphate Anion. From the above results, we expected that when such an oxoanion as the orthophosphate ion is present in the W phase, the transfer of $Mo_6O_{19}^{2-}$ from NB to W would be followed by the formation of a heteropoly complex at the interface. In Fig. 4, the dashed line indicates the cyclic voltammogram

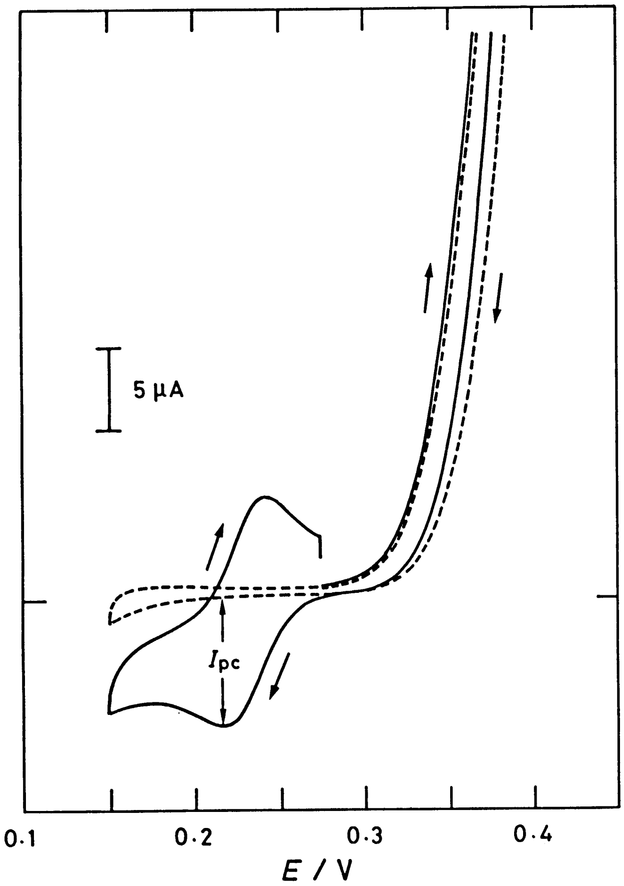

Fig. 4. Cyclic voltammograms of the transfer of $Mo_6O_{19}^{2-}$ at the NB/W interface in the presence (——) and absence (----) of 0.2 mM orthophosphate ion in the W phase (pH 3.1). The NB phase contained 5.0 mM $(TBA)_2Mo_6O_{19}$. The potential sweep was applied from 0.275 to 0.40 V in the anodic direction, followed by the cathodic to 0.15 V, then the anodic back to the initial potential. The potential-holding period at 0.40 V was 0 s in this case. Scan rate: 0.02 V s^{-1}.

obtained when $Mo_6O_{19}^{2-}$ was added in NB in a higher concentration (5.0 mM). On the initial anodic scan from 0.275 to 0.40 V, a large current due to $Mo_6O_{19}^{2-}$ transfer from NB to W was observed. As mentioned above, the anodic current was not followed by a cathodic current because of the rapid decomposition of $Mo_6O_{19}^{2-}$ in W. In the presence of orthophosphate ions in the W phase, however, a well-developed cathodic peak appeared at around 0.22 V on the succeeding cathodic scan, as shown by the solid line in Fig. 4. The cathodic peak was followed by an anodic peak at around 0.24 V. Obviously, these cathodic and anodic peaks were due to a phase transfer of certain molybdophosphate anions formed in the W phase in the vicinity of the interface. As the pH was raised, the wave shifted to negative potentials with a current change. In the following experiments, the pH was set at 3.1 so as to obtain the wave at a preferable potential, as shown in Fig. 4. Under these conditions, the cathodic peak current, i_{pc}, was proportional to the bulk concentration of orthophosphate ions in the range from 0.02 to 0.3 mM (shown in Fig. 5 by open circles). At concentrations higher than 0.3 mM, the cathodic current no longer increased, possibly because of a deficiency of Mo(VI). In this higher concentration range, the reproducibility of the currents was also poor. However, when the initial anodic scan was stopped at a switching potential of 0.40 V for a definite time, the lineality of the concentration dependence of i_{pc}, as well as the reproducibility, was much improved. At a potential-holding period of 60 s, i_{pc} was linear to the orthophosphate-ion concentration up to 0.5 mM (shown in Fig. 5 by full circles). In the lower concentration range (<0.3 mM), i_{pc} was virtually independent of the potential-holding period, indicating that the current was controlled only by the diffusion of orthophosphate ions to the interface.

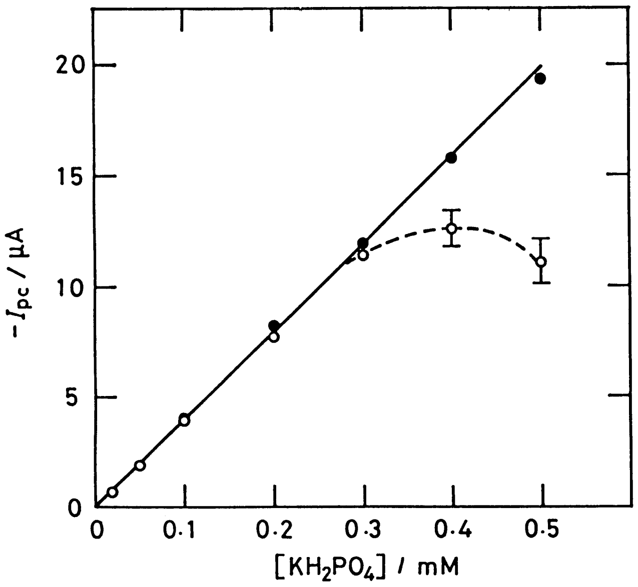

Fig. 5. Dependence of i_{pc} on the bulk concentration of orthophosphate ions added to the W phase. The potential-holding period: (○) 0; (●) 60 s.

These results clearly show that an NB/W interface containing $Mo_6O_{19}^{2-}$ in NB may function as a voltammetric ISE-surface for orthophosphate ions. An investigation is now in progress to develop a voltammetric sensor for practical uses based on such an oil/water interface.

Identification of the Heteropolyanion Formed at the Interface. For this purpose, a molybdophosphate anion formed at pH 3.1 in the aqueous molybdate solution was isolated as a TBA^+-salt, i.e. $(TBA)_4[H_3PMo_{11}O_{39}]$, as mentioned in the experimental section. By adding the salt to the NB phase, where the heteropoly complex was stable, a well-defined voltammogram for the phase transfer of the lacunary anion was observed at the same position as that in Fig. 4 (see Fig. 6). This shows that the heteropoly species formed predominantly as a result of the $Mo_6O_{19}^{2-}$ transfer was the lacunary anion. It should be stressed that the wave in Fig. 4 can never be assigned to the Keggin anion, $[PMo_{12}O_{40}]^{3-}$, whose ion-transfer potential was quite positive ($E^r_{1/2}$=0.475 V).[10]

In the voltammograms shown in Fig. 6, the anodic and cathodic peaks correspond to the transfer of anions from NB to W and their transfer back to NB,

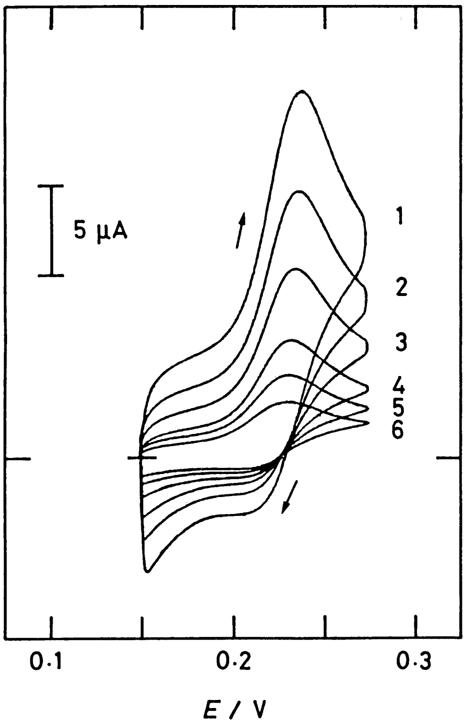

Fig. 6. Cyclic voltammograms of the transfer of $[H_3PMo_{11}O_{39}]^{4-}$ at the NB/W (pH 3.1) interface. The NB phase contained 0.18 mM $(TBA)_4[H_3PMo_{11}O_{39}]$. Scan rate: (1) 0.2; (2) 0.1; (3) 0.05; (4) 0.02; (5) 0.01; (6) 0.005 V s^{-1}.

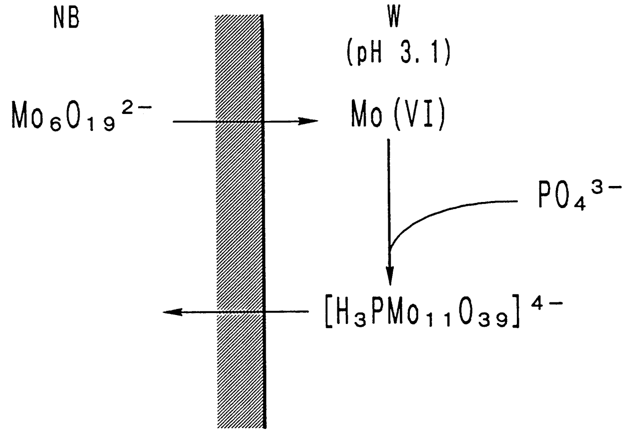

Fig. 7. Illustration of the electrochemical formation of a molybdophosphate anion at the NB/W interface. The succeeding transfer of the resulting $[H_3PMo_{11}O_{39}]^{4-}$ ion from W to NB can be utilized for the voltammetric determination of orthophosphate ions in W.

respectively. Compared with the anodic peak currents, the cathodic ones were small, particularly at lower scan rates. This shows that the complex anions decomposed partially in the W phase, even at pH 3.1. Accordingly, the same theory[21)] as that for $Mo_6O_{19}^{3-}$ transfer may be applied to this ion-transfer process. The slope (8 mV) of the E_{pa} vs. $\log v$ plot at pH 3.1 was close to the theoretical slope (7.4 mV) for $z = -4$. This suggested that the lacunary anion transferred across the interface as the tetravalent anion, i.e. $[H_3PMo_{11}O_{39}]^{4-}$ under these conditions.

Finally, the electrochemical formation of molybdophosphate anions at the NB/W interface may be illustrated graphically in Fig. 7. We would like to add that the present interface system possibly serves as a powerful tool for studying the dynamics of the heteropolyanion formation in aqueous solutions.

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