Electrochemistry of the Transfer of Isopoly and Heteropoly Anions across the Water/Nitrobenzene Interface: Isopolytungstate and Heteropolytungstate Anions

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The transfer behavior of the heteropoly anion \([H_3PW_{11}O_{39}]^-\) and the isopoly anion \([H_2W_{12}O_{40}]^-\) across the water/nitrobenzene interface was investigated by cyclic voltammetry and chronopotentiometry with linear current scanning. The transfer processes were diffusion-controlled. The effect of pH on the transfer behavior and the formation of isopolytungstates and heteropolytungstates anions in the water phase was studied. Parameters related to interface, the transfer half-wave potential and the standard transfer Gibbs energy, were estimated and transfer mechanisms are discussed.

Keywords Liquid/liquid interface, isopolytungstate and heteropolytungstate acids, chronopotentiometry with linear current scanning, cyclic voltammetry

In recent years, much attention is being paid to isopoly and heteropoly acids. They have been widely utilized as catalysts.\(^1\)\(^-\)\(^4\) Liquid-liquid extraction has been used most frequently for the selective separation of heteropoly and isopoly acids.\(^5\)\(^,\)\(^6\) Nevertheless, the mechanisms of the extraction and catalytic process have not yet been fully understood. Electrochemistry at the liquid/liquid interface offers a promising possibility for understanding the interfacial processes including extraction and phase transfer catalysis.\(^7\)\(^,\)\(^8\) Osakai et al. have studied the transfer of some isopoly and heteropoly anions across the water/nitrobenzene (W/NB) interface by cyclic voltammetry (CV) and normal pulse voltammetry.\(^9\)\(^-\)\(^12\) We have also investigated the transfer of some heteropoly and isopoly anions across the W/NB interface by CV and chronopotentiometry with linear current scanning (CLC).\(^13\)\(^-\)\(^15\)

In this paper, the transfer of \([H_3PW_{11}O_{39}]^-\) and \([H_2W_{12}O_{40}]^-\) across the W/NB interface has been studied. The effect of pH on the transfer behavior and the formation of isopolytungstate and heteropolytungstate anions in the water phase are discussed. Parameters related to interface were estimated and transfer mechanisms are discussed.

Experimental

Reagents

Phosphatungstic acid (H₄PW₁₂O₃₉, A.R.) was purchased from Huzhou Linhu Food Chemical Plant. Sodium tungstate (Na₂WO₄, A.R.) and lithium chloride (LiCl, A.R.) were used. The nitrobenzene (A.R.) used was washed with 0.1 M hydrochloric acid and twice-distilled water.

Tetrabutylammonium tetrphenylborate (TBATPB, Fluka AG Puriss) and tetrabutylammonium chloride (TBACl, Fluka AG Purum) were used. Other reagents were all analytical grade.

Dilute nitric acid or acetic acid-sodium acetate was used as buffer solution. Twice-distilled water was used.

Apparatus

An electrolytic cell and a cyclic voltammetric analyzer equipped with a four electrode potentiostat with a positive feedback system were used, as in the previous paper.\(^16\) Current vs. potential curves were recorded with a 3033-type X-Y recorder (Yokogawa, Hokushin Electric, Japan). The electrochemical cell used be represented as:

\[
\text{Ag/AgCl, 0.01 M LiCl} \quad \text{0.01 M LiCl sample buffer} \\
\text{RE1} \quad \text{(W)} \\
\text{0.01 M TBATPB} \quad \text{0.01 M TBACl, AgCl/Ag.} \\
\text{(NB)} \quad \text{(W)} \quad \text{RE2}
\]

The geometric area of the test interface between the
aqueous and nitrobenzene phases is 1.2 cm². The Galvanic potential difference between the water (W) and nitrobenzene (NB) phases is \( \Delta \phi = \phi(\text{w}) - \phi(\text{n}) \), related to TBA⁺ ion selective electrode. The potential difference of the cell, \( E \) is

\[
E = \Delta \phi - \Delta \phi_{\text{Na}^+}
\]

where \( \Delta \phi_{\text{Na}^+} = -0.248 \text{ V} \) (ref. 17).

All measurements were performed at room temperature (15±2°C).

**Results and Discussion**

**Heteropolytungstate anions**

Figure 1 shows cyclic voltammograms recorded at various scan rates when the W phase contained 0.3 mM PW₁₂O₄₀³⁻ (pH 3.0). A pair of anodic and cathodic peaks is obtained. The transfer half-wave potential \( E_{1/2} \) is 0.255 V. Both anodic and cathodic peak currents, \( i_{pa} \) and \( i_{pc} \), are proportional to the square root of the potential scan rate (10 - 200 mV s⁻¹) and the concentration of PW₁₂O₄₀³⁻ (10⁻³ - 10⁻⁵ M), indicating that the transfer process is diffusion-controlled. The difference between the anodic and cathodic peak potential \( \Delta E_p \) (\( = E_{pa} - E_{pc} \)), increases with increasing scan rate and is about 15 mV at the lower scan rate, which corresponds to the transfer of tetravalent ion.

When the pH was above 5.7, no transfer peak was observed. At the pH range from 5.7 to 1.5, the transfer half-wave potential shifts linearly to negative direction with decreasing pH. The slope of \( E_{1/2} \) vs. pH is 14.7 mV/pH (Fig. 2). This further demonstrated that the transfer species was tetravalent ion. Both \( i_{pa} \) and \( i_{pc} \) increase with increasing pH, and then decrease with increasing pH. At pH 4.2, the current reaches a maximum (Fig. 3).

According to the paper of Osakai et al.¹⁰ these transfer peaks do not correspond to the transfer of PW₁₂O₄₀³⁻, the transfer potential for which should be far more positive than the case shown above. PW₁₂O₄₀³⁻ is stable only below pH 1.5.¹⁸ When the pH is above 1.5, the following reaction occurs:¹⁹

\[
[\text{PW}_{12}\text{O}_{40}]^{3-} + (5 - x)\text{OH}^- \xrightarrow{\text{H}^+} [\text{H}_{x}\text{PW}_{11}\text{O}_{39}]^{3-x} + \text{HWO}_4^- + (2 - x)\text{H}_2\text{O}.
\]

Cyclic voltammograms for PW₁₂O₄₀³⁻ at pH<1.5 are

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Fig. 1 Cyclic voltammograms for PW₁₂O₄₀³⁻: W phase, 0.01 M LiCl+0.3 mM PW₁₂O₄₀³⁻ at pH 3.0 adjusted by nitric acid; NB phase, 0.01 M TBATPB; scan rate (mV/s), (1) 10, (2) 20, (3) 50, (4) 100, (5) 200.

Fig. 2 \( E_{1/2} \) vs. pH curve for PW₁₂O₄₀³⁻.

Fig. 3 \( i_{pc} \) vs. pH curve for PW₁₂O₄₀³⁻; scan rate, 20 mV/s; concentration of PW₁₂O₄₀³⁻, 0.38 mM.
The transfer peaks described above disappear. Only a cathodic peak ($E_0 = 0.43$ V) is observed, not very clearly. But owing to the large concentration of $H^+$ and the limits of our potential window, no distinct transfer peak was observed.

From these results and the hydrophobicity scale of polyanions proposed in ref. 11, we conclude that the transfer species responsible for the waves observed is a lacunary anion $\left[H_3PW_{11}O_{39}\right]^{4-}$. From the relation between pH and $E_{1/2}$, a protonation attends the reaction before the $\left[H_3PW_{11}O_{39}\right]^{4-}$ transfer across the W/NB interface. From the curve of peak current vs. pH and with the reference of Pope19, $PW_{12}O_{40}^{3-}$ can be transformed into other heteropolytungstate anions beside $H_3PW_{11}O_{39}^{4-}$.

Finally, the transfer process of $\left[H_3PW_{11}O_{39}\right]^{4-}$ at the W/NB interface may be illustrated by the schematic diagram shown below (Scheme 1).

**Isopolytungstate anions**

When W phase contains 0.01 M LiCl, 9.1×10$^{-4}$ M $WO_4^{2-}$ and acetic acid–sodium acetate buffer (pH 3.65), a pair of well-defined peaks are obtained in cyclic voltammetry.

![Fig. 4 Cyclic voltammograms for $PW_{12}O_{40}^{3-}$: W phase, 0.01 M LiCl+0.23 mM PW$_{12}$O$_{40}^{3-}$ at pH 1.1 adjusted by nitric acid; NB phase, 0.01 M TBATPB; scan rate (mV/s), (1) 10, (2) 20, (3) 50, (4) 100, (5) 200, (0) blank solution without PW$_{12}$O$_{40}^{3-}$, 10 mV/s.](image)

![Fig. 5 Cyclic voltammograms for $WO_4^{2-}$: W phase, 0.01 M LiCl+0.91 mM WO$_4^{2-}$+acetic acid–sodium acetate at pH 3.65; NB phase, 0.01 M TBATPB; scan rate (mV/s), (1) 10, (2) 20, (3) 50, (4) 100, (5) 200, (0) 10, blank solution without WO$_4^{2-}$.](image)

![Fig. 6 Chronopotentiometry with linear current scanning curve for $WO_4^{2-}$: W phase and NB phase as in Fig. 5; scan rate, 5 μA/s.](image)

Isopolytungstate anions

When W phase contains 0.01 M LiCl, 9.1×10$^{-4}$ M $WO_4^{2-}$ and acetic acid–sodium acetate buffer (pH 3.65), a pair of well-defined peaks are obtained in cyclic voltammetry.

$$W_\text{phase}: \quad PW_{12}O_{40}^{3-} + 3OH^- \rightleftharpoons HWO_4^- + \left[H_2PW_{11}O_{39}\right]^{4-} \rightleftharpoons \left[H_3PW_{11}O_{39}\right]^{4-}$$

$$NB\text{phase}: \quad \left[H_2PW_{11}O_{39}\right]^{4-} \rightleftharpoons \left[H_3PW_{11}O_{39}\right]^{4-}$$

Scheme 1
voltammetry (CV), as shown in Fig. 5. The transfer half-wave potential $E_{1/2}$ is 0.23 V. These peak currents, $i_{pa}$ and $i_{pc}$, are proportional to the square root of the potential scan rate (10 – 200 mV s$^{-1}$), indicating that the transfer is diffusion-controlled. The potential difference between two peaks is about 15 mV at a slow scan rate ($v<10$ mV s$^{-1}$). The peak potentials, $E_{pa}$ and $E_{pc}$, shift positively and negatively with increasing scan rate, respectively. These results show that the transfer species is tetravalent anion.

The chronopotentiogram for the transfer of isopolytungstate anion across the W/NB interface is shown in Fig. 6. The limiting current $i_l$ in chronopotentiometry with linear current scanning (CLC) is proportional to one-third power of the current scan rate $v^{1/3}$. A 4 o.63 is 0.23 V in agreement with CV. At lower current scan rates ($v<10$ µA s$^{-1}$), the curve of log$[i_{3/2}/(i_{3/2}^{-1/2})]$ vs. $E$ is linear with a slope of 15 mV. This demonstrates further that the charge number of the transfer species is four and that the transfer process is diffusion-controlled. The above results and reference20, allow us to conclude the transfer species is $[\text{H}_2\text{W}_{12}\text{O}_{39}]^{4-}$.

When the pH is above 4.0, no distinct transfer peaks are observed. At pH<4.0, a pair of well-developed peaks appear. The peak potentials are almost independent of pH. However, the peak currents firstly increase with decreasing pH, and then decrease with pH. The current is the highest at pH 1.5 (Fig. 7). At pH<1.5, another pair of peaks appear (Fig. 8). These results indicate that the $[\text{H}_2\text{W}_{12}\text{O}_{39}]^{4-}$ is converted to some other form of the anion rather than the protonated process. The transfer mechanism can be expressed by the following schematic diagram (Scheme 2).

From voltammetric data, the formal transfer potential and Gibbs energy for the $[\text{H}_2\text{W}_{12}\text{O}_{39}]^{4-}$ transfer across the W/NB interface can be calculated. The value of the transfer standard potential is $-0.018$ V and the Gibbs energy is calculated by the following equation:

$$
\Delta G(0, w \rightarrow n_0) = ZF\Delta\Phi_{0.63}^{o}
$$

where $Z$ is the charge number and $F$ is the Faraday constant. $\Delta G(0, w \rightarrow n_0)$ is calculated to be 6.95 kJ mol$^{-1}$.

In conclusion, PW$_{12}$O$_{40}^{3-}$ is transformed into H$_3$PW$_{11}$O$_{39}^{4+}$ at 1.5<pH<5.7, which can transfer across the W/NB interface with the pronotated process. The transfer process is diffusion-controlled. The transfer half-wave potential and Gibbs energy are 0.255 V (at pH 3.0) and $-2.70$ kJ/mol, respectively.

At pH<4.0, WO$_4^{2-}$ is transformed into H$_2$W$_{12}$O$_{39}^{4+}$, which can transfer across the W/NB interface. The transfer process is diffusion-controlled. The transfer half-wave potential is 0.23 V and the standard Gibbs
energy is 6.95 kJ/mol.
The pH ranges of H₃PW₁₁O₃₉⁴⁻ and H₂WO₁₂O₃₉⁴⁻ existing in solution are the same as those reported.¹⁹ This indicates further that electrochemistry at liquid/liquid interface is a promising method for studying isopoly and heteropoly acids, especially their formation in solution.

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References

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