Redox Properties and Basicity of Keggin-Type Polyoxometalate Complexes

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For Keggin-type polyoxometalate complexes (α-$[XMo_{12}O_{40}]^{n-}$ ($X = S$, P, As, Si, Ge; $n = 2$–4) and α-$[XW_{12}O_{40}]^{n-}$ ($X = S$, P, As, Si, Ge, B, Al; $n = 2$–5)), the conversion processes of the first two one-electron waves into a two-electron wave were investigated in dipolar aprotic solvents containing H^+, Li^+, or Na^+ as a Lewis acid. A simulation of the cyclic voltammogram indicated that the potential difference (ΔE_{mid}) between the first one- and two-electron redox waves served as a useful criterion for the basicity of the Keggin anions. According to the ΔE_{mid} values, the Keggin anions were classified into the following four groups: (1) $[SW_{12}O_{40}]^{2-}$; (2) $[SMo_{12}O_{40}]^{2-}$, $[XW_{12}O_{40}]^{3-}$ ($X = P$, As); (3) $[XMo_{12}O_{40}]^{3-}$ ($X = P$, As), $[XW_{12}O_{40}]^{4-}$ ($X = Si$, Ge); (4) $[XMo_{12}O_{40}]^{4-}$ ($X = Si$, Ge), $[XW_{12}O_{40}]^{5-}$ ($X = B$, Al). The voltammetric properties of the Keggin anions were systematized with reference to their basicities.

In general, the reduction of Keggin-type polyoxometalates proceeds in a complex manner.[1,2] The association of H^+, Li^+, or Na^+ with the reduced form of the Keggin anion at the electrode surface causes one-electron waves to be converted into two-electron waves in CH_3CN and CH_3COCH_3.[3–8] When the association is not sufficiently strong, the Keggin anion does not exhibit successive two-electron waves, but undergoes one-, one-, and two-electron reductions. Thus, the coalescence of the first two one-electron waves into a two-electron wave is necessary to obtain successive two-electron waves.

For either of the molybdenum- and tungsten-complexes, the Keggin anion with a greater ionic charge possesses a greater basicity. However, there is a big difference in the voltammetric properties between the molybdenum- and tungsten-complexes with identical anionic charge. In acidified CH_3CN–water media, $[PMo_{12}O_{40}]^{3-}$ undergoes successive two-electron reductions,[9] while $[PW_{12}O_{40}]^{3-}$ is electrochemically reduced by one-, one-, and two-electrons.[4] Thus, the voltammetric properties of the molybdenum- and tungsten-complexes still need to be systematically investigated. Besides, the voltammetric behaviors of the Keggin anions depend on the nature of the solvent, because the associating ability also depends on the donicity, expressed as the donor number (DN), and the relative permittivity (ε_r) of the solvent.[10,11]

Bond et al. simulated cyclic voltammograms for α-$[S_2Mo_{18}O_{62}]^{4-}$, γ^*-$[S_2W_{18}O_{62}]^{4-}$, α-$[P_2W_{18}O_{62}]^{6-}$, and α-$[H_2W_{12}O_{40}]^{6-}$ to quantitatively explain the acid–base equilibria coupled with electron-transfer in the two-electron reduction.[12–15] The effect of Li^+ on the voltammetric behavior of α-$[S_2Mo_{18}O_{62}]^{4-}$ was also investigated.

In the present study, the voltammetric behaviors of the Keggin anions prepared so far were investigated in acidified dipolar aprotic solvents. Upon the addition of H^+ to the solution, successive two-electron waves were obtained at potentials more positive than the original one-electron waves. This study focused on the potential difference (ΔE_{mid}) between the original first one-electron wave and the first two-electron wave in the presence of H^+. A simulation of the cyclic voltammogram showed that ΔE_{mid} could be used as a direct measure of the basicity of the Keggin anions. The present study was undertaken to relate the voltammetric properties and basicities of the Keggin anions.

Experimental

Cyclic voltammograms were recorded with a Hokuto Denko (Model HA1010mM1A) potentiostat interfaced to a microcomputer-controlled system. A Tokai glassy carbon (GC-30S) with a diameter of 5.0 mm was used as the working electrode and a platinum wire served as the counter electrode. The potentials are referred to the redox potential of ferrocene (Fc)/ferrocenium ion (Fc^+) as an internal reference. Prior to each measurement, the GC electrode was polished manually with 0.25 µm diamond slurry, and washed with distilled water in an ultrasonic bath. The solutions were deoxygenated with nitrogen. Unless otherwise noted, the potential scan rate was set at $100\ mV\,s^{-1}$. All voltammetric measurements were made at 25 ± 0.1 °C. The solution resistance was compensated for by positive feedback. A digital simulation of cyclic voltammograms was made with the simulation package DigiSim 3.0 (Bioanalytical Systems).

A 0.10 M $HClO_4$ solution in acetic acid (Wako Pure Chemical Industries) was used to study the effect of H^+ on the voltammetric behavior. Tetrabutylammonium perchlorate (n-Bu_4NClO_4) was prepared and purified according to a literature method.[16] Lithium perchlorate and sodium perchlorate were of analytical reagent grade, and were dried under a vacuum at 50 °C for 24 h. Other chemicals were of analytical grade, and were used as received. The n-Bu_4N^+ salts of Keggin anions ($[XMo_{12}O_{40}]^{n-}$ ($X = S$, P, As, Si, Ge; $n = 2$–4) and $[XW_{12}O_{40}]^{n-}$ ($X = S$, P, As, Si, Ge,

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B, Al; $n = 2$–5)) were prepared and purified according to methods obtained from the literature.[17–20] All of the Keggin complexes are referred to as the α-isomer. The electrode processes are diffusion-controlled because the reduction currents depend linearly on the square root of the potential scan rate (50–150 mV s^{-1}).

Results

Conversion of the First Two One-Electron Waves into a Two-Electron Wave in CH_3CN. All of the Keggin anions exhibited reversible one-electron redox waves in CH_3CN containing 0.10 M n-Bu_4NClO_4. The separation of E_{pa} and E_{pc} for each redox couple averaged 59 ± 3 mV, where $E_{mid} = (E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are the anodic and cathodic peak-potentials, respectively, and the peak-potentials were independent of the potential scan rate. These results indicate the reversible nature of each one-electron wave.

For either of the tungsten- and molybdenum-complex anions, the E_{mid} value for the first one-electron waves showed a linear dependence on their ionic charge with a common slope of 0.46 V/unit charge (Fig. 1). Since the ionic radius of the Keggin anion is independent of the ionic charge, the E_{mid} value reflects the surface charge density, and consequently the basicity of the molybdenum- or tungsten-complex anion.[21,22] However, the E_{mid} values cannot be used to compare the basicities of the molybdenum- and tungsten-complexes.

The conversion behavior of the one-electron waves into two-electron waves was investigated for a 0.30 mM solution of each Keggin anion in CH_3CN containing 3.0 mM $HClO_4$ + 0.10 M n-Bu_4NClO_4, 0.10 M $LiClO_4$, or 0.10 M $NaClO_4$. The results are given in Table 1, where 1e$^-$ and 2e$^-$ indicate the one-electron and two-electron behaviors, respectively. Of the Keggin anions, $[SW_{12}O_{40}]^{2-}$ should be the least basic, and the first two one-electron waves did not merge into a two-electron wave. For $[SMo_{12}O_{40}]^{2-}$ and $[XW_{12}O_{40}]^{3-}$ (X = P, As) belonging to group (2), successive two-electron waves were obtained only in the presence of H^+. For $[XMo_{12}O_{40}]^{3-}$ (X = P, As) and $[XW_{12}O_{40}]^{4-}$ (X = Si, Ge), the first two one-electron waves did not merge into the two-electron wave in the presence of Na^+, but the presence of Li^+ as well as H^+ produced two-electron waves.[6,8] Because of the strongest basicities, $[XMo_{12}O_{40}]^{4-}$ (X = Si, Ge) and $[XW_{12}O_{40}]^{5-}$ (X = B, Al) exhibited two-electron waves in the presence of H^+, Li^+, or Na^+. Since the Lewis acidity becomes greater in the order $Na^+ < Li^+ \ll H^+$, these results suggest that their voltammetric properties are strongly dependent on the Lewis acidity of such small cations and the Lewis basicity of the Keggin anion.

Table 1. Classification of Keggin Anions Based on Their Voltammetric Behaviors in CH_3CN

Group	Polyoxometalates	H^+	Li^+	Na^+
(1)	$[SW_{12}O_{40}]^{2-}$	1e$^-$	1e$^-$	1e$^-$
(2)	$[SMo_{12}O_{40}]^{2-}$ $[PW_{12}O_{40}]^{3-}$, $[AsW_{12}O_{40}]^{3-}$	2e$^-$	1e$^-$	1e$^-$
(3)	$[PMo_{12}O_{40}]^{3-}$, $[AsMo_{12}O_{40}]^{3-}$ $[SiW_{12}O_{40}]^{4-}$, $[GeW_{12}O_{40}]^{4-}$	2e$^-$	2e$^-$	1e$^-$
(4)	$[SiMo_{12}O_{40}]^{4-}$, $[GeMo_{12}O_{40}]^{4-}$ $[BW_{12}O_{40}]^{5-}$, $[AlW_{12}O_{40}]^{5-}$	2e$^-$	2e$^-$	2e$^-$

With the exception of $[SW_{12}O_{40}]^{2-}$,[20] the Keggin anions exhibited a two-electron wave at potentials more positive than the first one-electron wave in the presence of 3.0 mM H^+ (Table 1). The potential difference (ΔE_{mid}) between the first one- and two-electron waves became greater for either of the tungsten- and molybdenum-complex anions with greater ionic charges. It was found that plots of the ΔE_{mid} value against the ionic charge on the molybdenum- or tungsten-complexes gave straight lines with a common slope of −0.49 V/unit charge (Fig. 2). These observations suggest that the ΔE_{mid} value be used to evaluate the basicity of the Keggin anions.

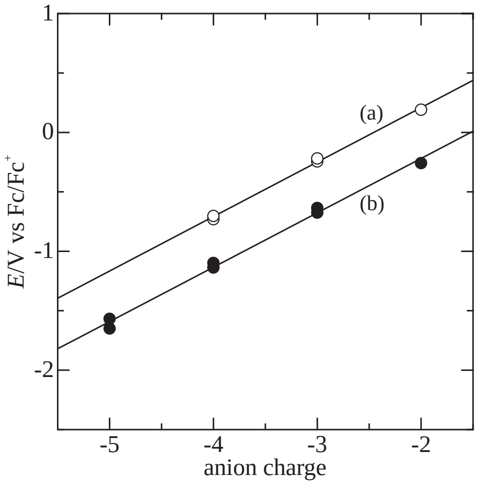


Fig. 1. The E_{mid} values for the first one-electron waves of (a) $[XMo_{12}O_{40}]^{n-}$ (X = S, P, As, Si, Ge; $n = 2$–4) and (b) $[XW_{12}O_{40}]^{n-}$ (X = S, P, As, Si, Ge, B, Al; $n = 2$–5) as a function of the anion charge in CH_3CN containing 0.10 M n-Bu_4NClO_4. For $[SW_{12}O_{40}]^{2-}$, 0.05 M $NaClO_4$ was used as the supporting electrolyte, owing to the solubility problem.

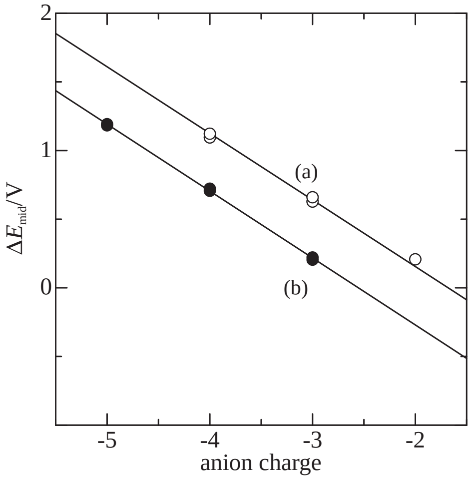


Fig. 2. The ΔE_{mid} values between the first one- and two-electron waves for 0.30 mM solutions of (a) $[XMo_{12}O_{40}]^{n-}$ (X = S, P, As, Si, Ge; $n = 2$–4) and (b) $[XW_{12}O_{40}]^{n-}$ (X = P, As, Si, Ge, B, Al; $n = 3$–5) as a function of the anion charge in CH_3CN containing 0.10 M n-Bu_4NClO_4 + 3.0 mM $HClO_4$.

Simulation of Cyclic Voltammograms. In order to further study the conversion process of the first two one-electron waves into the two-electron wave, cyclic voltammograms were simulated for $[SMo_{12}O_{40}]^{2-}$, $[PMo_{12}O_{40}]^{3-}$, $[GeMo_{12}O_{40}]^{4-}$, $[PW_{12}O_{40}]^{3-}$, $[GeW_{12}O_{40}]^{4-}$, and $[BW_{12}O_{40}]^{5-}$ in CH_3CN. As an example, Fig. 3 shows a cyclic voltammogram of 0.30 mM $[PMo_{12}O_{40}]^{3-}$ in CH_3CN containing 0.10 M n-Bu_4NClO_4. When the potential was scanned to a negative limit of −0.8 V, a two-step one-electron wave, denoted as A(0/I) and B(I/II), was obtained with $E_A{}^{\circ\prime}$ and $E_B{}^{\circ\prime}$ values of −0.244 V and −0.663 V, where $E_A{}^{\circ\prime}$ and $E_B{}^{\circ\prime}$ denote the E_{mid} values of A(0/I) and B(I/II), respectively. In the following, the number of electrons introduced to the oxidized form (0) is expressed in Roman numerals. As shown in Fig. 3, the addition of 3.0 mM H^+ caused the first two one-electron waves to be converted into a reversible two-electron wave with an E_{mid} value ($E_C{}^{\circ\prime}$) of 0.384 V.

The electrode process was analyzed quantitatively by a simulation of the cyclic voltammogram. After the treatment by Bond et al.,[13–15] the electrochemical reaction was assumed to be very fast, and the heterogeneous rate constant was set to $k_s = 1 \times 10^4$ cm s^{-1}. The diffusion coefficients of all the oxidized and reduced Keggin anions were regarded as identical ($D_{Keggin} = 2.3 \times 10^{-5}$ cm^2 s^{-1}), and the diffusion coefficient of H^+ (D_{H^+}) was set to 5×10^{-5} cm^2 s^{-1}. The rate constant for protonation (k_f) was also assumed to be fast, and was set at 1×10^{10} M^{-1} s^{-1}. A value of 1.6×10^{-5} F was used for the double-layer capacitance. The electrochemical and chemical parameters in Scheme 1 provid-

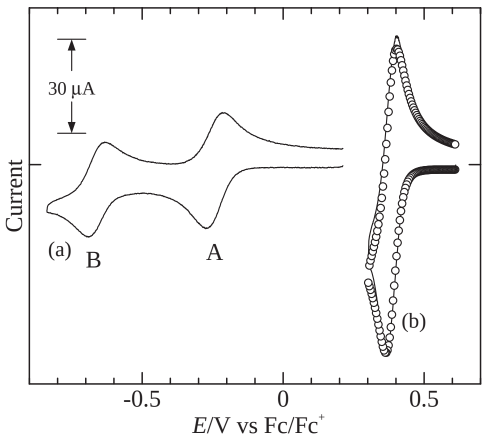
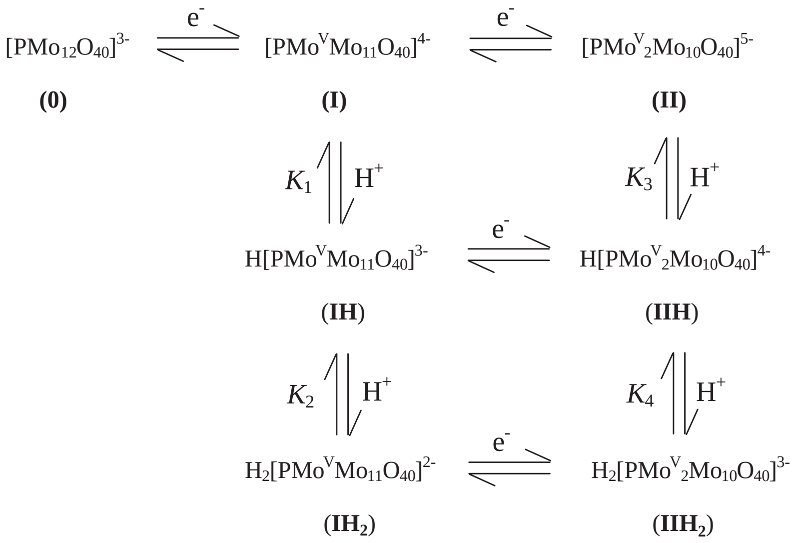


Fig. 3. Cyclic voltammograms of 0.30 mM $[PMo_{12}O_{40}]^{3-}$ in CH_3CN containing (a) 0.10 M n-Bu_4NClO_4; (b) (a) +3.0 mM $HClO_4$. line; experiment: dot; simulation.



couples	A(**0**/**I**)	B(**I**/**II**)
E_{mid}/V	-0.244	-0.663

protonation equilibria

(**I**) $+H^+$ = (**IH**) $K_1 = 4.5 \times 10^{12}$

(**IH**) $+H^+$ = (**IIH$_2$**) $K_2 = 1.5 \times 10^{2}$

(**II**) + H^+ = (**IIH**) $K_3 = 1.2 \times 10^{21}$

(**IIH**) $+H^+$ = (**IIH$_2$**) $K_4 = 2.0 \times 10^{12}$

disproportionation equilibrium

2(**IH**) = (**0**) +(**IIH$_2$**) $K_5 = 9.8$

Scheme 1.

Table 2. Cyclic Voltammetric Data and Protonic Constants

	$E_A{}^{\circ\prime}$/V	$E_B{}^{\circ\prime}$/V	ΔE_{mid}/V	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$
$[SMo_{12}O_{40}]^{2-}$	0.19	−0.16	0.21	5.6	−5.3	15.0	3.9
$[PMo_{12}O_{40}]^{3-}$	−0.24	−0.66	0.63	12.7	2.2	21.1	12.3
$[GeMo_{12}O_{40}]^{4-}$	−0.70	−1.11	1.12	21.1	2.9	31.7	18.3
$[PW_{12}O_{40}]^{3-}$	−0.68	−1.20	0.20	5.6	−4.0	16.4	4.3
$[GeW_{12}O_{40}]^{4-}$	−1.10	−1.61	0.72	14.2	3.4	25.2	12.9
$[BW_{12}O_{40}]^{5-}$	−1.65	−2.14	1.18	22.3	2.2	33.1	20.3

The $\log K$ values are within an error of ±0.1.

ed the best fit between the observed and simulated voltammograms, as shown in Fig. 3. Table 2 summarizes the protonation constants obtained for the six Keggin anions in CH_3CN (DN, 14.1; ε_r, 36.0).

Relationship between the ΔE_{mid} Value and the Basicity of the Keggin Anions. The following equations were derived to relate the ΔE_{mid} value with the protonation constants. The presence of H^+ produces a positive potential shift of the first one-electron wave:

$$E_1{}^{\circ\prime} = E_A{}^{\circ\prime} + 0.059\log(1 + K_1[H^+] + K_1K_2[H^+]^2), \qquad (1)$$

where $E_1{}^{\circ\prime}$ denotes the apparent E_{mid} value.
Since $K_1[H^+] \gg 1 + K_1K_2[H^+]^2$ (Table 2), we obtain the relationship

$$E_1{}^{\circ\prime} = E_A{}^{\circ\prime} + 0.059\log[H^+] + 0.059\log K_1. \qquad (2)$$

Similarly, the E_{mid} value of the second one-electron wave is shifted to

$$\begin{aligned} E_2{}^{\circ\prime} &= E_B{}^{\circ\prime} + 0.059\log\{(1 + K_3[H^+] + K_3K_4[H^+]^2) \\ &\quad /(1 + K_1[H^+] + K_1K_2[H^+]^2)\} \\ &= E_B{}^{\circ\prime} + 0.059\log\{(K_3 + K_3K_4[H^+])/K_1\}, \end{aligned}$$

where $E_2{}^{\circ\prime}$ denotes the apparent E_{mid} value.
Since $K_3K_4[H^+] \gg K_3$ and $K_1 \approx K_4$ (Table 2), we obtain

$$E_2{}^{\circ\prime} = E_B{}^{\circ\prime} + 0.059\log[H^+] + 0.059\log K_3. \qquad (3)$$

Because the peak-separation for the first two-electron redox wave averages (36 ± 3) mV, $E_2{}^{\circ\prime}$ was calculated to be about 6–50 mV more positive than $E_1{}^{\circ\prime}$. Since $E_C{}^{\circ\prime} = (E_1{}^{\circ\prime} + E_2{}^{\circ\prime})/2$,[23] the relationship of $E_C{}^{\circ\prime} \approx E_1{}^{\circ\prime} \approx E_2{}^{\circ\prime}$ holds within 25 mV. As a result, ΔE_{mid} can be expressed as

$$\begin{aligned} \Delta E_{mid} &= E_C{}^{\circ\prime} - E_A{}^{\circ\prime} \approx E_1{}^{\circ\prime} - E_A{}^{\circ\prime} \\ &= 0.059\log[H^+] + 0.059\log K_1. \end{aligned} \qquad (4)$$

Combining Eqs. 2 and 3, ΔE_{mid} is also given by

$$\begin{aligned} \Delta E_{mid} &\approx E_2{}^{\circ\prime} - E_A{}^{\circ\prime} = E_B{}^{\circ\prime} - E_A{}^{\circ\prime} \\ &\quad + 0.059\log[H^+] + 0.059\log K_3. \end{aligned} \qquad (5)$$

When the observed ΔE_{mid} values were plotted against $\log K_1$ and $\log K_3$ (Table 2), good straight lines were obtained with slopes of 0.059 and 0.056 V, respectively, as shown by the open circles in Fig. 4. A linear plot of ΔE_{mid} against $\log K_1$ gave an intercept of −0.12 V, which agrees with the theoretical value of −0.15 V, calculated with $[H^+] = 3.0 \times 10^{-3}$ M. The theoretical value of $(E_B{}^{\circ\prime} - E_A{}^{\circ\prime} + 0.059\log[H^+])$ averaged (−0.60 ± 0.04) V, the value also being in good agreement with the observed intercept value of −0.61 V. These agreements demonstrate the validity of Eqs. 4 and 5. Thus, the much greater K_3 relative to K_1 explains the coalescence of the first two one-electron waves into the two-electron wave.

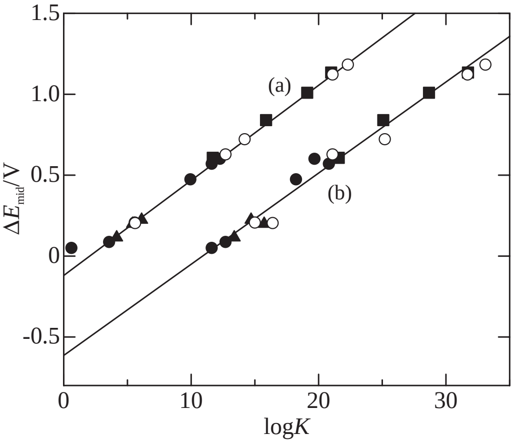


Fig. 4. Plots of ΔE_{mid} values against (a) $\log K_1$ and (b) $\log K_3$. ○: $[SMo_{12}O_{40}]^{2-}$; $[PW_{12}O_{40}]^{3-}$; $[PMo_{12}O_{40}]^{3-}$; $[GeW_{12}O_{40}]^{4-}$; $[GeMo_{12}O_{40}]^{4-}$; $[BW_{12}O_{40}]^{5-}$ in CH_3CN. ▲, $[PW_{12}O_{40}]^{3-}$; ●, $[PMo_{12}O_{40}]^{3-}$; ■, $[GeMo_{12}O_{40}]^{4-}$ in PC, MIPK, acetone, TMP, DMF, and DMA.

Relationship between the ΔE_{mid} Value and the Protonation Constants, K_1 and K_3, in Various Organic Solvents. In order to further study the relationship between the ΔE_{mid} value and the protonation constants, K_1 and K_3, cyclic voltammograms were measured for $[PW_{12}O_{40}]^{3-}$, $[PMo_{12}O_{40}]^{3-}$, and $[GeMo_{12}O_{40}]^{4-}$ in propylene carbonate (PC) (DN, 15.1; ε_r, 64.4), methyl isopropyl ketone (MIPK) (DN, 17.1; ε_r, 15.4), acetone (DN, 17.1; ε_r, 20.7), trimethyl phosphate (TMP) (DN, 23.0; ε_r, 16.4), *N*,*N*-dimethylformamide (DMF) (DN, 26.6; ε_r, 36.7), and *N*,*N*-dimethylacetamide (DMA) (DN, 27.8; ε_r, 37.8). The three Keggin anions represent groups (2), (3), and (4) in Table 1, respectively. Cyclic voltammograms were simulated to estimate the protonation constants; the results are summarized in Table 3. When the ΔE_{mid} values were plotted against $\log K_1$ and $\log K_3$, all of the data lay on the same linear lines, as shown by the dark dots in Fig. 4. Thus, the ΔE_{mid} values are directly related to the basicities of the one- and two-electron reduced forms of the Keggin anions, and consequently of the fully oxidized forms of the Keggin anions.

The relationship between the solution properties (DN and ε_r) and the observed ΔE_{mid} values was also studied for $[PW_{12}O_{40}]^{3-}$, $[PMo_{12}O_{40}]^{3-}$, and $[GeMo_{12}O_{40}]^{4-}$ in various

Table 3. Protonic Constants in Various Organic Solvents

Solvents	DN	ε_r	$[PW_{12}O_{40}]^{3-}$			$[PMo_{12}O_{40}]^{3-}$			$[GeMo_{12}O_{40}]^{4-}$		
			ΔE_{mid}/V	$\log K_1$	$\log K_3$	ΔE_{mid}/V	$\log K_1$	$\log K_3$	ΔE_{mid}/V	$\log K_1$	$\log K_3$
Acetonitrile	14.1	36.0	0.204	5.6	16.4	0.628	12.7	21.1	1.122	21.1	31.7
Propylene carbonate	15.1	64.4	0.115	4.2	13.4	0.474	9.9	18.2	1.009	19.1	28.7
Methyl *i*-propyl ketone	17.1	15.4	0.224	6.1	14.7	0.601	12.3	19.7			
Acetone	17.1	20.7	0.199	5.4	15.7	0.570	11.6	20.8	1.134	21.0	31.7
Trimethyl phosphate	23.0	16.4							0.840	15.9	25.1
DMF	26.6	36.7				0.087	3.6	12.7	0.607	11.7	21.6
DMA	27.8	37.8				0.050	0.6	11.6			

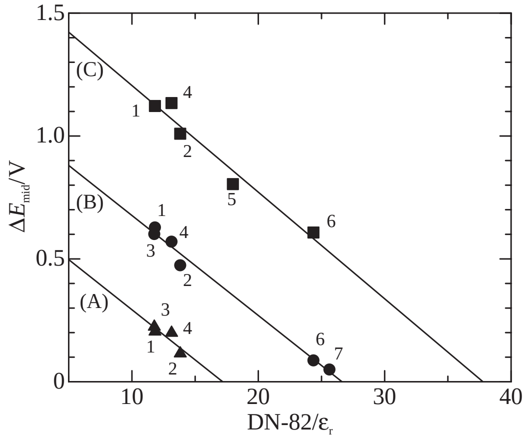


Fig. 5. Plots of ΔE_{mid} values for (A) $[PW_{12}O_{40}]^{3-}$; (B) $[PMo_{12}O_{40}]^{3-}$; (C) $[GeMo_{12}O_{40}]^{4-}$ against the (DN − 82/ε_r) value. (1) acetonitrile; (2) PC; (3) MIPK; (4) acetone; (5) TMP; (6) DMF; (7) DMA.

organic solvents. A regression analysis showed that parallel straight lines were obtained by plotting the ΔE_{mid} value against the value of (DN − 82/ε_r) (Fig. 5). Since the first and second one-electron waves are merged into the two-electron wave only when $\Delta E_{mid} \geq 0$, the extrapolation of the linear lines to $\Delta E_{mid} = 0$ can give a critical value of (DN − 82/ε_r) to obtain successive two-electron waves.

Discussion

The present study has demonstrated that protonation of the reduced forms at the electrode surface causes the two one-electron waves to be converted into the first two-electron wave, giving rise to successive two-electron waves. According to Barrows et al.,[24] the oxygen atom at the edge-shared contact is protonated. From two linear plots in Fig. 1 it follows that the oxidized forms of the Keggin anions are not protonated.

A simulation of the voltammogram confirms that the two-electron reduction is accompanied by the consumption of two protons, which is in line with the previous results.[3,13,22,25] For the Keggin anions, the values of K_1 are close to those of K_4, indicating that the basicities of the reduced anions, $[XM^{V}M_{11}O_{40}]^{(n+1)-}$ and $[HXM^{V}_2M_{10}O_{40}]^{(n+1)-}$, are comparable, where M = W or Mo. However, the ΔE_{mid} value is greater for the molybdenum-complex than for the tungsten-complex with an identical ionic charge, owing to the smaller ionic radius and, consequently, the greater basicity of the former complex anion.[7]

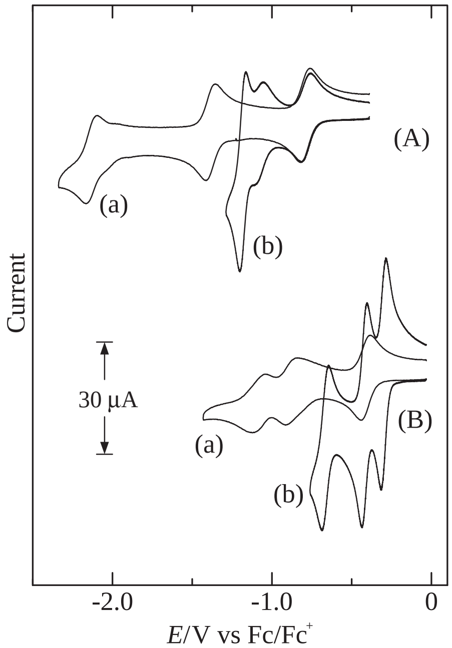


Fig. 6. Cyclic voltammograms for 0.30 mM solutions of (A) $[PW_{12}O_{40}]^{3-}$ and (B) $[PMo_{12}O_{40}]^{3-}$ in DMF containing (a) 0.10 M *n*-Bu_4NClO_4; (b) (a) +3.0 mM $HClO_4$.

Among the parameters, the protonation constants for the one- and two-electron reduced species, K_1 and K_3, are of the most important (Tables 2 and 3). When the K_3 values are about ten orders of magnitude larger than the K_1 values, the first two one-electron waves merge into the two-electron wave. The linear dependence of ΔE_{mid} vs $\log K_1$ or $\log K_3$ indicates that the ΔE_{mid} value can be used as a direct measure of the basicity of the Keggin anions.

As shown in Fig. 2, the basicity of the Keggin anions is in the order of $[SMo_{12}O_{40}]^{2-} \approx [XW_{12}O_{40}]^{3-}$ (X = P, As) $\ll$ $[XMo_{12}O_{40}]^{3-}$ (X = P, As) $<$ $[XW_{12}O_{40}]^{4-}$ (X = Si, Ge) $\ll$ $[XMo_{12}O_{40}]^{4-}$ (X = Si, Ge) $<$ $[XW_{12}O_{40}]^{5-}$ (X = B, Al). Since the ΔE_{mid} values of $[XMo_{12}O_{40}]^{n-}$ and $[XW_{12}O_{40}]^{(n+1)-}$ are almost identical, the Keggin anions can be classified into the following four groups: (1) $[SW_{12}O_{40}]^{2-}$; (2) $[SMo_{12}O_{40}]^{2-}$,

$[XW_{12}O_{40}]^{3-}$ (X = P, As); (3) $[XMo_{12}O_{40}]^{3-}$ (X = P, As), $[XW_{12}O_{40}]^{4-}$ (X = Si, Ge); (4) $[XMo_{12}O_{40}]^{4-}$ (X = Si, Ge), $[XW_{12}O_{40}]^{5-}$ (X = B, Al). As a result, the cation-effect in Table 1 can be accounted for in terms of the basicity difference of the Keggin anions.

Besides, the present study makes it possible to design the solution conditions to obtain successive two-electron waves. For Keggin anions belonging to groups (2)–(4), the ΔE_{mid} values are greater than zero in solvents of the $(\mathrm{DN} - 82/\varepsilon_{\mathrm{r}})$ value < 17 (Fig. 5), and successive two-electron waves can be obtained in acetonitrile, PC, MIPK, and acetone. However, Keggin anions belonging to group (2) cannot undergo successive two-electron reductions in solvents of the $(\mathrm{DN} - 82/\varepsilon_{\mathrm{r}})$ value > 17. As expected, $[PW_{12}O_{40}]^{3-}$ was electroreduced by one-, one-, and two-electrons in DMF with a $(\mathrm{DN} - 82/\varepsilon_{\mathrm{r}})$ value of 24 (Fig. 6(A)), in agreement with the observation by Keita and Nadjo.[26] On the other hand, the first two one-electron waves for $[PMo_{12}O_{40}]^{3-}$ merged into a two-electron wave (Fig. 6(B)), followed by two two-electron waves, because it belongs to group (3).

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