CUMULATIVE EXAMINATION IN ANALYTICAL CHEMISTRY

October 12, 2002

Dennis H. Evans, Principal Examiner

The following announcement was posted:

The examination will be based on the content and topics covered in "Difference in voltammetric properties between the Keggin-type [XW_{12}O_{40}]^{\text{m}}" and [XMo_{12}O_{40}]^{\text{n}} complexes", *Journal of Electroanalytical Chemistry*, 2002, 528, 17—174, by Sadayuki Himeno and Masayo Takamoto.

This will be a closed-book examination. A copy of the above paper will be provided.

Examination—Introduction

The content of the paper will be introduced into the examination in connection with questions about three topics that were covered: (a) chemistry of polyoxometalate complexes; (b) cyclic voltammetry; (c) ionic interactions in solution.

Examination—Questions

1. (20 points) Two types of polyoxometalate complexes were described in the paper, the Keggin-type and the Dawson-type, though results for only the first type were described.

   (a) Describe in as much detail as possible (but even in a very sketchy fashion if you don’t know the details) the structure of Keggin-type polyoxometalates. Take [PMO_{12}O_{40}]^{3-} as an example. This is a famous complex that has been exploited for the spectrophotometric determination of phosphate. Accordingly, the complex contains P^{V}.

   (i) What is the oxidation state of Mo in the complex?
   (ii) The complex contains Mo_{6} octahedra. Where are they in the structure and how are they bound?
   (iii) Where is the phosphorous atom located?
   (iv) On page 171, left column, line –5, the one-electron reduced form is described as [PMo^{V}Mo_{11}O_{40}]^{4+}. What does this tell you about the supposed site of reduction.

   (b) The Keggin-type anions were prepared as their tetra-\textit{n}-butylammonium salts (p. 171, left column, section 2.2) for their study in the nonaqueous solvent acetonitrile. Why did the authors bother to make the tetra-\textit{n}-butylammonium salts when alkali metal salts are easier to prepare?

   (c) A conclusion of this work is that the Mo complexes are smaller (5.4 Å radius) than the W complexes (5.6 Å). The elements fall in group VIA of the periodic table in the order Cr, Mo, W (top to bottom). Explain the difference in size.

2. (30 points).
Difference in voltammetric properties between the Keggin-type [XW_{12}O_{40}]^{n-} and [XMo_{12}O_{40}]^{n-} complexes

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Abstract

The voltammetric properties of the Keggin-type [XW_{12}O_{40}]^{n-} complexes were compared with those of the corresponding Mo-analogue, [XMo_{12}O_{40}]^{n-}, where X = P, Ge; n = 3, 4. The one-electron waves for the Keggin anions are converted into two-electron waves by the presence of small cations such as H^+, Li^+ and Na^+, and the conversion occurs much more easily for [XMo_{12}O_{40}]^{n-}, as compared with [XW_{12}O_{40}]^{n-} with an identical ionic charge. A comparison of the redox potentials for the V(V)/V(IV) couple of the mono-vanadium derivatives made it possible to estimate the ionic radius of [XMo_{12}O_{40}]^{3-} as 5.4 Å, with the ionic radius of [XW_{12}O_{40}]^{4-} = 5.6 Å as reference. The big difference in voltammetric behaviors between the Mo- and W-complexes was interpreted in terms of the smaller ionic radius and consequently greater basicity of [XMo_{12}O_{40}]^{3-}, as compared with [XW_{12}O_{40}]^{3-}. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Keggin-type polyoxometalates; Voltammetry; Size difference

1. Introduction

The so-called Keggin- and Dawson-type polyoxometalate complexes have been the subject of earlier voltammetric studies. It is known that the one-electron waves are converted into two-electron waves in acidified media where protonation accompanies the reduction [1,2]. However, there is a big difference between the voltammetric properties of the Mo- and W-complexes with an identical ionic charge. In acidified CH_3CN + water media, the Keggin-type [PMo_{12}O_{40}]^{3-} complex underwent successive two-electron reductions [3], while the corresponding W-analogue, [PW_{12}O_{40}]^{3-} was still electroreduced by one, one and two electrons [4]. In addition to the CH_3CN + water system, an acidified aqueous system also gave a different voltammetric behavior of the Dawson-type [P_2Mo_{12}O_{42}]^{6-} and [P_2W_{12}O_{42}]^{6-} complexes. The [P_2Mo_{12}O_{42}]^{7-} complex underwent a three-step two-electron reduction in aqueous media of pH < 4, whereas for the [P_2W_{12}O_{42}]^{5-} complex, a three-step two-electron wave was obtained only in aqueous media of 12.4 M HCl [2,5-10].

Recently, we found that the [PMo_{12}O_{40}]^{3-} and [SiMo_{12}O_{40}]^{3-} complexes underwent two-electron reductions in CH_3CN and CH_3COCH_3 containing Li^+ or Na^+ instead of H^+ [11]. The present study revealed that the one-electron waves for the corresponding W-analogues, [PW_{12}O_{40}]^{3-} and [GeW_{12}O_{40}]^{4-} were not converted into two-electron waves in such Li^+ or Na^+ containing CH_3CN solutions.

Since the conversion behavior into two-electron waves depends on the association ability of H^+, Li^+ or Na^+ with the reduced form of the polyoxometalate anion, the voltammetric results suggest a smaller ionic size of the Mo-complex than the W-complex with an identical ionic charge, resulting in greater basicity of the Mo-complex. According to Baker and Pope [12], however, the diffusion coefficients for [SiMo_{12}O_{40}]^{3-} and [SiW_{12}O_{40}]^{4-} are identical, indicating that both Keggin anions possess the same ionic radius.

In the present study, a linear relationship between the first one-electron redox potential and the surface charge density of the vanadium-substituted Keggin-type polyoxometalate anion enabled the estimation of the ionic size of the Mo-complex relative to the W-complex.

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2. Experimental

2.1: Apparatus and materials

Cyclic voltammograms were obtained with a Hokuto Denko Model HA1010mM1A potentiostat interfaced to a microcomputer-controlled system. A Tokai glassy carbon (GC-30S) electrode with a surface area of 0.071 cm² was used as a working electrode and a platinum wire served as the counter electrode. The reference electrode was an Ag/0.01 M Ag⁺ + CH₃CN electrode. Prior to each measurement, the working 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. All the measurements were made at 25 ± 0.1 °C. Unless mentioned otherwise, the voltage scan rate was set at 100 mV s⁻¹. Lithium perchlorate and sodium perchlorate were dried under vacuum at 50 °C. All the chemicals were of analytical grade.

2.2. Preparation of the Keggin complexes

The n-Bu₄N⁺ salts of the [PW₁₂O₄₀]³⁻, [PMo₁₂O₄₀]³⁻, [GeW₁₂O₄₀]³⁻ and [GeMo₁₂O₄₀]⁴⁻ complexes were prepared and purified according to slight modifications of the literature method [13]. The n-Bu₄N⁺ salts of the mono-vanadium derivatives; [S(VW₁₁)O₄₀]³⁻, [S(VMo₁₁)O₄₀]³⁻, [P(VW₁₁)O₄₀]⁴⁻ and [P(VMo₁₁)O₄₀]⁴⁻ were prepared by the literature methods [14–17].

3. Results

3.1. Voltammetric behavior of [PMo₁₂O₄₀]³⁻ and [PW₁₂O₄₀]³⁻

3.1.1. Effect of H⁺

Fig. 1(a) shows a cyclic voltammogram of 0.50 mM [PMo₁₂O₄₀]³⁻ in CH₃CN containing 0.1 M n-Bu₄NClO₄. In the absence of H⁺, a three-step one-electron redox wave was obtained with $E_{\text{mid}}$ values of -0.17, -0.58 and -1.31 V, where $E_{\text{mid}} = (E_{\text{pa}} + E_{\text{pc}})/2$; $E_{\text{pa}}$ and $E_{\text{pc}}$ are the anodic and cathodic peak potentials, respectively. With the addition of CF₃SOH, a new wave appeared at potentials more positive than the one-electron waves and grew as the CF₃SOH concentration was increased. The appearance of the new wave is ascribed to the protonation of the one-electron reduced form, [PMo⁴⁺Mo₁₁O₄₀]⁴⁻. Ultimately, a three-step two-electron redox wave with $E_{\text{mid}}$ values of 0.23, 0.13 and -0.16 V was obtained in the presence of 5.0 mM CF₃SOH (Fig. 1(b)). Each two-electron reduction proceeds with consumption of two protons [18].

Similarly, [PW₁₂O₄₀]³⁻ exhibited four one-electron redox waves with $E_{\text{mid}}$ values of -0.58, -1.10, -1.80 and -2.30 V in CH₃CN containing 0.1 M n-Bu₄NClO₄ (Fig. 2(a)). The presence of 5.0 mM CF₃SOH caused the one-electron waves to merge into two two-electron redox waves with $E_{\text{mid}}$ values of -0.53 and -0.68 V.

3.1.2. Effect of Li⁺

Fig. 3 shows cyclic voltammograms for 0.50 mM [PW₁₂O₄₀]³⁻ in CH₃CN containing n-Bu₄NClO₄ + LiClO₄, where the ionic strength is adjusted to 0.10 M. With the addition of Li⁺, the second one-electron wave moved slightly to more positive potentials, indicating the association of Li⁺ with the two-electron reduced species, [PW₁₂O₄₀]³⁻. In contrast to the behavior in the [PW₁₂O₄₀]³⁻/H⁺ system (Fig. 2(b)), the first one-electron reduction proceeds without consumption of Li⁺, because the first wave does not change the potential location. Since Li⁺ associated only weakly with the two-electron reduced form, the first and second one-electron waves did not merge into a two-electron wave. Ultimately, [PW₁₂O₄₀]³⁻ was electroreduced by one, one and two electrons in 0.1 M LiClO₄ (Fig. 3(e)).
and peak position, and a new wave appeared at more positive potentials than the original second one-electron wave. With an increase of the Na⁺ concentration, the new wave moved to more positive potentials, owing to the association of Na⁺ with the two-electron reduced form, [GeW₁²⁺W₁₀O₄₀]⁵⁻. The affinity of Na⁺ for [GeW₁²⁺W₁₀O₄₀]⁵⁻ was rather weak so that the first two one-electron waves remained even in 0.1 M NaClO₄; the associating ability becomes weaker as the concentration of the supporting electrolyte is further increased, owing to the increased relative permittivity [11,19].

For comparison, Fig. 5(a) shows a cyclic voltamogram of 0.50 mM [GeMo₁₂O₄₀]⁺ in CH₃CN containing 0.1 M n-Bu₄NClO₄. A two-step one-electron wave was obtained with \(E_{\text{mid}}\) values of −0.62 and −1.02 V. In the presence of 0.1 M NaClO₄, the two one-electron waves were merged into a two-electron wave with an \(E_{\text{mid}}\) value of −0.42 V.

3.3. Estimation of the ionic size of the Keggin-type Mo-analogue

The first one-electron redox potential is shifted to more negative potentials with an increase in the negative charge of the Keggin anion, and a linear relationship is found between the redox potential and the ionic charge [18,20–22]. The difference, \(\Delta E\), between the first redox potentials of two Keggin anions with ionic charges of \(-n\) and \(-(n+1)\) depends on the difference in the electron affinity; namely, \(\Delta E = e/4\pi\varepsilon_0 r\), where \(e\) is the electronic charge; \(\varepsilon_0\) is the permittivity in a vacuum; \(r\) is the ionic radius [20,21]. Since the ionic radius of the Keggin anion is independent of the ionic charge [21], the first one-electron redox potential is a measure of a surface charge density, \(D = -n\varepsilon_0 r^2\).

Since the direct comparison between the first one-electron redox potentials of the Mo- and W-complexes is of no use, the redox potentials due to the V(V)/V(IV) couples of the mono-vanadium substituted derivatives, which also show a linear dependence on their ionic...
charge [22], are used to estimate the ionic radius of the Keggin-type Mo-complex anion.

3.3.1. Voltammetric behavior of \([S(VW_{11}I)O_{4n}]^{3−}\) and \([P(VW_{11}I)O_{4n}]^{4−}\)

The mono-vanadium derivatives exhibit one-electron waves due to their V(V)/V(IV) redox couple at potentials more positive than those due to redox couples of Mo(VI)/Mo(V) and W(VI)/W(V) [15,22]. The peak separation for the redox couples averaged 65 mV and the peak potentials were independent of the voltage scan rate (50−150 mV s⁻¹), indicating the reversible nature of the one-electron waves. As an illustration, Fig. 6 shows a cyclic voltammogram of 0.50 mM \([P(VW_{11}I)O_{4n}]^{2−}\) in CH₃CN containing 0.1 M n-Bu₄NClO₄. The first wave with an \(E_{\text{mid}}\) value of −0.21 V corresponds to a reduction of V(V) to V(IV) in the peripheral position. Similarly, the \([S(VW_{11}I)O_{4n}]^{3−}\) complex exhibited the redox couple of V(V)/V(IV) with an \(E_{\text{mid}}\) value of 0.24 V.

On the basis of viscosity and diffusion coefficient measurements, the ionic radius of \([XW_{12}O_{40}]^{n−}\) \((n = 3, 4)\) is estimated to be \(r = 5.6 \text{ Å}\) [20,23]. With the use of \(r = 5.6 \text{ Å}\) for the \([XW_{12}O_{40}]^{n−}\) and \([X(VW_{11}I)O_{4n}]^{n−}\) anions, the \(E_{\text{mid}}\) values for the redox couples were plotted against the surface charge density, along with the \(E_{\text{mid}}\) values of the first one-electron wave for the \([PW_{12}O_{40}]^{5−}\) and \([GeW_{12}O_{40}]^{4−}\) complexes. As is shown in Fig. 7, two separate plots gave good parallel lines, indicating that the \(E_{\text{mid}}\) value for the redox couple of V(V)/V(IV) of the \([X(VW_{11}I)O_{4n}]^{n−}\) anion is also a measure of the surface charge density.

In order to estimate the surface charge density of the Keggin-type Mo-complex anion, a cyclic voltammogram was recorded for \([S(VMo_{11}I)O_{4n}]^{3−}\) in CH₃CN containing 0.1 M n-Bu₄NClO₄. The \([S(VMo_{11}I)O_{4n}]^{3−}\) anion shows a reversible redox couple of V(V)/V(IV) with an \(E_{\text{mid}}\) of 0.14 V, which is more negative by 100 mV than the corresponding value for \([S(VW_{11}I)O_{4n}]^{3−}\). This result indicates the greater surface charge density and thus shorter ionic radius of \([S(VMo_{11}I)O_{4n}]^{3−}\) as compared with \([S(VW_{11}I)O_{4n}]^{3−}\), because both vanadium-substituted complexes possess the same ionic charge of −3. As marked with an X on the line (b) in Fig. 7, the \(E_{\text{mid}}\) value for \([S(VMo_{11}I)O_{4n}]^{3−}\) lies between the corresponding values for the \([S(VW_{11}I)O_{4n}]^{3−}\) and \([P(VW_{11}I)O_{4n}]^{3−}\) anions, and the direct fitting of the \(E_{\text{mid}}\) value to the line (b) gives the ionic radius of \([S(VMo_{11}I)O_{4n}]^{3−}\) as 5.4 Å.

Since the ionic radii of the \([S(VMo_{11}I)O_{4n}]^{3−}\) and \([P(VMo_{11}I)O_{4n}]^{4−}\) complexes are regarded as identical, the linear line is extended to \(n = 4\). From the extended line, the \(E_{\text{mid}}\) value for the \([P(VMo_{11}I)O_{4n}]^{4−}\) complex was evaluated to be −0.328 V, which is in good agreement with the observed value of −0.32 V. This result demonstrates the validity of the present method.

4. Discussion

For the polyoxometalate anion, the number of transferred electrons and the potential location can be determined by the associating ability of small cations such as H⁺, Li⁺ and Na⁺ with the reduced form of the polyoxometalate anion. For small cations, the associating ability becomes greater in the order H⁺ > Li⁺ > Na⁺. The voltammetric behavior can be put into the following two categories:

1) when the one-electron reduced species is associated, the two-electron wave appears at potentials more positive than the first one-electron wave; with a given cation, the separation of the \(E_{\text{mid}}\) values is greater for a polyoxometalate anion with greater ionic charge [11];

2) when the two-electron reduced species is associated, (i) the two-electron wave appears at nearly the same potential as the original first one-electron wave (Fig. 1(c), Fig. 2(b)); (ii) the second one-electron wave does not merge into the first one-electron wave if the associating ability between the small cation and the
reduced form of the polyoxometalate anion is weak (Fig. 3(c), Fig. 4(c)).

As is shown in Fig. 1(b), Fig. 2(b), the presence of 5.0 mM H⁺ produced two-electron waves for [PMo12O40]³⁻ and [PW12O40]³⁻. The Eₘid value for the first two-electron wave was 0.50 V more positive than the original first one-electron wave for the former complex. On the other hand, the difference in the Eₘid values was only 0.03 V for the latter. In the presence of 0.1 M LiClO₄, [PMo12O40]³⁻ exhibited a two-step two-electron wave whereas [PW12O40]³⁻ underwent one-, one-, and two-electron reductions, owing to the much stronger association of Li⁺ with [PMo14O₄0]⁵⁻ than [PW12W₁⁰O₄0]⁵⁻ (Fig. 1(c), Fig. 3(e)). Similarly, a comparison of Fig. 4(c) with Fig. 5(b) indicated the greater association ability of Na⁺ with [GeMo12O₄0]⁴⁻ than [GeW12O₄0]⁶⁻. These results are in line with the fact that the difference in the Eₘid values between the first one- and two-electron waves is greater for [GeMo12O₄0]⁴⁻ (0.19 V) than [GeW12O₄0]⁴⁻ (0.09 V) in CH₃CN containing 0.1 M LiClO₄. The voltammetric results can be accounted for in terms of the greater basicity of the Mo-complex than the W-complex with an identical ionic charge. This is supported by the fact that the unit cell dimensions for the Ti⁺, K⁺ and NH₄⁺ salts of [PMo12O40]³⁻ are 1–2.5% smaller than those for the corresponding salts of [PW12O40]³⁻ [24].

As has already been described, the conversion of one-electron waves into two-electron waves occurs more easily for [P₂Mo₁₈O₆₂]⁶⁻ than [P₂W₁₈O₆₂]⁶⁻ in acidified aqueous media [2,5–10]. In CH₃CN containing 10 mM CF₃SO₃H, the first two-electron wave for [S₂W₁⁰O₆₂]⁴⁻ was split into two one-electron waves with the addition of 1% (v/v) water [25]. On the other hand, the two-electron waves for [S₂Mo₁⁰O₆₂]⁴⁻ were retained even in the presence of 5% (v/v) water [26]. In CH₃CN–water mixed solvents, preferential solvation of H⁺ by water caused the acidity strength to be decreased [27,28]. The voltammetric behaviors for Dawson complexes can also be interpreted in terms of the greater basicity of [X₂Mo₁⁰O₆₂]⁴⁻ than [X₂W₁⁰O₆₂]⁴⁻, where X = S, P; n = 4, 6. Papakonstantinou and Pope have pointed out the possibility of the smaller ionic size of the Mo-complex than the W-complex [6].

References

Two types of information are inferred from the cyclic voltammograms presented in this work. Both are drawn from the (relatively) reversible voltammograms that were obtained. The first is information about the formal potential of the reductions (called E_{mid} in the paper, page 171, left column, line -12). The second is information about the total number of electrons exchanged in the overall reaction that is occurring at a given voltammetric peak.

(a) At several places, a positive shift in E_{mid} is ascribed to interaction of the reduced form of the half-reaction that responsible for the peak, with an ion present in solution. The first example is found on page 171, left column, line -7: "...The appearance of the new wave [upon addition of the strong acid CF_{3}SO_{2}H] is ascribed to the protonation of the one-electron reduced form, [PMo^{V}Mo_{11}O_{40}]^{4-}...".

\[ \text{e.g. } [\text{PMo}^{V}\text{Mo}_{11}\text{O}_{40}]^{4-} + \text{H}^+ \rightleftharpoons [\text{PMo}^{V}\text{Mo}_{11}\text{O}_{40}][\text{H}]^{3-}. \] (1)

Explain how the example reaction (1) would cause the observed positive shift in potential. (You may use equations but a verbal explanation, if accurate, will be fully acceptable).

(b) Another example is seen in Figure 4, where the reduction of [GeW_{12}O_{40}]^{4-} is studied in the presence of (a) 0, (b) 1, and (c) 100 mM NaClO_{4}. In (b) the second reduction peak has moved in the positive direction compared to (a) and this shift is still larger in (c). The first peak is unchanged in position in (b) compared to (a) but undergoes a small shift on going from (b) to (c). What does this tell you about the relative degree of interaction of Na^+ with [GeW^{V}W_{11}O_{40}]^{3-} and with [GeW^{V}W_{10}O_{40}]^{5-}?

(c) The behavior cited in (b) above is carried to an extreme in Figure 5 where [GeMo_{12}O_{40}]^{4-} is studied in the absence (a) and the presence (b) of 100 mM NaClO_{4}. Here there is a single, sharp reduction peak that is approximately twice as high as either peak in the absence of Na^+ and is located over 200 mV positive of the first reduction peak seen in the absence of Na^+. Also explain this observation in terms of the relative degree of interaction of Na^+ with [GeMo^{V}Mo_{11}O_{40}]^{5-} and with [GeMo^{V}Mo_{10}O_{40}]^{6-}? Compare the degree of interaction of Na^+ with the Mo complexes to that with the W complexes.

3. (30 points). The second type of information extracted from the voltammograms is the total number of electrons exchanged in the overall reaction occurring at a given peak. First, here are some facts about reversible processes in cyclic voltammograms. (i) The peak height is proportional to n^{3/2} where n is the number of electrons exchanged. Thus an n = 2 process will have a peak current that is 2^{3/2} = 2.8 times larger than that of an n = 1 process (this is limiting behavior; actual two-electron peaks will be between about 2 and 2.8 times larger). (ii) When a compound shows multiple reduction peaks, the height of the second peak is measured from the extension of the first peak as illustrated in Figure 6.6.1 taken from Bard, A. J.; Faulkner, L. R. Electrochemical Methods: Fundamentals and Applications, 2nd Ed., John Wiley, New York, 2001, p. 244. (This figure pertains to the reduction of equal concentrations of a mixture of two substances, each requiring n electrons. However, the principle is the same for the reduction of a single substance in a series of steps).
(a) Do the voltamograms in Figure 5 support the conclusion of the authors that \([\text{GeMo}_{12}\text{O}_{40}]^{4-}\) undergoes a two-electron process in the presence of 100 mM NaClO\(_4\)? Please support your statement by measurements on the enlarged version of Figure 5 given below.

(b) When two peaks have not quite merged into a single peak, the relative heights can be deceiving. Reproduced below is Figure 6.6.4 from the aforementioned book by Bard and Faulkner, which shows the evolution of a two-step reduction process as the difference between the formal potentials, \(\Delta E^\circ = E^\circ_1 = E^\circ_2\), becomes smaller and eventually changes sign. \(\Delta E^\circ = -180\) mV in (a), -90 mV in (b), 0 mV in (c) and 180 in (d). Note in (b) that

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Fig. 5. Cyclic voltammograms for 0.50 mM \([\text{GeMo}_{12}\text{O}_{40}]^{4-}\) in CH\(_3\)CN containing (a) 0.1 M \(n\)-Bu\(_4\)NClO\(_4\); (b) 0.1 M NaClO\(_4\).
the two peaks are not quite fully merged and that the height of the first (the shoulder) appears to be larger than that of the second. Explain this observation in terms of the procedure described earlier for establishing the baseline for determining peak currents for consecutive peaks.

![Cyclic voltammograms](image)

Figure 6.6.4 Cyclic voltammograms for a reversible two-step system at 25°C. Current function is analogous to \( \chi(z) \) defined in (6.2.16). \( n_2/n_1 = 1.0 \).

(a) \( \Delta E^0 = -180 \text{ mV} \), (b) \( \Delta E^0 = -90 \text{ mV} \), (c) \( \Delta E^0 = 0 \text{ mV} \), (d) \( \Delta E^0 = 180 \text{ mV} \).


(c) With the answer to (b) in mind, show that Figure 4c is consistent with the first two reductions of \( \text{[GeW}_{12}\text{O}_{40}]^{+} \) occurring in a not quite completely merged peak with each step still involving one electron. You may make measurements or sketches on the enlarged version of Figure 4 on the next page.

(d) The authors conclude (page 173, right column, line -16) that the "...associating ability becomes greater in the order \( \text{H}^+ > \text{Li}^+ > \text{Na}^+ \). In fact the authors did not show results for the same polyoxometalate in the presence of all three of these ions. The order for two of them was established in one case. Where? What was the complex and which two associating ions were studied?

4. (20 points)

We will now move to the final topic, ionic interactions in solution.

(a) An inference that one may draw from the paper is that the authors believe that the association that is seen is a type of ion-pairing. Consider the interaction of \( \text{H}^+ \), \( \text{Li}^+ \) and \( \text{Na}^+ \) with a certain polyoxometalate complex of a given charge. What property of the three ions explains the order of interaction given in question 3d?
Fig. 4. Cyclic voltammograms for 0.50 mM $[\text{GeW}_{12}\text{O}_{40}]^{4-}$ in CH$_3$CN containing $n$-Bu$_4$NCIO$_4$ + NaClO$_4$, where the ionic strength = 0.10. [NaClO$_4$/mM, (a) 0; (b) 1.0; (c) 100.

(b) In terms of the principles of ion-pair interactions, rationalize the relative interactions of the ions with Na$^+$ described in question 2e.

(c) In Figure 7, the authors present an elaborate argument in terms of surface charge density, $D = -n/4\pi r^2$, where $n$ is the charge and $r$ is the radius of the assumed spherical polyoxometalate complex. Curves 7a and 7b are meant to show that there is a linear relationship between $E_{\text{mid}}$ and surface charge density. On the basis of the simplest principles of data analysis, offer your criticisms of these “linear relationships”.

(d) A general principle of polyoxometalate electrochemistry is that $E_{\text{mid}}$ depends on the composition of the oxometalate shell and the charge on the ion but depends very little on $X$. Show that the four points in Figure 7 are consistent with these conclusions. (ignore the point X).

5. **Extra credit.** For up to 10 additional points, answer the following:

An idiosyncrasy of the field of voltammetry is the lack of a consistent method of plotting voltammograms. The authors use the IUPAC-endorsed convention of plotting potentials from negative to positive, left to right, and plotting oxidation (anodic) currents as positive. The examples taken from Bard and Faulkner follow precisely the opposite convention. This is called the “polarographic” convention and it is widely used by electroanalytical chemists.

Explain why the “polarographic” convention arose and prospered during the early days of voltammetry.