The Reactivity of Selenite toward Methyl Viologen in Mildly Acidic Aquous Solutions

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The chemical and electrochemical reactivity of selenite, SeO\textsubscript{3}\textsuperscript{2−}, toward methyl viologen, MV\textsuperscript{2+}, has been examined in mildly acidic (pH 4) aqueous electrolytes. Solutions containing these two species heated at 60°C for ca. 2 hours, were found to yield both 1-methyl-[4,4′-bipyridine]-1-ium chloride and elemental Se as the main reaction products, as evidenced from information derived from mass spectrometric and spectroscopic techniques. Cyclic voltammetric measurements recorded in acetate buffer (pH 4) with a glassy carbon, GC, electrode bearing a self-assembled monolayer, SAM, of N-ethyl-N’-octadecyl-4,4′-bipyridinium (EOB), which had been exposed to a 100 mM SeO\textsubscript{3}\textsuperscript{2−} solution in aqueous acetate buffer (pH 4) for over 200 min and then rinsed with ultrapure water, displayed a significantly smaller redox peak ascribed to the reduction of the viologen moiety in the EOB SAM. This observation is consistent with the loss of the redox active species within the layer and supports the view that SeO\textsubscript{3}\textsuperscript{2−} can cleave the N-C bond in EOB leading to the release of the viologen group into the solution. Cyclic voltammetric experiments involving a freshly prepared EOB SAM on GC in 1 mM SeO\textsubscript{3}\textsuperscript{2−} in the same buffer yielded a large reduction current with an onset potential virtually identical to that associated with the reduction of the EOB SAM in SeO\textsubscript{3}\textsuperscript{2−}-free solutions. On this basis, the extraordinary shift in the onset of SeO\textsubscript{3}\textsuperscript{2−} reduction induced by the presence of MV\textsuperscript{2+} in the same electrolyte reported by Koshikumo et al. [Electrochemistry (Tokyo, Jpn.), 81(5), 350 (2013)], may be explained by invoking formation of MV\textsuperscript{2+} aggregates on the GC surface in amounts too small to be detected by conventional voltammetric techniques.

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Attention in our laboratory is currently being focused on the development of techniques for the quantitative detection and removal of various forms of selenium oxyanions in aqueous electrolytes which are often present as contaminants in drinking water thereby posing health risks to human populations.1 Our efforts culminated recently in the discovery of underpotential deposited copper on polycrystalline Au electrodes as a highly active electrocatalytic surface for the reduction of selenite, SeO\textsubscript{3}\textsuperscript{2−}(aq), in acidic electrolytes.2 In related studies, we have also examined the claims of Koshikumo et al.3 regarding the ability of methyl viologen, MV\textsuperscript{2+}, to reduce both selenite, SeO\textsubscript{3}\textsuperscript{2−}(aq), and selenite, SeO\textsubscript{2}\textsuperscript{3−}(aq), on glassy carbon, GC, electrodes, in aqueous buffered (pH 4) electrolytes. As will be shown in this work, no evidence for electrocatalytic activity other than that associated with the reduction and subsequent oxidation of MV\textsuperscript{2+}(aq) could be found in SeO\textsubscript{3}\textsuperscript{2−}(aq)-containing solutions which had been carefully purified to remove SeO\textsubscript{2}\textsuperscript{3−}(aq), a common contaminant in commercially available selenate salts. In stark contrast, very large negative currents at potentials far more positive than the onset for the reduction of either MV\textsuperscript{2+}(aq) or SeO\textsubscript{2}\textsuperscript{3−}(aq) were found in solutions containing both species. These observations do confirm the MV\textsuperscript{2+}(aq)-mediated reduction of SeO\textsubscript{2}\textsuperscript{3−}(aq), originally reported by Koshikumo et al.3 This contribution explores detailed aspects of the chemistry and electrochemistry of mixed mildly acidic (pH 4) MV\textsuperscript{2+}-SeO\textsubscript{3}\textsuperscript{2−} solutions, including experiments in which the viologen moiety was confined on the GC electrode surface within a self-assembled monolayer, SAM, of a judiciously functionalized alkyl derivative. As will be shown, the reaction between these two species in solutions heated at 60°C for over two hours leads to the unprecedented demethylation of MV\textsuperscript{2+} to yield 1-methyl-[4,4′-bipyridine]-1-ium (also known as monoquat) and the formation of elemental Se.

Experimental

Methyl viologen dichloride (Sigma-Aldrich, 98%), MVCl\textsubscript{2}, sodium selenite (Sigma-Aldrich, 99%), Na\textsubscript{2}SeO\textsubscript{3}, acetic acid (Fisher Scientific, certified ACS), sodium sulfate (Fisher Scientific, certified ACS), Na\textsubscript{2}SO\textsubscript{4}, selenium oxide (Acros, 99%), SeO\textsubscript{2}, potassium carbonate (Fisher Scientific, certified ACS), Na\textsubscript{2}CO\textsubscript{3}, methanol (Fisher Scientific, HPLC grade), CH\textsubscript{3}OH, and tetrahydrofuran (Fisher Scientific, certified), C\textsubscript{4}H\textsubscript{8}O\textsubscript{4}, were all used as received. Sodium selenate (Alfa Aesar, 99.9%), Na\textsubscript{2}SeO\textsubscript{4}, was purified by the method described by Gruebel et al.,4 a procedure that removes SeO\textsubscript{3}\textsuperscript{2−} impurities by adsorption on high area TiO\textsubscript{2} (Aldrich, 99.9+%; 1 μm particle size) in aqueous solutions of low pH.

A glassy carbon, GC, disk electrode (Pine Instruments, AFE2M050GC, cross sectional area 0.196 cm\textsuperscript{2}) attached to a rotator (Pine Instruments, AFMSRX) connected in turn to a speed controller (Pine, MSRX), and a carbon microelectrode (Basi, MF-2007, diameter 11 ± 2 μm) were used as working electrodes and a carbon rod (Alfa Aesar, diameter 6.15 mm) and a Ag/AgCl (Basi, MF2052) as counter and reference electrodes, respectively. Cyclic voltammetric and dynamic polarization measurements were performed in aqueous 0.2 M sodium acetate buffer (pH 4) prepared with ultrapure water (18.3 MΩ, Barnstead water purifier), using either a bipotentiostat (Pine Instruments, RDE3) or a Metrohm Autolab (PGSTAT302N).

Raman spectra were acquired with a Kaiser HOLOSPEC VPH system equipped with a Kaiser Optical, HOLOLAB B, Series 5000 microscope using a Kr+ laser (647.1 nm) as the excitation source. UV-visible absorption spectra were obtained with a Varian Cary 50 Bio UV-visible spectrophotometer. Electrospay ionization, ESI, mass spectra were collected with a Thermo Finnigan LCQ Deca XP instrument. NMR spectra were acquired on a 500 MHz Bruker Ascend III HD equipped with a Prodigy probe operating at 500 and 125 MHz for 1H and 13C, respectively, and referenced internally to residual solvent. A Phenomenex, Strata-X column was used for the reversed phase purification of the products of the reaction between MVCl\textsubscript{2} and Na\textsubscript{2}SeO\textsubscript{4}. FTIR spectra were obtained using an Agilent Cary 630 FTIR in ATR mode and diamond on ZnSe crystal.

The bromide salt of N-ethyl-N’-octadecyl-4,4′-bipyridinium, denoted hereafter as EOB, was synthesized5 and purified6 according to procedures reported in the literature, and further characterized by NMR and mass spectrometry. Self-assembled monolayers of EOB on GC were prepared by immersing the bare electrode into a solution of EOB for 24 h. Feasibility of the electrode was confirmed by cyclic voltammetry, noting the characteristic redox waves characteristic of the EOB species.

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The KSeO$_2$(OCH$_3$)$_2$ was synthesized and purified according to procedures reported in the literature, and further characterized by NMR and IR spectroscopies. It should be stressed that once a pungent odor was detected after the mixture of methyl viologen and selenite was added to the purified Na$_2$SeO$_4$ solution, a new peak centered at 251.4 and ca. 500 cm$^{-1}$ were detected. The aqueous phase eluant was collected in a vial, dried under vacuum at room temperature and the resulting solid then dispersed in methanol to exclude remaining solids, yielding a red clear solution. A few aliquots of the latter were then injected into a short reversed phase column using water as the eluent until no UV response was detected. The supernatant was dried under vacuum at room temperature and the resulting solid was redissolved in water, and syringe filtered through a $0.22 \mu$m filter, while allowing the Se particles to go through. The filtrate was then characterized by Raman scattering yielding a spectrum displaying prominent peaks centered at 251.4 and ca. 500 cm$^{-1}$ (see Fig. 3), consistent with those of amorphous elemental Se.9–11

This observation is consistent with the presence of tiny particles of elemental Se, an effect that will be addressed later in this work. The extraordinary ability of MV$^{2+}$ (aq) to reduce SeO$_3^{2-}$ (aq) is best illustrated by data collected in the acetate buffer solution with the GC disk rotating at a rate $\omega = 900$ rpm in a mixture of 1 mM MVCl$_2$ and 1 mM Na$_2$SeO$_3$ (blue line) and ca. 1 mM of the red suspension after heating a 1 M MVCl$_2$ and 1 M Na$_2$SeO$_3$ mixture for 2 h. (magenta line, see text for details). Also shown in the black line is the corresponding voltammogram of the GC electrode in neat buffer.

The cyclic voltammogram of a GC disk electrode recorded at a scan rate $v = 100$ mV/s in a quiescent 0.2 M NaOAc buffer solution (pH 4) containing 1 mM MVCl$_2$ displayed the characteristic redox peaks associated with this species (see magenta line in Panel A, Fig. 1). Also shown in the cyan curve in the same panel is the featureless voltammogram collected in a purified 30 mM Na$_2$SeO$_4$ solution under the same conditions, which was virtually identical to that of the GC electrode in the neat buffer. Moreover, hardly any changes were observed after introducing 1 mM MVCl$_2$ to the 30 mM purified Na$_2$SeO$_4$ solution (see green line in this panel). It may thus be concluded that, contrary to literature reports, MV$^{2+}$ (aq) does not catalyze the electrochemical reduction of SeO$_3^{2-}$ (aq) on GC electrodes under the conditions of these experiments. In contrast, a rather large negative current with an onset potential far more positive than that associated with the reduction of either MV$^{2+}$ (aq) or SeO$_3^{2-}$ (aq) solutions in the same electrolyte was clearly observed during the first cycle following addition of 1 mM Na$_2$SeO$_3$ to the purified Na$_2$SeO$_4$-MVCl$_2$ mixed solution (see gray curve in Panel A, Fig. 1). This finding affords unambiguous evidence that MV$^{2+}$ (aq) can induce the reduction of SeO$_3^{2-}$ (aq), as originally claimed by Koshikumo et al., and that the electrocatalytic effects reported by these authors in mixed Na$_2$SeO$_4$-MVCl$_2$ solutions can be ascribed to the presence of SeO$_3^{2-}$ impurities in the as received commercial Na$_2$SeO$_4$ used in that work. As shown in the gray curve in Panel A, Fig. 1, the first cycle yielded, in addition to the redox features associated with the reduction and oxidation of MV$^{2+}$ (aq), a new peak centered at $-0.59$ V, the magnitude of which decreased during the first few subsequent cycles relative to that of the MV$^{2+}$ (aq) reduction peak at $-0.7$ V, to finally reach a steady value. Also mentioned by Koshikumo et al., and verified in our laboratory was the development of a faint red coloration in the neighborhood of the GC electrode while cycling extensively in the mixed solution.

**Figure 1.** A. Cyclic voltammograms recorded with a GC disk electrode at a scan rate $v = 100$ mV/s, in a quiescent 0.2 M NaOAc buffer solution (pH 4) containing 1 mM MVCl$_2$ (magenta line), 30 mM purified Na$_2$SeO$_4$ (cyan line), 1 mM Na$_2$SeO$_3$ (purple line), a mixture of 1 mM MVCl$_2$ and 30 mM purified Na$_2$SeO$_4$ (green line), a mixture of 1 mM MVCl$_2$, 30 mM purified Na$_2$SeO$_4$ and 1 mM Na$_2$SeO$_3$ (gray line). B. Dynamic polarization curves ($v = 10$ mV/s) recorded at $\omega = 900$ rpm in the same buffer solution containing 1 mM MVCl$_2$ (magenta line), 1 mM Na$_2$SeO$_3$ (blue line), and a mixture of 1 mM MVCl$_2$ and 1 mM Na$_2$SeO$_3$ (black line).

**Figure 2.** Cyclic voltammograms ($v = 100$ mV/s) of a GC electrode recorded in 0.2 M NaOAc buffer solution (pH 4) containing a fresh mixture of 1 mM MVCl$_2$ and 1 mM Na$_2$SeO$_3$ (blue line) and ca. 1 mM of the red suspension after heating a 1 M MVCl$_2$ and 1 M Na$_2$SeO$_3$ mixture for 2 h. (magenta line, see text for details). Also shown in the black curve in Panel B, Fig. 1. A plausible explanation for this unique electrocatalytic behavior may be found in the formation of an adduct-type species, which is far more easily reduced than each of its constituents.
a vacuum oven and then characterized by NMR yielding $^1$H NMR (500 MHz; D$_2$O) δ 8.81 (d, 2H), 8.69 (m, 2H), 8.29 (d, 2H), 7.82 (m, 2H), 4.34 (s, 3H); $^{13}$C NMR (125 MHz; D$_2$O) δ 153.57, 149.92, 145.54, 142.64, 125.72, 122.42, 47.72; ESIMS m/z: 171.53 (calculated for C$_4$H$_7$N$_2$, 171.22). Lastly, the UV-visible spectrum of MQ in water (see red curve in Fig. 4) yielded a peak at 260 nm and a rather well-defined sharp peak at 205 nm. These features are similar to those of MV$^{2+}$ (see black line), although with somewhat different relative intensities. It may thus be concluded based on these information that the product of the reaction between MV$^{2+}$(aq) and SeO$_3^{2-}$(aq) is the monomethylated form of 1-methyl-[4,4'-bipyridine]-1-ium, known commercially as monoquat, MQ, with chloride as the most likely counterion.\(^{12}\) It should be emphasized that no changes were found in the spectrum of a solution of MVCl$_2$ in water (pH 4) heated at 60°C for about two hours developed a similar color to that of the heated suspension.

The electrochemical properties of MQ were characterized in 0.2 M NaOAc buffer (pH 4) using a carbon microelectrode. As shown in Fig. 5 (red line), the cyclic voltammogram displayed a rather reversible peak in the region −0.5 to −0.9 V and thus similar to that found for MV$^{2+}$ in the same solution (see magenta line in Panel A, Fig. 1), and a set of small redox peaks (not found for MV$^{2+}$) at much more positive potentials, which decreased in magnitude upon repeated cycling. No efforts were made to elucidate the nature of these features.

One of the issues that remains to be addressed relates to the fate of the leaving methyl group in MV$^{2+}$. One possible product is methyl selenite, SeO$_2$(OCH$_3$)$^-$ (in fact, an analogous methyl transfer reaction was reported between several methyl-containing quaternary ammonium species and acetate ion, which yielded the corresponding demethylated derivative and methyl acetate.\(^{13}\) Some of the properties of SeO$_2$(OCH$_3$)$^-$ have been investigated by Kim et al. as part of their efforts aimed at preparing alkyl imidazolium-SeO$_2$(OCH$_3$)$_2$ ionic liquids.\(^{7,14}\) In particular, the X-ray diffraction of KSeO$_2$(OCH$_3$) afforded unambiguous evidence that the methyl group is attached to one of the oxygen atoms and not to the Se center. Moreover, the cyclic voltamogram of KSeO$_2$(OCH$_3$)$_2$ and 1,3-dimethylimidazolium[SeO$_2$(OCH$_3$)$_2$] solutions in methanol yielded a rather large reduction current starting at −0.2 V vs Ag/AgCl. A similar behavior was found in our laboratory for 1 mM KSeO$_2$(OCH$_3$)$_2$ aqueous solutions in 0.2 M NaOAc (pH 4), which, as shown in red in Fig. 6, displayed a prominent reduction peak with a half wave potential, $E_{1/2}$, ca. −0.67 V, i.e. about 0.15 V more negative than $E_{1/2}$ for the mixture of 1 mM MVCl$_2$ and 1 mM Na$_2$SeO$_3$ in Panel A, Fig. 1 (see blue curve in this figure). It may be surmised on this basis, that the reduction of SeO$_2$(OCH$_3$)$_2$ cannot account for the remarkable enhancements in the rates of SeO$_2$(aq) reduction induced by MV$^{2+}$(aq). It should be stressed that no detectable changes in the appearance of a mixture of 1 mM MVCl$_2$ and 1 mM KSeO$_2$(OCH$_3$)$_2$ in water (pH 4) were noted after heating at 60°C for about two hours under otherwise the same conditions as those employed in the case of Na$_2$SeO$_3$. This observation strongly suggests that the transfer of the methyl group is required for the overall process to occur.

In summary, MV$^{2+}$(aq) was found to react with SeO$_2$(aq) at 60°C in water with the pH adjusted to 4 to yield elemental Se and monoquat as the only firmly identified products. Indirect evidence was also obtained for the methyl group in the MV$^{2+}$(aq) being transferred to the selenite to yield SeO$_2$(OCH$_3$)$_2$$. Although hardly anything is known about the thermodynamic potentials for the reduction and oxidation of alkyl selenites, it seems conceivable that MV$^{2+}$(aq) catalyzes the dismutation of SeO$_2$(aq) through a complex process that generates.

**Figure 3.** Raman spectrum of the red powder isolated following centrifugation (see text for details).

**Figure 4.** UV-visible spectrum of aqueous solutions of pure MVCl$_2$ (black line) and MQ (red line).

**Figure 5.** Cyclic voltammograms recorded at a scan rate of 5 V/s with a carbon microelectrode in 0.2 M NaOAc buffer (pH 4) containing a small amount of MQ (red line). The black curve shows the corresponding data collected in the neat buffer under otherwise the same conditions.
a yet to be identified species in solution that undergoes reduction at potentials more positive than the onset of the electrocatalytic process.

Further insight into some of these issues was obtained from analogous studies involving a self-assembled monolayer, SAM, incorporating a viologen moiety on GC to be described in the next section.

On the reactivity of selenite toward a viologen moiety confined within a self-assembled monolayer.—The rationale behind the experiments to be described in this section is three-fold:

i. According to data reported in the literature, the onset for the reduction of a EOBSAM self-assembled on a polycrystalline Au electrode in 0.5 M Na2SO4 is at about −0.2 V vs Ag/AgCl; a value which is very close to the onset for the reduction of SeO32− (aq) induced by MV2+(aq), described in Fig. 1 in the previous section. In order to explore this correlation further, we examined the electrochemical and electrocatalytic properties of an EOBSAM on GC prepared by the method specified in detail in the Experimental Section.

ii. As shown by the experiments described in the previous section, the reaction between MV2+(aq) and SeO32− (aq) led to the loss of one of the methyl groups. Hence, one might envision that exposure of the EOBSAM to SeO32− (aq) will lead to dealkylation and possibly to the desorption of the redox active group from the surface, which will result in a loss in the intensity of the redox peak.

iii. The experiments performed in solution phase provided unambiguous evidence for the formation of elemental Se. This species displays characteristic voltammetric peaks in aqueous solutions and, given its low solubility, might remain adhered to the electrode surface allowing its identification.

The cyclic voltammograms of a EOBSAM on GC (see Experimental Section) recorded in a 0.2 M NaOAc buffer solution (pH 4) at various scan rates, vs, displayed a set of fairly symmetric peaks centered at −0.39 V vs Ag/AgCl (see solid lines in Fig. 7). As expected, a plot of the peak currents, Ip, vs v corrected for the current associated with the substrate (see dotted line in Fig. 7) was found to be linear (see inset in this figure). The surface concentration of EOBSAM determined from a coulometric analysis of the reduction peak corrected by the (voltage independent) capacitive contribution due to the underlying GC substrate, yielded a value of 2.16 × 10−10 mol/cm², which is very similar to that reported in the literature for a self-assembled monolayer of N-methyl-N’-hexadecyl viologen on the same substrate (1.7 × 10−10 mol/cm²).15

Shown in Panel A, Fig. 8 are cyclic voltammograms curves recorded at v = 100 mV/s with a bare (black curve) and an EOBSAM functionalized GC, EOBSAM, disk electrode (red curve) in neat 0.2 M NaOAc buffer (pH 4). As evidenced therein, an increase in the negative current at about −0.2 V was found upon addition of 1 mM Na2SeO3 in the same buffer, which is virtually the same as the onset potential for the reduction of the EOBSAM layer in the neat buffer. Interestingly, this is also similar to the onset for the reduction of solution phase MV2+ found in the presence of 1 mM Na2SeO3. In fact, the current at −0.6 V was also comparable between the two media. One possible explanation for this effect may be found in a fraction of the MV2+ being adsorbed in the form of aggregates on the GC, which although not detectable by the voltammetric technique employed catalyze very effectively the reduction of SeO32− (aq). Additional experiments in which the amount of EOBSAM was small enough to yield non-detectable voltammetric features did show in fact the same onset potential toward the reduction of SeO32− (aq) as for the full EOBSAM layer, although the currents at −0.6 V were less than half those observed for the full monolayer. As shown in Panel B, Fig. 8, the magnitude of the overall electrocatalytic currents increased although not proportionally with the concentration of Na2SeO3 in solution.

Further insight into the interactions between EOBSAM and SeO32− (aq) was obtained by exposing a freshly prepared EOBSAM/GC electrode to a 0.1 M Na2SeO3 in 0.2 M NaOAc buffer (pH 4) under ambient light and an inert (Ar) atmosphere. After ca. 200 min, the EOBSAM/GC was taken out, rinsed with UPW water, transferred back to the neat buffer and a series of voltammograms were recorded over the range 0.0 and −0.6 V.

As shown in Fig. 9, the intensity of the reduction peak (see blue curves) associated with the fresh EOBSAM/GC in the neat buffer (see red curve) decreased, an effect consistent with the loss of the viologen moiety. This behavior would be analogous to that found for the reaction between MV2+(aq) and SeO32− (aq) in homogenous media, where in the present case the alkyl group in contact with the surface would cleave leading to the release of the remaining viologen fragment into the solution. Some support for this view was obtained in preliminary experiments involving aqueous solutions of EOBSAM and selenite heated under the same conditions as those described in the first section above.
which displayed a $^1$H NMR spectra containing new peaks with similar chemical shifts as those found in those experiments.

Most prominent in Fig. 9 was the well-defined peak centered at ca. $-0.56$ V, the magnitude of which decreased as the scanning was continued, and what appears to be a small oxidation peak centered at $-0.24$ V on top of a much broader feature during the scan in the opposite direction. The potential associated with the reduction peak is very similar to that found in the gray line in Panel A, Fig. 1. At least two lines of evidence point to elemental Se as being responsible for this overall behavior. First, the reaction between selenite and methyl viologen in solution was found to yield elemental Se as a product. Second, a large increase in the current starting at $-0.4$ V followed by a clearly defined oxidation peak centered at ca. $-0.2$ V was found in the voltammogram of a GC electrode first cycled in a selenite solution, removed from the solution, rinsed with UPW and then reintroduced into neat buffer (see red line in Fig. 10). The same behavior was found for a GC electrode cycled in a MV$^{2+}$-SeO$_3$$^{2-}$ mixture or in 1 mM KSeO$_2$(OCH$_3$)$_2$ following the same procedure (not shown here). These peaks have been associated with the reduction of elemental Se to selenide which is subsequently oxidized to regenerate Se.$^{16}$ It should be stressed that a coulometric analysis in all cases yielded a charge under the oxidation peak that was below a monolayer. In fact, similar features were also observed after the data in Panel B, Fig. 8 was collected, the electrode rinsed with UPW, and later immersed in a neat buffer (see black line in Fig. 10).

**Conclusions**

The major finding emerging from the experiments presented in this work relates to the ability of methyl viologen (MV$^{2+}$) to react
with SeO$_3^{2-}$ in mildly acidic (pH 4) aqueous solutions to yield elemental Se, a process that is coupled to the loss of a methyl group in MV$^{2+}$ generating 1-methyl-[4,4'-bipyridine]-1-ium, known as monoquat. Experiments in which a monolayer of the alkyl-substituted viologen cation N-ethyl-N'-octadecyl-4,4'-bipyridinium (EOB) was self-assembled on a glassy carbon electrode and then exposed to an aqueous Na$_2$SeO$_3$ solution also provided electrochemical evidence for a partial dealkylation of the EOB and the formation of elemental Se. Cyclic voltammetric measurements involving this modified electrode showed that the onset for the reduction of SeO$_3^{2-}$ coincided with the onset for the reduction of the viologen in the EOB and also with the onset for the same reaction on a bare GC electrode in a solution containing both MV$^{2+}$ and SeO$_3^{2-}$, as reported earlier by Koshikumo et al. The most likely explanation for the latter effect may be found in the formation of MV$^{2+}$ aggregates on the GC surface in amounts too small to be detected in solutions containing only MV$^{2+}$, which would be responsible for the electrocatalytic effects. Lastly, and in contrast to earlier claims, no electrocatalytic effects were found for the reduction of SeO$_3^{2-}$ in the presence of MV$^{2+}$ in solution.

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