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Adhering Homogeneous Molecular Electrocatalysts Entrapped in Micelles to Electrode Surfaces

by

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Honors Thesis

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Chemistry Department

University of Richmond

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Advisor: Dr. Michael Norris

Abstract

Heterogeneous catalysts are important to industrial use; however, mechanistic studies are difficult because they lack the easy tunability of homogeneous catalysts. One solution could be to immobilize homogeneous catalysts using micelles while maintaining catalytic properties and activities.

Introduction

The increasing effects of global warming and the threat of an energy crisis have made the search for an efficient pathway for the reduction of carbon dioxide an important research focus. Carbon dioxide is a harmful greenhouse gas emitted by burning fossil fuels and it can be reduced into products that can be used as fuel. There is a large energy barrier in the reduction of carbon dioxide[1], so to make the reaction energetically feasible and selective, it must be catalyzed.

Many homogeneous catalysts have been developed for CO_2 reduction, because they are easy to study in a laboratory and allow for a high level of control.[2] Electrochemistry is the most favorable method for CO_2 reduction, because the electricity used to drive the reaction can be obtained from renewable sources. However, for electrochemical reactions, homogeneous catalysts are not ideal because they are only active in the diffusion layer near the electrode surface, meaning much of the catalyst in solution will not be active. Additionally, homogeneous catalysts must be extracted from the solution after use which can be challenging and many of the catalysts that have been developed use expensive metals which are not cost-effective on an industrial scale. There are also photocatalysts that can be used for CO_2 reduction[3,4], but most are homogeneous and therefore also present some drawbacks.

For large and industrial scale CO_2 reduction, the use of heterogeneous catalysts is ideal. Immobilizing molecular electrocatalysts at an electrode surface allows all of the catalyst to be active at once and the catalyst can be easily removed from the solution after use. Turning homogeneous catalysts into heterogeneous catalysts by immobilizing them usually involves either covalent or non-covalent interactions between the catalyst and the electrode surface. Approaches using covalent interactions include “click” reactions with an azide-modified graphitic electrode surface[5,6,7,8] as well as the direct formation of carbon-carbon bonds between an electrode surface and the catalyst.[9] Non-covalent methods include π-stacking interactions between functionalized ligands and graphene surfaces.[10] Catalyst immobilization through the

electrochemical polymerization of vinyl functional groups has also been achieved with ruthenium complexes on metal-oxide electrodes in water.[11,12,13] In all of these types of modifications, the addition of functional groups can affect the catalyst's activity and can be difficult to successfully achieve.

Electroactive molecules have been successfully attached to electrode surfaces without changing the functional groups of the catalyst.[14] The immobilization was done by forming films on the surface of glassy carbon electrodes stabilized with HPU/TPU films. The project described in this thesis seeks to find a solution for making heterogeneous catalysts by forming reverse micelles that entrap homogeneous catalysts and allows the catalyst to be immobilized at the electrode surface without modifying its functional groups. In a nonpolar solution, reverse micelles will form around any water that is present, trapping it in the polar core and away from the nonpolar solvent. This allows any water-soluble catalyst or electroactive molecule to be trapped within the micelles. Since catalysis will occur in this microenvironment at the core of the micelles, it can be highly controlled and the functional groups on the surfactant molecules can be modified to promote reactivity and selectivity. Strategies for modifying the surfactant headgroup have demonstrated increased catalytic performance for various uses.[15]

In this work, a ruthenium complex and an iron catalyst were successfully captured inside micelles and adhered to glassy carbon electrode surfaces. Electrochemical activity and stability were maintained in aqueous environments at mid and high pH. The use of high surface area graphite electrodes was also explored, and initial results show potential for further research.

Experimental

The chemicals used in the experiment are as follows. For the surfactant synthesis, we used 4-hydroxybenzaldehyde (Alfa Aesar), 1-bromooctane (Oakwood Chemical), sodium borohydride (Millipore Sigma), phosphorus tribromide (Sigma-Aldrich), and triallyl amine (Sigma-Aldrich). In the micelle solution, Triton X-45 (Sigma-Aldrich) and cyclohexane (Millipore Sigma) were used. Lithium trifluoromethanesulfonate (Oakwood Chemical), iron(II) chloride (Sigma-Aldrich), 2,6-diacetyl pyridine (Chem-Impex International), triethylenetetramine (Sigma-Aldrich) were used for the iron catalyst synthesis.

To synthesize the surfactant to be used to form the reverse micelles, we followed a previously reported procedure[16] but changed the length of the carbon chain to eight rather than

ten. The surfactant, 4-octyloxybenzyltriallylammonuim bromide (**Image 1**), was synthesized in 37% yield and was able to be scaled up.

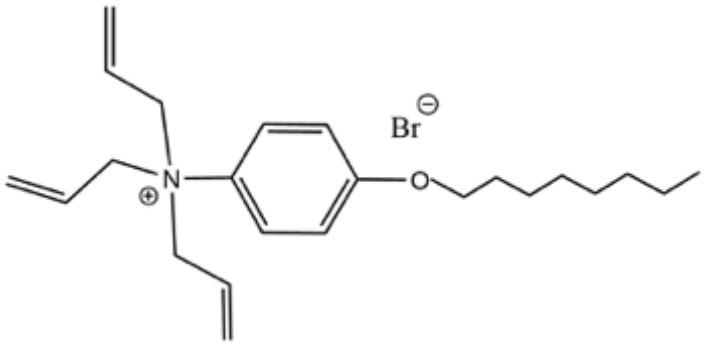

Image 1. Structure of 4-octyloxybenzyltriallylammonium bromide

The ruthenium(II) tris bipyridine (**Image 2**), $Ru(bpy)_3^{2+}$, used in this project was found in the lab from a previous project.

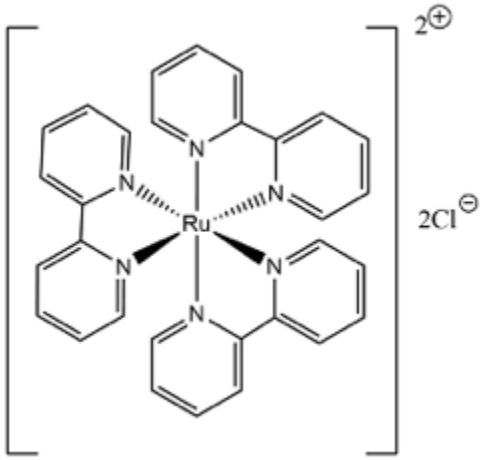

Image 2. Structure of Ruthenium(II) tris bipyridine

To form the micelles, $Ru(bpy)_3^{2+}$ was dissolved in a small amount of water and added to a solution of cyclohexane, Triton X-45, and 4-octyloxybenzyltriallylammonuim bromide. The solution, Solution 1, was stirred at room temperature until it became clear.

To adhere the reverse micelles to the electrode surface, films of Solution 1 were formed by dropping 3 or 5 10-μL drops of solution onto glassy carbon electrodes (GCEs) and graphite electrodes. The films did not dry completely even with extended time or with air blown over them.

For all electrochemistry experiments, a CH Instruments Electrochemical Analyzer potentiostat was used with a platinum counter electrode. An Ag/AgCl reference electrode was used for aqueous solutions, an Ag/$AgNO_3$ reference was used for acetonitrile experiments, and an Ag/Ag(s) pseudo-reference electrode was used for experiments done in DCM. Bulk electrolysis experiments at 1.4V for 3600s or 1800s at pH 7 were run on each GCE to initiate the radical polymerization of the micelles.

After the polymerization, cyclic voltammetry experiments were run on the GCEs in acetonitrile and in water at pH 7 and pH 12.5. For the CVs done in acetonitrile, 5 or 7 drops of a solution of 50/50 HPU/TPU, two polyurethanes, were dropped over the films to help secure the film on the electrode surface while maintaining the catalyst activity. CVs for the $Ru(bpy)_3^{2+}$ films were run from -2.3V to 0.8V in acetonitrile, and -0.5V to 1.4V in water.

The iron catalyst, $[Fe^{II}(L)(Cl_2)](OTf)$ (**Image 3**), was synthesized according to a previously reported procedure.[17] Lithium triflate was used for the precipitation rather than Lithium perchlorate. We were unable to confirm the structure of the catalyst with NMR because the iron is paramagnetic, but the electrochemical activity of the catalyst is consistent with what would be expected. The catalyst was dissolved in a small amount of water and was added to a solution of our surfactant, Triton X-45, and cyclohexane, the same conditions that were used with the ruthenium complex. After stirring overnight, the solution was clear. The same procedure for forming the GCE films was used, and polymerization was done at pH 7 for 30 min. CV scans were done at pH 7 under Ar and CO_2 from -1.5 to 1.4V. CVs were also taken in DMF under Ar and CO_2 from -2.1V to 1.0V.

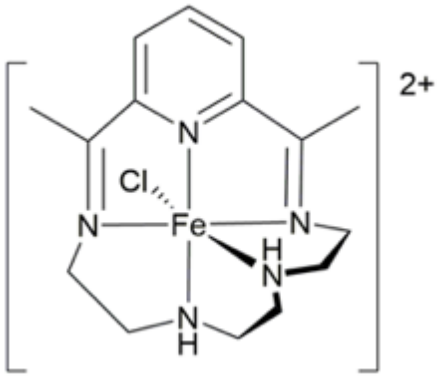

Image 3. Structure of $[Fe^{II}(L)(Cl_2)]^{2+}$

Results and Discussion

For initial experimentation, $Ru(bpy)_3^{2+}$ was used to determine if the micelles would capture the catalyst and to test the electrochemical activity of molecules trapped in the core of micelles. The ruthenium complex was chosen because it has known electrochemical activity and is water-soluble. Because of the long nonpolar tails on the micelles and the positively charged core, the aqueous solution of water and $Ru(bpy)_3^{2+}$ stayed inside the core of the reverse micelles. The Triton X-45 surfactant was added to the micelle solution to increase the solubility and help form the reverse micelles.

The polymerization of the micelles with bulk electrolysis (BE) was necessary to inhibit the individual surfactant molecules from coming off and on in solution. The electrons provided by the BE initiated the radical polymerization of the alkenes at the heads of the surfactant molecules. Constant potential BE was run for each film before the cyclic voltammetry experiments.

In acetonitrile, the films almost immediately fell off of the electrode surface, even after polymerization and with varied amounts of polyurethanes. However, even when the films fell off, there was still redox activity (**Figure 1)** and the $Ru(bpy)_3^{2+}$ did not diffuse into solution, indicating that it stayed trapped within the micelles.

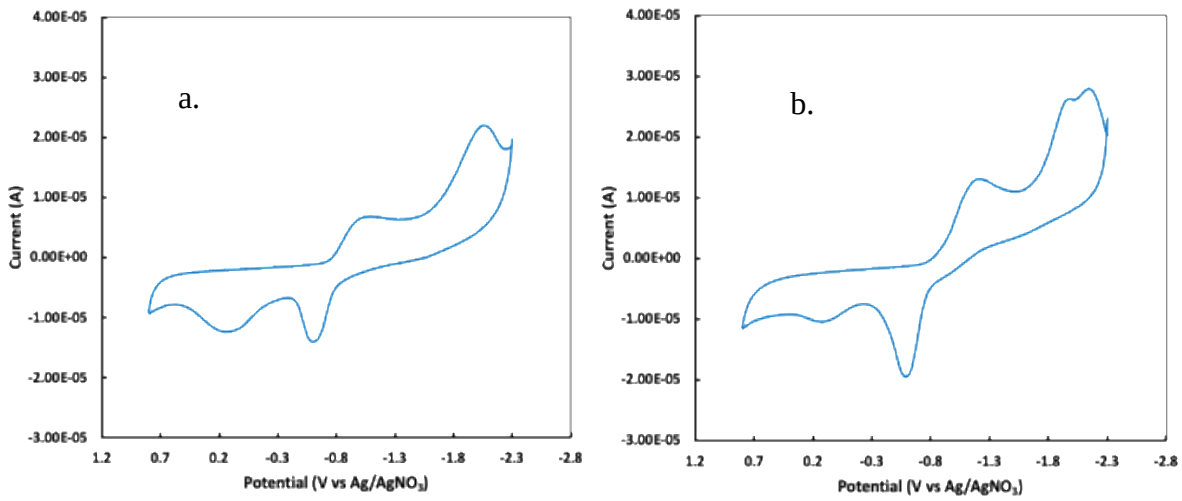

Figure 1. Voltammograms of micelle films contatining $Ru(bpy)_3^{2+}$ on GCEs in acetonitrile. CVs taken with scan rate of 100mV/s from -2.3V to 0.8 V under Ar (g). **a.** 5 drops HPU/TPU; **b.** 7 drops HPU/TPU

In the aqueous environment at pH 7, the films stayed at the electrode surface, likely because of the hydrophobic tails of the reverse micelles, and the $Ru(bpy)_3^{2+}$ was active over a long scan period of 100 sweeps (**Figure 2**). The same stability was seen at the higher pH of 12.5 (**Figure 3**). Decay in the ruthenium complex can be seen in the oxidations in the scans from remaining in solution for a long period of time.

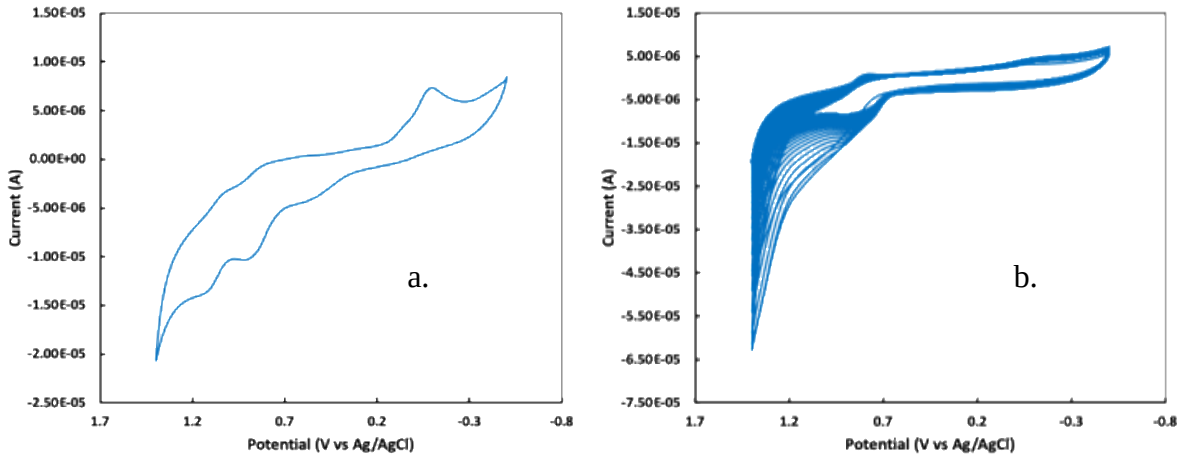

Figure 2. Voltammograms of micelle films containing $Ru(bpy)_3^{2+}$ on GCEs at pH 7 under Ar (g). **a.** Scan rate of 100mV/s from -0.5V to 1.4V, 5 scan segments; **b.** Scan rate of 100mV/s from -0.5V to 1.4V, 100 scan segments

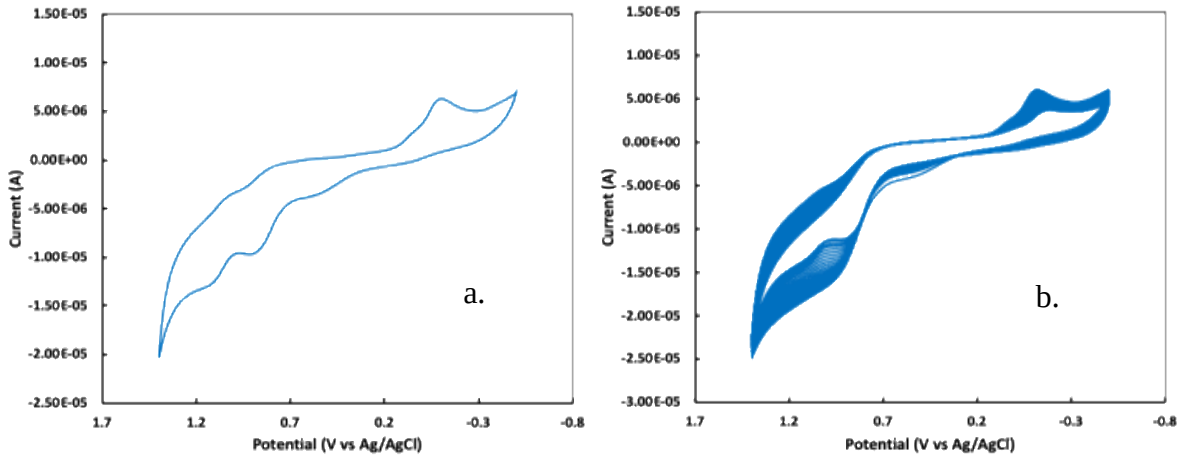

Figure 3. Voltammograms of micelle films containing $Ru(bpy)_3^{2+}$ on GCEs at pH 12.5 under Ar (g). **a.** Scan rate of 100mV/s from -0.5 to 1.4V, 5 scan segments; **b.** Scan rate of 100mV/s from -0.5 to 1.4V, 50 scan segments

For industrial purposes, high surface area electrodes are ideal because there is more surface area for electron exchange. For this project, we used graphite electrodes. The initial CVs of the graphite electrodes with micelle films containing $Ru(bpy)_3^{2+}$ showed large amounts of background current, but activity is still visible (**Figure 4**).

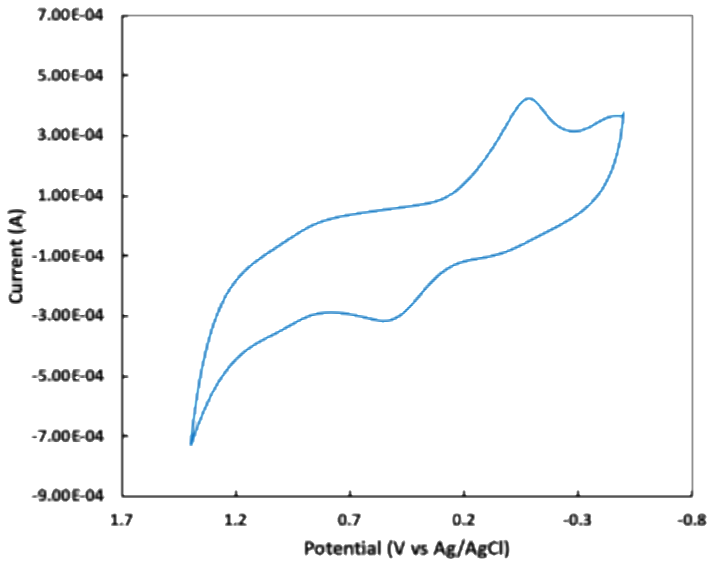

Figure 4. Voltammogram of micelle films containing $Ru(bpy)_3^{2+}$ on a graphite electrode under Ar (g). Scan rate of 50mV/s from -0.5V to 1.5V.

To remove some of the background current, electrolyte was added between drops of micelle solution when forming the films. **Figure 5** shows scans with 5 drops of micelle solution and pH 7 aqueous electrolyte. An additional electrode film was made with one drop of HPU/TPU solution added before the micelle solution and electrolyte. CVs of this electrode are shown in **Figure 6**. The addition of electrolyte was successful in reducing the background current and the films with and without HPU/TPU remained stable over 50 scans. The scans using the electrodes with and without HPU/TPU are very similar. The only notable difference is that the addition of the polyurethanes causes less current to be passed.

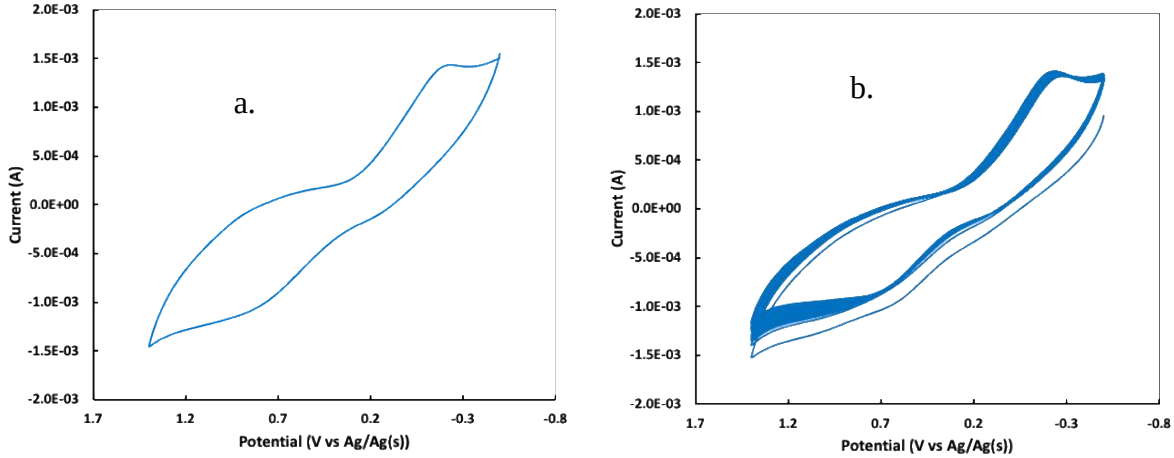

Figure 5. Voltammograms of micelle films containing $Ru(bpy)_3^{2+}$ with electrolyte on a graphite electrode under Ar (g) from -0.5V to 1.5V. **a.** Scan rate of 100 mV/s, 5 scan segments; **b.** Scan rate of 100 mV/s, 50 scan segments.

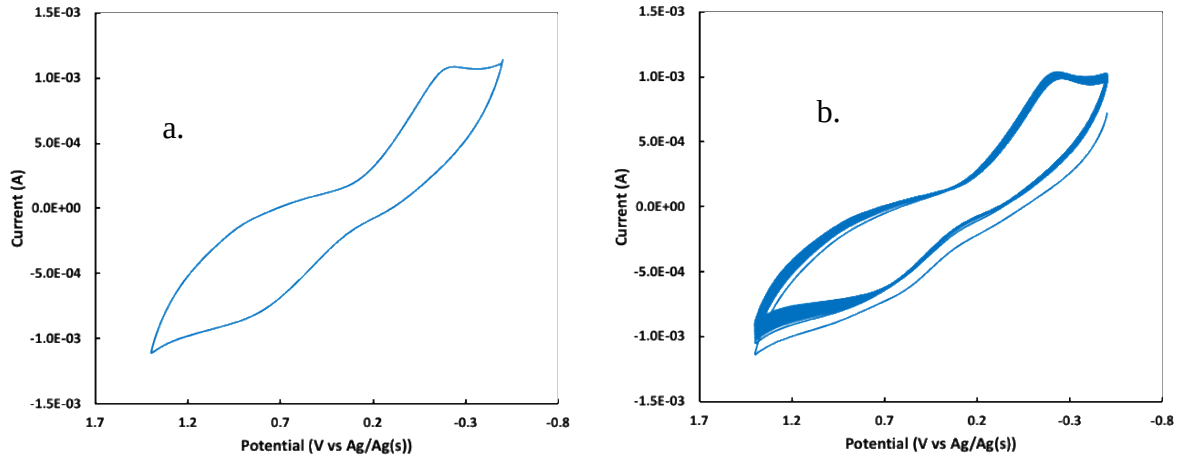

Figure 6. Voltammograms of micelle films containing $Ru(bpy)_3^{2+}$ with electrolyte and HPU/TPU on a graphite electrode under Ar (g) from -0.5V to 1.5V. **a.** Scan rate of 100 mV/s, 5 scan segments; **b.** Scan rate of 100 mV/s, 50 scan segments.

After experimenting with the ruthenium inside the reverse micelle core, we synthesized an iron catalyst, $[Fe^{II}(L)(Cl_2)](OTf)$, that has been reported to reduce CO_2.[14] This catalyst was chosen because it can be made to only produce formate/formic acid, which is easy to identify and quantify using NMR techniques. The micelle solution containing the catalyst was prepared in the same way as with the $Ru(bpy)_3^{2+}$ and was polymerized with BE under the same conditions. The CVs at pH 7 showed some activity under both Ar and CO_2 (**Figure 7**). In DCM, the activity was more clear (**Figure 8**). The major conclusion at this point is that the film stayed at the electrode surface and electrochemical activity was preserved with the catalyst trapped inside the micelles.

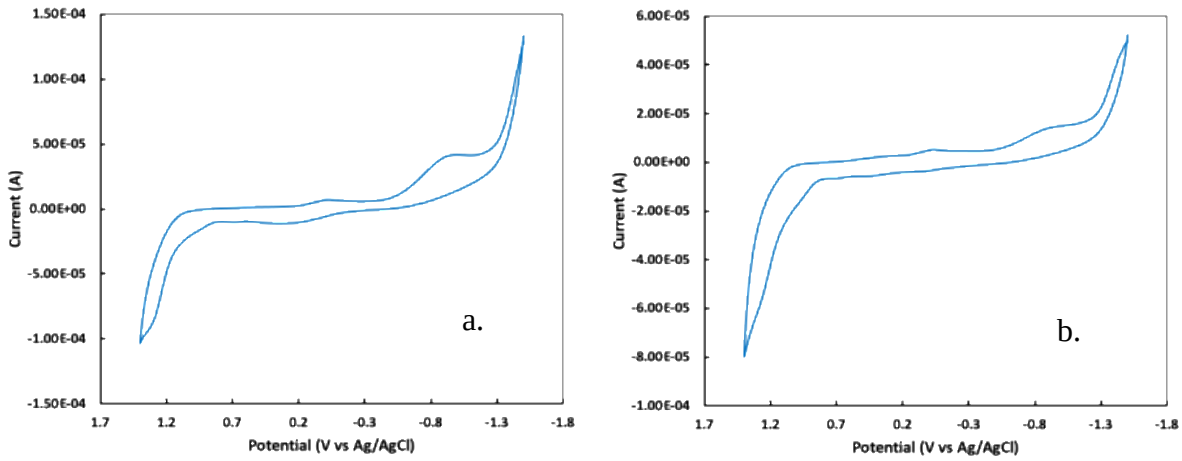

Figure 7. Voltammograms of micelle films containing $[Fe^{II}(L)(Cl_2)](OTf)$ on GCEs at pH 7. **a.** Scan rate of 100mV/s from -1.4V to 1.5V under Ar (g); **b.** Scan rate of 100mV/s from -1.4V to 1.5V under CO_2 (g)

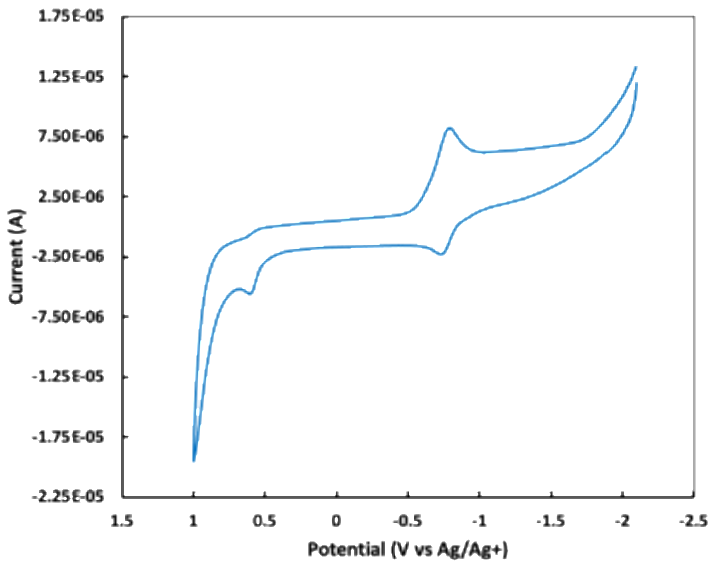

Figure 8. Voltammogram of micelle films containing $[Fe^{II}(L)(Cl_2)](OTf)$ on GCEs in DCM. Scan rate of 50mV/s from -2.1V to 1.0V under Ar (g).

Conclusion

This research yielded promising initial results and created many pathways for further study. First, characterization of the micelles must be done to verify that the polymerization occurs as expected. The structure of the surfactant headgroup can be further studied as well to ascertain the effects of the secondary coordination sphere on electrochemical and catalytic activity. The catalytic activity of the iron complex must be further analyzed, since all we have learned is that it remains active inside the micelles. Additionally, more experimentation needs to be done with high surface area electrodes such as the graphite since this has important implications for industrial use of this technique. Overall, this research project has concluded that micelles containing electroactive molecules can be successfully adhered to electrode surfaces while maintaining electrochemical activity.

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