

DETERMINATION OF DIFFUSION COEFFICIENTS FERROCENE IN MICELLAR SOLUTIONS

INTRODUCTION

The process of diffusion is important in a wide variety of chemical scenarios, including kinetics of rapid reactions, chromatographic and electrophoretic separations, and heterogeneous catalysis. Of especial interest in this experiment is the role of diffusion in electrochemistry. Mass transfer of the electroactive species to the electrode surface is a major factor in the rate of an oxidation/reduction reaction, and if there are no kinetic hindrances to the electron transfer step, movement through the solution becomes the rate-limiting step. Because of this dependence, electrochemical measurements are frequently used to determine diffusion coefficients of electroactive species.

According to Fick's first law, the diffusion coefficient, D , is the proportionality constant relating the number of moles, N , of a substance which cross an area, A , per second to the concentration gradient perpendicular to A , $\frac{\partial C}{\partial x}$:

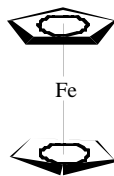
$$\frac{dN}{dt} = -AD \frac{\partial C}{\partial x} \quad (1)$$

In equation 1, D has units of cm^2/s if A is in cm^2 , C is in mol/cm^3 , and x is in cm . The negative sign indicates that the molecules move from the region of high concentration to the low concentration end. The change in concentration with time due to the diffusion process is given by Fick's second law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2)$$

This experiment involves the measurement of diffusion coefficients by two electrochemical procedures, chronocoulometry and cyclic voltammetry, which are described further below. The latter method provides additional information about the chemical system, most notably the half wave potential, $E_{1/2}$. In most cases, $E_{1/2}$ (after correction for the reference) is very close to E° , the standard electrode for the redox pair.

Aside from enabling predictions about behavior in the scenarios mentioned in the first paragraph, knowledge of diffusion coefficients provides insight into molecular structures and interactions. An instructive example is the organometallic compound ferrocene (Fc), dicyclopentadienyl iron (II), $(\text{C}_5\text{H}_5)_2\text{Fe}$,



which can be oxidized to the ferrocenium ion $(C_5H_5)_2Fe^+$. Ferrocene is not very soluble in water, but the compound can be solubilized by incorporating a surfactant into the solution. The resulting interactions also alter the diffusional and electrochemical character of the compound.

Surfactants are amphipathic molecules; this is, they contain both a polar region, called the headgroup, and a long-chain hydrophobic tail. The headgroup can be neutral or charged, and in this experiment both cationic $R-(CH_3)_3N^+$ and anionic $R-OSO_3^-$ surfactants will be used. In the latter case, R is a twelve carbon alkyl chain. The full formula is $CH_3(CH_2)_{11}OSO_3^- Na^+$, called sodium dodecyl sulfate, SDS, or sodium lauryl sulfate, SLS. For cationic surfactants, both 12 and 16 carbon compounds will be investigated: dodecyltrimethyl ammonium bromide, $CH_3(CH_2)_{11}(CH_3)_3N^+Br^-$ ($C_{12}TAB$) and cetyltrimethyl ammonium bromide, $CH_3(CH_2)_{15}(CH_3)_3N^+Br^-$ ($C_{16}TAB$). (Note: In literature references, CTAB with no subscript usually refers to $C_{16}TAB$.) For comparison, the behavior of Fc in a simple electrolyte, tetrabutyl ammonium bromide, $Bu_4N^+Br^-$, will also be investigated.

Above a certain concentration, called the critical micelle concentration or CMC, surfactant molecules come together to form globular aggregates called micelles. The hydrocarbon tails group together in the nonpolar interior with the headgroups facing the aqueous environment. Micelles are often roughly spherical with aggregation numbers of 50 to 100. Figure 1 shows a cut-away view of a typical $C_{16}TAB$ micelle.

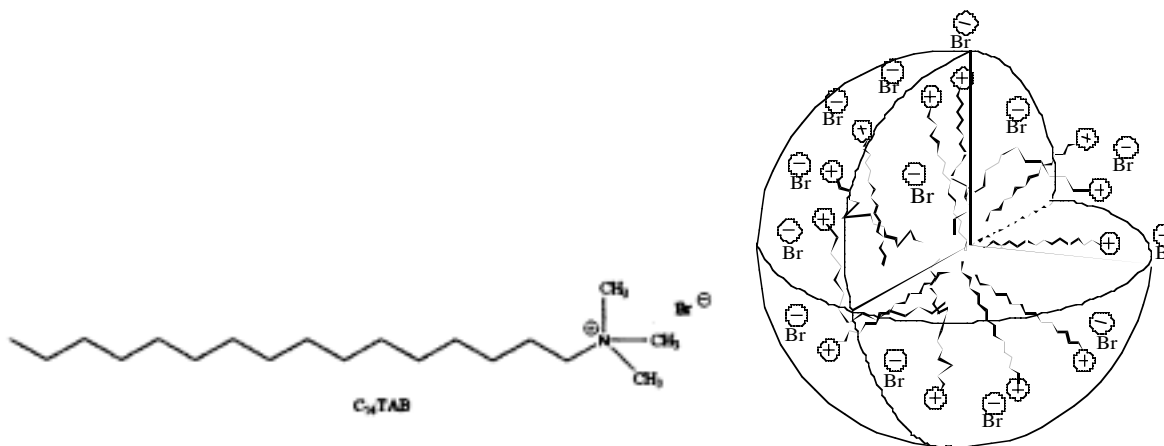


Figure 1. $C_{16}TAB$ micelle. This is a cut-away view of an overall roughly spherical structure. The Br^- counterions are distributed in the surface layer of the micelle and in the surrounding solution. The hydrophobic tails are tangled randomly, and some of them protrude on the surface to help shield the positive charges from each other.¹

Micelles are capable of solubilizing neutral ferrocene, which can reside in the hydrophobic micelle interior. Association with the bulky micelle slows the overall motion of the neutral compound, and the diffusion coefficient decreases as a result. This effect is more pronounced for larger (e.g., C₁₆TAB) micelles.

It will also be observed that the E_{1/2} is more positive in C₁₂TAB and C₁₆TAB solutions than it is in water or SDS solutions. Thus, it is more difficult to oxidize Fc (easier to reduce Fc⁺) in C₁₂TAB and C₁₆TAB. It is tempting to rationalize this behavior in terms of repulsion of the positive micelle from the anode for the oxidation process. However, the effect is really an example of Le Chatelier's principle; the concentration of free Fc in solution decreases when the molecule associates with the micelles. This "removal" of neutral Fc alters the favorability of the redox equilibrium.

Several research groups have treated the E_{1/2} shifts mathematically. The simplest method^{2,3} makes use of partition coefficients, K_R and K_O, for the reduced (Fc) and oxidized (Fc⁺) forms.

$$K_R = \frac{[Fc_w]}{[Fc_m]} \quad \text{and} \quad K_O = \frac{[Fc_w^+]}{[Fc_m^+]} \quad (3a,b)$$

in which subscripts w and m represent the water and micellar phases. (Note: In a strictly correct treatment, K_R and K_O should be written as activity ratios.) For C₁₂TAB and C₁₆TAB, K_R is very small (~10⁻²), but K_O is very large, because Fc⁺ is very soluble in water and is repelled from the positive micelles. Letting [Fc_T] and [Fc_T⁺] represent the total Fc and Fc⁺ concentrations, equations 3a and 3b may be rearranged to give

$$[Fc_w] = \frac{K_R [Fc_T]}{(1 + K_R)} \quad \text{and} \quad [Fc_w^+] = \frac{K_O [Fc_T^+]}{(1 + K_O)} \quad (4a,b)$$

and since K_O >> 1, [Fc_w⁺] ≈ [Fc_T⁺].

These expressions may be substituted into the Nernst equation for the Fc_w⁺ + e ⇌ Fc_w half-reaction:

$$E = E_w^0 - \frac{59.2}{n} \log \frac{[Fc_w]}{[Fc_w^+]} = \left\{ E_w^0 - 59.2 \log \frac{K_R}{1 + K_R} \right\} - 59.2 \log \frac{[Fc_T]}{[Fc_T^+]} \quad (5)$$

The bracketed term in equation 5 is a constant for a given micellar environment and is called the formal potential for ferrocene in the micellar solution. To convert the formal potential to a half-wave potential, an extra term containing the diffusion coefficients is needed:

$$E_{1/2m} = E_w^0 - 59.2 \log \frac{K_R}{1 + K_R} - 59.2 \log \left(\frac{D_O}{D_R} \right)^{1/2} \quad (6)$$

in which D_O and D_R are the observed diffusion coefficients of Fc^+ and Fc in the micellar solution.

In the absence of micelles, D_O is about equal to D_R (Fc_w and Fc_w^+ have similar sizes.), so that $E_w^0 \approx E_{1/2w}$. Thus,

$$E_{1/2m} = E_{1/2w} - 59.2 \log \frac{K_R}{1 + K_R} - 59.2 \log \left(\frac{D_O}{D_R} \right)^{1/2} \quad (7)$$

Incorporation of Fc into $C_{12}TAB$ and $C_{16}TAB$ micelles causes D_R to decrease, making the D_O/D_R ratio significantly greater than one. Thus, the third term in equation 7 tends to decrease $E_{1/2m}$. However, this effect is overwhelmed by the second term. Because $K_R \ll 1$, the fraction $K_R/(1+K_R)$ reduces to $K_R/1$, which is very small. Thus, the negative log is positive, and the overall effect is an increase in $E_{1/2}$ in $C_{12}TAB$ and $C_{16}TAB$ micelles.

The value of K_R in $C_{12}TAB$ and $C_{16}TAB$ may be calculated using the $E_{1/2}$'s in the presence and absence of micelles. In the third term, D_R is the diffusion coefficient of Fc in the micellar solutions. Since Fc^+ does not associate with the micelles,^{2,3} its diffusion coefficient is the same as in water, and D_O may be approximated by the value for Fc in the absence of micelles. Thus, K_R may be calculated using the observed $E_{1/2}$'s and D 's in the micellar ($C_{12}TAB$ or $C_{16}TAB$) and Bu_4NBr solutions.

The situation in the SDS solution is more complicated, because Fc and Fc^+ both associate with the negative micelles. This means that the second term in equation 5 must be rewritten as $-59.2 \log \frac{K_R(1 + K_O)}{(1 + K_R)K_O}$. The net effect is that the second and third log terms both become quite

small, so that the observed $E_{1/2m}$ is not shifted much compared to $E_{1/2w}$. It is not possible to evaluate K_R and K_O numerically without additional data.³

EXPERIMENTAL METHODS

Chronocoulometry

Chronocoulometry (CC) is a potential step method, in which the voltage applied to a microelectrode is instantaneously switched from a no-reaction value to a value at which the electrode reaction goes to completion and the rate is limited by diffusion. For a planar microelectrode, an equation for the diffusion is derived by solving Fick's second law (equation 2) using the boundary conditions

$$C^e = C^b \text{ at } t = 0 \quad (8)$$

$$C^e = 0 \text{ at } t \gg 0 \quad (9)$$

$$C = C^b \text{ at } x \text{ far from the electrode surface } (x \rightarrow \infty), \quad (10)$$

In these equations, C^e is the concentration of the electrochemical species at the electrode surface ($x = 0$), and C^b is the bulk concentration ($x \rightarrow \infty$).

Prior to the start of the experiment ($t < 0$) the potential of the electrode is maintained at a value at which the species does not react. Therefore, at time zero the concentration at the electrode, C^e , is equal to the bulk concentration, C^b (equation 8). At time zero, the potential is stepped to give a voltage sufficient to ensure complete reaction at the electrode surface. The concentration at the surface rapidly decreases to zero (equation 9). However, the concentration of the bulk solution is not affected as long as there is no stirring and the vessel is much larger than the electrode.

The mathematical result satisfying these conditions is given by:

$$C(x, t) = C^b \sqrt{\frac{z}{\pi}} \int_0^x \frac{1}{\sqrt{Dt}} e^{-z^2/2} dz \quad (11)$$

The seemingly formidable expression on the right is just the integrated form of the Gaussian curve with a lower limit of zero, because the diffusing species does not exist on the "negative" side of the electrode. The student may be accustomed to seeing the expression

$$\frac{1}{\sqrt{2\pi}} \int_{-\varepsilon/\sigma}^{+\varepsilon/\sigma} e^{-z^2/2} dz \quad \left(\text{or equivalently, } \sqrt{\frac{z}{\pi}} \int_0^{+\varepsilon/\sigma} e^{-z^2/2} dz \right)$$

which gives the probability of an observation within a certain number of standard deviations, σ , from the mean. When evaluated for ε/σ equal to one, the result is 0.68. In the case of diffusion, the upper bound (x / \sqrt{Dt}) is the distance from the surface in units of \sqrt{Dt} . Evaluation of the integral shows that, at the distance \sqrt{Dt} , the concentration of the solution is just 0.68 times the bulk concentration.

Experimentally the quantity which is measured is the current through or the charge collected by the electrode as a function of time. For a half-reaction involving transfer of n moles of electrons per mole of electroactive species, the current at any given time is

$$i = nF \frac{dN}{dt} \quad (12)$$

in which F is Faraday's constant. Substitution from Fick's first law gives

$$i = nFAD \frac{\partial C}{\partial x}, \quad (13)$$

which must be evaluated at $x = 0$ (i.e. at the electrode surface). (Note: The sign of i is determined by the half reaction at the working electrode. By convention, a positive current corresponds to a reduction.)

Equation 11 is differentiated as follows:

$$\begin{aligned}
 \left(\frac{\partial C}{\partial x}\right)_t &= C^b \frac{\frac{\partial}{\partial x} \int_0^{\frac{x}{\sqrt{Dt}}} e^{-z^2/2} dz}{\frac{\partial x}{\partial x}} \\
 &= C^b \left[\frac{\frac{\partial}{\partial x} \left(e^{-\left(\frac{x}{\sqrt{Dt}}\right)^2/2} \cdot \frac{1}{\sqrt{2Dt}} \right)}{\frac{\partial x}{\partial x}} \right]_{x=0} \\
 &= \frac{C^b}{\pi^{1/2} D^{1/2} t^{1/2}} .
 \end{aligned} \tag{14}$$

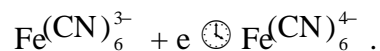
When inserted into equation 13, this gives the simple result

$$i = \frac{nFAD^{1/2}C^b}{\pi^{1/2}t^{1/2}} . \tag{15}$$

This equation may be integrated from time 0 to time t to give the total charge, Q, collected over the measurement period:

$$Q = \frac{2nFAD^{1/2}C^b t^{1/2}}{\pi^{1/2}} \tag{16}$$

Equation 16 shows that for a given electrode and solution, a plot of Q versus $t^{1/2}$ should give a straight line through the origin. The slope is equal to $2nFA\pi^{-1/2}D^{1/2}C^b$. Thus, if the electrode area is known, the diffusion coefficient can be calculated from the slope. Direct measurement of the electrode dimensions can give an approximate value of A, but surface irregularities usually cause the effective area for the electrochemical process to be considerably different. It is best to determine A by calibration of the electrode system with a solution of a species of known diffusion coefficient. The calibrant of choice is ferricyanide, which undergoes a reversible reduction to ferrocyanide:



At 25 °C the D values (\pm sigma) for $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ in 0.10 M KCl are $(7.63 \pm 0.05) \times 10^{-6}$ and $(6.50 \pm 0.02) \times 10^{-6}$ cm²/s, respectively.⁴

Cyclic Voltammetry

In cyclic voltammetry (CV) the current through a microelectrode is measured continuously as the potential is scanned through a voltage range in both the forward and reverse directions. The meanings of "forward" and "reverse" depend on the half-reaction at the microelectrode. For a reduction, the forward direction is towards more negative voltage; the opposite holds for an oxidation. A typical cyclic voltammogram is shown in Figure 2.

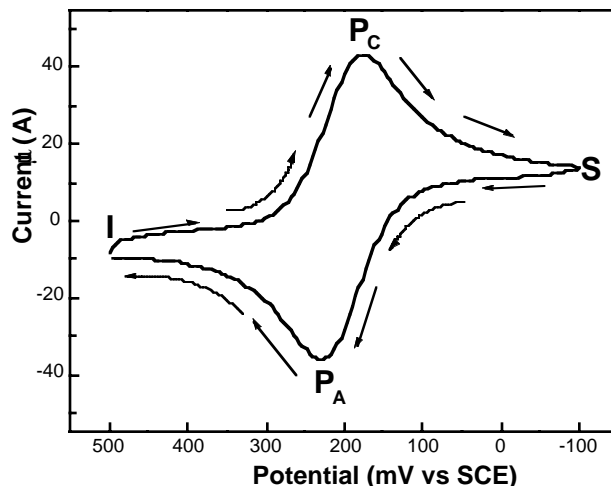
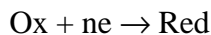


Figure 2. Cyclic voltammogram for 10mM $\text{Fe}(\text{CN})_6^{3-}$ in 0.5 M KCL. The voltage was scanned linearly from +500 mV to -100 mV at 50 mV/s. Note that the arrows in the figure attempt to show the time evolution of the output and do not correspond to the direction of the electron flow.

The CV may be explained in terms of a general reduction half-reaction:



(In the figure, Ox is $\text{Fe}(\text{CN})_6^{3-}$ and Red is $\text{Fe}(\text{CN})_6^{4-}$.) Starting at initial point I, the applied potential is first too positive to cause Ox to be reduced. Proceeding from I to S, the current increases as the potential is made less positive (or more negative, as the case may be), and Ox starts to be reduced. At P_C the forward (cathodic) current is maximum, because the rate of the reduction process is maximum. Past the peak, the current decreases, because the diffusion rate is not great enough to maintain a sufficient quantity of Ox at the electrode surface.

At point S, called the switching potential, the direction of the potential scan is reversed. The current continues to be positive (Ox continues to be reduced) for a brief segment of the reverse scan. Eventually, however, the potential is again sufficiently positive for the reduced

form, which has accumulated around the electrode as a result of the reduction process, to be reoxidized. The anodic current reaches its most negative value at P_A , where the rate of the oxidation process is most rapid. When the concentration of the accumulated Red has depleted, the current again decays to about zero. For a reversible electrode reaction it can be shown that $E_{PA}-E_{PC}$ is theoretically equal to $59/n$ mV, where n is the electron change. In most cases the value is slightly larger ($\Delta E_p \sim 60-70$ mV for $n = 1$). Another important parameter is the average of E_{PA} and E_{PC} which gives the half-wave potential, $E_{1/2}$, for the half-reaction.

Obtaining a cyclic voltammogram is a necessary part of a chronocoulometry experiment. As explained above, in CC the potential must be stepped from a voltage (V1) where little or no current flows to a value (V2) at which the current is diffusion limited. Referring to the CV for $Fe(CN)_6^{3-}$ shown in the figure, good choices would be 400 mV for V1 and 0 mV for V2.

The diffusion coefficient can also be obtained from CV measurements using the Randles-Sevcik equation, given here without derivation:

$$i_p = 0.4463nFAc \left(\frac{nF}{RT} \right)^{1/2} D^{1/2} v^{1/2} \quad (17)$$

In equation 17, i_p is the peak current in amperes, and v is the potential scan rate in V/s. For a one-electron transfer at 25° C, this becomes:

$$i_p = 2.69 \times 10^5 ACD^{1/2} v^{1/2} \quad (18)$$

Cyclic voltammograms are obtained at a series of voltage scan rates and a plot of peak current versus $v^{1/2}$ is prepared. The plot should be linear with zero intercept. The slope is equal to $2.69 \times 10^5 ACD^{1/2}$. Thus, the value of D can be obtained if the electrode area is known. A scan rate study of the ferricyanide system provides the data needed to calculate the area.

In voltammetric studies, it is imperative that the potential of the working electrode (the planar rough pyrolytic graphite, RPG, microelectrode in this case) be known and controlled. Modern electrochemical setups use a three-electrode system for this reason. The potential of the working electrode is measured relative to a constant reference, the saturated calomel electrode, SCE. The current is measured through another circuit containing the working electrode and a platinum wire auxiliary electrode. The potentiostat in the Bioanalytical Systems BAS 100A Electrochemical Analyzer controls the working/SCE voltage at the desired value. The instrument has internal software for acquisition and analysis of a large variety of electrochemical measurements, including CV and CC used in this experiment.

PRE-LAB EXERCISE

1. In this experiment, a planar RPG electrode with a 2.0 mm x 2.5 mm rectangular surface is used in a solution which is about 0.0010 M in $K_3Fe(CN)_6$ and 0.1 M in KCl. Assuming that the effective electrode area is the same as the geometric area, use equation 16 to calculate the

expected slope (in $(\mu\text{C})(\text{ms})^{-1/2}$) of the CC plot. Also, use equation 17 (not 18) to calculate the slope of the Randles-Sevcik plot.

- Using the Initial E, High E, and Low E values specified in procedure steps 2 and 7, sketch the approximate CV's for ferricyanide in 0.1 M KCl and ferrocene in 0.1 M C_{12}TAB . Referring to Figure 2, use arrows to show the time evolution of the data, and label the initial and switching potentials and the two peak potentials. Use 170 mV and 200 mV for the approximate $E_{1/2}$'s of $\text{Fe}(\text{CN})_6^{3-}$ and ferrocene, respectively.

PROCEDURE

- The major source of experimental problems in electrochemical work is a coated electrode surface. The instructor will polish the electrode prior to lab using a rotating grinding surface of 600 mesh SiC paper. (Hand grinding is possible, but the electrode surface will produce less reproducible results.) After grinding, the electrode must be sonicated for several minutes in deionized water. Use a ruler or calipers to measure the dimensions of the planar electrode surface.
- Fill the thermostatted cell with the 10^{-3} M $\text{K}_3\text{Fe}(\text{CN})_6$ solution. (Be sure to record the exact concentration of this and all other solutions. Estimated concentration uncertainties for all solutions are $\pm 1\%$ RSD.) Turn on the electrochemical analyzer. After entering the date and time, specify the cyclic voltammetry (CV) mode. Use the following acquisition parameters: Initial E = 500 mV; High E = 500 mV; Low E = -100 mV; Scan Rate = 50 mV/s; Sweep Segments = 2; Sensitivity = 10^{-5} A/V. In the BAS 100A, the CG (Change General parameters) command may be used if these need to be altered. Type R <return> to initiate the scan. After the run, use the B command to adjust the full scale and the QD command to obtain a hardcopy. Use the X command to obtain the anodic and cathodic peak potentials and currents. Choose the initial and final potentials for chronocoulometry from the CV. Make sure these are suitable for both the forward and reverse reactions.
- Repeat the CV measurements at the following scan rates: 5, 10, 20, 40, 60, 80, 100, 125, 150, 200, 400 mV/s. Obtain the peak potentials and currents, but do not print the CV's. Stir the solution briefly between runs.
- Use the CM (Change Mode) and CC (Chronocoulometry) commands to change to the chronocoulometry experiment. Specify the potentials chosen above and a Pulse Width of 250 ms. The default Sensitivity should be OK. Type R <return> as above. At the end of data acquisition, obtain the slopes and intercepts of the forward and reverse processes with the X command. (Pages 4.10-1 through 4.10-5, 5.3-3 and 5.4-5 of the BAS manual explain how these values are obtained. Be sure to note the units.) Obtain at least 4 good data sets for these and all subsequent CC measurements. Agitate the solution briefly between acquisitions.

5. Place the $\text{K}_3\text{Fe}(\text{CN})_6$ solution in the designated waste container. Clean the cell and electrodes with deionized water and blot dry. Then, fill the cell with the 0.1 M KCl, and repeat the CC measurements. Use the same potentials as those chosen for the ferricyanide runs. Clean and dry the cell and electrodes.
6. Pipet 10 mL 0.10 M C_{12}TAB /0.10 M NaCl into the cell. Perform CC measurements using 0 and +300 mV for the initial and step potentials. (Why is the step to a more positive value?)
7. Turn on the magnetic stirrer and use a pipetting device to add 400 μL of the 0.03 M ferrocene stock solution (prepared in ethanol). Obtain a CV using the following parameters: Initial E = -100 mV; High E = 500 mV; Low E = -100 mV; Scan Rate = 50 mV/s; Sweep Segments = 2; Sensitivity = 10^{-5} V/A. Obtain a hardcopy of the voltammogram. Use it to verify that the potentials used for CC in step 6 were good choices.
8. Perform a scan rate study using the scan rates specified in step 3.
9. Perform CC measurements using the potentials specified in step 6. Clean the cell and electrodes, but save the solution in a beaker or vial in case additional measurements are needed.
10. Repeat steps 6-9 with 10 mL 0.10 M C_{16}TAB / 0.10 M NaCl. Use the same potentials.
11. Repeat step 6 with 10 mL 0.10 M tetrabutylammonium bromide, $(\text{C}_4\text{H}_9)_4\text{N}^+\text{Br}^-$. Use +75 mV and +225 mV for the initial and step potentials.
12. Repeat steps 7 and 8, but add only 20 μL of the ferrocene stock solution, and use 400 mV for the high E. Visually observe the solution to be sure no precipitate forms. (This concentration is very close to the solubility limit in the absence of micelles.) Note that it may not be possible to obtain data at low scan rates.
13. Repeat step 9 (CC measurements) using +75 and +225 mV for the potentials.
14. Repeat step 6 with 10 mL 0.10 M SDS/0.10 M NaCl. Use +75 mV and +225 mV for the initial and step potentials.
15. Repeat steps 7 and 8, using 400 μL of ferrocene and 400 mV for the high E. Note that adsorption is a problem, and it may not be possible to obtain useful data at the very low scan rates. The CC measurements are not feasible due to the adsorption problem.
16. Verify that no further measurements are needed. Then place all ferrocene solutions in the appropriate waste container, and clean all glassware and electrodes. Leave the SCE and auxiliary electrode in 0.1M KCl. Leave the RPG electrode in air.

DATA ANALYSIS

1. Using the measured dimensions, calculate the geometric area of the electrode and its 95% confidence limits.
2. Using the ferricyanide data, prepare a plot of i_{pc} versus the square root of the scan rate. Use the known diffusion coefficient for $\text{Fe}(\text{CN})_6^{3-}$ and equation 18 to calculate the effective electrode area and its 95% confidence limits.
3. Using the CC data from Procedure steps 4 and 5, subtract the average forward slope for 0.10M KCl from the average forward slope for ferricyanide to obtain the corrected forward slope and 95% confidence limits. (Note: The reverse slopes will not be used for any of the CC runs.) Use equation 16 to calculate the effective electrode area and 95% confidence limits.
4. For each ferrocene solution, calculate $E_{1/2}$ and the 95% confidence limits.
5. Use the scan rate data for the ferrocene solutions and the effective electrode area obtained in step 2 to calculate the diffusion coefficient of ferrocene in the four different environments and the 95% confidence limits.
6. Use the CC data for the micellar electrolytes to correct the corresponding CC slopes for the ferrocene solutions. Calculate the diffusion coefficients for Fc using the electrode area obtained step 3.
7. Calculate the value of K_R in the C_{12}TAB and C_{16}TAB solutions.

DISCUSSION

Compare the effective electrode areas obtained by CV and CC to each other and to the geometric area, and discuss any differences.

Compare the diffusion coefficients for Fc obtained by CV and CC to each other and to literature values.^{2,3} Compare the $E_{1/2}$ values to those in the literature.^{2,3,5,6} (Note that values may depend on the identity of the added salt, NaCl in this experiment.) Discuss the relative magnitudes of the diffusion coefficients, the $E_{1/2}$'s, and the K_R 's in terms of the micellar environment.

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