

# Micelles in the Physical Chemistry Laboratory: Diffusion Coefficients and Half-Wave Potentials of Ferrocene

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The special properties of surfactants are important in a wide variety of applications in chemistry, biology, engineering, materials science, and other areas. These molecules are amphiphilic (amphiphathic); that is, they have distinct polar and nonpolar functionalities. Surfactants commonly form aggregates, which can be layered structures as in phospholipid membranes, or enclosed globules called micelles (1). The presence of micelles can have marked effects on thermodynamic favorability and reaction kinetics (2) as well as on many physical properties. A variety of articles on micelles, located via an online search for "micelle" in the title field, have appeared in this *Journal*. We have developed a new physical chemistry experiment, which demonstrates the effects of micelles on diffusion coefficients and voltammetric half-wave potentials.

Diffusion is important in many physicochemical processes, including reaction kinetics, electrochemistry, and chemical separations. The chemical education literature contains descriptions of several undergraduate experiments on diffusion coefficients of aqueous solutes using various procedures and chemical systems (3–16). This new experiment involves two electrochemical approaches: cyclic voltammetry (CV) and chronocoulometry (CC). The experiment reinforces lecture material on diffusion and introduces students to CV and CC. The chemical system, ferrocene in several different micellar environments, also demonstrates the effects of micellization on the diffusion process.

## Background

Cyclic voltammetry is described in analytical chemistry books (17–19) and texts on electrochemistry (20), as well as several *JCE* articles (21–22). The most important features of the CV curve are the cathodic and anodic peak potentials,  $E_{pc}$  and  $E_{pa}$ , and the associated peak currents. The average of  $E_{pc}$  and  $E_{pa}$  is the voltammetric half-wave potential,  $E_{1/2}$ . The diffusion coefficient,  $D$  ( $\text{cm}^2 \text{s}^{-1}$ ), of the electroactive species is given in the equation for the peak current,  $i_p$  in amperes, of a reversible system, often called the Randles–Sevcik equation:

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

In eq 1,  $n$  is the electron change,  $F$  is Faraday's constant,  $C$  is the concentration of the bulk solution in  $\text{mol cm}^{-3}$ ,  $R$  is the gas constant,  $T$  is the absolute temperature,  $A$  is the effective electrode area in  $\text{cm}^2$  (usually quite different from the geometric area, owing to surface irregularities), and  $\nu$  is the potential scan rate in  $\text{V s}^{-1}$ . The diffusion coefficient is determined by measuring the peak current for a series of scan rates (e.g., 5 to 200  $\text{mV s}^{-1}$ ). A plot of  $i_p$  versus  $\nu^{1/2}$  is prepared;  $D$  can be calculated from the slope if the electrode area is known.

The value of  $A$  is obtained from a similar plot for a species, usually ferricyanide, with known diffusion coefficient (23).

Chronocoulometry is an alternative electrochemical method for measuring diffusion coefficients (24, 25). The working electrode is initially held at a potential,  $V_i$ , at which there is no electrode reaction. It is then stepped to  $V_f$ , at which the reaction goes to completion at the electrode surface, and after a few hundred milliseconds the potential is stepped back to  $V_i$ . While the electrode is held at  $V_f$ , the total charge,  $Q$ , in coulombs, passed through the electrode is measured as a function of time,  $t$ , in seconds. For a planar working electrode, the relationship of charge to time is the integrated Cottrell equation:

$$Q = 2nFAC\pi^{-1/2} D^{1/2} t^{1/2} \quad (2)$$

which is derived from Fick's laws in the student handout.<sup>W</sup> The slope of a plot of  $Q$  versus  $t^{1/2}$  can be used to determine  $D$  after calibrating the electrode area from CC measurements of ferricyanide. It is also necessary to correct for the contribution from the supporting electrolyte by subtracting the average slope for  $Q$  vs  $t^{1/2}$  data of the electrolyte alone. This correction procedure is somewhat prone to uncertainty, and some authors prefer the CV method for this reason (26). However, in an undergraduate experiment, it is instructional to have students determine the diffusion coefficients by two methods and compare the results.

## Overview of the Experiment

Cyclic voltammetry and chronocoulometry are easily implemented on modern electrochemical instrumentation.<sup>1</sup> Because of the inherent speed of these procedures compared to other diffusion coefficient experiments (hours or days in several of the references listed above), students are able to measure a number of diffusion coefficients in a single laboratory period. In particular, they observe the importance of solution environment on the behavior of ferrocene,  $(\text{C}_5\text{H}_5)_2\text{Fe}$  (Fc), which is oxidized to the ferricenium ion,  $(\text{C}_5\text{H}_5)_2\text{Fe}^+$  ( $\text{Fc}^+$ ). Students investigate two cationic surfactants, dodecyltrimethylammonium bromide ( $\text{C}_{12}\text{TAB}$ ) and cetyltrimethylammonium bromide ( $\text{C}_{16}\text{TAB}$ ), and an anionic surfactant, sodium dodecylsulfate (SDS) (each in the presence of 0.10 M NaCl), as well as a simple background electrolyte, tetrabutylammonium bromide,  $\text{Bu}_4\text{NBr}$ . Because of the limited aqueous solubility of ferrocene, the latter sample is only ca.  $6 \times 10^{-5}$  M, and the data are very noisy. The neutral compound is readily incorporated in the nonpolar micelle interiors, allowing concentrations of ca.  $1 \times 10^{-3}$  M to be used in the surfactant systems. Thus, students observe the importance of surfactants as solubilizing media, as well as the effects of micelle size and charge on both the diffusion coefficient of the ferrocene molecule and the  $E_{1/2}$  of the  $\text{Fc}^+/\text{Fc}$  couple.

A major concern in electrochemistry is the electrode surface, and several materials were tried. For the student laboratory, Pt and glassy carbon proved to be inconvenient because they often required repeated cleaning during the laboratory period. The most reliable and reproducible material has been rough pyrolytic graphite (RPG) sealed in a glass tube with epoxy. Before each laboratory, the ca. 0.045-cm<sup>2</sup> surface is cleaned with 600 grit SiC paper and sonicated in deionized water, but no further treatment is needed.

According to the procedure, students first obtain background readings on 10.00 mL of the surfactant solution. They then add a 400- $\mu$ L (20  $\mu$ L for Bu<sub>4</sub>NBr) aliquot of 0.03 M Fc in ethanol and obtain the data for ferrocene. This procedure circumvents direct dissolution of solid ferrocene, which is slow even in the presence of micelles. Periodic checks by UV-vis spectrophotometry have indicated that ethanolic Fc solutions are stable for several months.

## Results and Discussion

Typical data for both the CV and CC studies are shown in Table 1, together with literature values obtained in similar media. Chronocoulometry cannot be performed on the SDS solutions, because there is noticeable adsorption of Fc<sup>+</sup> on the electrode surface (27). Since the adsorption peak occurs after the anodic maximum (more positive potential), the scan rate study is still possible. As shown in Table 1, separation of the anodic and cathodic maxima is acceptable for a one-electron reversible system (59 mV theoretically).

For the most part, the diffusion coefficients obtained by CV and CC are in reasonable agreement with each other and with literature values. Students observe that the diffusion coefficients are much smaller in the presence of micelles than in water. Partitioning of the neutral compound into the hydrophobic micelle interior slows its movement. Students also compare the results for the SDS, C<sub>12</sub>TAB, and C<sub>16</sub>TAB solutions and observe that, within experimental uncertainty, the diffusion coefficients are equal in SDS and C<sub>12</sub>TAB, which both have 12-carbon hydrophobic chains. However, the diffusion coefficient in C<sub>16</sub>TAB is well below that for the two smaller surfactants, owing to the larger overall size of the C<sub>16</sub>TAB micelle (31–34).

Students are also asked to discuss the  $E_{1/2}$  results. There is qualitative agreement with literature values. The order of  $E_{1/2}$ 's in the four systems is SDS  $\leq$  H<sub>2</sub>O < C<sub>12</sub>TAB < C<sub>16</sub>TAB. This indicates that oxidation of Fc to Fc<sup>+</sup> is less favorable (more properly, reduction of Fc<sup>+</sup> is more favorable) in the presence of positively charged C<sub>12</sub>TAB and C<sub>16</sub>TAB micelles than in water or negative SDS micelles. These results may be attributed to the decrease in concentration of the free ferrocene in solution when the molecule associates with the micelle. For positively charged C<sub>12</sub>TAB and C<sub>16</sub>TAB micelles, the Fc<sup>+</sup> remains in the aqueous part, and the  $E_{1/2}$  may

be modeled by a relatively simple equation (28, 29), which is derived in the student instructions. The situation is more complicated in the SDS solution, because both Fc and Fc<sup>+</sup> associate with the negatively charged micelles.

## Safety Concerns (35)

**CAUTION:** Ferricyanide is toxic if swallowed or by skin contact, and ferrocene is harmful if swallowed, but the masses used are very small. The surfactants and Bu<sub>4</sub>NBr are present at macro levels, however, and are classified as irritants to the skin, eyes, and (except for SDS) the respiratory system. SDS and C<sub>16</sub>TAB are harmful if swallowed. Therefore, students need to practice reasonable caution while performing this experiment, and waste should be collected for disposal by a suitable authority.

## Conclusion

The determination of diffusion coefficients and half-wave potentials is an excellent instructional experiment for the physical chemistry laboratory. Students gain experience with both cyclic voltammetry and chronocoulometry and are able to compare the results obtained by the two methods. The studies in surfactant solutions clearly show that physical properties can be varied in a micellar environment.

## Supplemental Material

Supplemental material for this article is available in this issue of *JCE Online*.

**Table 1. Half-Wave Potentials and Diffusion Coefficients for Ferrocene in Water and Micellar Solutions**

Surfactant	Electrolyte	$\Delta E_p/mV$ ( $E_{pa} - E_{pc}$ )	$E_{1/2}/mV$	$D/10^{-6} \text{ cm}^2 \text{ s}^{-1}$
None	0.1 M Bu <sub>4</sub> NBr <sup>a</sup>	55 $\pm$ 4	170 $\pm$ 6	38.4 $\pm$ 15.5 (CV) 18.5 $\pm$ 1.4 (CC)
	0.2 M Li <sub>2</sub> SO <sub>4</sub> (28)		165 $\pm$ 5	7.0 (CV)
	0.1 M NaCl (29)		155 $\pm$ 5 <sup>b</sup>	6.7 <sup>c</sup>
0.10 M C <sub>12</sub> TAB	0.1 M NaCl <sup>a</sup>	66 $\pm$ 3	199 $\pm$ 2	2.27 $\pm$ 0.21 (CV) 2.01 $\pm$ 0.12 (CC)
	0.2 M Li <sub>2</sub> SO <sub>4</sub> (28)		232	1.4 (CV)
	0.1 M KBr (30)		—	0.83 (CV)
0.10 M C <sub>16</sub> TAB	0.1 M NaCl <sup>a</sup>	72 $\pm$ 4	212 $\pm$ 2	0.88 $\pm$ 0.07 (CV) 1.20 $\pm$ 0.07 (CC)
	0.2 M Li <sub>2</sub> SO <sub>4</sub> (28)		242	0.92 (CV)
	0.1 M KBr (30)		—	0.22 (CV)
	0.1 M NaCl (29)		230 <sup>b</sup>	0.76 <sup>d</sup>
	0.1 M phosphate, pH 7 (27)		261 $\pm$ 12	—
	0.10 M NaCl (26)		239 $\pm$ 2	0.87 (CV)
0.10 M SDS	0.1 M NaCl <sup>a</sup>	66 $\pm$ 4	157 $\pm$ 2	1.92 $\pm$ 0.19 (CV)
	0.05 M NaCl (30)		—	0.59 (CV)
	0.1 M NaCl (29)		150 <sup>b</sup>	0.782 <sup>d,e</sup>
	0.1 M phosphate, pH 7 (27)		181 $\pm$ 12	—
	0.1 M NaCl (26)		153 $\pm$ 2	1.1 (CV)

<sup>a</sup>Typical results for this experiment; uncertainties as 95% confidence limits. <sup>b</sup>Potentials vs AgCl/Ag (satd NaCl). <sup>c</sup>Calculated from the Stokes-Einstein equation. <sup>d</sup>Limiting current measurements (Lewich equation). <sup>e</sup>0.138 M SDS.

## Note

1. The University of Florida laboratory has a BAS 100A Electrochemical Analyzer (Bioanalytical Systems, Inc., West Lafayette, IN, <http://www.bioanalytical.com>), which is equipped with all necessary software for implementation of both CV and CC. An alternate vendor is Cypress Systems, Inc., Lawrence, KA, <http://www.cypresshome.com>.

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