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THE ELECTROCHEMICAL CHARACTERIZATION OF FERROCENE AS A GUEST MOLECULE IN THE PRESENCE OF β -CYCLODEXTRIN

Anne T. Roberson

Abstract

This experiment involves the development of electrochemical experimental methods for the determination of the oxidation/reduction potentials of a guest ferrocene complex ($C_{10}H_{10}Fe$) hosted by β -cyclodextrin. The project was conducted so that the specific interaction of two molecules forming a unique inclusion compound can be used as a model for rapid analysis of other small molecules. In principle, the study is based on the expected equilibrium interaction of the iron compound with β -cyclodextrin resulting in a complexed and an uncomplexed species equilibrium. The project's experimental objective is to determine if the redox potentials of both complexed and uncomplexed iron compounds are influenced sufficiently by β -cyclodextrin to allow simultaneous determination of the redox potentials in equilibrium mixtures. This analysis will allow the determination of equilibrium constants for interaction of guest molecules with β -cyclodextrin.

Introduction

Cyclodextrins are a series of cyclic compounds constructed from at least six units of linked glucose. (β -cyclodextrin, the one under consideration, is made up of seven linked glucose units.) Cyclodextrins are torus-shaped molecules with central cavities in which guest molecules of suitable size can be accommodated. The requirement for this inclusion formation appears only to be spatial, because all kinds of guest molecules, ranging from molar to ionic in character, are accepted. One of the most distinctive characteristics of cyclodextrins is that they are hydrophilic outside owing to the primary and secondary hydroxyl groups occupying both rims, and they are hydrophobic within the cavity because it is lined by hydrocarbon groups and ether-like oxygens.¹

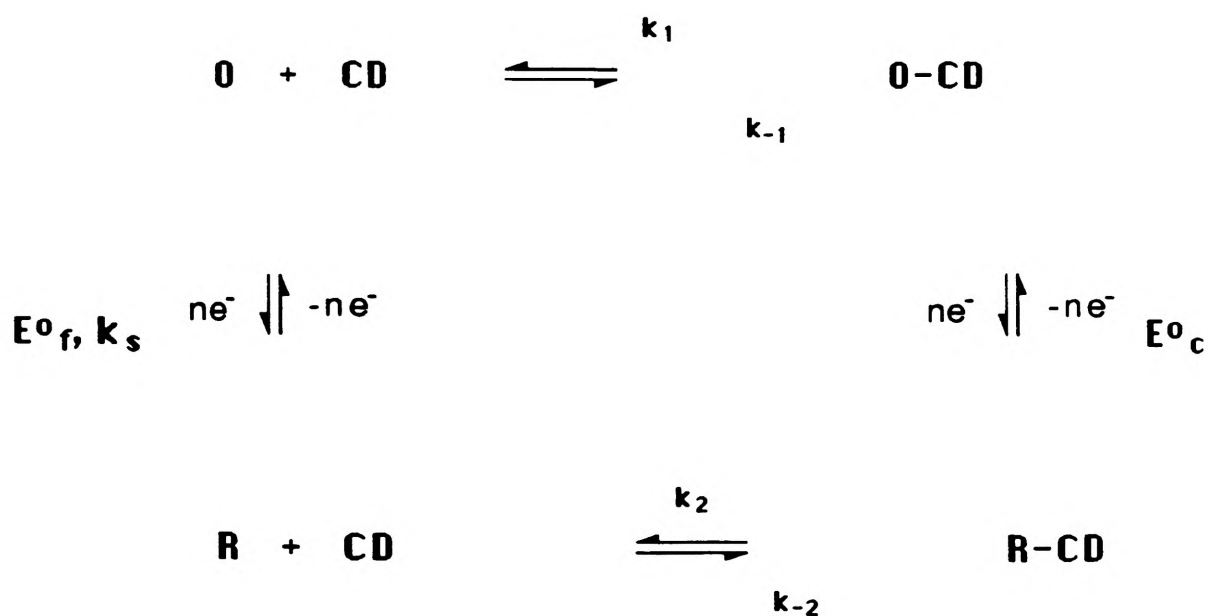
The inclusion reaction is promoted due to recognition of the guest molecules based on their size. It is also promoted upon hydrophobic interaction between the non-polar cyclodextrin interior and the guest molecule created on accommodation of the guest in the cyclodextrin cavity from the polar environment outside the cyclodextrin. Cyclodextrins become a host for guest molecules, and if the guests are electroactive in nature, this inclusion phenomena influences the electrochemistry of the guest molecules. This can be measured by cyclic voltammetry.

A cyclic voltammogram is analogous to conventional spectrum in that it conveys information as a function of an energy scan. Cyclic voltammetry is perhaps the most versatile electroanalytical technique for the study and identification of electroanalytical species.² It consists of cycling the potential of an electrode, which is immersed in an unstirred solution, and measuring the resulting current. Its effectiveness results from its capability for rapidly observing the oxidation/reduction (redox) potential over a wide potential range. The potential of the working electrode is controlled versus a reference electrode such as a saturated calomel electrode. The controlling potential which is applied across the two electrodes can be considered an excitation signal. A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan.³ A salt is used in the solution as a supporting electrolyte.

Cyclic voltammetry is capable of rapidly generating a new oxidation state during the forward scan, and then reducing the sample or producing a new species after the reverse scan. With a reversible reaction, the cyclic voltammogram forms a sort of square mechanism⁴ (Fig. 1).

Figure 1

The Square Mechanism



E°_c, E°_f ; Formal Potential

k_s ; Standard Electron Transfer Rate

O, R; Oxidized and Reduced Species

To perform a set of viable cyclic voltammetry experiments, two things must first be done. An appropriate test procedure must be developed, and an effective electrode cleaning procedure must be found.

Experimental

Ultra-clean (electrochemical grade) dimethyl formamide was found to be an appropriate solvent, and tetrabutylammonium fluoroborate was used as the supporting electrolyte. Ferrocene is the inclusion compound discussed because it depicts theoretical trends. It formed a documented inclusion compound with β -cyclodextrin,⁵ which resembles this (Fig. 2).

The testing procedure was as follows:

1. The electrode cleaning procedure was implemented. (This consisted of a documented, three-step process⁶ entailing treatment with aqua regia, pulsing, and flaming.)
2. All glassware was cleaned.
3. The solutions to be tested were prepared.
4. The fixed amount (25 mL) of solution was measured out and placed in the testing cup.
5. The liquid was flushed with Argon gas, in order to deoxidize the solution.
6. The scan was run.

Results and Discussion

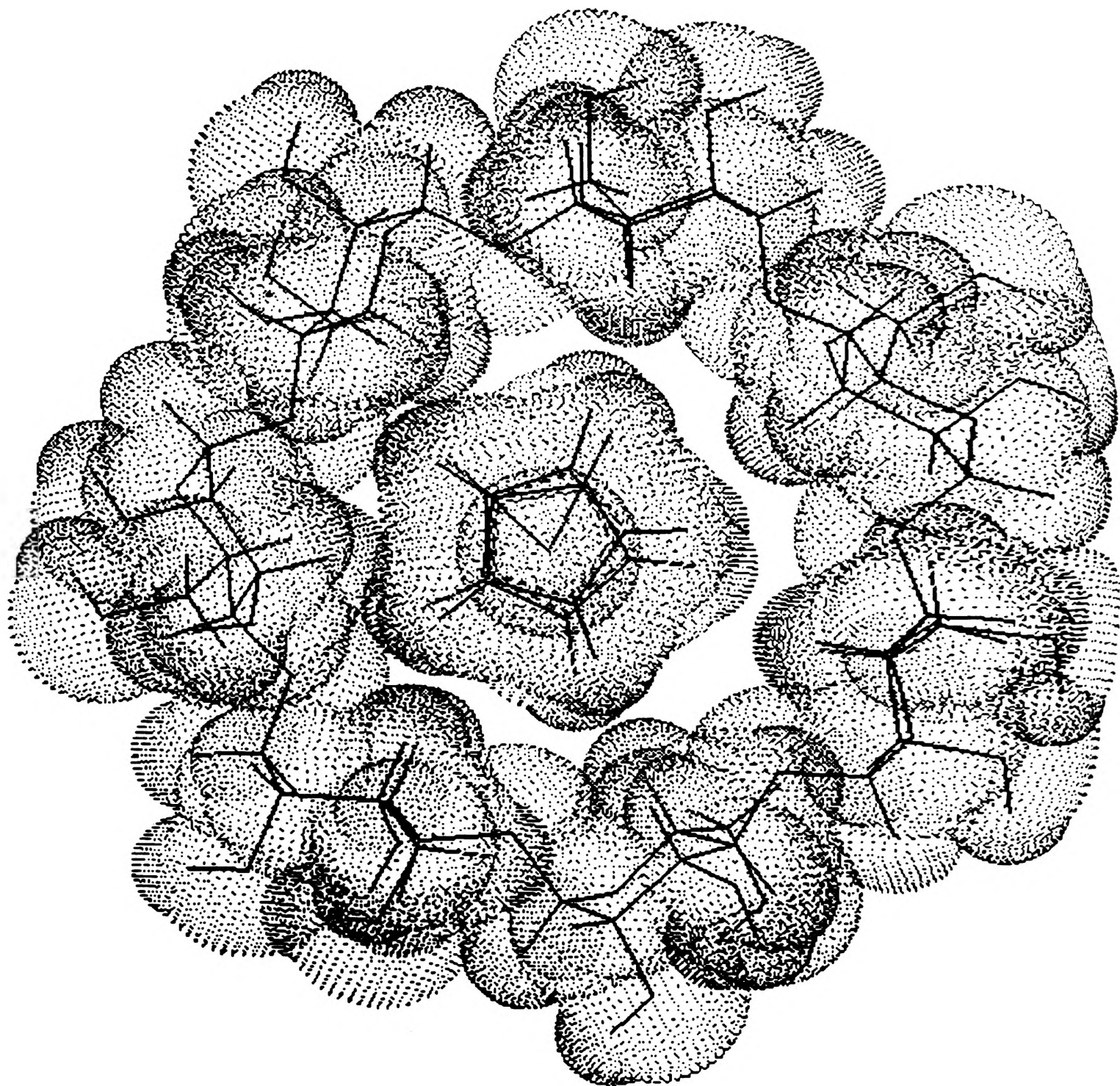
Inclusion phenomena do influence the electrochemistry of an electroactive guest molecule.⁷ Inclusion phenomena are usually characterized by the formation constant (equilibrium constant) and the formation rate constant (dissociation constant). When the guest molecule is electroactive, an electrochemical method is applicable for determining these constants and sometimes this method is superior to other methods, because information, not only on the substrate, but also on the electrogenerated species formed after the electron transfer reaction, can concurrently be obtained.

The shape of the voltammogram is sensitive to the heterogeneous electron transfer rate between the substrate and electrode, and also to the dissociation and formation rates. As demonstrated by the β -cyclodextrin/ferrocene data (Fig. 3), the addition of cyclodextrin to the electrolyte solution caused a decrease in the peak current.

Since cyclodextrin is a large macrocyclic compound, incorporation of a small guest molecule in the bulky cyclodextrin makes the apparent diffusivity of the guest lower. Diffusivity has the dimensions of a length times a velocity; obviously the greatly increased mass of the inclusion compound will slow any movement. Taking advantage of this phenomena, the formation constant of the inclusion complex can be easily determined by quantitative treatment of the variation of the peak current with a cyclodextrin concentration in solution.⁴ A much higher cyclodextrin concentration (an order of magnitude of about twenty times higher than that of the guest compound concentration) insures that all of the guest molecule goes into the inclusion state.

There is one more demonstrable change in the electrochemical nature of a transorganic metal upon the addition of cyclodextrin, and this is a shift in the apparent half-wave potential. This shift is dependent on the concentration of cyclodextrin. Detailed analysis of

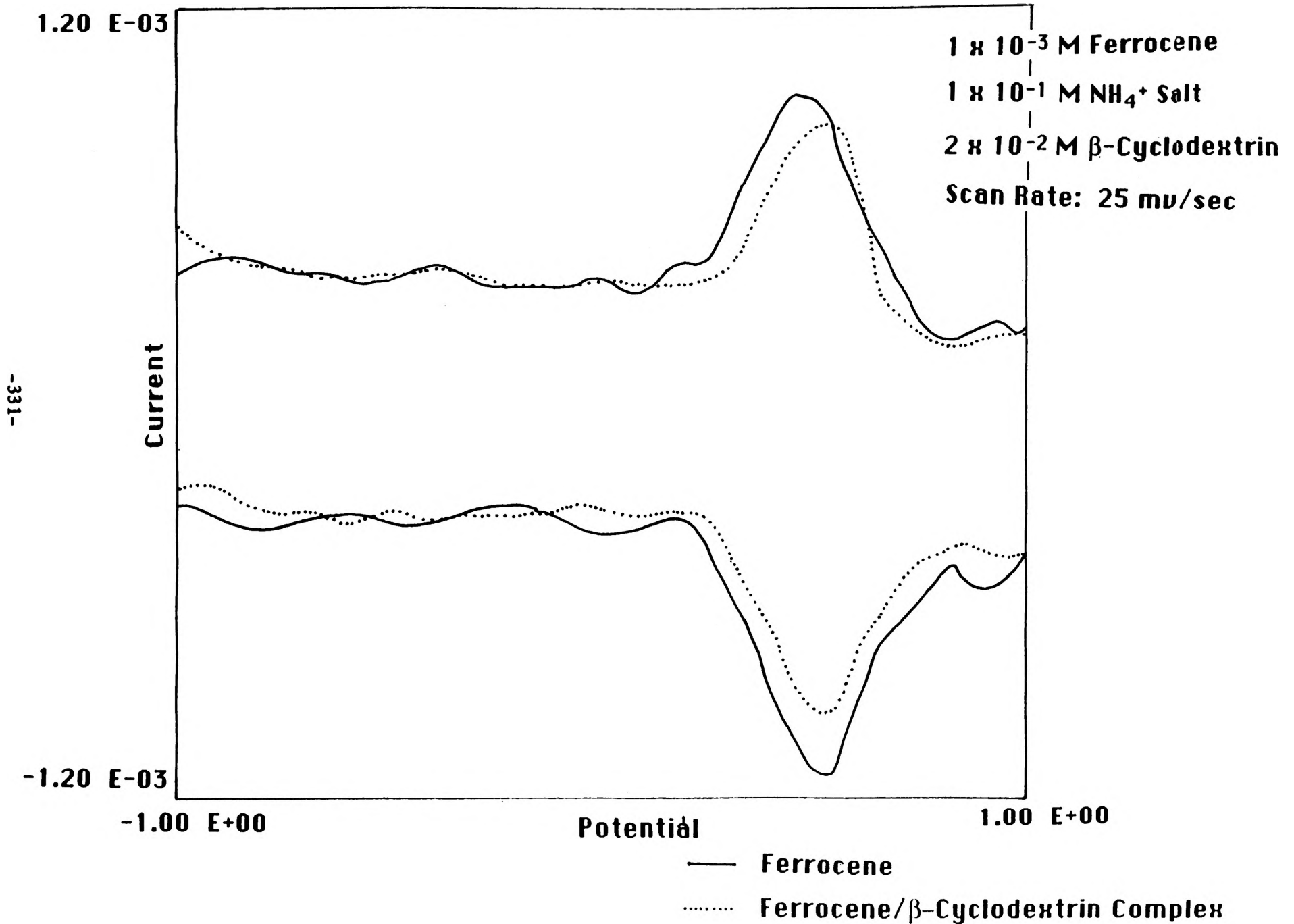
Figure 2



Ferrocene/ β -Cyclodextrin Inclusion Compound

Figure 3

Ferrocene/ β -Cyclodextrin Cyclic Voltammograms



this shift can also lead to the equilibrium constants of the cyclodextrin complexes.⁴ This was also readily observable in the β -cyclodextrin/ferrocene data (and can be seen in Figure 3).

Conclusion

The objectives of this study were to:

1. Discover the electrochemical conditions needed to monitor β -cyclodextrin and an inclusion compound.
2. Demonstrate the theoretical shift in electroanalysis of an active species upon bonding with β -cyclodextrin.

These were met successfully.

A third objective was to determine the equilibrium constant of the β -cyclodextrin/organometallic bonding. This is the point to which research has culminated. Future developments will include: the actual determination of the equilibrium constant for the ferrocene inclusion compound, the study of how species concentration affects the equilibrium constant, and expansion to consider other transorganometallic guest molecules.

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