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Evidence for Adsorption of the Cobaltocenium Cation and Precipitation of Uncharged Cobaltocene at the Platinum Microelectrode–Acetonitrile Interface in the Absence of Supporting Electrolyte

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The reduction of the cobaltocenium cation (Cc^+) to uncharged cobaltocene (Cc^0) and to the cobaltocenium anion (Cc^-) has been studied voltammetrically in acetonitrile in the presence and absence of supporting electrolyte using platinum microdisk electrodes of radii from 0.5 to 6 μm. In the presence of supporting electrolyte, the voltammetry is observed as two well-separated diffusion-controlled one-electron-reduction processes $Cc^+ + e^- \rightleftarrows Cc^0$ and $Cc^0 + e^- \rightleftarrows Cc^-$. However, precipitation of neutral cobaltocene formed as a result of the initial one-electron-reduction process and possibly adsorption of Cc^+ appears to be induced by the removal of supporting electrolyte. The precipitation leads to rapid electrode passivation at the reversible $Cc^{+/0}$ electrode potential and gives rise to the observation of a stochastic process at very small microelectrodes at more negative potentials. The voltammetry in the presence of electrolyte in higher dielectric solvent media such as water and dimethyl sulfoxide in which cobaltocene is known to be insoluble also exhibits features analogous to those observed in acetonitrile in the absence of electrolyte. The electrochemical behavior in the absence of supporting electrolyte is therefore consistent with the interfacial solvent having a higher dielectric constant than bulk solvent at negative potentials where reduction of the cobaltocenium cation takes place.

INTRODUCTION

Presently, there is considerable experimental and theoretical interest in undertaking voltammetric studies under steady-state conditions with electrolyte as well as in the absence of deliberately added supporting electrolyte or in the presence of very low concentrations of electrolyte.[1-24] The ohmic (iR) drop problem encountered in the absence of added electrolyte is commonly minimized via the use of steady-state measurements at microdisk electrodes having radii of the order of 5 μm.[1] The presence of electroreactant-electroproduct migration under steady-state conditions is usually accounted for by incorporating migration terms into the Nernst–Plank equations for mass transport,[2-13] and for some electrode processes, incorporation of migration terms into the theory has resulted in excellent agreement between experiment and theory.[7-11] However, discrepancies between experimental data and theory still exist in other systems even when the theory includes both diffusion and migration terms.[7,8,12,14] The identification of an increasing number of apparently anomalous results[8,14] implies that factors additional to mass transport may be altered when electrochemical experiments are performed in the absence of added electrolyte. In the case of oxidation of ferrocene, Drew et al.[12] proposed that convection terms should be added to the theory when only low levels of electrolyte are present. However, convection will not explain the other apparently anomalous data[7,8,14] so that further studies without electrolyte appear to be warranted.

In this paper, the anomalous voltammetry observed for the reduction of the cobaltocenium cation, Cc^+, in the absence of electrolyte is described in detail in acetonitrile at microdisk electrodes having variable radii. The initial one-electron-reduction process to form cobaltocene, Cc^0, is diffusion controlled in the presence of electrolyte. However, at very small radii microdisk electrodes data are consistent with cobaltocene precipitation onto the electrode surface and probably adsorption of Cc^+ *when no supporting electrolyte is present*. That is, the solvent properties in the absence of

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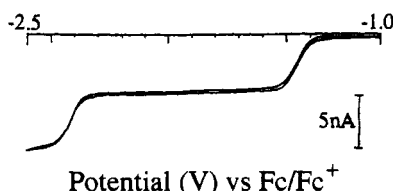(24) Oldham, K. B. *J. Electroanal. Chem.* 1992, *337*, 91.

Figure 1. Reduction of 1×10^{-3} M Cc^+ in acetonitrile (0.1 M Bu_4NPF_6) at a 5.8-μm glassy carbon disk microelectrode. Scan rate 10 mV s^{-1}.

electrolyte are modified at the electrode surface to the point where precipitation and nucleation of cobaltocene occurs at the solvent–electrode interface even though cobaltocene is extremely soluble in the bulk solvent. Finally, data in higher dielectric solvents such as water and dimethyl sulfoxide are presented to demonstrate that the behavior in acetonitrile without electrolyte has some analogies to that found in higher dielectric media.

EXPERIMENTAL DETAILS

Chemicals and Solvents. Cobaltocenium hexafluorophosphate and cobaltocene were synthesized and purified as described in the literature.[25] Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was synthesized by metathesis of tetrabutylammonium bromide (Aldrich) and potassium hexafluorophosphate (Aldrich) and purified by recrystallization three times from hot absolute ethanol followed by vacuum drying. Tetrabutylammonium tetrafluoroborate (Bu_4NPF_4) and lithium sulfate were obtained from Southwestern Analytical Chemicals (electrochemical grade) and BDH (analytical grade), respectively, dried under vacuum, and stored in a desiccator prior to use. Dimethylsulfoxide (Mallinckrodt, ChromAR HPLC grade) and formamide (Merck, Pro analysis grade) were used as received. Acetonitrile (Malinckrodt, ChromAR HPLC grade) was dried by passing down a 15 × 3 cm column of 4-Å Linde molecular sieves under nitrogen followed by a 15 × 3 cm column containing 70–230 mesh ASTM Merck neutral aluminium oxide under nitrogen. Both columns were activated at 200 °C under vacuum. The solvent was stored in a sealed flask under nitrogen containing 4-Å Linde molecular sieves. The procedure of White et al.[10] indicated that the ionic impurity level in acetonitrile was less than 10^{-6} M. Since this concentration is considerably less than the cobaltocenium hexaflurophosphate concentration used in all experiments, it is considered unlikely that ionic impurities contribute to data reported in this paper. Reagent-grade dichloromethane was distilled from calcium hydride and then treated in manner similar to that described for the acetonitrile solvent. Water was obtained from a Millipore 25TS reverse osmosis water purification system.

Instrumental Details. Voltammetric data were acquired at 20 ± 1 °C with either a Cypress Model CYSY-1 electroanalysis system using the cyclic staircase mode with a 1-mV step or a BAS Model 100A electrochemistry system used in conjunction with a BAS Model PA-1 preamplifier. For microelectrode experiments, a single-compartment cell with a conventional three-electrode arrangement was used where both counter and reference electrodes were platinum wires and the working electrodes were platinum or glassy carbon disk microelectrodes fabricated in these laboratories. A quasi-platinum reference electrode was used instead of a conventional reference electrode in order to minimize adventitious leakage of electrolyte from the reference electrode compartment. In some experiments in aqueous media, conventionally sized glassy carbon (area 0.021 cm^2) and Metrohm Model E411 hanging mercury drop (area ~0.02 cm^2) electrodes were employed. In organic solvents, the electrochemical cell was connected to a vacuum/nitrogen line for deoxygenation. High-purity CIG nitrogen was used after further purification by passing over two activated Ridox columns and one Linde 4-Å molecular sieve column. Sufficient deoxygenation was acquired after four to seven pump–purge cycles. Any volume lost during the evacuation procedures was corrected for by addition of more solvent. The background current obtained with the above purification procedures was negligible over the potential range

of interest in this work (+1.0 to -2.4 V vs Pt) In some of the solutions, ferrocene was added as an internal standard.

RESULTS AND DISCUSSION

(a) Mass Transport in the Presence and Absence of Added Electrolyte. In many solvents, the reduction of Cc^+ takes place[26] in two reversible electron-reduction steps as shown in eqs 1 and 2

$$Cc^+ + e^- \rightleftarrows Cc^0 \qquad (1)$$

$$Cc^0 + e^- \rightleftarrows Cc^- \qquad (2)$$

Under steady-state conditions, and in the presence of electrolyte, the limiting current for the two reduction steps in eqs 1 and 2 are diffusion controlled and for a disk electrode have equal limiting currents given by eq 3

$$i_d = 4nFCDr \qquad (3)$$

where i_d is the diffusion-controlled limiting current, n is the number of electrons in the charge-transfer step, F is the Faraday constant, C is the bulk concentration, D is the diffusion coefficient, and r is the electrode radius. Theoretically, in the absence of any specific double-layer effects and after correction for any influence of ionic strength on the diffusion coefficient, the limiting current for the first reduction step (eq 1) is expected to increase 2-fold when the supporting electrolyte is removed because of the contribution of the migration current associated with a cation (Cc^+) being reduced at a negatively charged electrode.[7,11,13] However, the theory for the second step is rather complex as the net process involves the reduction of a cation to an anion,[9,13,24] although at least in principle very large currents can be predicted.[24]

(b) Voltammetry in Acetonitrile. Bulk acetonitrile solvent has a dielectric constant of 37.5.[27] Voltammograms at a glassy carbon microdisk electrode for the reduction of Cc^+ in acetonitrile containing 0.1 M Bu_4NPF_4 as the electrolyte are shown in Figure 1. As expected from eqs 1 and 2, two reversible processes having equal limiting currents are observed at low scan rates where steady-state conditions prevail. Voltammograms at platinum microdisk electrodes of 6-, 1-, and 0.5-μm radii also were acquired with and without added electrolyte in acetonitrile solution containing 0.8 mM Cc^+. A 0.4 mM ferrocene (Fc^0) solution was used as either an internal[7] or external standard. The data obtained for reduction of Cc^+ were shown to be independent of the presence of Fc^0, so that the Fc^+/Fc^0 process could be used as a convenient internal standard.[7] With the above-mentioned concentrations of Cc^+ and Fc^0 in the presence of 0.1 M Bu_4NPF_6 electrolyte, and with electrode radii over the range 0.6–6 μm, the limiting current for both reduction process of Cc^+ (eqs 1 and 2) and the oxidation of Fc^0 (eq 4) while opposite in sign, were found to be equal in magnitude and obey eq 3.

$$Fc^0 \rightleftarrows Fc^+ + e^- \qquad (4)$$

Since eq 3 applies, this equivalence of the Cc^+ reduction and Fc^0 oxidation limiting currents is as theoretically expected because the diffusion coefficient of Fc^0 is approximately twice that for Cc^+[7,11] in acetonitrile (0.1 M Bu_4NPF_6), but the concentration Fc^0 is only half that of Cc^+. In Figure 2A a voltammogram for the reduction of 0.8 mM Cc^+ and oxidation of 0.4 mM Fc^0 in acetonitrile is shown without Bu_4NPF_6 electrolyte with a 6-μm-radius platinum microdisk electrode and using a scan rate of 10 mV s^{-1}. Under these conditions, a limiting current is reached for both oxidation of Fc^0 and

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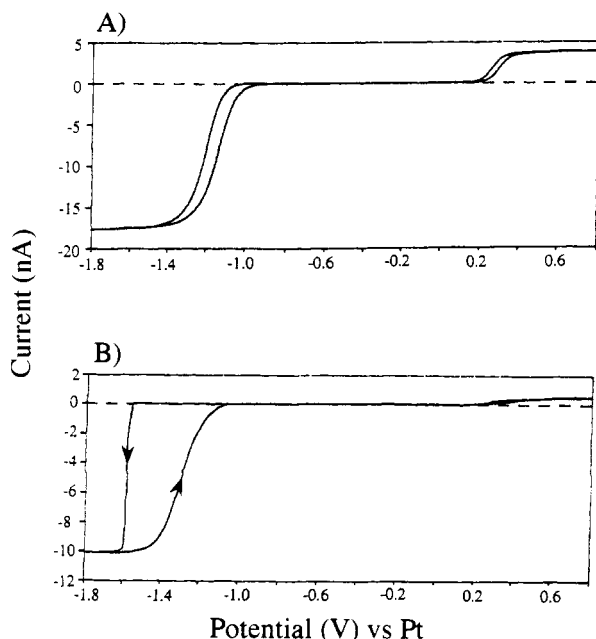(27) Sawyer, D. T.; Roberts, J. L. Experimental Electrochemistry for chemists; Wiley: New York, 1974; Chapter 4.

Figure 2. Reduction of 8 × 10⁻⁴ M Cc⁺ and oxidation of 4 × 10⁻⁴ M Fc in acetonitrile at (A) a 6- and (B) a 1-μm-radius platinum disk microelectrode in the absence of supporting electrolyte at a scan rate of 10 mV s⁻¹. Potential program is 0 mV/800 mV/−1800 mV/0 mV. The scans are consecutive with no electrode cleaning between each scan.

reduction of Cc⁺ and the magnitude of these limiting currents is independent of scan rate (10–50 mV s⁻¹) as required for a steady-state response. In the absence of added electrolyte, the ratio of the limiting current of the Cc⁺ reduction to that of the Fc⁰ oxidation at a 6-μm radius platinum microdisk electrode is approximately −4.7, which is significantly larger than the theoretically expected value of −2.[7,11] If the diffusion coefficient dependence on ionic strength were the only cause of the nonideality, the ratio would be independent of electrode radius, but as will be seen, this is not the case. Furthermore, the reduction potential relative to ferrocene has become considerably more negative, a small amount of unexpected hysteresis is observed in the forward and reverse scan directions, and there is no second reduction process prior to the solvent reduction step. In contrast, under the conditions of Figure 2A, the limiting current of the Fc⁰/Fc⁺ wave is in agreement with a diffusion-controlled theory with a diffusion coefficient of Fc⁰ in acetonitrile of (2.4 ± 0.1) × 10⁻⁵ cm² s⁻¹ so that the ferrocene oxidation process exhibits the expected characteristics when Cc⁺PF₆⁻ acts as the electrolyte.

When experiments shown in Figure 2A without added electrolyte are repeated with a smaller 1-μm-radius platinum microdisk electrode (Figure 2B), the shape, position, and normalized limiting currents of the voltammograms are all drastically changed relative to that observed at a 6-μm-radius electrode. At all scan rates examined (10–50 mV s⁻¹), both the Cc⁺ and Fc⁰ processes achieve limiting currents, but now the limiting current ratio for reduction of Cc⁺ and oxidation of Fc⁰ to is about −20. In addition, the onset of a measurable Cc⁺ reduction current now begins at a potential which is about 600 mV more negative than in the voltammograms obtained at the 6-μm-radius electrode, and the response is much steeper ($E_{1/4} - E_{3/4} \leq 30$ mV vs 60 mV in the presence of electrolyte). Finally, extensive hysteresis is now observed in the forward and reverse scans of potential. However, the decay of the Cc⁺ current back to zero on the reverse or positive potential scan direction still occurs at potentials similar to those found with the 6-μm electrode. Importantly, at all scan rates, the limiting current for the Fc⁰/Fc⁺ couple again is consistent with a diffusion-controlled process.
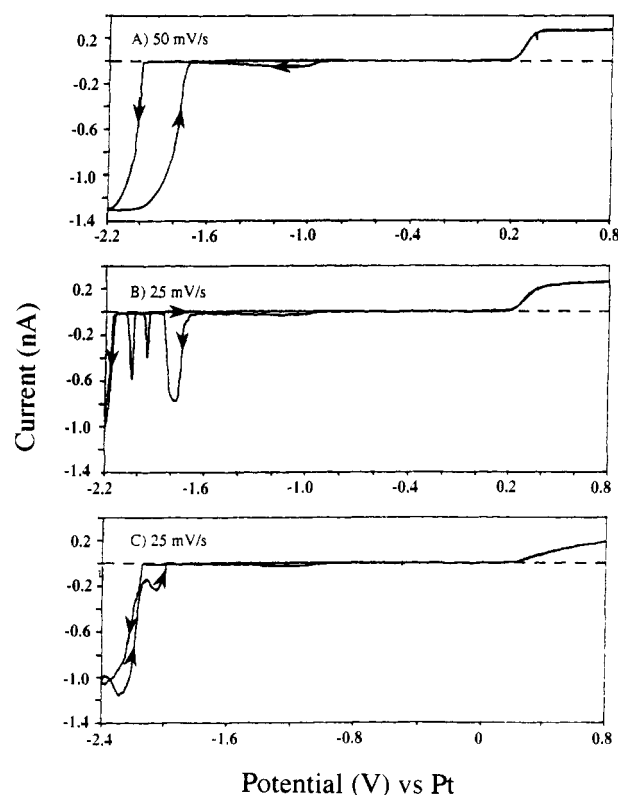

Potential (V) vs Pt

Figure 3. Reduction of 8 × 10⁻⁴ M Cc⁺ and oxidation of 4 × 10⁻⁴ M Fc in acetonitrile at a 0.5-μm-radius platinum disk microelectrode in the absence of supporting electrolyte at indicated scan rates. Potential program is 0 mV/800 mV/−1800 mV/0 mV. The scans are consecutive with no electrode cleaning between each scan.

Figure 3 shows voltammograms acquired with an even smaller 0.5-μm-radius platinum microdisk electrode in the absence of electrolyte, and it can be seen the response for reduction of Cc⁺ becomes still more complex. With a scan rate of 50 mV s⁻¹ (Figure 3A) the current rises transiently from zero as the potential approaches −1000 mV vs Pt, which is close to the value where the reversible Cc⁺/Co⁰ couple is observed in the presence of electrolyte. However, the current then decays until zero current is again reached at approximately −1600 mV vs Pt, but then increases abruptly and reaches a limiting value when a potential of about −2000 mV vs Pt is reached. On the reverse scan, the current does not decay back to zero current until a potential of about −1700 mV vs Pt is reached. In Figure 3B, where a slower scan rate of 25 mV s⁻¹ was used, the initial rise of the reduction current at −1000 mV is again followed by a return to zero current at −1600 mV vs Pt. At more negative potentials, a series of sharp current spikes is observed until the current rises to a limiting value at −2200 mV vs Pt. As shown in Figure 3C, a repeat experiment at the same scan rate shows an initial current increase at −1000 mV vs Pt followed by a return to zero current at −1600 mV vs Pt, where the current once again begins to rise and fall in what appears to have the characteristics of a classical stochastic, nucleation-precipitation process.[27] With the 0.6-μm electrode, the initial forward and reverse traces of the Fc⁰/Fc⁺ process still overlap and the limiting current remains consistent with a diffusion-controlled process, although for repeat experiments, the Fc⁰/Fc⁺ wave becomes more drawn out than for the first scan and electrode fouling is evident. For the 0.5-μm electrode, scanning to very negative potentials also results in the observation of stochastic current spikes which are not reproducible from scan to scan in the sense that they occur at random potentials (see Figure 3B,C). The sharp rise in current (Figures 2B and 3) at rather negative potentials is probably due to reduction of the
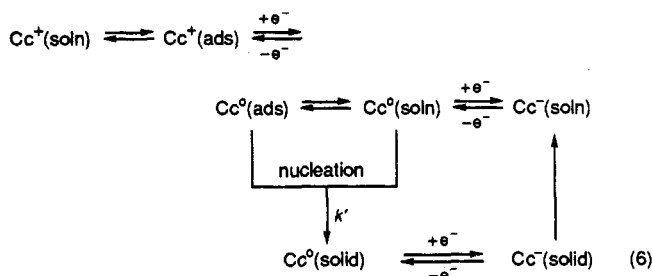
surface Cc^0 precipitate as the reduction potential of the process Cc^0 (solid) + $e^- \rightarrow Cc^-$ (soluble) is reached. The reduction of Cc^0 to Cc^- in the presence of electrolyte where all species are soluble occurs at about –900 mV vs the Cc^+/Cc^0 couple in most solvents. (Figure 1 and ref 26).

The postulated electrode processes in acetonitrile may be summarized as follows:

(a) In the presence of electrolyte the two well-separated reduction processes are both reversible (diffusion controlled) and correspond to eq 5:

$$Cc^+(soln) + e^- \rightleftharpoons Cc^0(soln) + e^- \rightleftharpoons Cc^-(soln) \qquad (5)$$
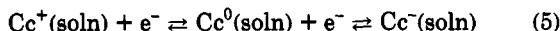
(b) In the absence of added electrolyte, the overall Cc^+ to Cc^- process can be written as the multistep mechanism presented in eq 6:

$$Cc^+(soln) \rightleftharpoons Cc^+(ads) \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}$$

$$Cc^0(ads) \rightleftharpoons Cc^0(soln) \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Cc^-(soln)$$

nucleation $\downarrow k'$

$$Cc^0(solid) \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Cc^-(solid) \qquad (6)$$

The concentration of Cc^0 also may be enhanced in the extended double-layer region in the absence of added electrolyte by the comproportionation reaction given in eq 7:

$$Cc^+ + Cc^- \rightarrow 2 Cc^0 \qquad (7)$$
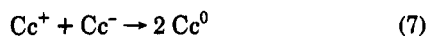
Homogeneous bimolecular reactions of this kind have been shown to have significant effects on the concentration profiles at a microelectrode at low supporting electrolyte concentrations.[9]

It is therefore postulated that the various components of the adsorption and precipitation processes that occur in the absence of electrolyte have been conveniently interrogated by using electrodes of different radii. At a 6-μm electrode, a limiting current is observed which is independent of scan rate but larger than that predicted when mass transport occurs solely by diffusion and migration. The enhanced limiting current at the 6-μm electrode can be attributed in part to the coupling of adsorption with the normal processes of mass transport, although it is possible that the single-step reduction observed in the absence of electrolyte may now involve formation of Cc^- (see later). Reduction of a cation to an anion is in fact predicted in some circumstances to produce large currents in the absence of electrolyte.[24]

When the electrode radius is decreased to 1 μm, there is an almost 40-fold reduction in the electrode area, so that single crystals of Cc^0 having an appropriate size can result in almost complete electrode coverage and concomitant electrode passivation. In fact, while no current can be detected at the Cc^+/Cc^0 reduction potential in the voltammograms shown in Figure 2B it should be noted that, by increasing the scan rate to 100 mV s^{-1}, a transient current response of about 25 pA can be detected near the reversible Cc^+/Cc^0 reduction potential (Figure 4). This result confirms that the rate of electrode blockage is rapid, but that the kinetics of precipitation may be outrun at sufficiently fast scan rates. Furthermore, as more negative potentials are reached, it is postulated that the surface precipitate (and/or adsorbed Cc^0) is reduced to Cc^- and dissolution occurs to a soluble product. At this very negative potential regime, the electrode-solution interface becomes very complex. Not only can the neutral Cc^0 at the surface be reduced, but bulk Cc^+ can migrate/diffuse to the surface and undergo a direct two-electron
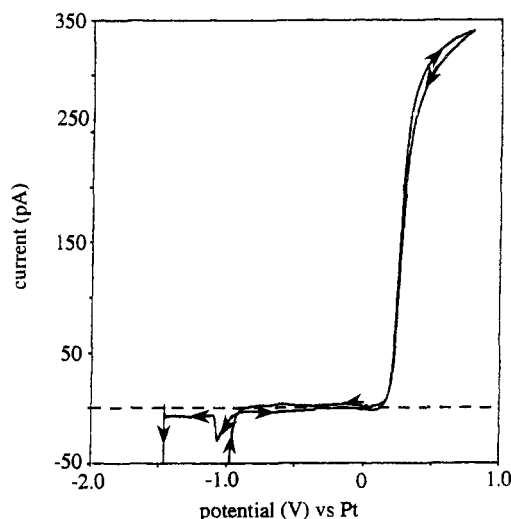

Figure 4. Reduction of 8 × 10^{-4} M Cc^+ and oxidation of 4 × 10^{-4} M Fc in acetonitrile at a 1-μm-radius platinum disk microelectrode in the absence of supporting electrolyte at a scan rate of 100 mV s^{-1}. Potential program is 0 mV/800 mV/–1800 mV/0 mV. The reverse scan of the voltammogram has been offset to show the small response obtained at –1100 mV (Cc^+/Cc^0 potential) on the forward scan.

reduction which, in the absence of electrolyte, is predicted to produce large currents.[24] In addition, the large concentration of Cc^- near the electrode surface may be involved in the comproportionation reaction mentioned in eq 7 as the soluble species diffuse and/or migrates.

At the smallest (0.5 μm) electrode examined, a transient faradaic current, which attains a value of about –50 pA (Figure 3) before decaying to zero current, is detected at the Cc^+/Cc^0 reduction potential even with a moderate scan rate of 25 mV s^{-1}. It may have been anticipated that, at the smallest electrode examined, precipitation of Cc^0 would have its most dramatic effect. However, the decrease in radius also results in an increase in the rate of radial mass transport of soluble product away from the surface, effectively leading to a lower concentration of soluble Cc^0 near the electrode surface. Consequently, even though it will only take a very small amount of precipitate to block the surface at a 0.5-μm-radius electrode, the effective rate at which this occurs at the electrode surface may be slower than with larger electrodes. Once precipitation occurs onto the electrode surface, current spikes can be occasionally observed as the crystals grow and fall from the electrode surface (Figure 3B). As would be expected, this blocking-unblocking process is observed less frequently in the shorter time scale experiments (Figure 3A, scan rate of 50 mV s^{-1}) than in longer time scale experiments (Figure 3B, scan rate of 25 mV s^{-1}). Nucleation processes at electrode surfaces have been studied in detail both theoretically and experimentally[28-31] and have been shown to be random, as is the case in this study.

Apparently, the adsorption, nucleation, precipitation, and related phenomena are all induced by removal of electrolyte from the electrode–acetonitrile solvent interface, since normal diffusion-limited current plateaus were obtained in acetonitrile in the presence of 0.1M Bu_4NPF_6 at each of the 6-, 1.0-, and 0.5-μm-radii electrodes, giving values of D_{Cc^+} of (1.3 ± 0.1) × 10^{-5} cm^2 s^{-1} and D_{Fc^0} of (2.4 ± 0.1) × 10^{-5} cm^2 s^{-1}, which is consistent with literature values.[7]

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(29) Bindra, P.; Fleischmann, M.; Oldfield, J. W.; Singleton, D. *Faraday Discuss. Chem. Soc.* **1973,** *56,* 180.
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Interestingly, the microelectrode voltammetry of cobaltocene in acetonitrile without electrolyte has some resemblance to the oxidation of Fc^0 in heptane. In their study in heptane, Murray et al.[32] reported that the oxidation currents for Fc are considerably larger than theoretically predicted steady-state values and the current decays rapidly when the potential is held at positive potentials due to formation of a passivating film of the Fc^+, which is insoluble in heptane. Furthermore, the film formation is thought to involve a nucleation period and nonquantitative precipitation of Fc^+ after the nucleation process. In heptane, Fc is soluble and the product of oxidation, Fc^+, is insoluble, so the parallel with reduction of soluble Cc^+ to what appears to be insoluble Cc^0 is expected if the proposed mechanism is correct.

A feature of data obtained in the absence of electrolyte is the apparently much lower solubility of cobaltocene at the electrode–acetonitrile interface than is the case in bulk solvent. This is intriguing since Cc^0 was found to be soluble at *molar concentrations* in bulk acetonitrile solvent, while the surface concentration of Cc^0 in the absence of supporting electrolyte, assuming mass transport occurs solely by diffusion and migration, should be <2 mM.[7] It appears that the key to unraveling this apparent dilemma may lie in the modified double-layer region that exists in the absence of supporting electrolyte, since normal diffusion-controlled limiting currents were obtained for all experiments performed in the presence of 0.1 M Bu_4NPF_6 supporting electrolyte.

(c) Voltammetry in Other Solvents. On the basis of the above results, it is reasonable to propose that the adsorption of Cc^+ and the small solubility *at the electrode surface* in the absence of supporting electrolyte could arise from an enhancement of the solvent dielectric within the double-layer region at the negative potentials where Cc^+ is reduced. For example, if the dielectric constant were to be raised to the value associated with solvents such as water, where Cc^0 is insoluble, then this would provide an explanation of the voltammetry in acetonitrile without electrolyte. With this concept in mind, voltammetry at a conventional hanging mercury drop electrode and a glassy carbon microelectrode was studied in water. The negative potential range available at platinum electrodes in water makes mercury and carbon the preferred electrode materials to study the reduction of Cc^+ in water. Figure 5A shows that, in water, and with a concentration of 1×10^{-3} M, the reduction of Cc^+ to Cc^0 passivates a mercury electrode surface in a very similar fashion to that observed in acetonitrile at a microelectrode in the absence of electrolyte. However, at lower concentrations of Cc^+, the voltammetry in water is simplified to that given by eqs 2 and 3 (Figure 5B,C). Similarly, at a conventionally sized glassy carbon electrode, reduction of Cc^+ (Figure 5D) has many of the features of the voltammetry in acetonitrile without electrolyte.

Data in dimethyl sulfoxide also were obtained and shown to have many of the features of voltammetry in acetonitrile without electrolyte. Voltammograms for reduction of 0.5 mM Cc^+ and oxidation of 0.5 mM Fc were obtained at a 6-μm-radius Pt electrode in dimethyl sulfoxide, which has a dielectric constant of 46.7.[27] In the presence of 0.1 M Bu_4NPF_6 electrolyte, the expected diffusion-limited current was obtained in both processes, with values of $D_{Fc} = 6 \times 10^{-6}$ cm^2 s^{-1} and $D_{Cc^+} = 3 \times 10^{-6}$ cm^2 s^{-1} being obtained using eq 4. That is, the diffusion coefficient for cobaltocenium is half that of ferrocene in dimethyl sulfoxide,[7] as is the case in the acetonitrile. In the absence of supporting electrolyte, it would again be predicted that the Cc^+/Cc limiting current would increase 2-fold due to migration whereas the Fc^0/Fc^+ ferrocene
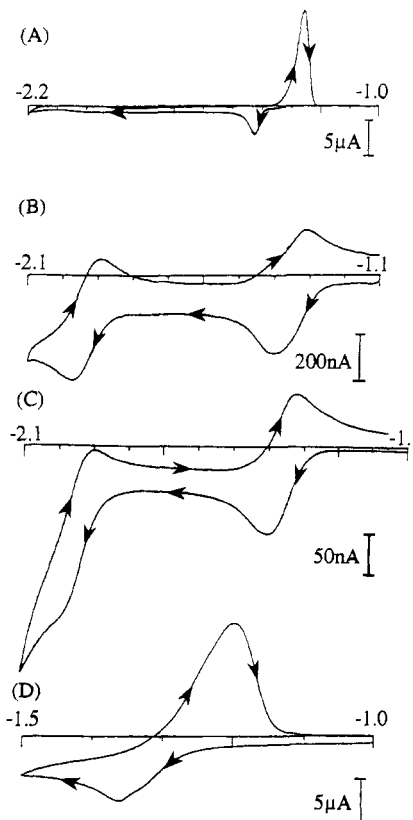
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Figure 5. Cyclic voltammograms for reduction of Cc^+ in water at 0.1 M Li_2SO_4 at (A–C) a conventionally sized hanging mercury drop: (A) 1×10^{-3} M, scan rate 100 mV s^{-1}; (B) 1×10^{-4} M, scan rate 100 mV s^{-1}; (C) 5×10^{-5} M, scan rate 10 mV s^{-1}; (D) a conventionally sized glassy carbon electrode (1×10^{-3} M, scan rate 100 mV s^{-1}).

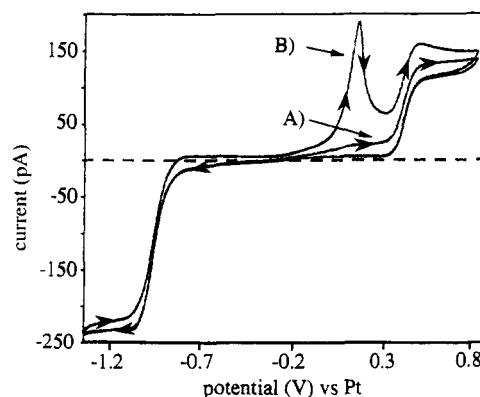**Figure 6.** Reduction of 5×10^{-4} M Cc^+ and oxidation of 5×10^{-4} M Fc in dimethyl sulfoxide in the absence of supporting electrolyte at a 6-μm-radius platinum disk microelectrode using a scan rate of 30 mV s^{-1}. For scan A, the potential program was 0 mV/800 mV/–1350 mV/0 mV. For scan B, the potential program was 0 mV/–1350 mV/800 mV/0 mV.

limiting current would remain essentially independent of electrolyte concentration. However, as was the case in acetonitrile, the Cc^+ limiting current in the absence of electrolyte is significantly larger than the theoretically expected value (Figure 6A). This again can be attributed in part to adsorption of Cc^+, which is not significant when electrolyte is present. Furthermore, a peak-shaped response can be seen on the reverse scan direction after reduction of Cc^+ (Figure 6B) which can be attributed to the oxidation of adsorbed or precipitated Cc produced at the electrode surface.

Given the complexity observed in the voltammetry in higher dielectric solvents, it was of interest to examine the reduction of Cc^+ in a low dielectric solvent in the presence and absence of electrolyte. The steady-state voltammograms obtained
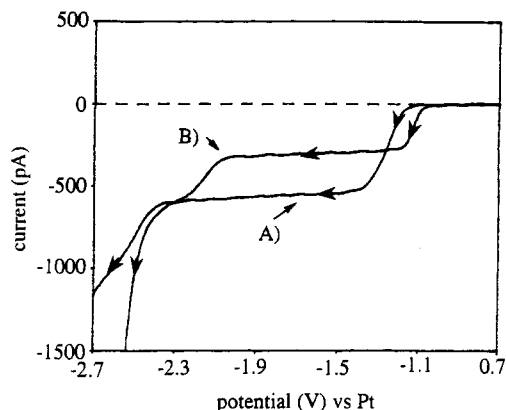
Figure 7. Reduction of 5 × 10⁻⁴ M Cc⁺ in dichloromethane in (A) the absence and (B) the presence of 0.1 M BU₄NPF₆ at a 1-μm-radius platinum disk microelectrode and a scan rate of 10 mV s⁻¹.

for the reduction of the cobaltocenium cation (Cc^+) to neutral cobaltocene (Cc) and to anionic Cc^- in dichloromethane at a 1-μm-radius Pt microdisk electrode in the presence and absence of any supporting electrolyte are shown in Figure 7. In this solvent, the theoretically expected 2-fold enhancement for the Cc^+/Cc^0 process is confirmed easily by noting that the limiting current for the first process in the absence of electrolyte is essentially equal to the sum of the limiting current for both processes in the presence of electrolyte. Dichloromethane, which has a low dielectric constant of 8.93,[27] therefore represents a voltammetrically ideal case, in both the presence and absence of added electrolyte. Presumably, changes in dielectric properties of this solvent are insufficient to cause Cc^0 to exceed its solubility and it is possible that ion pair formation inhibits adsorption of Cc^+.

Further support for the need to invoke a modified interfacial solvent region to explain voltammetry without added electrolyte may be gained from consideration of data reported very recently.[8] Experimental data on a wide range of charged species confirmed that for electrode reactions that occurred at moderately positive or negative potentials the limiting current in the absence of added electrolyte was enhanced or suppressed by migration (relative to the diffusion-controlled value) to within experimental error of the values predicted by the conventional model. However, for several processes, and particularly for those occurring at very positive potentials, a dramatic deviation from theory based on mass transport by diffusion and migration was found. For these compounds, it is possible that the existence of a polarized solvent layer may also provide a rationalization of the large suppression of current observed for the oxidation of several complexes in the absence of added electrolyte[8] since the effects of a modified solvent dielectric are predicted to be enhanced at *high redox potentials*. While we have tried to minimize water contamination, its presence at trace concentrations also could modify the double-layer region.

(d) The Double Layer in the Absence of Electrolyte. In conventional electrochemical experiments it is assumed that added electrolyte is present and that a potential dependent double layer involving the solvent and ions from the electrolyte is established in the electrode–solution interfacial region. Reference 33 may be consulted for general details of the many theoretical models that have been proposed to describe the double layer.

Classical theories of the double-layer region at the electrode–solution interface may be classified as primitive or nonprimitive, depending on the way in which polarization of

solvent molecules is deemed to contribute to the interfacial profile and as to how the ion distribution is represented.[34] Primitive models assume that the first monolayer of solvent adjacent to the electrode can be treated theoretically as a dielectric of varying permitivity, with the remainder of the solution being composed of ions embedded in a dielectric continuum having the bulk dielectric constant of the solvent. In nonprimitive models, distribution functions are calculated for solvent molecules as well as for ions, with the inclusion of appropriate interaction energies between species constituting the double layer.[34]

Most experimental data reported to date have been interpreted on the basis of primitive models in which the inner-layer capacitance has been described as a function of the overall metal electrode–solution potential difference or the surface charge, and electrode metal and nature of the solvent relationships [see refs 35–42 for example].

In all the double-layer models, the electrode is assumed to be in contact with an electrolyte solution containing molecules of the solvent and positive and negative ions of the electrolyte. The electrode–solution interfacial region is then considered to be populated with dipoles of the solvent oriented at the surface in a manner dependent on the electrode surface charge and any intrinsic affinity the electrode material may have for the solvent. Coupled with the interaction of the electrode surface with adjacent solvent dipoles is a potential-dependent adsorption of ions which themselves strongly interact with the solvent.[42]

From the above discussion it is obvious that the double-layer situation, even for the simple case when electrolyte is present, represents a very complex one. Rigorous theoretical treatments of even this conventional situation require consideration of the orientation (polarization) behavior of solvent dipoles as a function of electrode potential or surface charge and the influence of charge- and potential-dependent concentrations of charge species present.[33,40,41]

Most studies concerning microelectrode voltammetry have neglected to specifically explore consequences of the modified double layer in the absence of added electrolyte. However, it is well recognized that, with very low electrolyte concentrations, the diffuse layer will extend much further into the solution than when electrolyte is present at the commonly employed 0.1 M or higher concentration level.[2,11,20] Indeed, with a sufficiently small microelectrode and without added electrolyte, the diffuse double-layer region is expected to extend a very long way from the electrode interface,[42] and in this sense, it may be of even greater significance than in conventional studies conducted in the presence of electrolyte.

In the case of the voltammetry of Cc^+ in acetonitrile at a microelectrode, Cc^+ itself and its counterion (PF_6^-) and ions from self-dissociation of acetonitrile and from adventitious impurities will be present and all of these ions may contribute to an electrochemical double layer. Consequently, a modified form of solvent may be present in the absence of added electrolyte and could exert a profound influence on the voltammetry relative to the case when high concentrations of added electrolyte are present. Similarly, in the absence of

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a conventional compact double layer, it follows that adsorption of the electroactive species, particularly if they are charged, may be greatly enhanced. Thus, modifications relative to the case when electrolyte is added to both adsorption and solubility of electroactive components may occur.

Nonpolar, symmetrical, organometallic metallocenes such as ferrocene and cobaltocene, as is the case with the majority of nonpolar organic molecules, are highly soluble in organic solvents of relatively low polarity such as aromatic hydrocarbons, chlorinated hydrocarbons, and nitriles. However, in higher dielectric solvents such as water, dimethyl sulfoxide, or formamide, ferrocene and cobaltocene are only sparingly soluble or insoluble. Consequently, reduction of the soluble Cc^+ in the absence of electrolyte would be predicted to lead to formation of insoluble Cc^0 at the electrode surface if the kinetics of precipitation of Cc^0 are sufficiently rapid and the dielectric properties of the solvent are appropriate. Furthermore, if a sufficiently small microelectrode is used under steady-state conditions, then the probability of observing an individual nucleation and precipitation event[28] is optimized, as elegantly demonstrated in refs 29–31. Consequently, the combination of absence of electrolyte and steady-state microelectrode voltammetry may provide an optimal electrochemical combination to experimentally observe a dielectric-induced precipitation phenonmenon. Finally, in the absence of a compact double layer, adsorption of Cc^+ at the negative potentials, where it is reduced, is likely to be enhanced. In accordance with the above arguments, the data obtained at sufficiently small electrodes for the reduction of Cc^+ in acetonitrile without added electrolyte are consistent with adsorption of Cc^+ and precipitation of Cc^0 at a small-radius platinum microdisk electrode, which are induced by modification of the solvent dielectric in the absence of added electrolyte.

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