work, zinc acetate was used for the preparation of ZnO crystals, and adsorbed actate groups were found to strongly influence the visible luminescence. If other precursor compounds were used, one might expect different luminescence behavior.

A better understanding of the role of organic ligands in luminescence phenomena may lead to the development of luminescent semiconducting sensors for these ligands. The mechanisms of visible luminescence and the effects of different adsorbates, however, must be investigated further.

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Electron Transfer between Amphiphilic Ferrocenes and Electrodes in Cationic Micellar Solution

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Standard heterogeneous electron-transfer rate constants (k') for ferrocene (Fc) esters attached to the 2- and 5-carbon atoms (I and II) away from nitrogen on the hydrocarbon chain of dodecyltrimethylammonium ions were similar to each other and to ferrocene (Fc) in homogeneous organic solvent. However, in micellar solutions of cetyltrimethylammonium bromide (CTAB), differences were found for k' in the order Fc > I > II. Activation free energies from temperature dependences of k' and microenvironmental polarities from spectroscopic studies were similar for I and II in CTAB solutions, suggesting similar reorganization energies. The distance dependence of k' in micellar solution was consistent with predictions of Marcus theory using a through-space model with average distances of electron transfer estimated from molecular dynamics or a through-bond model assuming bonding of head groups to the electrode. Results suggest that CTAB adsorbed to the electrode helps to orient the electroactive surfactants with alkylammonium head groups down on the Pt surface prior to electron transfer. Electron transfer to Pt from Fc in cationic micellar solutions occurs over a shorter distance than for I.

Introduction

Electrochemistry in micellar media has received significant interest over the past two decades. Among various applications, micellar media have been used for redox titrations of proteins,¹ electrochemical synthesis and analysis,² and reductive dehalogenation of organohalide pollutants.³⁻⁵ Despite these applications, the exact way in which electrons are exchanged between micelle-bound solutes and electrodes is unclear.

Predissociation mechanisms have been used with some success to explain electrochemical results in which the solutes are physically bound to micelles. Ohsawa suggested that 5,10-dimethyl-5,10-dihydrophenazine in alkyltrimethylammonium solutions dissociates from the micelle before electron transfer. Eddowes and Gratzel⁷ concluded that tetrathiofulvalene dissociates from cationic micelles before accepting an electron from a Pt electrode. A predissociation mechanism explains both the solute and surfactant concentration dependence of electrochemically measured diffusion coefficients.8 These reports present convincing evidence that in certain cases dissociation of the reactant from the micelle occurs prior to electron transfer.

However, simple reactant dissociation followed by electron transfer may not tell the entire story. There is a great deal of evidence that, at surfactant concentrations well above the critical micelle concentration (cmc), charged surfaces tend to be fully coated with surfactant, thought to be at least a bilayer thick.^{3,9,10} There are several specific reports relating to the present study involving cationic surfactants and metal electrodes. Differential capacitance and ellipsometric studies^{9b,c,10a} indicated that tetraalkylammonium surfactants at concentrations well above their cmcs were adsorbed over nearly the entire available potential window of Hg electrodes. Octadecyltrimethylammonium ions were found to be strongly adsorbed to Pt and iodine-coated Pt electrodes.^{9d} This appears to be a general phenomenon for cationic surfactants on Pt, and head-group down orientations are proposed over the full potential window.² Surface-enhanced Raman spectroscopy (SERS) was used to show that cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride were adsorbed strongly to silver electrodes. A head-group down orientation was demonstrated by SERS results at potentials on both sides of the point of zero charge (PZC) of the Ag electrode.^{9e} Adsorption of cetyltrimethylammonium was found to occur over a wide potential range on Ag by using a fluorescence probe method.9

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$$(CH_3)_3N^+$$
-CH₂CHCH₂CH₂CH₂CH₂(CH₂)₆CH₃ I
|
00CFc

$$(CH_3)_3N^+$$
-CH₂CH₂CH₂CH₂CH₂CH(CH₂)₆CH₃ II
|
OOCFc

Figure 1. Structures of probes I and II.

Consider electron exchange with a reactant in solution assuming that a surfactant coating covers an electrode surface in a micellar solution. With a bilayer of a C12 surfactant on the electrode surface, electrons would have to transfer across a distance of about 4 nm. Outer-sphere electron transfer across such distances would be slow.¹¹ Since fast electron transfer has been observed for numerous solutes in micellar media, $2^{-8,9a}$ the possibility that reactants partition from micelles into a surfactant layer on the electrode prior to electron exchange needs to be considered.

Earlier work on the influence of surfactants on heterogeneous electron-transfer kinetics at electrodes considered the influences of physical inhibition of electron-transfer and electrostatic interactions.¹⁰ However, many experimental systems fail to fit quantitative models based on these concepts. In this paper, we investigate electron-transfer kinetics of model amphiphilic reactants in cationic micellar solutions. Electronic spectra are used to investigate differences in solvent effects. Kinetic results are explained by modern electron-transfer theory.

A large amount of literature exists on the effects of solvents on kinetics and thermodynamics of solutes and chemical reactions. Solvent interactions with solutes can be treated generally using linear solvation free energy relationships.^{12,13}

Many scales of solvent polarity have been developed. Most are single-parameter or multiparameter models based on spectrochemical shifts of indicator molecules in different solvents. Several single-parameter polarity scales have been applied to surfactant systems. In an early example, Mukerjee and Ray¹⁴ used charge-transfer absorbance bands to study the polarity of the Stern layer in alkylpyridinium micelles. Others have correlated the polarity of solute environments in micelles with Dimroth's ET(30) scale for a variety of surfactant systems.¹⁵⁻¹⁸

We recently correlated electron-transfer rate constants of ferrocene to a series of single- and multiple-parameter solvent models.^{19,20} By far, the best correlations were obtained using a linear free energy relationship proposed by Taft et al.²¹⁻²³ This includes terms for the hydrogen bond donor (α) and acceptor (β) properties and the electronic polarizability (π^*) of the solvent. In general, the properties of a solute or a reaction in a specific solvent, X, can be related to those in a standard solvent, X₀, by

$$X = X_0 + a\alpha + b\beta + s\pi^* \tag{1}$$

where a, b, and s are constants.

In the present work, dodecyltrimethylammonium surfactants with ferrocenyl groups in the 2- and 5-positions (Figure 1) on the alkyl chain were used to estimate π^* and β in CTAB micelles. Electron-transfer kinetics for these ferrocenyl surfactants were then measured in CTAB solutions at a platinum electrode. Results suggest that the ferrocenyl surfactants line up with their cationic head groups down on the electrode surface prior to electron transfer, presumably in an adsorbed CTAB layer.

Experimental Section

Chemicals. Propylene carbonate [PC] (Aldrich, HPLC grade), dimethylformamide [DMF] (Baker, analyzed reagent), dimethyl sulfoxide [DMSO] (Aldrich, Gold Label), dimethylacetamide [DMA] (Aldrich, 99%), 1,2-dichloroethane [DCE] (Aldrich, Gold Label), methyl acetate [MAC] (Aldrich), diethyl ether [DEE] (Aldrich), ethanol [EtOH] (USI Chemicals, 200 proof), hexane [Hex] (Baker, certified grade), lithium perchlorate (Aldrich), tetrabutylammonium perchlorate [TBAP] (Kodak), and cetyltrimethylammonium bromide [CTAB] (Kodak, 99.8%) were all used as received. Tetrahydrofuran [THF] (Baker) was distilled under vacuum before use. The surfactant solutions were all made with triply distilled water.

The ultraviolet spectra were measured using a Perkin-Elmer λ 4d spectrophotometer, and the wavelengths of peak maxima were obtained to ± 0.1 nm using a built-in curve fitting routine.

Cyclic voltammetry (CV) was done using a BAS-100 electrochemical analyzer with automated full compensation for Ohmic drop. The working electrode was a platinum disk of 0.5-mm diameter which was prepared as described previously.²⁰ The counter electrode was a large surface area platinum gauze, and all potentials were measured with respect to a reference saturated calomel electrode (SCE) in surfactant solutions and a Ag/AgClO₄ electrode in organic solvents. Temperature was maintained at the given value ± 0.1 °C using a thermostated cell. Apparent standard heterogeneous electron-transfer rate constants were obtained from CV peak separations as described previously.²⁰

Carboxylic Acid Chloride. Ferrocenecarboxylic acid (Aldrich) (10 g) was refluxed in thionyl chloride (Aldrich) (50 mL) for 30 min. At the end of this time the excess thionyl chloride was removed under vacuum. The last traces of thionyl chloride were removed by adding a small amount of benzene and again applying a vacuum.

[2-(Ferrocenylcarboxy)dodecyl]trimethylammonium Iodide (I). Dodecane oxide was formed by stirring perbenzoic acid (Aldrich, technical) (10 g) with 1-dodecene (Aldrich) (10 g) in THF at 0-5 °C for 30 min. This solution was extracted with dilute sodium bicarbonate to remove the excess perbenzoic acid. The THF was then evaporated from the product under vacuum. The hydroxyamine was formed by boiling the dodecane oxide in acetonitrile with an equal volume of 30% dimethylamine in water (Aldrich) for 3 h. Following this, the acetonitrile was removed under vacuum, and the aqueous solution was acidified with dilute hydrochloric acid. The unreacted starting materials were extracted back into ether, and the aqueous layer was made basic with dilute NaOH solution. The product was then extracted into ether and dried with sodium sulfate. The ferrocenyl ester was formed by reacting the hydroxy amine with ferrocenecarboxylic acid chloride in ether with a catalytic amount of pyridine. A dark brown precipitate was formed almost immediately. This was filtered and washed several times with ice cold ether. The product was dissolved in ethanol and stirred with methyl iodide (Aldrich) (2 mL) for 30 min. The precipitate thus formed was filtered and washed with ethanol. The overall yield was 5%, but no attempts were made to optimize the reaction, as only small amounts were needed. This compound decomposed above 220 °C.

[5-(Ferrocenylcarbonyl)dodecyl]trimethylammonium Iodide (II). A solution of $(+)-\delta$ -dodecalactone (Aldrich) (5 g) in acetonitrile (50 mL) was refluxed with an equal volume of 30% dimethylamine in water for 6 h. Following this, the acetonitrile was evaporated under vacuum, and the solution was acidified with dilute HCl. The unreacted lactone was removed by washing the solution with ether, and the aqueous layer was made basic with dilute sodium bicarbonate. The 5-hydroxy dimethylamide was extracted into ether and reduced to the hydroxy amine with lithium aluminum hydride by the method described in the literature.²⁴ The esterification of the hydroxy group and the quaternization of the amine were performed as described above. The overall yield was 8%. The compound decomposed above 240 °C.

Analyses of I and II. Structures were confirmed by IR and NMR spectroscopies and elemental analysis. No unassigned peaks were observed in the spectroscopic analyses, and proton NMR integrations agreed well with the proposed structures. Elemental percentages calculated for $C_{26}H_{42}O_2NFeI$: C, 53.5; H, 7.2; N, 2.4. Analysis found for I: C, 53.9; H, 6.5; N, 2.1. Analysis found for II: C, 53.0; H, 6.3; N, 1.9.

Results

Figure 2 shows the UV spectrum for probe I in 1,2-dichloroethane which is typical of spectra obtained in other solvents in this and previous work.^{25,26} The peak at about 230 nm has been ascribed to the $E_{1u}(e_{2u}-e_{2u})$ and that at about 260 nm to the



Figure 2. UV spectra of I in (a) 1,2-dichloroethane and (b) 0.05 M CTAB solution.

TABLE I: Wavelengths of UV Absorption Maxima of Probe I in a Series of Solvents

wavelengths, nm			nm			
solvent	E _{1u}	A _{2u}	СТ	π^{*a}	β	
DCE	217.1	246.1	304.0	0.82	0.00	
DMA		266.4	294.8	0.88	0.76	
DMF		270.4	294.3	0.88	0.69	
THF	230.4	262.0	304.3	0.58	0.55	
PC	236.1	258.3	294.4	0.83	0.40	
DEE	210.4	245.2		0.27	0.47	
MAc		262.2	295.3	0.60	0.42	
Hex		208.0	325.0	0.00	0.00	

^a π^* and β obtained from ref 22.

 $A_{2u}(e_{2g}-e_{2u})$. The broader band at about 300 nm is due to the charge transfer (CT) between the ferrocene group and the carbonyl moiety of the ester. A fourth band at 360 nm was only observed in a few solvents and is not discussed further since it did not give significant shifts in the solvents used.

Also in Figure 2 is the UV spectrum of probe I in a 0.05 M CTAB solution. This is a typical spectrum for all of the surfactant solutions investigated. Probe II gave spectra similar to those of probe I.

Wavelengths of absorption maxima of probe I in a series of solvents are listed in Table I. Equation 1 was fit to these data by forming sets of simultaneous equations for all of the solvents and solving them by a Gauss-Seidel method^{20,27} using commercial software.^{27b} Calculated and observed wavelengths were compared using the coefficient of correlation and the χ^2 test. All of the comparisons gave excellent correlations, and fits could be accepted at the 99% confidence level.

Figure 3 shows the correlation between the observed wavelengths (ν) and those calculated from eq 1 for all three sets of absorption maxima. The equations of best fit were

$$E_{1u} \qquad \nu = 175.7 + 50.5\pi^* + 46.2\beta \tag{2}$$

$$A_{2u} \qquad \nu = 230.9 + 20.9\pi^* + 28.3\beta \tag{3}$$

CT
$$\nu = 307.0 - 6.1\pi^* - 10.8\beta$$
 (4)



Figure 3. Correlation between the observed wavelengths for the absorbance maxima of probe I in a series of solvents and those calculated from eq 1.

TABLE II: Polarity Parameters for Different CTAB Solutions

			wavelength, nm				
surfac	tant	probe	E _{1u}	A _{2u}	π^*	β	
0.01 M	СТАВ	I	229.5	258.2	0.56	0.55	
		Π	229.2	258.0	0.56	0.54	
0.05 M	CTAB	I	226.8	256.5	0.72	0.38	
		II	224.1	254.1	0.63	0.30	
0.10 M	CTAB	Ι	226.1	257.7	0.64	0.41	
		II	225.9	256.5	0.51	0.52	

TABLE III: Apparent Standard Heterogeneous Electron-Transfer Rate Constants at Pt Electrodes at 30 °C

probe	solvent	k', cm s ⁻¹	$D,^{a} \text{ cm}^{2} \text{ s}^{-1}$	<i>E°′</i> , V
Ι	DMSO	1.2×10^{-2}	5.2 × 10 ⁻⁶	0.36 ^b
II		1.0×10^{-2}	5.0 × 10 ⁻⁶	0.42
ferrocene		3.0×10^{-2}	9.3 × 10⁻⁰	0.33
I	0.05 M CTAB	1.0×10^{-3}	1.0×10^{-7}	0.32 ^c
II		1.6 × 10 ⁻⁴	1.0×10^{-7}	0.38
ferrocene		2.0×10^{-2}	0.9 × 10⁻6	0.22

^aEstimated by cyclic voltammetry; D's in surfactant solutions are apparent^{8,9a} or conditional values. ^bVersus Ag/AgClO₄. ^cVersus SCE.

Table II lists the observed wavelengths of the absorption maxima of probes I and II in a series of CTAB solutions. Also listed are the π^* and β values calculated from eqs 2-4.

Table III shows heterogeneous electron-transfer rate constants (k') at formal potentials $(E^{\circ'})$ and diffusion coefficients for probes I and II in both DMSO and aqueous 0.05 M CTAB at 30 °C at a platinum electrode. Diffusion coefficients in CTAB were ≤ 10 -fold smaller than those in DMSO, showing that I and II diffuse to the electrode bound to micelles, as does ferrocene.⁸

Values of k' are consistent with those reported previously for ferrocene on Pt electrodes by a variety of techniques, as we recently discussed.²⁰ We also pointed out that some ultramicroelectrode studies give much higher measured rate constants for ferrocene. However, these results might be explained by uncharacterized irregular shapes and imperfect seals producing irregular diffusion at these tiny electrodes.²⁸ Experiments similar to those reported in detail previously²⁰ showed that the data in Table III were free from significant instrumental artifacts such as Ohmic drop. This being the case, our k' values are suitable for the comparative analysis that follows.

Figure 5 shows linear plots of $\ln k'$ against 1/T for probes I and II in 50 mM CTAB.

Discussion

Figure 3 shows very good correlation between observed and calculated wavelengths of the absorption maxima of probe I in the various solvents studied. Both the E_{1u} and A_{2u} peaks shift red with increasing solvent polarity whereas the CT band shifts blue. It is suggested that this arises because the species responsible for the CT band has a lower dipole moment in the ground state than



Figure 4. Possible orientation of surfactant probes on the electrode surface at the time of electron transfer.



(1/T)xE03, 1/K

Figure 5. Plot of $\ln k' vs 1/T$ for I and II in 0.05 M aqueous CTAB solution.

in the excited state, which is opposite to the other two transitions.

Values of β and π^* do not change significantly with the position of the ferrocene probe on the dodecyl chain or with surfactant concentration. This suggests that I and II feel similar average environments in the micellar solutions. Average values in CTAB solutions are $\beta = 0.60$ and $\pi^* = 0.45$, which resemble those of methyl acetate (cf. Table I).

This similarity of microenvironments does not agree with the classical model of the micelle, i.e., a sphere with head groups on the surface and hydrocarbon chains extending inside. If this were the case, the ferrocene group on II should be in the nonpolar interior of the micelle, while ferrocene in I would be closer to the micelle's surface in a more polar environment. It may be that the polar head groups of the surfactant molecules are staggered in the micelle allowing water penetration, as featured in alternative micelle models.²⁹ In such a dynamic structure, ferrocene groups in I and II may have similar average interactions with water molecules and CTAB head groups.

I and II show similar electron-transfer kinetics in homogeneous DMSO (Table III). Their rate constants are also similar to that of ferrocene in DMSO. The hydrocarbon chains of I and II do not hinder the ferrocenyl moiety from reaching the electrode surface. However, in CTAB solutions the electron-transfer rate is an order of magnitude smaller for probe I and 2 orders of magnitude smaller for probe II than in DMSO. The hydrogen bonding and polarizability characteristics of the two probes are similar in CTAB. Thus, the difference in kinetics may result from a longer electron-transfer distance for II compared to I.

Molecular dynamics calculations³⁰ revealed differences in the time dependence of the distance between the iron in ferrocene and the nitrogen of the head group. In 100-ps dynamic calculations, the Fe–N distance of I fluctuated randomly between 0.6 and 0.7 nm. Probe II showed pulsed variations between 0.7 and 1.2 nm in Fe–N distance with pulse widths of 15–30 ps. This suggests that ferrocene in I is held in place by interaction between the carbonyl group and the positive nitrogen. This was also reflected in the IR carbonyl stretching frequency of 1631 cm⁻¹ for I, indicating hindered vibration, compared to the value of 1730 cm⁻¹



Figure 6. Agreement of k' vs T data with eq 7. Points are experimental data; lines are best fits from nonlinear regression onto eq 7.

for II which is in the normal range for esters. The value for probe II suggests that ferrocene rotates freely around the C–O–C linkage of the ester to the surfactant hydrocarbon chain.

If molecules I and II were oriented normal to the electrode (Figure 4), their electron-transfer distances would differ. Extended electron transfer would occur, and a marked difference in the electron-transfer rates would be expected.

The effect of distance on electron-transfer kinetics can be estimated from Marcus theory.^{11,31-33} The rate constant for an outer-sphere electron-transfer reaction, k', is related to the activation free energy, ΔG^* , by

$$k' = K_{\rm p} \kappa_{\rm el} \nu_{\rm n} \exp(-\Delta G^* / RT)$$
 (5)

where K_p is the precursor equilibrium constant, κ_{el} is the electronic transmission coefficient, and ν_n is the nuclear collision frequency factor. The κ_{el} term is often assumed to be unity³³ for adiabatic reactions. Reorganization energy λ is a sum of inner and outer, solvent-dependent, energies.³³ It is related to ΔG^* by

$$\Delta G^* = (\Delta G^\circ + \lambda)^2 / 4\lambda \tag{6}$$

where ΔG° is the standard free energy for converting the precursor into successor states. The linearity of plots of $\ln k' vs 1/T$ for probes I and II in CTAB solution shows that the data agree with eq 5.

Long-distance electron transfer is usually considered to be nonadiabatic.¹¹ In this case, ν_n is much less than one, and the relevant expression is³³

$$k' = (\pi/\lambda kT)^{1/2} (1/h) |H_{\text{DA}}|^2 (d=d_0) \exp[\beta(d-d_0)] \exp(-\Delta G^*/RT)$$
(7)

where k is Boltzmann's constant, h is Planck's constant, $|H_{DA}|^2_{(d=d_0)}$ is the square of the exchange matrix element at the distance d_0 of closest approach of the reactant to the electrode, β (not the same as in eq 1) is the damping coefficient, and d is the tunneling distance.

Since all terms except T preceding $\exp(-\Delta G^*/RT)$ on the right-hand side of eq 7 are constant for an individual amphiphilic ferrocene, we can fit eq 7 to k'vs T data by nonlinear regression analysis.³⁴ The regression equation takes the form

$$k' = (B_1/T^{1/2}) \exp(-B_2/RT)$$

with the parameters $B_1 = (\pi/\lambda k)^{1/2} (1/h) |H_{DA}|^2 (d=d_0) \exp[\beta(d-d_0)]$ and $B_2 = \Delta G^*$. Experimental data showed good agreement with eq 7 (Figure 6). The quality of fit was slightly better than with eq 5. Standard deviation of the regression was 2% smaller with eq 7 than eq 5 for I and 14% smaller for II. Activation free energies obtained from regression analyses onto eq 7 were 56.2 \pm 7.3 kJ mol⁻¹ for I and 58.6 \pm 5.8 kJ mol⁻¹ for II. The difference in these values is not significant, suggesting from eq 6 that reorganization energies are similar for I and II. This is reasonable, since electron-donating centers are the same and since medium effects for I and II in CTAB micelles were shown to be similar by spectroscopic studies.

The preexponential factor in eq 7 was smaller for II than for I, consistent with a longer distance of electron transfer for II.

TABLE IV: Comparison of Rate Constants at 30 °C with Models for Distance Dependence of Electron Transfer^a

	$10^{3}k'$, cm s ⁻¹		
	probe I	probe II	
found	1.0	0.16	
eq 8, $\beta = 0.85 \text{ Å}^{-1}$	2.0	0.16	
eq 9, $\beta' = 1.12 \text{ Å}^{-1}$	1.2	0.23	

^a Parameters were $k_0 = 0.02 \text{ cm s}^{-1}$, d = 6.5 Å for I; 9.5 Å for II, d_0 = 3.8 $Å^{39}$ (see text).

However, large standard errors indicated by the regression program precluded using these values quantitatively.

Equation 7 predicts an exponential decay of k' with increasing tunneling distance. Numerous investigations of intramolecular elecron transfer involving donor and acceptor tethered by a rigid hydrocarbon spacer¹¹ and donor-acceptor reactions in modified proteins³⁵ have confirmed such an exponential dependence on distance. Similar approaches have been applied to long-distance electron transfer involving electroactive species attached to electrodes³⁶ and for electron transfer involving species in solution at gold electrodes coated with organic monolayers of different thicknesses.37

The following empirical expression^{11,35} can be used to relate k' to electron transfer over a distance d, relative to a rate constant k_0 at contact distance d_0 :

$$k' = k_0 \exp[-\beta(d - d_0)]$$
(8)

This expression is relevant to a through-space coupling mechanism. The predicted rate constant depends on β , which is between 0.85 and 2.6 Å⁻¹ for various systems^{11,35,37,38} but is more generally found^{11,37} in the range $0.85-1.15 \text{ Å}^{-1}$.

Assuming mean distances from the dynamics calculations of 6.5 Å for I and 9.5 Å for II, and using $d_0 = 3.8$ Å, the radius of ferrocene,³⁹ $k_0 = 0.02$ cm s⁻¹ measured for ferrocene in 0.05 M CTAB (Table III), and $\beta = 0.85 \text{ Å}^{-1}$, reasonable agreement with experimental k' values was found (Table IV).

Small values of β as used above have been associated with a through-bond electron-transfer pathway.^{11,37} The relevant empirical expression¹¹ is

$$k' = k_0 \exp[-\beta'(N-1)/2]$$
(9)

where N is the number of bonds through which the electron is transferred. Assuming that the quaternary nitrogens of I and II are bonded to the electrode surface, and using $\beta' = 1.12 \text{ Å}^{-1}$, values of k' predicted by eq 9 were again consistent with experimental data (Table IV).

Predictions of eqs 8 and 9 consistent with experimental k' values suggest that the differences observed for I and II in CTAB are caused by different distances of electron transfer. In CTAB solutions, the ferrocenyl surfactants probably orient head down on the electrode prior to electron transfer (Figure 4). Since kinetic differences in homogeneous DMSO were insignificant, we infer that, in CTAB solutions, surfactant molecules on the electrode surface help orient the amphiphilic reactants I and II. Head-down orientation is in agreement with the proposed orientation of alkylammonium surfactants on Pt electrodes² and the orientation of CTAB adsorbed onto Ag electrodes found by SERS,^{9e} at potentials on both sides of the PZC. Since electron transfer from ferrocene in CTAB solutions is much faster than from I, underivatized ferrocene most probably approaches the electrode more closely than the ferrocene group in I before donating an electrode.

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