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Cosurfactant-Induced Electron Transfer in Highly Resistive Microemulsions

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A cosurfactant-induced electron transfer phenomenon in reverse microemulsions of the quaternary water–acrylamide/bis(2-ethylhexyl) sulfosuccinate (AOT)/toluene system is reported, wherein electroactive electrolytes ($Ru(NH_3)_6^{3+}$ and $Fe(CN)_6^{4-}$) are incorporated in the water pools of these microemulsions. Threshold cosurfactant (acrylamide) levels exist, below which electron transfer to (from) Pt ultramicroelectrodes is retarded and above which electron transfer is greatly facilitated. This effect runs counter to the generally reported observation that organic additives retard or inhibit the rate of electrode reactions and appears physically related to changes in interfacial packing.

Introduction

Redox processes in only a few highly resistive microemulsion systems have been reported[1-5] since the advent of ultramicroelectrodes[6-8] (UME) has made such studies feasible. We examine the effects of acrylamide as a cosurfactant on the reduction of $Ru(NH_3)_6^{3+}$ and on the oxidation of $Fe(CN_6)^{4-}$ in highly resistive water/bis(2-ethylhexyl) sulfosuccinate (AOT)/toluene microemulsions. The behavior of acrylamide as a cosurfactant in the water/AOT/toluene system has been mapped by Candau and co-workers.[9] We have recently found that there exist threshold cosurfactant levels in these microemulsions, below which electron transfer is retarded and above which electron transfer is greatly facilitated. This threshold phenomenon appears physically related to changes in interfacial surfactant packing and has ramifications in electron and ion transport through cell, liposome, and vesicular membranes, through surfactant stabilized interfaces between immiscible fluids, through monolayers at solid/liquid interfaces, in microemulsion-based phase-transfer catalysis, and in reversibly self-assembled interfacial structures.

Experimental Section

Microemulsions were prepared by adding water or aqueous acrylamide (Eastman Laboratory Chemicals) solutions of $Ru(NH_3)_6Cl_3$ (Strem) or $K_4Fe(CN)_6$ (Matheson Coleman & Bell) to

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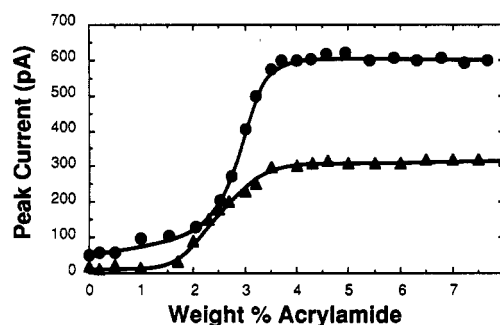(9) Candau, F.; Leong, Y. S.; Pouyet, G.; Candau, S. *J. Colloid Interface Sci.* **1984**, *101*, 167.

Figure 1. Reductive (●) peak currents for $Ru(NH_3)_6^{3+}$ and oxidative (▲) peak currents for $Fe(CN)_6^{4-}$ as a function of acrylamide concentration (weight %) measured by SWV in water–acrylamide/AOT/toluene microemulsions at a 10 μm diameter Pt UME.

solutions of AOT (bis(2-ethylhexyl) sulfosuccinate sodium salt, Fluka) in toluene (HPLC grade, Baxter Healthcare). These microemulsions were formulated with 1.84 g of AOT, 7.32 g of toluene, varying amounts of acrylamide (0–0.87 g) to cover the concentration range of 0–8% (w/w), and 0.833 g of aqueous 10.27 mM $Ru(NH_3)_6Cl_3$ or 10.25 mM $K_4Fe(CN)_6$.

Square-wave voltammetry (SWV; 71 Hz, 40 mV ac pulse width, 4 mV step) at a 10 μm diameter Pt UME (Bioanalytical Systems) was done with a BAS 100A electrochemical analyzer with a Faraday cage and a PA1 preamplifier (Bioanalytical Systems). Photon correlation spectroscopy (PCS, quasi-elastic light scattering) was done using a BI 240 goniometer and 128 channel BI 2030 correlator (Brookhaven Instruments) and Melles-Griot 632.8 nm He/Ne laser. Measurements were taken at detector angles of 45, 90, and 135°.

Proton nuclear magnetic resonance (NMR) spectra were acquired using a Varian VXR-300 with a four-nucleus 5 mm probe operating at 299.9 MHz. Spectra were obtained using a sweep width of 4039 Hz and 16K data points per acquisition. Trimethylsilylpropionic-d_4 sodium salt (TSP) in D_2O was used as an external reference. NMR was done at 30 °C; all other measurements were done at room temperature in the range of 23–24 °C.

Results and Discussion

The basic cosurfactant-induced electron-transfer phenomenon is illustrated by the SWV data in Figure 1 for the reduction (ca. −400 mV vs SCE, saturated calomel electrode) of $Ru(NH_3)_6^{3+}$ and for the oxidation (ca. +30 mV vs SCE) of $Fe(CN)_6^{4-}$. These data were obtained for a series of microemulsions containing varying amounts of the cosurfactant, acrylamide. The onset of facilitated $Ru(NH_3)_6^{3+}$ reduction occurs at about 2.3% acrylamide and

the onset of facilitated $Fe(CN)_6^{4-}$ oxidation occurs at about 1.7% acrylamide. Both of these transitions reach asymptotic peak currents with transition widths of approximately 1.2% and 1.6% acrylamide, respectively, for $Ru(NH_3)_6^{3+}$ reduction and $Fe(CN)_6^{4-}$ oxidation. It is known that peak currents in SWV depend both on diffusion rates and on electron transfer rates,[10] and it is important to try to understand whether this switching phenomenon depends critically on either of these two rate limiting processes. *Identical* behavior to that illustrated in Figure 1 was obtained for limiting currents in slow-scan cyclic voltammetry. This observation shows that this threshold phenomenon occurs under diffusion limiting conditions and is not a simple manifestation of changes in electron transfer kinetics. Moreover, explicit analysis[11] of the SWV data for $Ru(NH_3)_6^{3+}$ reduction yielded a standard (intrinsic or heterogeneous) rate constant that *increased approximately linearly* from 2.7×10^{-4} to 5.2×10^{-4} cm s^{-1} as acrylamide was varied from 1 to 5 wt %.[12,13] This variation corresponds to *less than a 40% change* in the standard rate constant over the transition interval (2–3.5% acrylamide) for this threshold phenomenon, where peak current increases by *400%*. Hence, this phenomenon appears only weakly correlated with the standard rate constant. Further, the symmetry factor β ($=1-\alpha$), of the Butler–Volmer equation for heterogeneous electron-transfer rates, was found to decrease *sigmoidally* from 0.61 to 0.43 with a transition width similar to the illustrated threshold current behavior (Figure 1). This transition in β may be interpreted[14] as corresponding to a decrease in the activation energy change $\Delta E^{\ddagger}$ upon cosurfactant addition. A precise definition of this symmetry effect in molecular (reaction) coordinates relative to the electrode is not yet possible. However, this decrease in the symmetry factor correlates strongly (negatively) with the presently reported phenomenon.

An explanation for this threshold phenomenon may be formulated in terms of electrode film models, colloidal models of complex fluid structure, and combinations of film and colloid models. Electrode film models involve the formation on the electrode of surfactant films by adsorption. Ion and electron transfer across monolayers of "surfactant" has been extensively reviewed by Lipkowski,[15] wherein "surfactant" comprises alcohols, phosphine oxides, quinolines, and other hydrophobic neutral molecules containing a polar functional group. Extant models[15] for the "surfactant" (inhibitor) surface coverage (θ) dependence of observed rates of electron or ion transfer in such films uniformly predict that *increasing* θ results in *decreasing* transfer rate. One of these models expresses a linear dependence of the standard rate constant on coverage

$$k_{\theta} = (1-\theta)k_{\theta=0} + \theta k_{\theta=1}$$

This equation can be simply modified to reflect an *increasing* rate with coverage if the saturation standard rate, $k_{\theta=1}$, is taken as greater than the rate obtained in the

absence of additive, $k_{\theta=0}$. In the highly resistive reverse microemulsions of the present report, the cosurfactant acrylamide functions as a catalyst rather than an inhibitor. The possibility of using this equation in such a catalytic context has been mentioned by Bard and Faulkner,[16] but we are unaware of any specific example having been reported. The main difficulty in applying this model to the present situation is the discrepancy in the magnitude of current change (discussed above) observed and the intrinsic nonlinearity of the threshold phenomenon. The saturation condition, however, does appear to be an example of a catalytic effect.

Little precedent exists for the characterization of adsorbed surfactant films on electrodes in microemulsions or in highly resistive solvents or for the characterization of charged surfactant adsorption onto solid state electrodes. Rusling and co-workers have identified interesting charge and electron transport phenomena[17,18] using electrodes covered with insoluble films of quaternary ammonium surfactants and have identified[19] key aspects of the interactions of these surfactants with the electrode surface. These systems involve electrochemical interactions with aqueous solution. We are aware of only one report of reverse hemimcelle formation, involving hemimicellization of 1-decanol at the heptane/graphite interface.[20,21] The characterization of anionic surfactant adsorption, particularly AOT, at electrodes is an area requiring much further study. Detailed adsorption studies[22] of charged ethenic molecules on platinum electrodes and the effects of this adsorption on aqueous reduction rates in 1 M $HClO_4$ of various Pt(IV) complexes indicate that standard rates for these reductions may be inhibited or catalyzed by adsorbates. Other studies[23] of naphthohydroquinone and anthraquinone sulfonate adsorption out of 1 M aqueous perchlorate on platinum have indicated that these aromatic molecules initially adsorb flat on the metal surface, with subsequent reorientation to edge-on adsorption possible in some cases at higher concentrations of adsorbate. In the present reverse microemulsions, it would seem most probable therefore that AOT molecules would adsorb with the charged head groups next to the electrode surface and with the double tails oriented toward the solution phase.

In our studies we have found that strong irreversible adsorption of AOT onto the electrode *did not occur*. Limiting oxidation currents measured for aqueous $Fe(CN)_6^{4-}$ at the UME before and after making measurements in the microemulsions of the present study were identical. Hence, the apparent electrode surface area was unchanged and the electrode was not covered with any film emanating from the microemulsion system. SWV peak currents varied linearly with the *square-root* of frequency (equivalently, scan rate), indicating that the respective electron transfer reactions were diffusion controlled and not confounded by specific adsorption of redox couples. Such adsorption yields a linear variation of

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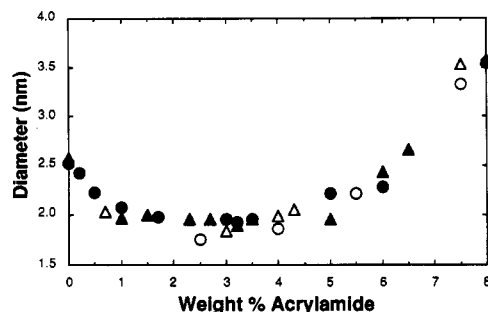
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Figure 2. Particle sizes as a function of acrylamide content (weight %) measured by photon correlation spectroscopy for water–acrylamide/AOT/toluene microemulsions containing Ru-$(NH_3)_6^{3+}$ and $Fe(CN)_6^{4-}$ (●, $Ru(NH_3)_6^{3+}$ series 1; ○, $Ru(NH_3)_6^{3+}$ series 2; ▲, $Fe(CN)_6^{4-}$ series 1; △, $Fe(CN)_6^{4-}$ series 2).

Figure 3. Proton magnetic resonance of AOT methyl protons in water–acrylamide/AOT/toluene microemulsions as a function of acrylamide concentration (weight %). The 0 ppm point is referenced to the TSP resonance.

current with frequency (scan rate[24]). It appears therefore that any electrode film component of the underlying threshold phenomenon involves reversibly formed surfactant/cosurfactant structures (most probably reverse hemimicelles).

Since microemulsions are complex fluids, colloidal models must be invoked to explain aspects of mass transport. This is especially the case since the electroactive species, electrolytes, as well as the cosurfactant acrylamide are essentially insoluble in the toluene pseudocontinuous phase. Since, as described above, redox currents in these microemulsions are diffusion limited, the complex fluid microstructure is expected to affect mass transport through the bulk to the electrode. The sigmoidal current transition might possibly be assignable to a morphological transition from a water-in-oil microemulsion to a bicontinuous microemulsion, where electroactive diffusion (and peak or limiting current) can increase by orders of magnitude. However, phase studies[9] of the water–acrylamide/AOT/toluene system indicate that only a water-in-oil type system exists over the composition range investigated here. Another possible explanation for such a phenomenon could involve a dramatic decrease in the water pool droplet sizes with a concomitant increase in the diffusion coefficient of these droplets. Photon correlation spectroscopy of these microemulsions yields droplet diffusion coefficients that can be converted directly to droplet diameters with the aid of the Stokes–Einstein equation and independent viscosity measurements.[25] The results of our PCS studies are illustrated in Figure 2 for two different series of Ru-$(NH_3)_6^{3+}$ microemulsions and for two different series of $Fe(CN)_6^{4-}$ microemulsions. There it is seen that the type of electrolyte has a negligible effect on the sizes, and the effect of added acrylamide is a modest one, with the diameter increasing to only 3.5 nm at high acrylamide over the initial size of 2.5 nm in the absence of added acrylamide. Hence, added acrylamide, after an initial modest decrease, leads to an increase in droplet size, and therefore a modest decrease in the self-diffusion coefficient. These changes run counter to the diffusion coefficient changes required to explain the phenomenon illustrated in Figure 1. Hence, colloidal morphology does not change significantly and cannot explain the threshold phenomenon of Figure 1.

None of these surfactant adsorption, cosurfactant adsorption, hemimicellization, or mass transport considerations (since a transition to dramatically higher diffusion
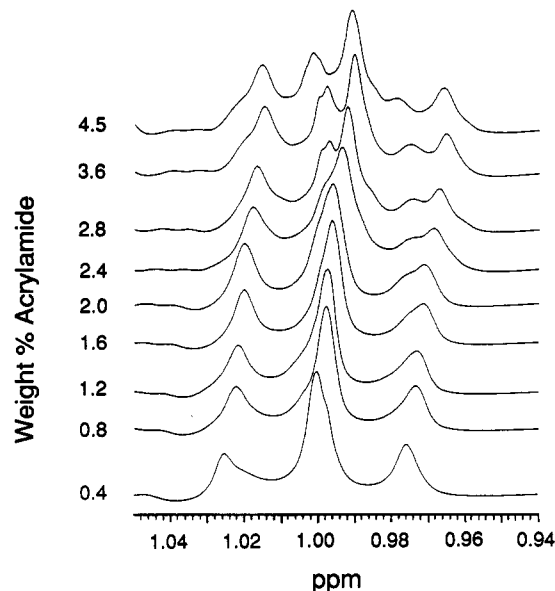
coefficients has been eliminated) explains the apparent catalytic effect of the acrylamide. In Figure 3 we illustrate proton magnetic resonance data for the protons of the AOT methyl groups as a function of acrylamide concentration. At low acrylamide levels, an upfield triplet characteristic of the methyl protons is evident. This triplet shifts upfield as acrylamide concentration increases. Concomitantly, these multiple peaks appear to split or separate. This apparent splitting is evident in the high field peak as the growth of a shoulder and separation into another peak over the 1.6–2.6% acrylamide range. A similar splitting is clearly evident in the center peak over the 2.0–2.6% range. This effect is noticeable, but less evident in the low field peak. At present it cannot be ascertained whether this is actually a splitting phenomenon or a disordering phenomenon. Either of these possibilities can be assigned to changes in interfacial structure and concomitant changes in the dynamical environment of the AOT hydrocarbon chains. Since the proton magnetic resonance data reflect a bulk property and the onset of "resonance splitting" coincides with the sigmoidal transition observed electrochemically, the present threshold phenomenon is strongly correlated with this transition in surfactant packing. It is reasonable to consider that a similar transition in packing may occur with any hemimicellar structure on the electrode surface, although direct evidence for such structures and transitions is not yet available.

We have observed similar threshold phenomena electrochemically using other cosurfactants in these systems, including the use of acetonitrile and alkylamides as cosurfactants, and we have observed, for a homologous series of alkylamides as cosurfactants, that the onset of facilitated electron transfer *decreases* as the interfacial activity of cosurfactant *increases*. This phenomenon appears based on partitioning of cosurfactant between the water pools and the oil/water interface. This partitioning has been extensively documented by Candau and her co-workers[9] for the acrylamide microemulsions of the present study, is inherent in the action of such cosurfactants,[26] is demonstrated by the NMR data of Figure 3 and chemical

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shift data to be published subsequently, and is supported by interfacial studies with a variety of alternative cosurfactants, including a homologous series of alkylamides. Accumulation of cosurfactant in the interfacial regions modifies surfactant packing and increases the local dielectric constant. These effects increase partitioning of charged or polar electroactive solutes into these regions, increase solute permeability through these regions, and change these interfacial regions from being ionically insulating to ionically conducting. These changes reasonably occur in *parallel* in the swollen micelles of the bulk and in any hemimicelles on the electrode surface and result in increased solute transport rates into and out of these micelles and hemimicelles. This dielectric/partitioning relation is a continuum effect that provides an equilibrium basis for increasing the concentration of electroactive solute (of any charge) in the AOT interfacial regions. The transition in surfactant packing, also an equilibrium effect, can be thought of in more local terms such as chain packing disorder, increased interfacial fluidity, and dynamical (molecular) pore opening, and formal analogy can be drawn in this regard to the leaky

insulating properties of monolayers on planar electrodes.[13,27-30] While the illustrated threshold transition in electron transfer is most probably related to changes in electrode-localized hemimicelle structure, the (parallel) packing or disorder transition identified by NMR in "bulk" interfacial regions suggests transitions in transport phenomena unrelated to electrode polarization may exist. Many aspects pertaining to these observations deserve more extensive characterization and will be described in greater detail subsequently.

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