J. Am. Chem. Soc. **1996,** *118,* 6499−6505

Dispensing Surfactants from Electrodes: Marangoni Phenomenon at the Surface of Aqueous Solutions of (11-Ferrocenylundecyl)trimethylammonium Bromide

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Received March 19, 1996⊗

Abstract: Electrochemical methods in combination with redox-active surfactants form the basis of a procedure to create gradients in surfactant-based properties of solutions. The gradients are created by the formation of surface-active species at controlled rates in spatially localized (<mm) regions defined by electrodes. Chemical removal of the surface-active species at rates competitive with their electrochemical formation permits the creation of surfactant molecules with lifetimes that can be manipulated from 10^{-2} to 10^3 s. Electrochemical reduction of a ferrocenium precursor ($\mathbf{I}^{2+}$) to a ferrocenyl surfactant (11-ferrocenylundecyl)trimethylammonium bromide ($Fc(CH_2)_{11}N^+(CH_3)_3$ Br^-; Fc = $[\eta^5\text{-}C_5H_5]Fe[\eta^5\text{-}C_5H_5]$) ($\mathbf{I}^+$) at a Pt electrode protruding from the surface of an aqueous solution caused the motion of fluid away from the electrode under the influence of a gradient in the surface tension of the solution (Marangoni phenomenon). The velocity of the solution increased as the potential applied to the electrode decreased from 0.1 V (vs SCE) to −0.2 V (vs SCE). The maximum velocity of the fluid was observed when the concentration of ferrocenium precursor was 0.6 mM; the change in dynamic surface tension of an aqueous solution upon reduction of $\mathbf{I}^{2+}$ to $\mathbf{I}^+$ was also maximal at a concentration of *ca*. 0.6 mM. Fluid was displaced back and forth across the surface of an aqueous solution by using two working electrodes. The lifetimes of ferrocenyl surfactants $\mathbf{I}^+$ formed electrochemically were manipulated from $\sim 10^{-2}$ to 10^3 s by changing the concentration of oxidizing agent (Fe^{3+}) dissolved within the bulk of the aqueous solution; the Marangoni flow of fluid was observed to result from a balance in the rates of electrochemical creation and chemical removal of $\mathbf{I}^+$ at the surface of the solution. The principles reported herein make possible the use of surfactants in environments in which their sustained and/or widespread presence is detrimental.

Introduction

We report that control of the oxidation state of a redox-active molecule permits the formation of surface-active species in localized regions of fluids thereby producing gradients in the surfactant-based properties of fluids. Temporal control of the potential applied to an electrode permits active control of both the location and the rate of delivery of surfactant in an aqueous solution. Herein we report one manifestation of the controlled delivery of a water-soluble surfactant to a localized region on the surface of an aqueous solution: control of the motion of fluid under the influence of a gradient in surface tension (Marangoni phenomenon). The principles we report—namely, the capability to deliver surfactant at a controlled rate to a defined location—can, we believe, be extended to form the basis of methods for the localized release of solubilizates, permeabilization of biological membranes, and control of the stability of thin films of liquid.

Surfactants affect both the interfacial and bulk properties of systems to which they are added in low concentrations and thereby influence phenomena such as wetting, foaming, detergency, solubilization, and heterogeneous catalysis.[1] They also form the basis of procedures for the extraction of proteins from biological membranes and for the preparation of liposomes.[2] The exclusion or removal of low concentrations of surfactants from solutions following their use can, however, be tedious and difficult (*e.g.*, dialysis). Low concentrations of surfactants can also denature proteins during extraction of biological membranes. Here we report methods and molecules that, when combined, permit the creation of surfactant molecules with lifetimes of $10^{-2}-10^3$ s in localized regions of solutions, thereby providing new principles for the use of surfactants in aqueous systems in which their sustained or widespread presence is detrimental.

Gradients in surface (or interfacial) tension can accelerate the spreading of fluids, enhance the stability of surfactant-laden films of liquid, emulsions, and foams, and increase rates of mass transport across interfaces.[3] The motion of fluid driven by a gradient in surface tension is referred to as a "Marangoni flow".[4,5] Here we report the Marangoni flow of an aqueous solution to result from the electrochemical reduction of a ferrocenium precursor ($\mathbf{I}^{2+}$) to a ferrocenyl surfactant ($\mathbf{I}^+$) at an electrode that protrudes from the surface of the solution.[6] Because the surface tensions of aqueous solutions of $\mathbf{I}^{2+}$ differ from those of $\mathbf{I}^+$, the localized transformation of $\mathbf{I}^{2+}$ to $\mathbf{I}^+$ can result in a gradient in the surface tension of an aqueous solution.[7,8] The gradient in surface tension causes the motion

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⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1996.

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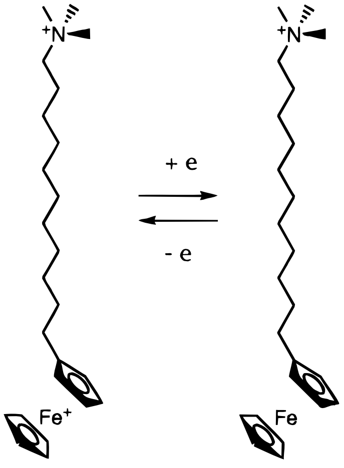
S0002-7863(96)00902-X CCC: $12.00



$\mathbf{I}^{2+}$ $\mathbf{I}^{+}$

of fluid at the surface of the solution and the displacement of solid particle tracers suspended on the surface of the solution. Consistent with the Marangoni effect, flow occurs in the direction of increasing surface tension (*i.e.*, in the direction of decreasing surfactant concentration).

The motion of fluid driven by gradients in surface tension has, in the past, been caused by chemical and thermal gradients.[4] First, gradients in concentration induced by nonuniform evaporation (or solubilization) of mixed fluid systems (*e.g.*, ethanol and water) whose components have different surface tensions in their pure states can cause the motion of fluid at the surfaces of their solutions.[9−12] The tears-of-wine phenomenon, for example, is a consequence of the flow of liquid from the bulk of the wine to its meniscus by preferential evaporation of alcohol at the meniscus.[9] Preferential solubilization of volatile components into one side of a drop of fluid can also cause the motion of the droplet.[10−12]

Second, gradients in composition formed by deposition of monolayers of surfactants can cause the motion of fluid at the surface of a solution.[13,14] When a drop of surfactant is deposited in a localized region on the surface of a fluid, the motion of the fluid is induced by transfer of momentum from the spreading surfactant to the underlying viscous liquid. For example, monolayers of both soluble and insoluble surfactants deposited onto aqueous subphases were reported to spread up thin films of water supported on the surfaces of inclined substrates of glass.[13−15] The velocity of spreading was influenced by the viscosity and depth of the aqueous subphase, and by the gradient in surface tension across the film.[13,16]

Third, gradients in temperature can force the spreading of liquids over the surfaces of solids[17] and liquids.[18] In the latter case, localized heating of a monolayer of insoluble surfactant under illumination from an optical microscope caused the surfactant to convect toward the edge of the field of view of the microscope where the monolayer underwent a transition from a liquid-expanded to a condensed phase.

Finally, McConnell and co-workers reported the motion of monolayers composed of binary mixtures of lipid under the influence of gradients in an electric field.[19,20] They attributed the motion to a difference in the density of dipoles between coexisting lipid phases induced by application of the electric field. Domains of lipid were formed about an electrode positioned orthogonally to the plane of the monolayer upon application of large electrical potentials (*e.g.*, 200 V).

In this paper, we report the capability to induce the motion of fluid on the surface of a solution by *in situ* control of the amphiphilicity of molecules dissolved within the solution. The principles we report for the creation of gradients in surface tension and control of the motion of fluid on the surface of a solution differ from those previously described: gradients in surface tension and the resulting motion of fluid can be easily controlled under arbitrarily chosen conditions of temperature, pressure, humidity, etc.; the velocity of fluid motion can be manipulated on time scales of milliseconds by control of the potential applied to an electrode; the sustained motion of fluid across a surface can be realized by competitive removal of the surface-active species from the surface of the solution; the source of surfactant can be localized to the dimensions of an electrode (*e.g.*, <1 mm); the direction of motion of the fluid can be manipulated by using arrays of electrodes distributed across the surface of a solution; introduction of chemical species across the system boundary is not required; and, the method can be realized using a simple experimental apparatus.

We use the Marangoni phenomenon at the surface of an aqueous solution of $\mathbf{I}^{2+}$ to demonstrate principles for the formation of surfactant with lifetimes that range from 10^{-2} to 10^{3} s. Surface-active $\mathbf{I}^{+}$ was generated electrochemically by reduction of $\mathbf{I}^{2+}$ at an electrode protruding from the surface of a solution of $\mathbf{I}^{2+}$ and Fe^{3+}. The lifetime of $\mathbf{I}^{+}$ so formed was controlled by its rate of formation at the electrode and its rate of oxidation by excess Fe^{3+}.[21] We observed the velocity of fluid motion near an electrode to reflect a balance between rates of formation and removal of $\mathbf{I}^{+}$ from the surfaces of solutions.

By using microelectrodes, the principles we report in this paper can, we believe, be extended to temporal resolutions of microseconds and spatial resolutions of micrometers and to phenomena such as creation of Marangoni flow on interfaces between immiscible fluids, the disruption of thin films of liquid into periodic arrays of droplets, the creation of complex fluid motions by control of the potential of arrays of electrodes, and the regiospecific permeabilization and extraction of biological membranes.

Experimental Section

The redox-active surfactant (11-ferrocenylundecyl)trimethylammonium bromide ($Fc(CH_2)_{11}N^+(CH_3)_3\ Br^-$; $Fc = [\eta^5\text{-}C_5H_5]Fe[\eta^5\text{-}C_5H_5]$) ($\mathbf{I}^{+}$) was synthesized according to the procedure of Saji *et al.*[22] The product of the synthesis was confirmed by ^1H NMR and elemental analysis. Solutions of surfactant in 0.1 M Li_2SO_4 (Aldrich) were prepared by using distilled water passed through a Milli Q Plus (Milli

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Pore Corp.) purification train (18.2 MΩ cm) and adjusted to pH 2.0 by addition of sulfuric acid. All glassware was cleaned in freshly prepared hot piranha solution (18 M H_2SO_4, 30% H_2O_2, 70:30, v/v). **WARNING:** *Piranha solution should be handled with extreme caution; in some circumstances (probably when it has contacted significant quantities of an oxidizable organic material), it has detonated unexpectedly.*

Measurements of dynamic surface tension were performed with a SensaDyne 3000 maximum bubble pressure tensiometer (Chem Dyne Research Corp., Mesa, AZ). The instrument was calibrated with Milli Q water (72.1 mN m^{-1}, 25 °C) and absolute ethanol (22 mN m^{-1}, 25 °C). Surface tensions of aqueous solutions of surfactants were measured by using a pair of glass capillaries with radii of 0.5 and 4.0 mm. The rate of formation of bubbles was *ca.* 1 Hz at the small capillary.

We used two methods to prepare solutions of **I**$^{2+}$. Unless otherwise noted, blue solutions of **I**$^{2+}$ were prepared by oxidation of yellow solutions of **I**$^{+}$ with *ca.* 1.5 equiv of Fe^{3+} (as $Fe_2(SO_4)_3 \cdot 5H_2O$, Aldrich). An excess of Fe^{3+} was used to ensure complete oxidation of the surfactants because equilibrium surface tension measurements indicated that a slight stoichiometric excess of Fe^{3+} was required to quantitatively oxidize solutions of the ferrocenyl surfactant at pH 2.0.

To permit an investigation of surface flows in the absence of Fe^{3+}, **I**$^{2+}$ was also formed by electrochemical oxidation of **I**$^{+}$ at 0.5 V (*vs* silver wire pseudo reference electrode). The electrochemical oxidation was performed by placing the working (platinum gauze, 52 mesh, Aldrich) and reference electrodes into a stirred solution of **I**$^{+}$ contained within a glass crucible. The counter electrode was placed in a compartment containing electrolyte (100 mM Li_2SO_4, pH 2.0) that was separated from the working electrode compartment by a sintered glass disk (fine porosity).

In a typical surface flow experiment, sulfur powder (*ca.* 30 mg; 200 mesh, Aldrich) was used to visualize the motion of fluid on the surface of a 20 mL solution of **I**$^{2+}$ contained in a glass Petri dish with a diameter of 9 cm. Sulfur powder sprinkled onto solutions of **I**$^{2+}$ remained on the surface for days. We observed particles of sulfur to sink through the surface of solutions of **I**$^{+}$. Talc (Shower-to-Shower) was used in initial experiments (not reported) but was observed to chemically reduce the solutions of **I**$^{2+}$. Initial experiments using chalk dust were also unsuccessful. Chalk dust readily forms rigid films on surfaces of aqueous solutions and thereby prevents the spreading of surfactant across the surfaces of solutions.

The surface of each aqueous solution of **I**$^{2+}$ was placed in motion by application of a reducing potential to a platinum gauze working electrode (*ca.* 1.2 cm × 1.2 cm, 52 mesh, Aldrich) positioned near one edge of a petri dish. The working electrode protruded from the surface of the aqueous solution. The potential was controlled by using a bipotentiostat (Pine Instruments, Grove City, PA) with a counter electrode formed from a platinum flag (*ca.* 1.5 cm^2) and a saturated calomel reference electrode (SCE). The motion of sulfur particles was imaged by using a CCD video camera (Sony) and recorded with a VCR.[23,24] Images were analyzed by using commercially available software (Rasterops Mediagrabber). The displacement of the sulfur particles from the working electrode at one edge of a Petri dish toward the opposite edge was typically measured over an interval of 20 s. Multiple trials were performed with each solution by redistributing the sulfur particles on the surface between each trial. A uniform redistribution of particles was achieved by gentle agitation of the Petri dish.

Although chloride ions are known to react with the ferrocenium group under oxidative conditions,[25−27] we observed no evidence for decomposition of **I**$^{2+}$ solutions over the course of the surface flow experiments when using the SCE. In expressing applied potentials, we have followed the convention that oxidizing potentials are positive and reducing potentials are negative. All potentials are expressed *vs* SCE unless otherwise noted. The half-wave potential for **I**$^{+}$ (1 mM in 100 mM Li_2SO_4, pH 3.5) was measured to be 0.17 V by cyclic voltammetry.

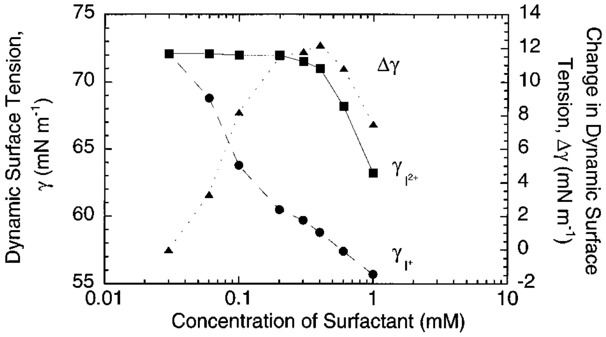

Figure 1. Dependence of dynamic surface tension (γ) and change in dynamic surface tension ($\Delta\gamma$) on concentration of **I** in aqueous solutions of 100 mM Li_2SO_4, pH 2.0: **I**$^{+}$ (●), **I**$^{2+}$ (■), and change in dynamic surface tension upon oxidation of **I**$^{+}$ to **I**$^{2+}$ (▲).

Results and Discussion

Measurements of Surface Tension. Dynamic Surface Tension. Large and reversible changes in the *equilibrium* surface tensions of aqueous solutions of **I**$^{+}$ have been reported to accompany electrochemical oxidation of **I**$^{+}$ to **I**$^{2+}$.[7,8] The change in equilibrium surface tension that accompanied oxidation of **I**$^{+}$ to **I**$^{2+}$ was maximal (23 mN m^{-1}) when **I**$^{+}$ was initially present at its critical micelle concentration (cmc, 0.1 mM): the surface tension increased from 49 mN m^{-1} to 71 mN m^{-1}.[7] The magnitude of the change in equilibrium surface tension diminished as the concentration of **I**$^{+}$ was either increased or decreased from its cmc. Although oxidation of **I**$^{+}$ to **I**$^{2+}$ is accompanied by large changes in equilibrium surface tension, it is the gradient in the *dynamic* surface tension that causes nonequilibrium phenomena such as the motion of fluid. The dynamic surface tension of a solution measured by the method of maximum bubble pressure depends on the rate of transport of surfactant to the surface of the bubble and on the rate of adsorption of surfactant to the surface.[28] Only at very slow bubbling rates will surface tensions measured by this method approach those determined under equilibrium conditions. At typical bubbling rates (1 Hz), the surface of the bubble does not reach equilibrium with the bulk solution of surfactant, and higher than equilibrium values of surface tension are observed. Figure 1 shows the change in dynamic surface tension upon addition of *ca.* 1.5 equiv of Fe^{3+} to an aqueous solution of **I**$^{+}$. The change in dynamic surface tension due to change in oxidation state of the surfactant, observed as a function of concentration, is similar to the change in equilibrium surface tension as a function of concentration reported in the past.[7,8] However, two differences do exist between the equilibrium and dynamic response of the solutions upon oxidation of **I**$^{+}$ to **I**$^{2+}$: the concentration at which the maximum change in surface tension occurs is greater for the dynamic surface tension than for the equilibrium surface tension (0.4 *vs* 0.1 mM); and the magnitude of the maximum change in the surface tension is *ca.* 50% lower for the dynamic surface tension than for the equilibrium measurements (12 *vs* 23 mN m^{-1}).

Marangoni Flow. Description of the Phenomenon. The Marangoni phenomenon is shown in Figure 2. Application of −0.3 V to a Pt gauze electrode immersed in a solution of 0.1 mM **I**$^{2+}$, 100 mM Li_2SO_4, pH 2.0 (*ca.* 3.2 mm depth), caused the surface of the fluid to move radially outward from the Pt gauze working electrode toward the edge of the Petri dish. Sulfur

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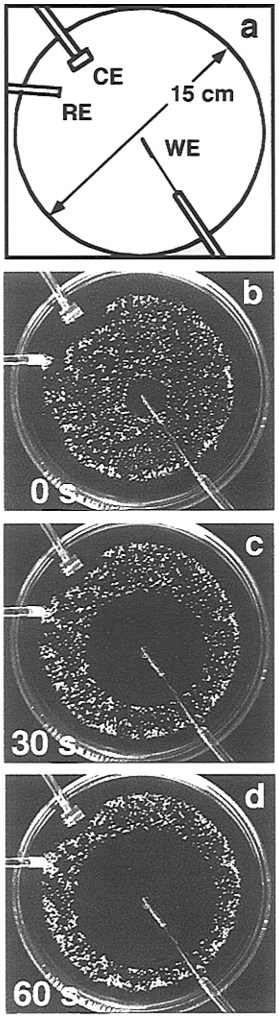

Figure 2. Top view of displacement of fluid on the surface of an aqueous solution of 0.1 mM $\mathbf{I}^{2+}$ (100 mM Li_2SO_4, pH 2.0) induced by application of −0.3 V to a Pt gauze working electrode (WE, 2 mm diameter cylinder) protruding from the surface of the solution. The surface of the solution was dusted with sulfur powder. Panel a is a schematic illustration of the arrangement of the electrodes. The reference electrode (RE) was a SCE, and the counter electrode (CE) was a platinum flag. Panels b−d show the distribution of sulfur powder on the surface of the solution before application of the reducing potential (b) and 30 s (c) and 60 s (d) after application of the reducing potential to the WE.

powder supported on the surface of the solution was displaced from the center of the dish toward the meniscus of the fluid at the vertical walls of the Petri dish. The motion of fluid was sustained for times greater than 10 min at −0.3 V as evidenced by displacement of sulfur powder sprinkled onto the surface of the solution near the working electrode.

Upon elimination of the potential applied to the electrode, the outward directed motion of fluid slowed, ceased, and finally reversed. The sulfur powder moved symmetrically back toward the center of the dish. The flow of fluid toward the center of the dish is plausibly due to the relaxation of the surface tension gradient as components of the monolayer are dissolved into the bulk solution or oxidized by excess Fe^{3+}. We measured identical values of equilibrium surface tension (72 mN m^{-1} at 0.1 mM $\mathbf{I}^{2+}$, Wilhelmy plate) before spreading of the surfactant across the surface of the solution, and following surface relaxation after spreading had occurred. This observation demonstrates that the monolayer of surfactant is eventually removed from the surface by dissolution into the bulk solution and suggests that transient generation of a surfactant monolayer at the surface of an aqueous solution is a potentially useful method of sweeping clean its surface.

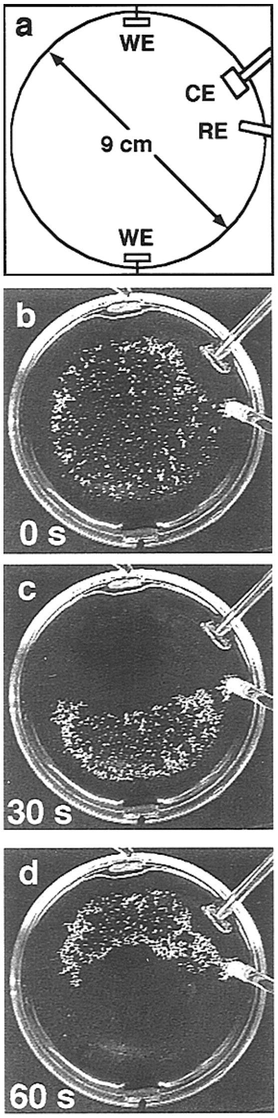

Figure 3. Top view of back and forth motion of fluid on the surface of an aqueous solution of 0.1 mM $\mathbf{I}^{2+}$ (100 mM Li_2SO_4, pH 2.0) induced by the application of potentials of opposite sign at two Pt gauze working electrodes (WE, planar squares, *ca.* 1.2 cm × 1.2 cm) placed at opposite sides of a Petri dish of diameter 9 cm. Panel a is a schematic illustration of the arrangement of the electrodes. The reference electrode (RE) was a SCE, and the counter electrode was a platinum flag. Panel b depicts the distribution of sulfur powder on the surface of the solution before application of potentials to the WEs. Panel c shows the displacement of sulfur powder caused by application of −0.3 V at the upper WE and +0.3 V to the lower WE for 30 s. Panel d shows the displacement of sulfur powder from the distribution shown in c caused by application of +0.3 V at the upper WE and −0.3 V to the lower WE.

By controlling the potentials applied to two working electrodes in a solution of 0.1 mM $\mathbf{I}^{2+}$, the sulfur powder coating the surface of the solution was moved back and forth between the electrodes. Figure 3 shows the displacement of sulfur powder across the surface of a solution between two Pt gauze working electrodes (planar squares, *ca.* 1.2 cm × 1.2 cm) positioned at opposite edges of the Petri dish. The sulfur powder was driven away from the top electrode, which was held at −0.3 V, toward the bottom electrode, which was held at +0.3 V; the motion of the sulfur powder was reversed by changing the potential at the top electrode to +0.3 V and the bottom electrode to −0.3 V. The islands of sulfur powder were repeatedly displaced across the surface of the solution (*e.g.*, 20 cycles over

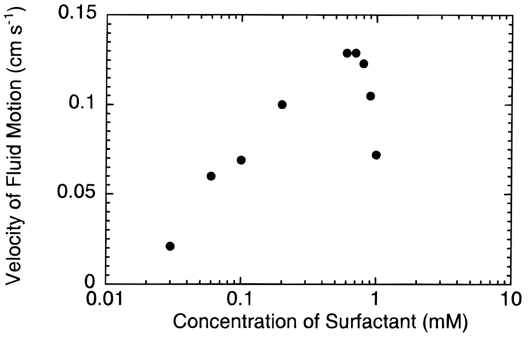

Figure 4. Dependence of velocity of fluid motion at the surface of an aqueous solution (100 mM Li_2SO_4, pH 2.0) of $\mathbf{I}^{2+}$ on the concentration of $\mathbf{I}^{2+}$. The motion of fluid was induced by application of a potential of −0.3 V to a Pt gauze electrode protruding from the surface of the solution.

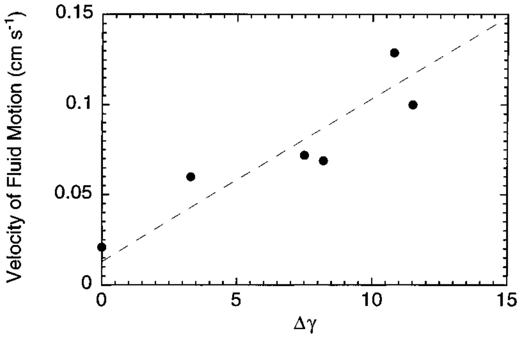

Figure 5. Correlation between the velocity of fluid motion at the surface of an aqueous solution (100 mM Li_2SO_4, pH 2.0) of $\mathbf{I}^{2+}$ and the change in the dynamic surface tension ($\Delta\gamma$) measured upon reduction of a solution of $\mathbf{I}^{2+}$ to $\mathbf{I}^{+}$. The fluid motion was induced at the surfaces of the solutions by application of −0.3 V to Pt gauze electrodes protruding from solutions of $\mathbf{I}^{2+}$ with concentrations shown in Figure 4.

10 min) without a measurable decrease in the velocity of the motion of the fluid.

The motion of fluid also occurred on solutions of $\mathbf{I}^{2+}$ prepared by electrochemical oxidation of $\mathbf{I}^{+}$ rather than by chemical oxidation with Fe^{3+}. Such flows were not sustained for times as long as those times observed when experiments were performed with solutions prepared by oxidation of $\mathbf{I}^{+}$ with Fe^{3+}. Flows with electrochemically oxidized $\mathbf{I}^{2+}$ solutions were typically sustained for several minutes with a −0.3 V potential applied to the platinum gauze working electrode.

Effect of Concentration of Surfactant. The effect of concentration of surfactant on the velocity of fluid motion was investigated by varying the initial concentration of $\mathbf{I}^{2+}$ and measuring the spreading velocities at a constant potential of −0.3 V, as shown in Figure 4. In control experiments, no motion of fluid was observed in the absence of surfactant or when $\mathbf{I}^{2+}$ was replaced by the redox-inactive surfactant dodecyltrimethylammonium bromide. The dependence of the velocity of fluid motion on the concentration of surfactant is similar to the dependence of the change in dynamic surface tension (upon reduction of $\mathbf{I}^{2+}$ to $\mathbf{I}^{+}$) on the concentration of surfactant (Figure 1). The maximal velocity in Figure 4 occurs at a concentration of surfactant (0.5−0.6 mM) that is similar to the concentration of surfactant corresponding to the maximum change in dynamic surface tension (0.4−0.6 mM). Figure 5 shows that the velocity of fluid motion is correlated with the difference in the dynamic surface tensions ($\Delta\gamma$) of solutions of $\mathbf{I}^{2+}$ and $\mathbf{I}^{+}$ over concentrations between 0.03 and 1.0 mM. The measurement of a nonzero velocity at a concentration of surfactant (0.03 mM) where $\Delta\gamma$ was zero does not mean that fluid motion occurs when the gradient in the surface tension of the solution is zero. Although the $\Delta\gamma$ values were measured under conditions similar to those used to determine velocities of fluid motion, these two quantities were measured in separate experiments. Our purpose in presenting Figure 5 is to emphasize that the velocity of fluid motion increased with the values of $\Delta\gamma$ measured by using the maximum bubble pressure method.

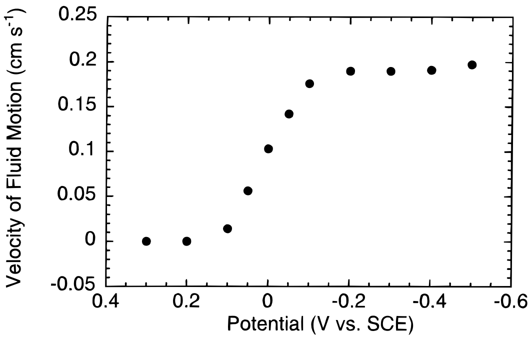

Figure 6. Dependence of the velocity of fluid motion at the surface of an aqueous solution (100 mM Li_2SO_4, pH 2.0) of 0.1 mM $\mathbf{I}^{2+}$ on the potential applied to a Pt gauze electrode (1.5 cm^2) protruding from the surface of the solution.

Effect of Applied Potential. The effect of the potential applied to the electrode on velocity of fluid motion was investigated by using a solution of 0.1 mM $\mathbf{I}^{2+}$ prepared by chemical oxidation of a solution of $\mathbf{I}^{+}$ with *ca.* 1.5 equiv of Fe^{3+} (Figure 6). The onset of the motion of fluid occurred between 0.2 and 0.1 V, which spans the half-wave potential measured for oxidation of $\mathbf{I}^{+}$ to $\mathbf{I}^{2+}$ (*i.e.*, 0.17 V). The velocity of fluid motion increased with increasingly negative (reducing) potentials up to *ca.* −0.2 V, where the velocity reached a plateau. Above −0.2 V, mass transport of the surfactant to the working electrode plausibly limits the rate of generation of surfactant and thereby limits the velocity of fluid motion.

When Pt wire with a diameter of 0.5 mm was substituted for Pt gauze as the working electrode, we did not observe the motion of fluid at potentials less reducing (more positive) than −0.6 V and concentrations of surfactant less than 1.0 mM. The small surface area of the Pt wire, as compared to the Pt gauze, appeared to limit the rate of formation of surfactant to a level that was insufficient to cause Marangoni flow. We did, however, observe the motion of fluid away from a Pt wire working electrode that was held at reducing potentials more negative than −0.6 V. We also observed the evolution of hydrogen gas at the Pt wire working electrode at potentials more negative than −0.6 V. The velocity of fluid motion increased as the potential was made more negative than −0.6 V and plateaued above *ca.* −2.0 V (data not shown). We believe that the motion of fluid at reducing potentials more negative than −0.6 V was caused by reduction of water to hydroxide ions, and not by the electrochemical reduction of $\mathbf{I}^{2+}$ to $\mathbf{I}^{+}$ at the Pt wire working electrode. Hydroxide ion reacts with $\mathbf{I}^{2+}$ to produce the surface-active species $\mathbf{I(OH)}^{+}$. We also observed rapid motion of fluid on both chemically oxidized and electrochemically oxidized solutions of $\mathbf{I}^{2+}$ at pH 2.0 when small aliquots of concentrated hydroxide ion (*i.e.*, 5−50% NaOH, w/v) were added to the surface of the solution from a capillary pipet. Decomposition of the ferrocenium ion and its derivatives *via* reaction with hydroxide ion in alkaline aqueous solutions has been reported.[26,29] We observed the velocity of fluid motion near an electrode to be slow under strongly acidic conditions (*i.e.*, pH 2.0) but rapid under weakly acidic (*i.e.*, pH 3.5) or

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(29) Pendin, A. A.; Zakharevskii, M. S.; Leontevskaya, P. K. *Kinet. Katal.* **1966**, *7*, 1074−1077.

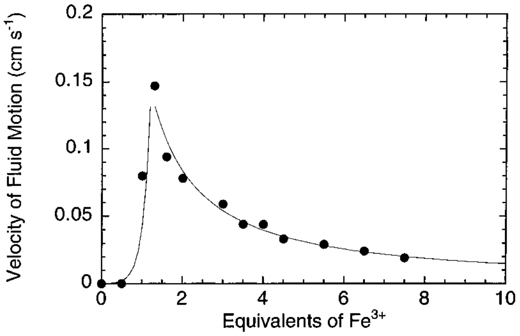

Figure 7. Dependence of the velocity of fluid motion at the surface of an aqueous solution (100 mM Li_2SO_4, pH 2.0) of 0.1 mM $\mathbf{I}^{2+}$ on the number of equivalents of Fe^{3+} added to the solution. The fluid motion was induced at the surface of the solution by application of -0.3 V to a Pt gauze electrode protruding from the surface of the solution.

neutral (pH 7.0) conditions. The marked effect of pH on the velocity of fluid motion induced by the application of -2.0 V at a Pt wire working electrode supports our belief that hydroxylation of $\mathbf{I}^{2+}$ is the mechanism responsible for the induction of Marangoni flow at potentials less than -0.6 V.[30]

Effect of Concentration of Oxidizing Agent. The dependence of the velocity of fluid motion on the equivalents of Fe^{3+} added to a solution of 0.1 mM $\mathbf{I}^{+}$, 100 mM Li_2SO_4, pH 2.0, is shown in Figure 7. The velocity of fluid motion increased on addition of Fe^{3+} up to *ca.* 1.5 equiv *vs* $\mathbf{I}^{+}$. Further addition of Fe^{3+} resulted in a decrease of the velocity of fluid motion and a diminished distance of movement of the sulfur powder from the working electrode.

The maximum in the plot of velocity of fluid motion *vs* equivalents of Fe^{3+} in Figure 7 corresponds to a maximum in the gradient in surface tension across the solution. The gradient in surface tension is influenced by the flux of $\mathbf{I}^{+}$ due to its electrochemical formation at the electrode and its subsequent removal upon oxidation by Fe^{3+}. The rate of oxidation of $\mathbf{I}^{+}$ by Fe^{3+} depends on the thickness (h) of the layer below the surface through which Fe^{3+} must diffuse in order to react with $\mathbf{I}^{+}$. We have estimated the time (t) required for the diffusion of Fe^{3+} from bulk solution to its surface from the relation[31]

$$t \approx h^2/2D \qquad (1)$$

where h^2 is the mean-square displacement of Fe^{3+} ions and D is the diffusion coefficient (estimated as 5×10^{-6} cm s^{-1}). The root-mean-square displacement, h, is approximated as the depth below the surface of the solution that defines a volume containing sufficient Fe^{3+} ions to oxidize a monolayer of $\mathbf{I}^{+}$ adsorbed at the surface of the solution. The number of Fe^{3+} ions contained in a volume defined by h was estimated as Ahc, where A is the surface area of the solution and c is the concentration of Fe^{3+} in bulk solution. The number of molecules of $\mathbf{I}^{+}$ within a monolayer at the surface of water was estimated as A/a, where a is the area occupied, on average, by each surfactant adsorbed at the surface (50 Å^2, corresponding to a monolayer of surfactant). By using eq 1, we estimated the time required for Fe^{3+} to diffuse from bulk solution to a monolayer of $\mathbf{I}^{+}$ at the surface of the solution to be 4.4, 1.1, and 0.28 s for bulk Fe^{3+} concentrations of 0.05, 0.1, and 0.2 mM, respectively (corresponding to 0.5, 1.0, and 2.0 excess equiv of Fe^{3+} *vs* equivalents of $\mathbf{I}^{+}$).[32] The maximum velocity of fluid motion is observed at *ca.* 0.5 excess equiv of Fe^{3+} (Figure 7). Because the motion of fluid occurred on time scales of seconds, these estimates of diffusion times suggest that the presence of only 0.5 excess equiv of Fe^{3+} may result in competitive consumption of the spreading monolayer—after it is produced—at a rate that maintains steady-state spreading of $\mathbf{I}^{+}$ across the surface of the solution. At concentrations of Fe^{3+} greater than *ca.* 1 mM, $\mathbf{I}^{+}$ is consumed by Fe^{3+} over time scales that are short (tens of milliseconds) compared to time scales associated with the spreading of the surfactant on the surface of the solution.

Continuous removal of $\mathbf{I}^{+}$ from the surface of the solution *via* reaction with Fe^{3+} is supported by two further observations. First, steady-state flow was not sustained for long times when the solution of $\mathbf{I}^{2+}$ was prepared electrochemically, whereas steady-state flow occurred for times longer than 10 min when an excess of Fe^{3+} was present. Second, the velocity of the backward motion of the fluid, which followed elimination of the applied potential, increased in magnitude with increasing concentration of Fe^{3+} (data not shown). The first observation suggests that the motion of fluid ceases following monolayer coverage of the surface by $\mathbf{I}^{+}$ in the absence of excess Fe^{3+}. The second observation suggests that, upon elimination of the applied potential, the monolayer of $\mathbf{I}^{+}$ is quickly removed by oxidation with Fe^{3+}.

General Considerations. We propose that two conditions must be fulfilled for the Marangoni phenomenon to be observed near electrodes protruding from the surfaces of solutions containing redox-active species. First, the *dynamic* surface tension of the solutions must change with the oxidation state of the redox-active species. We observed the velocity of motion of an aqueous solution of $\mathbf{I}^{2+}$ near an electrode to correlate closely with the change in dynamic surface tension of the solution measured upon reduction of $\mathbf{I}^{2+}$ to $\mathbf{I}^{+}$ (Figures 4 and 5).

Second, the rate of formation of surface-active species at the electrode must be sufficiently high to support a gradient in the concentration of surface-active species across the surface of the solution. We observed the velocity of the surface of a solution of $\mathbf{I}^{2+}$ to increase with the magnitude of the reducing potential applied to the electrode (Figure 6) and to increase with the surface area of the electrode. The gradient in concentration of surface-active species across the surface of the solution is, however, determined not only by the rate of formation of surfactant at the surface but also by the rate of removal of surface-active species from the surface. We manipulated the rate of removal of $\mathbf{I}^{+}$ from the surface of its solution by changing the concentration of Fe^{3+} within the aqueous subphase. The velocity of the fluid motion away from the electrode decayed to zero over minutes in the absence of Fe^{3+} within the aqueous subphase. Because we observed the transient (over minutes) motion of the surface of a solution of $\mathbf{I}^{2+}$ that contained no Fe^{3+}, we infer that spontaneous desorption of surfactant from the surface of the solution can support gradients in concentration of surfactant. Over long times (>minutes), however, $\mathbf{I}^{+}$ accumulates within a solution that contains no Fe^{3+}; the surface of the solution becomes saturated with $\mathbf{I}^{+}$, and the gradient in surface tension decays to zero. The presence of Fe^{3+} in the bulk of the solution prevents the accumulation of $\mathbf{I}^{+}$ near its surface by oxidizing $\mathbf{I}^{+}$ to $\mathbf{I}^{2+}$. The motion of the surface of solutions containing Fe^{3+} and $\mathbf{I}^{2+}$ was sustained over periods of time greater than 10 min. Concentrations of Fe^{3+} greater than ~0.7 mM, however, prevented the motion at all times (short

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[30] The evolution of gaseous H_2 at an electrode did not cause the motion of sulfur particles. The motion of sulfur particles was observed only in the presence of $\mathbf{I}^{2+}$.

[31] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 129.

[32] This analysis is approximate because it neglects the influence of convection on the mass transport of Fe^{3+} in the vicinity of the surface of the solution.

and long). By using eq 1, we estimate that $\mathbf{I}^+$ formed at an electrode will be competitively consumed by 0.7 mM Fe^{3+} on time scales of tens of milliseconds; $\mathbf{I}^+$ is plausibly oxidized to $\mathbf{I}^{2+}$ by 0.7 mM Fe^{3+} before a gradient in surface tension can be established across the surface of the solution.

Although we observed the motion of fluid to accompany the application of a reducing potential to an electrode positioned at the surface of a solution of $\mathbf{I}^{2+}$, we did not observe the motion of fluid to be induced, in general, by application of an oxidizing potential to an electrode positioned at the surface of a solution of $\mathbf{I}^+$. In the former case, $\mathbf{I}^+$ formed at the electrode establishes a gradient in surface pressure that results in its lateral convection across the surface of the solution at a rate that is comparable to its rate of desorption from the surface and vertical diffusion into the bulk of the solution. In the latter case, $\mathbf{I}^+$ oxidized to $\mathbf{I}^{2+}$ at the surface of the solution is plausibly replenished at the surface by diffusion of $\mathbf{I}^+$ from the bulk of the solution. The rate of replenishment of $\mathbf{I}^+$ at the surface of the solution appears to prevent formation of a gradient in surface tension at the surface of its solution. This conclusion is supported by observations described below.

Although fluid motion was not observed, in general, near electrodes held at oxidizing potentials in solutions of $\mathbf{I}^+$, we encountered a particular set of conditions that did lead to fluid motion by using oxidizing potentials. The motion of fluid toward an electrode held at an oxidizing potential (*e.g.*, +0.3 V) was observed when solutions were prepared by combining stoichiometric equivalents of $\mathbf{I}^+$ and Fe^{3+}. The experiment was performed by, first, applying a reducing potential to an electrode immersed in the solution until fluid motion away from the electrode was observed and, second, switching the potential of the electrode from reducing to oxidizing. The motion of fluid toward the electrode was observed to follow application of the oxidizing potential. Under conditions where little Fe^{3+} is present in the bulk solution, reduction of $\mathbf{I}^{2+}$ plausibly produces a monolayer of $\mathbf{I}^+$ that is sustained over time scales of seconds until it is removed by application of an oxidizing potential to the electrode.

Majda and co-workers have investigated the lateral diffusion of redox-active amphiphiles both in monolayers at the surface of water[33,34] and in supported bilayers.[35-38] Chronoamperometry was used to determine the diffusion coefficient of *N*-octadecylferrocenecarboxamide ($C_{18}Fc$) in Langmuir monolayers at the surface of water at different surface concentrations. The authors suggest that the method may be superior to FRAP (fluorescence recovery after photobleaching) for estimating diffusion constants in Langmuir monolayers because the electrochemical technique is free from convective interferences.[33] Our results demonstrate that oxidation of ferrocene-containing amphiphiles can lead to their convective transport across surfaces of aqueous solutions.

Control of the motion of fluid under the influence of gradients in surface tension that result from electrochemical transformations of redox-active surfactants can form the basis of principles to transport species within thin films of fluids. The use of arrays of electrodes allows active control of the velocity and direction of motion of particles at the surface of fluids (or species dissolved within the fluid). We used a pair of working electrodes to control the motion of fluid across an unconstrained solution, as depicted in Figure 3. We have also used pairs of working electrodes, positioned at the surfaces of reservoirs of surfactant solutions connected by a channel, to control the direction and velocity of fluid motion through the channel. This work will be described in a forthcoming paper.

In our system, steady-state motion of fluid over macroscopic spatial scales results from a balance between the rates of creation and removal of surface-active species. The rate of formation of surfactant was controlled by the potential applied to the electrode and the size of the electrode, and the rate of removal of surfactant was controlled by the concentration of Fe^{3+} in the bulk solution. The combination of electrochemical formation and chemical removal of surfactant provides the basis of a principle to control the lifetimes of surfactants. By changing the concentration of oxidizing agent present in this system, the lifetime of the electrochemically generated surface-active species can be tuned so that surfactant is created for times that range from 10^{-2} to 10^3 s. Because surfactants with lifetimes of tens of milliseconds will be confined to regions of solution within ~10 μm of the electrode at which they were formed (in the absence of bulk convection), the principles we report make possible the use of surfactants in environments in which the sustained or widespread presence of surfactants is detrimental (*e.g.*, biological membranes).

Conclusion

We have demonstrated that ferrocenyl surfactants in combination with electrochemical methods can be used to generate spatial gradients in surfactant-based properties of solutions by electrochemically generating surfactant in localized regions defined by electrodes. Because electrochemical reduction of a ferrocenium precursor to a ferrocenyl surfactant can reduce the dynamic surface tension of an aqueous solution by more than 10 mN/m, one phenomenon that results from the formation of ferrocenyl surfactant at an electrode that protrudes from the surface of an aqueous solution is the motion of the solution under the influence of a gradient in its surface tension. The velocity of fluid motion at the surface of the solution can be actively controlled by the potential applied to the electrode; fluid motion is directed between two electrodes by application of an oxidizing potential to one electrode and a reducing potential to another. This principle can plausibly be extended to arrays of electrodes so as to direct fluid—and solutes contained within the fluid—to multiple locations (*e.g.*, for sorting, mixing, or reacting of species contained within thin films of fluid). By changing the background concentration of oxidizing agent (Fe^{3+}) dissolved in solution, the lifetime of the electrochemically generated ferrocenyl surfactant can be controlled between 10^{-2} and 10^3 s. By tuning the lifetime of the ferrocenyl surfactant to *ca*. 1 s, steady-state gradients in surface tension can be maintained on the surfaces of aqueous solutions for tens of minutes. Extension of these principles to phenomena such as the disruption of thin liquid films into periodic arrays of droplets, the directed release of solubilizates,[39] and the permeabilization of membranes via a directed source of surfactants is under way.

Acknowledgment. Partial support of this research was provided by the Camille and Henry Dreyfus Foundation, the David and Lucile Packard Foundation, the donors of the Petroleum Research Fund, and the National Science Foundation (CTS-9410147 and CTS-9502263).

JA960902T

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