Gibbs Monolayers at the Air/Water Interface: Surface Partitioning and Lateral Mobility of an Electrochemically Active Surfactant

Andrew D. Malec, Deng Guo Wu, Mary Louie, Janusz J. Skolimowski,† and Marcin Majda*

Department of Chemistry, University of California, Berkeley, Berkeley, California 94720-1460

Received September 18, 2003. In Final Form: November 13, 2003

Monolayer films of a water-soluble surfactant, 4-octanamide-2,2,6,6-tetramethyl-1-piperidinyloxy (C8TEMPO) were investigated at the air/water interface. An electrochemical, horizontal touch method was developed to measure the equilibrium surface concentrations (Γ) of C8TEMPO. The dependence of Γ on the solution concentration followed a Langmuir isotherm and yielded the partition constant K = (2.3 ± 0.2) × 10^4 M^-1. The results were verified by surface tension measurements and Brewster angle microscopy. Within experimental error, the same K values were obtained. The lateral diffusion constants vs surface concentration of this molecule were measured by 2D voltammetry. In these experiments, the component of the oxidation current due to C8TEMPO in the bulk of the solution was subtracted from the total measured current to obtain the component due to the lateral surface diffusion. In the range of mean molecular areas from 120 to 400 Å²/molecule, the lateral diffusion constant of C8TEMPO increased from 1.0 × 10^-6 to 1.0 × 10^-5 cm²/s. The latter value is about 2.5 times larger than the C8TEMPO diffusion constant in bulk water. Comparison of the lateral mobilities of C8TEMPO and two longer alkane chain, water-insoluble homologues, C14TEMPO and C18TEMPO, showed no statistically significant differences.

Introduction

Surface equilibria and dynamics of water-soluble surfactants constitute fundamental elements of characterization of this important class of chemical systems. Specifically, understanding the bulk/surface partitioning, its dynamics, and the lateral surface mobility of water-soluble surfactants is essential to characterization of practical systems such as emulsions and foams. Understanding of these processes reflects also on our understanding of the properties of the aqueous liquid/vapor interfacial region, a subject of both fundamental significance and far-reaching significance in areas such as atmospheric sciences.

Here, we focus on redox-active, water-soluble surfactants represented in this study by an octane derivative of 4-amino-2,2,6,6-tetramethyl-1-piperidinyloxy (C8TEMPO). Taking advantage of the reversible and kinetically facile electroactivity of the nitroxide group, we developed electrochemical methods to measure the equilibrium surface concentration of this surfactant at the air/water interface, as well as its lateral mobility on the water surface as a function of its bulk concentration. To measure the surface concentration of C8TEMPO at the air/water interface, we broaden the horizontal touch methodology of Lipkowski and Bizzotto and co-workers. We used two time-resolved electrochemical techniques, cyclic voltammetry and chronocoulometry, to discriminate against electrochemical signal due to the C8TEMPO bulk population. In the second part of these investigations, the lateral diffusion constant of C8TEMPO is measured by 2D voltammetry. In those experiments, we take advantage of differences in the diffusion-limited processes governing transport to a microelectrode of the two C8TEMPO populations, that in the bulk of water and that at the air/water interface. We demonstrate that the signal due to the former can be independently recorded after the water surface is blocked by a compact monolayer of stearic acid, a redox-inactive and water-insoluble surfactant. When the resulting current—voltage curve is subtracted from that obtained in the absence of stearic acid, the differential signal can be interpreted to yield the lateral diffusion constant. The dependence of the lateral mobility of C8TEMPO on its surface concentration is compared to the surface mobility data of longer chain length, water-insoluble derivatives of this surfactant, C14TEMPO, and C18TEMPO.

* Corresponding author: e-mail majda@socrates.berkeley.edu, fax (510) 642-0269.
† Permanent address: Department of Organic Chemistry, University of Lodz, ul. Narutowicza 68, 90-136 Lodz, Poland.
Experimental Section

Materials. Synthesis of 4-octanamido-2,2,6,6-tetramethyl-1-piperidinylxoy free radical (C₈TEMPO) followed the same procedure as that used in the synthesis of the octadecane derivative (C₁₈TEMPO) described earlier. Briefly, octanoyl chloride was reacted with 4-amino-TEMPO in methylene chloride and the resulting carboxamide was oxidized with hydrogen peroxide in the presence of sodium tungstate/ethylene diamine-tetraacetic acid (EDTA) catalyst in a solution of 16 acetone/water. Purification of the product was performed by column chromatography (silica gel, eluted with 35% ethyl acetate in hexane) and characterized by thin-layer chromatography (TLC) and elemental analysis. The product crystallized slowly after vacuum evaporation. The crystals were then incubated in a vacuum to remove any traces of solvent remaining. The final results of the elemental analysis experiments were (calcd) C 68.6, H 11.2, N 9.4; (found) C 68.3, H 11.5, N 9.1. The melting point was 40 °C.

Octadecyltrichlorosilane (OTS) and 3-mercaptopropyltrimethoxysilane (MPS) were from Aldrich. OTS was vacuum-distilled into sealed glass ampules, which were opened as needed immediately prior to the individual experiments. Octadecylmethylcapran (OM) (Tokyo Kadei, Tokyo, Japan) was used without further purification. Reagent-grade 70% HClO₄ (Fisher, ACS-certified), LiClO₄ (99.99%, Aldrich), n-alkanethiols (CₙSH, n = 3, 6, 9, and 12), 0.1 M KCl, and 12 M HCl. The resistivity of the resulting water (DI water) was determined with a DuNouy tensiometer (model 70535, CSC Scientific Co. Inc.). The tensiometer's Pt ring was flamed between each measurement to increase the precision and reproducibility of these measurements.

Results and Discussion

Determination of Surface Concentration. The horizontal touch method of Lipkowski and Bizzotto is applicable to our system. Briefly, a flat surface of an unmounted gold single crystal (see Experimental Section) is brought into contact with the water surface and positioned slightly above the surface supporting a positive meniscus of water and thus limiting the exposed surface area of the gold crystal to its flat surface. In our case, featuring a solution of a water-soluble TEMPO surfactant, the gold surface is then contacting the C₈TEMPO monolayer. Since surface adsorption of a surfactant is driven by a decrease of the interfacial tension, the surface concentration of C₈TEMPO at the solution/gold interface can be expected to be different than the equilibrium concentration of C₈TEMPO at the air/water interface where the interfacial tension of the two interfaces is different. Therefore, our first goal was to chemically modify the gold surface by assembling a monolayer of an alkanethiol so that the energetics of the modified gold/water interface approximate the energetics of the alkane/water interface. Specifically, at 20 °C, the surface tensions of the air/water and alkane/water interfaces are 72.4 and 51.4 ± 0.5 mN/m (the latter is the average and the standard deviation of the nearly identical interfacial tensions of water and six liquid hydrocarbons of increasing chain length from hexane to dodecane). The interfacial tension of an alkanethiol-modified gold/water interface is likely to be somewhat smaller than that of the alkane/water interface. Consequently, in view of the thermodynamic argument mentioned above, we could expect a small negative error in the C₈TEMPO surface concentration determined at the modified gold/water interface relative to the air/water interface. We discuss this issue below.

In addition to surface thermodynamics, we were also concerned about the effect of the alkanethiol monolayer on the electron-transfer processes involved in the C₈TEMPO coulometric assay. As described in the Experimental Section, the assembly of C₈SH (n = 3, 6, 9, and 12) following each set of horizontal touch experiments, the gold surface was brought back to its initial state by several careful flaming cycles that increased the temperature of the gold crystal to just below melting point, visually recognized by a dark red color of the crystal followed by quenching in distilled water.

Electrochemical Measurements. All cyclic voltammetric and coulometric experiments were done with either a CH Instruments Model 620 electrochemical analyzer (Austin, TX) or a BAS Model 100A electrochemical analyzer (West Lafayette, IN) in a three-electrode setup under computer control with an SCE or an Ag quasi-reference electrode and a Pt counter electrode. A copper Faraday cage was used in 2D electrochemical experiments to minimize noise.

Brewster Angle Microscopy. Brewster angle microscopy (BAM) measurements were performed on a small active vibration table (MOD-2, Halconics GmbH, Goettingen, Germany), enclosed in a Plexiglas box on a large table within a thermostated, laminar flow enclosure operated under positive pressure with filtered air. The microscope (BAM 2plus, Nanofilm Technology GmbH, Goettingen, Germany) was equipped with a 50 mW Nd: YAG laser, typically operated at 50% power. BAM measurements were done in ca. 105 exposures interspersed by ca. 30 s for a total time of about 5–10 min for each concentration.
was limited to 10 s in order to decrease the extent of organization and thus potentially passivating character of the monolayer films. The resulting water contact angles measured on the modified gold surfaces were 92°, 96°, 99°, and 101°, respectively. We further determined that the surface concentrations of C8TEMPO measured with C12SH-modified gold electrodes were systematically ca. 14% lower than those obtained when a nonanethiol modification layer was used. We assigned this difference to partial blocking of the C8TEMPO electroactivity by the dodecanethiol monolayer. The C8TEMPO coverage obtained with nonanethiol-modified electrodes was ca. 3% and 22% greater than those obtained with the C6SH- and C3SH-modified surfaces, respectively. Consequently, all the data shown below were obtained with either the hexanethiol- or the nonanethiol-modified gold (C6,9S-Au) electrodes.

Initially, we tested the C6,9S-Au electrodes in the horizontal touch experiments involving water-insoluble monolayers of C18TEMPO.13 Figure 1 shows a cyclic voltammogram recorded in such experiments with the C18TEMPO surface coverage of 2.2 \times 10^{-10} \text{ mol/cm}^2 (corresponding to 75 Å²/molecule). Integration of the anodic or cathodic current above background yields the electrochemically determined surface coverage. The inset in Figure 1 is a correlation of the electrochemically determined coverage and that spread on the water surface by a standard Langmuir trough procedure with a chloroform solution of C18TEMPO of a precisely known concentration.13 The unit slope in that correlation in a range of the surface concentrations of (1.1 \times 10^{-10} \text{ mol/cm}^2) ensure us that the C6,9S-Au electrodes allow full electroactivity of C18TEMPO trapped at the C6,9S-Au/water interface.

Determination of the C8TEMPO surface concentration is only slightly more involved. Since the surface population of C8TEMPO is in equilibrium with its bulk population, the horizontal touch cyclic voltammograms reveal current contributions of both populations. The two components of the voltammetric current can be resolved by one of two methods. The first is voltammetry at a fast scan rate (v) such that the diffusion-controlled current due to oxidation of the bulk population (i_b \propto v^{1/2}) is insignificant relative to the surface current proportional to the C8TEMPO concentration at the C6,9S-Au/water interface (i_s \propto v).15

Figure 2 shows two cyclic voltammograms of C8TEMPO at a bulk concentration of 4.47 \times 10^{-5} \text{ M} recorded in the horizontal touch experiments at 0.01 and 2 V/s. The slow-scan voltammogram (Figure 2A) is dominated by the C8-TEMPO bulk component. As a result, its anodic and cathodic branches are of nearly identical magnitude. The symmetric shape of the anodic peak of the fast-scan voltammogram (Figure 2B) reveals the dominance of the C8TEMPO surface component. The asymmetry of the anodic and cathodic branches is of nearly identical magnitude. The symmetric shape of the anodic peak of the fast-scan voltammogram (Figure 2B) reveals the dominance of the C8TEMPO surface component. The asymmetry of the anodic and cathodic branches in this case reflects a greater solubility of the positively charged oxonium ion, C8-TEMPO+ a fraction of which leaves the C6,9S-Au/water interface before it can be reduced. Integration of the anodic current of the high-scan voltammograms yields the surface concentration of C8TEMPO. Analysis of the dependence of the surface concentration obtained in such experiments on scan rate (see inset in Figure 2B) showed that the anodic charge became independent of scan rate above ca. 1 V/s. Thus, at scan rates higher than 1 V/s, the contribution to the anodic current due to the bulk population of C8TEMPO becomes insignificant.

In this potential step experiment, the time dependence of charge $Q$ is given by

$$Q = Q_{dl} + nF\Gamma + 2nFAC^* \frac{D_b \theta}{\pi}$$

where $Q_{dl}$ is the double-layer charge associated with the potential change, $\Gamma$ is the surface concentration of C8-TEMPO at the C6,9S-Au/water interface, $D_b$ is the diffusion constant of C8TEMPO in water, and the other symbols carry their usual meanings. A plot of $Q$ vs $t^{1/2}$ gives $\Gamma$ from its intercept once the double-layer charge is independently determined. Figure 3 shows one such plot representing a chronocoulometric experiment carried out on a 4.47×10^{-5} M C8TEMPO, 0.05 M LiClO4, and 0.01 M HClO4 solution. To accurately measure the double-layer charge, similar experiments were carried out stepping the potential in a range negative of the formal potential of C8TEMPO where no faradaic current flows (see Figure 3, curve B). A blank voltammogram recorded between −0.05 and +0.55 V at 1 V/s at a modified gold electrode touching 0.05 M LiClO4 and 0.01 M HClO4 electrolyte solution showed that the capacitance ($C_a$) of the C6,9S-Au/solution interfaces is independent of the potential in this range. Therefore, the intercepts of the Anson plots such as those in Figure 3B represent the accurate value of $Q_{dl}$. We note that $C_a$ that can be obtained as $Q_{dl}/\Delta V$ is affected both by the modifying alkanethiol monolayer and by the adsorption of C8TEMPO.

For example, the average $C_a$ of the C6,9S-Au/water interfaces was found to be 5.6 ± 0.1 μF/cm². It decreases to 4.7 ± 0.1 μF/cm² when the electrode is exposed to the same electrolyte also containing 4.47×10^{-5} M C8TEMPO. The C8TEMPO surface concentration ($\Gamma$) data obtained by the fast-scan voltammetry and by chronocoulometry were statistically indistinguishable. We point out that surface coverage measured by these techniques does not depend on the time of equilibration of the C6,9S-Au electrodes at the surface of the C8TEMPO solutions from approximately 1 s to over an hour. Figure 4 shows the dependence of $\Gamma$ on C8TEMPO bulk concentration obtained by these electrochemical methods.

To validate our new electrochemical methodology, the dependence of the surface concentration of C8TEMPO on its bulk concentration was also deduced from the measurements of the integrated reflected light intensity in Brewster angle microscopy (BAM), carried out on the C8-TEMPO solutions of increasing bulk concentration, and from a set of surface tension ($\gamma$) measurements. We demonstrated earlier that the intensity of reflected BAM light integrated over the illuminated area of the air/water interface of 320 × 430 μm² is, indeed, proportional to the surface concentration of a surfactant at that interface. The surface tension measurements (shown in the inset of Figure 4) yielded the surface concentration of C8TEMPO by use of the Gibbs equation:

$$\Gamma = \frac{1}{RT} \frac{dy}{d\ln(C)}$$

Both sets of the $\Gamma$ vs C data are also shown in Figure 4. The solid lines in that figure represent the fits of the Langmuir isotherm to the three sets of data:

$$\Gamma = \Gamma_{max} \frac{KC}{1 + KC}$$

where $K$ is the partitioning constant and $\Gamma_{max}$ is the limiting surface concentration. The values of these parameters for each fit are listed in Table 1. Examination of Figure 4 and Table 1 shows clearly that there is very good agreement between the results of the three experimental approaches.

The comparison of the BAM, surface tension, and electrochemical data in Figure 4 requires some discussion. Unlike the first two methods, the electrochemical approach is specific to C8TEMPO. However, it relies on the determination of C8TEMPO at the C6,9S-Au/water interface rather than at the air/water interface. As mentioned above,
the fact that the former is expected to exhibit a smaller interfacial tension and thus presents a weaker driving force for C8TEMPO adsorption suggests that the electrochemical results in Figure 4 could be burdened with a systematic negative error. In comparison, the BAM and surface tension measurements could, in principle, be burdened with a positive error. While we do not believe that impurities play a significant role in the measurements reported in Figure 4, BAM and surface tensiometry are not specific to C8TEMPO but report rather an integrated effect due to all surface-active compounds including, potentially, impurities. Therefore, the agreement between the three sets of adsorption data suggests that they all accurately reflect the adsorption thermodynamics. Consequently, there likely exists an additional driving force in the C8TEMPO adsorption at the C8:5:3-Au/water interface that compensates for the somewhat lower interfacial tension of that interface relative to the air/water interface. We postulate that this additional effect is due to intercalation of C8TEMPO into the alkanethiol monolayer on gold. The latter is clearly not well organized (see the contact angle data above) because of the purposefully short self-assembly time and the relatively short alkane chain. Even a prolonged self-assembly of alkanethiols results in well-ordered monolayer films exhibiting contact angles with water of ca. 112° only when the chain length is at least 12 carbon atoms long. The decrease of C8 of the C8:5:3-Au/water interface in the presence of C8TEMPO reported above substantiates this hypothesis.

**Determination of the Lateral Diffusion Constant.**

Determination of the lateral diffusion constant of C8 TEMPO encounters a similar difficulty as that met in the measurements of the surface concentrations. Existence of two C8 TEMPO populations, on the water surface and in bulk of the aqueous solution, inevitably leads to the fact that the current density at a gold line microelectrode is a sum of two components contributed by the two C8 TEMPO populations.

The methodology of 2D voltammetry with line microelectrodes has been described in our previous reports. Briefly, in these experiments, the microband electrode obtained by fracturing a gold-coated glass slide (see Experimental Section) is touching the water surface so that only the cross-section of the newly generated glass slide and the ca. 100 nm wide edge of the vapor-deposited gold film are exposed to the electrolyte solution. Thus, the voltammetric current recorded with these microband electrodes (see Figure 5, curve A) contains a lateral component due to the surface population and a component due to the bulk population. The latter can be independently recorded when the water surface is covered by a monolayer of stearic acid, which blocks adsorption of C8TEMPO. A small volume of a chloroform solution of stearic acid is spread on the surface in the electrochemical cell. The amount of stearic acid applied was equivalent to a monolayer, and thus to obtain the 2D voltammogram due to the lateral diffusion of C8TEMPO, we relied on the equation derived by Aoki et al. for the case of linear sweep voltammetry at microband electrodes that considers, as in our case, a mixed linear and hemicylindrical diffusion control of the peak current. The necessary 2D reduction of dimensionality involved substituting the product of cylinder length (h) and bulk concentration

\[
i(t) = \frac{2\pi n F A D o C^*}{w \ln \left(\frac{64D_o t^2 w^2}{\tau}\right)} \tag{4}
\]

In a set of experiments carried out with stearic acid-covered water surface at different bulk C8TEMPO concentrations (C* was varied in the range shown in Figure 4), the average D0 value and standard deviation were found to be (3.9 ± 0.24) × 10^-6 cm²/s.

The ability to independently record the component of the voltammetric current due to the C8TEMPO diffusion in the bulk of electrolyte allows us then to subtract it from the current recorded in the absence of the stearic acid monolayer, and thus to determine the 2D voltammogram due to the lateral diffusion of C8TEMPO on the water surface (see Figure 5, curve C). The cathodic branch of the voltammogram C in Figure 5 is very small due to the fact that the oxonium cation, C8TEMPO+, generated in the forward, anodic scan is more soluble in water than its reduced, uncharged counterpart and desorbs from the air/water interface. The anodic branch of the 2D voltammogram bares a signature of a mixed linear and radial diffusion. This is expected since the width of the diffusion layer developing in the plane of the water surface in these slow-scan experiments is comparable with the 500 Å length of our line microelectrodes. Therefore, the observed 2D voltammogram (curve C in Figure 5) combines a hemicylindrical and a linear diffusion component. To extract the lateral diffusion constant (D L) of C8TEMPO, we relied on the equation derived by Aoki et al. for the case of linear sweep voltammetry at microcylinder electrodes that considers, as in our case, a mixed linear and hemicylindrical diffusion control of the peak current. The necessary 3D → 2D reduction of dimensionality involved substituting the product of cylinder length (h) and bulk concentration


particles decreases. This is consistent with the behavior of particle–fluid suspensions. A quantitative analysis of the data in Figure 6 will be a subject of a separate report. We note that in the case of the ferrocene-amide surfactants, which we investigated earlier, we did observe an alkane chain length effect on the surfactant mobility. However, in that case we showed that the effect was related to the dependence of the surfactant’s immersion depth on the chain length and not directly to the chain–chain interactions. In closing, we note that the C8TEMPO diffusion constant in low-density monolayers at the air/water interface of ca. 1.0 × 10⁻⁵ cm²/s is more than twice as large as its value in the bulk of the aqueous electrolyte of 3.9 × 10⁻⁶ cm²/s. This is the consequence of a rather shallow immersion depth of the TEMPO amphiphile at the air/water interface.

Conclusions

Our electrochemical, horizontal touch method of measuring surfactant’s surface concentration at the air/water interface was compared with surface tension measurements and Brewster angle microscopy. The very good agreement of the data obtained by these three techniques suggests that surface modification of gold electrodes with water, an interface that behaves similarly to the air/water interface, yielding the same partition constant for C₈-TEMPO. We hypothesize that the smaller interfacial tension of that interface relative to that of the air/water interface is compensated by the van der Waals interactions of C₈TEMPO with the alkane chains of the alkane thiol monolayer. Whether this property of the C₈S-Au/water interface can be extended to other classes of redox-active surfactant is a subject of our current investigations. We also showed that line microelectrodes can be used successfully in the measurements of the lateral mobility of water-soluble redox surfactants at the air/water interface. Finally, we demonstrated that the lateral mobility of C₈-TEMPO surfactants (with n = 8, 14, and 18) does not depend on the length of their alkane chain. It is instead determined by their immersion depth and by their concentration, which determines the level of intermolecular interactions in the headgroup region.

Acknowledgment. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Additional support was provided by the National Science Foundation (CHE-0079225).

LA035754G