A Direct Method of Studying Adsorption of a Surfactant at Solid–Liquid Interfaces

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A self-assembled monolayer of decyltrichlorosilane (Cl₃Si(CH₂)₉CH₃) supported on elastomeric polydimethylsiloxane (PDMS) was used as a model system to study the adsorption of a nonionic surfactant [H(CH₂)₁₂(OCH₂CH₂)₇OH] at the solid–liquid interface. The deformation produced on contacting a semispherical lens of the elastomer with a flat sheet under water varied systematically in response to the amount of surfactant added to the aqueous phase. The JKR theory of contact deformation in conjunction with the Gibbs’ theory of interfacial thermodynamics yielded the required interfacial tension and surface excess quantities at solid–liquid interface.

Introduction

Thermodynamic analysis of the adsorption of surfactant at a liquid–air interface can be done using Gibbs adsorption equation:

$$\Gamma = -(CIR)\frac{\partial y}{\partial C}$$  \hspace{1cm}(1)

where, $\Gamma$ is the surface excess of the adsorbed surfactant, $C$ is the concentration of the surfactant in the solution, $y$ is the surface tension at the liquid–air interface, and $R$ and $T$ are the molar gas constant and temperature, respectively.

By contrast, estimation of the surface excess quantities at the solid–liquid interface is not that straightforward because its interfacial tension is not readily measurable. The relevant surface excess quantities, in this case, are therefore obtained by spectroscopic and weight gain methods. Here we report a study where the interfacial tension of a solid–solution interface could be measured directly as a function of the bulk concentration of a surfactant, thus allowing a direct estimate of $\Gamma_{sl}$ from the Gibbs adsorption equation (eq 1).

The method of determining the interfacial tension is based upon measuring the deformation produced on bridging a semispherical elastomer of polydimethylsiloxane (PDMS) in contact with another flat sheet under aqueous solutions of a nonionic surfactant [H(CH₂)₁₂(OCH₂CH₂)₇OH]. Using the theory of Johnson, Kendall, and Roberts (JKR), the interfacial tension $\gamma_{sl}$ is calculated from the radius $(a)$ of contact deformation at zero load according to the equation:

$$\gamma_{sl} = K_0 a^3/12\pi R^2$$  \hspace{1cm}(2)

where $K$ is the composite modulus and $R$ is the radius of the hemisphere. Johnson et al. used the method of contact deformation to measure the interfacial tension of a surfactant solution/rubber interface. Later, using the same basic principles, Pashley et al. estimated the interfacial tension of a surfactant coated mica and water, and Chaudhury and Whitesides measured the interfacial tension of a silicone rubber and solutions of water and methanol. This method was also recently by Sharma et al. to measure the interfacial tension of a self-assembled silane monolayer and water.

In our current studies, the surface of polydimethylsiloxane was modified by a self-assembled monolayer of decylsiloxane according to a method described earlier. Silane modified PDMS surface is hydrophobic ($\theta_{water} = 112^\circ$) as well as oleophobic ($\theta_{hexadecane} = 42^\circ$). Furthermore, it provides a chemically homogeneous surface as evidenced by the relatively low contact angle hysteresis (ca. $8^\circ$) of water. The contact deformation experiments were performed by first bringing small semispherical lenses of PDMS into contact with flat sheets of PDMS under water and then injecting the surfactant [H(CH₂)₁₂(OCH₂CH₂)₇OH] in the aqueous subphase (Figure 1). Followed by the addition of surfactant, the area of contact at first decreases and then reaches an equilibrium value. The magnitude of the contact deformation at equilibrium varied systematically as a function of the concentrations of the surfactant. These contact deformations in conjunction with the JKR (eq 2) and Gibbs (eq 1) equations allowed estimation of $\Gamma_{sl}$ at the polymer–water interface.
Figure 2. Gibbs plot of the interfacial tension $\gamma$ versus $\ln C_b$ at 23°C. $C_b$ (mg/mL) is the bulk concentration of the surfactant (heptaethylene glycol mono-n-dodecyl ether) in water. The open circles represent the adsorption at the liquid-air interface and the closed circles represent the adsorption at the solid-liquid interface.

Results and Discussion

The surface tensions of the aqueous solutions of the surfactant were measured in air using the Wilhelmy plate method. The corresponding Gibbs plot of $\gamma_l$ versus $\ln C_b$ is shown in Figure 2. This plot shows a clear break at $C_b = 3.7$, giving a value of the critical micellar concentration (cmc) of the surfactant as $8.1 \times 10^{-5}$ M/L. The surface excess $\Gamma_v$ of the adsorbed surfactant at liquid–vapor interface, estimated from the linear portion of the plot, is $2.7 \times 10^{-10}$ mol/cm$^2$ giving the corresponding molecular area ($a_v$) of the adsorbed surfactant as 61 Å$^2$. These values of $\Gamma_v$ and $a_v$ are somewhat different from the corresponding values $^{12}$ ($\Gamma_v = 3.6 \times 10^{-10}$ mol/cm$^2$; $a_v = 46$ Å$^2$), measured at 55°C.

The results of the contact deformation experiments under aqueous solutions of the surfactant are summarized in Figure 4. When the surfactant is added to water, the contact area decreases after a brief induction period (1 to 3 min). In Figure 4, the decrease of the interfacial tension is shown by plotting $\gamma_{Sl}(t)/\gamma_{Sl}(0)$ versus time $t$. According to the arguments of fracture mechanics, $^{13}$ the stability of contact of a sphere on a flat plate is determined by the balance of the tensile stresses at the edge due to adhesion and the crack closing stresses resulting from the intermolecular forces present in the open surfaces of the crack. Adsorption of surfactant on the open surfaces reduces their attraction, causing the crack to open further and driving the interface to a new mechanical equilibrium. Since the polymer used here is elastic, it is reasonable to assume that the crack opens up instantaneously. Although, we have not proven the above hypothesis by direct measurement of crack speed, the time scale of crack propagation (less than a second), in experiments where change of contact area is induced by external loads, is much faster than what (minutes) is seen in the current experiments. The crack growth, thus, is expected to be in equilibrium with the local concentration of the surfactant. Although we have not analyzed these data in any detail, it is reasonable to expect that the kinetics of crack propagation, to a large extent, is limited by the bulk diffusion of surfactant. Recently, Parker and Rutland $^{14}$ studied the time-dependent adhesion between glass surfaces in a dilute surfactant solution, while keeping the surfaces in contact for different amounts of time. Since the surfactant increases the hydrophobicity of the glass/water interface, the adhesion increased with time following...
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**Experimental Section**

**Materials.** The plasma oxidation was carried out in a Harrick Plasma Cleaner (Model PDC-23G, 100 W). The silane was purchased from Petrich. The water used in these studies was purified using a Nanopure water purifier (Barnstead) and has a surface tension of 72.7 dyn/cm. The surfactant (heptaeethylene glycol mono-n-dodecyl ether) was purchased from Nikko Chemicals Co., Ltd. (Tokyo, Japan) and used without further purification. The contact radii \( a(t) \) were measured using an inverted microscope (Nikon, Daphot), which was equipped with a video camera and a video recorder. The surface tensions of the aqueous solutions of the surfactant were determined using a Cahn automatic electrobalance (DCA 312).

**Methods.** The PDMS elastomers were prepared from the clear components of Dow Corning Sylgard-170A and 170B at proportions of 1:3. The surfaces of PDMS elastomers were modified by first exposing them to an oxygen plasma (45 s, 0.2 Torr) to generate a thin superficial oxide layer, which was derivatized by reacting it with the vapor of decyltrichlorosilane under reduced pressure. The details of the surface modification are described in refs 8, 10, and 11. The experimental cell (a polystyrene petri dish) contained a known volume \( (V_1) \) of water, in which the initial contact between the semisphere and flat sheet was made. The final volume of solution was adjusted to 40 mL by injecting a weighted volume \( (40 - V_1) \) of a surfactant stock solution to meet the desired final bulk concentration \( C_b \). After a short induction time, the contact area started to decrease and finally reached an equilibrium value. The contact areas were recorded in a video recorder and analyzed at leisure. Surface tensions at the liquid–air interface were measured at 23°C (±0.5°C) and a constant speed (5μm/s) of immersion of the platinum plate. The mean standard deviations corresponding to these experimental data are 0.5 erg/cm² for \( \gamma_{hv} \) and 1 erg/cm² for \( \gamma_{sl} \).

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**References and Notes**

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