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From superhydrophobic to superhydrophilic surfaces tuned by surfactant solutions

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The wettability of hydrophobic surfaces is generally improved by surfactant solutions. The wetting behavior of superhydrophobic surfaces can be classified into two types, in terms of the variation of contact angle with surfactant concentration c_s. Contact angle is controlled by surface tension for common linear surfactants and becomes independent of c_s as $c_s >$ critical micelle concentration. Consequently, superhydrophobic surfaces remain in hydrophobic range, as reported. However, for branch-tailed surfactants such as sodium-bisethylhexylsulfosuccinate and didodecyldimethylammonium bromide, superhydrophobic surfaces can turn superhydrophilic by increasing c_s owing to continuous reduction of solid-liquid interfacial tension. The superhydrophobicity is recoverable simply by water rinsing. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2779092]

Wetting phenomena of water droplets on substrates are of crucial concern in our daily life as well as in engineering and science. Wetting contact angle (CA) between the liquid-gas (l-g) and liquid-solid (l-s) interfaces is used to characterize the nature of solid-fluid interactions. Conventionally, a surface is termed superhydrophobicity when water contact angle is greater than 150°.[1] The opposite effect is superhydrophilicity whereby a droplet is converted into a film. Superhydrophobic and superwetting surfaces have potential use in the microfluidic and sensor applications.[2] In capillarity-related applications, however, surfaces with strong water repellency make wetting and spreading very difficult to control. In general, specific surfactants can be added to tune the wetting and spreading behavior of the liquid on hydrophobic interfaces. Nevertheless, it was reported that superhydrophobic surfaces remain in hydrophobic or superhydrophobic range for common surfactants, such as nonionic octaethylene glycolmono-*n*-decyl ether ($C_{10}E_8$) and ionic sodium dodecyl sulfate (SDS).[3,4] As a result, the traditional approach (surfactant addition) seems unable to turn superhydrophobic surfaces into highly wettable surfaces (less than 20°), and the superhydrophobic surface cannot be easily cleaned.

The wetting behavior is governed by two factors, the chemical composition and the roughness of the solid surfaces. The wettability of an ideal *flat* solid is depicted by Young equation,[5] $\cos\theta = (\gamma_{s\text{-}g} - \gamma_{l\text{-}s})/\gamma_{l\text{-}g}$, where $\gamma_{s\text{-}g}$, $\gamma_{l\text{-}s}$, and $\gamma_{l\text{-}g}$ represent the interfacial tensions of solid-gas, l-s, and l-g interfaces, respectively. The highest contact angle for a water droplet on a smooth substrate, such as–CF_3 groups with surface-free energy of 6.7 mJ/m^2, is generally about 120°.[6] Beyond this angle, the fine surface roughness becomes the dominant factor in increasing the contact angle. The mechanisms responsible for the effect of surface roughness were addressed by Wenzel[7] and later by Cassie and Baxter.[8] The superhydrophobic surface can be regarded as a surface composed of two types of homogeneous patches that have different solid-fluid interfacial tensions. Because the rough structure is mainly filled with air, the openings of the grooves can be regarded as nonwetting patches with the contact angle $\theta = 180°$. According to the Cassie-Baxter model,[8] the apparent contact angle is given by $\cos\theta_a = f\cos\theta + (1-f)\cos 180°$, where f represents the fraction of the projected area that is wetted by the liquid. On the other hand, Wenzel[7] considered that the liquid fills up the grooves on the rough surface and generalized Young equation to obtain the apparent contact angle $\cos\theta_a = r\cos\theta$, where r is termed the "roughness factor" and defined as the ratio of the actual area of a rough surface to the projected area. As a result, in addition to enhance hydrophobicity, surface roughness can lead to superhydrophilicity on intrinsically hydrophilic surfaces as well.

Surfactant molecules tend to adsorb onto l-g and l-s interfaces and therefore alter the interfacial tensions and wetting behaviors. In this letter, the modifications of the wettabilities of superhydrophobic surfaces by surfactant solutions have been studied. The shapes of sessile drops were recorded at an elapsed time of 90 s and analyzed at room temperature on a Krüss DSA10 contact angle measuring system. Reported contact angles are the average of at least four mea-

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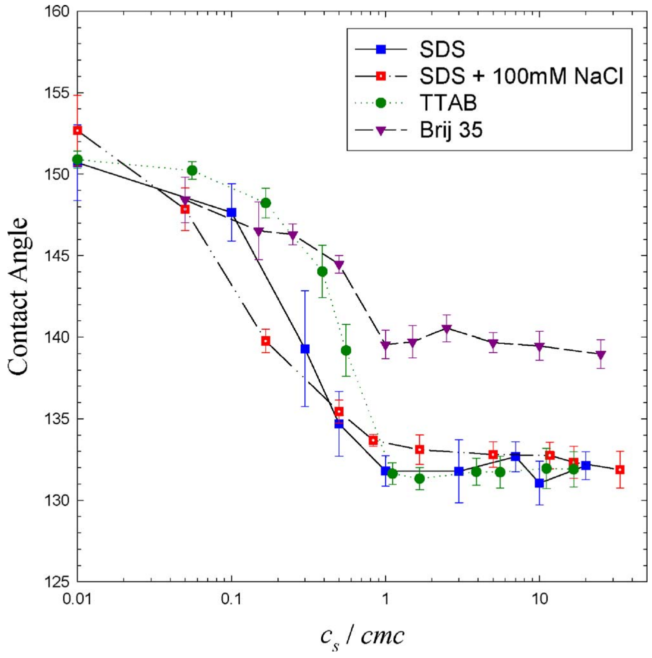

FIG. 1. (Color online) Variation of contact angle with surfactant concentration for surfactants with a linear alkyl tail. When c_s is increased, CA declines and then becomes insensitive to c_s for $c_s >$cmc. The surface always remains in hydrophobic range because $\gamma_{l\text{-}g}$ is dominant.

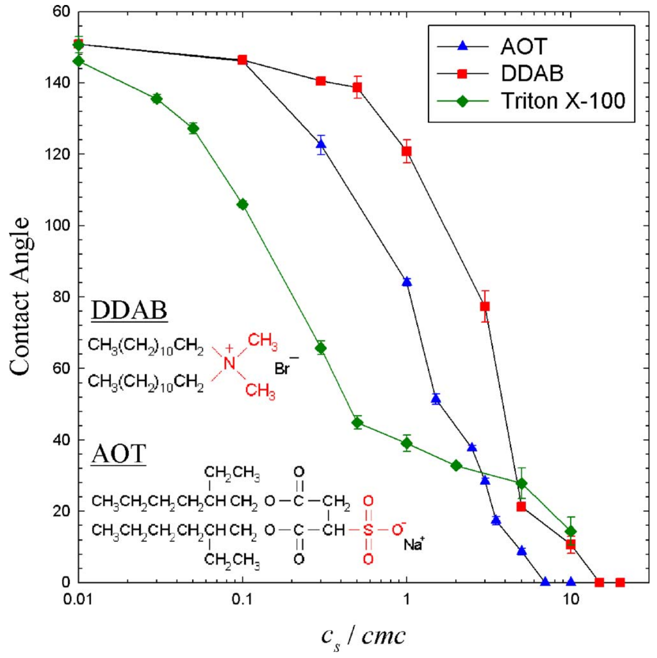

FIG. 2. (Color online) Variation of contact angle with surfactant concentration for surfactants with a branched tail. With increasing c_s, CA continues decaying and becomes a hydrophilic surface because $\gamma_{l\text{-}s}$ is dominant. Eventually, the surface reaches superwetting due to surface roughness associated with superhydrophobic behavior.

surements. Investigated surfactants include nonionic and ionic surfactants. The former has polyoxyethylene lauryl ether (Brij 35) (Acros, >99%) and Triton X-100 (Sigma, 10%) while the latter contains SDS (Sigma, 99%), tetradodecylammonium bromide (TTAB) (Aldrich, >99%), sodiumbisethylhexylsulfosuccinate (AOT) (Sigma, 99%), and didodecyldimethylammonium bromide (DDAB) (Acros, 99%). The superhydrophobic silica-based thin film has been prepared by a combination of sol-gel process and poor solvent addition after casting process.[9] The chemical modification yields CH_3-terminated surfaces and leads to water contact angle greater than 150° with a low CA hysteresis (less than 4°). The effective solid-gas interfacial tension determined by the Owen-Wendt-Rabel-Kaelble method[10,11] with water and ethylene glycol is $\gamma_{s\text{-}g} \approx 10\ \mathrm{mJ/m^2}$. According to the Wenzel theory, the roughness factor can be estimated by depositing the ethylene glycol droplets on the *smooth* and *rough* surfaces with the same chemical composition. The rough surface possesses micron-size particles while the smooth surface does not. Since the contact angles are about 120° (rough) and 101° (smooth), the roughness factor of the rough surface is $r \simeq 2.6$.

The wetting behavior on the superhydrophobic surface is expressed in terms of the variation of contact angle with surfactant concentration, as shown in Figs. 1 and 2. Depending on the architecture of the surfactant tail, two types of wetting behaviors can be clearly identified. The first type shows CA reaching a constant value in the hydrophobic range while the second type exhibits a continuous decay of CA.

Type I is surface tension ($\gamma_{l\text{-}g}$) control. Typical surfactants consist of a *linear*, hydrophobic tail (alkyl chain). The hydrophilic headgroup is generally polyethylene oxide or polyol headgroup for nonionic surfactants and sulfonic acid salt or quaternary ammonium salt for ionic surfactants. The wetting behavior associated with the typical surfactants is shown in Fig. 1. As surfactant concentration c_s is increased, contact angle drops at first. However, CA becomes independent of surfactant concentration for c_s greater than critical micelle concentration (cmc). Consistent with previous studies,[2,4] a superhydrophobic surface remains in hydrophobic or superhydrophobic range for typical surfactants. Consequently, increasing c_s furthermore is useless in turning the wettability from superhydrophobicity to hydrophilicity. Since it is known that $\gamma_{l\text{-}g}$ remains constant for $c_s \geqslant$cmc, this consequence reveals that $\gamma_{l\text{-}s}$ becomes insensitive to c_s as well, according to Young equation.

The interfacial tension modified by surfactant addition is caused by the adsorption of surfactant onto the interface and can be described by the Gibbs adsorption equation, which relates the surface excess concentration Γ_s to the interfacial tension γ by $\Gamma_s = -(1/k_B T)(d\gamma / d \ln c_s)$. Therefore, for $c_s \geqslant$cmc, the surfactant monolayer of *l-g* or *l-s* interface becomes saturated because both $\gamma_{l\text{-}g}$ and $\gamma_{l\text{-}s}$ are unchanged. Such surfactants are unable to reduce $\gamma_{l\text{-}s}$ further to satisfy the condition, $\gamma_{l\text{-}s} < \gamma_{s\text{-}g}$, at saturation and thus the surface remains in hydrophobic range. Since *l-s* interface is saturated before *l-g* interface is, CA reduction for common surfactants is controlled by surface tension ($\gamma_{l\text{-}g}$). In this study, we focus mainly on the advancing contact angle. Contact angle hysteresis has also been observed by 20% reduction of the drop volume. CA hysteresis is generally increased with the linear surfactant concentration (but no more than 20°). This result agrees with the previous study in terms of surface tension.[3] Nonetheless, like advancing contact angle, CA hysteresis becomes independent of surfactant concentration as $c_s \geqslant$cmc.

Type II is liquid-solid interfacial tension ($\gamma_{l\text{-}s}$) control. Some surfactants have a *branched*, hydrophobic tail. For example, the hydrocarbon tail of Triton X-100 is 4-(1,1,3,3-tetramethylbutyl)-phenyl group. Moreover, AOT and DDAB are ionic surfactants, each with two identical, hydrocarbon tails (see Fig. 2). The wetting behavior associated with the branched surfactants is displayed in Fig. 2. Different from the typical surfactants, the contact angle declines continuously with increasing surfactant concentration even as $c_s > \text{cmc}$. When c_s is high enough, e.g., 5 cmc, CA becomes less than 20° and eventually the droplet is able to form a film (superwetting) on the supposedly superhydrophobic surface. Because $\gamma_{l\text{-}g}$ remains unchanged for $c_s > \text{cmc}$, a continuous decay of CA indicates that $\gamma_{l\text{-}s}$ modified by surfactant adsorption decreases with increasing c_s. That is, while the surfactant monolayer formed at *l*-*g* interface reaches saturation at $c_s = \text{cmc}$, it is not saturated at all at *l*-*s* interface. In fact, the surface excess $\Gamma_s^{(l\text{-}s)}$ is increased further as c_s rises. Eventually, one might has $\gamma_{l\text{-}s} \to 0$ as $\Gamma_s^{(l\text{-}s)}$ is maximum.

Double-tailed surfactants are often employed to form thermodynamically stable, bicontinuous microemulsions, which consist of an interconnected network of water and oil channels, stabilized by surfactant films. In order to reduce the interfacial-free energy associated with microscopic water/oil contacts, double-tailed surfactants experience stronger excluded volume interactions than single-tailed ones[12] and therefore lead to an ultralow interfacial tension.[13] This consequence reveals that double-tailed surfactants may have greater adsorption at the water/hydrophobic solid interface than at the water/air interface. In other words, addition of double-tailed surfactants can reduce $\gamma_{l\text{-}s}$ drastically and lead to the liquid imbibition into grooves.

Since $\gamma_{l\text{-}s}$ continues decreasing with increasing c_s, it will satisfy the condition $\gamma_{l\text{-}s} < \gamma_{s\text{-}g}$ eventually. That is, the intrinsic CA of the surfactant solution becomes smaller than 90° on a smooth surface (of identical material). As the surfactant monolayer of *l*-*s* interface reaches saturation, the minimum intrinsic CA is simply $\cos\theta_{\min} = \gamma_{s\text{-}g}/\gamma_{l\text{-}g} > 0$ with $\gamma_{s\text{-}l} \to 0$. For example, one has $\theta_{\min} \approx 65°$ for DDAB at 10 cmc ($\gamma_{l\text{-}g} \simeq 24\ \text{mJ/m}^2$) and it is still far from superhydrophilicity. According to the Wenzel mechanism, however, the hydrophilicity can be reinforced by the roughness. In fact, superhydrophobic surfaces turn superwetting when pure liquids with intrinsic CA below 90° are deposited on rough surfaces.[4] Since the superhydrophobic behavior is always characterized by low $\gamma_{s\text{-}g}$ coupled with high roughness, superhydrophilicity is naturally resulted at high enough c_s. Indeed, we have showed that the branched surfactant solution penetrates the grooves and wet the rough surface. It switches the surface from superhydrophobic to superhydrophilic range. Nonetheless, the superhydrophobicity can be recovered simply by rinsing with water.

In conclusion, the wetting behavior on superhydrophobic surfaces can be modified by surfactant solutions due to the reduction of $\gamma_{l\text{-}g}$ and $\gamma_{l\text{-}s}$ by surfactant adsorption onto interfaces. Two types of wetting are identified, depending on the architecture of the surfactant tail. For linear alkyl tails, CA is reduced mainly by $\gamma_{l\text{-}g}$. Since both *l*-*g* and *l*-*s* interfaces are saturated with surfactants for $c_s \geqslant \text{cmc}$, CA becomes independent of c_s and the surface remains in hydrophobic range due to the fact that $\gamma_{l\text{-}s}$ cannot be lower than $\gamma_{s\text{-}g}$ by surfactant addition. However, for branched tails, $\gamma_{l\text{-}s}$ continues decreasing for $c_s > \text{cmc}$ and can be lower than $\gamma_{s\text{-}g}$. Consequently, CA goes on decaying and the surfaces can be switched into hydrophilic ones, eventually reaching superwetting at high enough c_s owing to roughness. The superhydrophobicity can be recovered simply by water rinsing.

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