Effect of Surfactants on Wetting of Super-Hydrophobic Surfaces

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The effect of surfactants on wetting behavior of super-hydrophobic surfaces was investigated. Super-hydrophobic surfaces were prepared of alkylketene dimer (AKD) by casting the AKD melt in a specially designed mold. Time-dependent studies were carried out, using the axisymmetric drop shape analysis method for contact angle measurement of pure water on AKD surfaces. The results show that both advancing and receding contact angles of water on the AKD surfaces increase over time (∼3 days) and reach the values of about 164 and 147°, respectively. The increase of contact angles is due to the development of a prickly structure on the surface (verified by scanning electron microscopy), which is responsible for its super-hydrophobicity. Aqueous solutions of sodium acetate, sodium dodecyl sulfate, hexadecyltrimethylammonium bromide, and *n*-decanoyl-*n*-methylglucamine were used to investigate the wetting of AKD surfaces. Advancing and receding contact angles for various concentrations of different surfactant solutions were measured. The contact angle results were compared to those of a number of pure liquids with surface tensions similar to those of surfactant solutions. It was found that although the surface tensions of pure liquids and surfactant solutions at high concentrations are similar, the contact angles are very different. Furthermore, the usual behavior of super-hydrophobic surfaces that turn super-hydrophilic when the intrinsic contact angle of liquid on a smooth surface (of identical material) is below 90° was not observed in the presence of surfactants. The difference in the results for pure liquids and surfactant solutions is explained using an adsorption hypothesis.

1. Introduction

Surfaces with contact angles of larger than 150° with water are called super-hydrophobic or super-water-repellent.[1,2] Such surfaces are important in practical applications such as glass covers for solar cells, satellite dishes, microfluidics, windshields of automobiles, roofing, eyeglasses, and generally anywhere that reduced wettability or adhesion is desirable[3−5] (small contact area between liquid and surface is an important factor contributing to reduction in adhesion).

It is known that surface energy, surface roughness, and homogeneity are the three main factors that control the wetting of a solid.[6−8,9(Ch.1)] Surfaces with a high degree of roughness and low surface energy show super-hydrophobicity.[1,2,5] It should be noted that the highest contact angle for water on a smooth surface obtained by lowering the surface energy is about 120°.[10,11] Beyond this angle, the fine surface roughness produced by a fractal structure, for example, can be a dominant factor in increasing the contact angle. Contact angles of more than 170° have been obtained for water by roughening the low surface energy materials through chemical treatment or photolithographic methods.[3,12,13]

Many researches have focused on producing super-hydrophobic surfaces. Different methods such as microwave plasma-enhanced chemical vapor deposition[1,14] and aligning the synthesized polyacrylonitrile nanofibers[15] were used to produce such surfaces. Silica and oxidized alumina films were made with a high degree of transparency and hydrophobicity.[3,16,17] Tsujii and co-workers[18] and Onada et al.[19] investigated the wettability of surfaces prepared from synthesized alkylketene dimer (AKD). A very recent method proposed by Erbil et al.[20] has resulted in a super-hydrophobic surface made of polypropylene. The contact angle of water obtained on the surfaces produced by different methods mentioned above is in the range of 150−174°. Although different methods have been used to produce super-hydrophobic surfaces, systematic and focused studies into wetting with various liquids are scarce.

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The cleanliness of the super-hydrophobic surfaces and the purity of the water droplet are important factors in wetting of these surfaces; a small amount of surfactant on the surface or in the test liquid could potentially change the wettability in practical applications. An investigation of the effect of surfactants on wettability of super-hydrophobic surfaces is needed to assess the performance of such surfaces in the applications mentioned above. The objective of this paper is to investigate the change of hydrophobicity of super-hydrophobic surfaces (made of AKD) over time and to study the wetting of these surfaces by measuring the contact angle of different aqueous solutions containing different surfactants (anionic, cationic, and nonionic). The contact angles of the surfactant solutions were compared to those obtained for seven different pure liquids with surface tensions in the range of surfactant solutions used.

2. Theoretical Background

When a liquid droplet is placed on a homogeneous smooth solid surface, the contact angle, θ, can be obtained using Young's equation:[9(Ch.3)]

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \tag{1}$$

where γ_{sv}, γ_{sl}, and γ_{lv} are the interfacial tensions of the solid−vapor, solid−liquid, and liquid−vapor phases, respectively.

Wenzel[6] modified Young's equation and proposed a well-known equation for the contact angle of liquids on a rough homogeneous surface (θ_w), which is as follows:

$$\cos\theta_w = r\left(\frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}\right) = r\cos\theta \tag{2}$$

where r is the roughness factor defined as the ratio of the actual surface area of the rough surface to the geometric projected area. This equation implies that when the intrinsic contact angle of a liquid on a rough solid surface is larger (smaller) than 90°, the surface will become super-hydrophobic (super-hydrophilic) because r is always larger than 1.[5] However, it should be noted that the morphology of the surface has a significant influence on the observed contact angle for rough surfaces.[12,21] Roughness, in simple terms, by itself cannot explain the high hydrophobicity of very rough surfaces, and Wenzel's equation is not necessarily applicable (depending on the r value, eq 2 will become inapplicable to calculate θ_w as $r\cos\theta > 1$). For very rough surfaces, a composite surface structure made of air (trapped in undulations of a rough surface) and the primary surface material (e.g., AKD) are often observed. The wetting for such heterogeneous surfaces is traditionally described by the Cassie equation:[7]

$$\cos\theta_c = f_1\cos\theta_1 + f_2\cos\theta_2 \tag{3}$$

where θ_c is the Cassie contact angle; f_1 and f_2 are the fractions of materials 1 and 2 on the surface, respectively. Angles θ_1 and θ_2 represent the intrinsic contact angles of the liquid with materials 1 and 2 that can be found from eq 1. Equation 3 can be rewritten as follows where the contact angle of liquid with air is considered to be 180° (θ is the intrinsic contact angle for the primary surface material, e.g., AKD):

$$\cos\theta_c = f(\cos\theta + 1) - 1 \tag{4}$$

where f is the fraction of the solid surface in contact with liquid; the fraction of air (trapped in the surface roughness) in contact with liquid at the surface is $1 - f$. Equation 4 can be used to calculate the fraction of the air pockets at the surface (see section 4).

Quéré et al.[12,22,23] studied rough hydrophobic surfaces; the roughness had the form of fine microtextures (e.g., pillars) with different geometries. To understand the wetting behavior of such surfaces, they combined eqs 2 and 4 and obtained the following equation for a liquid droplet on a textured solid substrate:

$$\cos\theta_{cr} = \frac{f - 1}{r - f} \tag{5}$$

In eq 5, θ_{cr} is the critical intrinsic contact angle that delineates the wetting regime (Wenzel or Cassie). Equation 5 shows that for $90° < \theta < \theta_{cr}$, the Wenzel mode is applicable although some cases have been observed with the metastable Cassie mode.[23] For $\theta_{cr} < \theta < 120°$, however, the Cassie mode will be applicable because of the air pockets trapped below the liquid drop in the undulations of the rough surface. It should be noted that 120° is the highest possible intrinsic contact angle for water on a surface obtained by lowering the surface energy (see section 1).

3. Experimental Procedure

3.1. Fabrication of Super-Hydrophobic Surfaces. We followed the basic approach used by Shibuichi et al.[17,18] to produce the super-hydrophobic surfaces. To produce the surfaces, pellets of AKD (Hercules, Inc., Wilmington, U.S.A.) were heated to 90 °C in a beaker on an electric hot plate. Twenty milliliters of the melt was poured into a clean and dry stainless steel mold with a special design to ascertain the rapid cooling of the melt. The mold was placed in a dry nitrogen environment for 30 min to prevent possible reaction of the melt with air during solidification. After solidification of the melt, holes were made on the surface using a heated pin. These holes are needed for the contact angle measurements using the axisymmetric drop shape analysis (ADSA) method (see section 3.4). The surfaces were then cured for 3 days under a nitrogen environment to become super-hydrophobic. The super-hydrophobicity of these AKD surfaces results from the development of a prickly structure. Environmental scanning electron microscopy (ESEM, Philips/FEI LaB6) images were used to verify the formation of this structure (see Figure 1). As can be seen in the image of day 3 (super-hydrophobic AKD), the surface has a very rough microstructure. Therefore, a high roughness factor would be expected for the AKD surface in the super-hydrophobic state.

3.2. Surfactants. Four different surfactants with different properties (anionic, cationic, and nonionic) were used to investigate the effect of surfactants on wetting of super-hydrophobic AKD surfaces. The anionic surfactants used are sodium acetate (Merck, Darmstadt, Germany, hereafter denoted as SA) and sodium dodecyl sulfate (Fisher Scientific, NJ, U.S.A., hereafter referred to as SDS). Hexadecyltrimethylammonium bromide (Sigma-Aldrich, St. Louis, U.S.A., hereafter called HTAB) and *n*-decanoyl-*n*-methylglucamide (Sigma-Aldrich, St. Louis, U.S.A., hereafter denoted as MEGA 10) were used as cationic and nonionic surfactants, respectively. The molecular structures of these surfactants are shown in Figure 2.

3.3. Experimental Design. For each surfactant, seven aqueous solutions of different concentrations were prepared. For each concentration, at least three surfaces were used for contact angle measurements with three replications on surfaces from each batch, that is, a total of nine surfaces. Seven pure liquids: water, ethylene glycol, *cis*-decaline, hexadecane, ethylcinnamate,

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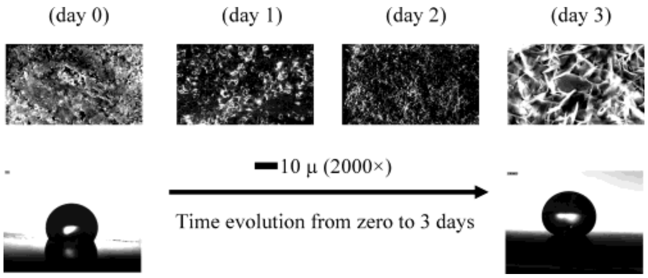

Figure 1. ESEM images of the AKD surface taken every 24 h for 3 days. The magnification is 2000× . The images, from left to right, confirm the formation and growth of the prickly structure. The image of day 3 shows the topography of the AKD surface that results in super-hydrophobicity. The images of the two drops show the water drop on the AKD surface on day 0 (left image) with a contact angle of about 126° and on the AKD surface on day 3 (right image) with a contact angle of about 164°.

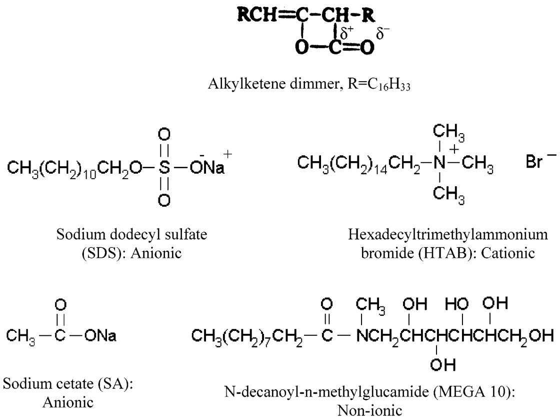

Figure 2. Molecular structures of AKD and the different surfactants used.

Table 1. Advancing Contact Angle (with 95% Confidence Limits) for Distilled Water on an AKD Surface (a Sample Run for Measurement on a Single Surface)

measurement no.	contact angle		contact radius (mm)
	deg	95% CL	
1	166.3	0.51	0.79
2	166.9	0.34	0.85
3	166.2	0.22	0.93
4	166.6	0.22	0.98
5	166.5	0.28	1.09
6	167.0	0.29	1.12
7	166.4	0.48	1.19
8	167.1	0.46	1.35
9	166.1	0.35	1.47
10	167.1	0.36	1.52

dibenzylamine, and 1-bromonaphthalene (all of them from Sigma-Aldrich, St. Louis, U.S.A., except for pure water) were used for comparison purposes. Three surfaces, with at least two replications on the surfaces from the same batch, were used to measure the contact angles of these pure liquids. Overall, for each surfactant type at various concentrations, at least 63 runs were performed, and a total of 42 experimental runs were performed for pure liquids (for a sample run see Table 1). It should be noted that the drop sizes were consistent for all of the systems studied to minimize the possible line tension effects.[24]

3.4. Surface Tension and Contact Angle Measurements. Surface tension measurements were made using an axisymmetric drop shape analysis-profile (ADSA-P) for pendent drop while contact angle measurements were done using ADSA-P for sessile drop. For more details on the ADSA method, see ref 9, Chapter 10.

The experimental setup used for contact angle measurements for sessile drop is shown in Figure 3. A similar setup was used to measure the surface tensions of different surfactant solutions and pure liquids by ADSA-P for pendent drop. The low-rate dynamic advancing and receding contact angles were measured using a motorized syringe. Every 2 s, drop images were captured for a total period of 30 s. After this 30 s, drops were followed for 5 min when surfactant solutions were used. Except for MEGA 10 at concentrations near the critical micelle concentration (CMC), no changes were observed in contact angles after 5 min. To measure the surface tension, the image of a well-deformed pendent drop produced at the tip of a capillary tube was taken and stored in a computer for analysis by ADSA-P (pendent drop). For each liquid (or solution), surface tension was measured by averaging the measurements for at least four droplets.

Time-dependent studies of contact angles (advancing and receding) were carried out on AKD surfaces to study the wetting implications of the formation of prickly structures at the surface. The hydrophobicity of the AKD surfaces was monitored from the time of solidification, in 6 h intervals, for 3 days. The contact angles of water were measured on three surfaces, with three replications on surfaces from the same batch.

4. Results and Discussion

The results of time-dependent studies of hydrophobicity for AKD surfaces are shown in Figure 4. This graph shows that both advancing and receding contact angles of distilled water on AKD surfaces increase with time and reach the final values of about 164 and 147°, respectively, after ~57 h. For each run, the observed contact angles were very consistent, as can be seen in Table 1. This table shows a sample run for measurement of the advancing contact angle of distilled water on an AKD surface using ADSA. Similar consistency in data was observed for contact angles (advancing and receding) of the other liquid systems on AKD surfaces. The time-dependent super-hydrophobicity of the AKD surfaces (Figure 4) corresponds to the SEM images taken from an AKD surface (Figure 1); that is, both the advancing and receding contact angles increase with the development and formation of the prickly structures. The images of these prickly structures shown in Figure 1 were taken for 3 days starting from solidification of the AKD melt. The images, from left to right, show the progressive formation of the prickly structures, which cause the AKD surface to become super-hydrophobic. The image from day 3 corresponds to the super-hydrophobic surface with a high advancing contact angle (~164°). It can be seen from Figure 4 that the contact angle hysteresis, defined as the difference between advancing and receding contact angles, increases and then decreases over time as prickly structures form. This behavior is the result of a transition from the Wenzel wetting regime to a composite Cassie regime.[8] In the prickly structures shown in the SEM images, small micrometer-sized pores can be observed. When the solid is hydrophobic, for thermodynamic energetic reasons it can be shown that water cannot enter the small pores and air becomes trapped in the pores.[8,12] Therefore, one will have a composite (heterogeneous) surface of air and hydrophobic material (AKD).

Using eq 4, one can calculate the percentage of the solid in contact with liquid (f) on the composite surface. With an assumed intrinsic contact angle (θ) of 126° (from Figure 4) for a relatively smooth AKD surface (almost without any prickly structures) and the final value of 164° for the advancing contact angle of water on the rough super-hydrophobic surface, one can find that f is 0.094 (i.e., ~90.6% of the liquid is in contact with air trapped on the surface with a prickly structure). This means that a combination of a large fraction of air and a small fraction of AKD makes the surface super-hydrophobic. It should be noted that considering the contact angle of 126° for an

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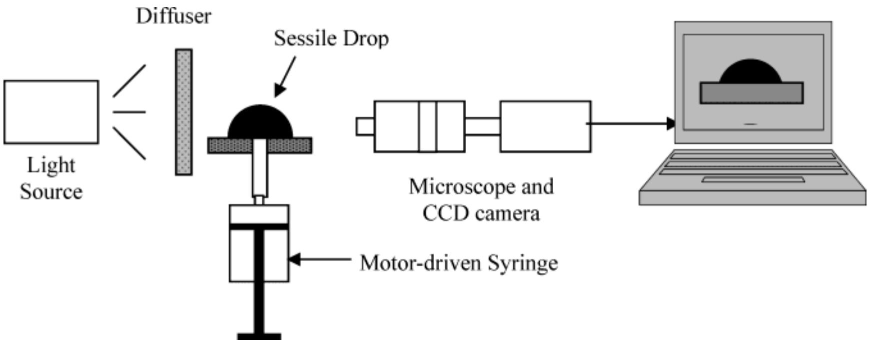

Figure 3. Schematic of the experimental setup for ADSA-P (sessile drop). A motorized syringe is used to inject or withdraw the liquid from a drop placed on the surface, allowing the measurement of advancing and receding contact angles, respectively. Drop images were taken every 2 s for 30 s.

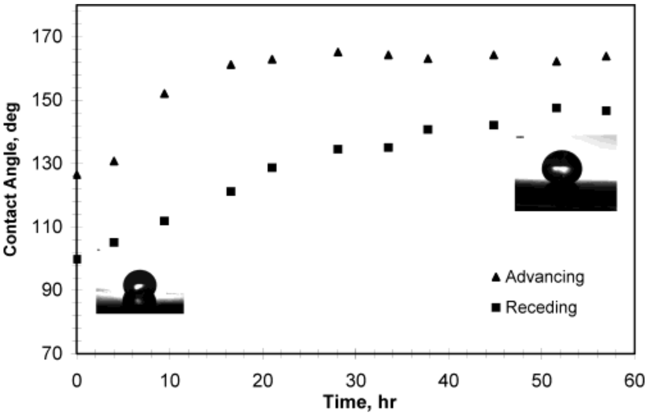

Figure 4. Advancing and receding contact angle change for distilled water on AKD surfaces over time. Both advancing and receding contact angles increase with time to reach the final values of about 164 and 147°, respectively, after 3 days. Error bars are generally less than 1° and are not shown. The images of the two drops show the water drop on a relatively smooth AKD surface (left image) with a contact angle of about 126° and on a super-hydrophobic AKD surface (right image) with a contact angle of about 164°.

ideally smooth AKD may not be realistic (see section 1); this value is used for having internally consistent data. If the reported contact angle value for a smooth AKD surface is used from ref 18, that is, 109°, the calculated fraction of air trapped in the surface pores will not change very much, that is, ∼94%.

According to Quéré et al.,[12,22] the critical contact angle (θ_{cr} in eq 5) is the minimum intrinsic contact angle required for transition from the Wenzel to the Cassie regime. In the transition point from Cassie mode to Wenzel mode, either eq 3 or eq 4 can be used to calculate θ_{cr}. From Figure 4, the average apparent contact angle is about 156° at maximum contact angle hysteresis (where transition occurs);[8] when this value for the apparent contact angle and the value of 0.094 for f are used, the critical intrinsic contact angle was calculated to be 94.5° from eq 4. Because the intrinsic contact angle of water on AKD is larger than the critical contact angle, one can conclude that the Cassie regime prevails and the Cassie equation can be applicable, that is, $\theta_c = 164°$. When f and θ_{cr} values of 0.094 and 94.5°, respectively, are used, the r value is found as 11.5 from eq 5. This high r value shows that the AKD surface is very rough, as can be seen in the image of day 3 (super-hydrophobic AKD) of Figure 1.

Advancing and receding contact angles for various concentrations of four surfactant (SA, SDS, HTAB, and MEGA 10) solutions in water are shown in Figure 5a−d. These graphs show that for all aqueous solutions of the surfactants, both advancing and receding contact angles decrease when the concentration of surfactants in water increase. However, even at very high concentrations of surfactant solutions corresponding to significant reduction in surface tension for water (e.g., 50%), the surface remains very hydrophobic. The only exception to this observation is MEGA 10 at concentrations very close to the CMC (7−8 mM). From Figure 5, one can also find that the contact angle hysteresis decreases with concentration for SA, HTAB, and MEGA 10 solutions. For SA and HTAB at high concentrations (0.6 M and 0.5 mM, respectively), the contact angle hysteresis starts to increase somewhat. The contact angle hysteresis is consistent, however, for SDS over the range of concentrations. It should be noted that the addition of a small amount of nonionic surfactant (e.g., 0.6 mM MEGA 10) seemingly could improve the sliding behavior of a drop on an inclined surface (lowering contact angle hysteresis), without much change in the observed advancing contact angle (see Figure 5d).

Figure 6 shows the changes in surface tension and advancing contact angle with concentration for the surfactants in water. It can be seen from Figure 6a that the surface tension decreases when the concentration of the surfactant in water increases and then starts to level off at the CMC for SDS (7−8 mM), HTAB (0.8−0.9 mM), and MEGA 10 (6−7 mM). This behavior is not observed for SA. SA does not reach a plateau over the range of its solubility in water. The behavior of the advancing contact angle versus concentration for all of the surfactant solutions is, to some extent, similar to that of surface tension (Figure 6b); that is, it decreases with concentration (this is of course expected). However, each surfactant solution shows a different behavior in the advancing contact angle at high concentrations (e.g., near the CMC) possibly as a result of different interactions of the surfactant with the AKD surface. Depending on the molecular structure and ionic properties of the surfactants (see Figure 2), the penetration of liquid into the air-filled surface pores can be somewhat held back, giving rise to a difference in the observed contact angles for liquids with similar surface tensions. The data obtained for the surface tension and contact angle of different surfactant solutions on AKD surfaces (Figure 6) were compared with those of the pure liquids shown in Table 2. This table shows surface tensions of pure liquids and their advancing contact angles with AKD surfaces.

Figure 7 shows the surface tension versus advancing contact angle for different surfactant solutions and pure liquids. Although the surface tensions of surfactant solutions at high concentrations are close to those of some of the pure liquids (see the region enclosed in the dotted rectangle in Figure 7), the contact angles are very different.

On the smooth AKD surface, the contact angle of a liquid with a specific surface tension can be below or above 90°.

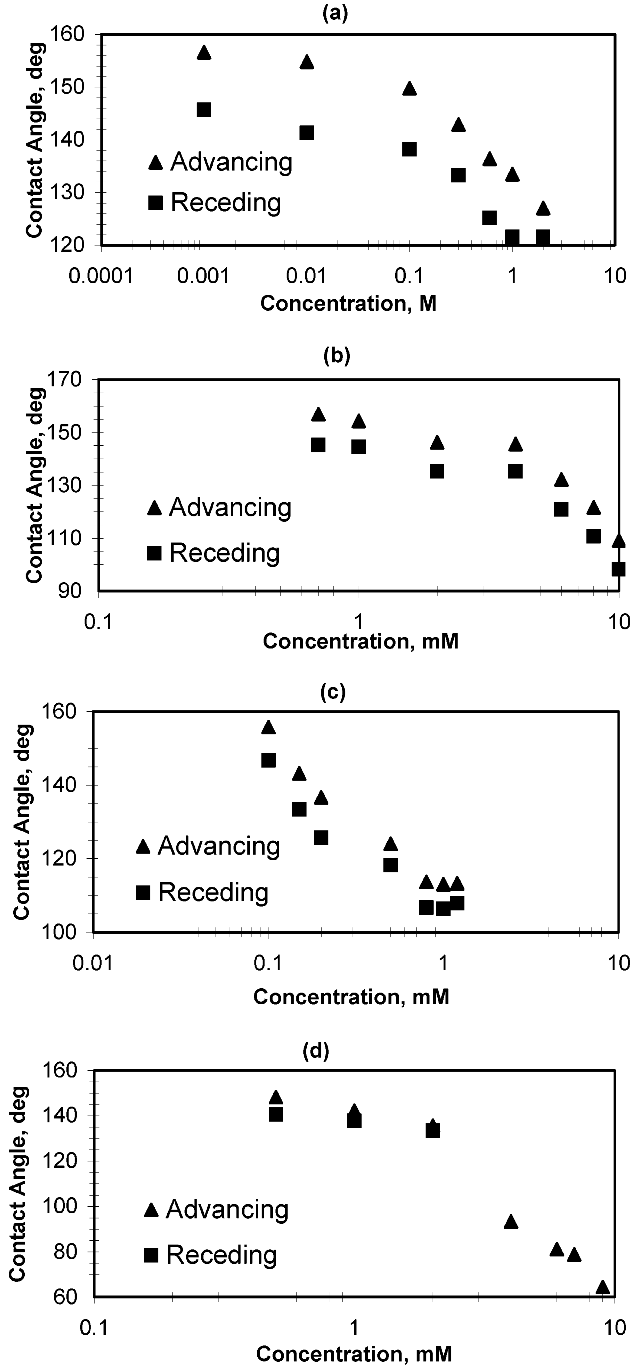

Figure 5. Advancing and receding contact angles versus concentration for four surfactant solutions with different chemical properties. (a) SA, (b) SDS, (c) HTAB, and (d) MEGA 10. All of the contact angles decrease by increasing the concentration of the surfactants in water, but even at a high concentration of surfactants (representing about 50% reduction in surface tension), the surfaces remain hydrophobic. Error bars are generally less than 1°.

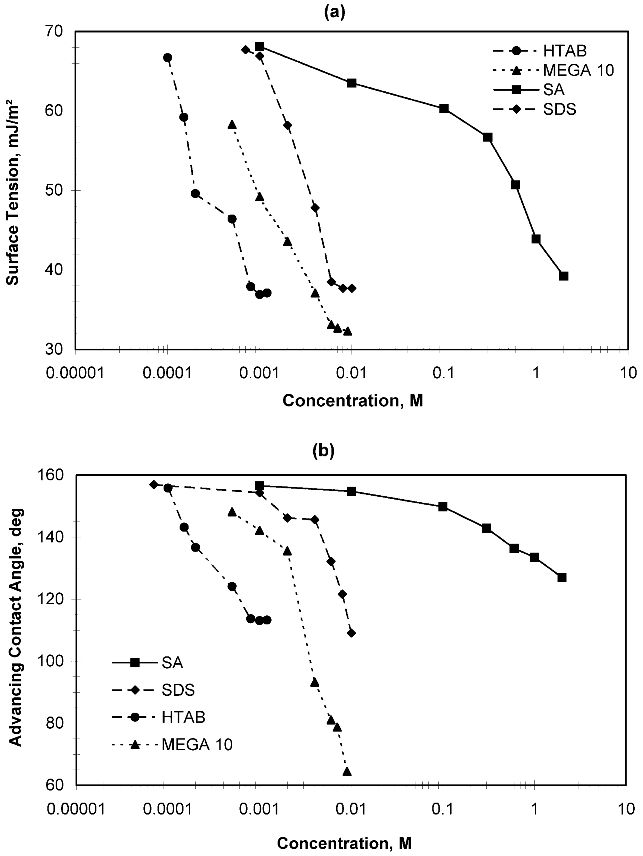

Figure 6. (a) Surface tension versus concentration in water for SA, SDS, HTAB, and MEGA 10. The surface tension decreases with concentration and levels off at the CMC for SDS (9−10 mM), HTAB (0.8−0.9 mM), and MEGA 10 (7−8 mM). (b) Advancing contact angle versus concentration in water for the aforementioned surfactants. Error bars are generally less than 1°. Lines are to guide the eye.

Table 2. Average Surface Tensions and Contact Angles (with 95% Confidence Limits) of Pure Liquids on the Super-Hydrophobic AKD Surfaces[a]

liquid	average surface tension (mJ/m^2)	average contact angle (deg)
water	72.2	160.3 ± 0.65
ethylene glycol	47.0	133.3 ± 0.43
1-bromonaphthalene	44.3	<20
dibenzylamine	40.8	<10
ethylcinnamate	37.2	<10
cis-decalin	32.3	0
hexadecane	27.0	0

[a] A contact angle of 0 indicates free spreading of the liquid.

Pure liquids with contact angles of below 90° on smooth AKD surface show contact angles of less than 20° on super-hydrophobic AKD surface (e.g., dibenzylamine and hexadecane in Table 2 and Figure 7). Such an observation indicates that the Wenzel mode (eq 2) is applicable, in which a rough solid surface will become super-hydrophilic, if the intrinsic contact angle of a liquid on the surface is smaller than 90°. Pure liquids with contact angles on smooth AKD surfaces of above 90° (e.g., ethylene glycol or water) show contact angles higher than 90° with rough AKD, and the Wenzel or Cassie mode is valid (see above). In this case, the existence of the Wenzel or Cassie mode depends on the critical contact angle (see section 2). Surfactant solutions that have surface tensions similar to those of pure liquids (with expected intrinsic contact angles of less than 90° on smooth AKD) show contact angles generally above 90° on rough AKD surfaces (Figures 6 and 7). Therefore, the wetting behavior (characterized by the contact angle) of surfactant solutions is not similar to what was seen for pure liquids.

The difference between the wetting of the AKD surface with pure liquids and the wetting with surfactant solutions (showing super-hydrophobic behavior) is attributed to the effect of surfactants available in the solutions. It is well-documented that surfactants available in a droplet on a surface are adsorbed to the surface.[25−29] This interaction of surfactants with the AKD surface and their accumula-

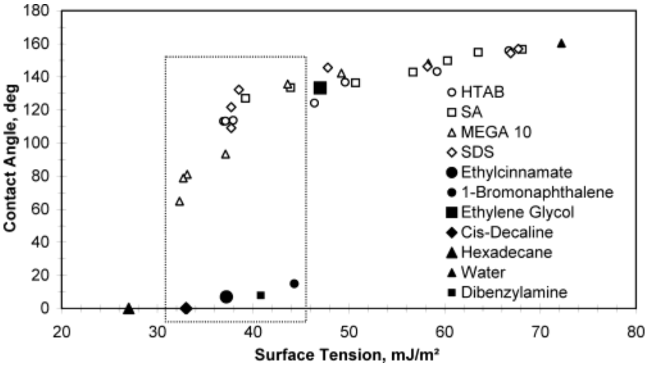

Figure 7. Surface tension versus contact angle for different surfactant systems and pure liquids. The dotted rectangle highlights the liquids (pure liquids shown with solid symbols and aqueous solutions of surfactants shown with open symbols) with close surface tensions having very different advancing contact angles. Error bars are generally less than 1°.

tion at the surface pores can hinder the penetration of the solution to the microcapillary surface pores. Therefore, it could be thought that it is thermodynamically unfavorable for the surfactant solution (liquid) to enter the surface pores and wetting would be kept in the composite mode (air-filled surface pores). High contact angles, therefore, result for surfactant solutions when compared to pure liquids with similar low surface tensions. In comparing the contact angles of surfactant solutions with those of pure liquids it should be noted that the adsorption of the surfactants to the surface might change the solid surface energy and, hence, influence the observed contact angle to a limited degree (however, the authors have not found a study that has examined the issue of changing the solid−vapor surface energy, due to adsorption of surfactants ahead of an advancing drop, for very rough superhydrophobic surfaces; all the data are for model smooth surfaces, for example, ref 30).

In comparing the contact angle data from various surfactant solutions, one can see that MEGA 10 solutions behave somewhat differently. MEGA 10 is a nonionic surfactant and perhaps would interact more weakly with the AKD surface when compared to the other surfactants used.[29] This weak interaction, considering the above explanation (i.e., hindering the penetration of liquid into surface pores by surfactants), would result in a reduced contact angle of about 60° (liquid can more freely enter the surface pores) at concentrations near the CMC (Figures 6 and 7). In the case of pure liquids, however, the liquid with a low surface tension and low intrinsic contact angle can easily enter the surface pores. Therefore, the mode of wetting changes from composite, Cassie mode, to the Wenzel mode (reduce contact angle to less than 20°), in which the surface will become super-hydrophilic.

5. Summary and Conclusions

Time-dependent studies were conducted to follow the formation of the prickly structures on the AKD surfaces. The hydrophobicity of the prepared AKD surfaces was monitored from the time of solidification for 3 days in approximately 6-h intervals. The results indicate that the advancing contact angle increases over time and reaches a final value of 164° for water. SEM images were taken to verify the progressive formation of prickly structures on the AKD surfaces. The changes in contact angle hysteresis over time show that, as the surface roughness increases with time (resulting from the formation of a prickly topography), the wetting behavior changes from the Wenzel to the Cassie regime.

The effect of surfactants on the wetting behavior of super-hydrophobic surfaces was investigated. Aqueous solutions of SA, SDS, HTAB, and MEGA 10 were used to investigate the wetting behavior of the super-hydrophobic surfaces in the presence of surfactants. Advancing and receding contact angle results show that when the concentration of surfactants in water increases, the contact angles and surface tension decrease.

Contact angles from surfactant solutions were compared with those of different pure liquids (with a range of surface tensions). The results of contact angle measurements reveal that for pure liquids with intrinsic contact angles smaller than 90° on smooth AKD, the rough AKD surface (r value of 11.5) becomes super-hydrophilic and the Wenzel mode prevails. However, for surfactant solutions that have similar surface tensions and intrinsic contact angles to those of the pure liquids, the contact angles are above 90° on super-hydrophobic AKD. Therefore, the composite (Cassie) mode is predominant. This behavior of the surfactant solutions can be due to the adsorption of surfactants on the surface. The adsorbed surfactants at the mouth of the surface pores (possibly by forming a double layer membrane) could hinder liquid penetration into the pores because of unfavorable thermodynamic conditions. Therefore, a composite Cassie regime with air trapped in pores is applicable, resulting in high contact angles.

Although the contact angle of MEGA 10 solutions on the AKD surface was lower than those of the other surfactant solutions, the surface still remains hydrophobic when compared to the case of the pure liquids with almost the same surface tensions. The weak interaction of MEGA 10 with the surface could lead to lower adsorption at the surface pores. This, in turn, would result in partial penetration of the solution into the pores and reduced hydrophobicity in comparison with the other surfactant solutions.

The presence of a small amount of anionic and cationic surfactants on the super-hydrophobic surface or in the test liquid, therefore, decreases the hydrophobicity of the surface. The advancing contact angle of solutions on the surface decreases from 164 to about 110° depending on the structure and concentration of the surfactants in the solution. This decrease is large, however, for the nonionic surfactants (from 164 to about 60° for MEGA 10).

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