Time-dependent Dynamic Receding Contact Angles Studied during the Flow of Dilute Aqueous Surfactant Solutions through Fluorinated Microtubes

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We report on the time-dependent dewetting behavior of dilute surfactant solutions of hexadecyltrimethylammonium bromide (CTAB) during forced flow in fluorinated ethylene–propylene (FEP) microtubes. The dynamic receding contact angle of the solution at a given velocity decreased as the solid–liquid contact time increased. Kinetics with long relaxation time of several hundred seconds led to a final state displaying a 0° dynamic receding contact angle. This effect was absent in the case of 2-propanol, where the dynamic receding contact angle did not depend on the contact time.

In the last two decades, increased attention has been paid to the investigation of the dynamics of wetting and dewetting.[1] Despite the significant effort, the precise mechanism by which a liquid front advances across a solid surface is not yet fully understood.[2] Even the well-studied wetting of simple one-component liquids is still not satisfactorily explained. The wetting of complex fluids[3] (including surfactant solutions, colloidal dispersions, and polymer solutions) is much less explored and far more complex.[4,5]

In many practical applications, such as coating, detergents, and those involving imbibition of liquids in porous materials, the spreading/wetting of aqueous liquids on hydrophobic solid surfaces needs to be controlled. One way to do this is to add surfactants to the liquid, and this alters the balance of forces acting on the three-phase contact line. However, the introduction of surfactants makes the wetting more complex, because time-dependent processes such as diffusion and adsorption of the surfactants come into play.[6] Surfactants adsorb onto the liquid–vapor (LV) and solid–liquid (SL) interface; adsorption onto the solid–vapor (SV) interface is still under debate.[7,8]

The dynamic wetting of surfactant solutions on hydrophobic solids has been mostly studied through drop-spreading[9,10] and spontaneous capillary-filling experiments.[11,12] In the latter category of experiments, penetration of surfactant solutions into hydrophobic capillaries showed different kinetic regimes. For concentrations, c, above the critical micellar concentration (CMC), two relatively fast kinetic regimes were found. The corresponding fast rise rates depended on the solution bulk concentration. Regimes with long relaxation time (with lower rise rates) were also identified, presumably caused by the relaxation of surface tension at the LV interface and adsorption equalization across the SL interface.[12] Churaev and co-workers had also previously reported on high rise rate kinetic regimes in solutions with concentrations above CMC. In cases where $c <$ CMC, the rise rate was much lower and was controlled by the meniscus concentration (reduced compared to the bulk). At even lower bulk concentrations and for thin capillaries, the rise rate was controlled by surface diffusion of surfactants in front of the meniscus. Forced rise was claimed to be ineffective at high

Peclet (Pe) numbers.[11] $Pe = LU/D$, where L is the characteristic length of the system, U is the velocity, and D is the diffusion coefficient.

Here, we report on the dynamic wetting behavior of aqueous dilute solutions with a cationic surfactant, which are forced to flow through polymeric tubes. In contrast to the spontaneous capillary-filling experiments (where the rise height is measured as a function of time), we directly measured the dynamic contact angles. The importance of direct measurements compared to indirect (calculated) ones has been pointed out in a previous study.[13] Moreover, by regulating the gravity-induced pressure difference that causes the liquid motion, the desired wetting speed could be achieved (possible range is $\mu m\,s^{-1}$–$cm\,s^{-1}$). This allowed for studying the time-dependent wetting behavior for a broad time range (seconds to hours). We show that the liquid–solid contact time strongly affects the dynamic receding contact angles (θ_{rec}), leading to unexpectedly slow kinetics (taking up to several hundred s). This dynamic wetting behavior is compared to the one of a simple liquid (2-propanol), where θ_{rec} remains constant over time.

The liquids utilized here were aqueous solutions of hexadecyltrimethylammonium bromide (CTAB, Sigma-Aldrich), in concentrations below CMC ($= 9 \times 10^{-4}$ M). Solutions were prepared in pure milli-Q water (resistivity: $18.2\,M\Omega\,cm$). 2-Propanol was used as a reference simple liquid (Sigma-Aldrich). θ_{rec} was measured using a dynamic capillary-wetting setup (Figure 1). Before starting the experiments and between experiments with different wetting liquids, the whole setup was thoroughly cleaned by flushing ca. 150 mL of milli-Q water and ca. 150 mL of acetone. For measuring the virgin θ_{rec} ($\theta_{rec,V}$) (see
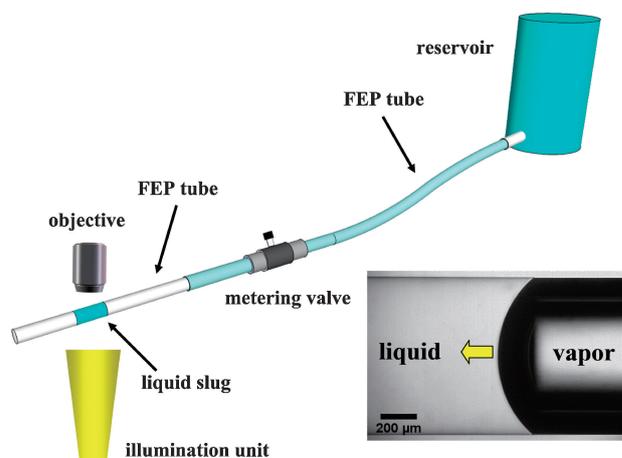
Figure 1. Schematic illustration of the dynamic capillary wetting setup. A typical image of the receding meniscus of a 2-propanol slug moving (in the direction of the arrow) in the fluorinated ethylene–propylene microtube is also shown.

below) of the same liquid, the FEP tubes were washed with ca. 20 mL of acetone and were carefully dried with N_2 subsequently. This ensured clean (virgin) surfaces, as verified using contact angle measurements of milli-Q water.

The setup consisted of four main parts: the liquid reservoir, a metering valve (for flow regulation), polymeric capillary tubes, and an upright optical microscope (Olympus BX 51) to image the moving liquid slugs (Figure 1). The microtubes are made from fluorinated ethylene–propylene (FEP) with an inner diameter of $855\,\mu m$ (Bohlender GmbH, Germany). The mean surface roughness of the tubes was $R_q = 50\,nm$, as measured with confocal microscopy. The driving force for the liquid motion is the pressure difference between the elevated reservoir and the capillary outlet. The microscope is equipped with a fast CMOS camera (Olympus i-speed, maximum frame rate 2000 fps), enabling image capturing even at high wetting speeds. To avoid light distortion in the cylindrical FEP microtube (refractive index $n_{FEP} = 1.34$), the microtubes were immersed in an index-matching flat glass cell filled with water ($n_{H_2O} = 1.33$).

Imaging of the moving liquid slugs provided snapshots of the receding liquid menisci (Figure 1). The wetting speed during each experiment was calculated by recording the receding meniscus displacement over a defined time-lapse. The menisci shapes were fitted with a circular sector function (by using an appropriate MATLAB algorithm and ImageJ software) to get the radius of curvature R_c. By geometric considerations, the receding contact angle is given by $\theta_{rec} = \arccos(R_c/R_t)$, where R_t is the inner microtube radius. All θ_{rec} values obtained in this work were the average of the values calculated from at least 40 images; the error bars (typically smaller than the symbols) represent the corresponding standard deviations.

In order to explore the effect of the solid–liquid contact time on the wetting behavior of the CTAB solution/FEP surface system, two types of experiments were performed. First, $\theta_{rec,V}$, was recorded as a function of the wetting velocity U. $\theta_{rec,V}$ is the dynamic contact angle of the receding (back) part of a liquid slug (typical lengths: ca. 2 cm) traveling in a clean microtube ("virgin" denotes that the liquid had never contacted the surface before). Second, the aged (long contact times) dynamic receding contact angles, $\theta_{rec,A}$ were recorded. Strictly speaking, a contact time of $t = 0\,s$ can never be valid for a receding meniscus. By definition, the receding meniscus will meet a point on the surface at a finite liquid–solid contact time t. If a slug of length L_s is moving with a velocity U, the contact time is given by $t = L_s/U$. For short slugs ($L \approx 2\,cm$), the contact times were typically short for the velocities used ($t < 10\,s$ for $U \approx 2$ $mm\,s^{-1}$). $\theta_{rec,V}$ corresponds to such short contact times, and $\theta_{rec,V} = \theta_{rec,A}$ as contact time $t \to 0$.

The dynamic receding contact angles of 2-propanol slugs traveling in a virgin surface decreased very slowly with increasing U in the measured velocity range (squares in the inset of Figure 2). To check if previous contact of 2-propanol with the microtube walls affected the wetting behavior, $\theta_{rec,A}$ (circles, inset to Figure 2) was measured in the same speed range (0–3 mm s^{-1}). The 2-propanol–FEP tube contact times varied between 0 and 3200 s. An identical velocity dependence was revealed, as shown from the overlap of $\theta_{rec,A}$ and $\theta_{rec,V}$. These findings indicate that the wetting history (prewetting) of the FEP microtubes with 2-propanol does not alter the wetting behavior of the system.
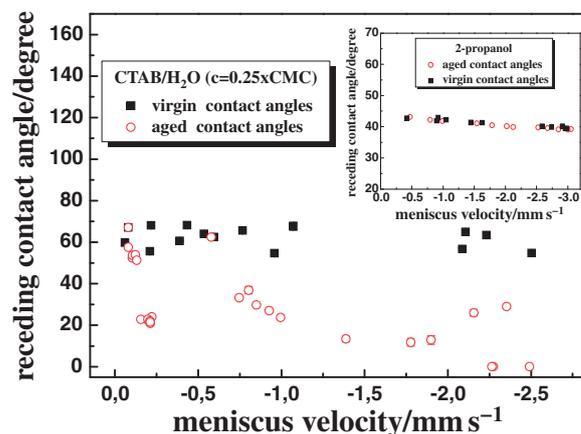
Figure 2. Meniscus velocity dependence of virgin ($\theta_{rec,V}$) and aged ($\theta_{rec,A}$) dynamic receding contact angles of an aqueous CTAB solution ($c = 0.25 \times CMC$) flowing through a FEP microtube. Inset: Meniscus velocity dependence of $\theta_{rec,V}$ and aged $\theta_{rec,A}$ of the reference simple liquid, 2-propanol, flowing through a FEP microtube.
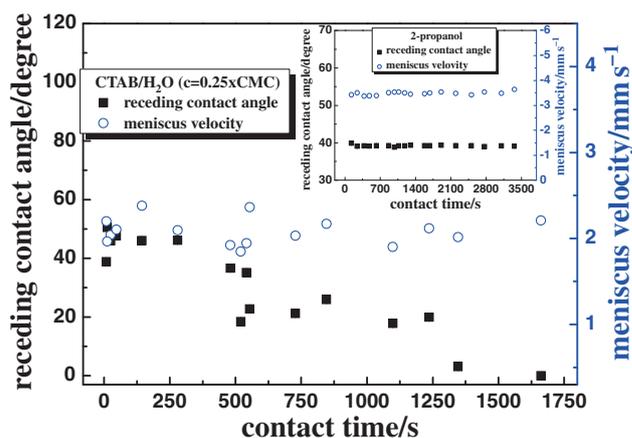
Figure 3. Dynamic receding contact angle and meniscus velocity dependence on solid–liquid contact time of an aqueous CTAB solution ($c = 0.25 \times CMC$) flowing through a FEP microtube. Inset: Dynamic receding contact angle and meniscus velocity dependence on solid–liquid contact time of the reference simple liquid 2-propanol traveling in FEP microtubes.

An opposite behavior was revealed when the wetting of CTAB solutions was considered. Figure 2 shows the dynamic wetting behavior of a dilute CTAB/H_2O solution ($c = 0.25 \times CMC$), measured by introducing air pockets in the flow at random times, traveling in a virgin FEP microtube. $\theta_{rec,V}$ (squares) slightly decreased with increasing U. Figure 2 also shows $\theta_{rec,A}$ (circles) of the solution moving over the previously wetted microtube. In contrast to the simple liquid case (inset in Figure 2), the $\theta_{rec,A}$ values for the CTAB solution are smaller than $\theta_{rec,V}$.

To get more insight into the evolution of the receding contact angle as a function of time, we performed experiments using CTAB solution slugs moving at an almost constant wetting velocity of $U \approx 2\,mm\,s^{-1}$ (Figure 3). The slug length was varied

in order to achieve different contact times. Each experiment using the surfactant solution was carried out using a clean microtube in order to avoid the effect of wetting history on the measurements. For 2-propanol, the measurements were done in a continuous way by simply introducing air pockets (typically ca. 2 mm long) in the liquid flow. Findings from these experiments correlated with the observations from Figure 2. The inset in Figure 3 shows that for 2-propanol, the contact angle is independent on the contact time. On the contrary, for the case of the CTAB solution (Figure 3), there was a strong dependence of the dewetting on the contact time. Starting from receding contact angles ranging between ca. 40–50° for very short contact times ($t < 50$ s), θ_{rec} decreased with increasing contact time. After some fluctuations, a state of long relaxation time with $\theta_{rec,A} = 0°$ for $t > 1660$ s was attained. In other words, the threshold for film formation was strongly changed during contact with the surfactant solution. The meniscus velocity (circles) during each measurement is also indicated. The observed contact-angle changes were clearly stronger than the minute velocity-induced changes as expected from the trend observed in Figure 2. This strong modification in the dewetting behavior of the system presumably points toward a time-dependent adsorption of surfactant molecules onto the solid. For short SL contact times (short slugs), surfactants were partially adsorbed onto the FEP wall during flow. For prolonged SL contact times, more surfactants were adsorbed on the solid surface, rendering it essentially hydrophilic ($\theta_{rec} = 0°$).

FEP, like other fluorinated solids (i.e., Teflon), is a low-energy surface. Therefore, no strong affinity between the CTAB molecules and the solid is expected, provided that electrostatic interactions do not play a role. To check the role of Coulomb interactions, first experiments with a negatively charged surfactant, namely, sodium dodecyl sulfate (SDS), were carried out. We found that $\theta_{rec,A}$ also decreased with contact time, similar to the case of CTAB solutions (at equal concentrations relative to CMC). A preliminary conclusion is that irrespective of the electrostatic interactions, adsorption of surfactants onto the FEP surface during liquid flow is a common feature, leading to a time-dependent wetting behavior. The detailed role of various parameters affecting the wetting behavior, such as the effect of fluid flow,[14] the development of surfactant self-assemblies at the interfaces[15] and the solid–surfactant interactions,[16] has to be investigated. This research is ongoing and will be the subject of an upcoming publication.

In summary, we have experimentally investigated the effect of solid–liquid contact time on the dynamic receding contact angles of slugs of 2-propanol and dilute CTAB/H_2O solutions during forced flow inside FEP microtubes. We showed that the dynamic receding contact angles of CTAB solutions decreased with increasing solid–liquid contact times. Eventually a value of 0° was reached through a process with very slow kinetics of the order of ca. 1700 s. In contrast, the dynamic wetting behavior of the reference simple liquid (2-propanol) did not depend on the solid–liquid contact time. Elucidating the long time scales involved, as well as the exact adsorption mechanism, will lead to a better understanding of the dynamic wetting of surfactant solutions.

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