ADSORPTION AND DESORPTION STUDIES OF SOME MODEL SURFACTANTS FROM OIL-BASED DRILLING FLUIDS

by

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ABSTRACT

Characterization of reservoir wettability is an important part of assessment of potential oil recovery. Oil-based drilling fluids include surfactants, which can alter the wettability of mineral surfaces. Cores exposed to these fluids may not reflect the true wettability of the reservoir materials.

The focus of this study was to observe wettability changes induced by adsorption and removal of surfactants of known structure on mica surfaces using tools that are applicable to studies of wetting alteration by crude oil components. The surfactants used were polyethoxylated coconut and tallow amines with chain lengths of 12 and 18 carbons and head groups consisting of two to five ethoxy groups. Mica was exposed to decane solutions of the surfactants. The treated mica was characterized macroscopically using contact angle measurements and microscopically using atomic force microscopy (AFM).

Upon exposure to the surfactant solutions, the mica became oil-wet (~170° for both water-advancing and receding conditions). AFM examination of similarly treated surfaces imaged in air revealed surfactant layers that were easily disrupted or surfaces that showed no surfactant at all. Contact angles were in the intermediate to water-wet range if the mica samples were removed from the surfactant solution, rinsed with non-aqueous solvents, and submerged in decane for measurements of water/decane contact angles. These results suggest only weak surfactant adsorption occurred from non-aqueous solutions. Sorption was less for increased levels of ethoxylation, which was concluded from the difference in the contact angles of TAM-2 and TAM-5; differences due to hydrocarbon chain length were negligible, which was evident when comparing CAM-2 and TAM-2 contact angle results. Stronger adsorption, higher contact angles,

and more stable surfactant layers could be demonstrated when mica was exposed to aqueous solutions after surfactant sorption, depending on the pH of the aqueous phase. Low-pH conditions that promote protonation of the surfactants' amine headgroup produced the greatest wetting alteration. Above a pH of 8 or 9, no surfactant remained adsorbed on mica surfaces.

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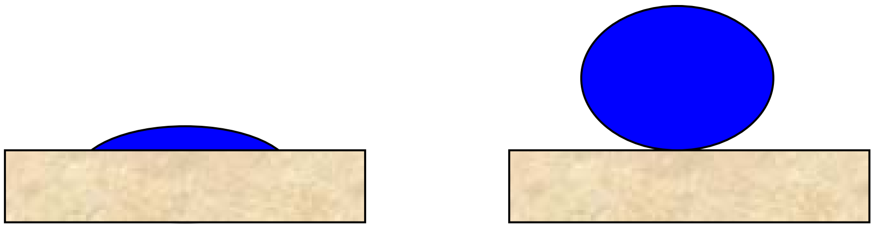
Chapter 1 : Background and Introduction

The wettability of an oil reservoir controls how fluids flow and where fluids reside in the reservoir (Anderson, 1986; Morrow, 1990). Thus, it is important to know the wettability of the reservoir in order to estimate oil that might be recoverable by different technologies. Cores are used to characterize properties of an oil reservoir including the wettability. Drilling fluids (muds) can alter the wettability of a core taken during drilling, resulting in improper characterization of reservoir properties. Surface active agents (surfactants) are the primary wettability-altering components of the drilling muds.

Wettability is the preference for contact with one or the other fluid (Rosen, 1978). It determines whether a surface is wetted by a fluid or not. Figure 1-1a shows a surface being wetted by a fluid and Figure 1-1b shows a fluid that is non-wetting to a surface. A wetting fluid spreads across the surface while a non-wetting fluid will bead up on a surface.



a) wetting

b) non-wetting

Figure 1-1. Wettability of a surface. a) Wetting fluid on a surface. b) Non-wetting fluid on a surface. In both a) and b) the system is submerged in another fluid.

During oil drilling, fluids called drilling muds are used in lubrication of the drill bit, stabilization of the borehole, and for easy removal of cuttings while drilling. There are many types of drilling muds, but in this study the focus was oil-based muds. Oil-based muds were the focus of this study because they are one of the more common types of muds used. Oil-based muds are composed of many components which include: oil, asphalt, water, emulsifiers, surfactants, weighting materials, and other chemical additives (Chilingarian and Vorabutr, 1983). Oil-based muds are usually made from diesel, mineral oil, or synthetic oil (Hyne, 2001).

A surfactant is made up of a hydrophilic, water loving, head group and a long hydrocarbon, hydrophobic, water hating, tail as shown in Figure 1-2.

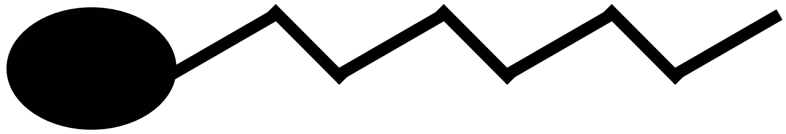


Figure 1-2. A surfactant with a long hydrophobic tail and a hydrophilic head group.

Surfactants can serve multiple functions in drilling muds. They can be used as emulsifiers, wetting agents, foamers, defoamers, and to decrease the hydration of clay surfaces (Darley and Gray, 1988). Emulsifiers are used to suspend oil in water or water in oil. Wetting agents are sometimes used to reduce the torque of the drilling bit, prevent bit- balling, or inhibit corrosion (Darley and Gray, 1988). Foams are used to facilitate the removal of water encountered during air or gas drilling (Darley and Gray, 1988). The surfactants can sorb onto the clay surface and alter the wettability, thereby reducing the hydration of the clay surface. Surfactants can also reduce the rate of drilling by reducing the rock hardness by altering the wettability (Chilingarian and Vorabutr, 1983).

In this study, the surfactants were characterized by their critical micelle concentration (CMC). Below the CMC, surfactants are generally present as monomers, while above the CMC the surfactants are present as aggregates known as micelles. The interfacial tension (IFT) can be used to estimate the CMC of a surfactant by plotting the IFT vs. log of surfactant concentration. When the surfactants are present primarily as monomers, the IFT is decreased as the surfactant concentration decreases. When the surfactants are present as micelles, the monomer concentration and IFT are no longer reduced with increasing concentration. Usually the surface tension is used to determine the CMC, but these surfactants dissolved only in the oleic phase, so the surface tension did not change with concentration. Therefore it was assumed that the IFT could be used instead of the surface tension.

Bobek et al. (1958) and Amott (1959) both observed that oil-based muds make cores more oil-wet. Since then numerous studies have focused on the wetting effects of the muds, their filtrates, or components of oil-based muds (Thomas et al., 1984; Gant and Anderson, 1988; Ballard and Dawe, 1988; Cuiec, 1989; Menezes et al., 1989; Yan et al., 1993; McCaffery et al., 2002; and Skalli, 2003). Menezes et al. (1989) examined the effects of commercial blends of surfactants on the wettability of quartz surfaces. Yan et al. (1993) examined wetting effects in sandstone cores and on quartz surfaces, while Skalli (2003) used mica as a model surface. All found the surfactants used in oil-based muds tended to alter water-wet siliceous surfaces to intermediate-wet or even oil-wet conditions. Since commercial blends of surfactants were used in those studies, the actual chemical structures of the surfactants were not known.

Patel and Ali (2003) suggested the use of ethoxylated amines as emulsifiers in drilling muds because it is possible to change their Hydrophilic-Lipophilic Balance (HLB). The HLB values indicate the emulsification behavior of a surfactant and are related to the hydrophilic and lipophilic properties of the surfactant (Rosen, 1978). An HLB value of 3 – 6 is recommended for a water-in-oil emulsion while an HLB value of 8 – 18 is recommended for an oil-in-water emulsion based on a 0 – 40 HLB scale (Rosen, 1978). Being able to manipulate the HLB value would allow one to alternate between an invert emulsion (water-in-oil) and an emulsion (oil-in-water).

Atomic force microscopy (AFM) can be very useful in understanding surfical features sorbed onto a mica surface by measuring the force between the tip (imaging source) and a surface. This force is measured by the instrument, which then can be used to determine the height, deflection, and/or phase signal by the instrument. The height signal (measured in contact or tapping mode) shows the topography of the surface. The deflection signal measures how much the voltage is changed from a set voltage due to surfical features (set point voltage) resulting in an error signal.

In this study, two modes of the AFM were used, contact and tapping mode. In contact mode, the tip of the AFM stays in contact with the surface during a scan, while in tapping mode, the tip taps the surface as it moves along. Contact mode tends to be more invasive than tapping mode since the tip is always in contact during contact mode causing the tip to apply a fairly strong, constant force across the surface. The deflection signal can only be measured in contact mode. The phase signal (measured only in tapping mode) is able to distinguish different materials on the surface due to varying elasticity.

Using an AFM, one is able to image surfaces under air or a liquid. When a surface is imaged under a liquid, the tip and the portion of the surface that is being imaged is submerged under a liquid. It is sometimes advantageous to examine a surface under a liquid to be able to vary conditions of the surface to see if there is any change, especially if a surface that is being examined is generally not in air in its natural environment.

Mica was used as a model surface for this study. Mica does not represent all reservoir pore surfaces, but it is similar in surface properties to the clay mineral illite. It is important to have a mineralogical surface with constant mineralogy and chemistry so that the surface heterogeneity would not affect the adsorption and desorption of the surfactant. Mica is also easily cleavable to produce a clean, molecularly smooth surface. Smooth surfaces are required for contact angle measurements (to avoid contact-line pinning and hysteresis due to roughness) and for AFM imaging because the AFM has a working distance that is limited to about 1μm.

In this study, polyethoxylated amines with known structures were used to gain a better understanding of how the surfactants interact with a siliceous (mica) surface. The ultimate goal of the study was to evaluate wetting changes and possible cleaning techniques designed to regain the original mica wettability after exposure to the surfactants. Mica was treated with a 5% by volume surfactant/decane solution and then washed with various solutions. The surface properties were characterized macroscopically and microscopically before and after washing. Wettability was determined by measuring contact angles using the captive drop method. Microscopically, surfical features were examined using (AFM). Macroscopic and microscopic properties were compared to obtain a consistent picture of wetting alteration.

Chapter 2 : Materials and Methods

2.1 Materials

2.1.1 Mica

Muscovite mica ($KAl_2(AlSi_3)O_{10}(OH)_2$, S&J Trading, Inc., Glen Oaks, NY) was used as a model surface. The mica was cut into rectangles of approximately 1.5 cm by 2 cm for the contact angle measurements while a disc punch was used to cut circular samples with a diameter of 12.7 mm for AFM tests. All mica was cleaved with adhesive tape to obtain a smooth, clean surface prior to treatment. Care was taken at all times to handle mica samples only by their edges so that the freshly cleaved surfaces were not contaminated.

2.1.2 Buffered aqueous solutions

Three buffered brines were used: pH 4, pH 8, and pH 10. NaCl was added as needed to maintain a constant ionic concentration of 0.1 M. The compositions of the buffers are listed in Table 2-1.

Table 2-1. Buffer compositions

Buffer:	pH 4, 0.1 M NaCl	pH 8, 0.1 M NaCl	pH 10, 0.1 M NaCl
NaCl (g/L)	3.74		3.76
Na Acetate (g/L)	2.95		
Glacial HAc (mL/L)	3.7		
Na_2HPO_4 (g/L)		6.21	
NaH_2PO_4 (g/L)		0.32	
$NaHCO_3$ (g/L)			2.10
NaOH (g/L)			0.43

2.1.3 Surfactants

Three liquid surfactants were obtained from Ethox Chemicals, LLC (Greenville, South Carolina): CAM-2, TAM-2, and TAM-5 (Figure 2-1). CAM-2 is composed of coconut amine (chain length of 12 carbons, C 12) along with two ethylene oxides. TAM-2 is composed of tallow amine (chain length of 18 carbons, C 18) along with two ethylene oxides, and TAM-5 is composed of tallow amine along with five ethylene oxides. TAM-5 has two possible arrangements of the ethylene oxides on the amine. It is not known whether our sample was one or a mixture of both of these structures. The purity of the surfactants is not known; surfactants were used as received.

2.1.4 Decane

All decane (>99.3% purity, Fisher Scientific) used was purified by passing it through a column containing silica (grade 62, 60 – 200 mesh, Aldrich, Milwaukee, WI) and alumina (80 – 200 mesh, Fisher Scientific). Before the silica was used, it was placed into an oven set at 200 °C for at least eight hours to remove any sorbed water.

2.1.5 Double Distilled Water

All water used in this study was double distilled before it was used. It is mentioned either as double distilled water or water. The pH of the water was 6.5 – 6.8.

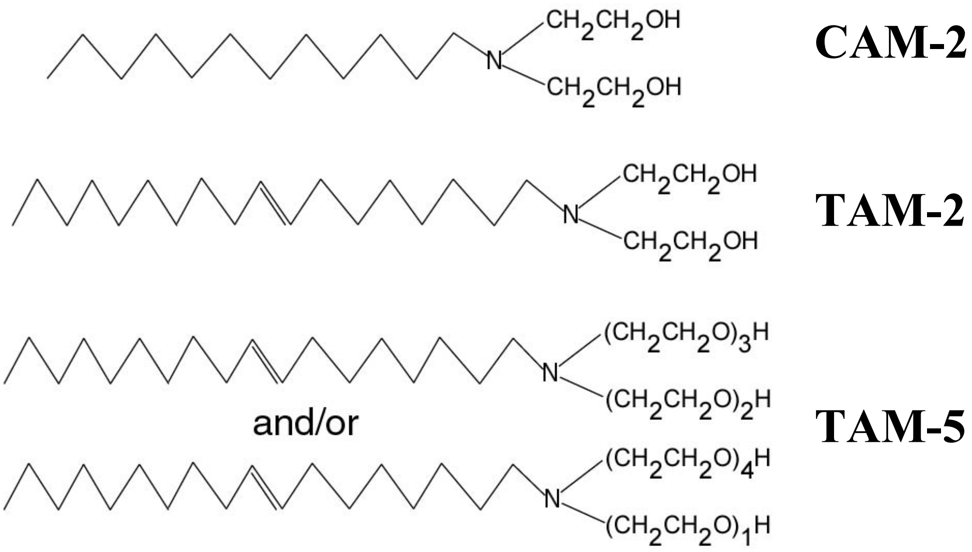


Figure 2-1. Chemical structures of the surfactants used in this study

2.2 Experimental Methods

2.2.1 Surfactant mixtures

Solutions of 5% by volume surfactant were prepared by diluting 5 mL of surfactant with decane in a 100-mL volumetric flask. Some of the surfactant/decane solutions were pre-equilibrated with buffer solutions. One-hundred milliliters of buffer and 100 mL of 5% surfactant/decane solution were mixed in a separatory funnel. Emulsions formed that required varying amounts of time (hours to weeks) to separate. After phase separation, the upper phase was used as the surfactant/decane solution and the lower phase as the aqueous buffer. Contact angle measurements using pre-equilibrated fluids were indistinguishable from those with non-equilibrated solutions for a given aqueous solution. Since pre-equilibration does not appear to affect the results, distinction between equilibrated and non-equilibrated fluid results will be omitted in most cases. Complete descriptions of the full suite of experiments are in the Appendices, as described in the Results section.

2.2.2 Interfacial tension measurements

The pendant drop method (Padday, 1969; Miller and Neogi, 1985) was used to measure the interfacial tension (IFT) between varying concentrations of surfactant solutions in decane and an aqueous drop of pH 4, pH 8, or double-distilled water using an OCA20+SCA20 (DataPhysics Instruments GmbH, Germany). In the pendant drop method of measuring the interfacial tension, a drop is formed at the end of a capillary; the shape of the drop is then fitted to the Young-Laplace equation to calculate the interfacial tension (Padday, 1969; Miller and Neogi, 1985). An inverted needle was used with an interdiameter of 0.64 cm (DataPhysics Instruments GmbH, Germany). An inverted needle was used because the fluid introduced into the needle was the surfactant/decane solution. The solution was less buoyant than the aqueous solution the IFT was measured with. Six measurements were made for each surfactant solution with each with a new drop being formed before the measurement was taken.

The critical micelle concentration (CMC) was determined for the surfactants with pH 4, pH 8, and double-distilled water from the interfacial tension measurements. The CMC is determined from the intersection of the two linear portions of the interfacial tension vs. log surfactant concentration plot. It was assumed that the IFT has a similar dependence on surfactant monomer concentration to that of the surface tension in an aqueous system, but in reality this may not be true since surfactants tend to not affect the surface tension. A 1% by volume surfactant/decane solution was made for each surfactant and diluted to yield lower concentrations.

2.2.3 Contact angle measurements

Clean mica. To test the initial condition of mica, contact angles were measured with a captive drop of double-distilled water on freshly cleaved mica submerged in purified decane. The water-advancing angle (θ_A) and water-receding angle (θ_R) of clean mica were found to be approximately 10°, indicating water-wet conditions.

Contact angles between surfactant solutions and water. Mica was submerged in about 10 mL of 5% by volume surfactant/decane solution and contact angles were measured using the captive drop method with a water drop produced by a Gilmont pipette. The drop was allowed to remain motionless on the surface for 2 minutes before the advancing angle measurements were taken. The receding angles were measured by drawing the water back into the pipette after advancing angles were recorded. All contact angles reported are an average of 6 measurements at various locations on three separate pieces of mica for a total of 18 measurements.

Contact angles on surfaces after surfactant sorption. Mica was soaked in the 5% by volume surfactant/decane solution for 40 to 70 min. The treated mica was then washed with one solvent or a sequence of solvents. The solvents tested included toluene, hexane, isopropanol, decane, acetone, water, and pH 4, 8, and 10 buffers. Details of washing sequences are described in the Results section. For each solvent, mica was washed by swirling it in the solvent three times followed by touching the edge of the mica with a Kimwipe to remove excess solution. The washed mica was placed into either decane or water and the contact angles were measured using the captive drop method as described above. If the contact angles were measured in water, the fluid delivered by the pipette (i.e. the drop) was decane.

The exposure time to the solvent was also examined by placing the washed mica into a solvent for approximately 60 min and 24 hours. The contact angles were then measured either in decane with water as the drop or in water with decane as the drop. It was found the exposure time to the solvent did not affect the contact angles (see Appendices, as described in the Results section).

2.2.4 Atomic forces microscopy

Mica was soaked in a 5% by volume surfactant/decane solution for approximately 45 minutes. Mica samples were removed from the surfactant solution and allowed to dry thoroughly in air. The mica was then mounted onto an AFM magnetic puck using a small amount of Super Glue Gel (Ace Hardware, Oak Brook, IL).

The AFM samples were imaged at ambient temperature in contact mode in air or under a liquid (pH 8 brine, pH 10 brine, or water) using methods described by Lord and Buckley (2002). Some samples were imaged using tapping mode. The set up of the AFM for the tapping mode was used as described by Thornton et al (2000).

The AFM used was a NanoScope IIIA (Veeco Instruments, Santa Barbara, CA), and the probes used were Olympus Oxide-Sharpened Silicon Nitride (Model OTR4-35 (contact mode and tapping mode under a fluid) or Model MPP-111000 (tapping mode under air), both from Veeco Instruments).

Some of the mica samples were washed with a solvent before they were glued to a puck and imaged. All AFM images shown using contact mode are of the deflection signal and images using tapping mode are of the height and phase signal. The height and phase signals were taken during the same scan.

Chapter 3 : Results

3.1 Characterization of the surfactants

Figure 3-1 shows the results of measurements of IFT as a function of surfactant concentration. These results were used to determine the critical micelle concentration (CMC) of the three surfactants with pH 4 brine. The CMC with pH 4 was 0.20 mM (0.06% by volume) for CAM-2, 0.04 mM (0.02% by volume) for TAM-2, and 0.0047 mM (0.003% by volume) for TAM-5, where the molar concentrations were calculated assuming the surfactants were pure as received. The CMCs for the surfactant/decane solution with pH 8 buffer or double-distilled water were greater than the values reported here for pH 4 buffer (see Appendix A for details). The concentration (5% by volume) of surfactant solution used for treatment of the mica was much greater than the CMCs of the surfactants.

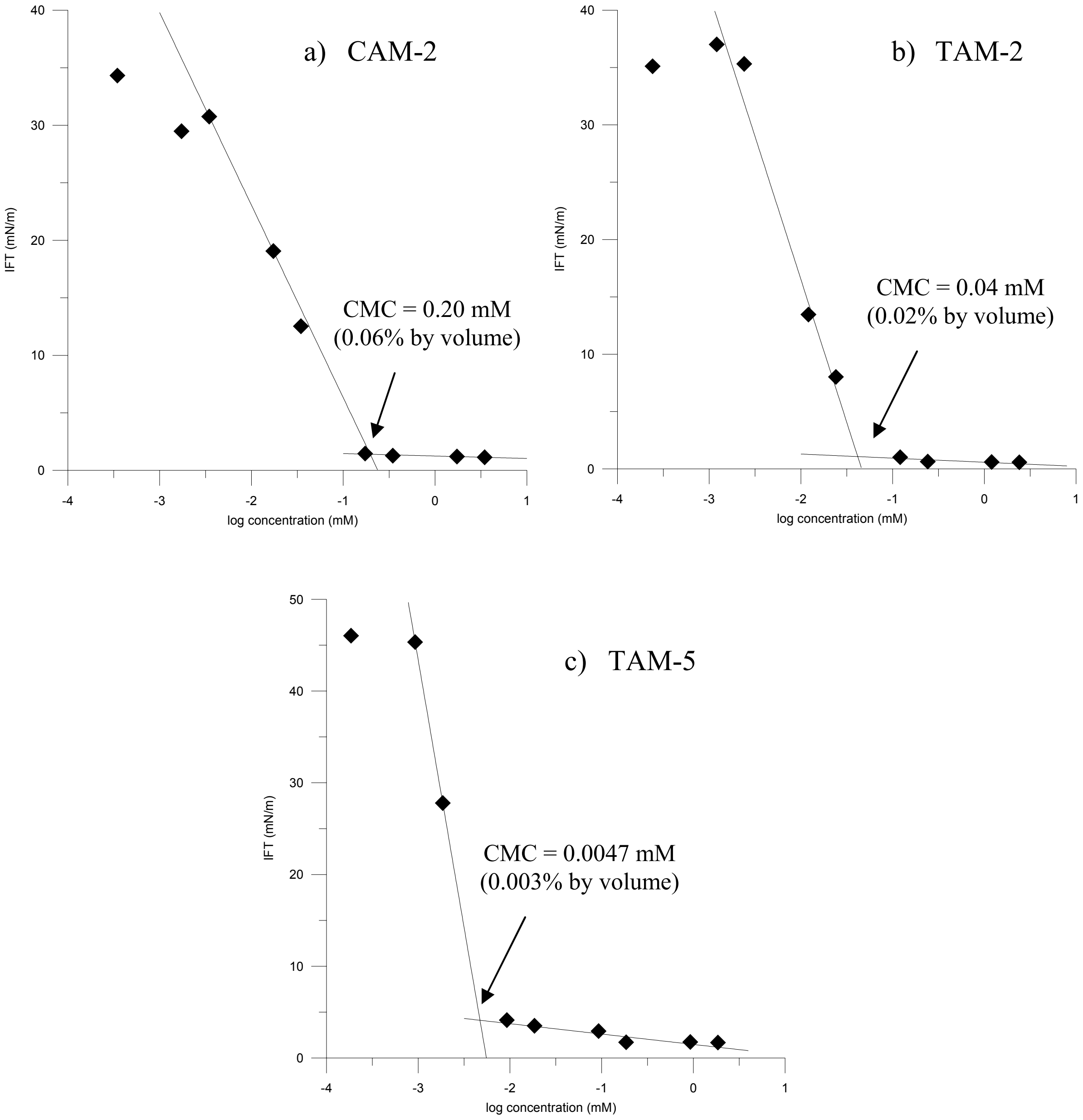


Figure 3-1. Plots of interfacial tension (IFT) as a function of log surfactant concentration were used to determine the CMC for a) CAM-2 b) TAM-2 and c) TAM-5 with pH 4 buffer.

3.2 Contact angle measurements

Table 3-1 and Figure 3-2 summarize the contact angle measurements on mica surfaces during and after exposure to the 5% by volume surfactant/decane solutions for all three surfactants. In general CAM-2 and TAM-2 gave similar results while TAM-5 differed from the other two. Appendices D – M have details of contact angle results for many different conditions.

Table 3-1. Summary of contact angle measurements for CAM-2, TAM-2, and TAM-5.

Sample	Advancing Angle		Receding Angle	
CAM-2	**Average**	**Std dev**	**Average**	**Std dev**
no wash measured in 5% by volume surfactant/decane solution	159	13	167	0
toluene wash measured in decane	91	22	34	6
hexane wash measured in decane	115	2	37	6
acetone wash measured in decane	114	0	33	4
acetone wash measured in water	161	2	141	10
acetone and water wash measured in water	160	2	142	3
TAM-2				
no wash measured in 5% by volume surfactant/decane solution	162	14	170	1
toluene wash measured in decane	132	9	84	5
hexane wash measured in decane	128	16	63	23
acetone wash measured in decane	102	3	37	2
acetone wash measured in water	165	3	155	12
acetone and water wash measured in water	167	5	167	5
TAM-5				
no wash measured in 5% by volume surfactant/decane solution	180	0	180	0
toluene wash measured in decane	17	3	14	1
decane wash measured in decane	10	1	10	1
acetone wash measured in decane	14	2	13	2
acetone wash measured in water	161	3	137	16
acetone and water wash measured in water	157	4	122	24
acetone and pH 8 wash measured in water	149	1	109	17
acetone and pH 10 wash measured in water	141	15	77	13
acetone, pH 4, acetone wash measured in water	85	8	32	0
acetone, water, acetone wash measured in water	82	7	30	2
acetone, pH 10, acetone wash measured in water	11	2	11	2

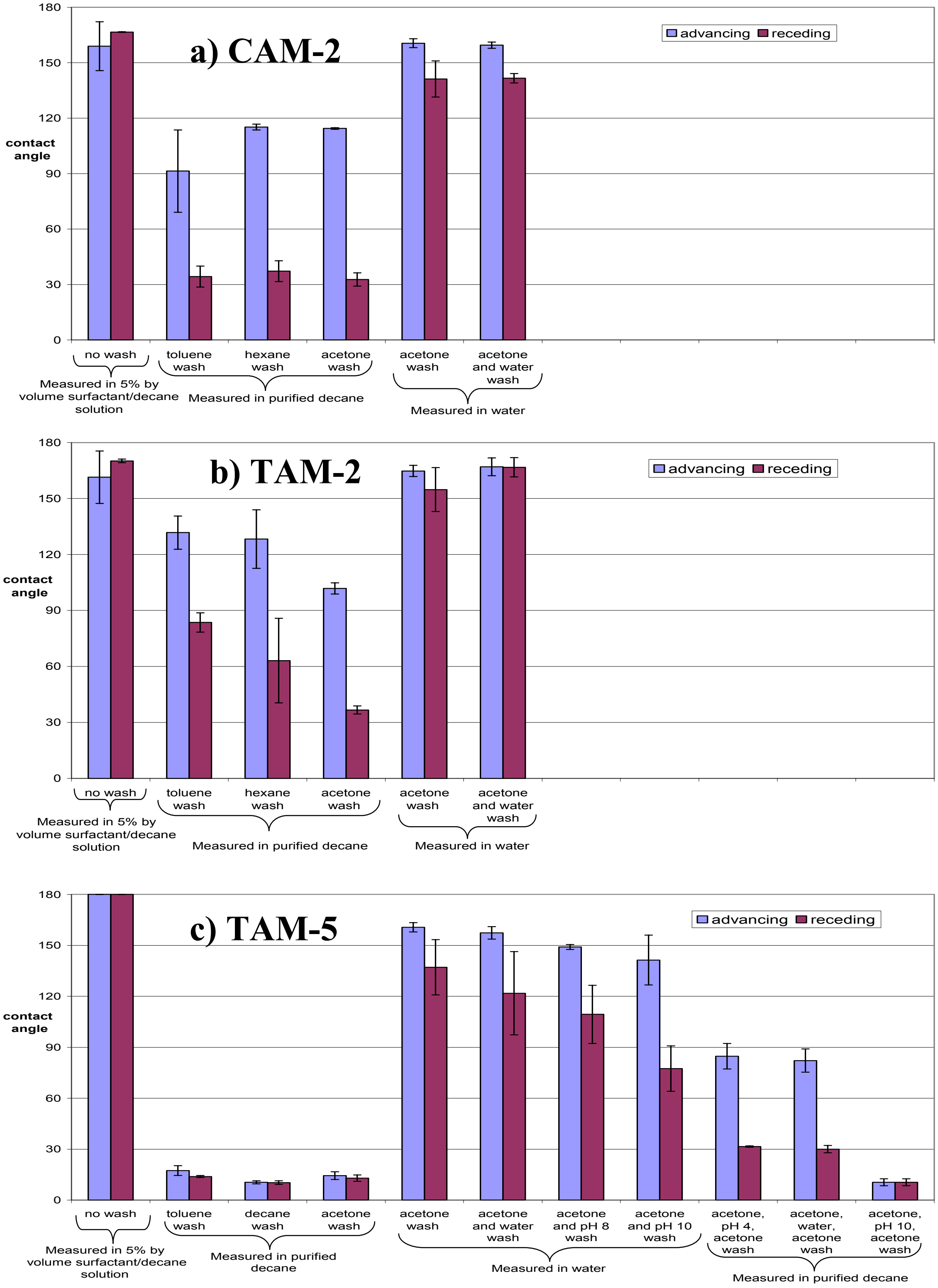


Figure 3-2. Contact angle results for a) CAM-2 b) TAM-2 and c) TAM-5. Error bars are standard deviations of 18 replicate measurements.

3.2.1 Contact angles between surfactant solutions and water

The leftmost results in Fig. 3-2 show the contact angles measured with a drop of water on mica that was submerged in surfactant/decane solution. Mica treated with CAM-2 or TAM-2 had a θ_A of approximately 160° (oil-wet) and a θ_R of approximately 170°, while mica treated with TAM-5 had an θ_A and θ_R of approximately 180° (oil-wet). An exact contact angle for TAM-5 could not be measured because the IFT was very low for this 5% surfactant/decane solution and water, which caused the water to stream continuously out of the pipette. This caused the water drop to grow continuously; therefore the contact angle was estimated from a moving contact line. Error bars represent the standard deviations of 18 replicate measurements.

3.2.2 Decane/water contact angles after surfactant sorption

When measured using purified decane after washing, the contact angle of the mica tended to be intermediate (CAM-2 and TAM-2, $\theta_A \sim 32\text{-}83°$) to water-wet (TAM-5, $\theta_A \sim 10\text{-}18°$) regardless of the washing procedure (Figure 3-2). When the contact angle was measured in water, surfaces appeared to be more oil-wet ($\theta_A \sim 141\text{-}167°$) regardless of which solutions were used to wash the mica (Figure 3-2).

An additional set of contact angle measurements was made on TAM-5-treated surfaces (using a decane surfactant solution that was pre-equilibrated with pH 8 buffer) with the water phase replaced by pH 8 and pH 4 buffers. Table 3-2 and Figure 3-3a summarize the contact angles for pH 4 brine while Table 3-2 and Figure 3-3b summarize the results measured with the pH 8 brine. The pH 4 contact angle results were generally less water-wet than comparable measurements with pH 8. The pH 4 measurements are comparable to similar measurements with double-distilled water. With pH 8, the mica surface appeared to be water-wet, while with pH 4, the mica surface was intermediate in wetting.

Table 3-2. Summary of contact angle measurements for TAM-5 pre-equilibrated with pH 8 buffer.

Sample	Advancing Angle		Receding Angle	
TAM-5 pre-equilibrated with pH 8 brine	**Average**	**Std dev**	**Average**	**Std dev**
measured in pH 4 buffer				
no wash measured in 5% by volume surfactant/decane solution	**161**	**34**	**161**	**34**
toluene wash measured in decane	**76**	**3**	**34**	**3**
acetone wash measured in decane	**62**	**6**	**27**	**3**
acetone and water wash measured in pH 4 brine	**144**	**0**	**93**	**18**
acetone and pH 8 wash measured in pH 4 brine	**133**	**8**	**58**	**6**
acetone and pH 10 wash measured in water	**133**	**15**	**65**	**25**
measured in pH 8 buffer				
no wash measured in 5% by volume surfactant/decane solution	**161**	**34**	**161**	**34**
toluene wash measured in decane	**13**	**7**	**12**	**5**
acetone wash measured in decane	**14**	**2**	**14**	**2**
acetone and water wash measured in pH 8 brine	**21**	**1**	**21**	**1**
acetone and pH 8 wash measured in pH 8 brine	**18**	**1**	**18**	**1**

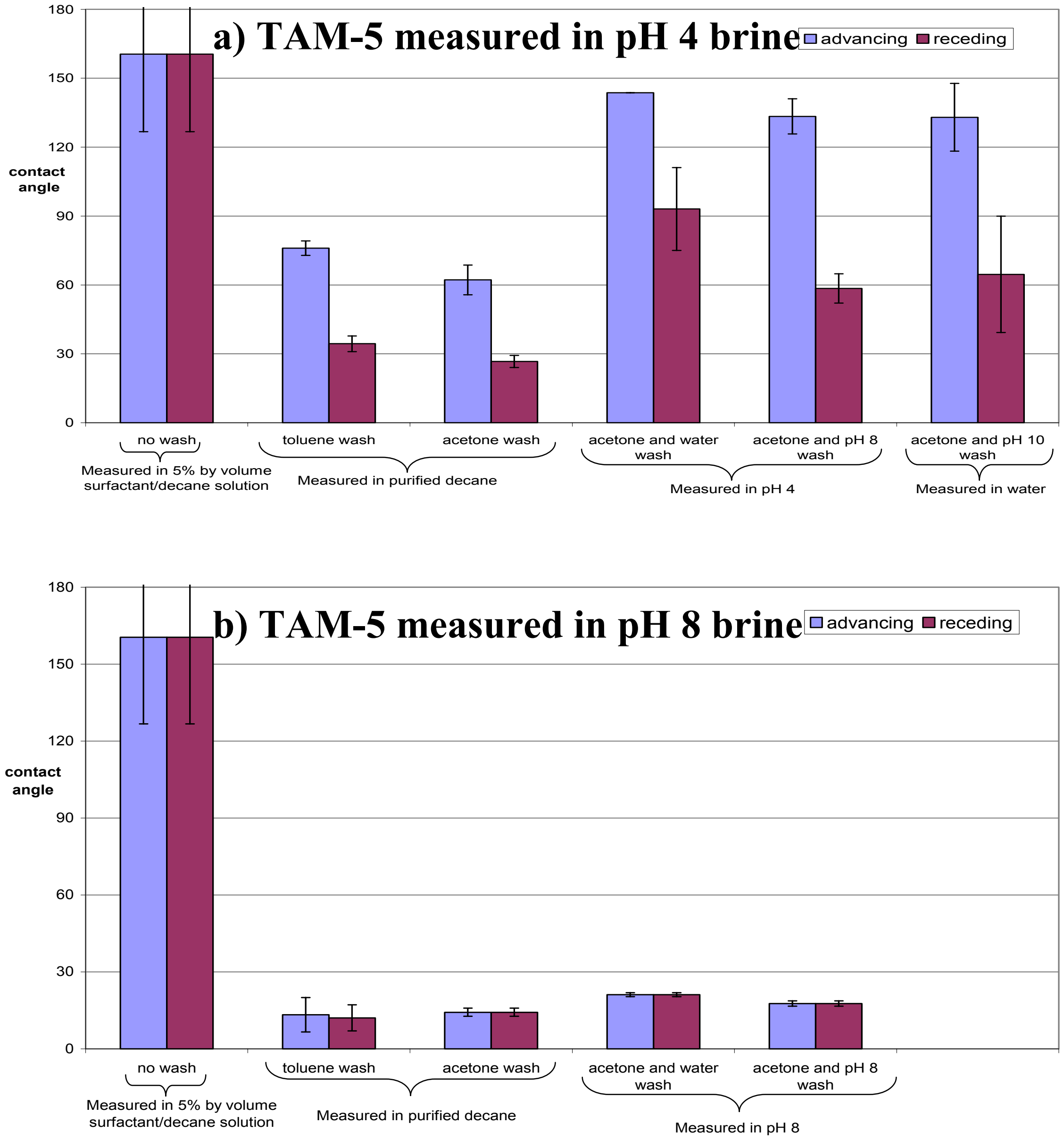
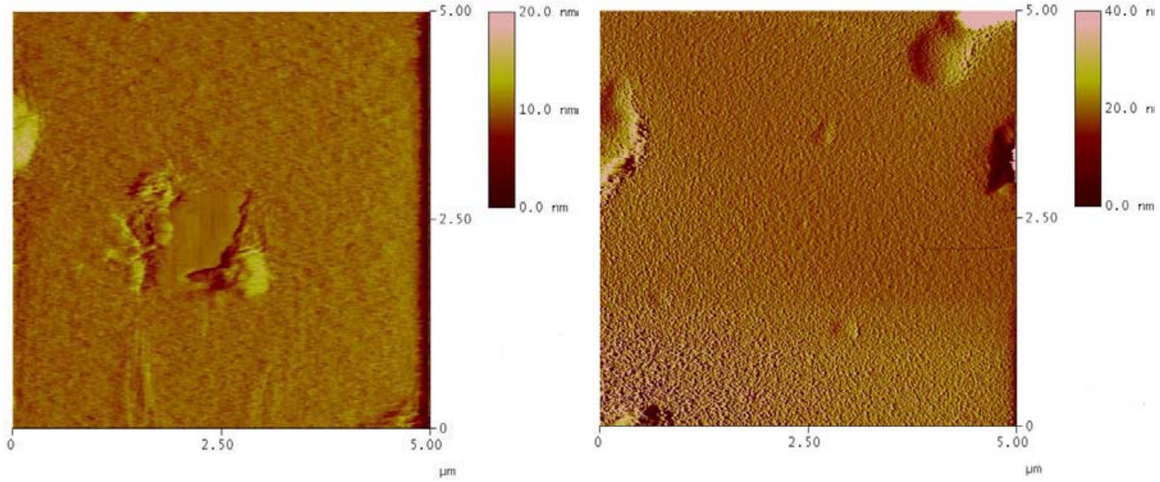


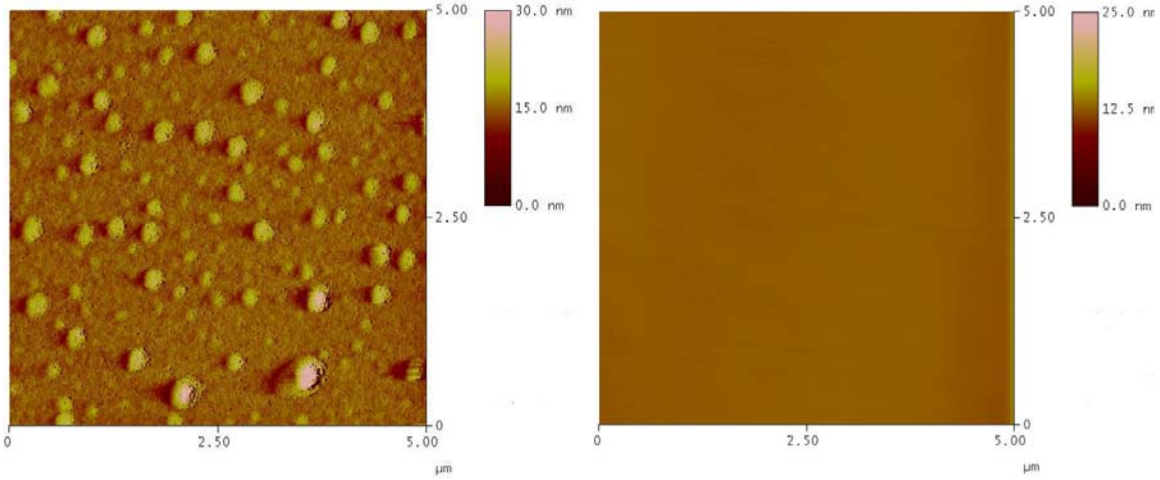
Figure 3-3. TAM-5 pre-equilibrated with pH 8 buffer measured in a) pH 4 buffer and b) pH 8 buffer. Error bars are standard deviations of 18 replicate measurements.

3.3 Atomic Force Microscopy

Figure 3-4 shows AFM images of mica treated with TAM-5. All images are of the deflection signal and are 5-μm by 5-μm scans. Figure 3-4a shows the TAM-5-treated mica surface imaged under air. The feature in the middle of the image was scraped by the tip during a previous scan of a 1-μm by 1-μm area. Figure 3-4b was imaged under water. The features on this surface were more stable than under air; a previous 1-μm by 1-μm scan produced no scraping of the surface. Figure 3-4c was imaged under pH 8 brine. It appeared the pH 8 brine caused some of the features to coalesce while others remained on the surface of the mica. The mica surface was imaged approximately 5 min after the pH 8 buffer came into contact with the surface. Other images were compared to see if time the mica surface was exposed to the fluid made any difference on the desorption of the surfactant, but no solid conclusion could be drawn. Figure 3-4d was imaged under pH 10 brine; this image has the same appearance as clean mica, suggesting that all the surfactant desorbed from the surface at this high pH. A more complete set of AFM images is in Appendices N – Q.


a) imaged under air

b) imaged under water


c) imaged under pH 8 buffer

d) imaged under pH 10 buffer

Figure 3-4. Mica treated with a 5% by volume TAM-5/decane solution imaged under a) air b) water c) pH 8 buffer or d) pH 10 buffer.

Chapter 4 : Discussion

The difference between CAM-2 and TAM-2 is their respective hydrocarbon chain lengths. Surfaces of mica treated with CAM-2 and TAM-2 had contact angles that were very similar; varying the chain length of the surfactant appeared to have little or no impact on surfactant adsorption on the mica surface. TAM-5, which has the same hydrocarbon chain length as TAM-2 but has five ethylene oxides attached to the nitrogen instead of two, adsorbed less efficiently on mica. Changing the polar head groups does appear to affect adsorption of polyethoxylated amine surfactants.

Exposure of dry mica to high concentrations of these surfactants produced wetting changes that were readily reversed by washing with any of the non-aqueous solvents, if followed by immersion in decane. It appears that any surfactant remaining on the surface after washing can diffuse back into the decane, in which it is quite soluble. Subsequent contact angle measurements indicate water-wet to intermediate-wet surfaces.

If, however, the washed surface is immersed in an aqueous phase, the results can be quite different. This can be seen in Fig. 3-2 by comparing acetone-washed surfaces immersed in decane with acetone-washed surfaces immersed in water for subsequent contact angle measurements. For all three surfactants, the contact angles measured under water are much higher than those measured under decane. Apparently there is some surfactant remaining on the acetone-washed surfaces. In the presence of water at low or neutral pH, the surfactant nitrogen is protonated and can adsorb much more strongly on the negatively charged mica surface than did the surfactant in a non-polar solution. Diethanol amine, a compound analogous to CAM-2 and TAM-2 without the hydrocarbon chain, has a pK_a (pH at which the concentrations of protonated and neutral forms are equal) of 8.88 (Dean, 1999); the pK_as of the surfactants tested here are likely close to this value. The limited effect of increasing hydrocarbon chain length on the value of pK_a is demonstrated by a comparison of diethylamine ($pK_a = 10.8$) and didodecylamine ($pK_a = 10.99$) (Dean, 1999). Sorption of the protonated forms of the surfactants produces intermediate to oil-wet conditions. The neutral form of the surfactant that dominates at pH 10 has much less ability to sorb strongly on the mica surface, producing water-wet conditions.

AFM generally confirms the interpretation derived from contact angle measurements. In air, with no water to ionize the surfactant, surfactant is weakly adsorbed and easily moved by the AFM tip. Imaged under water, surfactant adsorption appears much more stable. Imaging under pH 8 starts the process of surfactant removal, while imaging under a pH 10 buffer—where the surfactant is in its neutral form—completes the surfactant removal process.

Since water is present in oil reservoirs, adsorption of surfactants like the polyethoxylated amines in this study is likely to occur in cores obtained with oil-based drilling fluids. The possibility that adsorption of this class of surfactants might be reversible at high pH is encouraging, however, and worthy of additional study.

Chapter 5 : Conclusions and Suggestions for Future Research

5.1 Conclusions

Polyethoxylated amines adsorb to mica much more strongly in the presence of water (below a pH of about 8 or 9) than in the absence of water. Changing the hydrocarbon chain length from 12 to 18 had little effect on surfactant adsorption, whereas changing the extent of ethoxylation from two to five significantly reduced adsorption. Above pH 10, the presence of water inhibits or even reverses adsorption.

AFM images obtained in contact mode on mica surfaces treated with polyethoxylated amine surfactants under air, distilled water, pH 8 and pH 10 buffers were qualitatively consistent with interpretations of macroscopic contact angle measurements.

5.2 Suggestions for future research

When the surfactant solutions were pre-equilibrated, it was found that temperature affected how long it took for the emulsions to break. If these experiments were to be run again, I suggest that all pre-equilibrated solutions be placed in an oven (~30 °C) so that the emulsions break in a reasonable and predictable amount of time (hours to days).

Some of the AFM samples appeared to have liquid drops of decane remaining on the surface. It would be better to let the mica surface dry for about six months before imaging with the AFM to ensure the mica surface was indeed dry.

High performance liquid chromatography (HPLC) was used to determine if relative concentrations of the surfactant in the aqueous phase could be quantified (see Appendix B). It is suggested that all pre-equilibrated solutions be run through the HPLC to determine relative amounts of surfactant in the aqueous phase. A new method would have to be created to be able to determine the relative amounts of surfactant in the non-aqueous phase of the pre-equilibrated solutions. Knowing the relative amounts of surfactant in each of the pre-equilibrated phases would be helpful, because it may indicate which phase the surfactant prefers.

The surfactants used in this study focused on one family of surfactants, polyethoxylated amines. Other families of surfactants need to be investigated to determine if their adsorption and desorption are dependent on the pH of the solution and if the solubility of the surfactants affects the contact angle measurements. This may not be the case, especially for non-ionic surfactants since they will probably not be affected by the pH of the solution.

The wettability was examined on mica for this study. The wettability of these surfactants needs to be examined on core that is more representative of an oil reservoir to see if the results are similar to that found in this study. Also, mica is only representative of siliceous reservoirs and other types of material like calcite to simulate carbonate reservoirs should be used to investigate the effect of surfactant adsorption and desorption.

Generally in the drilling fluids, many different types of surfactants are used, therefore the combinations of surfactants and their effect on each other need to be investigated.

The interaction of the surfactants in the drilling fluids and crude oil need to be examined to see if the possible surfactants and/or asphaltenes present in the crude oil have any affect on the adsorption and/or desorption of the surfactants on a mineral and rock surface.

It would be useful to examine the effect of the surfactants in reservoir conditions. All measurements were carried out at ambient temperatures and pressures with mica. It is recommended these surfactants be examined at higher temperatures and pressures with a surface more representative of the reservoir like a sandstone or carbonate core. Also the presence of crude oil needs to be examined to simulate reservoir conditions since it is not known how these surfactants would interact with the crude oil. To simulate the introduction of the surfactant to the crude oil saturated rock, one could soak a mineral surface in crude oil and then expose the surface to a surfactant/oil solution and measure the contact angle to see the affects on the wettability of the surface. The surfactants could possibly behave differently depending on the crude oil compositions. Some crude oils contain surfactants which in themselves could alter the wettability more strongly than the surfactants used in this study. Also the presences of asphaltenes can alter the wettability of a surface and the interaction of the surfactants and asphaltenes needs to be examined. Suggested cleaning solvents for the crude oil system are toluene followed by acetone followed by a high pH buffer solution similar to the pH 10 buffer used in this study.

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Appendix A : Determination of the CMC for CAM-2, TAM-2 and TAM-5 with double distilled water and pH 8 buffer.

Figures A-1 and A-2 show the results of the IFT for all three surfactants with double distilled water and pH 8 buffer respectively. Table A-1 summarizes the CMC for all three surfactants with pH 4 buffer, double distilled water, and pH 8 buffer. Tables A-2, A-3, and A-4 show the data used to generate the graphs in Figure 3-1, A-1, and A-2, respectively. The CMC with double distilled water may not be too accurate since there were insufficient points above the CMC. Greater surfactant solution concentrations could not be measured with the pendant drop method with the needle sized used because the IFT was too low and a drop of the surfactant solution could not be formed at the end of the needle (indicated as “too low” in Tables A-1 – A-4).

The CMC’s tended to increase with increasing pH. This is due to the protonation of the head groups at a lower pH, making the surfactants more hydrophilic and prone to form micelles.

Table A-1. The CMCs for CAM-2, TAM-2, and TAM-5 with pH 4 buffer, double distilled water, and pH 8 buffer.

	CAM-2	TAM-2	TAM-5
pH 4 buffer	0.20 mM (0.06% by volume)	0.04 mM (0.02% by volume)	0.0047 mM (0.003% by volume)
Double distilled water	1.25 mM (0.36% by volume)	2.02 mM (0.34% by volume)	0.037 mM (0.02% by volume)
pH 8 buffer	0.25 mM (0.072% by volume)	2.77 mM (1.15% by volume)	0.065 mM (0.035% by volume)

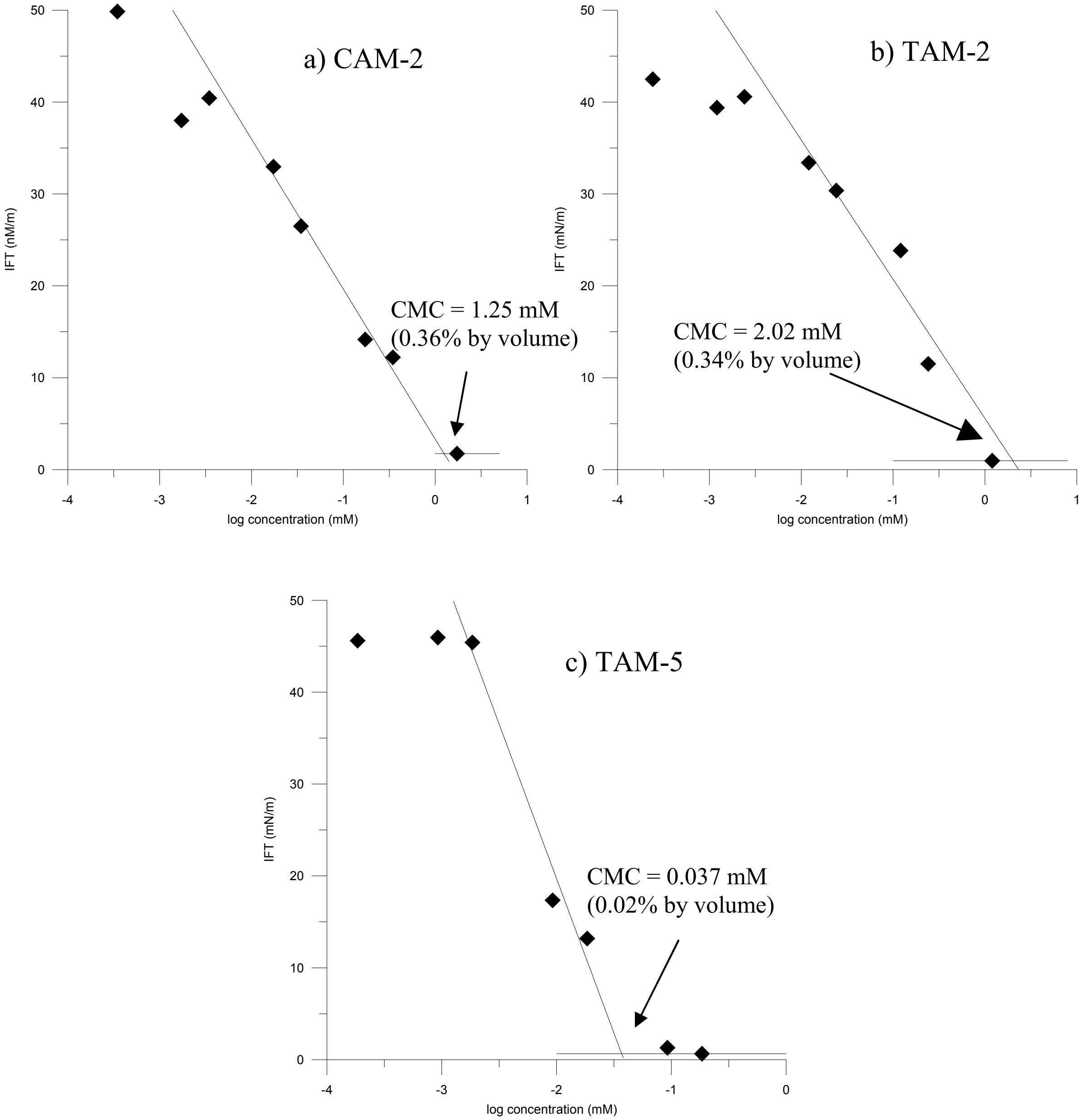


Figure A-1. The graph of interfacial tension (IFT) as a function of log concentration used to determine the CMC for a) CAM-2 b) TAM-2 and c) TAM-5 with double distilled water.

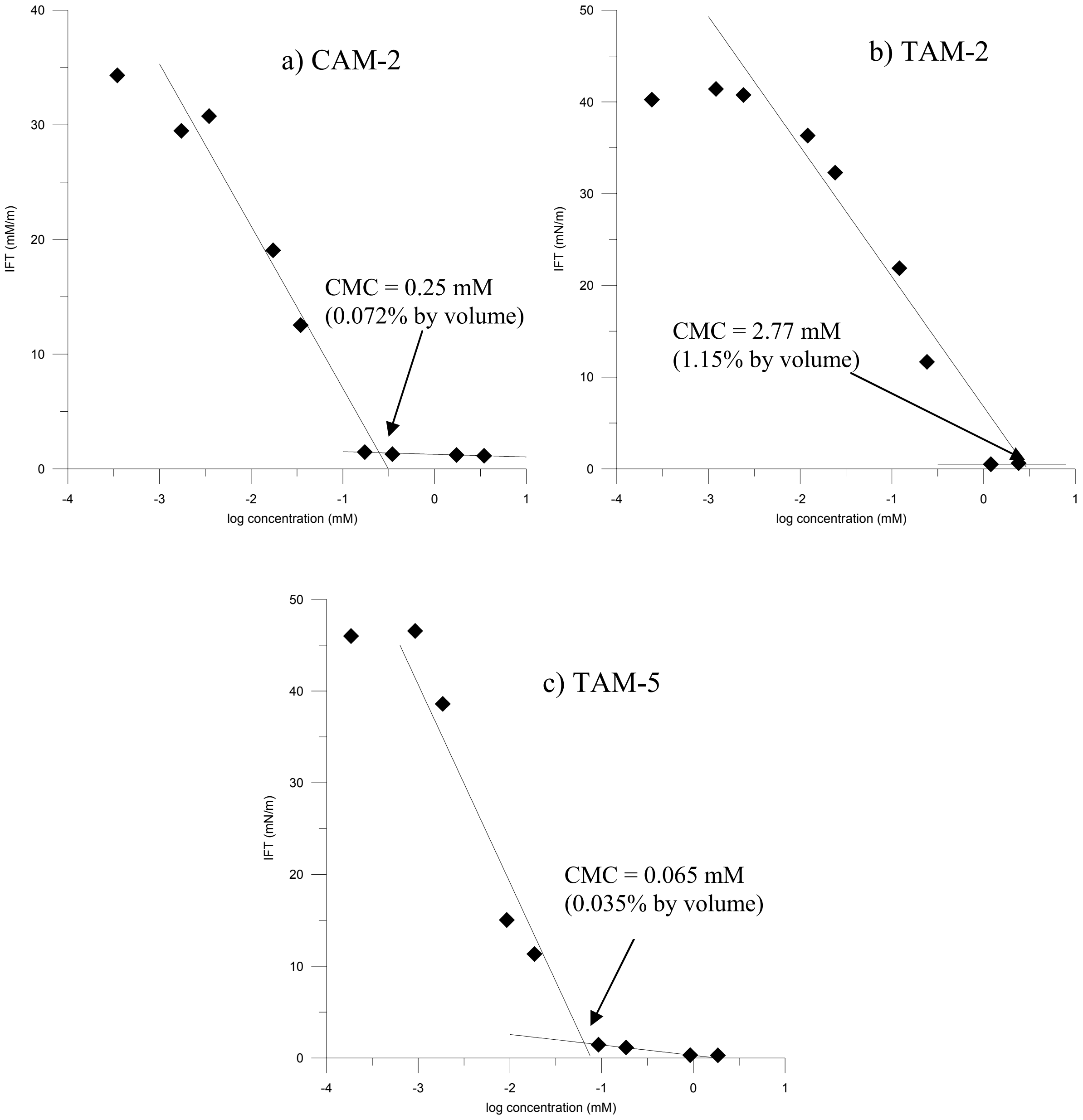


Figure A-2. The graph of interfacial tension (IFT) as a function of log concentration used to determine the CMC for a) CAM-2 b) TAM-2 and c) TAM-5 with pH 8 buffer.

Table A-2. IFT data used to plot graphs to determine the CMC for CAM-2 and pH 4 buffer, double distilled water, and pH 8 buffer.

	IFT (mN/m)		
log concentration (mM)	pH 4 buffer	double distilled water	pH 8 buffer
0.54	1.14	too low	0.49
0.24	1.21	1.73	1.17
-0.46	1.28	12.22	11.31
-0.76	1.46	14.16	12.85
-1.46	12.53	26.5	24.1
-1.76	19.06	32.97	30.84
-2.46	30.76	40.43	37.69
-2.76	29.48	38	36.83
-3.46	34.32	49.86	41.51

Table A-3. IFT data used to plot graphs to determine the CMC for TAM-2 and pH 4 buffer, double distilled water, and pH 8 buffer.

	IFT (mN/m)		
log concentration (mM)	pH 4 buffer	double distilled water	pH 8 buffer
0.38	0.58	too low	0.62
0.08	0.6	0.96	0.5
-0.62	0.64	11.51	11.66
-0.92	1.02	23.84	21.87
-1.62	8.02	30.37	32.29
-1.92	13.46	33.4	36.33
-2.62	35.32	40.58	40.76
-2.92	37.02	39.39	41.42
-3.62	35.11	42.49	40.25

Table A-4. IFT data used to plot graphs to determine the CMC for TAM-5 and pH 8 buffer, double distilled water, and pH 8 buffer.

	IFT (mN/m)		
log concentration (mM)	pH 4 buffer	double distilled water	pH 8 buffer
0.27	1.68	too low	0.28
-0.03	1.75	too low	0.31
-0.73	1.72	0.64	1.14
-1.03	2.93	1.29	1.44
-1.73	3.52	13.18	11.33
-2.03	4.13	17.34	15.04
-2.73	27.79	45.41	38.6
-3.03	45.34	45.95	46.55
-3.73	46.03	45.61	46

Appendix B : Analysis of Aqueous Surfactant Solution via High-Performance Liquid Chromatography

B.1 Methods

5% by volume surfactant/decane solution was prepared and pre-equilibrated with an aqueous solution (pH 4 buffer, double distilled water, or pH 8 buffer) as mentioned in the Methods section. After the two solutions had been separated after pre-equilibration, only the aqueous solution was used for the high-performance liquid chromatography (HPLC). One milliliter of the aqueous solution that had been pre-equilibrated with the 5% by volume surfactant/decane was placed into a Kimble amber 1-mL glass vial (Fisher Scientific). This was considered the 100:0 solution. The 50:50 solution was made by placing 0.5 mL of the 5% by volume surfactant/decane solution into the vial and then diluted with 0.5 mL of the aqueous solution (double distilled water or pH 4 or pH 8 buffer). The 25:75 solution was made by placing 0.25 mL of the 5% by volume surfactant/decane solution into the vial and then diluted with 0.75 mL of the aqueous solution. For each of the above solutions, three vials were made to have triplicates of the sample.

The samples were then run using a model 717 plus Autosampler, model 501 pump, and model 486 detector (all from Waters Corp., Milford, MA). The column used was a Nucleosil CN 5 µm, 150 mm x 4.6 mm (Sigma-Aldrich). The wavelength used was 254 nm and the mobile phase was 5 mM aqueous solution of p-toluenesulfnate and methanol (45:55 by volume), at a flow rate of 1 mL/min.

B.2 Results

Figures B-1 – B-4 show representative chromatographs for CAM-2, CAM-2 pre-equilibrated with pH 8 buffer, TAM-2 pre-equilibrated with pH 8, and TAM-5 pre-equilibrated with pH 4 buffer. Tables B-1 – B-4 and Figures B-5 – B-8 show the results from the triplicates run for CAM-2, CAM-2 pre-equilibrated with pH 4 buffer, TAM-2 pre-equilibrated pH 8 buffer, and TAM-5 pre-equilibrated with pH 4 buffer. All results show that with dilution there is a smaller area under the curve except for TAM-2 pre-equilibrated with pH 8 buffer. It was expected that as the surfactant solution was diluted the area under the curve would be less. It is not known why TAM-2 pre-equilibrated with pH 8 buffer showed an trend opposite than was expected.

It was shown that HPLC can be used to determine relative amounts of surfactant in the aqueous solutions. This could be helpful when comparing different pre-equilibrated aqueous solutions to determine how much surfactant was in each solution.

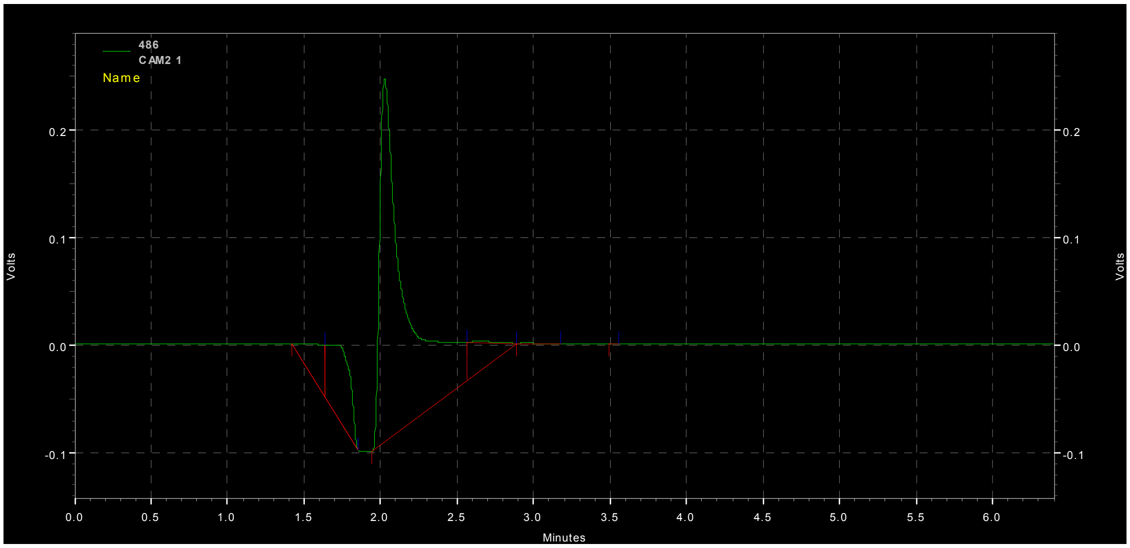


Figure B-1. HPLC chromatogram for CAM-2 100:0 aqueous solution 100:0.

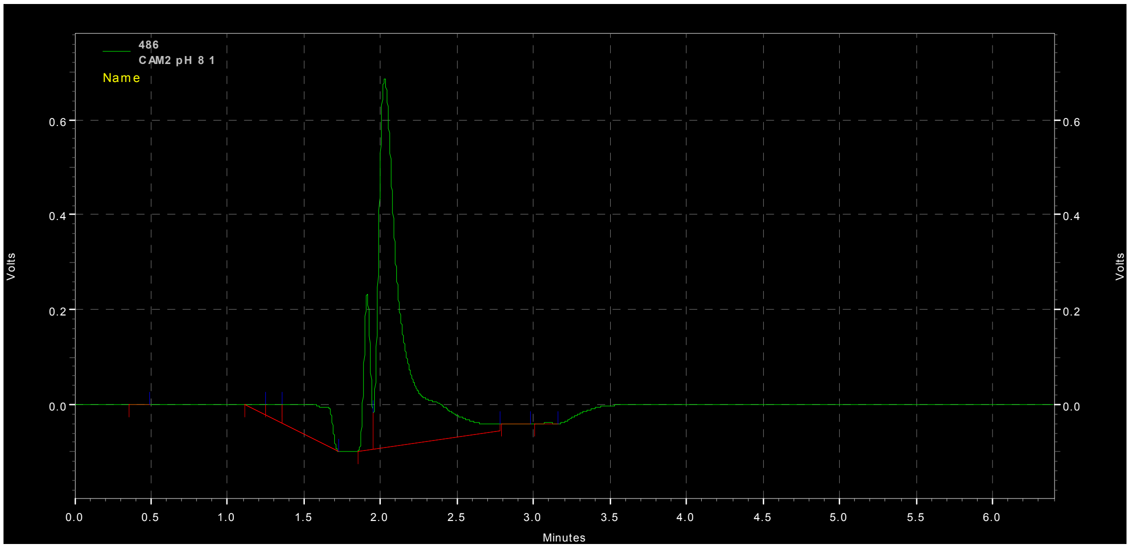


Figure B-2. HPLC chromatogram for CAM-2 pre-equilibrated with pH 4 buffer 100:0.

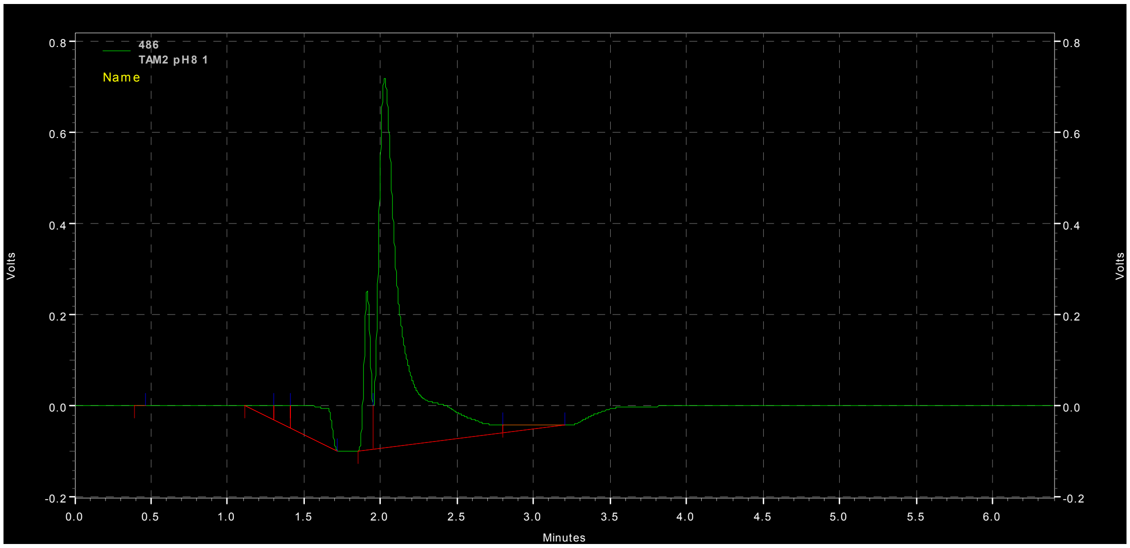


Figure B-3. HPLC chromatogram for TAM-2 pre-equilibrated with pH 8 buffer 100:0.

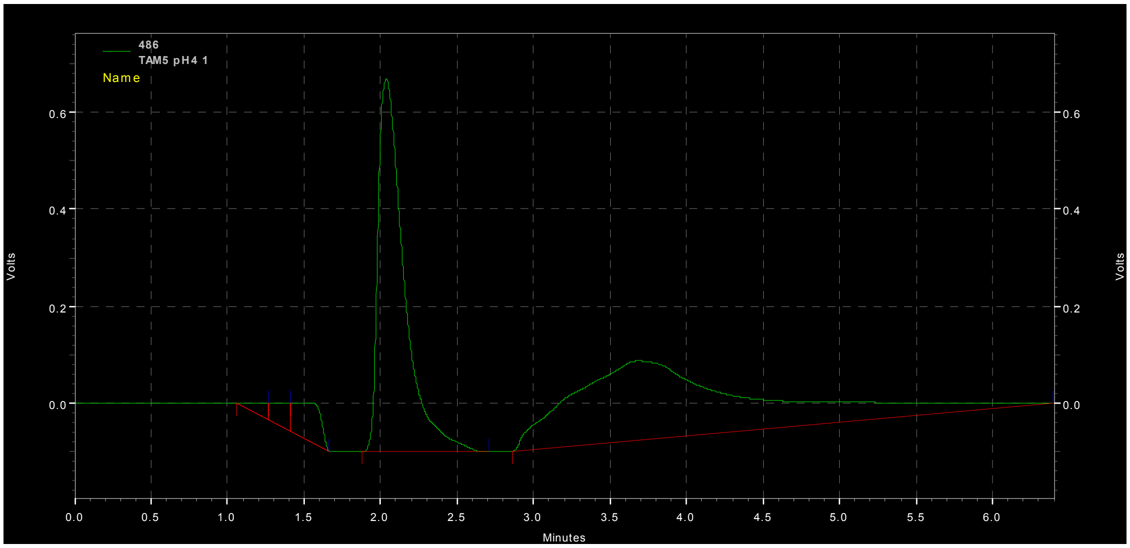


Figure B-4. HPLC chromatogram for TAM-5 pre-equilibrated with pH 8 buffer 100:0.

Table B-1. The area under the curve as reported by the HPLC for the peak around 2.6 min for CAM-2. If no value is reported, no measurement was taken.

sample number	1	2	3	average	Std. Dev.
100:0	17944	18177		18061	165
50:50	9029	5720	8259	7669	1732
25:75	3263	3361	3065	3230	151

Table B-2. The area under the curve as reported by the HPLC for the peak around 3.1 min for CAM-2 pre-equilibrated with pH 8 buffer.

sample number	1	2	3	average	Std. Dev.
100:0	4229	7576	3350	5052	2230
50:50	1538	1291	1761	1530	235
25:75	2366	1590	2006	1987	388

Table B-3. The area under the curve as reported by the HPLC for the peak around 2.9 min for TAM-2 pre-equilibrated with pH 8 buffer.

sample number	1	2	3	average	Std. Dev.
100:0	3352	1978	3421	2917	814
50:50	3521	1031	3778	2777	1517
25:75	4018	5178	3398	4198	904

Table B-4. The area under the curve as reported by the HPLC for the peak around 3.2 min for TAM-5 pre-equilibrated with pH 4 buffer.

sample number	1	2	3	average	Std. Dev.
100:0	13290357	11141551	13337375	12589761	1254407
50:50	11019058	9255758	9082722	9785846	1071492
25:75	5722924	6652402	5958078	6111135	483272

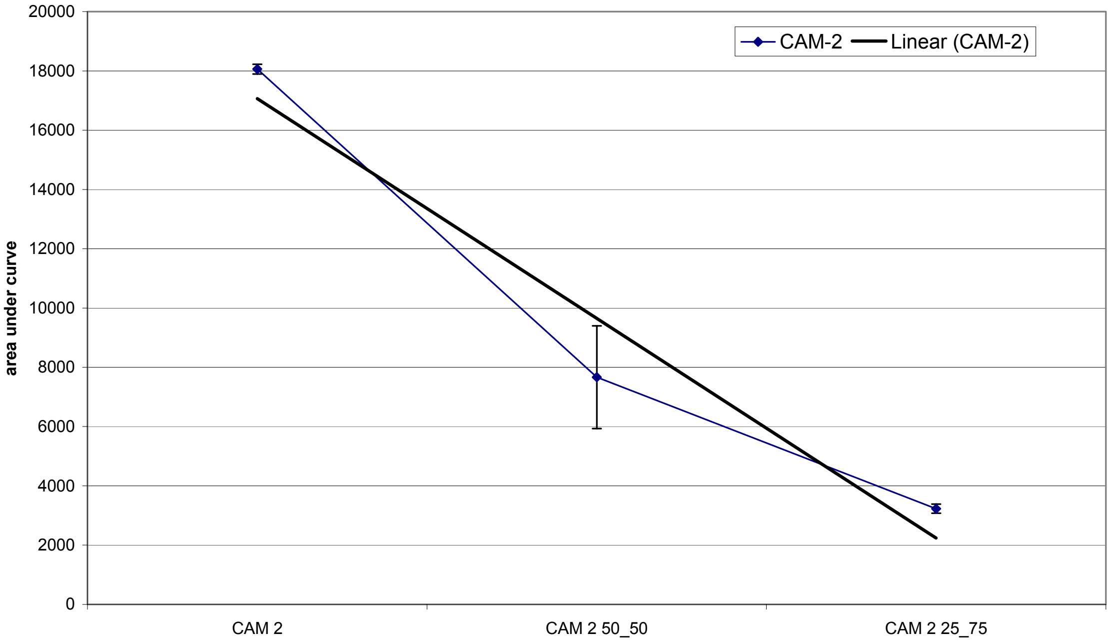


Figure B-5. Concentration graph for CAM-2 using the area under the curve from the HPLC.

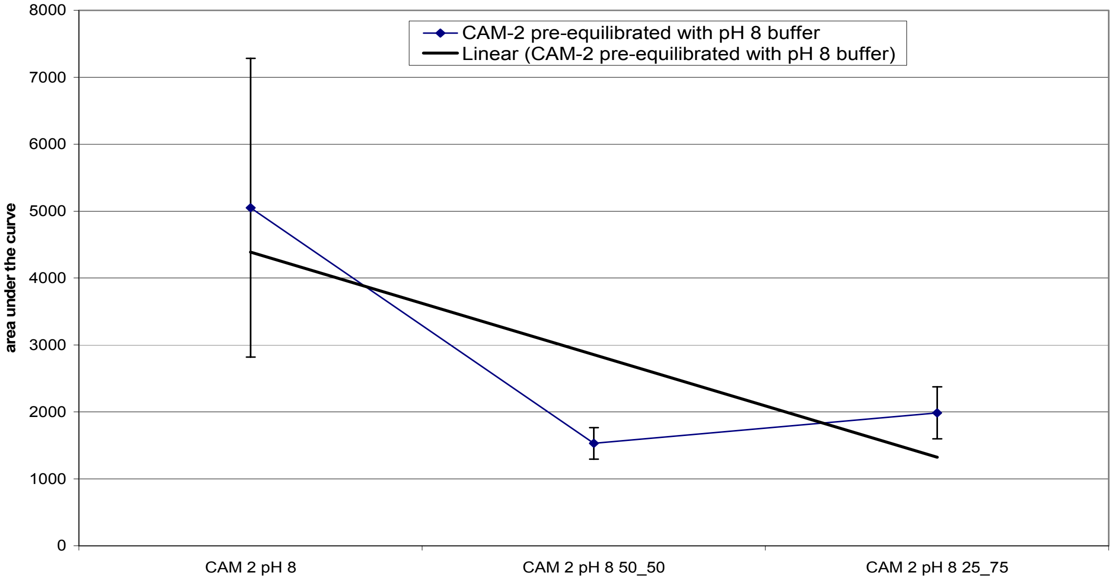


Figure B-6. Concentration graph for CAM-2 using the area under the curve from the HPLC.

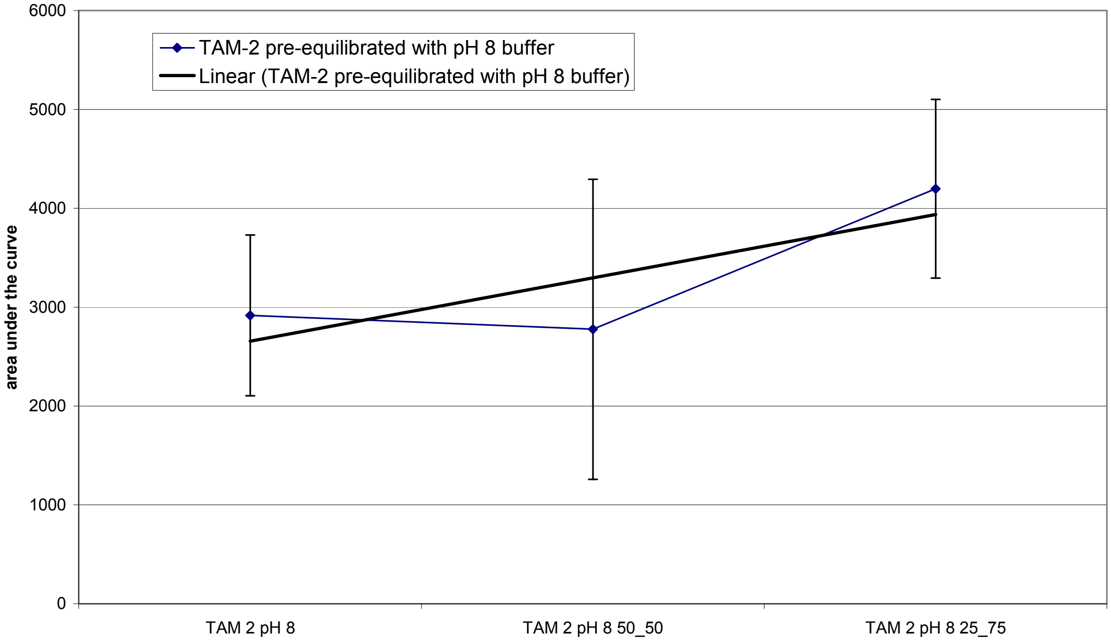


Figure B-7. Concentration graph for TAM-2 pre-equilibrated with pH 8 buffer using the area under the curve from the HPLC.

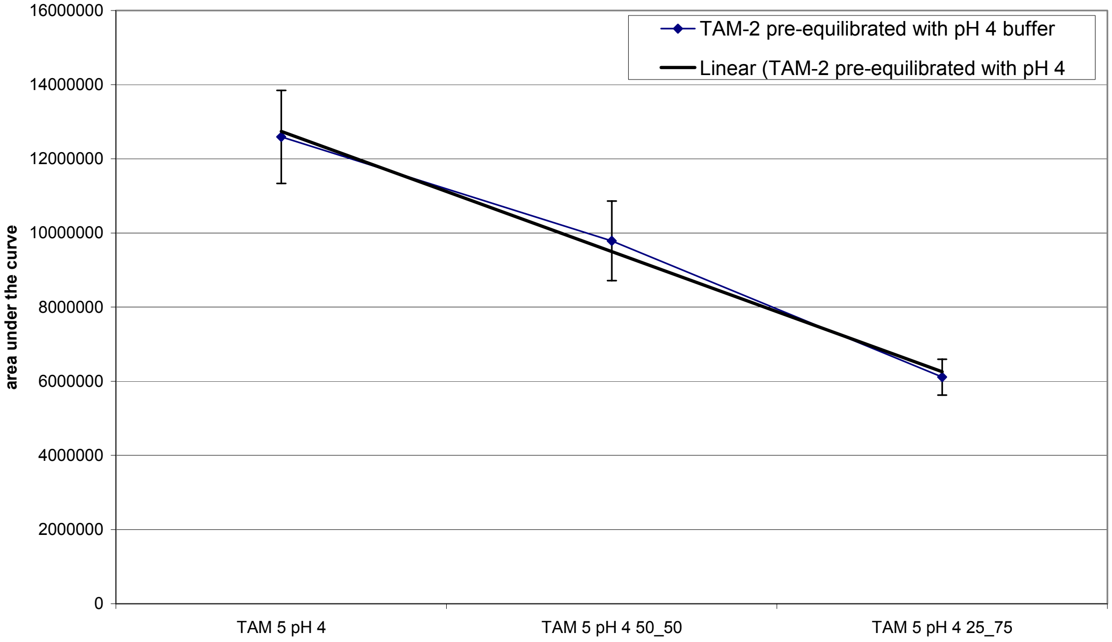


Figure B-8. Concentration graph for TAM-5 pre-equilibrated with pH 4 buffer using the area under the curve from the HPLC.

Appendix C : Surface tension data for pre-equilibrated fluids.

C.1 Methods

The surface tension was measured for some pre-equilibrated solutions. A surfactant/decane solution was pre-equilibrated with an aqueous fluid as mentioned in the Methods section. The surface tensions of the pre-equilibrated aqueous fluids were then measured using the DCA-312 Cahn Dynamic Contact Angle Analyzer using the duNouy Ring method. The ring used was a Platinum-Iridium Ring (Fisher Scientific) with a mean circumference of 5.925 cm. The Cahn Dynamic Contact Angle Analyzer would measure the force to detach the ring from the surface of a liquid. The surface tension was determined by the following formula:

$$\text{Surface tension (dynes/cm)} = \frac{(F * 0.981)}{P}$$

Where F = force determined by the balance (mg)

P = Perimeter of the sample at the interface = 11.85 cm

0.981 = conversion factor from mg to dynes

The Cahn Dynamic Contact Angle Analyzer was always calibrated with a 500 mg weight before any measurements were taken for the day. Before and after any measurements the ring was placed in a flame for 5 seconds to burn off any impurities.

C.2 Results

Table C-1 shows the results of the surface tensions of aqueous solutions pre-equilibrated with CAM-2, TAM-2 or TAM-5. The surface tension was lower for the pre-equilibrated solution than for the pure aqueous solutions. The presence of a surfactant tends to reduce the surface tension of an interface.

Table C-1. The surface tension of aqueous solutions pre-equilibrated with CAM-2, TAM-2, or TAM-5. The bold values were obtained from Dean (1999).

solution	Surface tension (dynes/cm)
Brine pH 4	**74**
Brine pH 4/CAM-2	32
Brine pH 4/TAM-2	34
Brine pH 4/TAM-5	41
Brine pH 8	**76**
Brine pH 8/CAM 2	34
Brine pH 8/TAM-5	34
Water	**72**
Water/CAM-2	32

For Appendices D-M all of the graphs indicate the fluid the contact angle was measured in. If the fluid the contact angle was measured in was decane, then the drop was an aqueous fluid (pH 4 buffer, double distilled water, pH 8 buffer). If the contact angle was measured in an aqueous fluid, the drop was decane. The solutions indicated as surfactant/aqueous solutions means the aqueous solution has been pre-equilibrated with the surfactant/decane solution.

Appendix D : The contact angle results for CAM-2, TAM-2, or TAM-5 pre-equilibrated (both fluids).

The mica was

- treated with CAM-2, TAM-2, or TAM-5 solutions (all solutions were pre-equilibrated
- washed with one of the following
    - toluene
    - hexane
    - acetone
    - acetone then water
    - acetone then pH 8 buffer
    - acetone then isopropanol
- contact angles measured with decane or aqueous solution (all solutions were pre-equilibrated with an aqueous solution)

Figures D-1, D-2, and D-3 show the contact angle results for CAM-2, TAM-2, or TAM-5 that have been pre-equilibrated with pH 4 buffer, double distilled water, and pH 8 buffer, respectively. For any given treatment of the mica, it was noticed that the contact angle depended on what the aqueous solution the surfactant had been pre-equilibrated with. The greater the pH the surfactant was pre-equilibrated with the greater the contact angle. For example, for mica that was treated with TAM-2 and washed with toluene and then measured in decane, the mica was oil-wet ($\theta_a \sim 155°$) when the TAM-2/decane solution had been pre-equilibrated with pH 4 buffer and intermediate-wet ($\theta_a \sim 85°$) when pre-equilibrated with pH 8 buffer. This can be attributed to the pK_a of the surfactants. At low pH, the surfactant is protonated, while at high pH's the surfactant is less protonated and therefore is less attracted to the negative mica surface.

It was noted earlier that the pre-equilibration of the solutions did not appear to affect the results of the contact angles. This was for the comparison of pre-equilibrated and non pre-equilibrated solutions for a given aqueous solution. For example, if a solution was pre-equilibrated with pH 4 buffer the non pre-equilibrated solutions gave approximately the same results. Here, it was pointed out there is a difference the contact angles of the pre-equilibrated solutions of different aqueous solutions. For example, if a solution was pre-equilibrated with pH 4 buffer and another was pre-equilibrated with pH 8 buffer, there was a difference in the contact angle results.

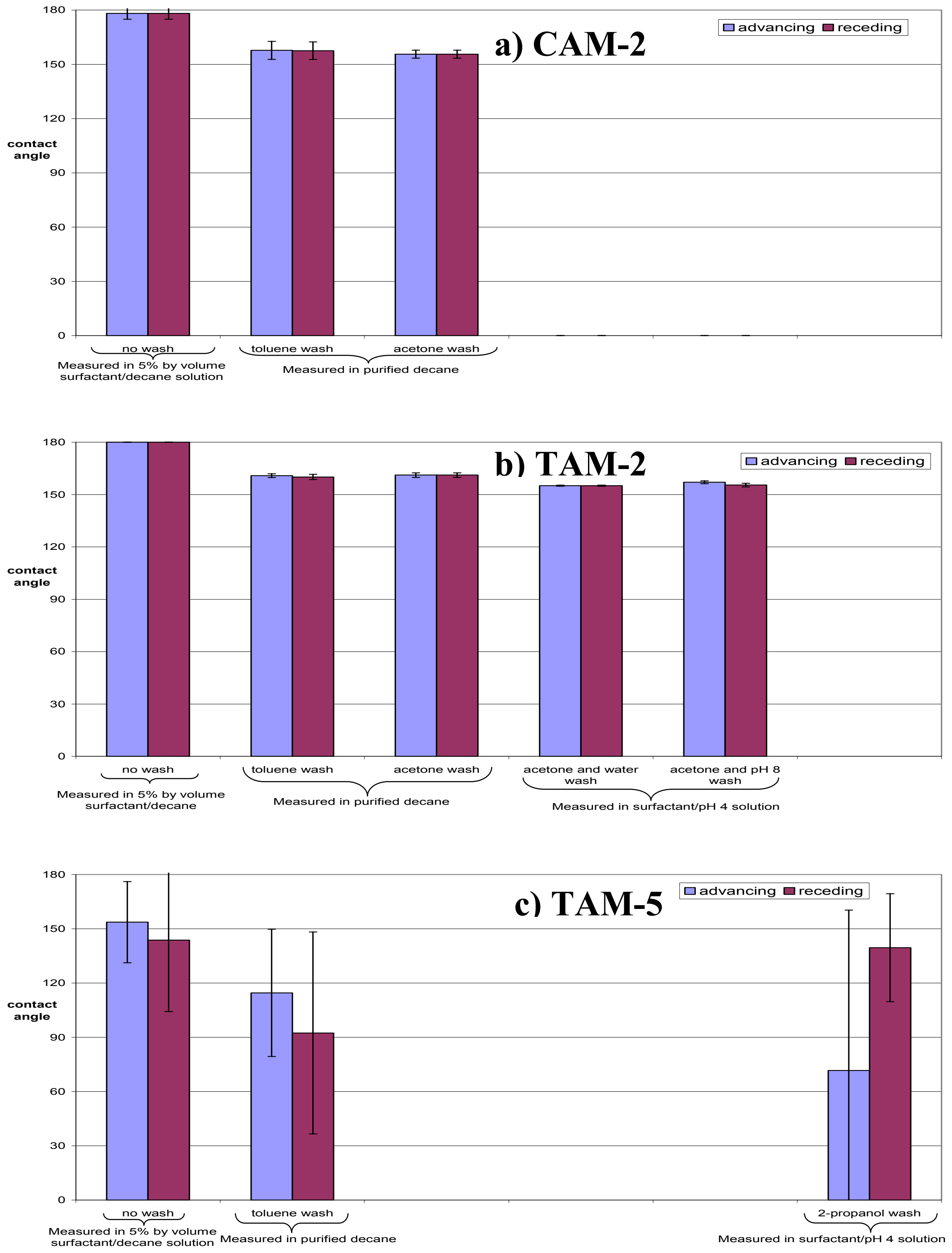


Figure D-1. Contact angle measurements for a) CAM-2 b) TAM-2 and c) TAM-5 pre-equilibrated with pH 4 buffer.

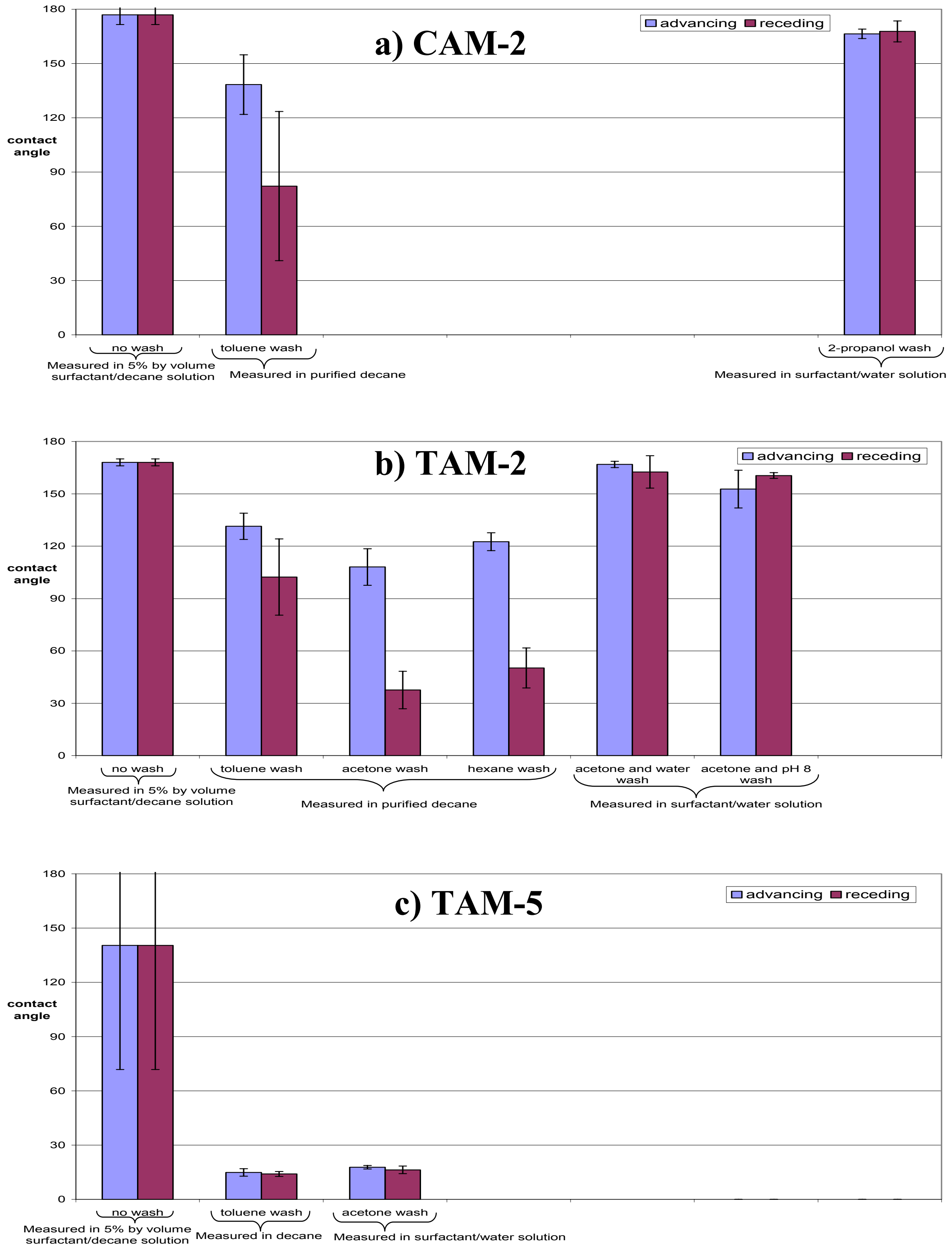


Figure D-2. Contact angle results for a) CAM-2 b) TAM-2 and c) TAM-5 for pre-equilibration with water (water has been pre-equilibrated with surfactant).

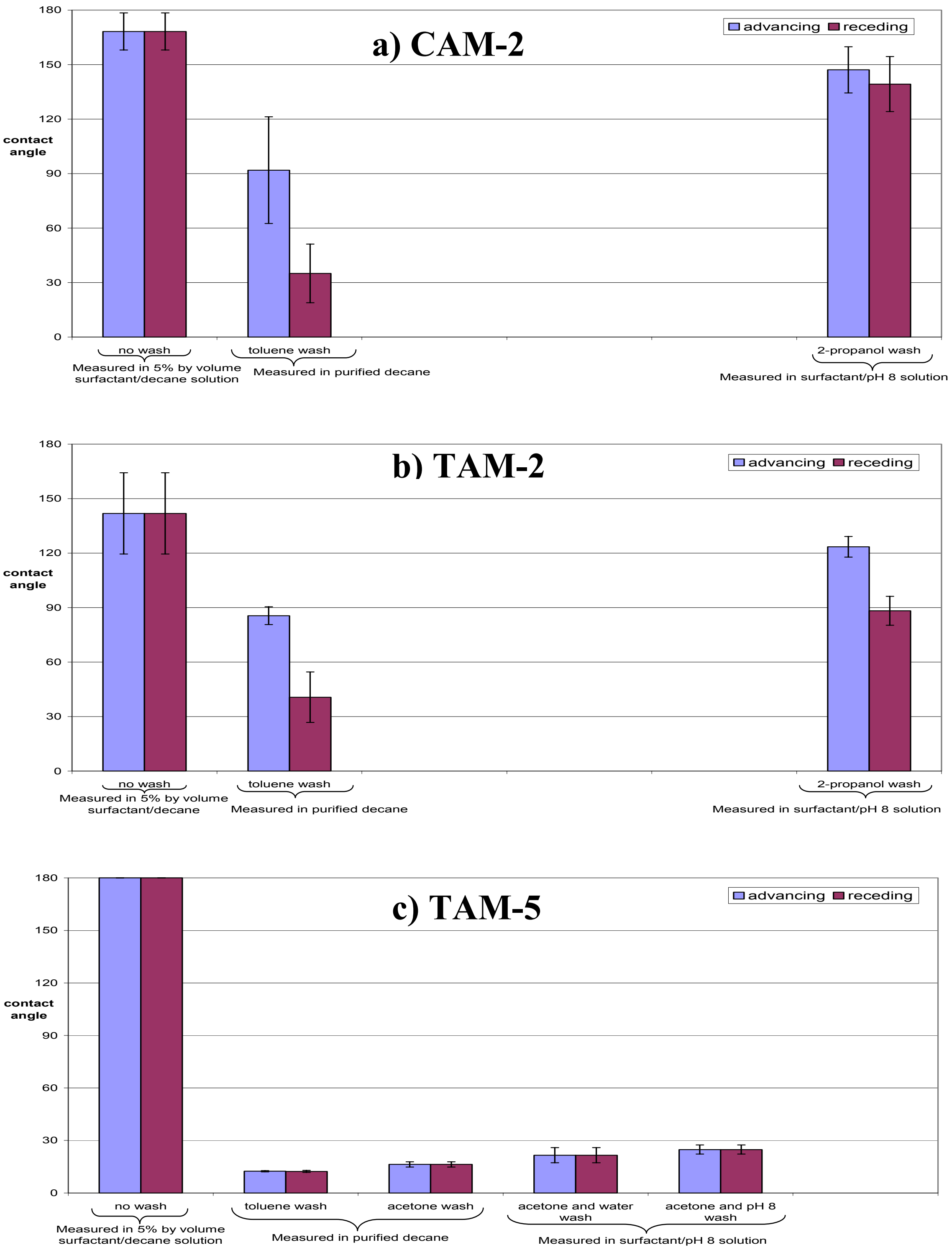


Figure D-3. Contact angle measurements for a) CAM-2 b) TAM-2 and c) TAM-5 pre-equilibrated with pH 8 buffer.

Appendix E : The contact angle results for CAM-2, TAM-2, or TAM-5 for pre-equilibration (decane only).

Mica was

- treated with CAM-2, TAM-2, or TAM-5 solutions in decane (decane was pre-equilibrated with an aqueous solution while the aqueous solutions (pH 4 buffer, double distilled water, or pH 8 buffer) used were not pre-equilibrated with decane)
- washed with one of the following
    - toluene
    - acetone
    - hexane
    - acetone then water
    - acetone then pH 8 buffer
    - acetone then pH 10 buffer
    - acetone then isopropanol
- contact angles were measured with decane (pre-equilibrated with pH 4 buffer, double distilled water, or pH 8 buffer) or an aqueous solution

Figures E-1, E-2, and E-3 show the contact angle measurements for CAM-2, TAM-2, or TAM-5 after only the decane solution had been pre-equilibrated with pH 4 buffer, water, and pH 8 buffer, respectively. The contact angles tended to be lower when measured in decane which was independent of which solvent the mica was passed through then when the contact angle was measured in the aqueous solution (pH 4 buffer, water, or pH 8 buffer). This was due to the greater solubility of the surfactant in decane than in water.

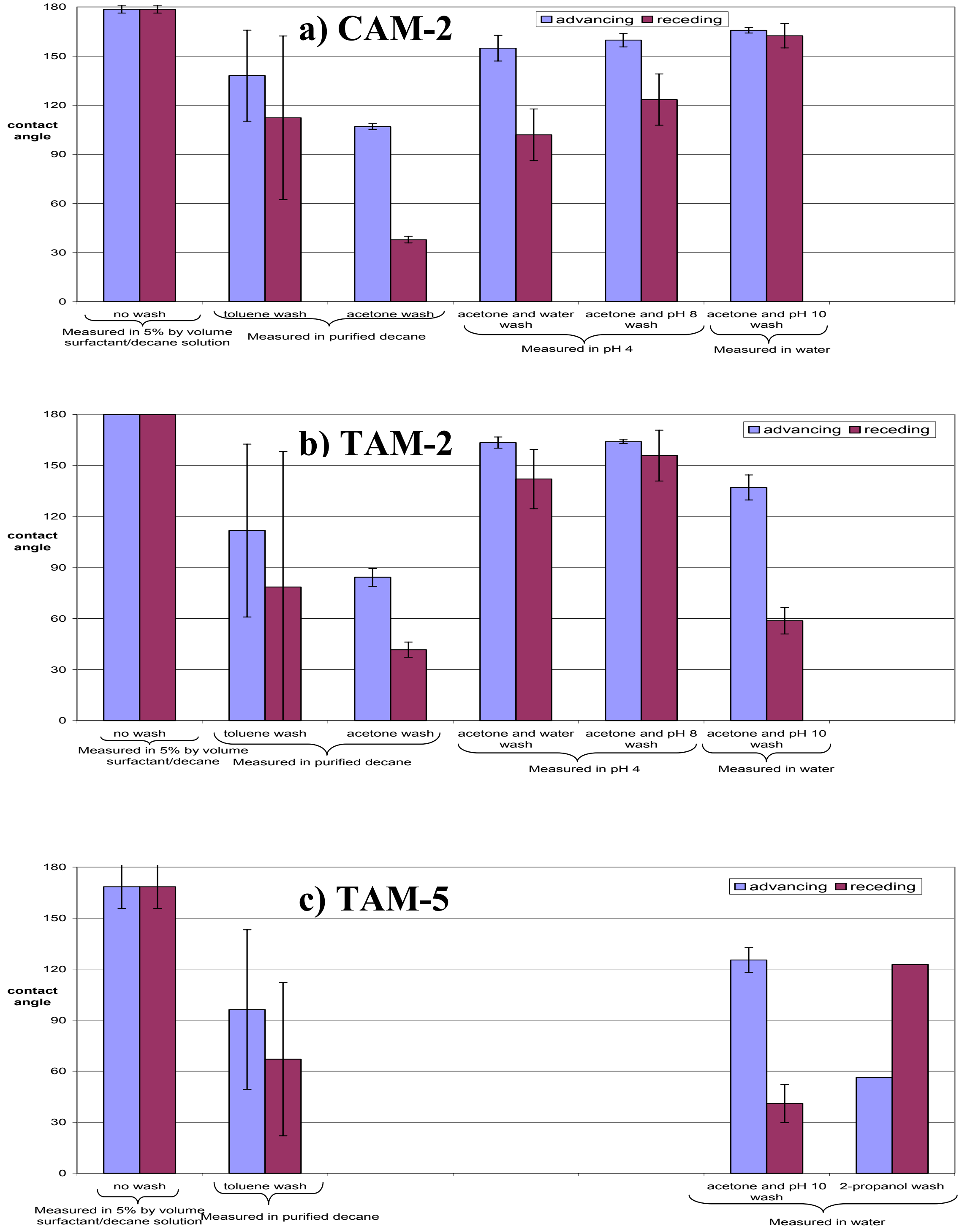


Figure E-1. Contact angle measurements for a) CAM-2 b) TAM-2 and c) TAM-5 pre-equilibrated with pH 4 buffer (decane only).

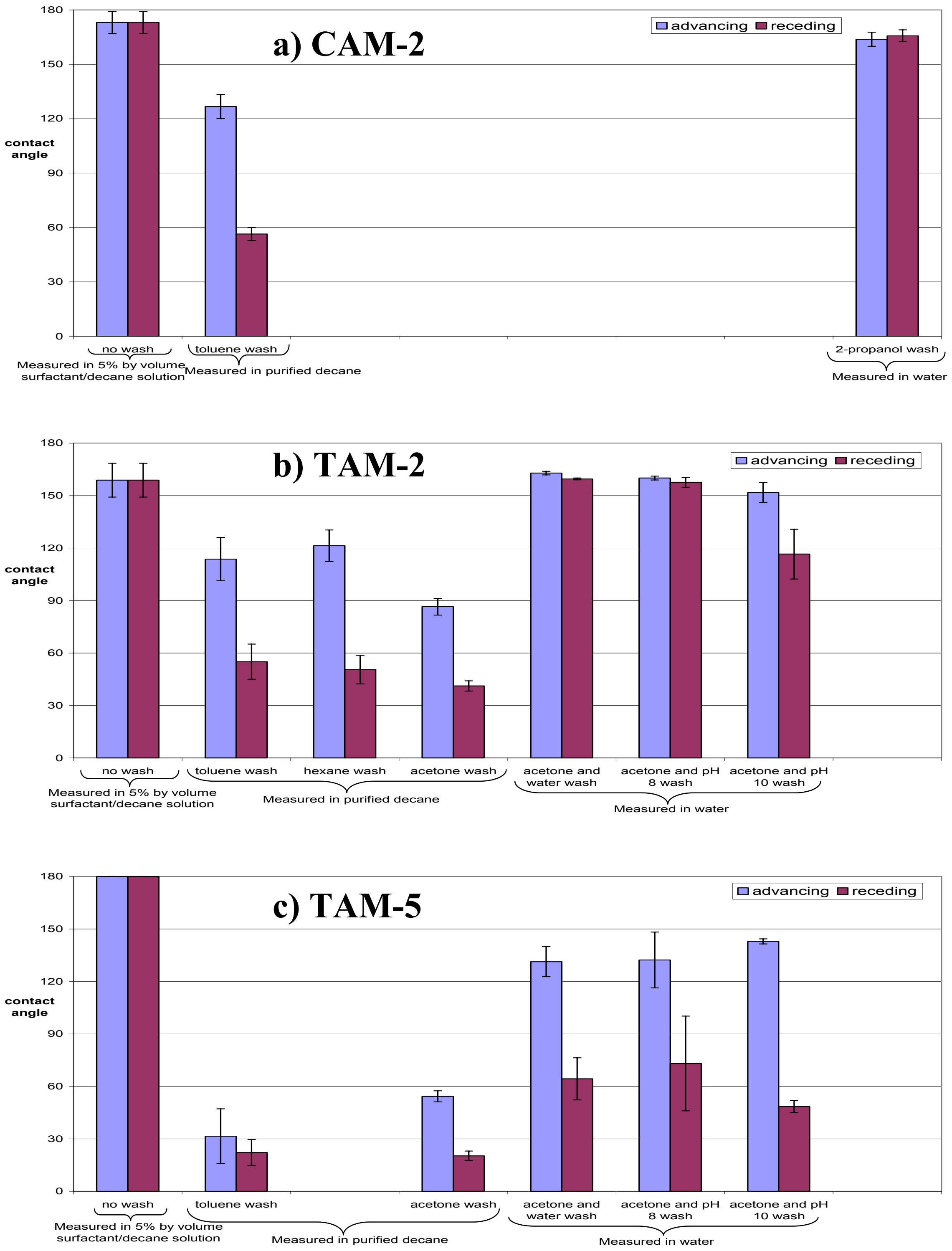


Figure E-2. Contact angle measurements for a) CAM-2 b) TAM-2 c) TAM-5 pre-equilibrated with water (decane only).

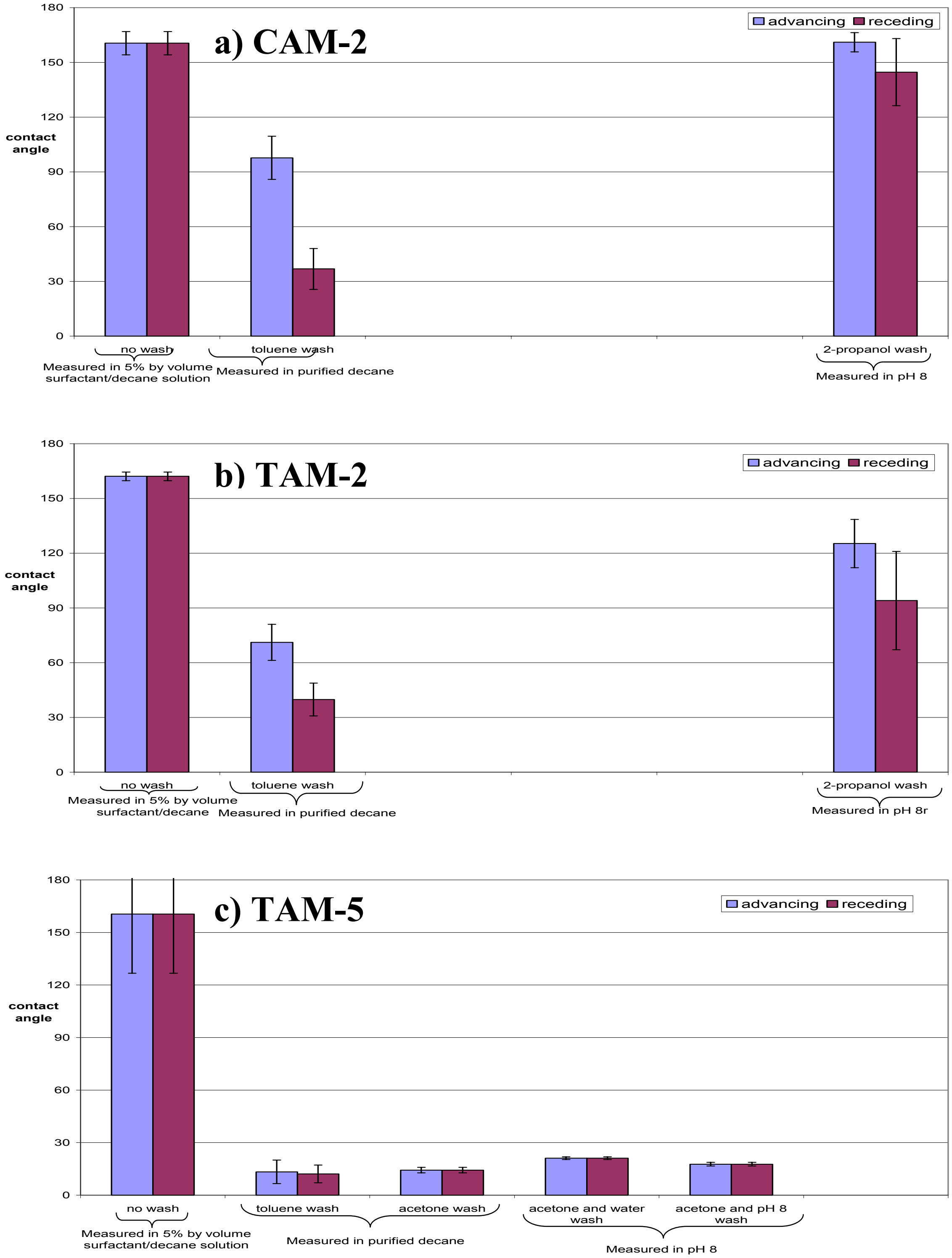


Figure E-3. Contact angle measurements for a) CAM-2 b) TAM-2 and c) TAM-5 pre-equilibrated with pH 8 buffer (decane only).

Appendix F : Contact angles after mica was treated with CAM-2, TAM-2, or TAM-5 then washed/soaked in solvents

Mica was

- treated with CAM-2, TAM-2 or TAM-5 solution in decane
- washed/soaked with one of the following
    - toluene
    - hexane
    - acetone
    - acetone then isopropanol (soaked in isopropanol)
    - acetone then water (soaked in water)
    - acetone then pH 10 (soaked in pH 10 buffer)
- contact angle was measured with decane or an aqueous solution

Mica was treated with CAM-2, TAM-2 or TAM-5 for 40-70 min then washed with a solvent (or series of solvents) and soaked in the solvent (or final solvent) for about 60 min or 24 hours. The contact angles were then measured.

Figures F-1 – F-7 show the contact angles after mica was treated with CAM-2, TAM-2, and TAM-5 and washed and soaked in toluene, hexane, acetone, isopropanol, acetone and water, acetone then pH 8 buffer, or acetone then pH 10 buffer, respectively. The were no significant changes in the contact angle when the mica was soaked for 60 min or 24 hours therefore it was concluded that soaking the mica in the solvent does not remove more surfactant from the mica surface.

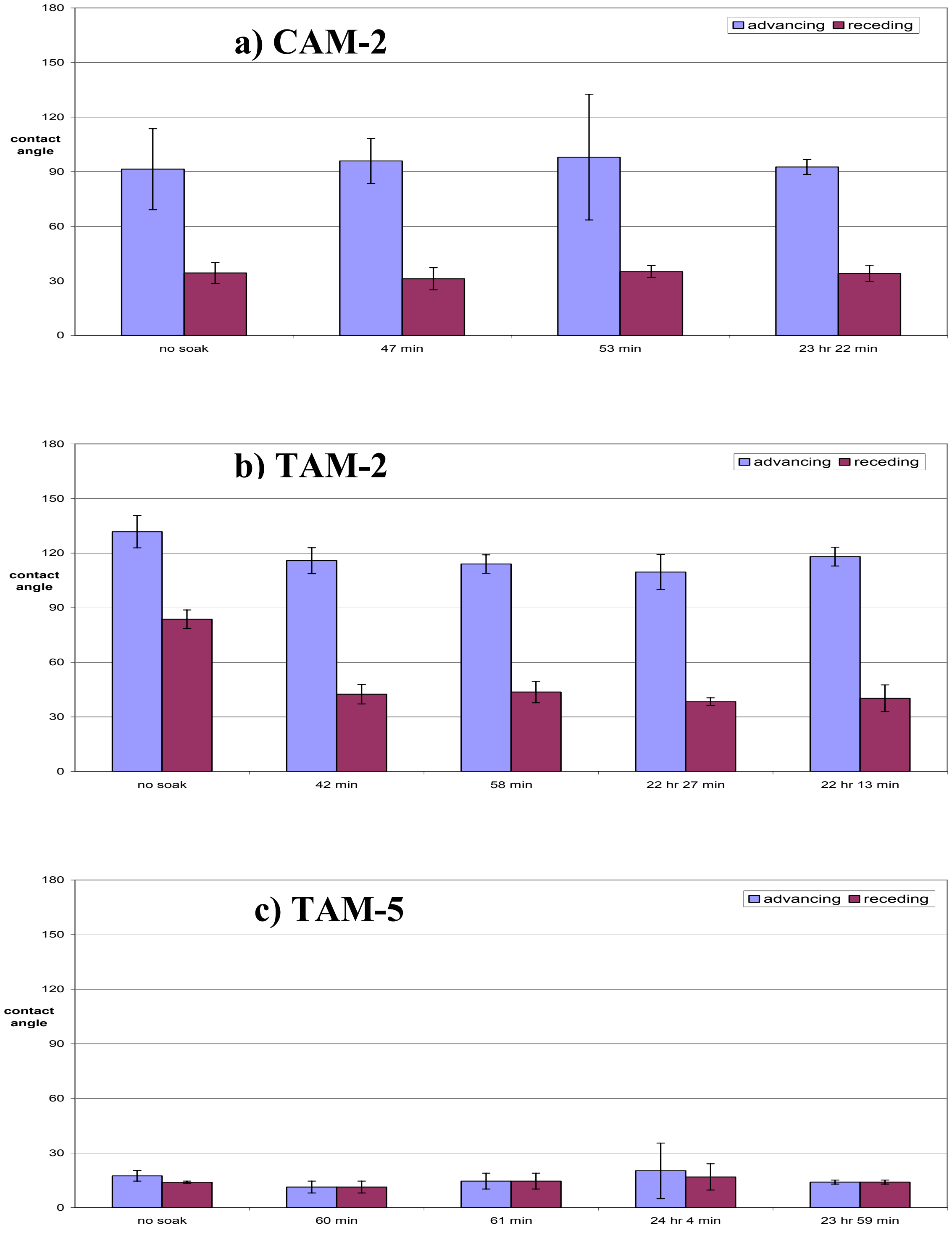


Figure F-1. Contact angle measurements for a) CAM-2 b) TAM-2 and c) TAM-5, washed/soaked in toluene, measured in decane (water drop).

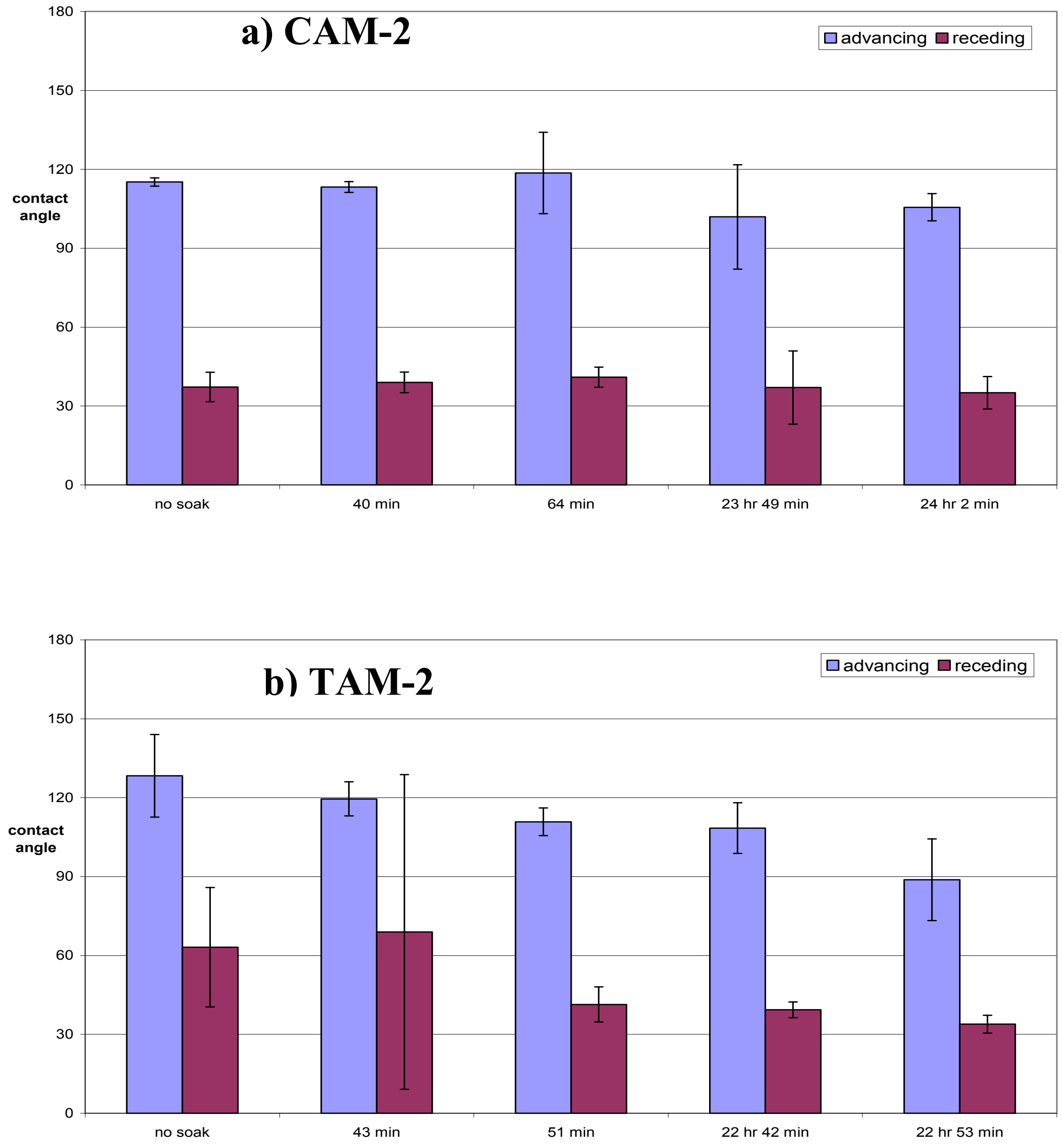


Figure F-2. Contact angle measurements for a) CAM-2 and b) TAM-2, washed/soaked in hexane, measured in decane (water drop).

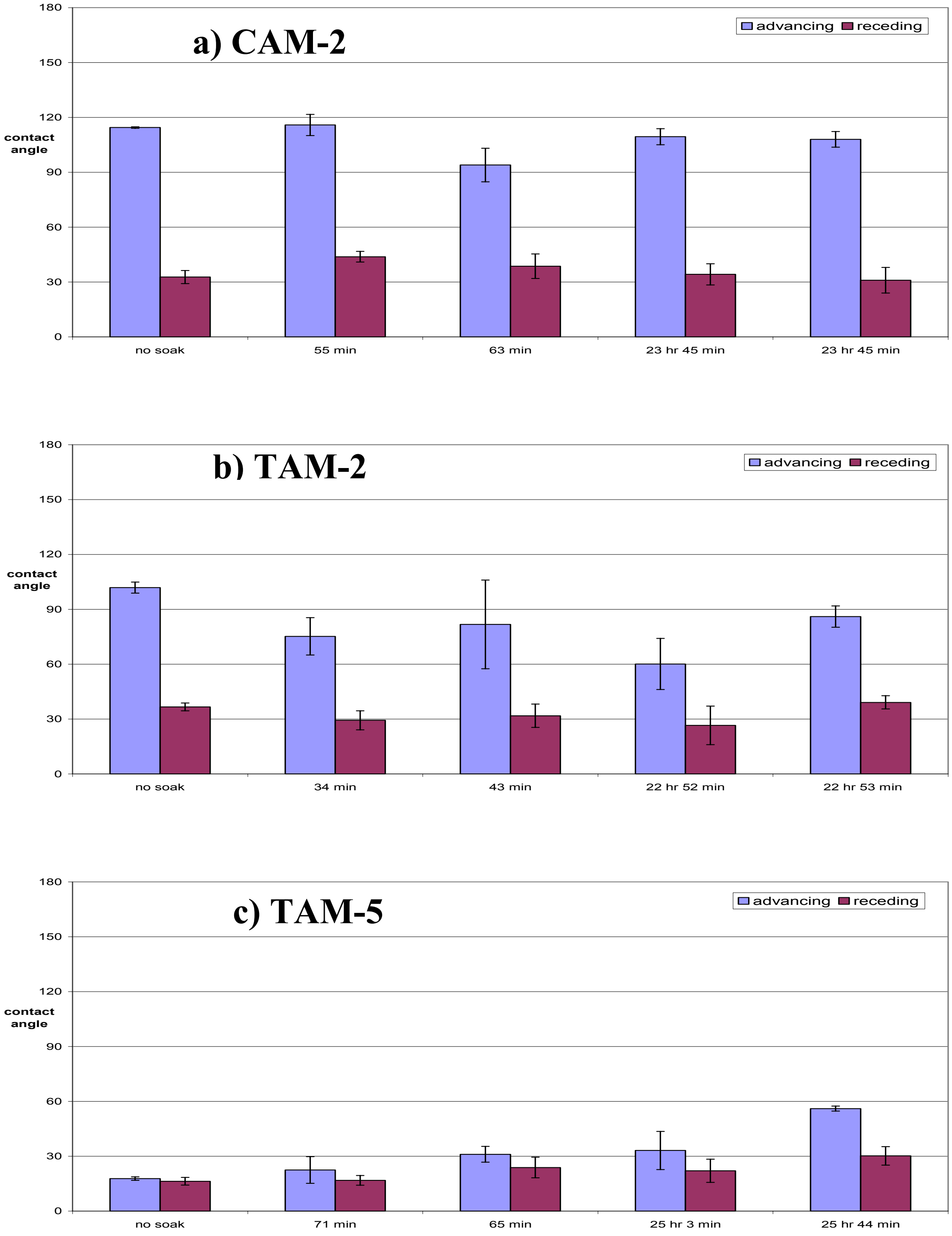


Figure F-3. Contact angle measurements for a) CAM-2 b) TAM-2 and c) TAM-5, washed/soaked in acetone, measured in decane (water drop).

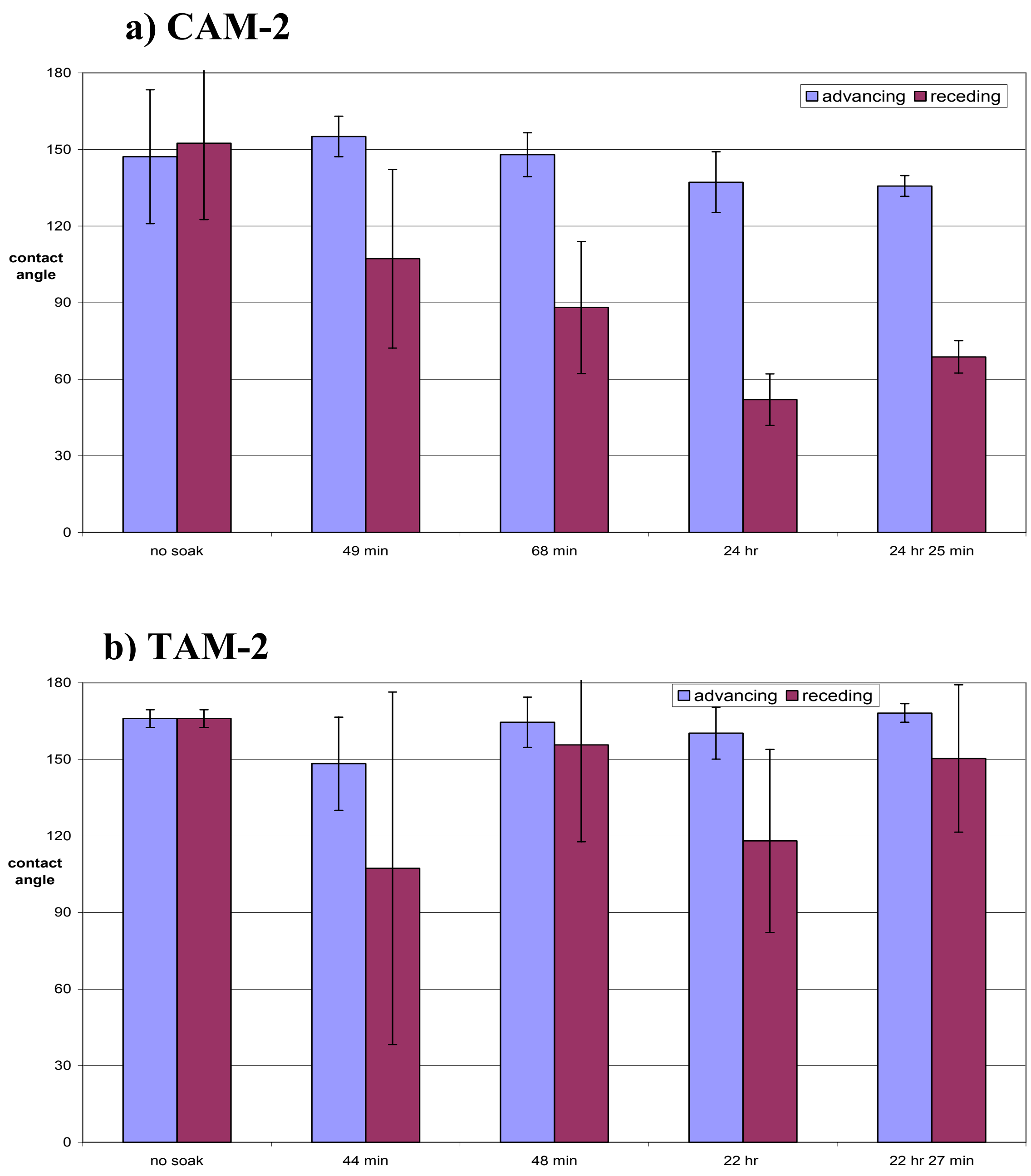
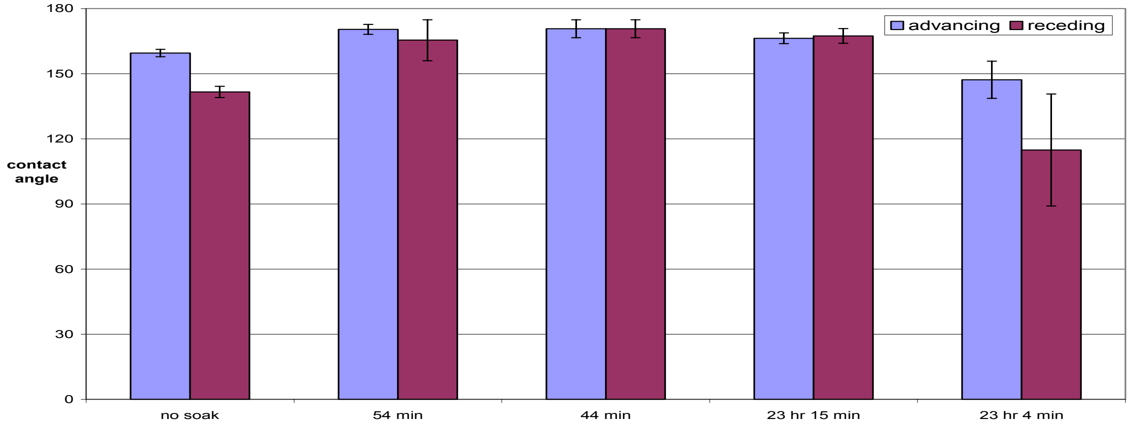
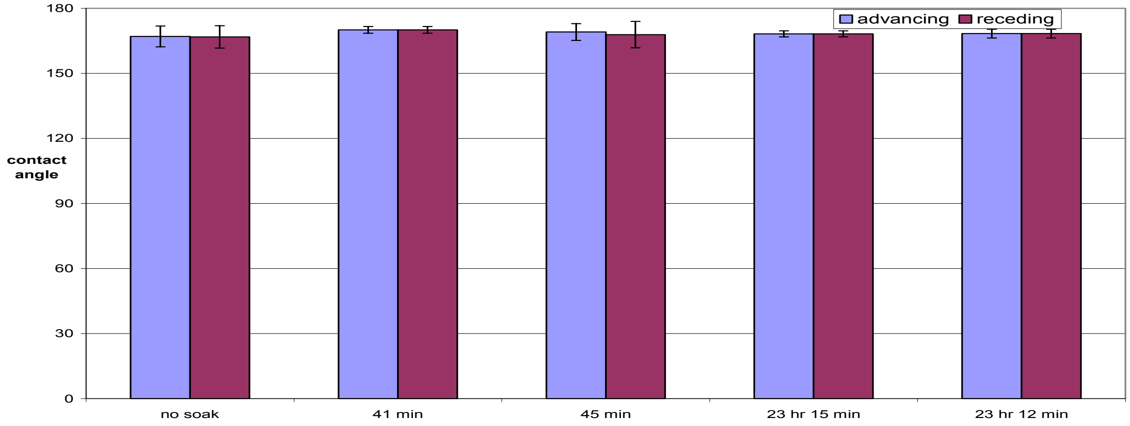


Figure F-4. Contact angle measurements for a) CAM-2 and b) TAM-2, washed/soaked in isopropanol, measured in water (decane drop).

a) CAM-2



b) TAM-2



c) TAM-5

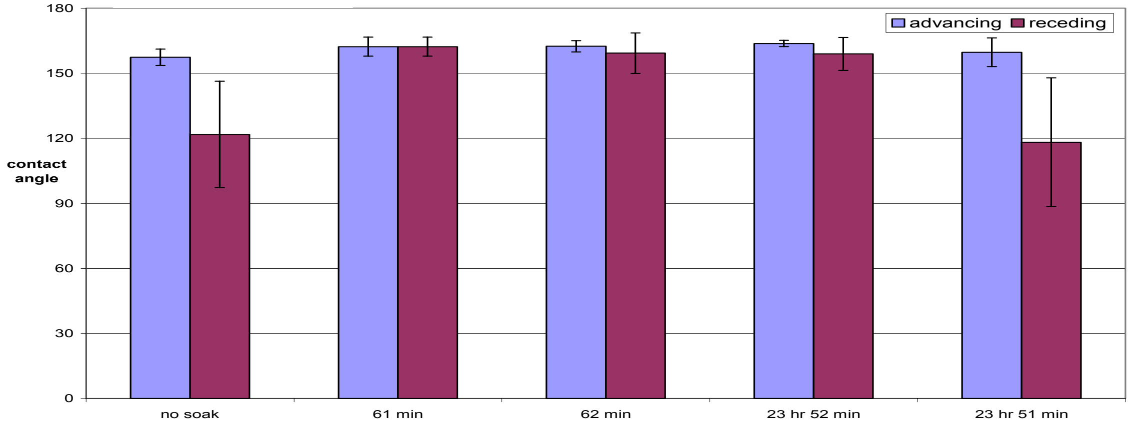


Figure F-5. Contact angle measurements for a) CAM-2 b) TAM-2 and c) TAM-5, washed in acetone and water, washed/soaked in water measured in water (decane drop).

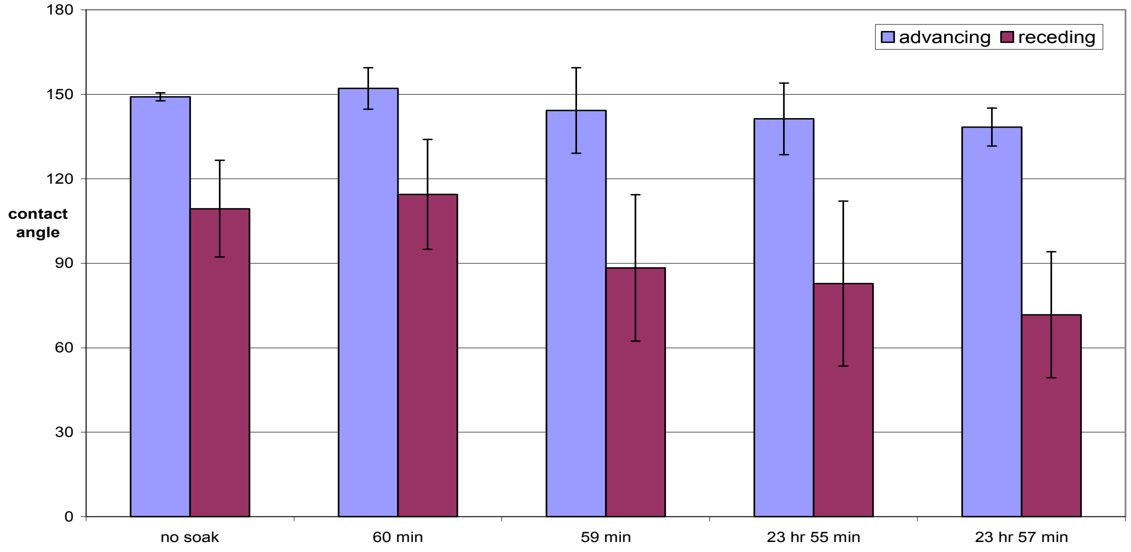


Figure F-6. Contact angle measurements for TAM-5 washed in acetone and pH 8 buffer, washed/soaked in pH 8 buffer, measured in water (decane drop).

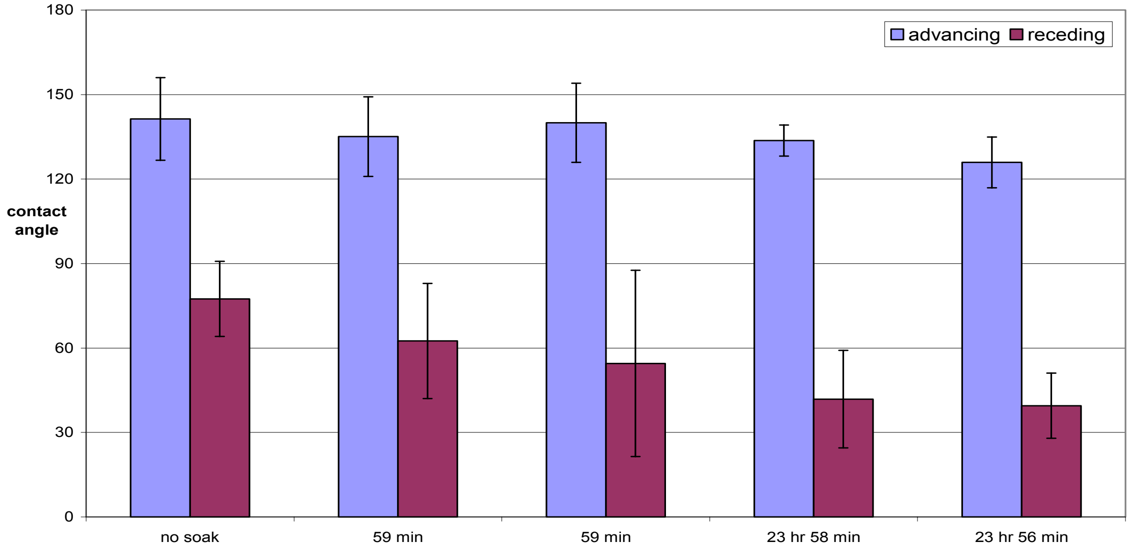


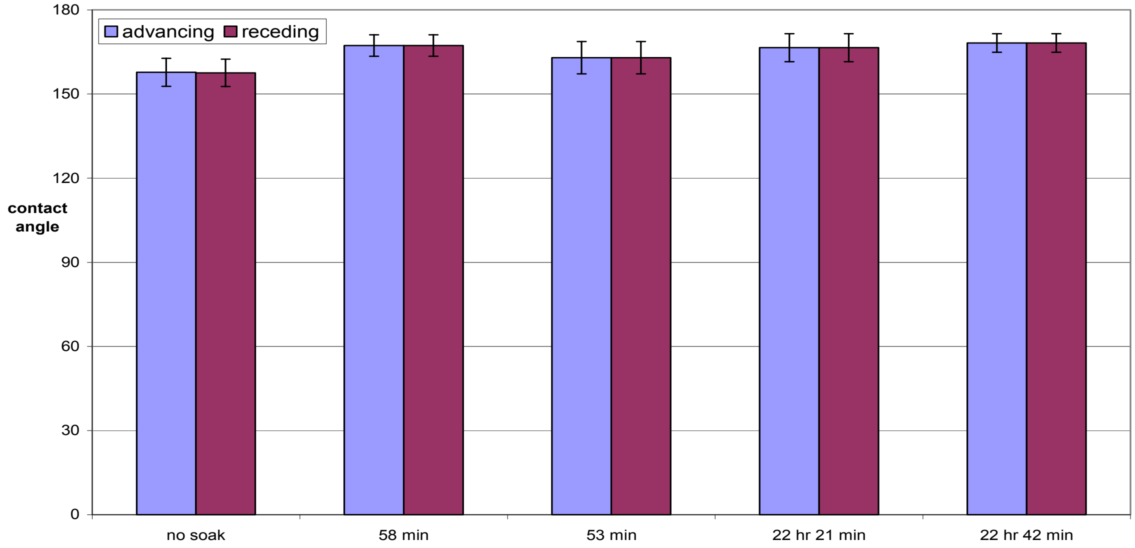
Figure F-7. Contact angle measurements for TAM-5, washed in acetone and pH 10 buffer soaked in pH 10 buffer, measured in water (decane drop).

Appendix G : Contact angles results for CAM-2, TAM-2, or TAM-5 pre-equilibrated with pH 4 buffer (both phases) then washed/soaked in various solutions.

Mica was

- treated with CAM-2, TAM-2, or TAM-5 solutions in decane pre-equilibrated with pH 4 buffer.
- washed/soaked with one of the following
    - toluene
    - acetone
    - acetone then water (soaked in water)
    - acetone then pH 8 buffer (soaked in pH 8 buffer)
    - acetone then pH 10 buffer (soaked in pH 10 buffer)
- contact angles were measured with decane or pH 4 (all solutions were pre-equilibrated)

Figures G-1 – G-5 show the contact angles for mica that has been treated with CAM-2, TAM-2, or TAM-5 pre-equilibrated with pH 4 buffer and washed and soaked in toluene, acetone, acetone then water, acetone then pH 8 buffer, or acetone then pH 10 buffer. There were no significant differences in the contact angles for different exposure times, therefore it was concluded that any surfactant removal occurred quickly.


a) CAM-2

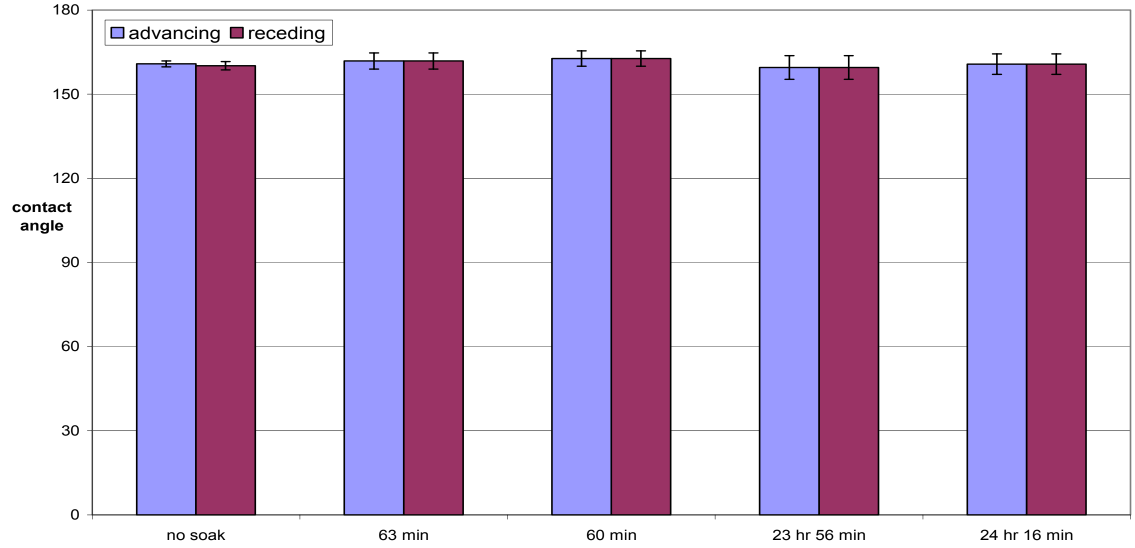
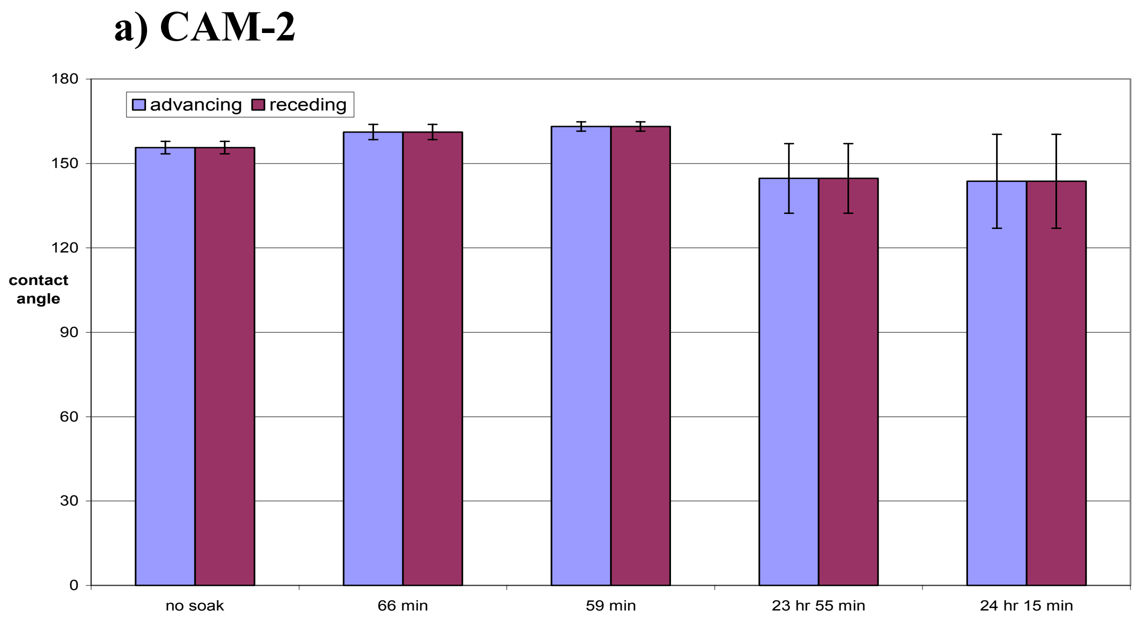

b) TAM-2

Figure G-1. Contact angle measurements for a) CAM-2 and TAM-2 pre-equilibrated with pH 4 buffer, washed/soaked in toluene, measured in decane (pH 4 that has been pre-equilibrated drop).


a) CAM-2

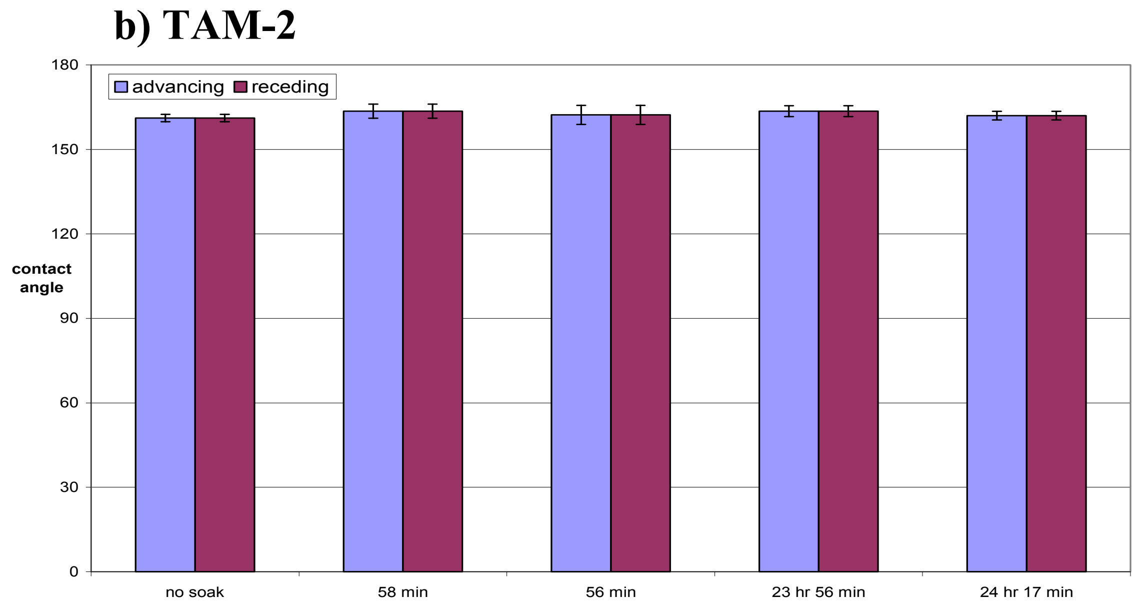

b) TAM-2

Figure G-2. Contact angle measurements for a) CAM-2 and b) TAM-2 pre-equilibrated with pH 4 buffer, washed/soaked in acetone, measured in decane (pH 4 that has been pre-equilibrated drop).

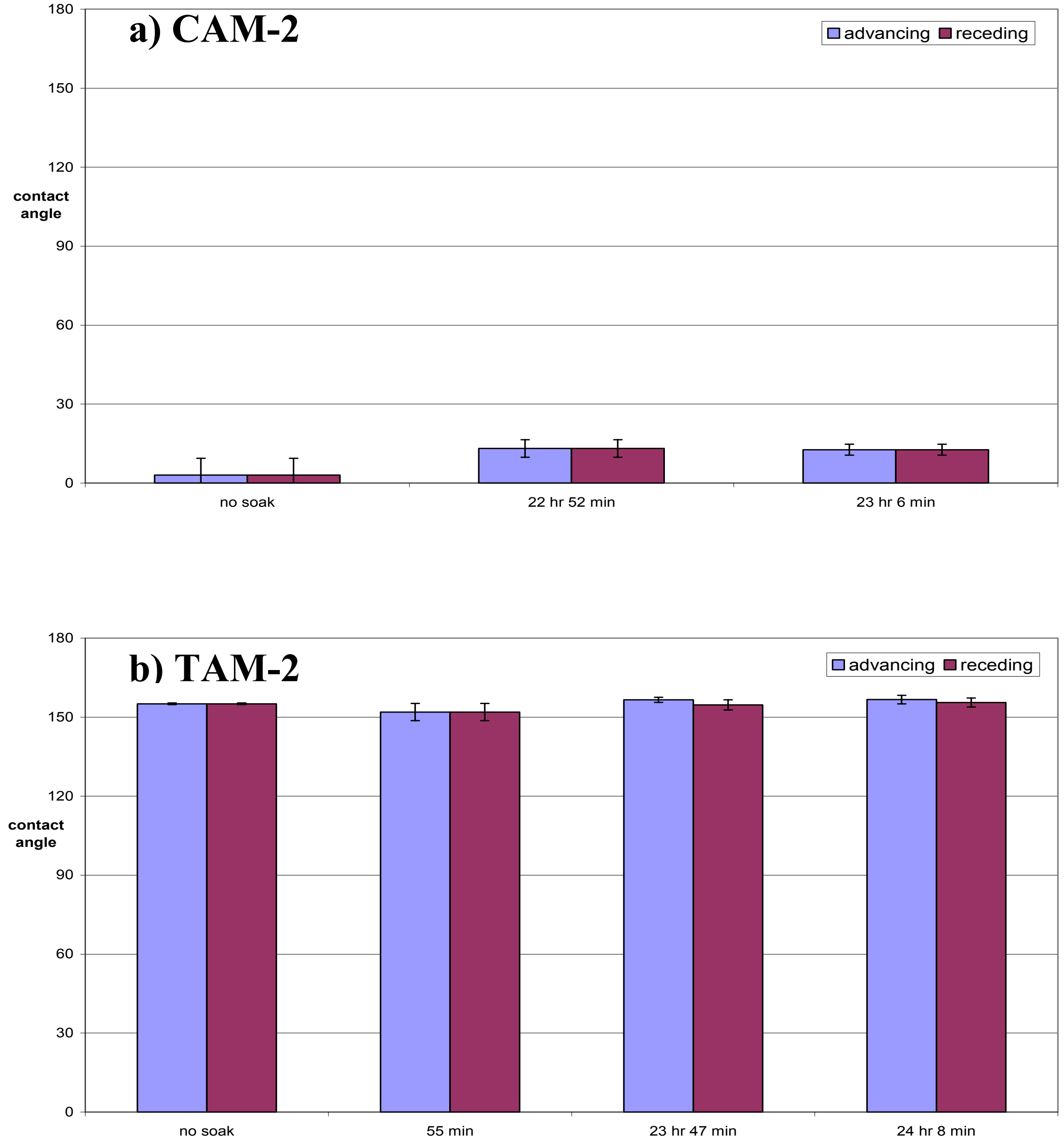


Figure G-3. Contact angle measurements for a) CAM-2 and b) TAM-2 pre-equilibrated with pH 4 buffer, washed with acetone and water (soaked in water), measured in pH 4 buffer that has been pre-equilibrated (decane that has been pre-equilibrated drop).

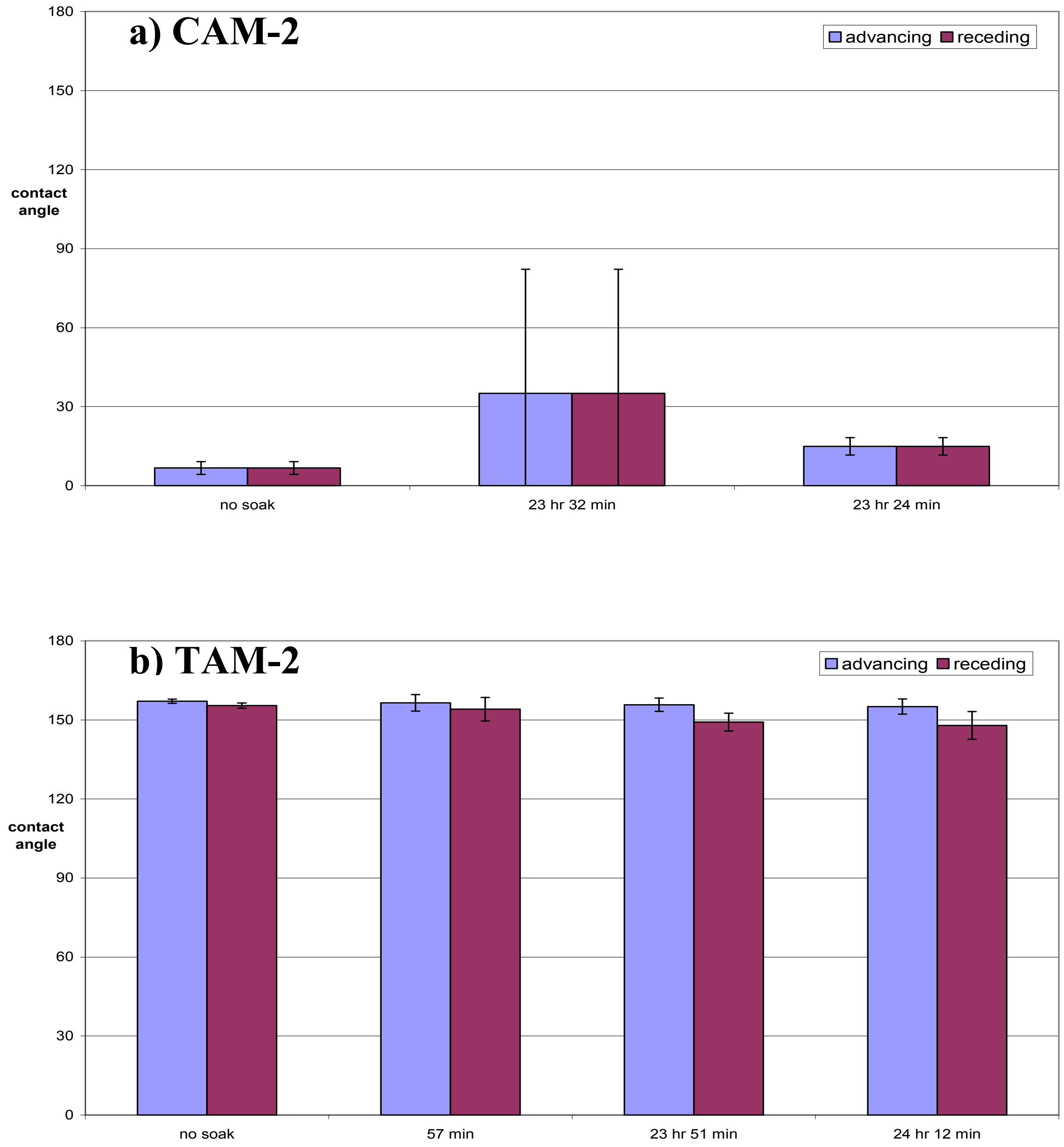


Figure G-4. Contact angle measurements for a) CAM-2 and b) TAM-2 pre-equilibrated with pH 4 buffer, washed with acetone and pH 8 buffer (soaked in pH 8 buffer), measured in pH 4 buffer that has been pre-equilibrated (decane that has been pre-equilibrated drop).

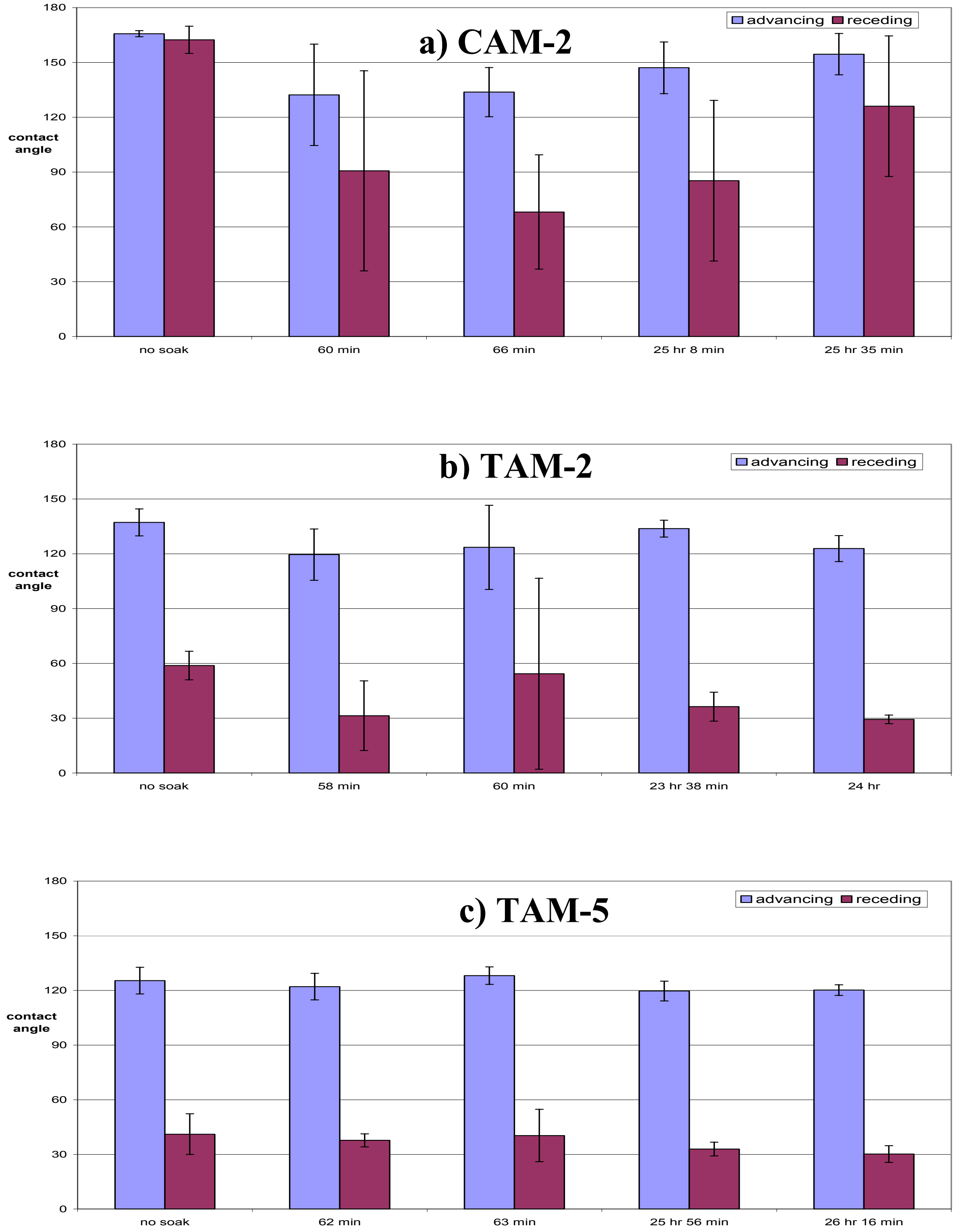


Figure G-5. Contact angle measurements for a) CAM-2 b) TAM-2 c) TAM-5 pre-equilibrated with pH 4 buffer, washed with acetone and pH 10 buffer (soaked in pH 10 buffer), measured in pH 4 buffer that has been pre-equilibrated (decane that has been pre-equilibrated drop).

Appendix H : Contact angle results for CAM-2, TAM-2, or TAM-5 pre-equilibrated with pH 4 buffer (decane only) then washed/soaked in various solutions.

Mica was

- treated with CAM-2, TAM-2, or TAM-5 solutions in decane pre-equilibrated with pH 4 buffer.
- washed/soaked with one of the following
    - toluene
    - acetone
    - acetone and water (soaked in water)
    - acetone and pH 8 buffer (soaked in pH 8 buffer)
- contact angles were measured with decane (pre-equilibrated) or pH 4

Figures H-1 – H-4 show the contact angle measurements for mica that has been treated with CAM-2, TAM-2, or TAM-5 pre-equilibration with pH 4 buffer (decane only) washed/soaked in toluene, acetone, acetone then water, or acetone then pH 8 buffer, respectively. The contact angles all fall within the error bars of each other therefore it was concluded that the time the mica soaked in the solvents did not impact how much surfactant was removed from the surface.

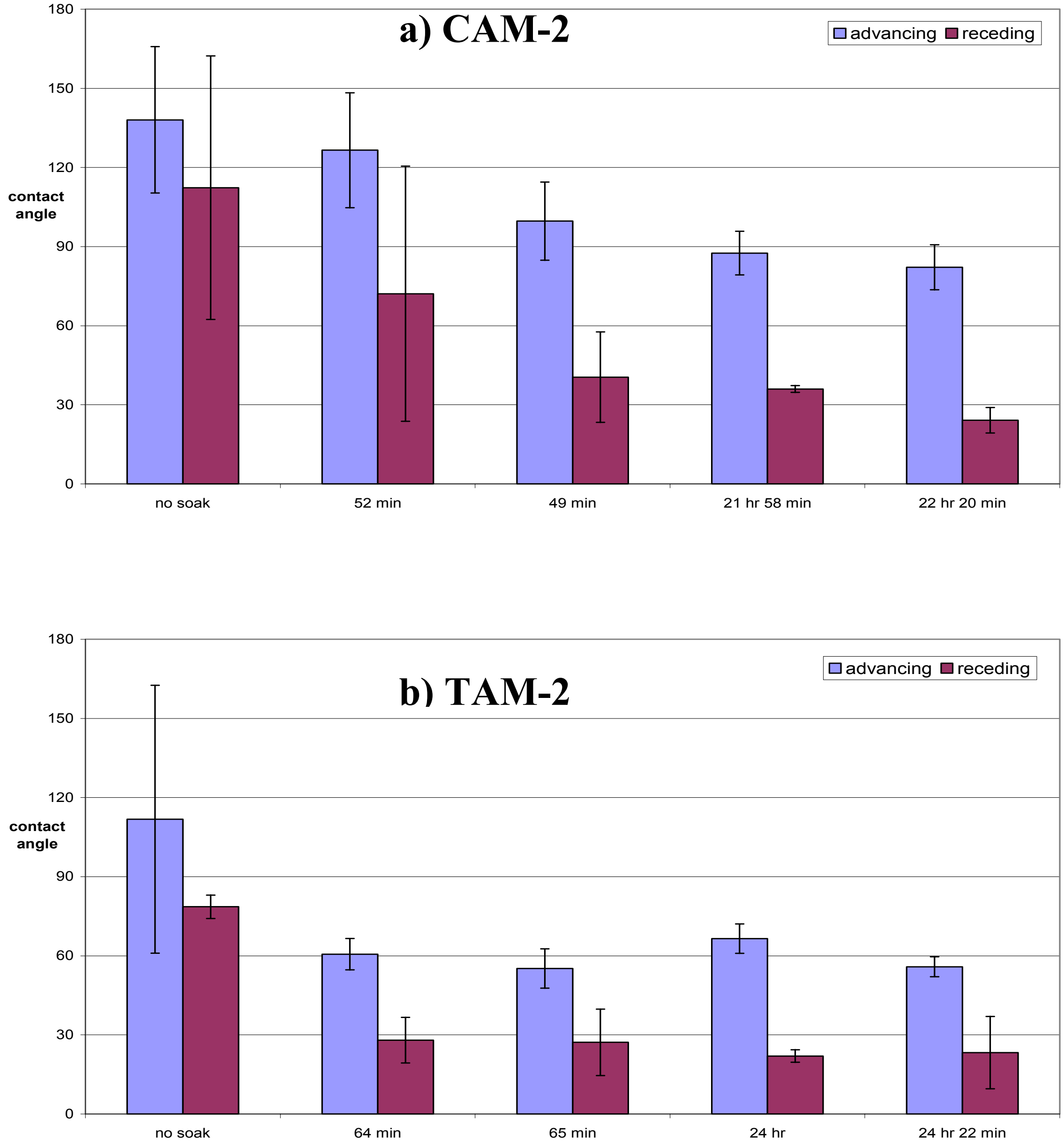


Figure H-1. Contact angle measurements for a) CAM-2 and b) TAM-2 pre-equilibrated with pH 4 brine (decane only), washed/soaked in toluene, measured in decane (pH 4 drop).

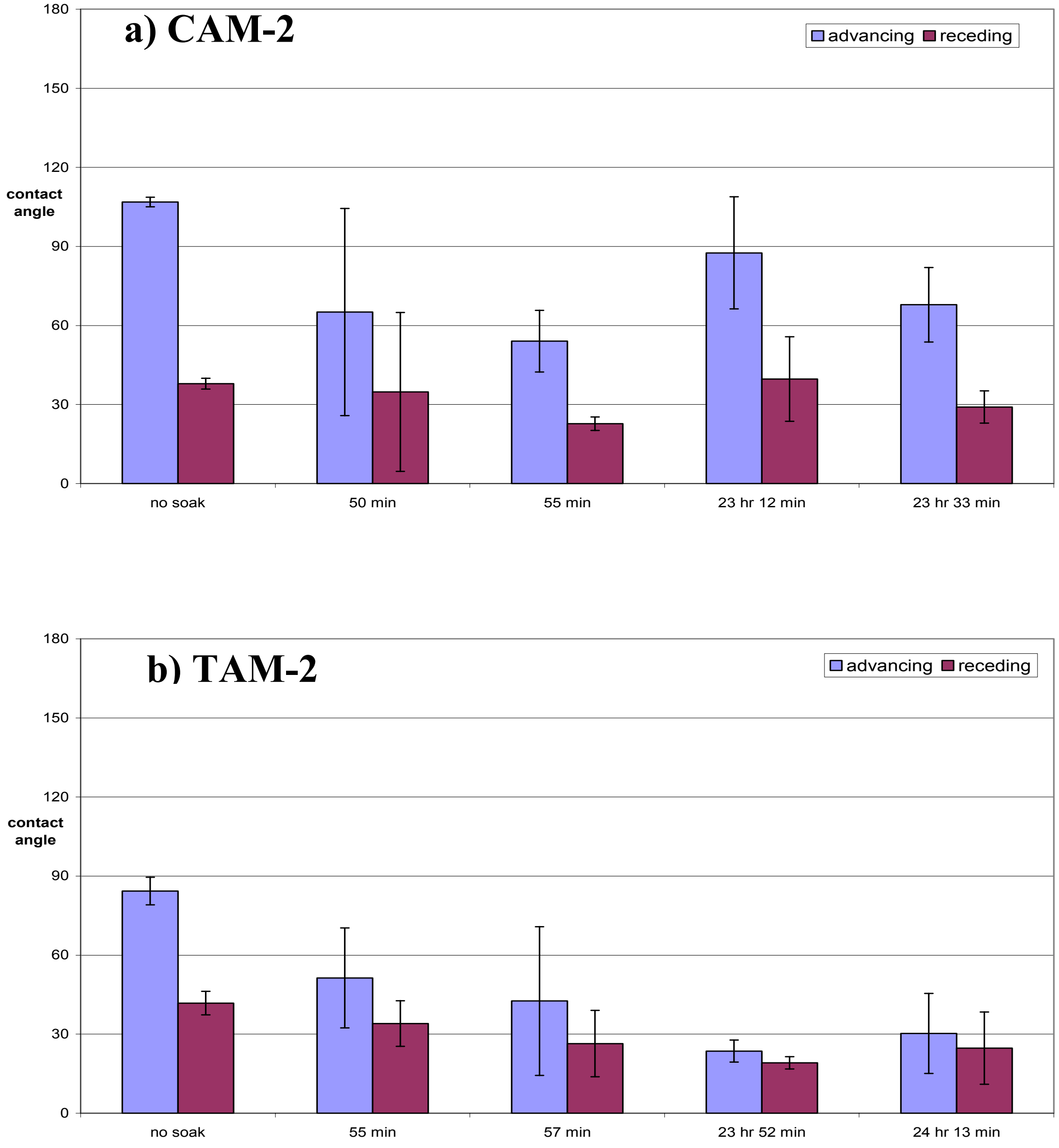
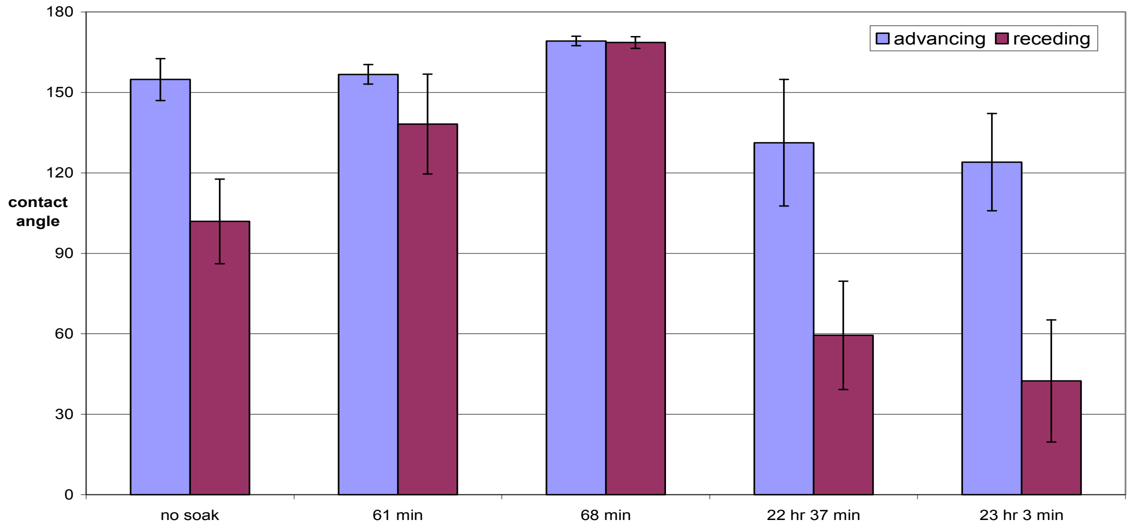


Figure H-2. Contact angle measurements for a) CAM-2 and b) TAM-2 pre-equilibrated with pH 4 buffer (decane only), washed/soaked in acetone, measured in decane (pH 4 drop).

a) CAM-2



b) TAM-2

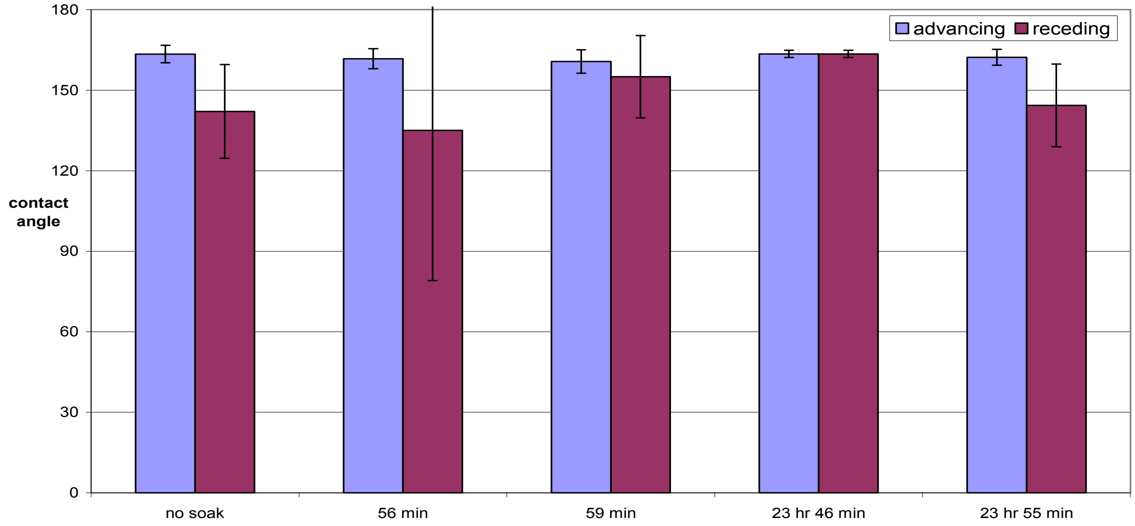
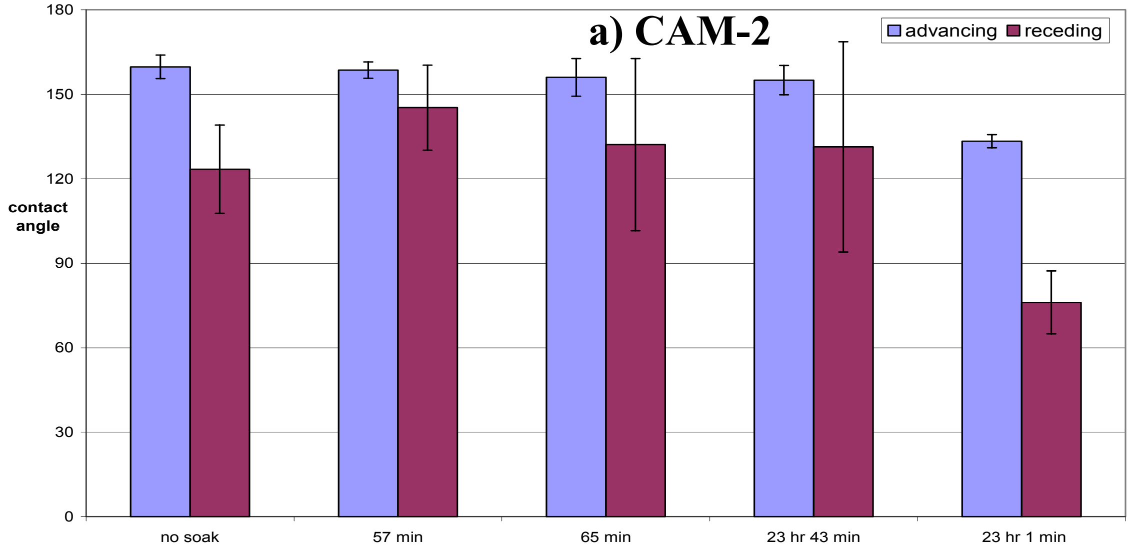


Figure H-3. Contact angle measurements for a) CAM-2 and b) TAM-2 pre-equilibrated with pH 4 buffer (decane only), washed with acetone and water (soaked in water), measured in pH 4 buffer (decane that has been pre-equilibrated drop).



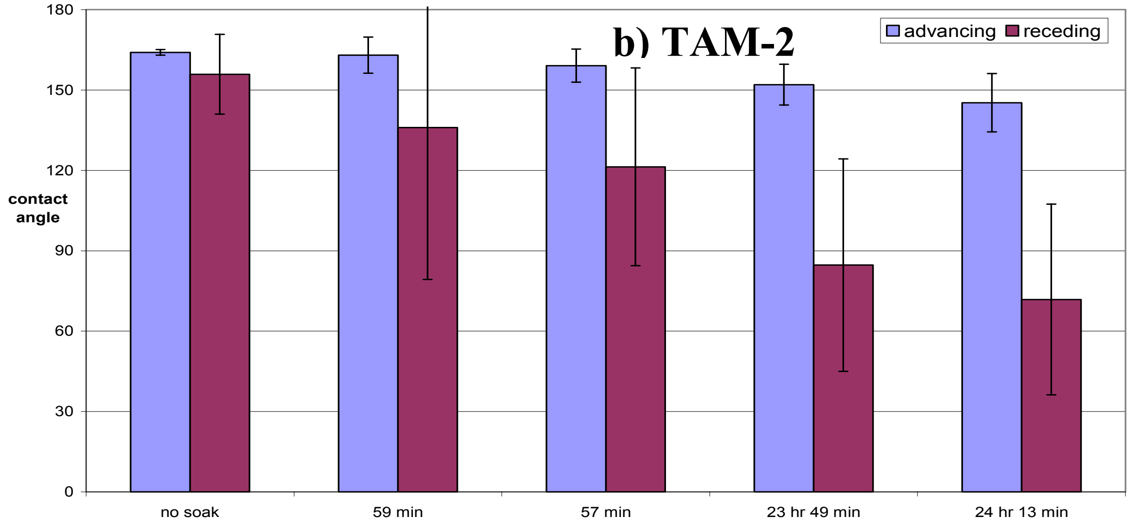


Figure H-4. Contact angle measurements for a) CAM-2 and b) TAM-2 pre-equilibrated with pH 4 buffer (decane only), washed with acetone and pH 8 buffer (soaked in pH 8 buffer), measured in pH 4 buffer (decane that has been pre-equilibrated drop).

Appendix I : Contact angle results of CAM-2, TAM-2, or TAM-5 pre-equilibrated with water (both phases) then washed/soaked in various solvents.

Mica was

- treated with CAM-2, TAM-2, and TAM-5 solution in decane (all solutions have been pre-equilibrated)
- washed/soaked with one of the following
    - toluene
    - acetone
    - acetone and isopropanol (soaked in isopropanol)
    - acetone and pH 8 buffer (soaked in pH 8 buffer)
    - acetone and pH 10 buffer (soaked in pH 10 buffer)
- contact angles were measured with decane or aqueous solutions (all solutions have been pre-equilibrated)

Figures I-1 – I-7 show the contact angle measurements for CAM-2, TAM-2, and TAM-5 pre-equilibrated with water and washed/soaked in toluene, acetone, hexane, isopropanol, acetone and water, acetone and pH 8 buffer, or acetone and pH 10 buffer, respectively. The contact angles were generally within the error bars no matter how long the mica was soaked in the solvent, therefore the surfactant was assumed to desorb from the mica surface fairly quickly.

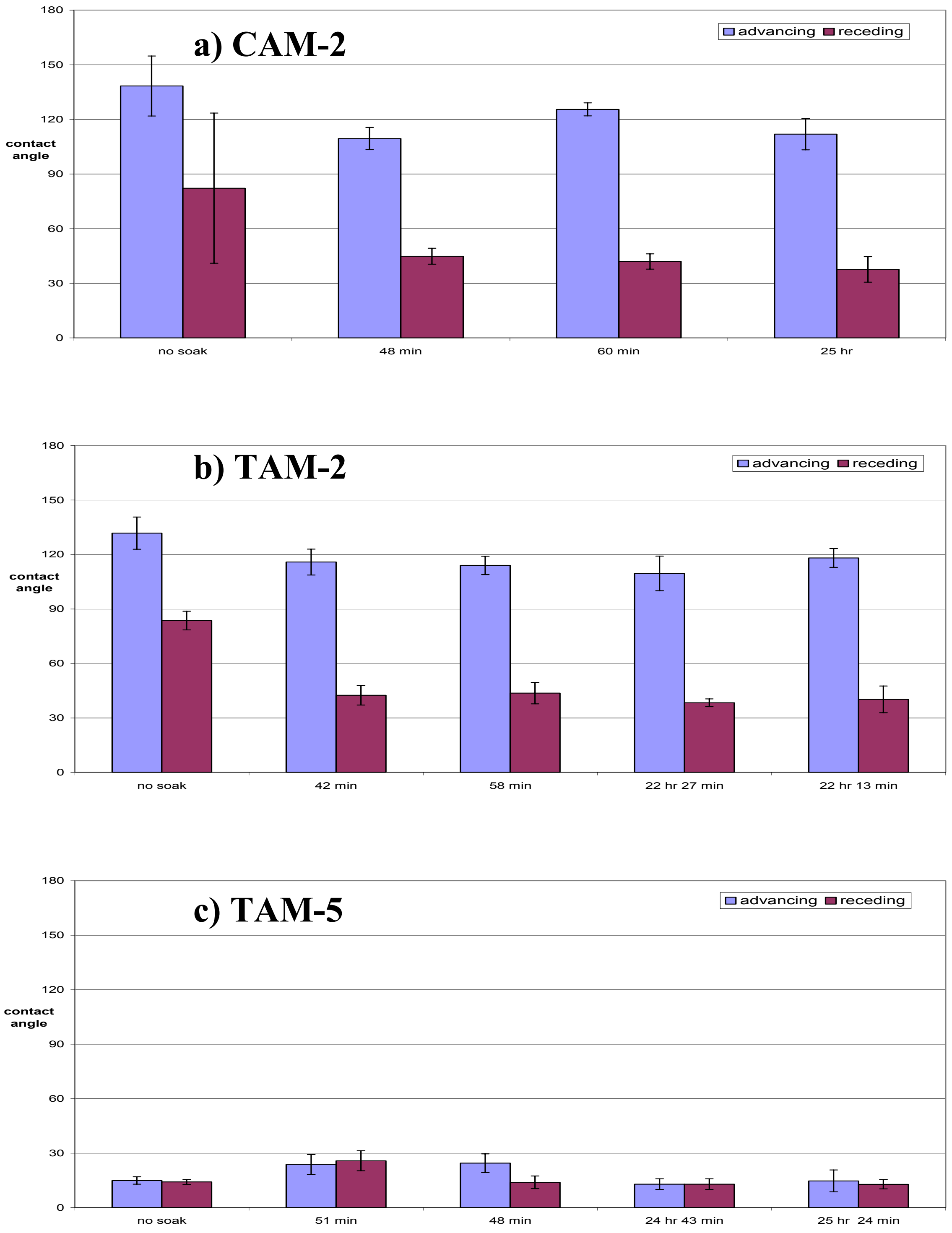
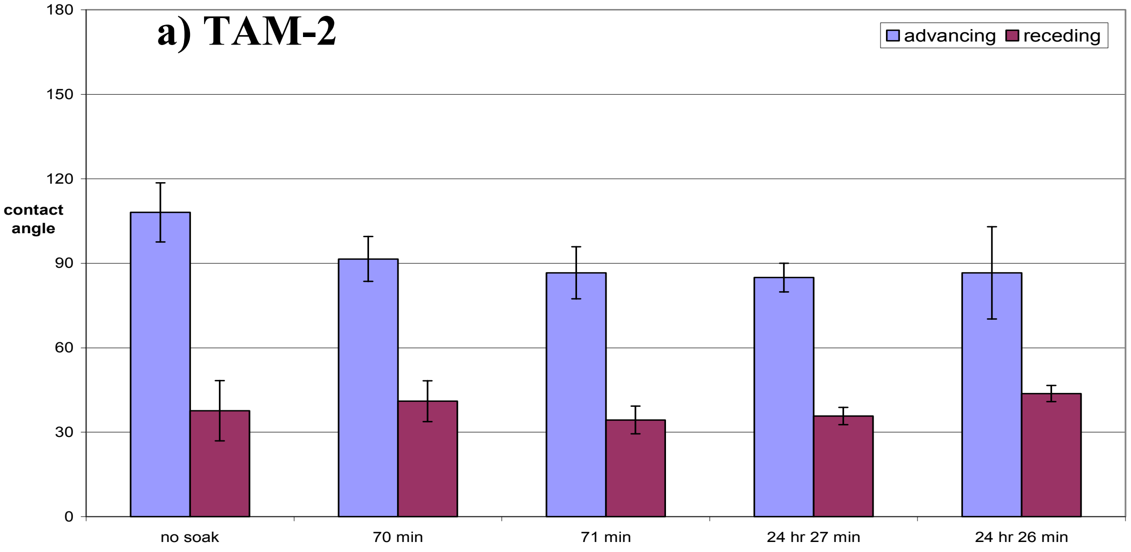


Figure I-1. Contact angle results for a) CAM-2 b) TAM-2 and b) TAM-5 for pre-equilibration with water, washed/soaked in toluene, measured in decane (water that has been pre-equilibrated drop).



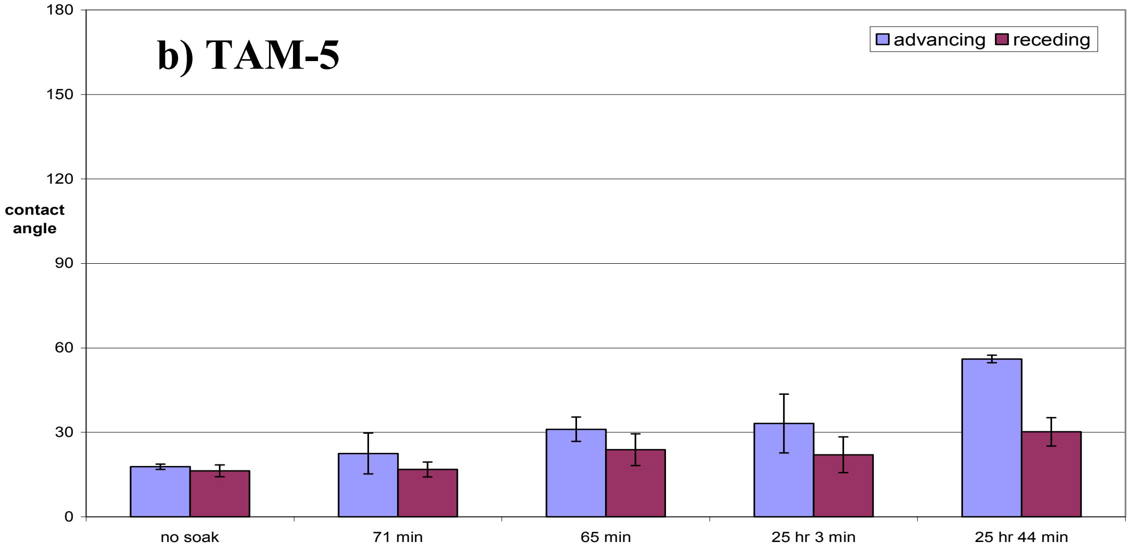


Figure I-2. Contact angle results for a) TAM-2 and b) TAM-5 for pre-equilibration with water, washed/soaked in acetone, measured in decane (water that has been pre-equilibrated drop).

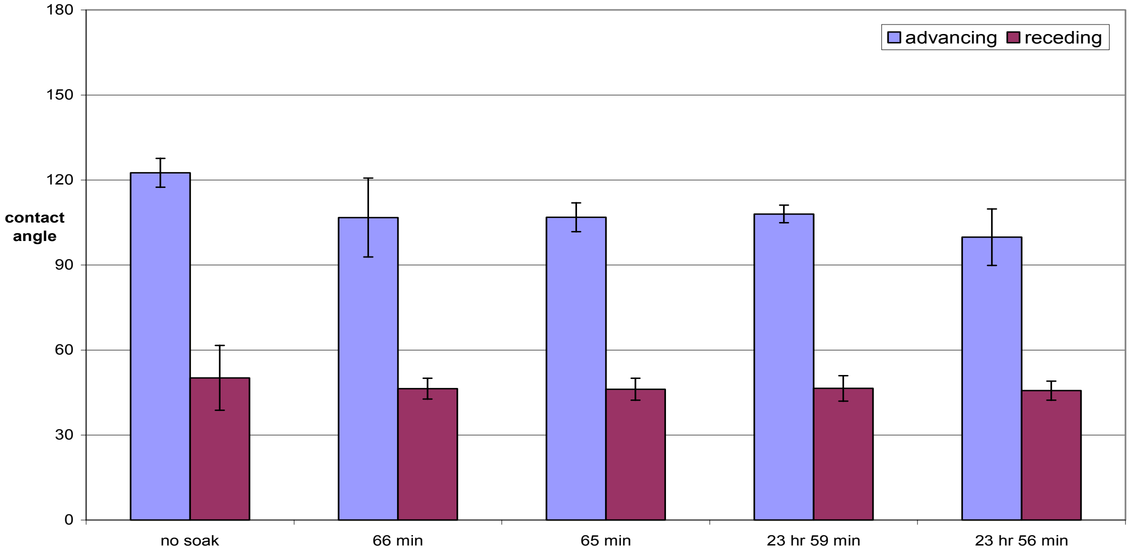


Figure I-3. Contact angle results for TAM-2 for pre-equilibration with water, washed/soaked in hexane, measured in decane (water that has been pre-equilibrated drop).

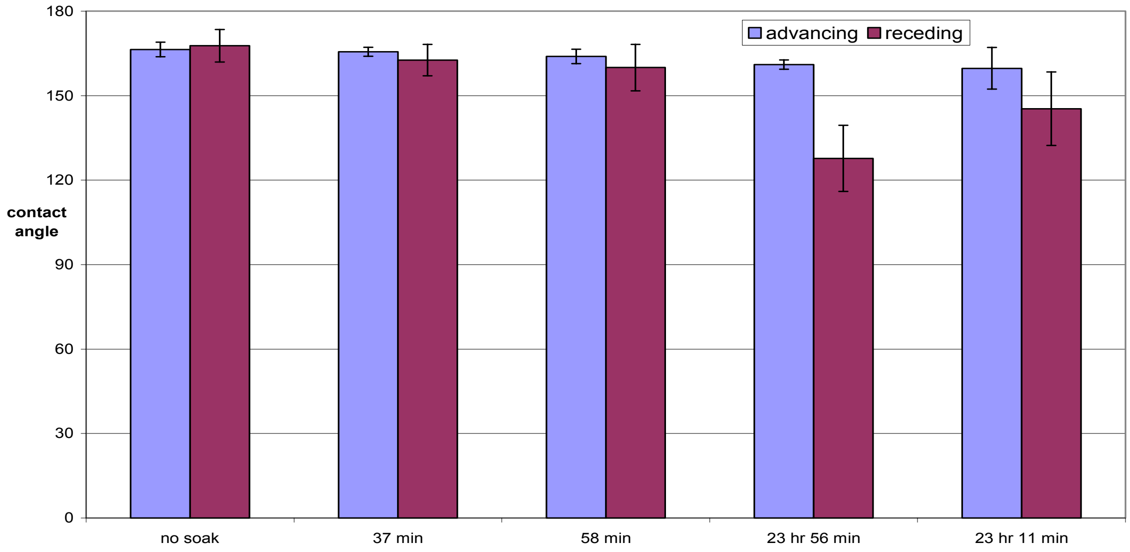


Figure I-4. Contact angle results for CAM-2 for pre-equilibration with water, washed/soaked in isopropanol, measured in water (decane that has been pre-equilibrated drop).

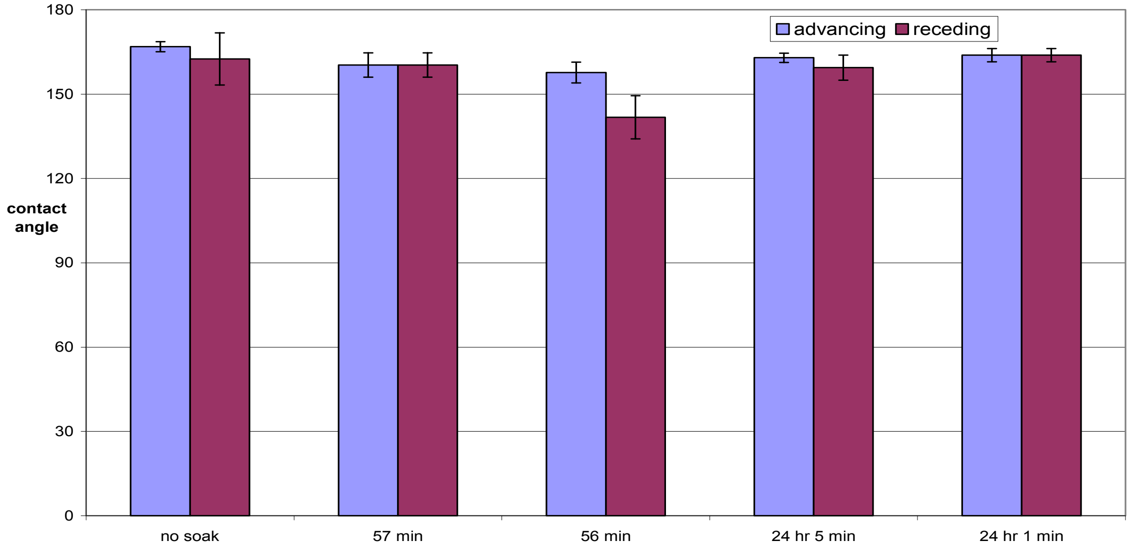


Figure I-5. Contact angle results for TAM-2 for pre-equilibrated with water, washed in acetone and water (soaked in water), measured in water (decane that has been pre-equilibrated drop).

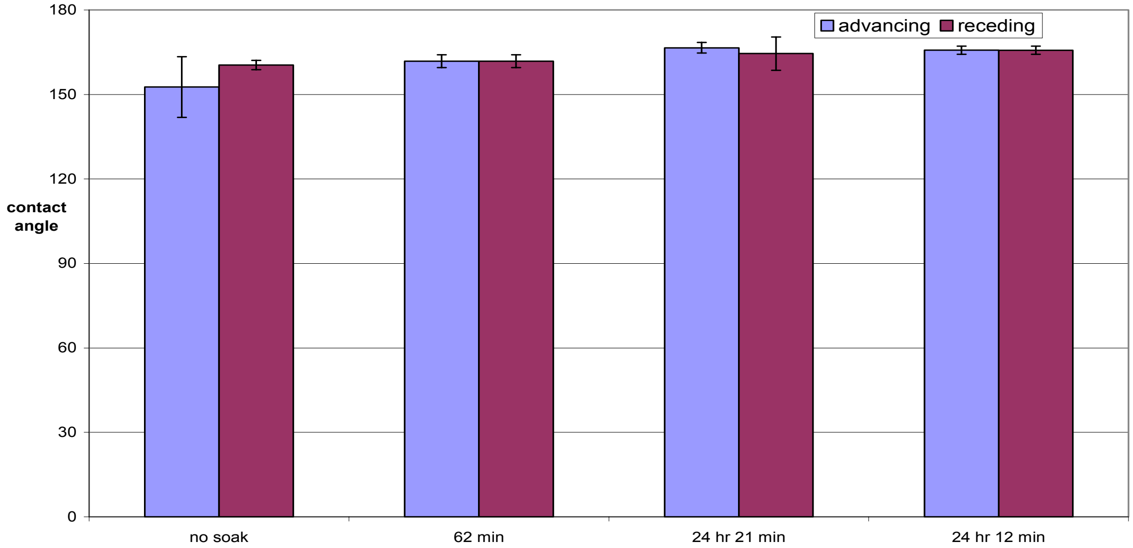


Figure I-6. Contact angle results for TAM-2 for pre-equilibration with water, washed in acetone and pH 8 buffer (soaked in pH 8 buffer), measured in water (decane that has been pre-equilibrated drop).

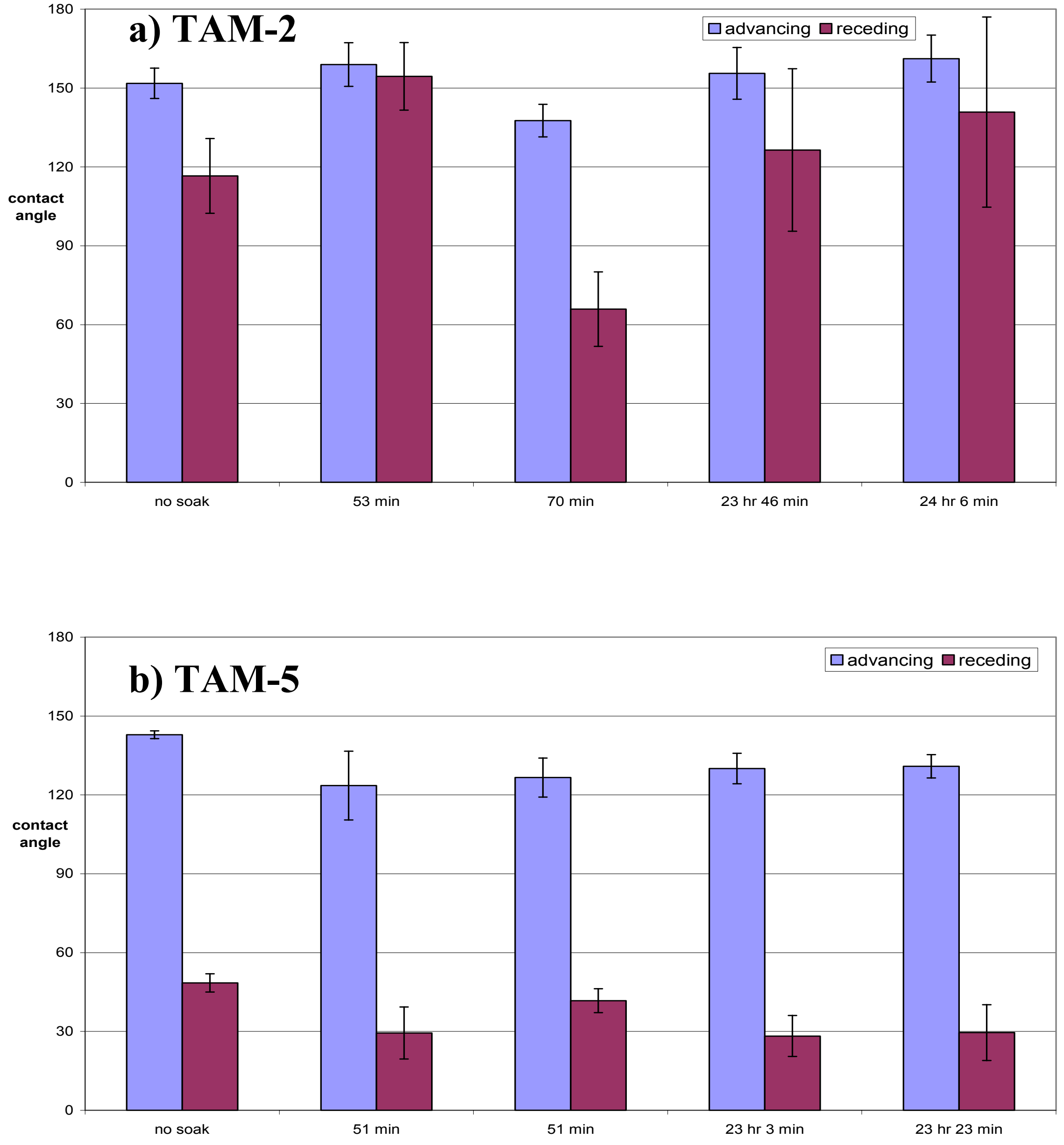


Figure I-7. Contact angle results for a) TAM-2 b) TAM-5 for pre-equilibration with water, washed in acetone and pH 10 buffer (soaked in pH 10 buffer), measured in water (decane that has been pre-equilibrated drop).

Appendix J : Contact angle results of CAM-2, TAM-2, or TAM-5 pre-equilibrated with water (decane only) then washed/soaked in various solvents.

Mica was

- treated with CAM-2, TAM-2, or TAM-5 solutions in decane (decane had been pre-equilibrated and the aqueous solutions were not pre-equilibrated)
- washed/soaked with one of the following
    - toluene
    - acetone
    - acetone then isopropanol (soaked in isopropanol)
    - acetone then water (soaked in water)
    - acetone then pH 8 buffer (soaked in pH 8 buffer)
- contact angles were measured with decane (pre-equilibrated) or water

Figures J-1 – J6 show the contact angles for CAM-2, TAM-2, and TAM-5 pre-equilibrated with water (decane only) washed and soaked in toluene, acetone, hexane, isopropanol, acetone then water, or acetone then pH 8 buffer, respectively. Generally, the contact angles were within the error bars therefore the surfactant desorbed quickly from the surface of the mica.

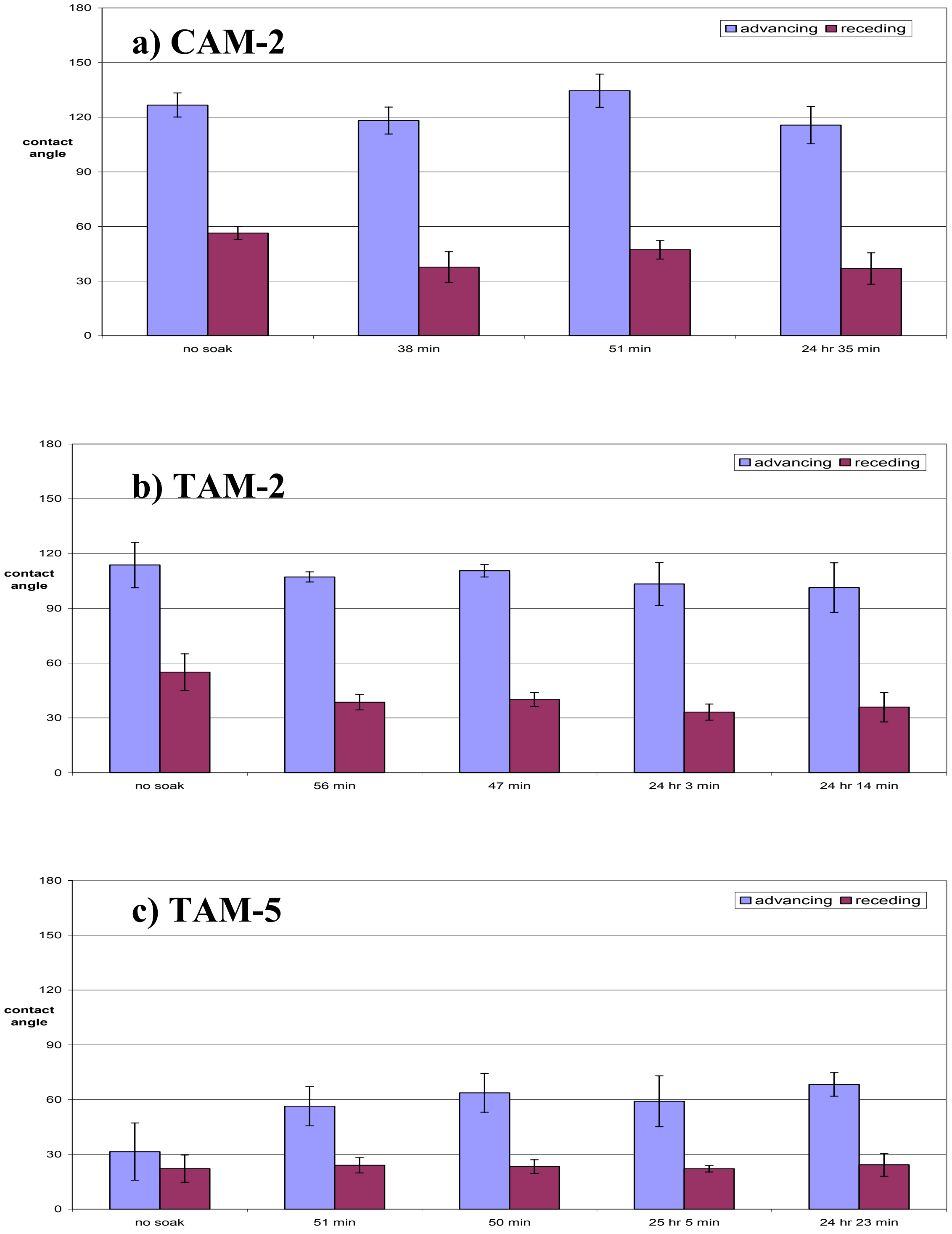
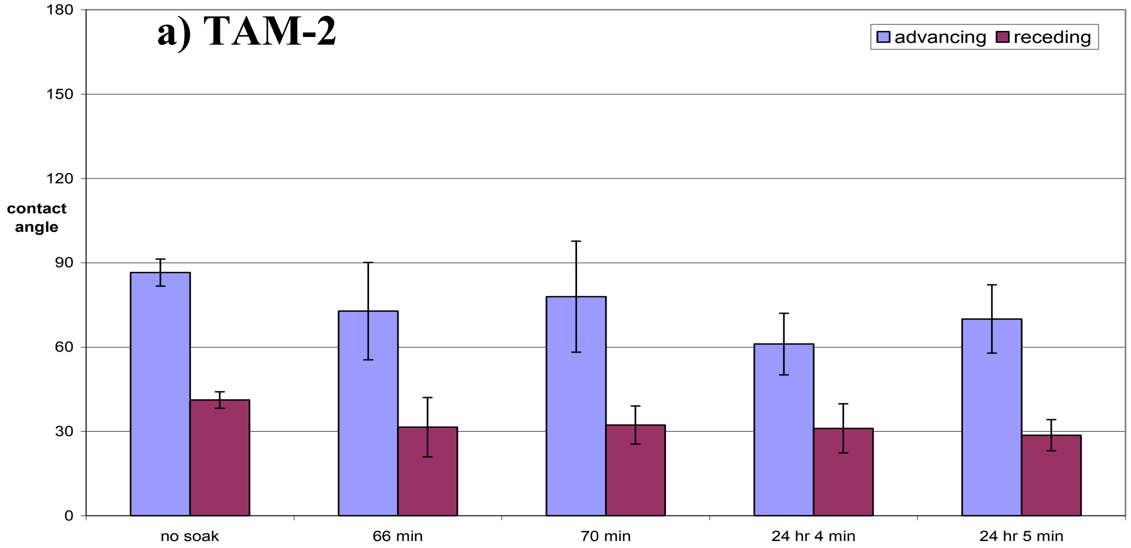


Figure J-1. Contact angle results for a) CAM-2 b) TAM-2 and b) TAM-5 for pre-equilibration with water (decane only), washed/soaked in toluene, measured in decane (water drop).



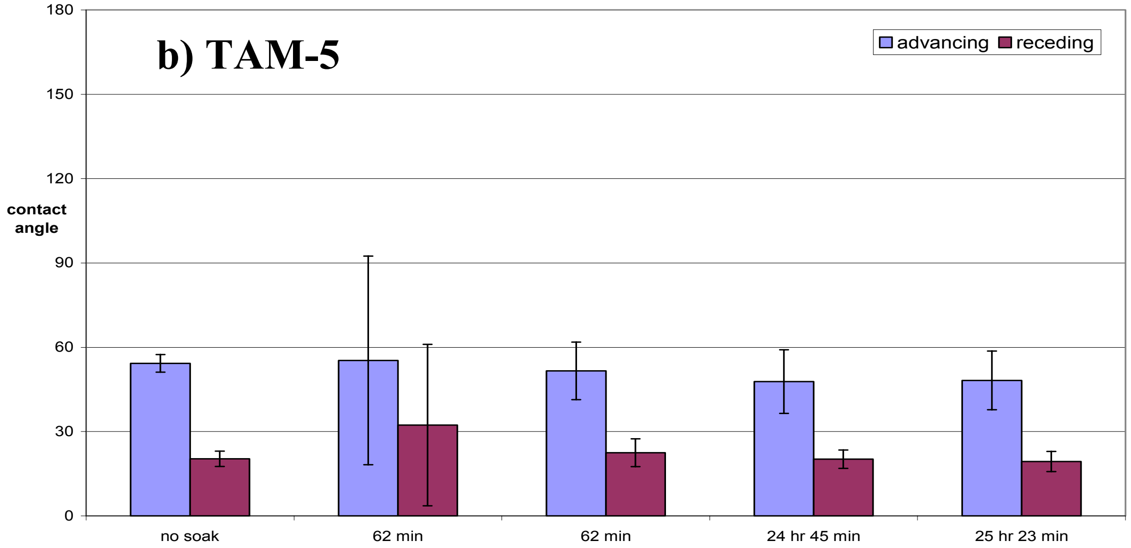


Figure J-2. Contact angle results for a) TAM-2 and b) TAM-5 for pre-equilibration with water (decane only), washed/soaked in acetone, measured in decane (water drop).

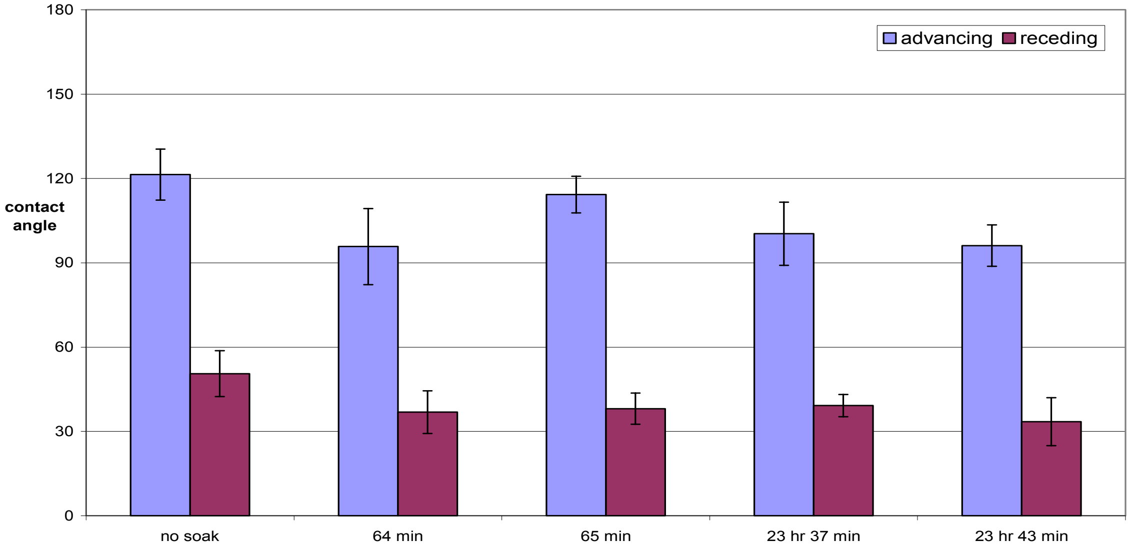


Figure J-3. Contact angle results for TAM-2 for pre-equilibration with water (decane only), washed/soaked in hexane, measured in decane (water drop).

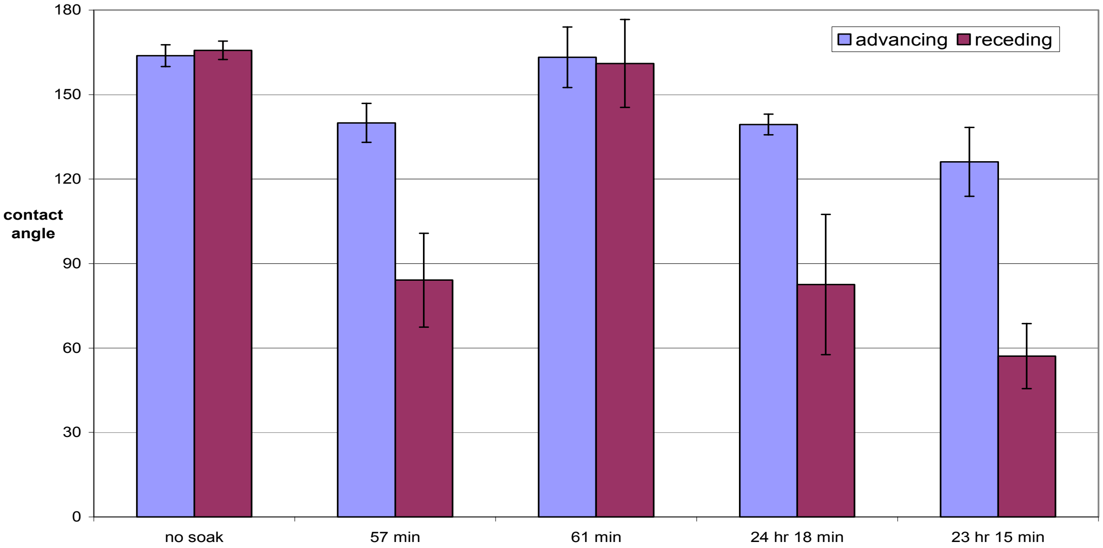
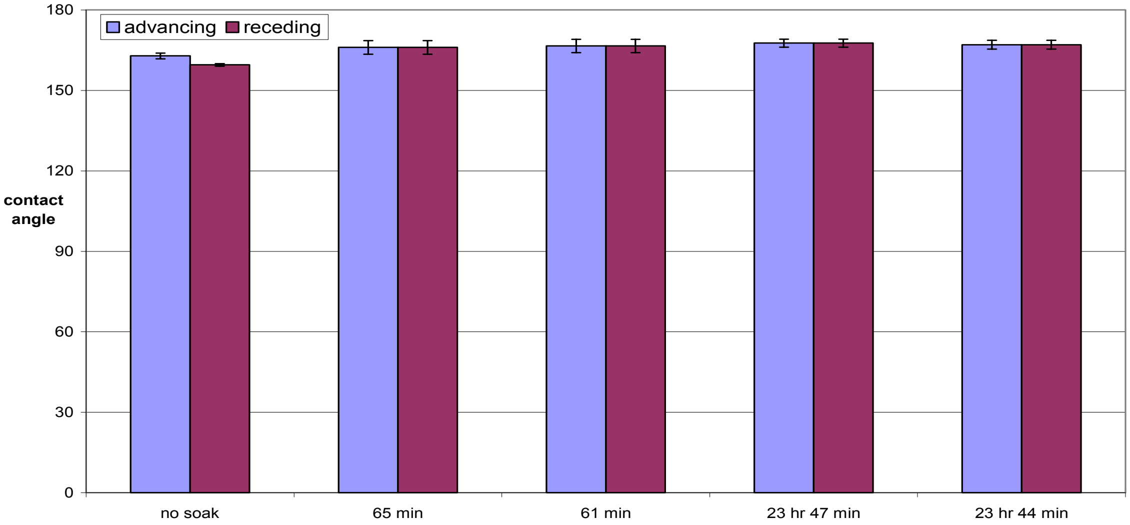


Figure J-4. Contact angle results for CAM-2 for pre-equilibration with water (decane only), washed/soaked in isopropanol, measured in water (decane that has been pre-equilibrated drop).

a) TAM-2



b) TAM-5

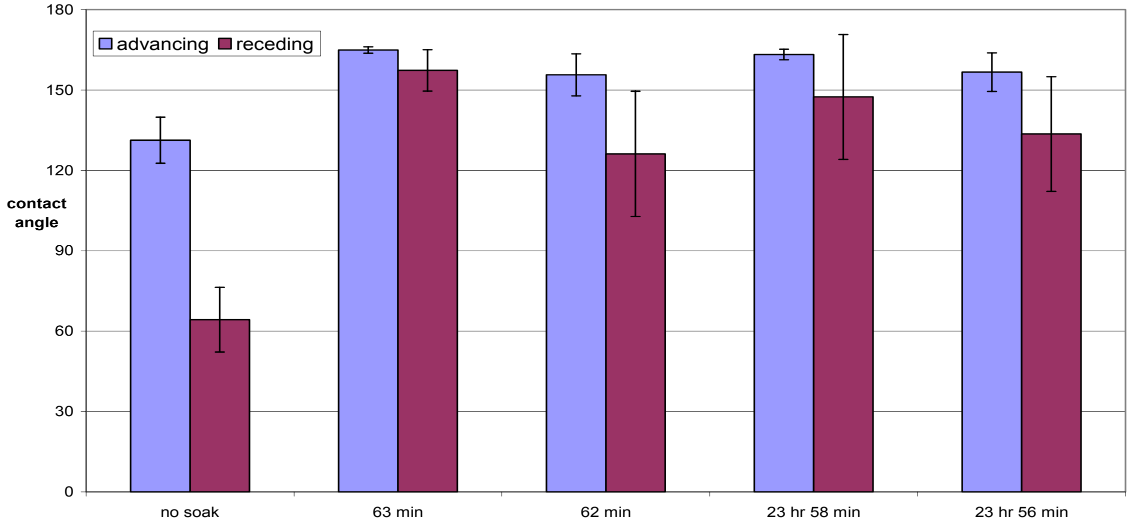
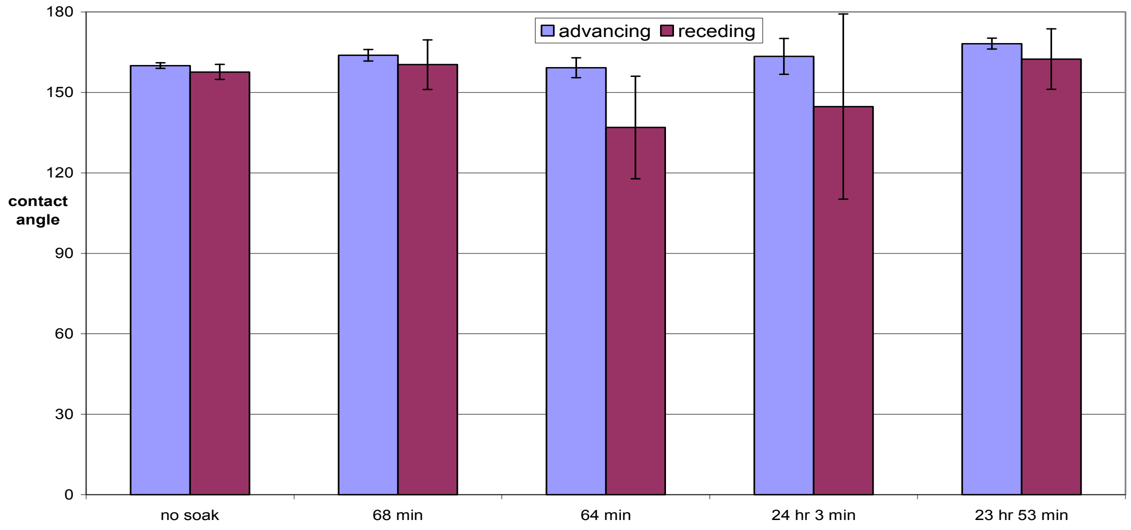


Figure J-5. Contact angle results for a) TAM-2 and b) TAM-5 for pre-equilibration with water (decane only), washed in acetone and water (soaked in water), measured in water (decane that has been pre-equilibrated drop).

a) TAM-2



b) TAM-5

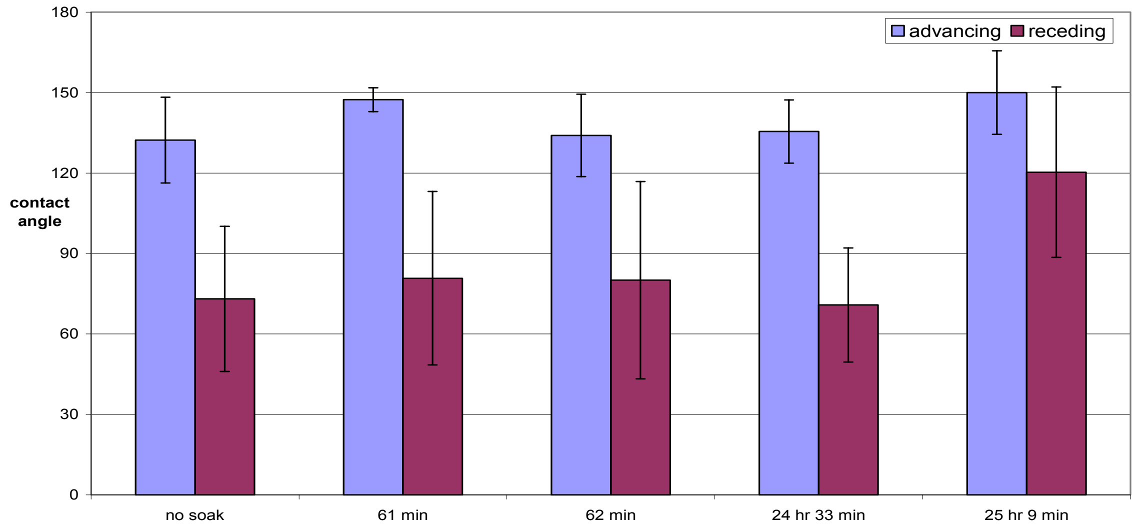


Figure J-6. Contact angle results for a) TAM-2 and b) TAM-5 for pre-equilibration with water (decane only), washed in acetone and pH 8 buffer (soaked in pH 8 buffer), measured in water (decane that has been pre-equilibrated drop).

Appendix K : Contact angle results for TAM-5 pre-equilibrated with pH 8 buffer (both phases) then washed/soaked in various solutions.

Mica was

- treated with TAM-5 solutions in decane (all solutions were pre-equilibrated)
- washed/soaked with one of the following
    - toluene
    - acetone
    - acetone then water (soaked in water)
    - acetone then pH 8 buffer (soaked in pH 8 buffer)
    - acetone then pH 10 buffer (soaked in pH 10 buffer)
- contact angles were measured in decane or pH 8 buffer (all solutions were pre-equilibrated)

Figures K-1 – K-5 show the contact angles for TAM-5 pre-equilibrated with decane washed and soaked in toluene, acetone, acetone then water, acetone then pH 8 buffer, and acetone then pH 10 buffer, respectively. The variations in the contact angle measurements are all within the error bars therefore the time soaked in the solvents did not change the contact angles greatly.

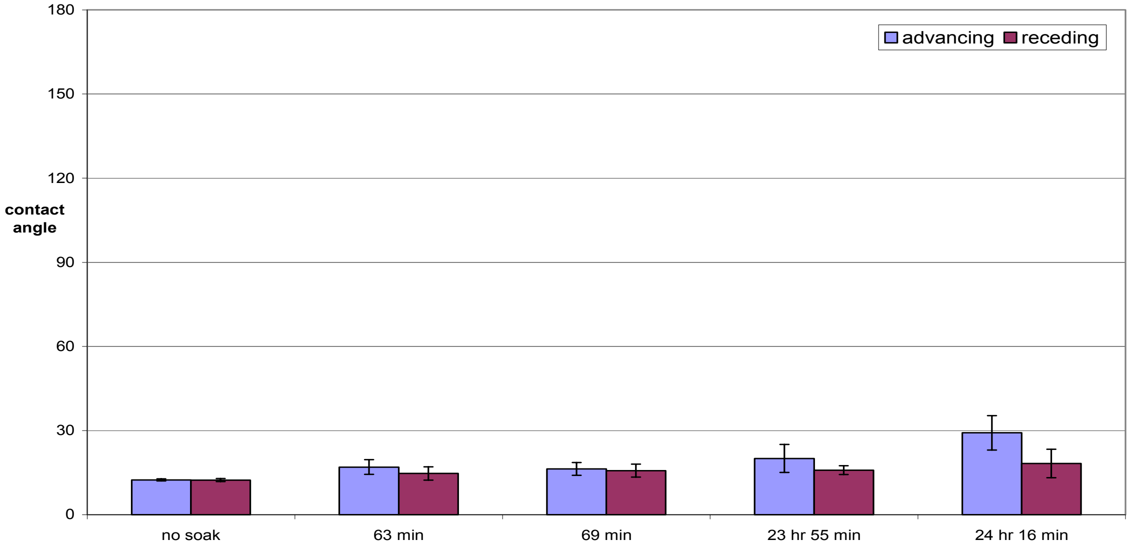


Figure K-1. Contact angle measurements for TAM-5 pre-equilibrated with pH 8 buffer, washed/soaked in toluene, measured in decane (pH 8 buffer that has been pre-equilibrated drop).

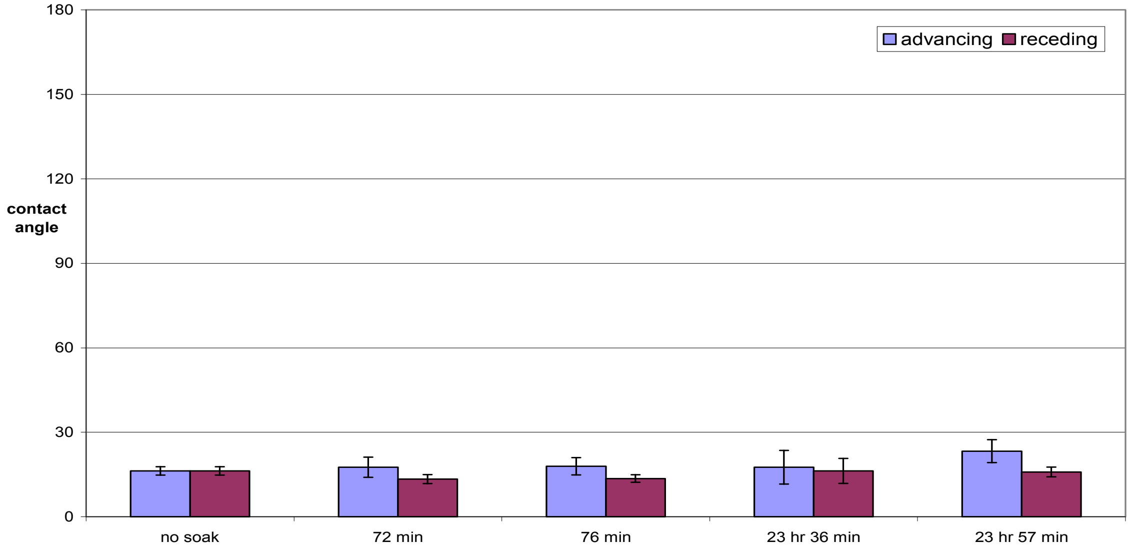


Figure K-2. Contact angle measurements for TAM-5 pre-equilibrated with pH 8 buffer, washed/soaked in acetone, measured in decane (pH 8 buffer that has been pre-equilibrated drop).

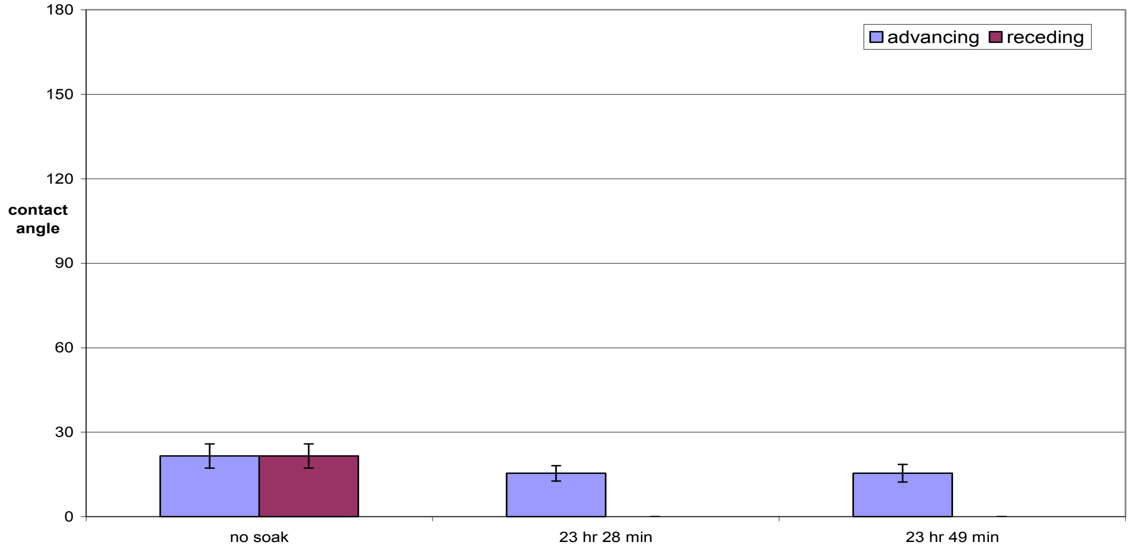


Figure K-3. Contact angle measurements for TAM-5 pre-equilibrated with pH 8 buffer, washed with acetone and water (soaked in water), measured in pH 8 buffer that has been pre-equilibrated with TAM-5 (decane that has been pre-equilibrated drop).

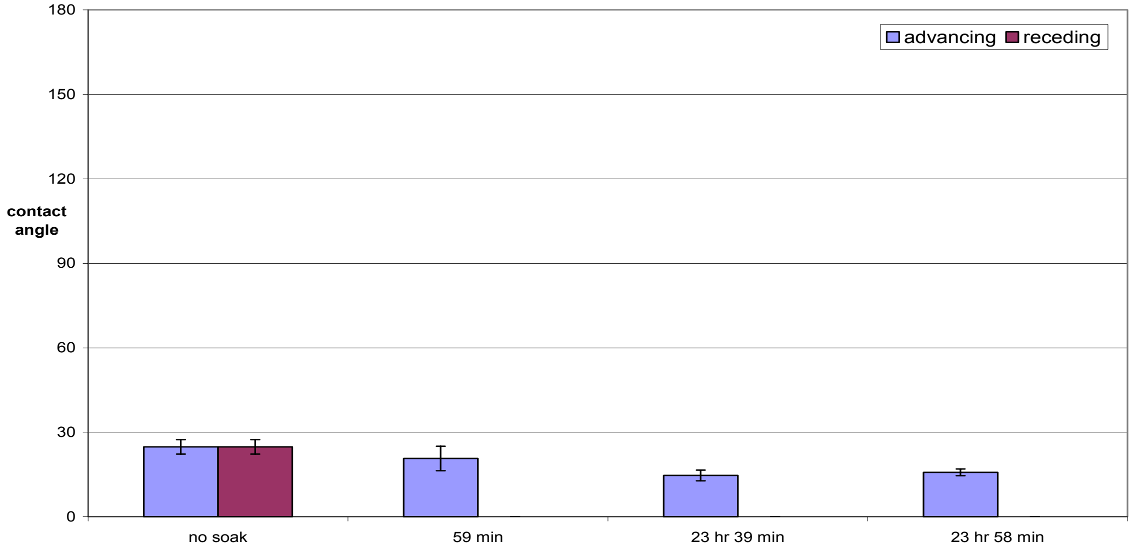


Figure K-4. Contact angle measurements for TAM-5 pre-equilibrated with pH 8 buffer, washed with acetone and pH 8 buffer (soaked in pH 8 buffer), measured in pH 8 buffer that has been pre-equilibrated with TAM-5 (decane that has been pre-equilibrated drop).

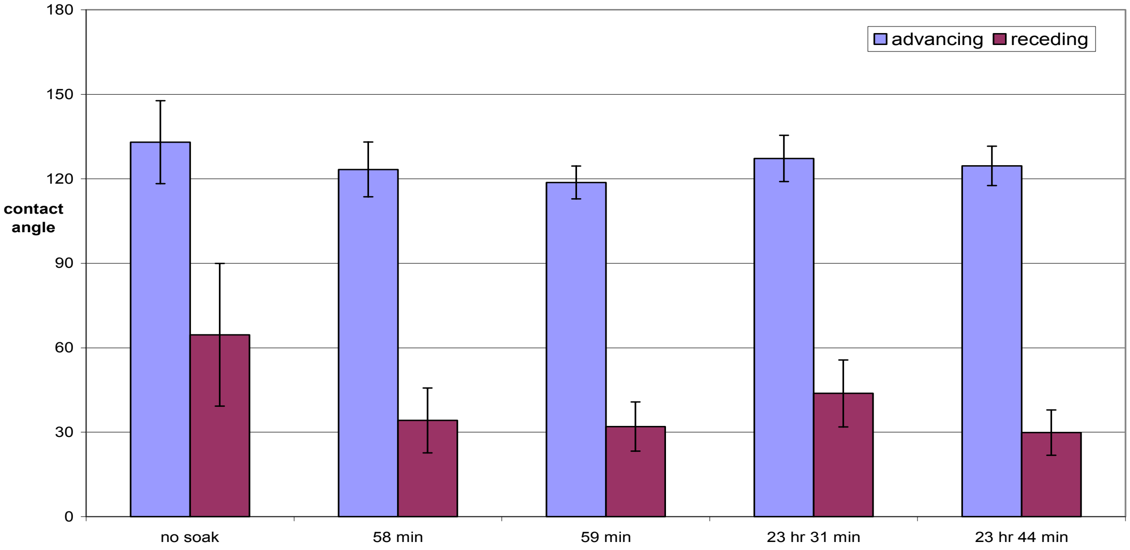


Figure K-5. Contact angle measurements for TAM-5 pre-equilibrated with pH 8 buffer, washed with acetone and pH 10 buffer (soaked in pH 10 buffer), measured in pH 8 buffer that has been pre-equilibrated with TAM-5 (decane that has been pre-equilibrated drop).

Appendix L : Contact angle results for TAM-5 pre-equilibration with pH 8 buffer (decane only) then washed/soaked in various solvents.

Mica was

- treated with TAM-5 solution in decane (decane was pre-equilibrated and pH 8 buffer was not pre-equilibrated)
- washed/soaked with one of the following
    - toluene
    - acetone
    - acetone then water (soaked in water)
    - acetone then pH 8 buffer (soaked in pH 8 buffer)
- contact angles were measured with decane (pre-equilibrated) or pH 8 buffer

Figures L-1 – L-4 show the contact angle measurements for TAM-5 pre-equilibrated with decane only washed with toluene, acetone, acetone then pH 8 buffer, or acetone then pH 10 buffer, respectively. The contact angles do not vary past the error bar therefore the time the mica is soaked in the solvents do not affect the contact angles.

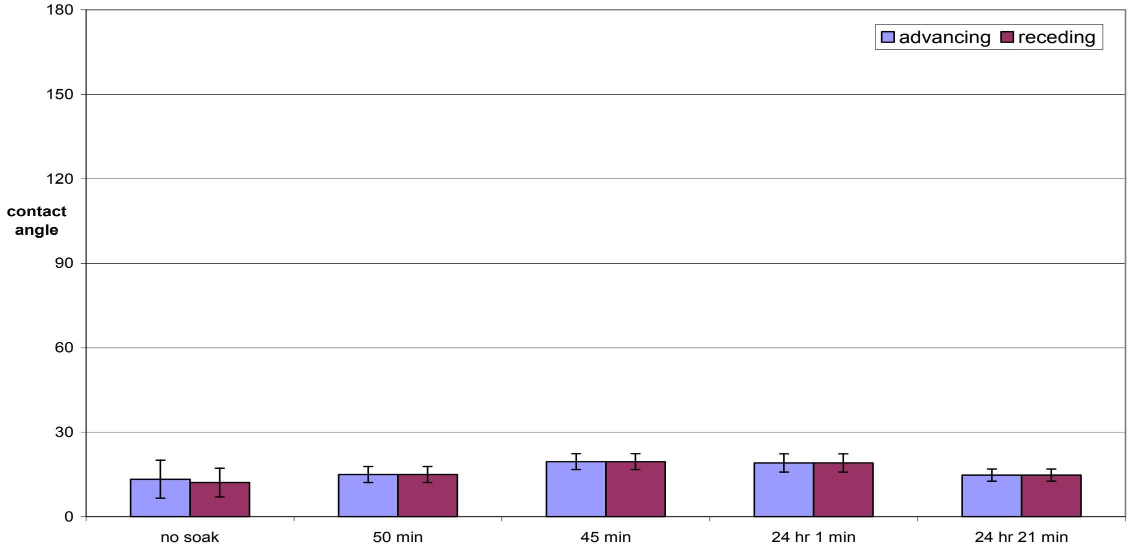


Figure L-1. Contact angle measurements for TAM-5 pre-equilibrated with pH 8 buffer (decane only), washed/soaked in toluene, measured in decane (pH 8 drop).

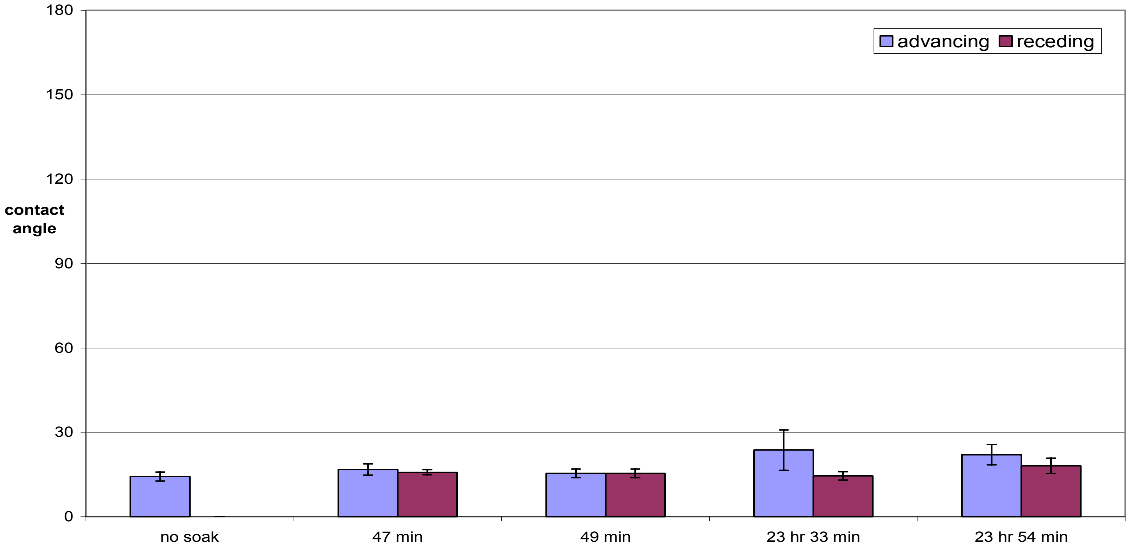


Figure L-2. Contact angle measurements for TAM-5 pre-equilibrated with pH 8 buffer (decane only), washed/soaked in acetone, measured in decane (pH 8 drop).

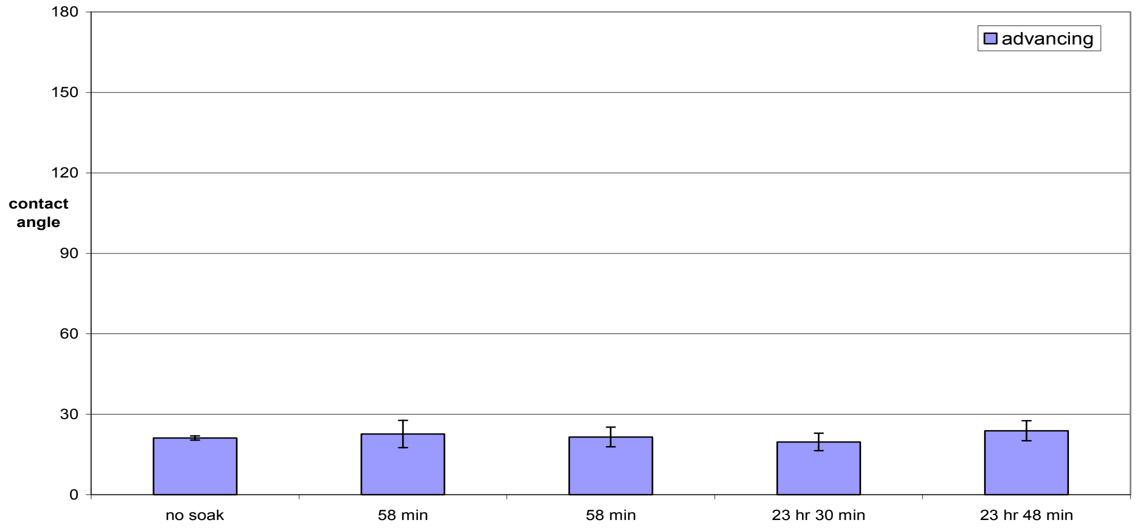


Figure L-3. Contact angle measurements for TAM-5 pre-equilibrated with pH 8 brine (decane only), washed with acetone and water (soaked in water), measured in pH 8 brine (decane that has been pre-equilibrated drop).

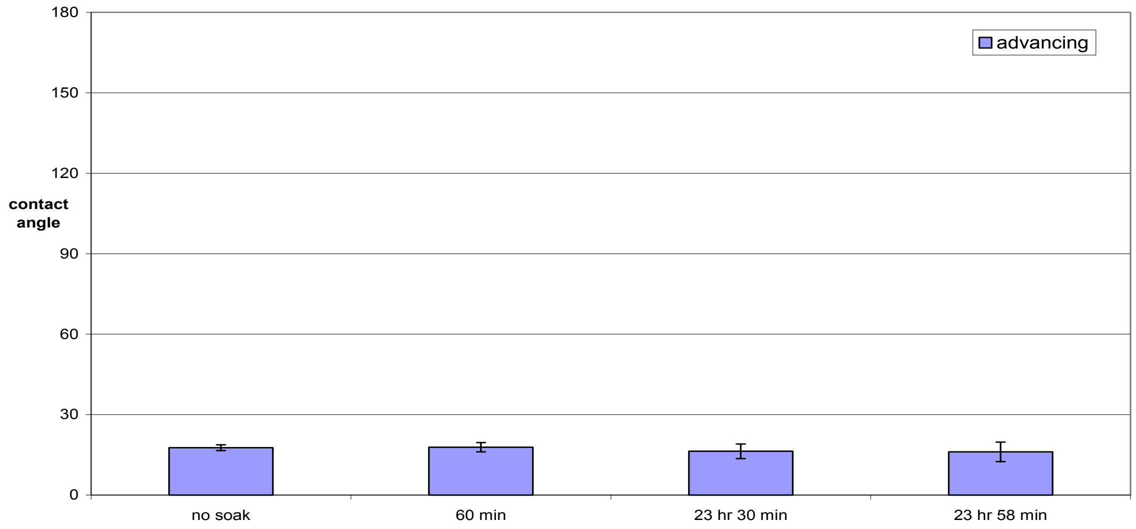


Figure L-4. Contact angle measurements for TAM-5 pre-equilibrated with pH 8 buffer (decane only), washed with acetone and pH 8 buffer (soaked in pH 8 buffer), measured in pH 8 buffer (decane that has been pre-equilibrated drop).

Appendix M : AFM image of clean mica

Figure M-1 shows an AFM image of clean mica. An image of clean mica was needed to be able to compare a clean surface to that of a surface with surfactant on it. There appears to be nothing on the surface of clean mica. Clean mica was only imaged under air in contact mode.

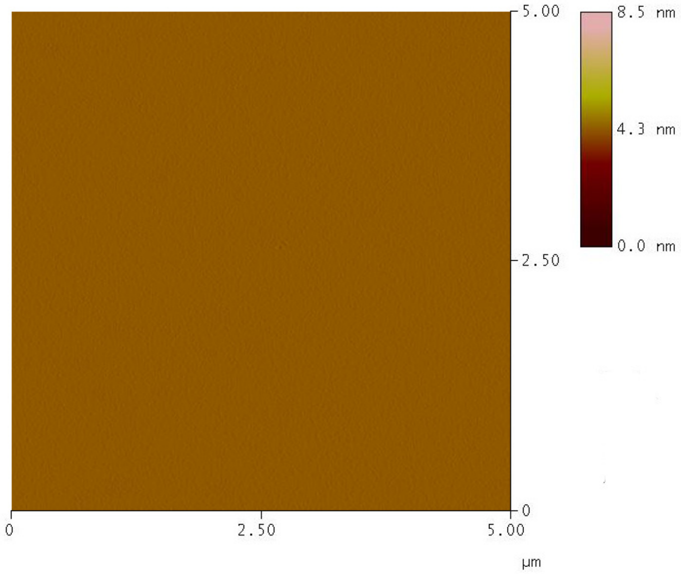


Figure M-1. AFM image of clean mica (contact mode) imaged under air.

Appendix N : AFM images of mica exposed to CAM-2 and TAM-2.

Figures N-1 and N-2 show the AFM images of mica exposed to CAM-2 or TAM-2, respectively. When mica exposed to CAM-2 was imaged under air (Figure N-1a) only circular features were on the surface. The vertical line approximately in the middle of the image was from a pervious scan (1 μm) without the force being increased. Therefore it was concluded that the surfactant was fairly easy to move on the surface. When mica exposed to CAM-2 was imaged under water in contact mode (Figure N-1b), there appeared to be nothing on the surface. It is possible that under water the surfactant is less stable. Therefore in contact mode the force of the tip removed the surfactant on the surface. It is possible that the features in Figure N-1a are actually not the surfactant but instead decane that was not removed by. When mica exposed to CAM-2 was imaged under water in tapping mode (Figures N-1c and N-1d), there appeared to be spots of what is presumed to be surfactant. When mica was exposed to CAM-2 was imaged under pH 8 in tapping mode (Figures N-1e and N-1f), the surfactant seemed to coalesce into linear features. The vertical orientation of what is presumed to be surfactant could be due to the scanning of the surface by the tip. There are fewer features on the surface imaged under pH 8. This is due to the pK_a of the surfactant. At higher pHs the surfactant is less protonated therefore it is less attracted to the surface of the mica.

When mica exposed to TAM-2 was imaged under air (Figure N-2a), there appeared to be complete coverage of the mica by the surfactant (small features) with the large features presumably being decane with surfactant on the surface that was not complete dry. Figure N-2b shows an area of the mica that was scraped by increasing the force of the tip. The part of the image that does not have any features was clean mica. When mica was exposed to TAM-2 was imaged under water in contact mode (Figure N-2c), the surface looked very similar to the surface imaged under air. When mica was exposed to TAM-2 was imaged under pH 8 (Figure N-2d), there appeared to be nothing on the surface, because the image looked similar to that of clean mica. This again was concluded to be due to the pK_a of the surfactant. The images of mica exposed to TAM-2 imaged under water in tapping mode (Figures N-2e and N-2f) were not too helpful, because the smooth area on the bottom left of the image is probably a tear in the mica, therefore it was concluded the water had not only been exposed to the surface of the mica but also underneath the mica.

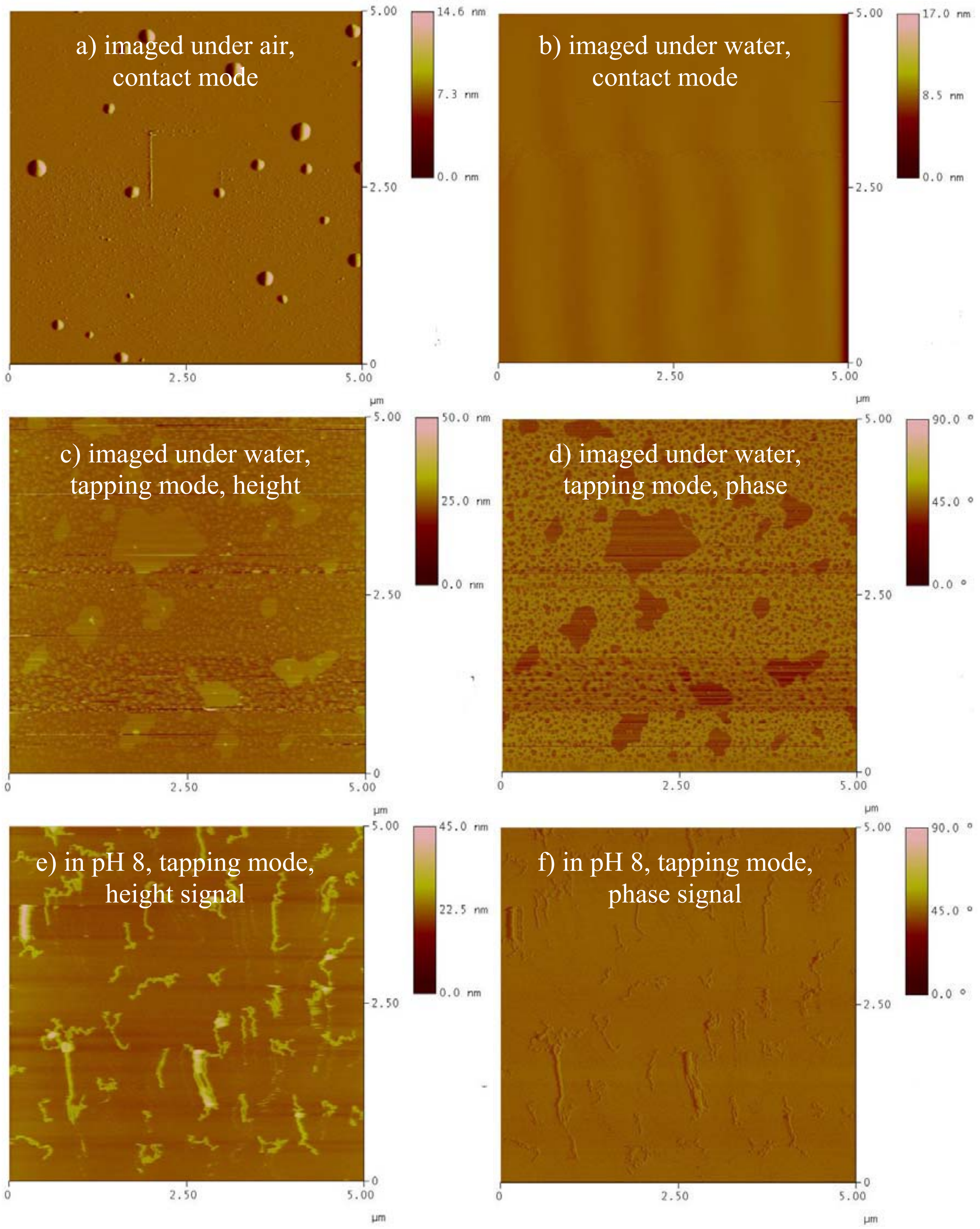


Figure N-1. AFM images of mica exposed to CAM-2 a) under air b) under water, contact mode, c) under water, tapping mode, height signal, d) under water, tapping mode, phase signal, e) under pH 8, tapping mode, height signal, and f) under pH 8, tapping, mode, phase signal.

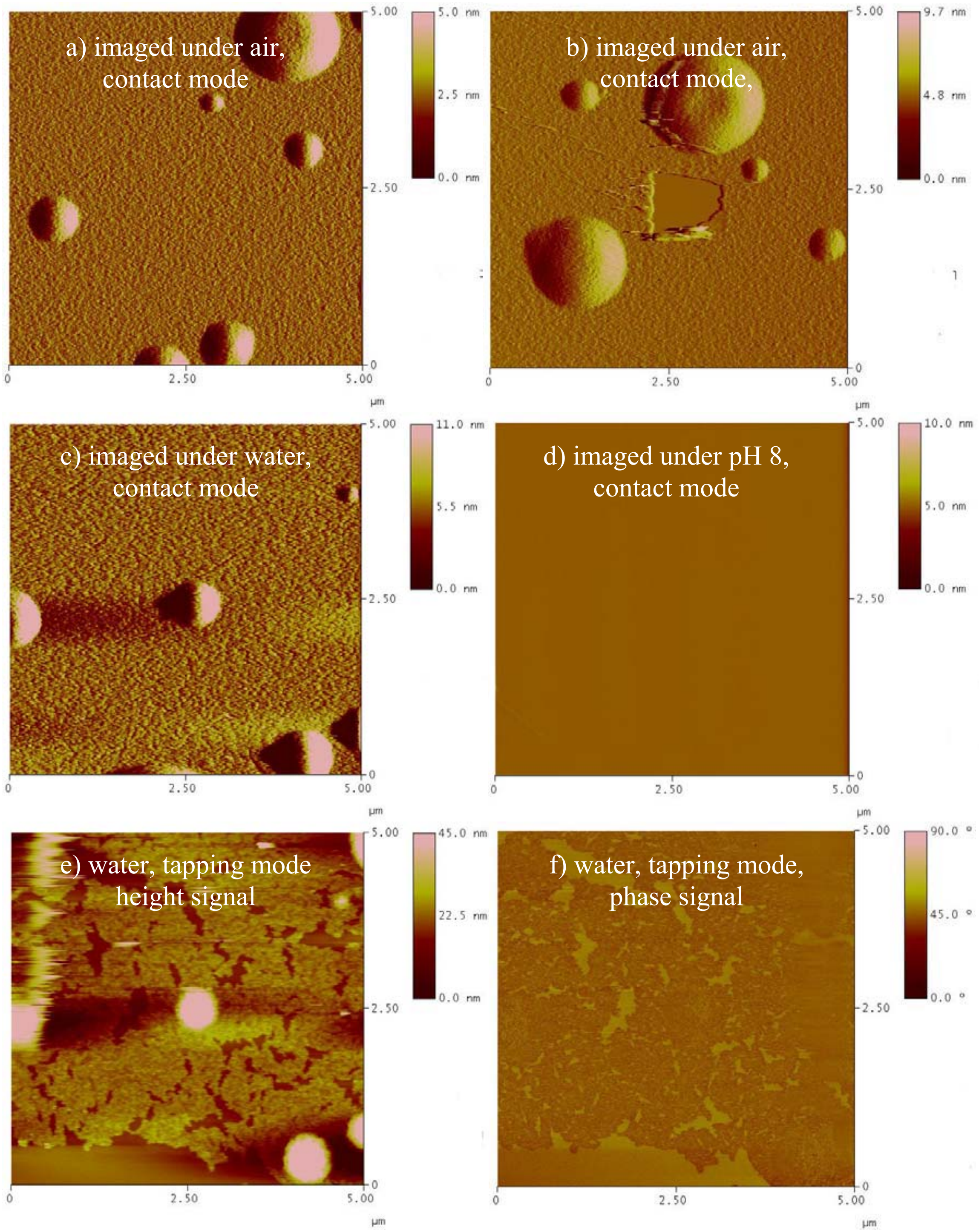


Figure N-2. AFM image of mica exposed to TAM-2 imaged under a) air, b) air with increased force, c) water in contact mode, d) pH 8 in contact mode, e) water in tapping mode, height signal, and f) water in tapping mode, phase signal.

Appendix O : AMF images of mica exposed to CAM-2, TAM-2, and TAM-5 pre-equilibrated with water.

Figures O-1 – O-3 show the AFM images for mica exposed to CAM-2, TAM-2, and TAM-5, respectively, pre-equilibrated with water. Figure O-1a shows the mica surface after it had been exposed to the CAM-2 pre-equilibrated with water solution. There appear to be some circular features on the surface, which are presumably surfactant. The larger circular features could possibly be decane that was not dried when the surface was imaged. Figure O-1b shows the mica surface after it had been washed with toluene. The horizontal orientation of some of the features is due to surfactant being moved by the scanning of the tip. The vertical feature near the middle of the image was due to the force being increased at a 1-μm scan, which caused the surfactant to gather on the left side of the smaller scan. The surface washed with hexane (Figure O-1c) looks like that of clean mica. It is possible the hexane washed the surfactant off the surface, but that is probably not the case since the water advancing angle was approximately 120° (Figure E-2b). A contact angle of 120° suggests there is surfactant on the surface. Figure N-1d shows the mica surface after it had been washed with toluene then hexane. The surface shows a fair amount of surfactant on the surface. Figure O-1e shows the mica surface after it had been washed with toluene then hexane. An increased force was used to image a 1-μm portion of the image. Since the 1-μm portion could be cleaned of the surfactant, it was assumed the surfactant was not that stable on the mica surface.

Figure O-2a shows the mica surface that had been treated with TAM-2 pre-equilibrated with water. There appeared to be nothing on the surface of the mica, but this could have been a result of the decane not being completely dry. When imaging this surface, the tip was actually placed into a decane drop that was not dry (this was witnessed through an optical microscope, but not recorded). Figure O-2b shows the mica surface after it had been washed with toluene. The box in the middle of the image was due to the increased force used when imaging at 1 μm. Mica was not exposed by the intentional scraping, therefore it was concluded that the surfactant was tightly bound to the mica surface.

Figure O-3a shows the mica surface that has been treated with TAM-5 pre-equilibrated with water. The very small features were surfactant adsorbed onto the surface. Figure O-3b shows the mica surface after it had been washed with toluene. The surface seems to have more surfactant on the surface than the non-washed surface. This could be due to the fact the non-washed surface may not have been completely dry (i.e. the decane was not completely evaporated). The blurred square in the middle of the image was from a pervious image scan at 1 μm where the forces were not increased. The apparent smearing of the surfactant suggested the surfactant is not strongly bound to the mica surface. Figures O-3c and O-3d show the non-washed surface imaged in tapping mode. The tapping mode images look similar to the contact mode images except for the presence of a few large circular features in the tapping mode images. These large features could have been present when imaging in contact mode but could have been scraped away. The circular features could have possibly been decane on the surface of the mica. Contact mode tends to be invasive to the surface by the fair amount of force that is constantly applied to the surface compared to tapping mode, even though at times it was possible to see the effects of a 1-μm scan in tapping mode (for example, Figure P-2d). Figures O-3e and O-3f show the toluene-washed surface imaged in tapping mode.

Figure O-3e shows there was full coverage of the surfactant remaining on the surface of the mica, while Figure O-3f shows there is not much difference in the phases present on the surface. This could suggest there is full coverage of the surfactant on the surface of the mica therefore resulting in no relief in the phase image.

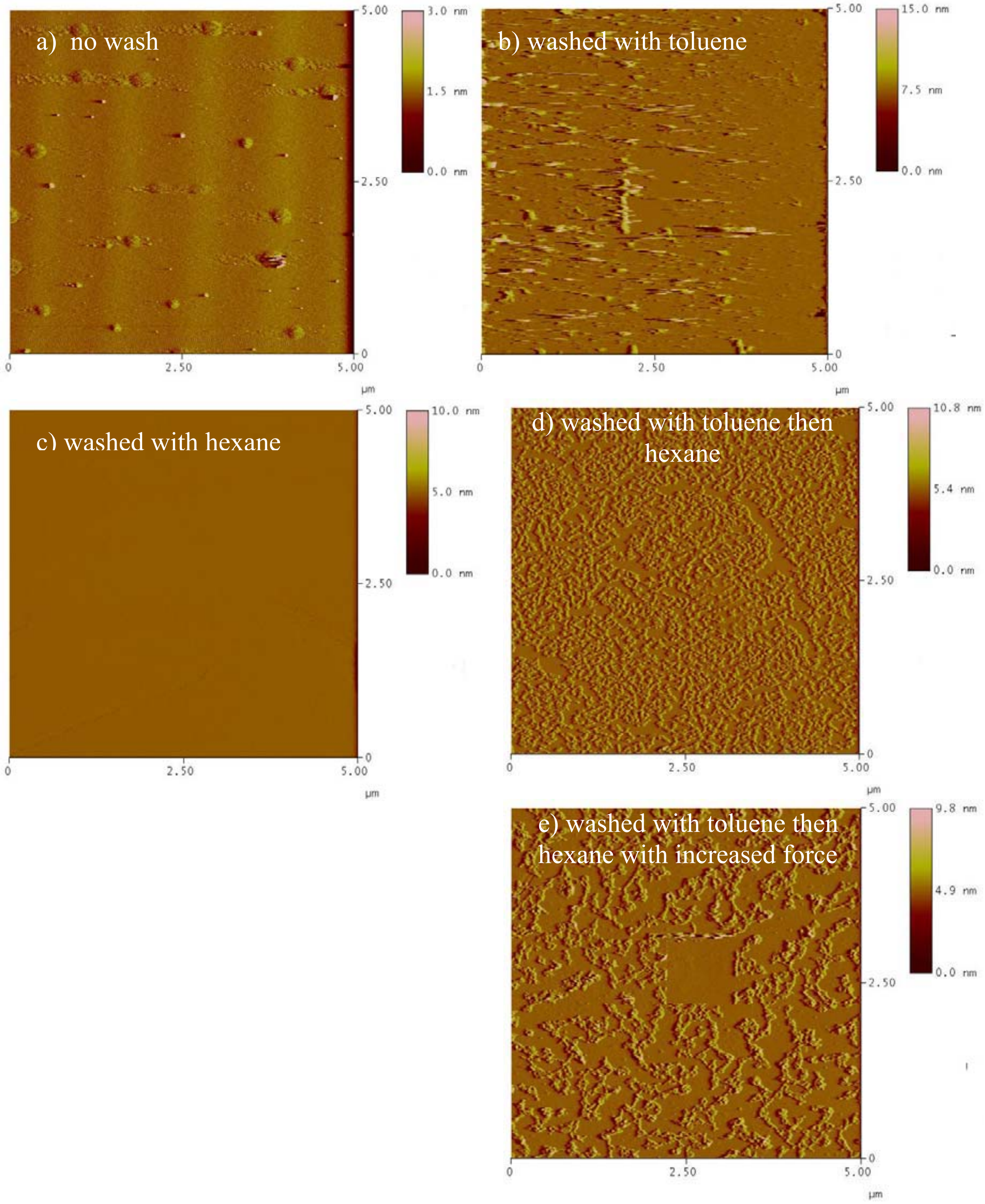


Figure O-1. AFM images of mica exposed to CAM-2 pre-equilibrated with water imaged under air a) non-washed surface, and surface washed with b) toluene, c) hexanes, and d) and e) washed with toluene then hexane.

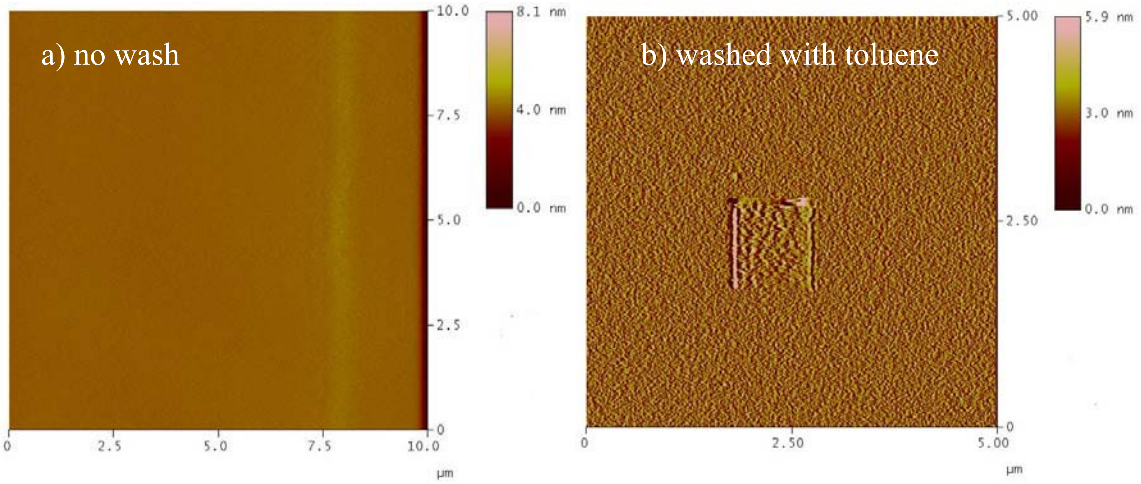


Figure O-2. AFM images of mica exposed to TAM-2 a) no wash and b) washed in toluene in contact mode.

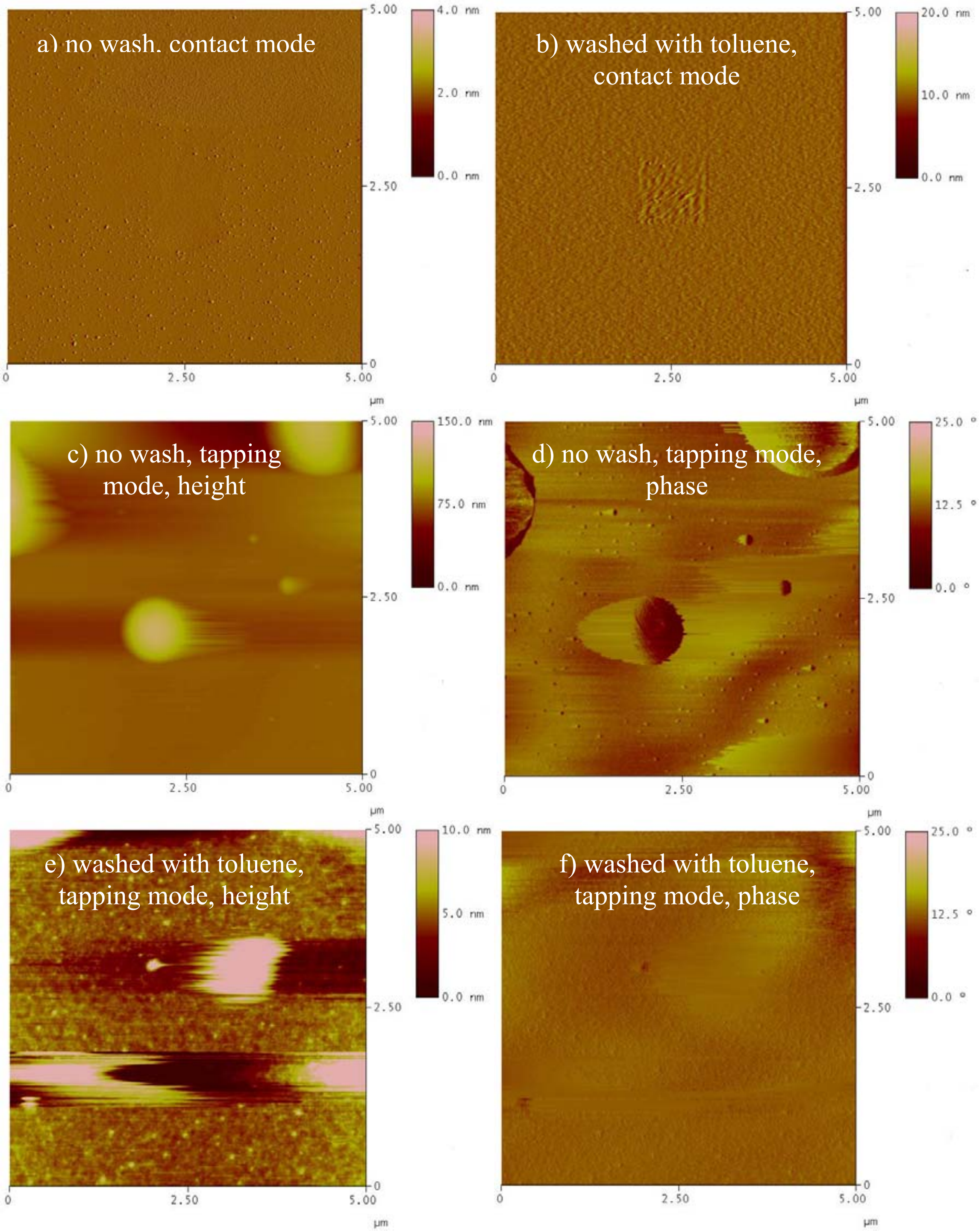


Figure O-3. AFM images of mica exposed to TAM-5 a) no wash (contact mode), b) washed with toluene (contact mode), c) no wash (tapping mode, height signal), d) no wash (tapping mode, phase signal), e) washed with toluene (tapping mode, height signal), and f) washed with toluene (tapping mode, phase signal).

Appendix P : AFM images of mica exposed to CAM-2, TAM-2, or TAM-5 pre-equilibrated with pH 4 buffer.

Figures P-1- P-3 show the AFM images of mica exposed to CAM-2, TAM-2, or TAM-5, respectively, pre-equilibrated with pH 4 buffer. Figure P-1a shows the mica surface after it had been exposed to CAM-2 that had been pre-equilibrated with pH 4 buffer. This image looks similar to that of clean mica. This could have been a result of the decane not being dry. Figure P-1b shows the mica surface after it had been washed with toluene. The features are presumably surfactant on the surface. Figure P-1c shows the mica surface after it had been washed with toluene with a 1-μm image taken with an increased force. The apparent piling of the surfactant on the left hand side of the image shows that the surfactant was easily movable and therefore was not tightly bound to the mica surface.

Figures P-2a and P-2b show the mica surface that had been treated with TAM-2 pre-equilibrated with pH 4 buffer then washed with hexane imaged in tapping mode. There appeared to be a complete coverage of the surfactant on the surface of the mica. Figures P-2c and P-2d show the mica surface after it had been washed with toluene and imaged in tapping mode. There appears to be more surfactant on the toluene-washed surface than on the hexane-washed surface. This could be due to the fact the surfactant is more soluble in hexane, therefore the surfactant could have been partially washed off the surface when washed with hexane. The square in the middle of both of the phase signal images (Figures P-2b and P-2d) are from imaging at a smaller scan (1 μm). This suggested the surfactant was fairly easy to flatten on the surface of the mica and therefore is not too tightly bound.

Figures P-3a and P-3b show the mica surface after it had been treated with TAM-5 pre-equilibrated with pH 4 buffer then washed with hexane and imaged in tapping mode. There appeared to be complete coverage of the surfactant on the surface of the mica. Figures P-3c and P-3d show the mica surface after it had been washed with toluene. These two images look fairly similar. The boxes in Figures P-3b and P-3d are again from imaging at a smaller scan, therefore it was concluded the surfactant was easily moved on the surface of the mica.

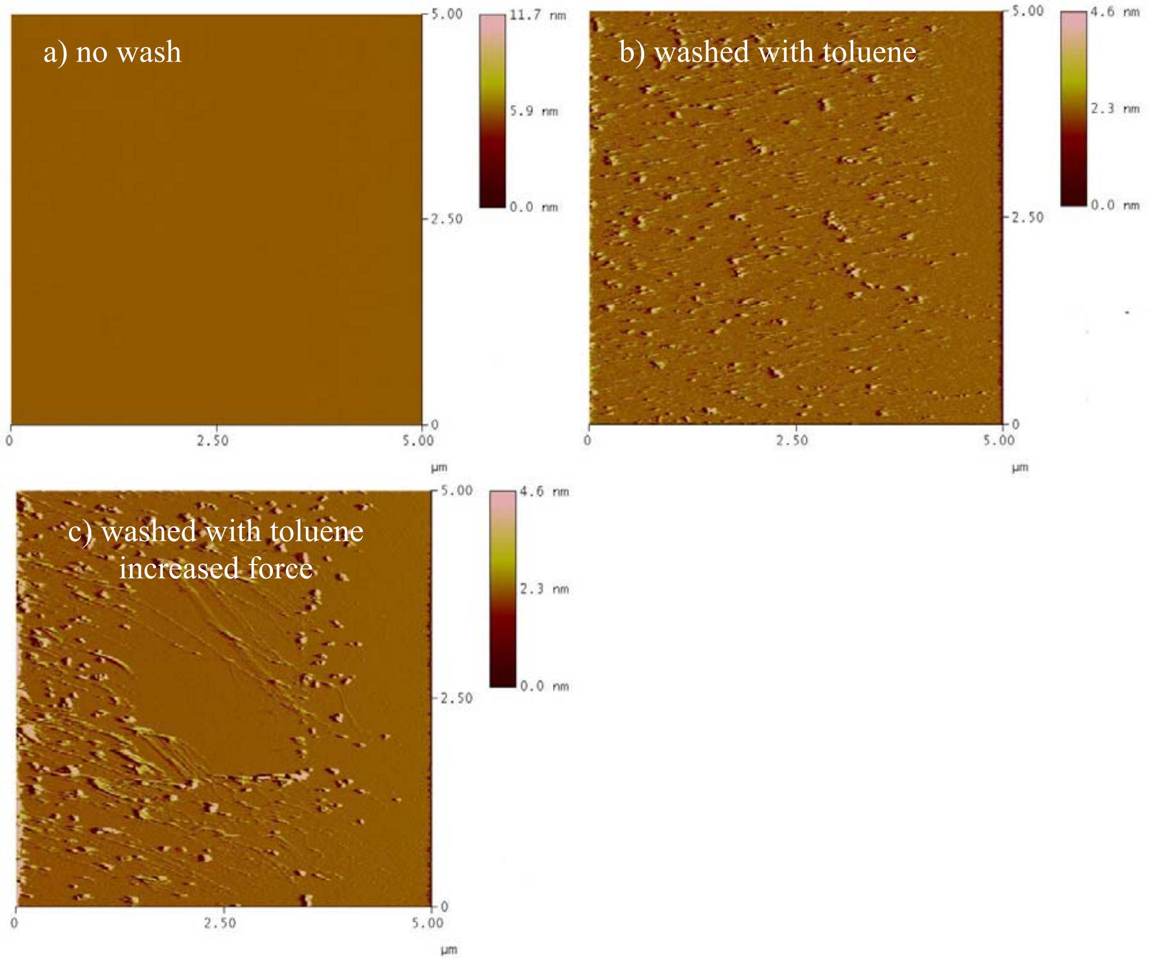


Figure P-1. Contact mode AFM image of mica exposed to CAM-2 pre-equilibrated with pH 4 buffer a) no wash and b) and c) washed with toluene.

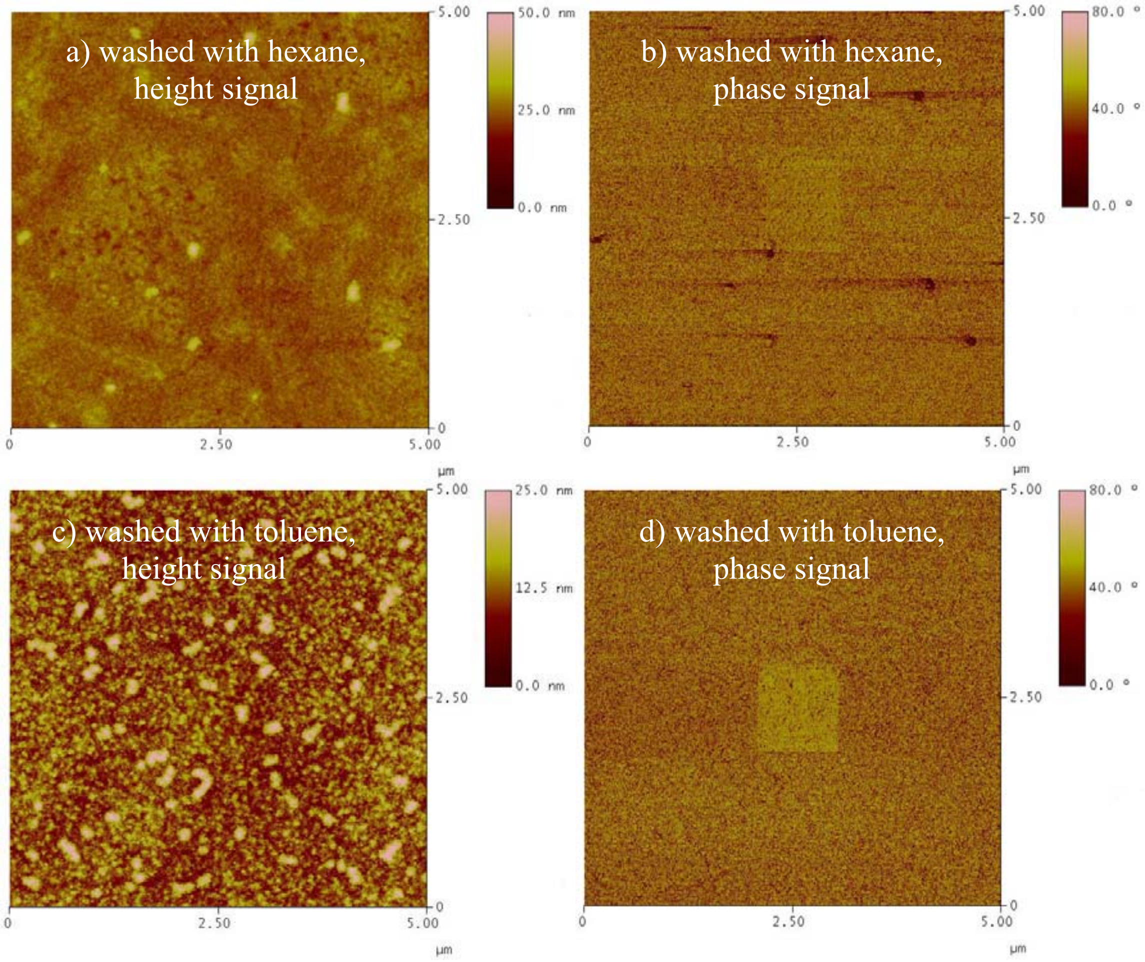


Figure P-2. Tapping mode AFM images of mica exposed to TAM-2 pre-equilibrated with pH 4 buffer washed with a) hexane (height signal), b) hexane (phase signal), c) toluene (height signal), and d) toluene (phase signal).

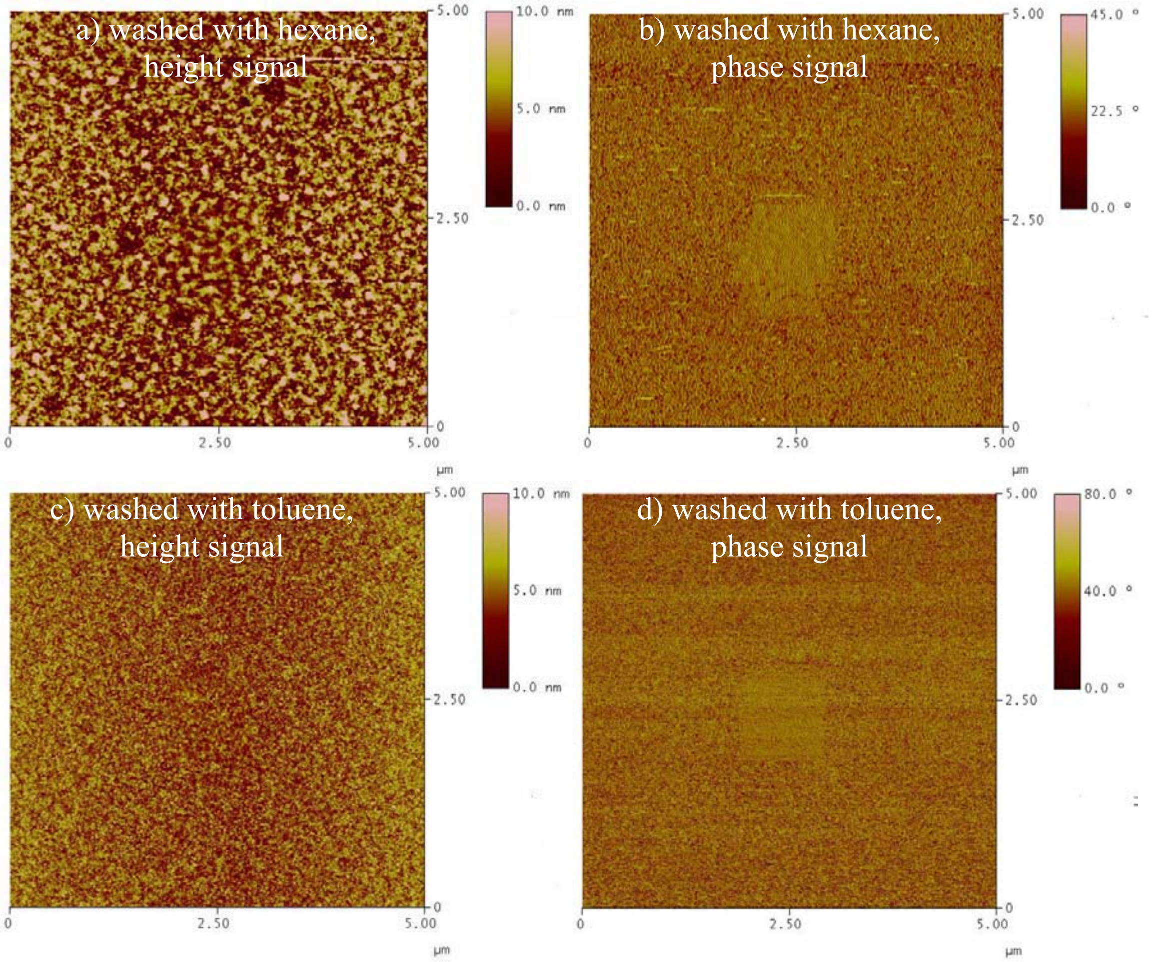


Figure P-3. Tapping mode AFM images of mica exposed to TAM-5 pre-equilibrated with pH 4 buffer washed with a) hexane (height signal), b) hexane (phase signal), c) toluene (height signal), and d) toluene (phase signal).

Appendix Q : AFM images of mica exposed to CAM-2, TAM-2, or TAM-5 pre-equilibrated with pH 8 buffer.

Figures Q-1 – Q-3 show the AFM images of mica exposed to CAM-2, TAM-2, or TAM-5, respectively, pre-equilibrated with pH 8 buffer. Figure Q-1a shows a mica surface that had been treated with CAM-2 pre-equilibrated with pH 8 buffer. There appears to be nothing on the surface except two circular features. This could be due to the fact the decane was not dried and therefore when the surface was imaged the features on the surface were all scraped off. Figures Q-1b, Q-1c, and Q-1d show the mica surface after it had been washed with toluene. There is complete coverage of the mica surface by what is presumed to be surfactant with a couple of large features which could possibly be toluene or even decane that was not dried. Figure Q-1c had a square feature in the middle of the image, which was due to an earlier scan at 1 μm without increasing the force, whereas Figure Q-1d shows a case where the force was intentionally increased. The ease of alteration of the surface by the tip suggested the surfactant was not tightly bound to the mica surface.

Figures Q-2a and Q-2b show the AFM images of mica exposed to TAM-2 pre-equilibrated with pH 8 buffer imaged in tapping mode. There were some features on the surface which were presumed to be surfactant. Figures Q-2c and Q-2d show the mica surface after it had been washed with hexane and Figures Q-2e and Q-2f show the mica surface after it had been washed with toluene. The images look fairly similar and have more features than the non-washed surface. This is presumed to be because the non-washed surface was likely not dried and therefore when it was imaged the tip scraped off most of the features on the surface. Figures Q-2g and Q-2h show the mica surface after it had been washed with acetone and imaged in tapping mode, while Figure Q-2i shows the mica surface after it had been washed with acetone imaged in contact mode. The images do not look similar to the mica surface washed with hexane or toluene, but the image size for the acetone-washed surface is smaller (1 μm for acetone and 5 μm for hexane and toluene). A larger image of the acetone-washed surface that would have been more directly comparable was not taken.

Figures Q-3a and Q-3b show the AFM images of mica exposed to TAM-5 pre-equilibrated with pH 8 buffer washed with hexane imaged in tapping mode, while Figures Q-3c and Q-3d show the AFM images of mica exposed to TAM-5 pre-equilibrated with pH 8 buffer washed with toluene imaged in tapping mode. The images looked similar. It was assumed there was complete coverage of the surfactant on the surface of the mica. The square feature in the middle of the images was due to imaging of a smaller 1 μm scan. This suggested the surfactant was not bound tightly to the surface of the mica.

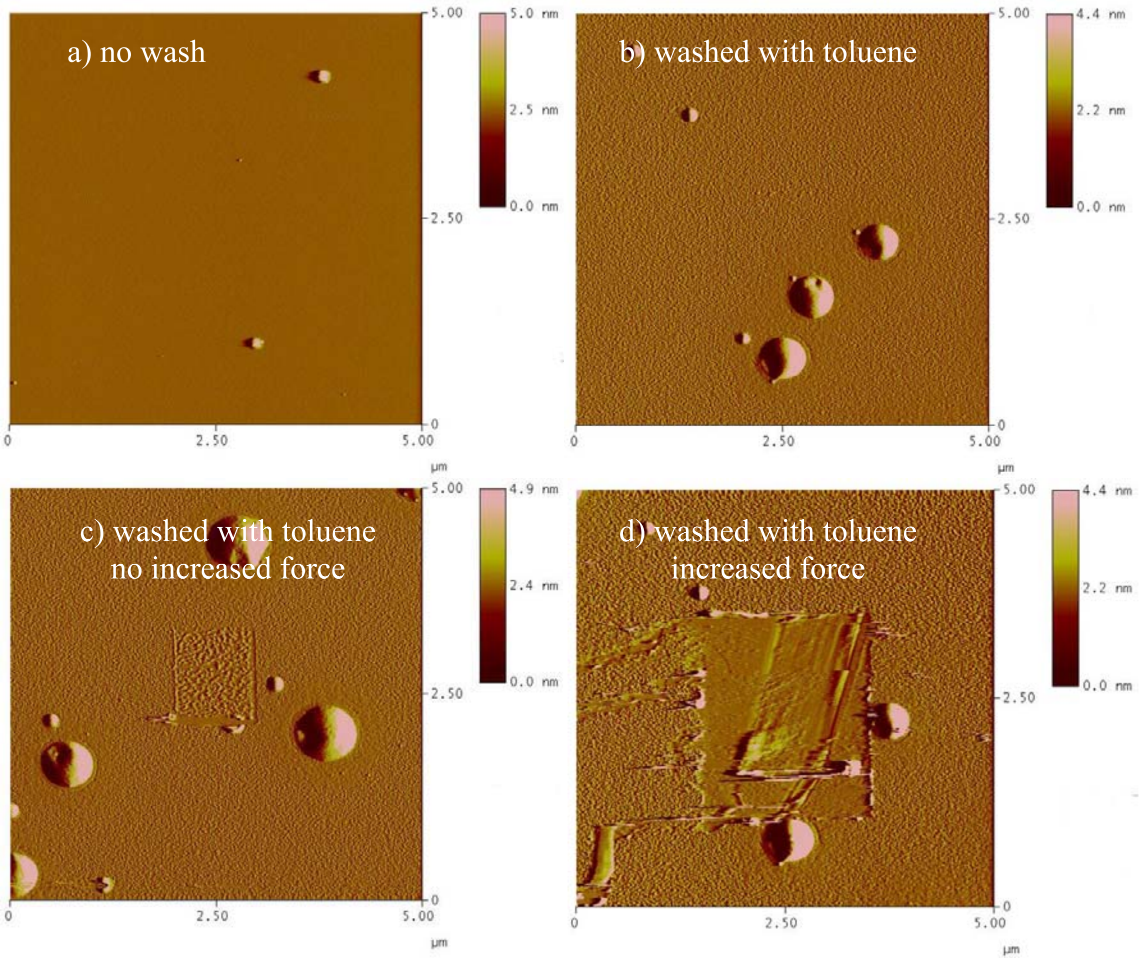


Figure Q-1. Contact mode AFM images of mica exposed to CAM-2 pre-equilibrated with pH 8 buffer a) no wash, b) washed with toluene, c) washed with toluene with an initial smaller scan shown, and d) washed with toluene with a scrapped portion of the image.

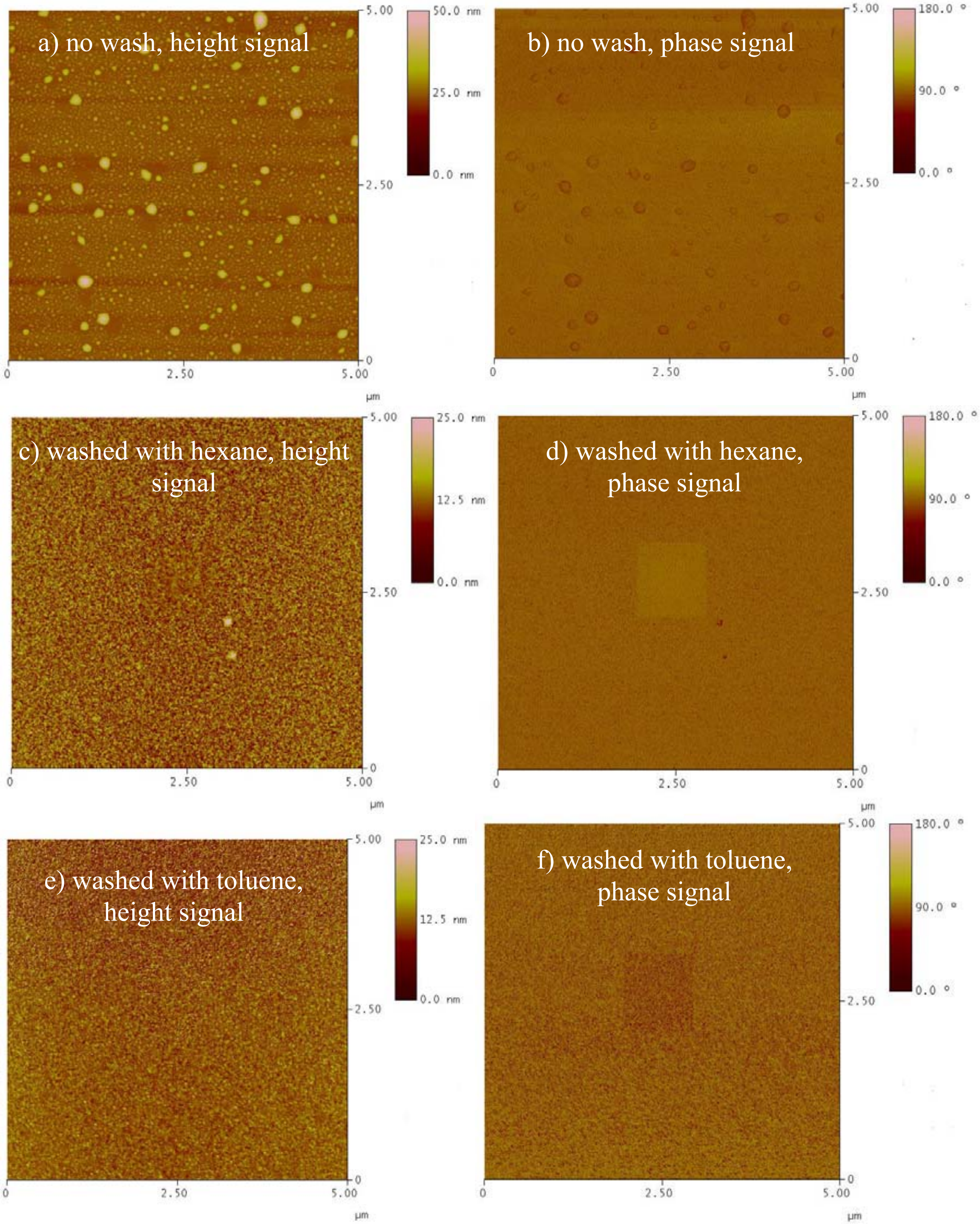


Figure Q-2. Tapping mode AFM images of mica exposed to TAM-2 pre-equilibrated with pH 8 buffer a) no wash (height signal), b) no wash (phase signal), c) washed with hexane (height signal), d) washed with hexane (phase signal), e) washed with toluene (height signal), f) washed with toluene (phase signal).

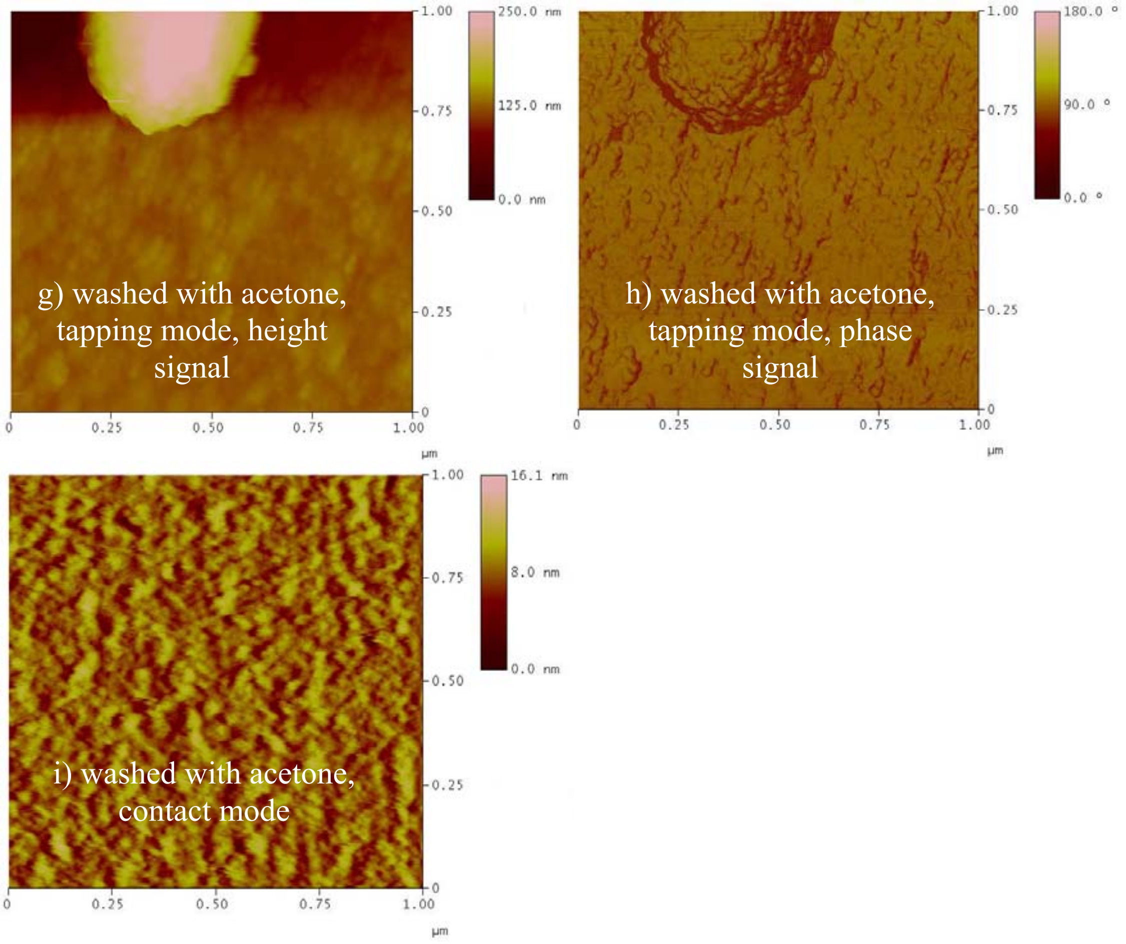


Figure Q-2 cont.

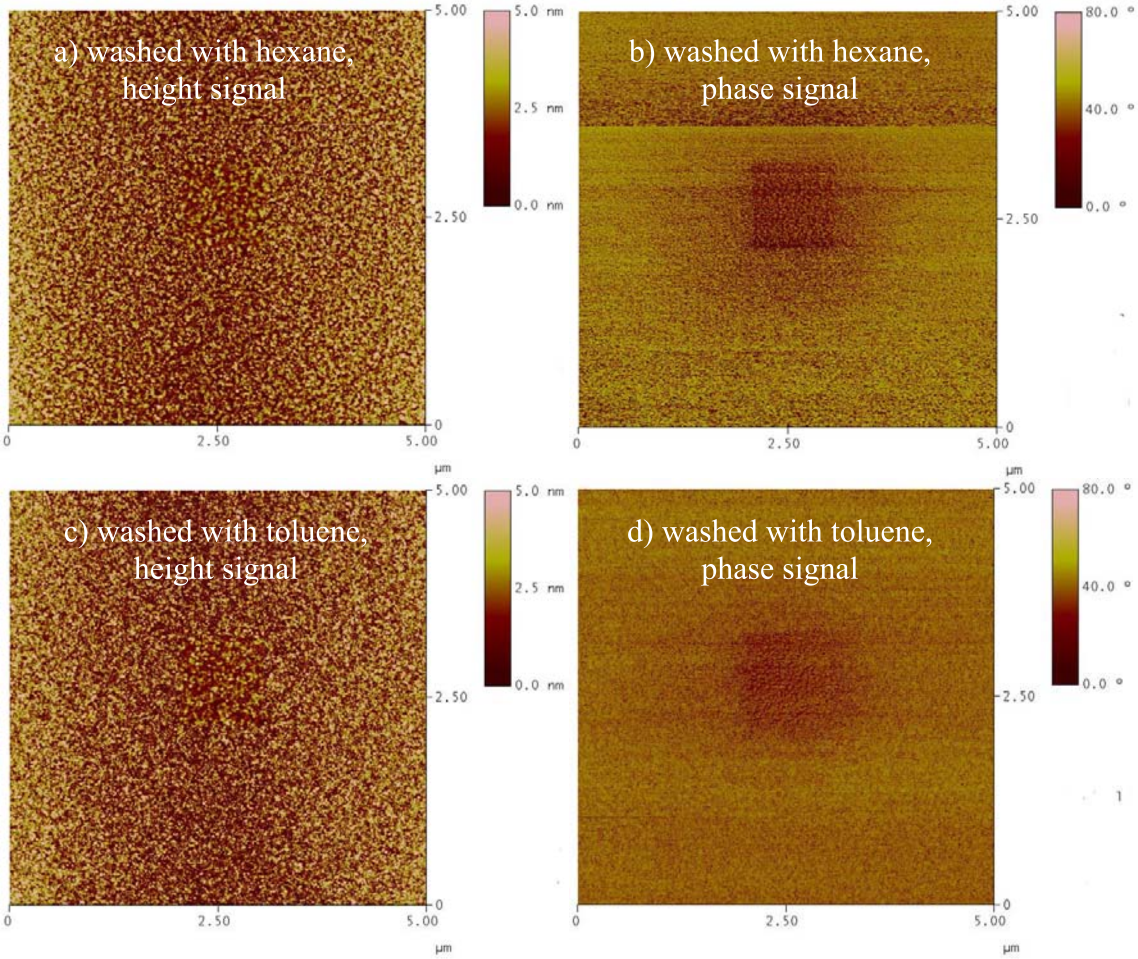


Figure Q-3. Tapping mode AFM images of mica exposed to TAM-5 pre-equilibrated with pH 8 buffer washed with hexane a) height signal and b) phase signal and toluene c) height signal and d) phase signal.