The interaction forces provided by silicone polyether (SPE) surfactants, adsorbed at the interface of octadecyltrichlorosilane monolayer and aqueous surfactant solution, were measured by atomic force microscopy. Changes in the forces in the presence of ethanol were examined for a series of comb-type SPE surfactants. It was found that the steric repulsion provided by the SPE molecules persisted up to an 80% or higher ethanol level. Conversely, conventional hydrocarbon surfactants such as dodecyl polyoxyethylene ether lose their interfacial activity at much lower ethanol levels. The force measurement results were compared favorably with the findings from emulsion-stability and interfacial-tension measurements. The difference between the conventional hydrocarbon surfactants and the SPE surfactants is attributed to the polysiloxane moiety being hydrophobic but not oleophilic. The polyoxypropylene units in the polyether chain were found to add unique characteristics to the surface behavior of the SPE surfactants by modifying the hydrophile's solubility in the alcoholic media. The surface activity and colloidal stability can be fine-tuned by the ratio of polyoxypropylene to polyoxyethylene. In general, emulsion and colloidal products and processes that contain alcohol or other nonaqueous media will benefit from the unique properties of this special class of SPE surfactants.

Key Words: surface forces; silicone surfactant; amphiphilic polymer; emulsion; colloidal stabilization; atomic force microscopy.

INTRODUCTION

The applications of silicone surfactants range from the manufacture of polyurethane foam to coatings; household, personal-care, and cosmetic products; and foam control and wetting agents (1). One of their applications as emulsifiers and stabilizers, in particular, has gained considerable market importance over the past decade. Silicone emulsifiers and stabilizers perform better than their hydrocarbon counterparts in cases where their unique silicone characteristics are utilized. For example, the siloxane chain is highly flexible, which enables molecules of high molecular weight to reach equilibrium configurations at interfaces in a short time. The siloxane moiety of sufficient length is hydrophobic and oleophobic, which allows for application in both aqueous and nonaqueous emulsions. The versatility of silicone surfactants comes from the many organic functional groups that can be incorporated into the molecule. Currently, silicone polyethers (SPEs) are the most commonly used silicone surfactants. SPEs consist of one or more polyoxyalkylene chains, most commonly homopolymers or copolymers of polyoxyethylene and polyoxypropylene, attached to the siloxane hydrophobe. The structure of SPEs can be either comblike with the polyoxyalkylene chain side-grafted to a siloxane backbone, or linear, either of the AB type or the ABA type, with A representing the polyoxyalkylene hydrophile and B the siloxane hydrophobe. Oligomeric and polymeric SPEs prove to be more effective emulsifiers and stabilizers and are believed to adsorb strongly at interfaces with multisegment attachments. For instance, in oil-in-water emulsions, the polysiloxane portion attaches to the oil phase while the polyoxyalkylene chains provide steric stabilization.

This study stems from a need to design surfactants for optimum colloidal or emulsion applications. Industrial emulsions are prepared largely on a trial-and-error basis. It is indeed difficult to optimize emulsifier formulations, since industrial emulsions contain many components in addition to oil and water. It is found that a mixture of surfactants often works better than a single, pure surfactant. In order to implement new experimental techniques and gain fundamental insights into the optimization of industrial emulsions, we carried out surface-force, interfacial-tension (IFT), and emulsion-stability measurements using industrial-grade silicone surfactants. The hydrophile chain length and the solvent quality were varied gradually and independently. Despite the presence of impurities and polydispersity, our study shows that data comparison from different surface-characterization techniques can delineate contributions from specific molecular moieties. This study was also initiated by the discovery that oil-in-water emulsions made by certain SPEs are stable against salts, alcohols, and other organic solvents (2). The behavior of SPEs in this case differs significantly from that of hydrocarbon surfactants. Salts, alcohols, and solvents are in fact routinely used to break emulsions made with hydrocarbon surfactants in order to extract the contents. We characterized a
series of SPE surfactants in order to understand the fundamental attributes that differentiate this class of SPE surfactants from the conventional hydrocarbon surfactants in media that contain a significant amount of alcohol. The understanding will impact many products or processes that involve alcohol or other non-aqueous mixtures used in personal, household, and automotive care, in coatings, and in petroleum industries.

The surface forces between adsorbed polymers play an important role in colloidal and emulsion stabilization (3). In this study, the force curves were measured in a liquid cell using atomic force microscopy (AFM). AFM (4) is a force-measuring device complementary to the traditional surface forces apparatus (SFA) (5). For a long time, SFA has been the primary technique used to measure the forces between adsorbed polymers on mica (6, 7) and surface interactions in micellar, emulsion, and liposome solutions (8, 9). It is found that the interaction between the solvated segments at opposing surfaces in a good solvent is monotonically repulsive. This steric repulsion between adsorbed polymers is the primary colloidal stabilization mechanism of polymers, and it is believed to originate from the osmotic interactions and solvent exclusion. The experimental results have generally agreed with theoretical predictions (10). The primary difference between AFM and SFA force measurements is the radius of curvature of the interacting area prior to contact, around 10,000 μm for SFA, 5 μm for AFM with a colloidal tip, and 0.02 μm for AFM with a commercial silicon nitride tip. Therefore, AFM force curves tend to be shallower in the region of high compression than those from SFA, and more sensitive to solvent quality and film inhomogeneity (11, 12). Because of its high spatial resolution and ease of operation, increasing numbers of polymer adsorption studies have been carried out by AFM. For example, steric repulsions were measured between adsorbed micelles and hemimicelles of nonionic dodecyl polyoxyethylene surfactants C_{12}E_n (n = 5–23) (13–15). C_{12}E_n film was believed to be removed from the contact zone at a discontinuity point during compression, called the jump-in point. The presence of the jump-in allows the film thickness to be estimated. In the study by Eskilsson et al. (16), poly(oxyethylene)-polytetrahydrofuran-poly(oxyethylene) adsorbed on hydrophilic silica largely as micelle-like aggregates. The surface aggregate size was found to decrease with increasing hydrophilic chain length as a result of competitive single molecule adsorption. The steric force profiles of polymer films do not always display the jump-in point. For example, the jump-in was not observed between polyacrylic acid (molecular weight = 750,000) adsorbed at zirconia surfaces (17). In this case, the layer thickness was estimated from the onset of the repulsion to the region of high and constant compliance. In the study of the adsorption of block copolymer poly(oxyethylene)/polystyrene (18), the onset of the repulsive force measured by AFM was consistent with the film thickness measured by SFA and neutron reflection. However, the AFM force curves were shallower, displayed a discontinuity near the substrate, and varied with topography compared with those from SFA. Review of the literature concludes that AFM even with the commercial tip is capable of providing quantitative spatial and height analysis of adsorbed polymer films.

In this study, AFM was employed to measure the interaction between an AFM silicon nitride tip and a methyl-terminated surface in the solution of comb-type SPE surfactants above the critical micelle concentration (CMC). The methylated surface was created by depositing a self-assembled monolayer (SAM) of organosilane on an oxidized silicon wafer. The adsorbing chain of the SPE is the polysiloxane backbone and the nonadsorbing chain is the cooligomers of oxyethylene and oxypropylene. The ratio of the two in the side chains was varied. The solvent quality was raised gradually by the addition of ethanol to water. Therefore, the effects of molecular chain structure and solvent on the steric repulsion curves can be studied separately. We also tried to relate the steric repulsion curves to emulsion-stability and IFT data where SPE surfactants were used as the emulsifiers for oil-in-water emulsions in the absence and in the presence of ethanol.

**MATERIALS AND METHODS**

**Materials.** Polished silicon (111) wafers (test grade, N-type with resistivity of 1–2 Ω·cm) were purchased from Wafer World. n-Octadecyltrichlorosilane (OTS) was purchased from United Chemical Technologies and vacuum distilled before use. USP grade 190-proof and 200-proof ethanol were purchased from Pharmco Products and AAPER Alcohol and Chemical Co., respectively. Carbon tetrachloride (>99.9%, HPLC grade) and n-hexadecane (>99%) were purchased from Aldrich. Chloroform (99.9%) was purchased from Fisher Scientific. Deionized water with resistivity of 18 MΩ·cm was obtained from Barnstead Nanopure System. Polyoxyethylene dodecyl ether C_{12}E_{23} (Brij35) was purchased from Aldrich. The SPE surfactants were synthesized by Michael R. LaFore of the Dow Corning Corporation, Midland, MI, and used without further purification. The general chemical structure of the SPEs is illustrated in Scheme 1, and the nominal values for x, y, m, n, and Cap are listed in Table 1, where x, y, m, and n are average numbers for the degree of polymerization in the copolymers. In this paper, we use the abbreviation Comb-\(m\)-\(n\)-Cap. \(m\) and \(n\) are the numbers of oxyethylene (EO) and oxypropylene (PO) repeating units in the side chain, respectively, and Cap denotes the end-cap functional group of the side chain. The siloxane backbone is the same in all the SPEs studied here. The concentration of all SPE solutions

![Scheme 1](image-url)
studied was fixed at 0.2% w/w, above the CMC of the SPE surfactants (CMC = 0.134% w/w for Comb-18-18-OH), while the ethanol-to-water ratio was varied gradually. All the SPE solutions were used within 1 week of preparation. The solution was filtered by a syringe-driven filter unit with a pore size of 0.45 μm (Millipore Co.) prior to injection into the AFM liquid cell. The pH of the solution was measured to be between 3.84 and 8.07 (Cole–Parmer pH benchtop meter).

**Substrate surface treatment.** The silicon wafer was cut to around 1 × 1 cm², and the pieces were rinsed with water and acetone, followed by the RCA clean procedures described previously (19). The treated substrate has a water contact angle close to zero (NRL contact angle goniometer, Model 100, Rame–Hart). The wafer pieces were then immersed in the OTS solution for 10 min. The wafer substrate after OTS deposition has a water contact angle between 104° and 109°. The characterization of the OTS monolayer was reported previously (19). The OTS substrate was stored in water prior to use. Its water contact angle was checked before and after an AFM experiment.

**Emulsion preparation and stability study.** A typical recipe for the preparation of the oil-in-water emulsion is as follows. (i) Part A was mixed in a container at 80°C. It contained 12 g of stearic acid (Hystrene 4516, Witco), 12 g of glyceryl stearate and PEG-100 stearate (Arlacel 165, ICI), and 30 g of mineral oil light. (ii) Part B was mixed in another container at 60°C. It contained 406.6 g of water and 7.4 g of triethanolamine (85% active in water). (iii) Part A was poured into part B, and the mixture was agitated with a mixer at 400 rpm at 60°C for 0.5 h and then cooled to room temperature. This is called the thick phase. (iv) Part C was made in a separate container. It contained 120 g of water and 12 g of SPE surfactant or polyoxyethylene dodecyl ether C12E23. (v) The mixture made in step (iii) was poured into part C, and the final emulsion was agitated with a mixer at 350 rpm for 0.5 h. The above procedures were repeated for each of the SPEs. An emulsion-stability test was conducted by slowly adding an ethanol and water mixture to the emulsion while stirring. The final mixture was left standing for observation of phase separation.

**Interfacial tension measurement.** Liquid/liquid interfacial tensions were measured using a drop volume tensiometer (model DVT-10, Kruss). Hexadecane (99%, Fluka) was used as the oil phase and surfactant solution in the water/ethanol mixture was used as the other phase. Measurements were conducted at a flow rate of 0.5 cm³/h.

**RESULTS AND DISCUSSION**

The adsorption of surfactants was studied by directly measuring the surface force versus surface separation profile between a hydrophobic OTS monolayer on oxidized silicon and a silicon nitride AFM tip in the water/ethanol solution containing 0.2% w/w surfactant. The hydrophobic substrate was chosen so that we can estimate the interaction barrier due to surfactant adsorption at water/particle and water/oil droplet interfaces, since it is difficult to measure forces between spheres in emulsions and colloidal dispersions. The Derjaguin approximation (21) allows the interparticle interaction potential energy to be calculated from that between a particle and a flat surface, as in the AFM force measurement. The data presented here address the effect of molecular-chain composition and solvent quality on the force-versus-separation profile, and the role of interaction barrier on emulsion stability provided by the SPE surfactants. In order to compare the behavior of SPEs with that of hydrocarbon surfactants, we also chose to study C12E23 (Brij35).

Before the discussion of force curves in various surfactant solutions, it is necessary to describe the interaction between the bare OTS substrate and AFM tip in pure water. A typical force curve is presented in Fig. 1. The measured force curve is plotted together with the van der Waals (VDW) interaction calculation.
FIG. 1. Force curves measured by AFM and calculated by van der Waals theory interaction between an AFM tip and OTS monolayer in pure water. The arrow indicates the jump-in. (22). The force curve displays pure attraction at a surface separation of 10 nm. The jump-in point, marked by the arrow, is caused by spring mechanical instability (i.e., force gradient larger than spring constant). This jump-in distance is larger than that resulting from pure VDW attraction (<5 nm) presumably owing to the hydrophobic OTS surface.

AFM imaging of both C₁₂E₂₃ and SPEs in the soft-contact mode (14, 15) yielded flat, featureless images. This means that the surfactants either from planar structure on OTS monolayer or the structure is too mobile to be imaged. The force measurement was reproducible from one area to another, which suggests that the adsorbed surfactant structure is uniform at the nanometer scale. The force curves in various surfactant solutions are presented in Figs. 2–5. The surfactant adsorption on the AFM silicon nitride tip is unknown. Our study of nonionic hydrocarbon and silicone polyoxyalkylene surfactants found that they generally form a thin, disorganized layer on oxidized silicon. The adsorption of the SPE surfactants on the AFM tip, whose composition is similar to that of oxidized silicon, should be significantly less than on the OTS surface. Here we assume that the monotonous repulsion comes largely from the adsorbed layer on the OTS surface. In most cases, the force-versus-distance curves showed a discontinuity in data acquisition near the maximum force value. After the jump-in process, the high-compliance region was reached, where the deflection is linear with the expansion of the piezoelectric crystal. The surfactants were either highly compressed into an incompressible state or were pushed out of the contact zone. Previous study of polyoxyethylene surfactants suggests that most physically adsorbed surfactant molecules are removed from the contact zone (15). Here we ignore the thickness of the surfactant film if any is left in the contact zone after the jump-in, and we determine the adsorbed film thickness by the separation distance at the onset of the steric repulsion. In order to select the force onset uniformly, we arbitrarily use the separation value at a force of 0.2 nN. This separation value corresponds to the thickness of an “uncompressed” film, also called the barrier thickness. The magnitude of the steric force maximum near the jump-in point corresponds to the force necessary to remove the physically adsorbed layer from the contact zone. The height of the repulsive force barrier was shown to be equal to the surface pressure exerted by the adsorbed surfactant films (23). It is proportional to the binding strength of a surfactant molecule to the substrate times the surface density of the surfactant. The rate of colloidal coagulation is found to increase with the magnitude of the energy barrier. In order to extract useful information from the force curves, we tabulate both magnitude and thickness of the steric force barrier.

In Fig. 2, the steric repulsion of C₁₂E₂₃ started at 11 nm and increased monotonically until the jump-in point at 4 nm, when ethanol was between 0 and 23% v/v in the water/ethanol mixture. The maximum force barrier in pure water was about 14 nN. The adsorption behavior of C₁₂E₂₃ is similar to that found on graphite surface (14). On graphite, AFM imaging showed a flat surface with the onset of repulsion around 9.5 nm, identical to the fully extended polyoxyethylene hydrophilic chain length. However, the thickness of polyoxyethylene films measured by neutron reflection at a hydrophobic solid surface (24) and X-ray reflection at the air/water interface (25, 26) is smaller than that measured by AFM. Several factors may contribute to this discrepancy. (i) C₁₂E₂₃ may form a micelle- or bilayerlike structure on the hydrophilic AFM tip. Our study on small-molecular-weight triblock type of silicone polyether surfactants showed that these surfactants form a thin layer (<2 nm) on oxidized silicon that can be continuously compressed by the AFM tip (27). The lack of a second jump-in point also suggests that either C₁₂E₂₃ adsorbs little on the tip or the adsorbed film on the tip is not removed from the contact zone. It is possible that the film on the tip may add up to 2 nm to the apparent film thickness. (ii) The other factor is the polydispersity of the sample that tends to lengthen the tail portion of the force curve. Despite the uncertainty in the exact film thickness, it can be concluded that C₁₂E₂₃ forms a monolayer at the OTS surface.
since a trilayer film of C$_{12}$E$_{23}$ on OTS does not agree with the force curve measured here. The steric repulsion decreased gradually with increasing ethanol content. In the same range, the data showed that the film thickness changed only slightly with alcohol. Assuming the force-barrier height is proportional to the adsorbed amount, as shown in the study of Eskilsson et al. (23) on the adsorption of low-molecular-weight triblock surfactants on hydrophobic surfaces, we can conclude that the addition of alcohol reduces the amount of surfactant at the interface without affecting the extended chain configuration of the adsorbed surfactant. Organic solvents such as alcohol solubilize hydrocarbon moieties and therefore reduce their attraction to the hydrophobic surface, while the film thickness is mostly determined by the hydrophilic polyoxyethylene configuration that is expected to extend into a good solvent such as water or water/ethanol mixture. At about 30% or more ethanol, the repulsion was completely diminished. This agrees well with the typical behavior of conventional hydrocarbon surfactants. Nonionic surfactants lose their surface activity and the ability to form micelles in the presence of 25% ethanol (28).

Figures 3–5 are the force curves of three SPEs on OTS substrate as a function of ethanol percentage. Figures 6 and 7 summarize the force barrier magnitude and thickness values. All display monotonic repulsions up to the jump-in point, as in the case of C$_{12}$E$_{23}$ in pure water. The maximum force barrier ranges from 1.3 to 3.2 nN, much smaller than that of C$_{12}$E$_{23}$. The long backbone of a comb-polymer probably prevents close packing of polyoxyalkylene chains. The film thickness of SPEs in water is slightly larger than that of C$_{12}$E$_{23}$. The film thickness is also larger than the calculated side chain length assuming fully extended configuration of the polyoxyethylene units. It is likely that the adsorbed SPEs form aggregates rather than monolayers. However, the film thickness should be contributed mostly by the hydrophilic moieties of the surfactants. Polydispersity of the SPE samples may also contribute to the longer than expected film thickness. It is interesting that the barrier thickness values for the three SPE surfactants are similar to each other at low ethanol content (~12 nm), and diverge to reflect the expected chain length values only at high alcohol content (~11 nm for Comb-18-18-OH and Comb-21-21-OAc, and 7 nm for Comb-10-4-OH). The fully extended chain lengths of Comb-21-21-OAc, Comb-18-18-OH, and Comb-10-4-OH, including both oxyethylene and oxypropylene units, were calculated to be 16, 13, and 5 nm, respectively. This first suggests extended chains when solvent quality is improved by ethanol. It also hints at an aggregate-like structure at low ethanol content, and a monolayer structure at high ethanol content. The SPE adsorption behavior in water/ethanol mixture differs from that of C$_{12}$E$_{23}$. In Fig. 3, the repulsive barrier in Comb-10-4-OH decreases monotonically with increasing ethanol/water ratio as expected, but remains positive (0.5 nN) up to 70% v/v ethanol. This is true for all three SPEs studied here. The surface activity of silicone surfactants in organic solvents is largely due to the oleophobic property of siloxane. The fact that the surface activity of the SPEs is
not completely diminished by a significant amount of ethanol makes them ideal emulsifiers and stabilizers in the formulations containing alcohol, such as fixative hairsprays.

Within the silicone surfactant class, we investigated whether some SPEs are better than others in alcoholic media. The emulsion system is more stable and versatile if its emulsifier can maintain its surface activity in a wide range of organic content. Here we compare surfactants with the same siloxane backbone but different side chains. In Fig. 3, the steric barrier of adsorbed Comb-10-4-OH decreased both in magnitude and thickness with increasing ethanol content. In Figs. 4 and 5, there was no significant decrease in the adsorption of Comb-18-18-OH and Comb-21-21-OAc, as determined by both the barrier height and thickness. In fact, the adsorption seemed to increase with ethanol content in low-to-intermediate ethanol content. The steric barrier height reached a maximum of between 20 and 40% v/v ethanol, while the barrier thickness remained almost constant up to 80% v/v ethanol. The effect of end caps (i.e., hydroxy (OH) versus acetoxy (OAc)) was investigated by comparing the force curves for Comb-18-18-OH and Comb-18-18-OAc. The two sets of force curves overlapped each other closely, with the Comb-18-18-OAc showing a slightly higher steric barrier (2.3 nN for Comb-18-18-OAc and 1.7 nN for Comb-18-18-OH in pure water) and higher film thickness (14.1 nm for Comb-18-18-OAc and 12.5 nm for Comb-18-18-OH). Similar conclusions were obtained in the emulsion-stability and IFT measurements. In summary, the force curves support the findings that silicone surfactants with a good balance of oxyethylene and oxypropylene units in the side chains can improve the tolerance of emulsions or dispersions to organic cosolvents and additives.

Next we compared the force measurement data with those from emulsion-stability and IFT measurements. Emulsion stability in water and water/ethanol mixtures was evaluated for the same group of SPE surfactants. We should point out that the emulsion protocols described under Materials and Methods were not optimized to achieve the maximum stability of the same emulsion system but were used as a quick check of the relative effectiveness of different surfactants. The emulsion stability was followed up to 2 weeks, and the data are tabulated in Table 2. In order to compare the surfactant adsorption at the liquid/solid interface with that at the liquid/liquid interface, we measured the IFT between hexadecane and water/ethanol solutions containing the various surfactants. The IFT data are tabulated in Table 3. In addition to emulsion-stability and IFT measurements, we calculated the hydrophile–lipophile balance (HLB) number and cohesive energy (CER) number for different surfactants. Both sets of numbers are tabulated in Table 2. The HLB number has been used widely as an empirical scale to match emulsifiers with emulsions and applications (29). It should be pointed out that the HLB scale works less satisfactorily with silicone emulsifiers or nonaqueous systems. For instance, some of the SPEs studied here should form water-in-oil emulsions according to their HLB values, but instead they form oil-in-water emulsions. This

<table>
<thead>
<tr>
<th>SPE</th>
<th>HLB&lt;sup&gt;a&lt;/sup&gt;</th>
<th>CER&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Pure water</th>
<th>30% ethanol</th>
<th>80% ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comb-10-4-OH</td>
<td>5.48 0.74</td>
<td>&gt;2 weeks</td>
<td>7 days (R)</td>
<td>20 h (PR)</td>
<td></td>
</tr>
<tr>
<td>Comb-18-18-OH</td>
<td>5.72 0.32</td>
<td>&gt;2 weeks</td>
<td>21 h (R)</td>
<td>19 h (PR)</td>
<td></td>
</tr>
<tr>
<td>Comb-18-18-OAc</td>
<td>5.63 0.31</td>
<td>3 days (R)</td>
<td>19 h (R)</td>
<td>21 h (PR)</td>
<td></td>
</tr>
<tr>
<td>Comb-21-21-OAc</td>
<td>5.93 0.32</td>
<td>6 days (R)</td>
<td>8 days (R)</td>
<td>21 h (PR)</td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;12&lt;/sub&gt; E&lt;sub&gt;23&lt;/sub&gt;</td>
<td>16.9 0.20</td>
<td>&gt;2 weeks</td>
<td>&lt;3 h (R)</td>
<td>&lt;1 min (I)</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> HLB values were calculated by the molecular weight percent of the oxyethylene portion divided by 5.

<sup>b</sup> CER values were calculated by the method developed by Beerbower and Hill (30).

<sup>c</sup> Emulsion samples were prepared and their stability tested following the protocols described under Materials and Methods. R, reversible phase separation (i.e., the emulsion was flocculated instead of coalesced after the indicated amount of time and was redispersible on shaking); PR, partially reversible phase separation; I, irreversible phase separation.
Interfacial Tensions in Dyne/centimeters Between Hexadecane and Various Solutions of Surfactant in Water/ethanol Mixture

<table>
<thead>
<tr>
<th>Ethanol/water (w/w)</th>
<th>Without surfactant C12E23 (0.2 mM)</th>
<th>Comb-10-4-OH (0.2% w/w)</th>
<th>Comb-18-18-OH (0.2% w/w)</th>
<th>Comb-21-21-OAc (0.2% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0:1</td>
<td>47.61</td>
<td>11.12</td>
<td>21.91</td>
<td>17.27</td>
</tr>
<tr>
<td>1:9</td>
<td>31.66</td>
<td>11.83</td>
<td>17.32</td>
<td>12.83</td>
</tr>
<tr>
<td>3:7</td>
<td>16.99</td>
<td>11.90</td>
<td>11.92</td>
<td>10.86</td>
</tr>
<tr>
<td>8:2</td>
<td>5.49</td>
<td>6.26</td>
<td>1.90</td>
<td>3.30</td>
</tr>
</tbody>
</table>

The data show that Comb-18-18 and Comb-21-21 reduce the IFT significantly whereas other surfactants and emulsifiers of other chemical classes do not. In the presence of 30% ethanol, the emulsion broke up instantly and irreversibly. The difference is not surprising since the HLB scale was originally developed for fatty alcohol ethoxylates and later adopted for emulsifiers and surfactants of other chemical classes. On the other hand, the CER number is calculated based on the solubility parameters and therefore provides a measure of the solubility “balance” of the emulsifier between the two phases (30). The CER scale was reported to work better for silicone surfactants and for non-aqueous emulsions than the HLB scale. Nevertheless, the CER method is still oversimplified. One can find cases where different molecules with different molecular structure share the same CER value but display different emulsification efficiency.

From Table 2, we can conclude that C12E23 is an effective emulsifier for oil-in-water emulsion made with pure water. In the presence of 30% ethanol, phase separation occurred 3 h after making of the emulsion, and in the presence of 80% ethanol, the emulsion broke up instantly and irreversibly. The interfacial tension data in Table 3 show that while C12E23 significantly reduces the IFT of oil and water (about 76% of initial value), the reduction became less as the ethanol content was increased (about 63% in 10% ethanol, 30% in 30% ethanol). Finally at 80% ethanol, the presence of C12E23 no longer affected the IFT of oil and water. Further increase in the C12E23 concentration by an order of magnitude did not reduce the IFT. This is typical of conventional hydrocarbon surfactants, nonionic or ionic. They are only effective dispersing agents for water or water with a small amount of organic cosolvents. We attribute the reduced surface activity to an increase in the solubility of the lipophilic part of the hydrocarbon surfactant in the alcohol media. Instead of forming self-associating aggregates or adsorbing at interfaces, surfactant molecules are increasingly solubilized in the bulk phase. Other evidence by cryotransmission electron microscopy showed that micellar aggregates of conventional hydrocarbon surfactants disappear when a significant level of ethanol was reached (31). In the case of C12E23, AFM force measurement indicates complete loss of surface activity below 30% alcohol, while according to the IFT measurement, the surfactant is still somewhat surface active. The difference may suggest that either the AFM has a lower sensitivity to surfactant adsorption or that the surfactant surface activity is lower at the solid/liquid interface than at the liquid/liquid interface with the addition of organic cosolvents.

In contrast, the SPE surfactants are capable of reducing the oil-water IFT even with ethanol as high as 80% of the water phase (Table 3). The emulsions made with SPEs are more stable than those made with C12E23 in intermediate to high alcohol content. Moreover, even when flocculation occurs, SPE-containing emulsions were redispersed on partially redispersed on shaking the solution. On the contrary, the phase separation in emulsions made with C12E23 was irreversible. The difference in emulsion stability between C12E23 and SPEs is supported by both AFM and IFT data. The main difference between a conventional hydrocarbon surfactant and a SPE surfactant is the composition of the hydrophobe. The siloxane chain is both hydrophobic and oleophobic at a molecular weight above 1000, so neither water nor ethanol is a good solvent for the polysiloxane chain. Their aversion toward water and hydrocarbon solvents increases with the siloxane molecular weight. The adsorption of SPEs at interfaces decreases gradually with increasing alcohol content because of the increased solubility. But unlike hydrocarbon surfactants, the surface activity of SPEs is not diminished until close to 100% ethanol in the water phase. Therefore, SPE surfactants can be used to make emulsions to withstand a higher level of alcohol in the formulation. On the other hand, for the same reason that siloxane is not oleophilic, SPE surfactants are often found less efficient than hydrocarbon surfactants in emulsifyng hydrocarbon oil-in-water emulsions. Oil-in-water emulsions made with both Comb-18-18-OAc and Comb-21-21-OAc display no phase separation (Table 2). The reduction in IFT provided by the SPEs is less significant than that provided by C12E23 in pure water. AFM measurement shows the steric barrier of C12E23 to be at least four times that of the SPEs in pure water (Figs. 2–5). Two factors may contribute to the difference in interfacial activities between comb SPE surfactants and C12E23 in aqueous environment. One factor is the lower affinity to the hydrocarbon surfaces of SPEs due to their oleophobicity. The other is due to the ease of packing of the C12E23 single-chain configuration as opposed to the comb-type. The long backbone of a comb-polymer prevents close packing of polyoxyalkylene chains and therefore causes less force in compressing and confining the chains. Therefore, the most advantageous application for the SPE surfactants is in the emulsification and stabilization of silicone oil/water emulsions where the water phase contains high level of alcohol cosolvents (2).

The other interesting feature displayed by the SPEs is the maximum steric barrier experienced at the intermediate ethanol level. This feature is only displayed by Comb-18-18 and Comb-21-21 (i.e., the SPEs with a significant portion of the oxypropylene unit). Correspondingly, emulsion-stability measurement showed that while the stability of emulsions made with C12E23 and Comb-10-4 decreases monotonically with ethanol percentage, the stability of emulsions made with Comb-18-18 and Comb-21-21 was almost unchanged in up to 80% ethanol. The IFT data show that Comb-18-18 and Comb-21-21 reduce the IFT...
more than the others when ethanol content becomes significant (i.e., their surface activity was more pronounced at the interface between oil and ethanol-rich aqueous phase). We attributed this to the different degree of solubilization between the oxyethylene and the oxypropylene unit by ethanol. Figure 8 describes a possible outcome due to the addition of ethanol. The grafted side chains of the SPEs are random copolymers of oxyethylene and oxypropylene. While oxyethylene is hydrophilic, oxypropylene is hydrophobic. Therefore, in pure water the oxyethylene units in the side chain extend into the solution while the oxypropylene units prefer to adsorb on the hydrophobic substrate or to self-associate. The copolymeric side chain of the SPEs can be viewed schematically either as undulating loops pinned to the substrate by the oxypropylene units or as a knotted coil tied by the self-associating oxypropylene units. The addition of ethanol improves the solvent quality of oxypropylene. In the mixed solvent of ethanol and water, polyoxypropylene interacts more favorably with the solvent and progressively desorbs from the substrate, or dissociates from each other with increasing ethanol content. The solubilized (yet still surface-bound) oxypropylene units contribute to the steric barrier in addition to the oxyethylene units. This may explain the observed force increase between 20 and 40% ethanol for Comb-18-18 and Comb-21-21. However, the film thickness dependence on the balance between the chain desorption and chain unwinding in the presence of ethanol may be different from that of the steric barrier height. Knowledge of the adsorbed amount is needed in order to understand this delicate balance quantitatively. The siloxane chains are soluble in pure ethanol and therefore the steric barrier decreases eventually with enough ethanol added to the water phase. It seems intuitive that this ethanol-induced steric barrier increase should be more pronounced for comb-copolymers with a significant percentage of oxypropylene units such as Comb-21-21 and Comb-18-18 and less pronounced for those with a small portion of oxypropylene units such as Comb-10-4. It can be concluded that in order for a surfactant to maintain a constant surface activity and surfactancy in aqueous phase with varying ethanol percentage, one type of surfactant segments should have balanced oxyethylene and oxypropylene units and the other type should be both hydrophobic and oleophobic.

The force-versus-separation curves presented here were obtained between 1 and 2 h after the injection of the surfactant solution. We studied the time effect by recording force curves in a sealed liquid cell as a function of time. In Fig. 9, the force curves were plotted as a function of time ranging from a few minutes to 13 h after the injection. The data showed little change. We concluded that the adsorption of SPEs is fast and the system reached equilibrium in under 10 min. We also did not observe any hysteresis in force curves measured during consecutive compression. Despite the relatively high molecular weight of the SPEs, the extreme flexible siloxane chain should aid the adsorption and packing of the surfactants at a solid/liquid interface. Figure 9 also displays typical AFM force measurement errors in our system, with an estimated error bar for the force magnitude of ±0.16 nN and an error of ±0.5 nm for the separation distance determination.

These unique properties provided by SPE surfactants can have profound impact in industrial applications. As emulsifier and stabilizer, the SPE provides stability for colloidal systems that contain a significant amount of alcohol, while most conventional hydrocarbon surfactants cannot. For example, the SPE can be
used as a stabilizer in hairspray products that sometimes contain as high as 80% short alkyl alcohol. The same mechanism responsible for emulsion stability in alcohols should also apply to systems involving other organic solvents. Therefore SPEs may provide stability in general for emulsion and colloidal products or processes involving organic solvents.

**SUMMARY**

The interaction forces provided by silicone polyether surfactants adsorbed at the interface of n-octadecyltrichlorosilane monolayer and aqueous surfactant solution were measured using atomic force microscopy. Response of the steric repulsion to the presence of ethanol in the surfactant solution was examined for a series of comb-type SPEs with varying side chain length, oxyethylene/oxypropylene ratio, and end-capping functionality. It was found that the steric repulsion provided by the SPE molecules persisted up to 80% or higher ethanol levels. In contrast, a hydrocarbon surfactant, C12E23, desorbed and lost its interfacial activity at much lower ethanol content. The force measurement results were consistent with the findings in the interfacial tension results between oil and water phase, and the stability measurement of emulsions made with the various surfactants. While emulsions made with a conventional hydrocarbon surfactant broke up irreversibly with 30% or more ethanol, SPE-containing emulsions sustained an ethanol level of at least up to 80%, and showed partial redispersibility even after the eventual breakup. The difference between the conventional hydrocarbon and SPE surfactants in emulsion stability and force measurements is largely attributed to the polysiloxane moiety of molecular weight larger than 1000 being hydrophobic but not oleophilic. The presence of polyoxypropylene in the polyether chain of the SPE surfactant also brings unique characteristics in alcohol-containing emulsions through its modification of the hydrophile’s solubility. The SPEs with a significant portion of oxypropylene show a remarkable ethanol tolerance up to high level, and can be used to tune the stability of emulsions and dispersions. In general, colloidal and emulsion products or processes that involve alcohols or other organic solvents can utilize the unique property of the SPE surfactants in order to improve their shelf life or efficiency.

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**REFERENCES**

22. The van der Waals (VDW) interaction was calculated by modeling the tip as a sphere with a seminfinite plane, F = −κR, was used, where the value of the Hamaker constant A was taken as 3.04 × 10−20 J and the value of the tip radius R was taken as 20 nm.