

# Chapter 9

## Silicone Surfactants

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### 9.1 Introduction

The energetic and commercially relevant topic of silicone surfactants was extensively reviewed by Hill in 1999 [1] with a series of follow-up, more specialized reviews between 2001–2011 by Henning et al. [2]; Hill [3]; Ruiz et al. [4]; Fleute-Schlachter and Feldmann-Krane [5]; Long and Wang [6]; Kamei [7]; Huang [8]; Hill [9]; Huang et al. [10]; O’Lenick and O’Lenick [11]; Han et al. [12]; Han et al. [13]; Huang et al. [14]; Somasundaran et al. [15]; Huang [16]; and Rodriguez-Abreu and Esquena [17]. With this in mind, and within the context of being part of the larger topic of silicon-based surface science, this chapter aims to carry out the following:

- Give an overview of the molecular structures, synthetic chemistry, interfacial activity and solution aggregation behavior of silicone surfactants.
- Make reference to the previously published reviews.
- Cover new developments in the field in the last twelve years.
- Discuss how these properties tie into the application science for these materials.

Silicone surfactants were first introduced into the marketplace in the 1950’s as stabilizing agents for polyurethane foam [18]. This application was unusual in that more traditional surfactants, based on hydrocarbon residues as the “hydrophobic” portion of the molecule, did not act as effective stabilizers in this media. The experimental verity of surface activity in a non-aqueous media suggested that silicone surfactants would have some significant differences in physico-chemical behavior from their hydrocarbon analogues.

Over the next 60 years, both striking similarities and differences were observed between the behavior of silicone surfactants and their hydrocarbon analogues. Ta-

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**Table 9.1** Similarities and differences between siloxane based and hydrocarbon based surfactants

Similarities between silicone and hydrocarbon-based surfactants	Differences between silicone and hydrocarbon-based surfactants
Surfactants are formed using most common hydrophilic moieties including non-ionic (polyether-based) and ionic (cationic/anionic/zwitterionic)	The great majority of commercial products containing silicone surfactants are based upon the non-ionic, polyether hydrophile
Aqueous surface activity including the marked reduction of aqueous surface tension	Silicone surfactants can routinely reduce the surface tension of water to values 10–20 % lower than measured with organic surfactants and display surface activity in organic media
Formation of a rich variety of aggregated structures in aqueous media including micelles and liquid crystalline phases	Silicone surfactants show a pronounced tendency to form bilayer-structured aggregates in aqueous dispersions including plate-like micelles, vesicles and lyotropic liquid crystalline phases
Stabilization of aqueous-based disperse systems such as foams and emulsions	Silicone surfactants can also stabilize dispersions in organic media
Wetting agents for aqueous mixtures	“Superwetting” of aqueous mixtures of specific silicone surfactants

ble 9.1 lists the similarities and differences between siloxane-based surfactants and hydrocarbon-based surfactants.

The physical behavior of silicone surfactants, as outlined in Table 9.1, has been the basis for a rich variety of commercial applications. Along with the fore-mentioned example of the stabilization of polyurethane foams, the following appli-cations have achieved significant commercial success:

- Process aids in fiber manufacturing.
- Spreading agents and emulsifiers in personal care and cosmetic formulations.
- Wetting agents, flow promoters, lubricants and foam control agents in paint and coating products/processes.

Therefore, this review of the field of silicone surfactants focuses on the following topics:

- The molecular structures of silicone surfactants and how they are synthesized.
- The interfacial activity of silicone surfactants.
- The aqueous aggregation behavior of silicone surfactants.
- The commercial applications of silicone surfactants.

This review also highlights areas of high activity which have begun in the last 12 years or have greatly intensified during this period:

- All aspects of research and product development of carbohydrate-functional sili-cone surfactants including synthesis, characterization, interfacial science, aggre-gation in aqueous solution and product conceptualization and development. This work is driven by environmental concerns, specifically the desire to work with

amphiphiles based on “natural” products, such as sugars/carbohydrates. This focus is highly relevant for the potential application of these materials into personal care, household care and health care markets.

- The intense work carried out on the bulk solution aggregation properties of silicone surfactants has yielded a number of exciting avenues of research and development. These areas lie in the exploding field of nanoscience and technology. For example:
  - The science and technology of nanoscale silicone surfactant vesicles has been extensively developed in the subsequent years. These materials are the first robust alternative to the highly established field of organic-surfactant-based vesicles/liposomes which are well-established in the personal care product and health care fields. By contrast to these organic materials, silicone vesicles are formed by a wide range of materials, under mild conditions and bring the benefit of silicone aesthetics to the skin care market.
  - The concentrated interest in and application of silicone emulsifiers in the personal care market has driven the discovery of novel methods of dispersion stabilization employing silicone surfactants. Specifically, a number of silicone surfactants act as nanoparticulate stabilizers at interfaces.
  - Silicone surfactant aggregates have been employed to “template” the formation of specific nanoscopic structures of metal oxides.

## 9.2 Molecular Structure

Silicone surfactants feature an amphiphilic molecular structure consisting of a non-polar/hydrophobic moiety, silicone, and various polar/hydrophilic moieties. The silicone moiety can vary from a linear to a highly branched (network) structure. The hydrophilic groups, including both non-ionic (polyether and carbohydrate) and ionic (cationic, anionic and zwitterionic) species can attach to the siloxanes in a wide variety of ways.

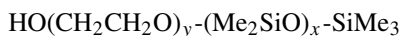
### 9.2.1 Silicone Structure

As discussed extensively in this book, “silicones” contain non-polar, hydrophobic groups composed of combinations of the monomer species  $R^1R^2R^3SiO_{1/2}$ ,  $R^1R^2SiO$ ,  $RSiO_{3/2}$ , and  $SiO_2$ . Common, minimally polar R groups bonded to silicon include methyl, longer chain alkyl, phenyl and  $\gamma,\gamma,\gamma$ -trifluoropropyl, with (by far) the most common R group being methyl. In order to satisfy the requirements of amphiphilicity, some of the R groups are highly polar and hydrophilic. These groups are discussed below.

### 9.2.1.1 Linear Silicone Structures

Many silicone surfactants are based upon a linear silicone structure featuring the oligomeric silicone group,  $-(R_2SiO)_x-$ . The typical R group is methyl and  $x$  can range from one to multiple hundreds. Hydrophilic groups can be attached to one (an "AB" structure) or both (an "ABA" structure) ends of this linear silicone. One can consider a linear structure BAB, where the hydrophilic group is in the middle. Examples of all three linear type structures are shown below, where the A group is a poly(oxyethylene) group. These have either a C-O-Si bond (hydrolytically unstable) or a O-C-C-C-Si bond (hydrolytically stable) as the linkage between the polyether portion and the silicone portion.

#### AB Structures:



Structure 9.1

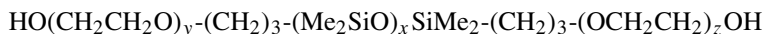


Structure 9.2

#### ABA Structures:

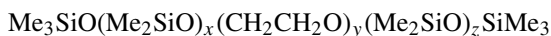


Structure 9.3

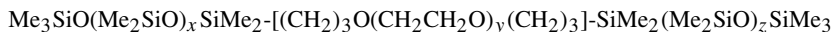


Structure 9.4

#### BAB Structures:



Structure 9.5



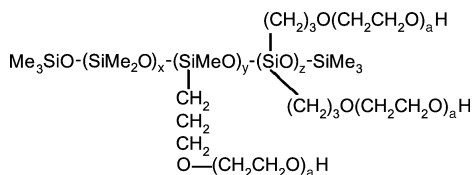
Structure 9.6

### 9.2.1.2 Branched Silicone Structures

Silicone branched structures can be further grouped according to the "degree" of branching. Examples with a lower degree of branching include "graft", "comb" or "rake" structures. Examples with higher degrees of branching usually feature some silicon atoms of the general formulas  $RSiO_{3/2}$ , and  $SiO_2$ , where R can be the hydrophilic moiety. These examples have been further grouped into the categories "resins", "dendrimeric structures" and "surface-active nanoparticles".

(a) "Graft", "Comb" or "Rake" branched silicone structures

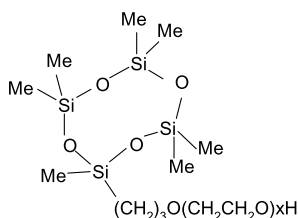
The general representation of a “graft”- or “rake”-structured silicone surfactant is displayed in Structure 9.7. As in Structures 9.1–9.6, the hydrophilic group of choice is the poly(oxyethylene) group.



**Structure 9.7**

One specific case of the general formula in Structure 9.7 is worthy of further mention; specifically, the case where  $x = 0$ ,  $y = 1$  and  $z = 0$ . This specific example, often referred to as a “branched” trisiloxane structure, appears frequently in the literature on silicone surfactants.

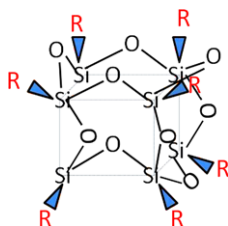
Another variation of structure on the theme of “graft” structure is where the siloxane backbone is in a cyclic, rather than a linear form. This is shown as Structure 9.8.



**Structure 9.8**

(b) Network silicone structures

The term “branching” within a silicone surfactant can also refer to materials containing  $\text{RSiO}_{3/2}$  and/or  $\text{SiO}_2$  units within their structure. The R group in the  $\text{RSiO}_{3/2}$  unit can feature either a hydrophobic (typically methyl) or hydrophilic group. Gentle and Bassindale reported [19] a series of materials of the molecular formula  $[(\text{polyether})\text{SiO}_{3/2}]_8$ . These materials featured a cubic cage structure as depicted in Structure 9.9, also known as a polyhedral oligomeric silsesquioxane, POSS (see also Chaps. 6 and 7), where the polyether groups are the “R” groups attached to each corner of the cube. The interfacial activity of these compounds was not reported; however, interfacial activity was observed in cases where the R groups were a mixture of alkyl and polyether [20]. In a related study Deng and coworkers reported [21] that the species  $[(\text{isobutyl})\text{SiO}_{3/2}]_8$  was not amphiphilic in behavior; however, they observed amphiphilic behavior in the case of the open cage species  $[(\text{isobutyl})\text{SiO}_{3/2}]_4[(\text{isobutyl})\text{SiO}(\text{OH})]_3$ .



**Structure 9.9**

In Structure 9.9, R represents a polyether group. For simplicity of presentation, one vertex Si atom, the one behind the plane of paper, is not shown.

Most investigators consider the  $[\text{RSiO}_{3/2}]_8$ -based structures to be “molecular” surfactants. However, as the highly branched siloxane structure attains a much greater size and molecular weight, typically through incorporation of  $\text{SiO}_2$  units, one might consider them to function as surface-active nanoparticles. Commercial materials are available which are best considered to be silica nanoparticles whose surfaces are covered with a mixture of organic and OH (silanol) groups. For example, amphiphilic behavior has been observed in the case where the organic group was methyl [22].

### 9.2.2 Silicon-Centered Hydrophobic Groups Other than Silicone

There are two such cases worthy of mention, both of which are structurally related to the siloxane (Si-O-Si-O-) backbone. The first example is a polysilane, where the backbone is Si-Si-Si and a carbosilane, where the backbone is Si-C-Si-C-. A small number of surfactants have been prepared from this backbone, as reviewed previously [23]. Since this review, one study reported [24] the synthesis and characterization of mixed fluoroalkyl/hydroxyl functional carbosilane dendrimers which demonstrated amphiphilic behavior. In a related study, Krska and Seyferth [25] reported the synthesis, characterization and amphiphilic behavior of carbosilane dendrimers decorated with a variety of hydrophilic groups. Kim et al. reported [26] the synthesis, characterization and amphiphilicity of dendrimers build around a cyclic siloxane core with silyl ether-based linkages (comprising the “generations” of the dendrimer structure) and capped with hydroxyl groups. For more detail about these and other silicon-containing dendrimers see Vol. 2 of this book series.

### 9.2.3 Hydrophilic Group Structure

Within the category of “silicone surfactants” one can also make distinctions based on the structural classification of the hydrophilic group. A first point of distinction would be between “non-ionic” and “ionic” hydrophilic groups. The two major categories of non-ionic groups are polyethers and carbohydrates. Within the category of ionic groups there are cationic, anionic and zwitterionic members.

### 9.2.3.1 Non-ionic Hydrophilic Groups

The vast majority of silicone surfactants feature the polyether group. Typically the polyether group is that of a poly(ethylene oxide)-PEO. However, a substantial number of silicone surfactants contain some poly(propylene oxide)-PPO in their polyether portion. PPO is generally used for non-aqueous applications of silicone surfactants [18] as it would be essentially a slightly polar hydrophobic material. For an alternative hydrophilic group, much work has been carried out on silicones containing hydrophilic carbohydrate moieties [27–49]. A small amount of work has also been carried out using phosphine oxides as the hydrophilic moiety [50].

### 9.2.3.2 Ionic Hydrophilic Groups

Although silicone surfactants containing ionic hydrophilic groups have not attained the commercial significance of their polyether-based, non-ionic cousins, there has been effort expended to synthesize, characterize and develop applications for these materials. A number of aspects of this field were covered in the afore-mentioned treatise on silicone surfactants [50]; however, this effort had a rather limited scope.

#### 9.2.3.2.1 Cationic Silicone Surfactants

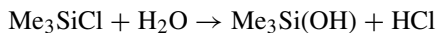
Silicone surfactants with a range of cationic hydrophilic moieties have been synthesized, characterized and their application potential assessed. The great majority of these materials have a quaternary ammonium moiety for the cationic group [51–60].

#### 9.2.3.2.2 Anionic Silicone Surfactants

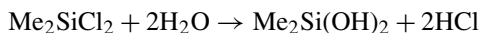
Silicone surfactants with a range of anionic hydrophilic moieties have been synthesized, characterized and their application potential assessed [61–66]. A wide variety of hydrophilic groups were investigated including sulfate, sulfonate, sulfosuccinate, carboxylate and phosphonate.

#### 9.2.3.2.3 Zwitterionic Silicone Surfactants

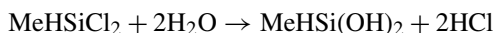
A small number of silicone surfactants featuring zwitterionic hydrophilic groups have been prepared. Those reported included both betaine [67] and sulfobetaine [68] moieties.



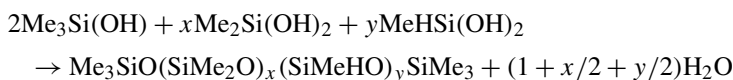
**Scheme 9.1** Hydrolysis of Methyltrichlorosilane



**Scheme 9.2** Hydrolysis of Dimethyldichlorosilane



**Scheme 9.3** Hydrolysis of Methylhydrogendichlorosilane



**Scheme 9.4** Condensation of Silanol Functionality

## 9.3 The Synthesis of Silicone Surfactants

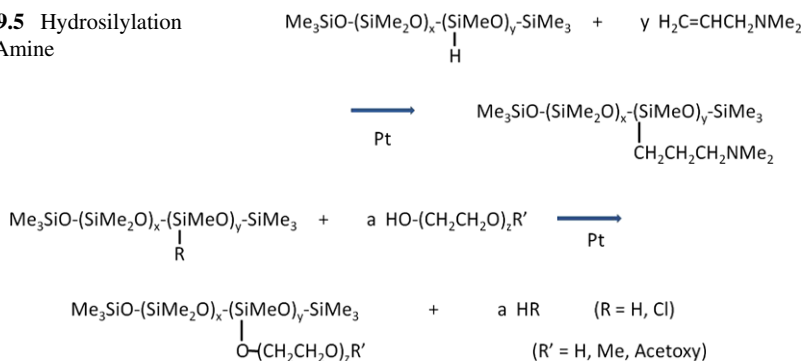
Because of the amphiphilic nature of silicone surfactants, their hydrophobic and hydrophilic parts are usually separately synthesized and subsequently linked together. This section mirrors that logic as we cover (1) Silicone synthesis, and (2) Linkage of the hydrophilic group to the silicone. In some cases the hydrophilic group is directly linked to the siloxane in one step. In other cases, the silicone is converted to an intermediate organofunctional silicone, which is then converted into the surfactant via traditional organic chemistry routes.

### 9.3.1 Silicone Synthesis

The broad topic of silicone synthesis has been extensively reviewed in many publications and the reader is advised to consult some of the classic publications in this field [69–71]. Nevertheless, we briefly outline here some of the key steps:

- The key raw material for the synthesis of silicones is silicon metal. The metal is treated with mixtures of methyl chloride and hydrogen chloride producing chlorosilanes such as  $\text{Me}_3\text{SiCl}$ ,  $\text{Me}_2\text{SiCl}_2$ ,  $\text{MeSiCl}_3$ ,  $\text{HSiCl}_3$  and  $\text{MeSiHCl}_2$ .
- As can be seen in Schemes 9.1, 9.2 and 9.3, chlorosilanes readily hydrolyze producing silanol species such as  $\text{Me}_3\text{Si(OH)}$ ,  $\text{Me}_2\text{Si(OH)}_2$ ,  $\text{MeSi(OH)}_3$  and  $\text{MeHSi(OH)}_2$ . As Scheme 9.4 shows, these silanol species, with the concurrent elimination of water, readily condense together to produce silicones. Within the silicone (Scheme 9.4), the Si-H functional group is introduced in order to provide an attachment point for a hydrophilic moiety.
- In some cases, in an intermediate step, an organic moiety is directly attached to the siloxane backbone via hydrosilylation reaction (the addition of an Si-H bond to an olefin). This moiety will be used as a synthon to link a hydrophilic



**Scheme 9.5** Hydrosilylation of Allyl Amine**Scheme 9.6** Silylation of Hydroxy Terminated Polyether

group to the siloxane moiety. An example [72, 73] is shown in Scheme 9.5. This reaction, like the great majority of hydrosilylations, is catalyzed by a platinum-based catalyst.

### 9.3.2 Linkage of the Hydrophilic Group to the Silicone

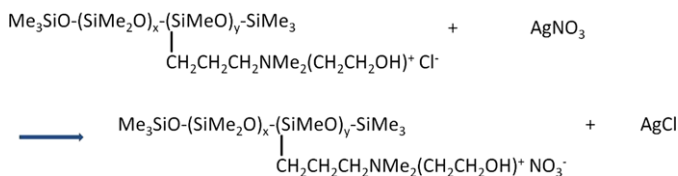
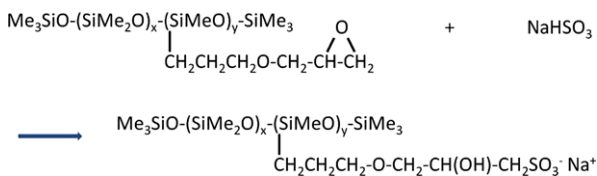
In the final step to produce the silicone surfactant, there are two general synthetic approaches. First, one can directly convert an Si-X-functional silicone (X = H, Cl) to the surfactant (Schemes 9.6 and 9.7). Secondly, one can convert an organofunctional silicone in one step to the surfactant (Scheme 9.8).

#### 9.3.2.1 Direct Linkage of the Hydrophilic Group to an Si-H Functional Silicone

There are two general methods to directly link a hydrophilic group to an Si-H functional silicone. First, as shown in Scheme 9.6, is the reaction between the hydroxyl group at the end of a polyether and the Si-R (R = H, Cl) group on a siloxane [74]. This silylation process is catalyzed by platinum compounds and yields H<sub>2</sub> gas as a by-product if R is H. Handling of the evolved hydrogen gas must be considered as part of the safety assessment of any material produced via this route. The resulting surfactants are typically used in non-aqueous applications as the Si-O-C linkage formed by the reaction is hydrolytically unstable.

The second method to directly link a hydrophilic group to a silicone is through hydrosilylation chemistry [74]. As seen in Scheme 9.7, an Si-H functional silicone is exposed to an olefin containing hydrophilic functionality, in this case an ethoxy polyether, in the presence of a platinum-based catalyst compound. This is a highly exothermic reaction (+28 kcal mole<sup>-1</sup>), so in many cases care must be taken to ensure adequate dissipation of the heat generated. This can be done via external



**Scheme 9.9** Preparation of Cationic Silicone Surfactant**Scheme 9.10** Preparation of Sulfate Functional Silicone Surfactant

an epoxy-functional silicone by sodium bisulfate yields the sulfate-functional surfactant [85].

Although the authors are not aware of literature describing the synthesis of analogous anionic silicone surfactants, as generated by standard cation exchange chemistries, they postulate that this would be a feasible synthetic methodology.

## 9.4 Interfacial Behavior of Silicone Surfactants

Silicone surfactants are widely acclaimed for their exceptional activity at a wide range of interfaces. This activity is manifested by (1) the reduction of equilibrium surface tension, (2) the orientation of the surfactant at an interface, (3) interfacial viscosity, dispersion stability and lubrication, (4) dynamic interfacial tension, and (5) the “superwetting” behavior of silicone surfactant solutions.

### 9.4.1 The Reduction of Equilibrium Interfacial Tension

Regarding the activity of silicone surfactants at the air/water interface, a defining feature of this behavior is the extraordinarily low equilibrium/static surface tensions that are routinely measured. Many silicone surfactants can reduce the surface tension of water down to 21–30 mN m<sup>-1</sup> [86–92]. This value is significantly lower (by *ca.* 10 mN m<sup>-1</sup>) than those commonly achieved with hydrocarbon surfactants and is generally only bettered by fluorocarbon-containing surfactants.

To a first approximation, the minimal tension achieved by surfactants at the air/water interface reflects the nature of the cohesive forces existing between the hydrophobic portions of the molecule. The higher the cohesive forces, the higher the degree of tension at the interface (or, alternatively, the energy required to

stretch/extend the interface). As discussed extensively throughout this treatise silicones, particularly methyl silicones, have low intermolecular cohesive forces. Furthermore, the extraordinarily low energy barrier to rotation of the siloxane backbone allows the methyl groups of the silicone to adopt the lowest energy conformation possible [93]. This is also a reasonable explanation as to why methylated silicone surfactants with significant degrees of branching in the siloxane backbone generally have higher surface tension values than their linear analogs; the barrier to rotation of the siloxane network is much higher due to steric hindrance [93].

One result of the low interfacial tension of silicone surfactants is their vigorous adsorption at the organic/air interface [94–98].

### 9.4.2 *The Orientation of Siloxane Surfactants at the Interface*

As mentioned in the previous section, it has been well-established that silicone surfactants robustly adsorb at a variety of interfaces, including the following:

- Water/air.
- Organic liquid/air.
- Water/organic liquid.
- Many solid/liquid interfaces.

The adsorption of branched trisiloxane surfactants at the air/water interface has been extensively documented. A key principle underlying many of these studies is that the packing of the surfactant molecules at the air/liquid interface is a function of the nature of the hydrophilic group [99]. This principle is probably operative given that the siloxane moiety is relatively small in area. Within this category, one can separate the relative influences of ionic and non-ionic hydrophilic groups. For the ionic trisiloxane surfactants, the area per molecule at the interface is strongly determined by shielded electrostatic interactions between the solvated hydrophilic group and its counter ion. For non-ionic species, specifically the polyether-based trisiloxane surfactants, in the absence of strong electrostatic interactions, a much more complicated picture comes into play. Generally, the area/molecule scales with the length of the polyether chain [100]. For non-ionic carbohydrate-functional silicone surfactants the size of the carbohydrate groups strongly influences the area/molecule at the interface [101, 102]. Unlike for small trisiloxane surfactants, for polymeric silicone surfactants both the silicone and hydrophilic moieties have an effect on the area/molecule at the interface [103].

The case where the area per molecule at the interface is strongly determined by the dimension of the siloxane portion of the amphiphile is the general case for silicone surfactants based on  $[\text{RSiO}_{3/2}]_4[\text{RSiO}(\text{OH})]_3$  [104] or  $(\text{R}_3\text{SiO})_x(\text{SiO}_{3/2}\text{OH})_y(\text{SiO}_2)_z$  [105] ( $\text{R}$  = short chain alkyl) molecules. In these cases, the hydrophilic group is OH, specifically the Si-OH (silanol) group. The  $[\text{RSiO}_{3/2}]_4[\text{RSiO}(\text{OH})]_3$  ( $\text{R}$  = isobutyl) species [a “pseudo-cube” (a cube missing one vertex) structure with Si atoms at each vertex of the pseudo-cube] was demonstrated to adsorb at the air/water interface with a near-saturation area/molecule of

1.35 nm<sup>2</sup> (approx. 180 Å<sup>2</sup>) consistent with the size of the isobutyl-substituted POSS molecule.

### 9.4.3 Interfacial Viscosity, Dispersion Stability and Lubrication

Along with extraordinarily low liquid/air interfacial tensions, another result of the presence of the low energy cohesive forces between the methylated siloxane chains is *low interfacial (air/liquid) viscosity*. Measurements of the surface viscosity of spread polydimethylsiloxane monolayers put this value close to zero. In some cases, surface viscosity can be built up at a silicone surfactant-adsorbed interface by interactions of the hydrophilic groups with either the underlying liquid or with each other. However, typically the surface viscosity values are nevertheless quite low.

One example of this was observed in the stabilization of polyurethane foam. Model studies [106–108] of the stabilization process, employing free-standing silicone surfactant-containing polyol films (“soap films”), showed that the foam drainage process was governed by the processes of “marginal regeneration” and highly turbulent surface flows. These phenomena are signatures of a low surface viscosity film [109, 110].

Conversely, highly viscous surface films have also been produced employing silicone surfactants. For example, surface films of the  $(R_3SiO)_x(SiO_{3/2}OH)_y(SiO_2)_z$  species. These films, featuring a highly packed surface layer of amphiphilic silica nanoparticles, have a high surface viscosity [109, 110]. In accordance, polyurethane foams produced using this material as a surfactant were extraordinarily stable.

In a related study, Hill and coworkers employed an interfacial stress rheometer to study the rheological properties of a silicone oil/water interface in the presence of siloxane surfactants that are used in the personal care industry as water-in-silicone-oil emulsifiers [111]. They appeared to stabilize water-in-silicone-oil emulsions in a fashion similar to that of Pickering emulsions, in which solid particles, such as silica or clay, accumulate at the oil/water interface forming a solid like “eggshell” that resists coalescence.

Regarding using silicone surfactants as dispersion stabilizers, along with the considerations of interfacial viscosity, one might consider the other traditional mechanisms of stabilization as well. These include bulk visco-elastic effects, electrostatic (double layer) stabilization and steric repulsion. Regarding bulk viscoelastic effects, Mehta and Somasundaran [112] studied the mechanism of emulsion stabilization where ionic silicone surfactants were employed as the stabilizer. Non-Newtonian behavior with viscosities an order of magnitude higher than that measured with non-ionic silicone emulsifiers was observed. This was explained by network formation at the droplet interface by weak interactions between the ionic functional groups. Bulk viscoelastic stabilization effects were also reported by Brook et al. in their investigation of the silicone surfactant stabilization of elastomeric silicone foams [113]. Liu and coworkers investigated the adsorption of “comb”-type silicone polyether (SPE) surfactants at the interface between water and a hydrophobic,

self-assembled monolayer [114, 115]. They concluded that SPEs showed significant oleophobic behavior and were therefore capable of stabilizing dispersions in organic media. They postulated that the stabilizing behavior was the result of a steric repulsion mechanism. This stabilization mechanism might also be operative in the case of castor oil-in-silicone emulsions stabilized by cyclomethicone/dimethicone copolyether surfactants [116] (see Chap. 13 for explanation of this terminology).

The adsorption and interfacial rheology of silicone surfactants adsorbed onto a solid surface is an active area of investigation, particularly in terms of the resulting lubricity of the solid surface. For example, Liu and coworkers [117] reported on interactions of an amphiphilic block copolymer of polyalkylene oxide-modified polydimethylsiloxane with thin films of polypropylene (PP), poly(ethylene terephthalate) (PET), and nylon, as well as with reference hydrophilic silica surfaces. They found that the silicone surfactant adsorbed following a Langmuir isotherm and that the adsorbed layers significantly improved fiber wettability and lowered friction.

#### ***9.4.4 Dynamic Interfacial Tension***

Historically, the dynamic interfacial tension (air/water interface) or alternatively, the rate of interfacial tension reduction, has been a subject of intense interest in the silicone surfactant field. A likely reason for this interest is that dynamic interfacial tension plays a significant role in many processes and surfactant applications including wetting and dispersion stabilization, which are of special interest in the silicone surfactant field.

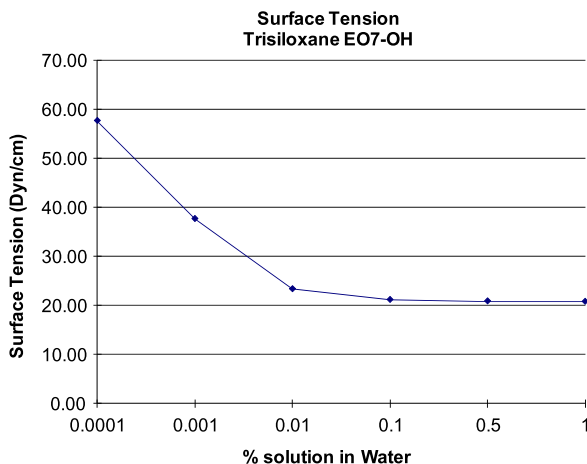
Generally, as expected, the rate of interfacial tension reduction of silicone surfactants scales inversely with the molecular weight (as expressed by the solvodynamic radius) of the surfactant. This conclusion is consistent with a model where the rate-determining step(s) of the interfacial adsorption process is the diffusion of the surfactant through solution or its rate of orientation at the interface. This has been recently confirmed in two independent studies [118, 119].

#### ***9.4.5 The “Superwetting” Behavior of Silicone Surfactant Solutions***

For the last 30 years one of the most investigated phenomena regarding silicone surfactants has been that of “superwetting” of aqueous mixtures of certain low molecular weight, trisiloxane-based, silicone polyethers. This fascinating topic has been reviewed in a number of publications [120, 121]. “Superwetting” refers to the extraordinarily rapid wetting of low energy, hydrophobic surfaces (such as parafilm) by these aqueous surfactant mixtures. This phenomenon has been correlated to a number of the physical properties of the surfactant including:

- Low equilibrium interfacial tension. As seen below in Fig. 9.1.
- Low dynamic interfacial tension (high rate of interfacial tension lowering).

**Fig. 9.1** Gibbs free energy plot of a trisiloxane-EO7-OH superwetter



- The presence of lamellar phases of surfactant bilayer aggregates (more information on surfactant aggregation is presented in Sect. 9.5.2).
- Marangoni flow.

Key to understanding superwetting is the assumption of rapid surfactant transport and surface reorientation. There is a strong correlation between a high rate of interfacial tension reduction (low dynamic surface tension) and superwetting [122]. Furthermore, in order to achieve a high rate of interfacial tension reduction, one should be using a relatively small surfactant, which as a result of its compact size will have high linear transport- and rotational-diffusion coefficients. This hypothesis has been quite robustly confirmed including in a recent study that demonstrated that for trisiloxane surfactants of the general formula  $(\text{Me}_3\text{SiO})_2\text{Si}(\text{Me})-(\text{CH}_2)_3(\text{EO})_x\text{OH}$  (where EO is  $(\text{CH}_2)_2\text{O}$ ), the highest initial spreading rate and largest spreading area were measured for the  $x = 6$  derivative [122].

Regarding the presence of lamellar phases of surfactant bilayer aggregates in superwetting, informal observations made in the authors' laboratories over 20 years ago showed that the superwetting solutions were often "cloudy", hinting at some type of two-phase system and the presence of lamellar surfactant aggregates [123]. More recently, a correlation between the ability of a silicone surfactant in aqueous media to aggregate into bilayer structures and a tendency to act as a "superwetter" was reported [124]. However, regarding this conceptual linkage of bilayer formation and superwetting, there is a significant amount of controversy with other authors disputing it [125, 126].

The role of surface tension gradient-stimulated flows (i.e. "Marangoni flows") in the superwetting phenomenon has also been discussed [127]. For example, the spreading front of the surfactant solution droplet causes the formation of a surface tension gradient which stimulates Marangoni flow. Furthermore, experiments [128] showed a correlation between the value of the gradient and the rate of flow.

## 9.5 Aqueous Solution Behavior—Hydrolysis and Aggregation

### 9.5.1 Hydrolytic Stability

An early and enduring observation about silicone surfactants was that they had a tendency to hydrolyze in aqueous solutions, a process that was quite slow at neutral pH and rapid at pH values below 4 and above 9. The hydrolysis process can be viewed as being the “reverse” chemical reaction to the siloxane condensation depicted in Scheme 9.4. The pH dependence of this phenomenon is explained by the consideration that acids and bases are catalysts for siloxane bond condensation and hydrolysis.

Hence, many studies and inventions in this field have been concerned with lessening the rate of hydrolysis of these surfactants. A common approach to this problem has been to consider the substitution of carbosilane (-Si-C-Si-)-based surfactants for their siloxane counterparts. However, carbosilane species are expensive and often do not have the favorable interfacial behavior of silicones.

Alternative approaches to diminish the rate of hydrolysis of silicone surfactants have been proposed by a number of authors. For example, Peng and coworkers demonstrated [129], while investigating the behavior of novel double-tail polyether-functional trisiloxanes, that some of the species were stable for more than 270 days in a neutral environment (pH 7.0). They concluded that the hydrolysis resistance of the double-tail trisiloxane surfactants can be improved by a weaker hydrophilicity of the surfactant molecule, and a larger volume of the hydrophobic groups. Another approach to lowering the rate of hydrolysis was reported by Pollicello and coworkers [130]. They claimed that the use of (presumably bulkier) alternative groups on both the siloxane backbone and the hydrophilic group achieved the purpose.

A less documented aspect of hydrolysis of silicone surfactants is the hydrolysis of silicone polyethers where the silicone-to-polyether linkage was a Si-O-C bond. Recently this hydrolytic “instability” was exploited by Lin and coworkers in order to prepare deliberately “cleavable” silicone surfactants [131–133]. The hydrolysis of these surfactants was, in some cases, accelerated by exposure to catalysts such as TiO<sub>2</sub>, radiation or plasma sources. In these applications the siloxane fragment with silanol (Si-OH) functionality resulting from the cleavage, could be profitably applied as water-proofing and anti-bacterial coatings.

### 9.5.2 Aggregation

Due to the well-known “hydrophobic effect” [134], silicone surfactants exhibit a pronounced tendency, in aqueous media, to self-assemble into various aggregates including micelles, vesicles and liquid crystalline phases. An extraordinary number of these aggregates are characterized by the presence of surfactant bilayers. These aggregates include non-spherical, oblate-ellipsoidal, disk- or plate-like micelles [135–138], vesicles, lamellar liquid crystal phase [139] and microemulsion “middle” phase.



For example, since the original reports [140–147], many workers [148–153] have documented the ubiquitous tendency of silicone surfactants (different siloxane structures, different hydrophilic groups) to form bilayer vesicles in aqueous mixtures. This formation, properties and application potential of silicone vesicles has been extensively investigated and the following key features have been identified:

- In some cases, silicone vesicles spontaneously form upon the mixing of the specified silicone surfactant with the correct amount of water.
- The bilayers of silicone vesicles are quite fluid and do not show the gel-to-fluid phase transition ubiquitous to hydrocarbon-based vesicles/liposomes.
- A variety of materials can be encapsulated into silicone vesicles [154–158].
- The width of the bilayer corresponds to the length of the siloxane portion of the silicone surfactant [159, 160].

Other studies involving silicone surfactant bilayers include:

- The presence of an AB-structured silicone polyether surfactant, as a co-surfactant with an alkyl ethoxylate, in a surfactant/dodecane/water mixture, causes a striking increase in the solubilization power of either a lamellar liquid crystal (LC) phase or else a microemulsion “middle” phase [161]. This increase in solubilization capacity correlated with an increase in the structural length scale of the microemulsion.
- The bilayer-forming tendency of silicone surfactants has also been exploited in the fabrication of surfactant-templated, mesostructured metal oxide phases [162–168]. In a series of intriguing studies the investigators found that the templating process often leads to the formation of lamellar phases with long-range order. In one case, a silica mesophase was prepared featuring the largest lattice constant reported for lamellar materials to that date [169]. The authors concluded, consistent with other studies, that the lamellar structuring was the result of the virtually unrestricted chain mobility within the silicone surfactant.

This “flexibility factor” favoring the self-assembly of silicone surfactants into bilayer structures has been mentioned by a number of investigators in the field. For example, siloxane chain conformations with surfactant bilayer aggregates have been proposed including coiled (based on micelle aggregation numbers and small angle neutron scattering (SANS) data) [170], flexible [171], and folded ones (Hill and colleagues have also found that the bilayer thickness of vesicles formed by comb-type silicone surfactants is significantly smaller than their extended molecular length) [172].

Finally, we also wish to cite the following:

- As expected, the cloud point of SPE surfactants scales with the degree of hydration of the EO chain. This was confirmed in a recent study [173].
- For a series of AB-structured silicone polyether surfactants in water, a number of unusual aggregate structures were observed including reverse discontinuous cubic phase ( $I_2$ ), reverse hexagonal phase ( $H_2$ ), and discontinuous cubic ( $I_1$ ) phases along with the common lamellar ( $L_\alpha$ ) and hexagonal ( $H_1$ ) phases [174].

The authors rationalized the correlation of the appearance of these phases by considerations of the entropy gain/loss of the silicone chain. Specifically, the entropy loss of a long hydrophobic chain (such as the silicone chain) would be largely increased when it is stretched, and thus, long hydrophobic chains tend to be in a shrunk-bulky state. This shrinkage affects the surfactant parameter, which heavily influences the state of aggregation.

## 9.6 Applications

The unique combination of physical and surface properties of ethoxylated siloxane copolymers (or silicone polyethers (SPEs)) results in the specification of these materials in numerous industrial applications. Inherently the SPEs provide a means to deliver silicone properties to an aqueous system. These properties can be expressed in terms of surfactancy by delivering the low surface energies, as described earlier, to the end application. This can make the materials effective as emulsifiers, wetting agents, foam control agents, or surface modifiers. The flexibility in the product chemistries allows these properties to be tailored to specific end uses. Materials within the SPE family can be effective at emulsifying water in oil or oil in water emulsions. Alternatively the structure can be tailored to demulsify these same two-phase systems. Similarly, the SPEs can be designed to be pro-foaming and stabilize foam systems, or can be designed to be effective foam control agents.

However, the low surface energies are not the only feature that makes these materials of commercial interest in so many applications. The inclusion of polyether groups onto a siloxane backbone allows these materials to treat surfaces and render them hydrophilic. The functionality present on the terminal end of the polyethers can make the SPE copolymer reactive with other cure chemistries. The siloxane portion of the copolymer allows the delivery of silicone feel into aqueous systems. In total, the combinations of these properties offer multiple benefits to the individual application.

Each of these end uses for silicone surfactants is unique and is summarized in the next few sections of this chapter. Many of these applications have been reviewed in other publications. The intent of this portion of the chapter is not to further review, but to summarize these applications and how the surface behavior of the silicone surfactants enables them to provide benefits in these applications. In addition, new developments are also highlighted.

### 9.6.1 *Personal Care*

Silicone surfactants have been used in the personal care industry for a number of years, beginning primarily in the mid-1980s. Mainly, these have been silicone polyether copolymer-based products although many other functional compositions

have been developed and commercialized. The unique surface properties have allowed these products to be incorporated into a broad spectrum of personal care uses. These include antiperspirant formulations, skin care, facial care, as well as hair care applications. The primary functions of these materials are to provide emulsification, humectancy, and overall aesthetics to the personal care formulations.

Several review articles have been written on the use of silicone surfactants in personal care. Floyd described a range of silicone surfactant structures and their ties to specific applications and the resulting intellectual property in a review in Hill's book on silicone surfactants [175]. He describes the foundational patents for this application and considers specific segments which utilize these materials and the claims they provide in these segments. O'Lenick has also published extensively in this field. He has described the use of silicone surfactants in various personal care formulations [176]. He has also published a review that describes the nomenclature system used in this industry and summarizes many of the properties important to various personal care applications [177]. This review details his work not only with non-ionic silicone polyethers, but also with other amphiphilic silicone copolymers that he has developed. Many of the patents on these compositions are described in Floyd's review [181].

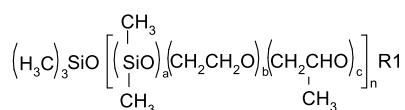
One of the major uses of silicone surfactants in personal care is in the area of emulsification. They have been used as emulsifiers for several years, beginning in the early 1980s. The initial work was in the antiperspirant segment where a series of unique silicone polyethers were utilized to stabilize water in silicone emulsions. Most specifically these were emulsions in which the external phase was based on cyclosiloxanes. The initial use of silicone surfactants as emulsifiers for water in silicone emulsions was described by Keil and Starch [178, 179]. The low surface energy of the siloxane external phase, as well as solubility parameters, did not allow the conventional hydrocarbon-based emulsifiers to stabilize this form of emulsion. The siloxane portion of a silicone surfactant is sufficiently low in surface energy, and is sufficiently compatible with the external phase to prevent coalescence of internal aqueous phase droplets. Key to this stabilization is managing the structural architecture of the silicone surfactant by balance of the dimethylsiloxane segments to the methyl/polyether siloxane segments of the copolymer. This provides the right solubility parameter of the silicone surfactant. Gruning and Bungard describe the use of hydrophile lipophile balance (HLB) methods to help predict the silicone surfactant composition best suited for stabilizing a water in silicone, as well as other types of emulsion (water-in-oil (W/O), oil-in-water (O/W), multiple emulsions) in their review article on silicone emulsifiers [180]. O'Lenick gives an additional perspective with a method called the three dimensional HLB system. This takes into account the consideration of the siloxane's unique solubility parameters and the fact that the silicones are hydrophobic, and yet not lipophilic [181]. Dahms and Zombeck collaborated on a series of papers in which they described how these molecular architectures are varied and used to prepare a range of personal care formulations, creams, and emulsions [182, 183].

Modifications of the basic structures of silicone oxyalkylene copolymers to include grafts of various alkyl functionalities and chain lengths have also been found

to stabilize water-in-oil emulsions, where the oil phase is hydrocarbon oil. Because of the non-lipophilic nature of the siloxane hydrophobe, there is little compatibility of the traditional silicone polyether graft copolymer with an oil phase, and these are not suitable for stabilizing W/O formulations. However, the added alkyl functionality to the composition provides for a proper solubility balance to effectively stabilize these systems [184].

Utilizing silicone surfactants as a primary surfactant in O/W formulations is not as common, as many organic-based surfactants are suitable for stabilizing these emulsions. Nevertheless, silicone surfactants can effectively perform in these formulations as well. Generally, the higher HLB silicone surfactants (HLB 10–18) are required to stabilize these formulations. More recently, non-polyether-based silicone modified carbonic acid surfactants have been shown to effectively stabilize O/W emulsions as well [185]. Further, efforts have shown how O/W emulsions containing pigment dispersants can be formed utilizing silicone surfactants with glycoside radicals as the key hydrophilic component in the surfactant composition. These are particularly useful in sun care products where the pigments help block harmful UV radiation [186].

Other recent developments in the field of silicone emulsifiers have focused on different architectures and improved understanding of emulsion fundamentals behind the preparations of various emulsions. Dimitrova et al. published two papers in which they describe the use of  $(AB)_n$  type silicone polyether copolymers as emulsifiers for water in oil systems, and compare these with the more traditional graft or rake type structures [187]. These  $(AB)_n$  materials are shown below as Structure 9.10 where the dimethylsiloxane block is the “A” component of the block copolymer and the “B” block is the combined EO and PO segments. These are prepared by the platinum catalyzed hydrosilylation of a silicon hydride end-blocked siloxane and an allyl end-blocked polyether. The EO/PO portion is prepared independently. The R1 simply signifies an end-blocking group.



**Structure 9.10**

The data suggested that these  $(AB)_n$  type emulsifiers require less shear energy to produce W/O emulsions vs. rake type SPEs of similar solubility parameters. These conclusions were further supported in a second paper in which a variety of personal care formulations were prepared and the fundamental stability studied [188]. Broader descriptions of how to use these fundamental properties in the preparation of stable formulations have also been described in a series of Society of Cosmetic Chemists papers [189, 190]. These papers describe how to prepare a range of formulations including glycerin in silicone, glycerin + water in silicone, and water in silicone emulsions and their stability and aesthetic properties.

Beyond the use as emulsifiers, the silicone-based surfactants have found utility as humectants, surface modifiers, and conditioning agents. In hair care applications,

a range of silicone surfactant structures has been shown to provide conditioning effects. The non-ionic polyether type surfactants confer a light conditioning. The lower HLB value silicone polyethers tend to be more effective in 2-in-1 conditioners [191]. In other cases, higher HLB surfactants improve conditioning on the hydrophilic portions of hair strands. Cationic silicone surfactants, like silicone quaternary amine compounds, give excellent conditioning properties as well as an improvement in hair body and curl retention [192]. The non-ionic polyether materials provide benefits to skin care and shave formulations by contributing humectancy and lubrication properties to the formulations [193].

### 9.6.2 Coatings

A second major application area for silicone-based surfactants is in the coatings industry. Here, they are primarily used as additives to various coating formulations to improve surface properties. The low surface energies provide for good leveling, wetting, spreading and gloss properties of the coating. The type of coatings where these materials are utilized is far reaching and includes: architectural, industrial protective coatings, wood, marine, cookware, and coil coatings. They are also used in many printing inks. The use of these additives significantly increased with the advent of more water borne systems which have inherently higher surface energies than solvent-based systems. Many of the desired coating properties were compromised with aqueous formulations without the use of additives. Easton provided an overview of silicone surfactants and their uses in waterborne coatings describing how they impacted the coating performance [194]. Perry published an updated review of these properties and discussed how dynamic surface tension and the rapid wet out provided by trisiloxane-based superwetters impact primarily aqueous-based coating formulations [195]. Her work also showed higher molecular weight copolymers tend to improve the slip and mar resistance of the coatings. This can be attributed to the orientation of the polysiloxane portion of the copolymer segments to the polymer/air interface yielding a lower energy surface. Ferritto et al. further developed this approach by extending the technology of branched silicone polyether copolymers into coatings [196]. These polymers utilized branched polyethers in the composition in place of pure linear ethoxylated or propoxylated ethers. The branching is derived from glycidol being utilized in the preparation of the polyether intermediates. These were shown to impact overall dirt pick up when formulated into wood coatings.

Another parameter that these materials provide is in reducing the propensity of these formulations to foam and to eliminate the appearance of microfoams in the resulting coatings, which can significantly impact end coating quality as well as processing when a coating is being applied. Semmler describes how the use of specialty silicone polyether additives in an overall formulation of a silicone antifoam helped to reduce the occurrence of microfoam when the coating was spray applied [197]. Van Dam describes the use of antifoams containing silicone polyether additives in printing inks [198]. These additives were more defoaming at the ink surface

and had good dynamic properties to eliminate foam build up during the printing process. Further, they had good durability and persistency in the process. O'Neil reviews the various mechanisms of foam destabilization by silicone surfactants and antifoam compounds. He describes differences between rake and ABA type silicone surfactants and their performance, as well as their uses in clear overprint varnishes, flexographic inks, wood parquet lacquers and automotive clear basecoats [199].

### 9.6.3 *Household Care*

The primary use of silicone surfactants in household care applications is again related to the control of foam. Unlike the applications in coatings where the target is to prevent the formation of foam, or to defoam a system in which foam has been created, the goal here is to control the foam to fit specific profiles. This is especially true in laundry applications. Fey has described the mechanism of foam control provided for with silicone fluids and silicone polyethers [200]. He suggested three main requirements for a material to behave as an effective antifoaming agent: (1) it must be insoluble in the foaming medium, (2) it must be readily dispersible in the foaming medium, and (3) it must have a lower surface energy than the foaming medium. This allows for the fluid to enter the air/liquid interface and spread over that interface. This allows for bridging of particles and eventual rupture (see Chap. 13).

In most cases, the silicone surfactant is used as part of an overall antifoam compound or composition. They are normally of the non-ionic polyether type and their role is to assist in the dispersion of the antifoam compound into the foaming media and to aid in the reduction and/or control of the foam. McGee et al. first showed this effect and described the impact of the incorporation of the silicone surfactant in combinations with silicone resins, fluids, silica particles and catalyst [201, 202].

Much of this knowledge has been applied to the development of antifoams specific for control of foam in liquid and powdered laundry detergents. In these products it has been found that branching in the polymer composition aids in the overall control of the foam. This branching can be introduced into the polymer chain by hydrosilylation of vinyl terminated polydimethylsiloxanes with a silicone polyether containing residual silicon hydride groups. Alternately, the crosslinking can be conducted in advance of the introduction of the allyl polyether to the polymer in the formation of the silicone polyether [203]. Elms et al. further developed this concept with formulated antifoam compounds containing linear and branched silicone polyether copolymers. These were shown to be more effectively dispersed in the detergent medium and to provide improved foam control profiles [204].

Beyond antifoaming there have been other uses of silicone surfactants in household care applications. Henning described the use of a range of silicone materials, especially silicone polyethers, in polishes and household cleaning products [205]. These included uses in car, furniture and shoe polishes, and in household and industrial cleaning applications. In some cases these uses are limited due to the inherent hydrolytic instability of silicone polyether copolymers under acidic or basic conditions. Panandiker described the use of low HLB type silicone polyethers in liquid

detergent formulations [206, 207]. These low HLB polymers were part of an overall formulation and were designed to deposit onto fabric in the washing cycle to improve fabric feel and hand.

### 9.6.4 Textiles

Silicone surfactants are used in numerous textile applications to impart hydrophilic properties to the textile. In this sense they are not specifically being utilized for their surfactancy properties; rather, their bulk structural properties allow them to orient at the interface of the textile to impact the feel. Often, these silicone materials contain amino groups to provide for excellent anchoring and hand to the fabric, and also polyether functionality to impart hydrophilicity [208]. More recently efforts have been focused on linear  $(AB)_n$  type block copolymers containing both amino and polyether functionalities. Czech published the initial work in this area [215]. The polymers were block copolymers prepared from the addition of end-blocked diepoxysiloxane fluids to various amines and diepoxy end-blocked polyethers. They imparted good softening and hydrophilicity to cotton [209]. Favresse prepared versions of these via different routes based on grafting functional groups on to  $(AB)_n$  block silicone polyether compounds utilizing free radical polymerizations. These showed improvements in hand on cotton, non-wovens, as well as synthetic fibers [210]. Kennan prepared different materials based on a process where an epoxy terminated  $(AB)_n$  silicone polyether was initially prepared and then aminated. These too showed excellent hand and provided improved hydrophilicity [211].

Silicone polyethers and silicone polyether terpolymers with other functionalities have also been used to treat non-woven textiles. Non-woven fabrics are traditionally made from polypropylene and are very hydrophobic. They are used as backing on many textile substrates as well as synthetic leathers, feminine care products and baby diapers. Improving the hydrophilicity of these non-woven products can significantly improve end performance. Sabia discussed the use of standard graft silicone polyethers to improve the finish of non-woven fabrics [212]. One detriment has been the durability of the treatment. Since there is no reactive functionality on the silicone polyether copolymers, they tend to wash off if exposed to water and then render the fabric hydrophobic once again. This is particularly of concern in diaper applications where it results in leakage. To address this durability issue, multiple functionalities are often incorporated onto the silicone. Most common are epoxy groups and polyethers. The epoxy can open and provide for improved durability to the non-woven substrate.

Standard silicone grafts and ABA type silicone polyethers are also used as fabric treatments to aid ironing. For example, the use of these materials in iron spray solutions for cotton and synthetic fabrics has been shown to significantly reduce the difficulty in removing wrinkles from fabric [213].

### 9.6.5 Oil and Gas

Applications of silicone surfactants in the oil and gas industry primarily center on demulsification and foam control. One concern that dictates the type of silicone and application of silicones in the oil recovery, transportation and refining processes is the potential of silicones to foul the catalysts used in the hydrocracking process [214]. However, this is somewhat limited to more oil soluble silicones and not necessarily silicone surfactants. It is critical that the silicone does not enter the oil phase in the refinery where it can be converted into silica upon heating in the cracking process thereby impacting the catalyst activity.

Most of the references relating to the use of silicone foam control agents in the oil and gas industry are centered on pure polydimethylsiloxane- (PDMS) based technologies. Foams in the oil and gas industry are primarily non-aqueous foams stabilized by naturally occurring asphaltenes. The gas phases are generally low molecular weight hydrocarbons. High molecular weight PDMS fluids tend to lower surface energies and allow for coalescence of the gas phase droplets resulting in foam rupture [215]. Because of the need for high oil solubility, silicone surfactants are not generally utilized in foam control formulations in the oil and gas industry, although there have been some efforts with low HLB-based silicone polyethers, but this is not widely practiced [216].

Silicone surfactants are more broadly utilized in the field of crude oil demulsification. In the recovery and transportation of crude oils, there is an undesired formation of various emulsions of oil in water and water in oil. The exact type is dictated by many factors, but depends heavily on the type of crude, salinity of the aqueous/brine phase, level of stabilizing asphaltenes, age of the well, and extraction process. The emulsions are generally formed as part of the oil extraction due to high turbulence in the production process [217]. Before the recovered oil is sent to a refinery for further processing the emulsion must be broken, oil recovered, and the produced water treated and then generally re-injected back into the recovery process or treated/cleaned and released. Many types of surface-active material are used in this demulsification process. Most are organic and include polymers of EO, PO phenols, and nonylphenols. Oil service companies formulate demulsification cocktails and tailor them to specific field conditions. The demulsifiers are generally formulated into organic solvents such as aromatic naphtha. By far, the greatest volumes of demulsifiers utilized in the industry are of these types.

Silicone polyethers are also utilized and a wide range of product offerings and technologies are available. Early investigations and use in this application for silicone surfactants dates back to the early 1970s [218]. However, widespread use has not resulted, primarily due to cost considerations as the silicone materials typically have a higher in-use cost than organic-based options. In some cases efforts have been made to overcome this issue by blending or by the incorporation of solid particles such as silica [219, 220]. The silicone materials do find utility when the crude oil/water emulsions are difficult to break, such as heavy crudes, or under cold conditions [221]. This has not deterred further development of new silicone surfactant compositions and improved understanding of the mechanism of how they behave as



emulsion breakers. David et al. described efforts to better understand destabilization mechanisms and proposed two possible scenarios: dissolution of the stabilizing asphaltene aggregates thereby removing the natural occurring surfactant, and displacement of these asphaltenes with a more surface-active silicone component. Further, these components are inherently not designed to be stabilizing, thereby allowing coalescence [222]. More recently, Phukan et al. described a new composition type of a silicone demulsifier that contains multiblocks of silicone and polyether with amino groups in the backbone that introduce further silicone branching sites [223].

### ***9.6.6 Pulp and Paper Applications***

Within the pulp and paper industry silicone surfactants are used as various process aides. These applications include pulp drainage, pulp digestion, antifoaming/defoaming, cleaning, and paper deinking. Silicone polyethers are used in many of these applications either directly or as part of an overall formulation component.

One of the first steps in the papermaking process is cooking which liberates the cellulosic fibers from the wood chips. This is done under highly alkaline conditions and is referred to as the Kraft process. In a simplified description of this process the wood chips are hydrated and impregnated with pulping chemicals (mainly highly alkaline sodium hydroxide and sodium sulfide) called white liquor. These are cooked to remove the lignin and recover the individual cellulosic fibers [224]. The used white liquor is referred to as the 'black liquor'. It is separated from the fibers by washing and recycled. The fibers are then screened and the resulting brownstock pulp is washed and bleached before the final conversion to paper. Process aids, surfactants, and additives are added throughout this process to aid in the paper production.

In the first part of this cooking, digester additives are commonly added to aid delignification. Silicone polyethers have been used in this process to reduce the digestion/cook time, to increase the yield of the pulp, and to reduce the level of undigested fibrous materials [225]. The low surface energies provided by the inclusion of the silicone surfactant allow the cooking chemicals to better impregnate the wood chips, thereby increasing their effectiveness.

Silicone defoaming agents are used in the washing of the brownstock. During delignification, many types of surface-active agent are formed. This causes severe foam control issues downstream during the pulp washing steps. Silicone-based defoaming agents are highly effective due to their inherent low surface activity and spreadability at the air/liquid interface. They exhibit good foam knock-down and persistence and are used at very low concentrations [226]. Silicone polyethers are included in many of these antifoam formulations to aid in the delivery of the primary silicone active, or to act as secondary antifoam fluids. The low surface energies have also been shown to aid in pulp drainage [227]. Compositions with branching in the siloxane backbone have also shown effectiveness in this application [228].

Silicone polyethers aid in the process of treating paper making equipment which helps to eliminate the need for frequent shut-down and cleaning of the equipment.

In this stage of the paper making process, dilute cleaned pulp is applied to a forming fabric and begins to drain and dry. The resulting paper web comes into contact with felt presses to further dry the pulp web to the desired moisture content. These felts become fouled with various deposits from the pulp drying process which can significantly decrease the process on-line time as a result of frequent cleaning. Solutions of silicone polyethers have been shown to reduce the amount of time required to clean when spray applied on these press felts [229].

Another segment in the pulp and paper industry that is growing in significance is in the area of paper deinking as part of the overall paper recycling process. Existing technologies often lead to inferior quality pulp that limits the applications for the recycled pulp to low value forms of paper or cardboard. Hence, removal of the ink from the recycled paper is critical in achieving a high quality recycled pulp that can be used for higher end paper products. Silicone polyethers have been shown to be effective in deinking flotation processes [230]. In this process the ink is removed utilizing more mild conditions vs. caustic treatments. SPEs help to emulsify the ink and are then skimmed off from the deinking bath [231].

### ***9.6.7 Other Foam Control Applications***

In addition to the foam control applications that are described in the sections on detergent foam control, pulp and paper, and in defoaming and antifoaming of coating formulations, silicone polyethers are also used in other foam control applications such as defoaming of diesel fuel. Silicone polyether copolymers that had the terminal carbinol functionality present on the polyether capped with succinic anhydride provide for excellent foam control in diesel and jet fuels. These polymers had good stability in the hydrocarbon liquid and retained their defoaming ability during storage [232]. Adding branching or crosslinking to the siloxane portion of the silicone polyether was also shown to impart improved foam control properties [233].

### ***9.6.8 Agriculture***

The use of silicone surfactants in the agricultural industry is mainly based on the wetting and penetration behavior of the trisiloxane-based silicone polyethers. As described earlier, the trisiloxane polyether copolymers are commonly referred to as superwetters. The unique, spontaneous wetting achieved by the use of these materials allows them to be very effective wetting agents and adjuvants in aqueous-based pesticide formulations. Penner et al. provided a comprehensive review of this application in Hill's book on silicone surfactants [234]. They described how the ultra low surface tension allows the aqueous pesticide solution to spontaneously wet the surface of leaves and aids in the penetration of the pesticide solution through the leaf cuticle into the active cell structure. This can impact the rate of pesticide applied

and can also provide for the pesticide to be resistant to wash off by rain, as the rate of pesticide uptake is significantly increased.

A common issue with trisiloxane-based superwetters is the inherent hydrolytic instability of the siloxane bond when solubilized into acidic or basic formulations. Under these conditions the siloxane bond will rearrange and surfactancy and superwetting behavior is lost. To combat this issue, non-siloxane-based Si containing materials have been suggested. Letherman et al. proposed a series of M–M' disiloxanes modified with ionic functionalities to combat the hydrolysis [235]. Additionally, they also proposed *t*-butyl substitutions on the terminal silicon groups to stabilize the trisiloxane groups to hydrolysis [236]. Klein et al. also addressed this issue by developing polyether-modified trimethylsilanes [237].

### 9.6.9 Polyurethane Foams

The final application in this review is the use of silicone surfactants as stabilizers for polyurethane foams. This was the original use of these materials and was the initial reason for their development. It still remains today the largest use of silicone surfactants although other applications discussed in this review are of growing importance. The primary functions these materials play in this application is to compatibilize the polyol and isocyanate intermediates, blowing agents and catalysts, and then to aid in the stabilization of the bubbles/cells during the foam formation until the final cure of the foam. This prevents coalescence of the cells and provides for the desired foam density and cell structure. Snow and Stevens have provided a thorough review of the types of silicone surfactant used to stabilize flexible, rigid and molded foams [18].

## 9.7 Conclusions

Silicone surfactants are a broad class of surface-active silicone compounds. The unique surface properties contributed by the siloxane structure are the result of the siloxane bonds and the free rotation of functional groups grafted onto the silicon atoms. This allows these materials to uniquely orient at interfaces, drive surface energies to very low values, and to form structured systems in aqueous formulations and solutions. This gives them a set of unique properties that allows them to be utilized in a diverse set of end applications ranging from polyurethane foam stabilization to personal care emulsifiers. The structural variations are many and will continue to develop and expand as new applications continue to evolve.

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