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Review on Silicone Surfactants: Silicone-based Gemini Surfactants, Physicochemical Properties and Applications

The increasing use of silicone polymers has attracted the interest of many researchers and manufacturers for the past three decades. The silicone surfactants have excellent surface properties, of which the wetting and spreading ability is particularly noteworthy. So silicone surfactants are used in various fields, starting with textiles to agriculture. Because of this particular wetting and spreading property, silicone surfactants will be used together with conventional surfactants to achieve the desired throughput. In this paper we describe in detail the origin of silicone surfactants and various silicone surfactant compounds, as well as their physicochemical properties. We also handle various applications of silicone surfactants in agriculture, textile manufacturing, personal care and cosmetics, polyurethane foam, metal extraction, foam floatation and other industrial applications. However, the main focus is on the latest syntheses, developments and applications of newly developed tailor-made molecules.

Key words: Silicone surfactants, physicochemical properties, trisiloxane polyether, wetting, spreading

Übersichtbeitrag zu Silikontensiden: Gemini-Tenside auf Silikonbasis, physikalisch-chemische Eigenschaften und Anwendungen. Die zunehmende Verwendung von Silikonpolymeren hat seit den letzten drei Jahrzehnten das Interesse vieler Forscher und Hersteller angezogen. Die Silikontenside besitzen ausgezeichnete Oberflächeneigenschaften, von denen die Fähigkeit zur Benetzung und Spreitung besonders hervorzuheben ist. So werden Silikontenside in verschiedenen Gebieten eingesetzt, beginnend mit Textilien bis zur Landwirtschaft. Aufgrund dieser speziellen Benetzungs- und Spreitungseigenschaft werden Silikontenside zusammen mit herkömmlichen Tensiden verwendet, um den gewünschten Durchsatz zu erreichen. In dieser Arbeit beschreiben wir ausführlich die Herkunft der Silikontenside und verschiedener Silikontensid-Verbindungen, sowie deren physikalisch-chemischen Eigenschaften. Wir behandeln auch verschiedene Anwendungen von Silikontensiden in der Landwirtschaft, der Textilherstellung, der Körperpflege und Kosmetik, im Polyurethanschaum, bei der Metallextraktion, der Schaumflotation und anderen industriellen Anwendungen. Der Hauptfokus liegt jedoch auf den neuesten Synthesen, Entwicklungen und Anwendungen neuer entwickelter, maßgeschneiderter Moleküle.

Stichwörter: Silikontenside, physikalisch-chemische Eigenschaften, Trisiloxanpolyether, Benetzung, Verbreitung

1 Origin of the silicon and silicones

Silicon (Si) is a chemical element obtained naturally from the earth's crust in the combined form. It is the second most (~28% by mass) abundant element present in the earth's crust after oxygen. All silicone compounds which are unique material in terms of chemistry, properties and their wide variety of useful application are the outcomes of the silicon derivatives. There are processes for conversion of combined silicon (from the earth's crust) into the pure silicon element. The technical confusion about the difference between "silicon" and "silicone" is that silicon is used to refer elemental material (Si) and when it comes to bonding between oxygen and silicon, it becomes "silicone". The extraction of silicon from quartz is the starting of the silicone chemistry. Silicon is produced by the heat treatment of quartz (SiO_2) with carbon at around 1700 °C temperature. The huge amount of heat is required for the conversion SiO_2 to Silicon. Hence, it is advisable to manufacture silicon where all the resources such as power, transportation, labor etc. are cheap and easily available. Silicon obtained by this method is generally a solid metallic material with at least 99% purity.

For further reaction, the solid metallic material is crushed into fine powder (200 to 400 nm particle size) in the fluidized bed also called silicon crusher. Once silicon is prepared from the above method, it is used for the conversion of the value added silicones. Rochow process is the most important commercial process in silicone chemistry. In this process, silicon solid metallic powder is reacted with methyl chloride in presence of copper catalyst and promoter. A mixture of chlorosilanes is obtained with dichlorodimethylsilane (approximately 75% to 80%) as a predominant compound. This reaction is very complex and requires 300 °C temperature and 3 bar pressure. It is also important to maintain the reaction temperature in the fluidized bed reactor once the reaction is started at high temperature as it is exothermic and need to control the temperature.

The hydrolysis is the further step of converting chlorosilanes into the siloxanediol which gives hydrochloric acid (HCl) as a byproduct. HCl shows high corrosive properties so it is essential to remove it properly. The reaction rate and product mixture are highly dependent on the Rochow process product mixture, pH and temperature of the reaction. The dehydration of the siloxanediol results into forma-

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tion of cyclomethicone and silanol (dimethicone) which are used in the various sectors as raw material, solvent and additive. The cyclomethicone is separated from dimethicone by distillation. D4 is a predominant cyclomethicone obtained by this reaction with the minor amount of D5 and D6. The lower cyclomethicones (D4, D5, D6) are volatile in nature hence they are used in applications such as antiperspirants, a solvent for cleansing purposes, whereas higher cyclomethicones are not volatile in nature. These are often blended with perfumes, creams, lotions, skin care lotions and currently researchers have been proved the application of the cyclomethicone in the products which tend to provide dryness on the skin. When formulation with this ingredient is applied to the skin, this leaves skin to feel smooth and lubricated. This class of silicones can be used to replace some of the petroleum-based solvents.

Silanol or dimethicone is another product from the dehydration reaction of siloxanediol. It contains a terminal Si-OH reactive group which has an analogy with organic alcohol i. e. $-CH_2$-OH. It has tendency of homopolymerization to generate water and high molecular weight silanols having different viscosities which are used mainly in the health and cosmetic products as emollient. These intermediate silicones are used as starting materials for the synthesis of higher molecular weight silicone compounds such as silicone fluid also known as silicone oil. The various silicones can be constructed using lower silicone molecules with suitable catalysts to produce multifunctional silicones, terminal silicones, reactive silicones etc. for the synthesis of various functional silicones which are used in the versatile applications.

2 Introduction

Silicone surfactants are a group of small-molecule and polymeric surfactants that find a wide variety of applications due to their unusual properties. It consists of a silicone backbone coupled with one or more polar groups. Many types of polar groups have been described, but nonionic groups based on polyoxyethylene and polyoxypropylene are the most common types [1]. Some of their larger applications are in the manufacture of plastic foams, as spreading and wetting agents, and in personal care products. Foaming, wetting, emulsification, and phase behavior are basic properties relevant to these applications. The unusual ability of certain trisiloxane surfactants to facilitate wetting of aqueous solutions on very hydrophobic surfaces called superwetting was reviewed by Hill [2].

3 HLB system

When selecting emulsifiers for various applications, hydrophilic-lipophilic balance (HLB) is of particular importance. Since a surfactant molecule consists of a hydrophilic and a hydrophobic part, the HLB value indicates the contribution of each part in the molecule and the value calculated by the following equation, that is generally applicable to conventional surfactants as they have distinct hydrophilic and hydrophobic parts in the surfactants molecules.

$$\mathrm{HLB} = \frac{20 \times \mathrm{Mh}}{\mathrm{M}} \tag{1}$$

Where,

M_h is a molecular mass of the hydrophilic part of the surfactant and M is total molecular weight of the surfactant.

Equation (1) cannot directly applied to the silicone surfactants due to the fact that silicones surfactants are hybrids of organic and inorganic components which neither fall into the conventional hydrophilic nor the hydrophobic category. Hence, it is necessary to the formulators to understand the concept of HLB of silicone surfactants. Since the last three decades various modifications have been carried out to design new silicone molecules which results in setting a difficult job to understand the HLB system of those molecules. Furthermore, it is a challenge when blends of silicone surfactants and hydrocarbon surfactants to be used in the formulations.

The difficulties mentioned above have led to the development of a concept called "3 dimensional HLB" (3D HLB). This approach was first developed by Anthony O'Lenick [3]. This system is an extension of the two dimensional HLB concept, and since it involves the three different chemical components in the same molecules which are soluble in silicone, oil or water. This 3D HLB system is represented on triangular coordinates (X, Y, Z) instead of a linear (2-component) HLB scale which is used for conventional surfactant system. The three components of the 3D HLB system can be determined using the equations (2)–(4):

$$\mathrm{X} = \frac{20 \times \mathrm{M_h}}{\mathrm{M}} \tag{2}$$

$$\mathrm{Y} = \frac{20 \times \mathrm{M_l}}{\mathrm{M}} \tag{3}$$

$$\mathrm{Z} = 20 - \mathrm{X} - \mathrm{Y} \tag{4}$$

where,

X – represents the coordinate of a water-loving portion, Y – represents the coordinate of an oil-loving portion Z represents coordinate of the silicone-loving portion and, M_h, M_l and M are the molecular weights of the hydrophilic part of the molecule, lipophilic part of the molecule and whole molecule.

The 3D HLB system is explained in triangular coordinates as shown in Fig. 1. This is well expressed in the right angle triangle with oil, water and silicone at the corners of the triangle. The hypotenuse of the right angle triangle represents the 2D HLB system which is a line connecting between oil and water portions and it is labeled from 0 – 20 like the other sides. The other two sides of the triangle are the lines connecting water-silicone and oil-silicone portions. This model of 3D HLB system was developed and experimentally tested by Tony O'Lenick [3] by developing several formulations with different molecules comprises of hydrocarbon and silicone based components including dimethicone copolyol isostearate, dimethiconol stearate, cetyl dimethicone. The phase diagram of the silicone oil-water emulsion stabilized by polymeric functionally modified silicone emulsifiers has studied in [25]. In this paper amino silicone copolymer, methylated amino silicone ter-polymer, acid modified silicone ter-polymer and EO modified silicone copolymer are used.

4 Properties of silicone surfactants

4.1 Surface tension

The surfactants are able to reduce the surface tension in solutions because of their hydrophilic and hydrophobic groups. The chemical configuration is that the hydrophilic groups attract to the water and the hydrophobic groups protrude into the water surface to form a molecular layer that reduces the internal force pulling the surface molecules of the solution's surface molecules. Hydrophobic groups cannot tightly align on the liquid surface when the surfactants concentration is below the CMC. As a result, the forces act unevenly on the liquid's surface, and surface tension is reduced ineffective. Figure 2 shows a diagram of surfactants surface tension at CMC. When the surfactant concentration exceeded the CMC, the surface tension value was shown to reach stability, indicating that the liquid surface tensions achieved a stable equilibrium. Among all surfactants, the silicone surfactant AG-pt (it is a commercial product of Elkay Chemical Private Limited, India, it is a trisiloxane based nonionic surfactant with 7–8 ethylene oxide units attached to the silicone backbone at the pendant position) possesses very low water surface tension reduction capability due to the quick optimal orientation of silicone surfactants molecule at the surface. Also the silicone surfactants possess a tighter molecular arrangement as compared to other hydrocarbon surfactants; and this degree of tightness in the molecular orientation affects the value of surface tension of an individual silicone surfactant and blend where silicone surfactants (AG-pt) are present. When AG-pt is blended with other hydrocarbon surfactants, they exhibit lower surface tension than the individual surfactants. Hence, surface tension reduction capability of AG-pt contributed to enhance the surface properties like detergency in presence of other hydrocarbon surfactants such as sodium dodecylbenzene sulfonate (SDS), lauryl alcohol ethoxylate-10 (LA-10) and nonylphenol ethoxylate-10 (NP-10).

Bonnington et al. have synthesized the trisiloxane ethers with a different number of oxyethylene units in the molecules and studied their applicability with the agrochemicals. The authors also studied the effect of the number of EO units on the surface tension and spreading capacity. A trisiloxane ether with 7.5 EO units possesses the lowest surface tension (21.35 mN/m) whereas a trisiloxane ether with 3 EO units possesses the highest surface tension (27.7 mN/m). More EO units in the trisiloxane molecules than 7.5 EO units resulted in a slightly increase of the surface tension (22.73 mN/m) hence they have concluded that trisiloxane ether with 7.5 EO units is the most effective molecule as an agrochemical adjuvant. Moreover, they have correlated the relationship between the surface tension and spreading capability and found that a low surface tension does not necessarily provide an efficient spreading as there are certain surfactants which show a lower surface tension but a reduced spreading capacity [4].

Dae won Chung et al. extensively studied the effect of the EO units in the silicone surfactants and length of the silicone backbone on the surface activities by grafting various molecules studying their surface properties. They have shown that when a number of EO units increases in the silicone surfactant molecule, the surface tension was reduced because the increase in the hydrophilicity results in a lower concentration of the surfactant at the air-solution interface and thus the area per molecule increases. In another category of product, they kept the EO content equal, varied the length of the silicone

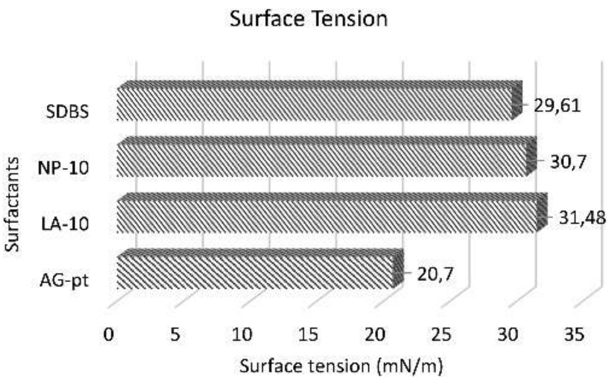

Figure 2 The surface tension of the trisiloxane polyether surfactant and other hydrocarbon surfactants (Results for this figure have been taken from our previously published work [10])

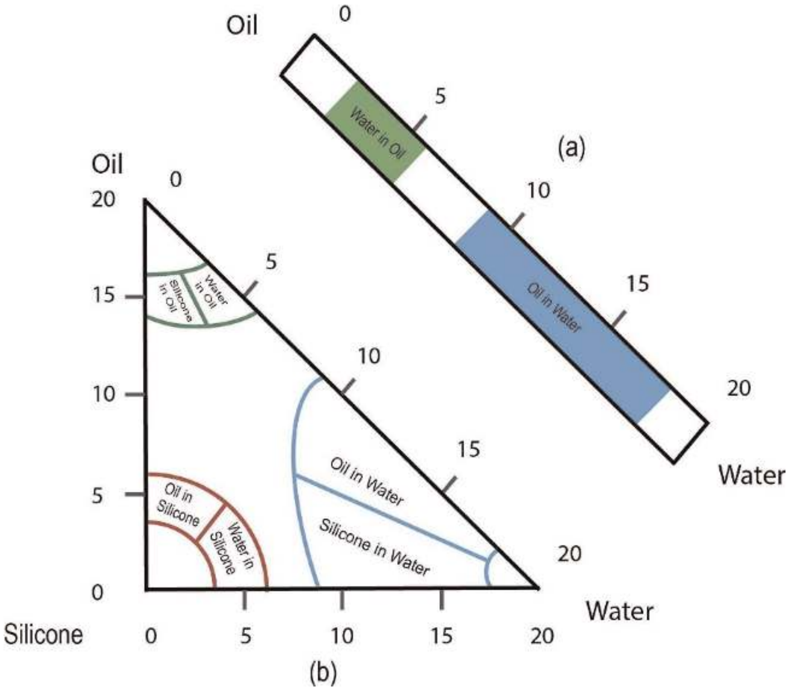

Figure 1 Schematic representation of (a) 2D HLB system and (b) 3D HLB system

backbone and studied the surface tension of these products. It has been found that as the length of the silicone backbone reduced, surface tension decreased. The lowest average surface tension has been observed at the shortest silicone backbone mainly due to efficient packing at the air-solution interface [5]. In these days, various research groups are aggressively working on the designing of novel trisiloxane based surfactants in order to get superior surface activities [1, 6–9]. Zhongli Peng et al. have developed a novel double tail trisiloxane surfactants range by attaching EO chain to the pendant position of silicone backbone and modifying the pendant position by adding some functionalities like amines. They designed a double tail trisiloxane molecule which provide a surface tension of 17.7 mN/m [6].

4.2 Contact Angle

Every solid surface is full of air molecules which are adsorbed on it; therefore, for liquids to expand on the surface, they must first push out the existing air. This phenomenon is called wetting. It typically creates a problem for water to dampen glasses with hydrophobic surfaces. However, this problem can be mitigated by adding surfactants to the water. Wettability of surfactants on the different substrates can be determined by observing their contact angles, where smaller contact angles imply less difficulty in wetting of a solid surface.

Figure 3 shows the contact angles of surfactants solutions. It can be observed that the contact angles of surfactant mixtures are less than the contact angle of hydrocarbon surfactant but more than AG-pt indicating that AG-pt assisted to reduce contact angle on both substrates i.e. Teflon and glass. As the length of hydrophobic group chains in the surfactant molecules increases, the ability to reduce the contact angle enhances up to certain length due to the optimal solubility and the balanced force exerted at the surfaces. Silicone surfactant comprises hydrophobic as well as an oleophilic characteristic which provides optimal solubility and balanced orientation results into a reduction in the contact angle individually and in the mixtures. The contact angle is the quantitative measurement of wettability as mentioned before; hence we could be able to comment that mixtures of hydrocarbon surfactants with AG-pt exhibit good wettability which enhances the detergency by allowing the detergent solution to reach to the bottom of the stain to dislodge in a fewer time span.

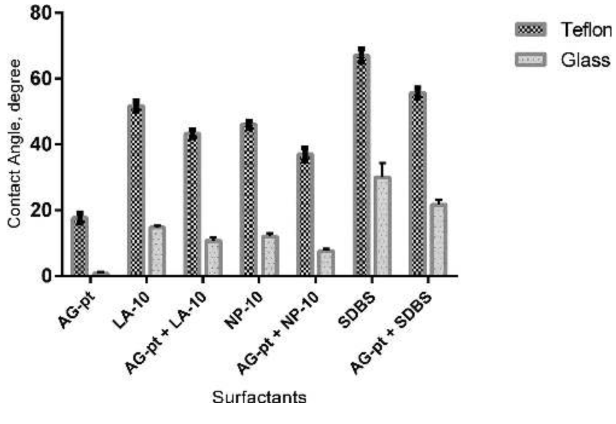

Figure 3 Contact angle of the trisiloxane polyether surfactant and other hydrocarbon surfactants (The results have been taken from [10] with prior permission)

4.3 Wetting/Superwetting/Superspreading

Interest in the spreading and wetting process has been dramatically enhanced during the last 20–25 years due to the importance of this phenomenon in the agricultural field, industrial application, medical sectors etc. Spreading or wetting can be achieved by incorporation of the surface active polymers, surfactants in the solvents usually in the water. It is known that the silicone surfactants are present as superspreader on the hydrophobic substrates. Trisiloxane surfactants are commonly denoted as M(D'En)M, where M stands for the trimethyl siloxy group, $(CH_3)_3\text{–}SiO_{1/2}\text{–}$, the term D stands for the $\text{–}O_{1/2}Si(CH_3)(R)O_{1/2}\text{–}$, where R is a polyoxyethylene group attached to the silicone, and En stands for polyoxyethylene, $\text{–}(CH_2\text{–}CH_2O)_nR\text{–}$ [11]. The trisiloxane surfactants with varied level hydrophilicity (i.e. the number of ethylene oxide units present at the pendant position of trisiloxane) showed spreading characteristic due to the following possible reasons speculated by K. P. Ananthapadmanabhan et al. [12]: a) packing molecular geometry of the trisiloxane molecule lead to the orientation of the molecules towards the interface, b) surface tension reduction capability, c) trisiloxane surfactants possess a greater level of affinity for low energy substrates, d) and also possess the quick adsorption kinetics at multiple interfaces. The spreading mechanism of the aqueous surfactant droplet has been depicted in Fig. 4. The different wetting/spreading situations such not-wetting case Fig. 4(a), partial wetting case Fig. 4(b), and complete wetting case Fig. 4 (c) have been shown in the figure with facile representation of the adsorption of the surfactant molecules at the air-solution interface as well as solution-solid substrate interface.

In 2011, Venzmer had extensively reviewed the study and development in the super-spreading characteristic of trisiloxane based surfactants since 1990 [13]. The spreading of the trisiloxane surfactants has studied with the aid of two different experimental setups to understand the underlying mechanism by Anoop Chengara et al. [14]. A few years ago, the same authors have shown that the initial rate of the spreading is dependent on the surface tension gradient

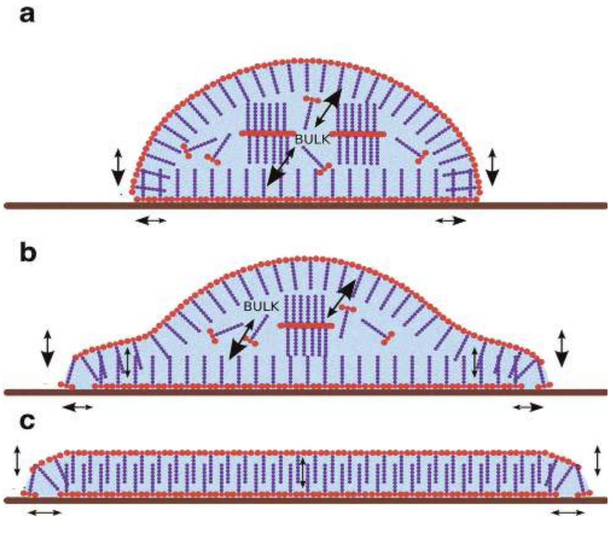

Figure 4 Spreading mechanism of trisiloxane polyether surfactant (a) the non-wetting case where the contact angle is more than 90°, (b) the partial wetting case where the contact angle is in between 0 to 90°, (c) the complete wetting case where drops completely spread out and only the dynamic contact angle can be measured.

which develops spontaneously at the air- solution surface due to the lack of the surfactant at the surface as surface stretching happens in spreading. On the basis of the conducted experiments, they have drawn up the hypothesis made initially that the initial spreading rate is not influenced by the forces at the interface between solid surface and solution which leads them to conclude that surface tension gradient of the air-solution surface plays a vital role in the spreading of the trisiloxane surfactant solution on hydrophobic surfaces such as Teflon tape, lotus leaf etc. K. S. Lee et al. have given an overview of the dynamic wetting and spreading phenomena in the presence of the various silicone surfactants on the different types of substrates such as smooth, porous materials etc. [15, 16]. In this study they have discussed the instability problems with spreading on thin aqueous layers and wet/dry hydrophilic surfaces. They also studied the capillary imbibition into the partially wetted porous medium and they have concluded that for all concentrations, the penetration rate obeys the Lucas-Washburn law. This law marks out the penetration length (L) of a liquid into the capillary pore with time (t) according to the equation, $L = (Dt)^{1/2}$. The diffusion coefficient (D) depends on the properties of the liquid to be penetrated and geometrical shape of the capillary. By taking into consideration of these parameter, the penetration length would be described by this law as follows:

$$D = \sqrt{\frac{\tau 2rt \cos(\phi)}{4\eta}} \tag{5}$$

where τ is the surface tension of the liquid, r is the pore radius, ϕ is the contact angle between the liquid and substrate (solid), and η is the dynamic viscosity of the liquid.

Interestingly, Sett. et al. have shown that the super spreading trisiloxane surfactants show a very good foaming capability when they are used together with organic surfactants such as sodium dodecyl sulfate (SDS) in mixtures having various proportions [17]. Caleb Chong Wei Ping et al. have studied the kinetics of different aqueous silicone surfactants on the different hydrophobic polymer substrates such as Teflon AF, Parafilm, and polystyrene. They applied trisiloxane polyether with 6 and 8 ethylene oxide units at a concentration close to the critical micelle concentration (CMC) and critical wetting concentration (CWC). They have concluded that the wetting and spreading behaviors are a function of hydrophobicity or roughness of the substrates and surface properties of the surfactants which were employed [18]. The chemical modifications in the trisiloxane molecules have been conducted to prepare a wide range of trisiloxane based surfactants which provides better surface properties and better compatibility required by the targeted applications. Wenshan Qu et al. designed a molecule which shows excellent surface tension i. e. 19.9 mN/m and superior spreading ability. They synthesized a novel molecule i. e. trisiloxane dicephalic surfactant and studied their physicochemical parameters [1].

Natalia Ivanova et al. have studied the importance of the CWC to wetting and spreading phenomenon. CWC is a concentration above which a transition from partial wetting to complete wetting happens as spreading over partial hydrophobic surfaces. They have found that the CWCs are many times higher than the corresponding CAC values for all trisiloxanes tested. This means that knowledge of CWCs is important when investigating the spreading capacity of surfactants. On the basis of experimental study they have proved that CWC is independent on the hydrophobicity of the substrates but it is a distinct surface property of surfactants that provide information on the higher limit of their spreading capability [19, 20].

The spreading/wetting of the trisiloxane based surfactants has wide applications in various sectors. The application of trisiloxane based surfactants on the hydrophobic leaf has been depicted in Fig. 5. During pesticide/insecticide/herbicide spraying on the various crops, the spreading agents can be used along with these solutions in order to get a

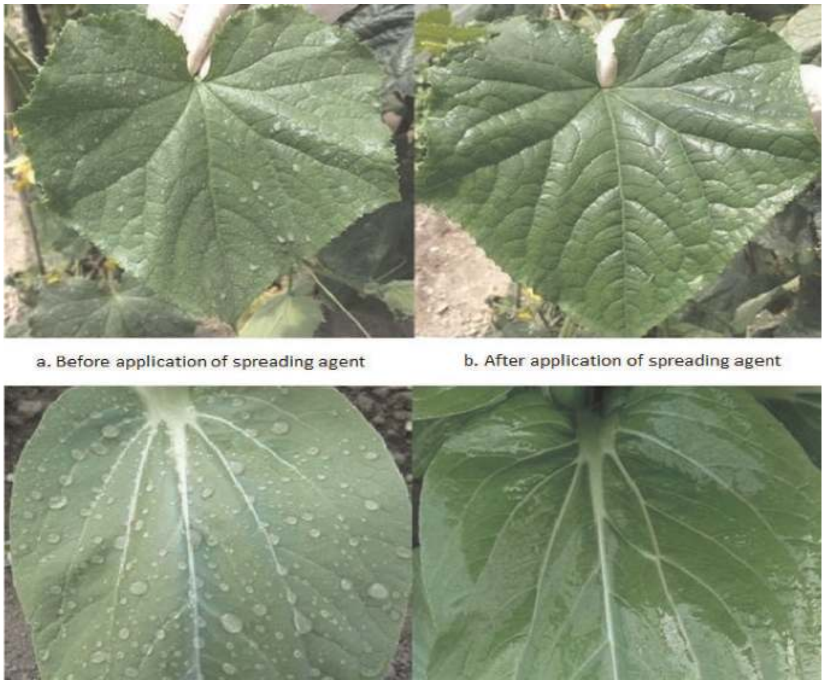

Figure 5 Spreading/wetting of the pesticide solution on the hydrophobic leaf a. before the application of trisiloxane based spreading agent, b. after application of trisiloxane based spreading agent

more effective spreading to cover a full portion of the leaf to kill the targeted insects. It can be easily seen from the Fig. 5(a) that drops of the pesticide solution are not properly wet on the leaf because of the hydrophobic nature of leaf whereas drops completely spread out (Fig. 5(b)) when trisiloxane based spreader applied with the pesticide.

4.4 Dispersion/emulsification

Emulsions are heterogeneous systems containing two different immiscible phases dispersed in each other in the form of droplets with the help of emulsifier/s. Nowadays emulsions have a tremendous demand in various sectors such as textiles, personal and home care, agricultural, industrial in order to deliver the actives in a facile manner. Emulsions provide us with a very high interfacial area due to the smaller droplet size which is beneficial for the applications where actives need to be transferred at the micro/core level of the substrate. The different types of emulsifiers are required to stabilize the emulsions by reducing the interfacial tension between the two immiscible liquids. There are organic/hydrocarbon surfactants available which possess the capability to reduce the interfacial tensions [21, 22].

Emulsions can be stabilized by using silicone surfactants. The silicone surfactants have their own characteristic properties which provide the superior emulsification capability because of following aspects: a. They possess very high flexibility which results into quick optical orientation at the interface in very less timespan, b. They show unique kind of orientation at the interface as they are hydrophobic as well as oleophobic, c. The main beauty of this category of surfactant is that molecules can be designed as per requirements by varying the silicone backbone length, group attached at the pendant position, position pedant group, length of the attached group at the pendant position, nature group to be attached etc. [23]. The nature of the silicone surfactants can be ionic or nonionic depending upon the functional group attached to the silicone backbone. These emulsifiers can be polymeric or oligomeric. The lower molecular weight silicone emulsifiers attach at the interface only over one/few segment/s hence the adsorption energy at the interface is relatively lower and leads to a weak adsorption at the interface of the two liquids. In contrast, polymeric, higher molecular weight, multifunctional emulsifiers adsorb at the interface via several segments. The total adsorption is the sum of adsorption energy of all the adsorption by different segments which is larger than the obviously individual adsorption energy by individual segments. These emulsifiers can serve emulsification in very low dosages and will be very effective for the emulsion stability. The stability of emulsion prepared using silicone polymeric emulsifiers will be very high because of the higher adsorption. They generally neither prefer to desorb from the interface nor migrate in to bulk [24].

The hydrophilic group such as ethylene oxide (EO), propylene oxide (PO) can be attached to the silicone backbone in order to increase the water solubility of the silicone molecules. The kind of molecules can be prepared using various numbers of EO and/or PO to the silicone backbone to prepare copolymers or block polymers to get different surface properties. Hence it is very important to know the molecular weight dependent surface properties of nonionic silicone surfactants. These molecules can be further modified into various molecules with a fatty alkyl group to make them compatible for hydrocarbon oil which will be useful to stabilize the emulsion of those oils. Though nonionic silicone surfactants are more effective in lowering interfacial tensions, they are least tolerant towards the pH variation and start hydrolyzing to long chain alcohol. Hence these molecules are not suitable for use under all pH conditions. All of these disadvantages of nonionic silicone emulsifiers can be avoided by using ionic silicone surfactants; however, only few studies have been carried out on these compounds. The added advantage of the ionic surfactants is that they behave as polyelectrolytes and hence can modify the rheological properties of their formulations, as desired particularly in cosmetic products.

Somasundaran's research group has studied the extensive application of polymeric silicone emulsifiers for emulsion preparation for the various uses such as textiles, cosmetics etc. They used different types of silicone polymers such as amino silicone copolymer, methylated amino silicone polymer, acid modified silicone polymer, EO-modified silicone copolymer etc. to prepare emulsions for fabric softening [25]. The observed behavior of emulsion stabilization is explained based on the hydrophilic-hydrophobic balance of the hybrid silicone polymers. It is postulated that with an increase in hydrophilicity of hybrid silicones, its tendency to stabilize water-in-oil emulsion decreases and oil-in-water emulsion increases [26, 27]. Further, this tendency for switching from water-in-oil emulsifier to oil-in-water emulsifier depends on the nature and the extent of functional modification. In order to be able to predict quantitatively emulsion stabilities, the stability of emulsions was correlated with the structure of the emulsifier using the 3D-HLB concept.

Various researchers are now working on the synthesis of silicone-based Gemini surfactants which exhibit good emulsification capability along with other surface properties [28, 29]. In some emulsions silicone surfactants are used as an active component to deliver the required properties in that particular application. In our previous research work, we have prepared a nanoemulsion of amino-modified silicone oil and pine using tridecanoic alcohol ethoxylate with 10 EO unit and AG-pt (trisiloxane polyether). In the nanoemulsion we have incorporated AG-pt to serve the wetting and penetration property when the nanoemulsion is applied to the fabric. Because of the AG-pt droplets of the nanoemulsion reach to the textile pore in order to obtain maximum benefits in terms of retaining the effect over a high number of washing cycles.

5 Silicone-based Gemini surfactant

Gemini surfactants are prepared from multiple hydrophobic or hydrophilic groups which are connected by a spacer to form a structure either with symmetrical or with asymmetrical sides. The surface properties of the Gemini surfactants are superior as compared to conventional surfactants in terms of lowering the critical micelle concentration, reducing surface tension, providing better foaming ability and foaming stability and also they act as a better emulsifying agent by reducing interfacial tensions between two phases. These days lot of research has been conducted on the Gemini based surfactant synthesis and application as it requires in lesser amount when it is formulated in any formulation with other ingredients. That means that Gemini surfactants serve the purpose e.g. cleaning, emulsifying in the lesser amount than conventional surfactants without compromising the desired throughput.

The work on silicone based Gemini surfactants has been initiated due to the potential characteristics provided by silicone linkage (Si-O-Si). The methyl group present in the siloxane surfactants tangle at the interface due to the high flexibility of silicone linkage results into the improvement in the surface properties. The conventional surfactant lacks this flexibility in the molecules as they contain only hydrocarbon bonds.

Li-Huei Lin et al. have synthesized silicone-based surfactant and studied the physicochemical properties of prepared molecules. In his study, PEG, PDMS and various chains of alcohols were connected by the glycidyl ether as a spacer. This prepared molecule possesses 0.061 mmol/L CMC and 22.1 mN/m surface tension which is considered as one of the good surface active agents as compared conventional surfactants [28]. Fu Han et al. studied the glucosamide-based trisiloxane surfactant, a new family of Gemini surfactant. The surface properties of the prepared dimeric compound i.e. glucosamide-based trisiloxane have been compared with the corresponding monomers and a dramatic improvement has been reported. This family of the Gemini surfactant obtained special attention as a part of the required raw material can be obtained from renewable sources [31]. Wang Guoyong et al. reported the adsorption and aggregation behaviors of tetrasiloxane-tailed Gemini molecules with ethylene oxide as a spacer. They reported that due to the incorporation of a short chain bulky siloxane moiety in the molecules, the molecule exhibited better surface properties in terms of lowering surface tension and CMC to the greater extent. This group also analyzed vesicle structure using TEM and DLS and found that vesicles are sphericle in nature, further they have confirmed the vesicle nature by encapsulating water-soluble compounds [32]. Guoyong Wang et al. reported the spontaneous vesicle formation from trisiloxane tailed Gemini surfactants. They confirmed that the formation of the vesicle is mainly due to the trisiloxane-tailed component and Gemini structure present in the Gemini molecule. Due to this vesicle formation capacity of these molecules, this surfactant can be utilized as a promising vehicle in the drug delivery system and in facile transport in the biomembrane [33]. Xiaohui Zhao et al. have studied the surface activity and thermodynamic properties in aqueous solutions of surfactants. They have compared tetrasiloxane Gemini imidazolium surfactants, the counterpart monomer and organic-based Gemini imidazolium surfactant on the basis of surface tension and electrical conductivity methods. This group has concluded that the tetrasiloxane Gemini imidazolium surfactant has a higher capacity to reduce surface tension as well as has a greater capacity to form micelles as compared to its corresponding monomer and organic-based Gemini imidazolium surfactant [30].

6 Applications

6.1 Agricultural

The study on the application of silicone surfactants in the agrochemicals has been extensively done since 1990. Due to their capability to provide a lower surface, good wetting and spreading properties on the hydrophobic leaves, silicone surfactants have a lot of scope in this application. Knoche, M. has written an extensive review on the effect of organosilicone surfactants on the spray solution in terms of their physicochemical properties [34]. In this review, foliar uptake and field performance of the agrochemicals have been discussed with the precautions to be taken during application.

The spray droplets containing silicone surfactants spread completely on the moderately hydrophobic leaf to encounter the insects present on the leaf [35]. Some silicone molecules degrade in the acidic/alkaline condition of spray solution which affects adversely on the performance. Murphy et al. have studied the performance of the four different silicone surfactants and two hydrocarbon surfactants for the agrochemical applications. They have proved that silicone surfactants possess superior properties in term of lowering surface tension, quick wetting and spreading etc. as compared to hydrocarbon surfactants on the paraffin film hence suggested that concluded that with the prior knowledge and precautions silicone surfactants can be applied in agrochemicals to get maximum utilization [36]. Sieverding et al. have proved that both super-spreader silicone surfactant and non-super-spreader silicone surfactant provide the same rainfastness performance and efficacy on herbicide. They also highlighted the reduced risk of ran off of non-super-spreader as compared to super-spreader which can result in low dosage [37]. Fu Xing Zheng et al. have optimized the organosilicone dosage for the correction of citrus zinc deficiency along with zinc fertilizers. Recently, they have studied the effect of foliar application of various fertilizers with various dosages with and without silicone surfactants and observed that appropriate quantity of these surfactants benefits to obtain the desired effect [38]. Toxicity to the mites and insects of the trisiloxane surfactants have studied along with pesticide. Due to their supreme surface properties, they allow wetting and either suffocate them or disrupt the physiological processes the mites and insects [39].

In the last almost 30 years, many researchers have studied the mechanism of wetting and spreading of silicone surfactants and proved them compatible, effective, efficient adjuvant for agrochemicals [36, 38, 40–45]. In 2016, Amandine Michel et al. have studied the different aspect of trisiloxane surfactant i.e. the mobility in the soil when it is applied as an adjuvant. They have proved that the trisiloxane surfactant possesses very slightly mobility in the soil on the basis of distribution coefficient between water and soil along with the surfactant. They also studied the worst case scenario by applying trisiloxane surfactant on the quartz sand followed by rainfall. From this study, they have concluded that this surfactant is least likely to percolate/leach in the soil when it is applied as an adjuvant hence there would not be any risk for groundwater contamination [46].

6.2 Textiles

Silicone surfactants have been used in the textile finishing since many decades in order to enhance the texture, appearance and to impart various morphological properties such as softness, smoothness, fluffiness, bounciness to the fabric. Silicone surfactants are responsible to make fabric hydrophobic, hydrophilic, wet feel, dry feel etc. when they are applied to the fabric. The effect of these finishing agents on the fabric is durable, long-lasting hence they are considered as effective finishing agents. The Somasundaran research group has worked on the various aspects of silicone treatment on the fabric [24]. Purohit et al. have studied the mechanism involved in the modification of the fabric surfaces with various silicones. In this study they applied amino silicones with a certain degree of quaternization on the fabric and studied the electro-kinetic properties as a function of pH and morphology of the fabric has been investigated using sophisticated techniques such as atomic force microscopy (AFM) [26, 47]. Somil C. Mehta et al. have studied the change in the behavior of emulsion stabilization by using various silicone polymers with the different molecular structure using phase diagrams. They developed emulsions with various systems including hybrid silicone surfactants and amino silicones for the textile finishing [48]. In our recent study, we have developed a nanoemulsion of silicone oil and pine oil using a binary surfactant system in order to impart various properties to the fabric such as softness, bounciness, fluffiness, antibacterial and mosquito repellency [49]. The binary surfactant system included a surfactant from hydrocarbon category (tridecanoic alcohol ethoxylate with 6 EO units (TDA-6)) and another surfactant from silicone based category (AG-pt). The purpose of incorporating AG-pt in the emulsion is to enhance the wetting and penetration ability of the emulsion in order to carry the active to the fabric pore which will result into long-lasting effect. The treated fabric with the prepared solution was analyzed by AFM and observed the physical modification of the fabric caused due to the emulsion as shown in Fig. 6. We have also studied the applicability of the silicone surfactant in a laundry detergent in our previous research and we have found that silicone surfactants are responsible to accelerate the washing mechanism removing various complex stains compared to other conventional surfactants [10].

6.3 Polyurethane foam

The surfactant is one of the components used while preparing polyurethane foam. It is required for uniform distribution of air in the cells and this property improves the consistency of foam by reducing surface tension. The silicone surfactants are widely used in polyurethane foam for many decades. The silicone surfactant protects the accumulation of gases generated during blowing operation by blowing agents so the foam does not collapse during rising.

Recently, A. Hasani Baferani et al. have studied the effect of the silicone surfactants on the mechanical, thermal, and acoustical properties of flexible polyurethane foams and proved that these properties can be improved using suitable silicone surfactant along with proper foam formulation [50]. X. D. Zhang et al. have shown that silicone surfactants have an important impact on both the bubble generation and the cell window stabilization stage. They have studied a range of silicone surfactants from lower to higher molecular weight and showed that a surfactant with a high content of silicone has a tendency to create a bubble with smaller size [51]. Eilbracht et al. have optimized the preparation of spray polyurethane foam with silicone isocyanate surfactants [52]. Few researchers have studied the importance of the silicone surfactants on the cell size and thermal conductivity of rigid polyurethane foam [53, 54]. Sayyeda M. Hasan et al. developed siloxane-based amphiphiles as cell stabilizers for porous shape memory polymer systems [55]. In the future, new silicone-based molecules for the polyurethane foam will be developed in order to get the desired properties in a more effective manner.

6.4 Personal Care and Cosmetic

Silicone oil, silicone copolyols and silicone surfactants are widely used in the formulation of creams, lotions, skin care products and hair care products etc. in order to improve the aesthetic performance of the formulations due to unique chemical and physical properties of silicone compounds

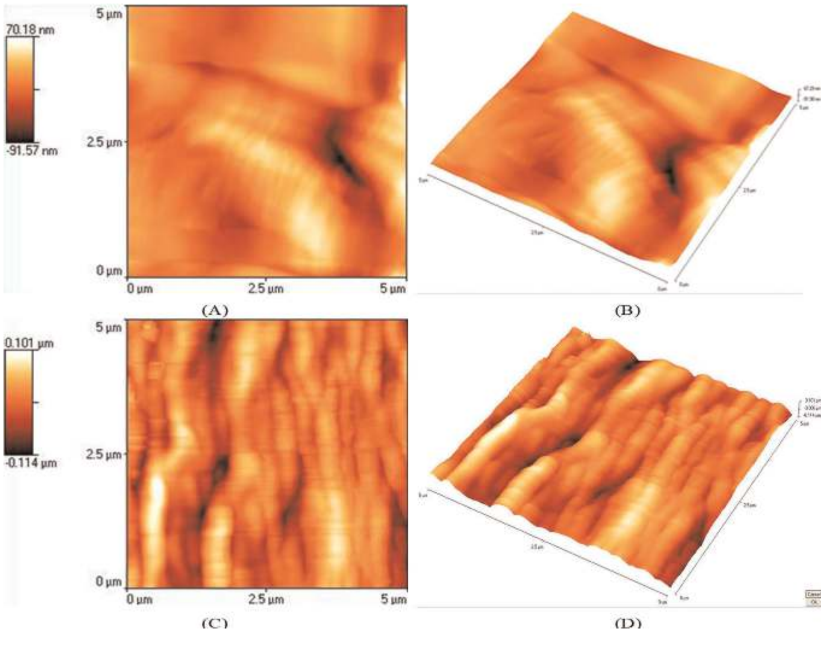

Figure 6 AFM images of fabrics (A) untreated fabric 2D image (B) untreated fabric 3D image (C) treated fabric 2D image (D) treated fabric 3D image (Image has been taken from our previously published work [49])

[56]. Dahms et al. have explored the new possibilities offered by silicones in the formulations. They studied how silicone polyoxyethylene compounds also called as silicone emulsifiers stabilize personal care formulations [57]. Moreover, they prepared different types of personal care formulations and studied rheology and stability along with applications. H. Nazir et al. have written an extensive review article on the various strategies to stabilize the silicone oil emulsions which are used in the hair care products using different conventional as well as silicone emulsifiers [58]. Silicone compounds with judicious modification with organic counterpart provide formulators an alternative to the conventional hydrocarbons with superior properties [59]. Rojas Wahl et al. have shown that in order to design formulations for shower/ bath purposes, it is very essential in order to get maximum throughput by optimizing the interaction study of the ingredients [60]. Anseth et al. have studied rheological properties of the silicone oil-water emulsion stabilized by siloxane based surfactant using an interfacial stress rheometer [61].

6.5 Metal extraction

The application of silicone surfactants in the metal extraction was not extensively studied until 2015. Silicone surfactant can be modified with certain groups such as imidazole and pyridine groups which will interact with a metal ion and can extract them from the aqueous solution. In 2016, Liying Fang et al. have designed novel cationic silicone surfactants to extract the metal ion from the aqueous system. They have speculated that cationic silicone surfactants can increase the lipophilicity i.e. hydrophobicity of the metal ion complexes which will accelerate the metal extraction process [62]. They have studied the metal extraction capability of prepared molecules and effective results have been observed in the case of gold and palladium ions from the acid solution. This study has opened the new vertical for the application of silicone surfactants by architecting judiciously silicone molecule.

Recently, X.Y. Yu, et al. have shown that cationic organosilicon collectors can be used for the floatation of the aluminosilicate minerals. They also studied the reverse floatation process of low-grade bauxite ore using cationic silicone collector and concluded it as an effective collector [63]. In froth floatation process, silicone surfactants with suitable functionalities can be used to generate a large amount of foam and providing hydrophobicity at the same time to the ions to be separated.

6.6 Other applications

The silicone surfactants have widespread applications in various sectors where low surface tension, wetting, spreading, foaming, antifoaming, penetration properties are required. These surfactants with a wide range of molecules can be applied in the construction industry, automotive industry, paper and pulp industry, leather industry, rubber industry etc. to serve above-mentioned properties. The antifoaming silicone surfactants are widely used in the petroleum industry to reduce or prevent the foam occurred during crude transportation from one place to another place for facile operation. The silicone emulsions with the various compositions are widely used to create water-resistant roofs. In the construction industry, the foaming silicone agents can be used to create foam to construct warehouses or buildings where strength is not the constraints.

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