

# Effect of functional groups on surface pressure – area isotherms of hydrophilic silicone polymers

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## ABSTRACT

The special Si – O bond characteristics of organic/inorganic hybrid silicone polymers have widened their applications in cosmetics, drug delivery, inks & paints, rubbers, hydraulic fluids and fabric care applications. Though they are widely used, the utilization of hydrophilically modified silicones on a large scale has mainly been empirical due to lack of fundamental knowledge about variation in their properties with systematic variation in their structure. The choice of moieties for hydrophilic modification of silicones in most of the earlier works has been non-ionic based on ethylene oxide and propylene oxide groups, however very little is known about their ionic counterparts. The current work focuses on understanding the behavior of functionally grafted silicone polymers with respect to variation in hydrophilic part of the grafting chain.

Hydrophilically grafted silicone polymers form monolayers at air – water interface, which are stabilized by interactions of functional groups that are submerged in water. The present work elucidated the

effects of functional group modifications on the conformational behavior of chains at the interface. It was observed that the shape of the chain depends on the available area at interface (or surface pressure) and there are conformational changes with increase in number of molecules per unit area. While PDMS chain may undergo stretched to helix transition as predicted earlier, this may not be true for hydrophilically grafted chains. Based on the shape of the surface pressure – area isotherm and correlation with the scaling theory, a gradation in hydrophilicity of functional groups and hence modified silicone chains is predicted.

## INTRODUCTION

Silicone surfactant is a generic name given to the molecules consisting of permethylated siloxane chain joined to one or more hydrophilic groups. The choice of hydrophilic moiety in most of the works in the past has been poly(ethylene oxide) to give a non-ionic silicone surfactant[1, 2]. A recent review in surfactant science series[3] describes the synthetic methods and surface active & phase behavior studies along with various applications such as deemulsification in oil production, defoamers in fuels and foam stabilizers in polyurethane foams. Other work describes the utility of silicone surfactants in other industrial formulations such as inks, paints and coatings[4], textiles, agricultures and personal care products[5]. While much effort has been made to understand the non-ionic silicone surfactants, very little is known about their ionic counter parts. Few preliminary works focused on cationic[6, 7] and anionic[8] trisiloxane surfactants and they found these trisiloxane surfactants to behave as excellent foaming agents[9]. Another work reported the synthesis and surface properties of zwitterionic silicone surfactant[10]. The objective of the current study is to understand the structure – activity relationship of functional polymeric silicone surfactants with respect to variation in hydrophilic part of the grafted chain. Since most of the applications of modified silicones involve modification of interfacial properties, the present work focuses on the effect of functional groups on conformational behavior of the polymer at air – water interface.

The surface pressure – area isotherm of poly(dimethylsiloxanes) (PDMS) have been investigated by many researchers in the past[11-19]. The initial work by Bank[11] and Zisman[12] focused on understanding the PDMS film on organic substrates. Newing[16] initiated work on modified siloxane showing the anchoring effect by terminal OH group. It was shown by Jarvis[14] that polarity of subphase liquid is important for stability and insolubility of PDMS film. From conformation point of view, several different structures have been proposed for conformation of linear PDMS chain. Damaschun[20] proposed a 6/1 helix with six backbone atoms per turn of the helix. Based on NMR spectra of crystalline PDMS, Flory[21] suggested a more extended conformation than Damaschun. An extended helical conformation was suggested based on cis-trans arrangements in PDMS[22]. All the three theories suggests helical

conformations, but Bernett and Zisman[23] showed trifluoro modification prevents formation of perfect helices because of steric hindrance of the bulky groups. A relatively recent work by Koberstein et. al.[19] have shown effect of functional groups on monolayer of end-group modified PDMS at air-water interface. They have also shown solubility of low molecular weight components in polydisperse systems[24]. While much work has been done on understanding air-water interface behavior of PDMS and end functionalized siloxanes, very little is known about hydrophilically grafted silicone chains. The present work reports the effect of functional graftings on siloxane polymers at air-water interface.

## **EXPERIMENTAL**

### **Materials**

PDMS was used as the reference compound in this study. PDMS of viscosity 50cSt was purchased from sigma chemical co. and was used as received. Amino modified polymeric silicone was synthesized from decamethyl cyclopentasiloxane (D5), tetramethyl ammonium hydroxide, and amino siloxane using equilibration process. The reactants were selected such that to have only one amino group per side chain. The ratio of reactants was selected to give m:n ratio of approximately 7.5:1 (figure 1) and the viscosity of the polymer was adjusted to 65 cps.

The cationic polymeric silicone surfactant was synthesized by methylation of the amino modified polymeric siloxane (figure 1). The quaternization reaction was carried out using methyl tosylate by stepwise addition method. The stoichiometric ratio was selected to obtain only 50% quaternization of amino groups as confirmed from amine value determination. The temperature of this exothermic reaction was maintained below 50°C by cold water-jacketing to reduce the yellowing of the compound.

The reaction to synthesize the anionic polymeric silicone (figure 1) has been carried out by reacting the amino modified silicone polymer with itaconic acid as previously reported in US Patents US5596061 and US5807955. The reaction was carried out above 90°C under controlled conditions for 3-4 hours till the desired acid value is reached. Here also the stoichiometric ratio was adjusted to have only 50% acid modification and was confirmed from acid value and amine value analysis. Solvents were avoided in order to eliminate any contamination of the product.

All modifications were performed at Elkay Chemicals Pvt. Ltd., Pune, India. Anionic and cationic silicone surfactants were synthesized by modification of amino modified compound; and hence the polymers are expected to have the same chain length. The structures and properties of the four compounds are listed in table 1. The products were characterized by nuclear magnetic resonance (NMR) and infrared (IR) spectroscopic methods (data not shown). The absolute molecular weights of polymers are not known but they are approximately 5000 based on viscosity measurements.

Langmuir isotherms were measured on Millipore water (18M $\Omega$  resistivity) subphase. Ionic strength was adjusted in some of the experiments using 99% pure sodium chloride purchased from Ruger chemical Co. and used as received. Urea (> 99% pure) was purchased from sigma-aldrich and was used as received to study the effect of hydrogen bonding. 1N hydrochloric acid and sodium hydroxide purchased from fisher scientific were used for pH adjustments.

### **Measurement of Langmuir isotherms**

Nima mini-langmuir trough (model 601 M) with vibration isolation was used for surface pressure measurements. The trough and barriers are made of Teflon to avoid any contamination of the subphase. Wilhelmy plate method using a paper plate (20mm perimeter) provided by Nima technology was employed for surface pressure measurement. Perfect wetting was ensured by first allowing the subphase solvent to completely wet the plate. The changes in surface pressure were measured using a pressure sensor, which was connected to a computer. The least count of the instrument is 0.1mN/m. The surface of water was cleaned by using micropipette aspirator. Chloroform, HPLC grade (with minimum purity of 99.9%) purchased from Pharmco products inc., was used as a spreading solvent. A solution containing 0.15mg/ml concentration of a given polymer in the spreading solvent was fixed for all experiments after a series of experiments done at different solute concentrations. 25 $\mu$ l of 0.15mg/ml solution was spread on water surface and chloroform was allowed to evaporate for 20mins. The surface pressure measurements were initiated only after ensuring that pressure sensor was reading zero surface pressure. This also makes sure that the spreading solvent was free of any non-volatile surface-active impurities. Constant temperature was maintained at 20 $^{\circ}$ C ( $\pm$ 0.1 $^{\circ}$ C) using Neslab water bath recirculator. The compression rate of barriers was fixed at 5cm<sup>2</sup>/min.

## **RESULTS AND DISCUSSION**

### **Conformation of silicone chain at air-water interface:**

The surface pressure – area isotherm obtained for the reference compound PDMS is shown in figure 2. The isotherm presents four regions. This data is in accordance with the PDMS isotherms of different molecular weights reported earlier[19, 25]. From the isotherms and from other spectroscopic techniques the following conformations are proposed in various regions

Region I: The individual polymer chains are far apart and there is no chain-chain interaction in this region. The polymer lies in a fully stretched conformation where the oxygen atoms of the – O-Si(CH<sub>3</sub>)<sub>2</sub>- units are in contact with water and methyl groups are pointing outwards.

- Region II: In this region, the polymer chains come close to each other and begin to touch. The rise in surface pressure indicates compactation of the polymer film.
- Region III: The plateau in this region corresponds to gradual transformation or phase change of the monolayer. The individual stretched chains have no further means to compress, and hence they are forced to change their conformation to a new one occupying a smaller surface area. The plateau represents transition of stretched chain to helices.
- Region IV: Slight increase in surface pressure reflects the formation of densely packed layer of helices. Once dense packing is achieved, there is no further place for helices to compress. Hence rather than deforming the stable helical conformation, the chains prefer to slide over one another giving rise to another plateau region.

It should be noted that all amino, quaternary, and acid modified compounds have one hydrophilic grafting chain per approximately 7.5 dimethylsiloxane units. Hence in order to have comparable repeat units, one repeat unit of PDMS includes about 8.5 dimethylsiloxane units. The area per repeat units observed in figure 2 is accordingly adjusted.

The isotherm of amino modified silicone chain is similar to PDMS isotherm in region I and region II (figure 3). But in region III, instead of plateau, further increase in surface pressure is observed in the case of amino modified silicone polymers. Similar regions I and II indicate that the amino modified siloxane, like PDMS, is fully stretched in region I and in region II the chains compress without any conformational change. In the case of region III in PDMS, there is change in conformation from straight chain to helix, which necessitates pulling some of the oxygen atoms out of water subphase. It is relatively easy to pull oxygen atoms out of water and form helix since there is no strong interaction between PDMS chain and water subphase. Whereas in the case of amino modified siloxane, the amino grafts stabilize the polymer chain on surface of water and hence act as tying points or anchors for the chains to water. To form helices of amino siloxane in region III, it is required to pull some of these anchors out of water. Since it will be relatively difficult to pull out amino groups from water, the amino chains further compresses and this leads to an increase in surface pressure. The slope of the line in region III is decided by the competitiveness of two simultaneous phenomena – compression of amino silicone chains and pulling out amino anchors from water.

The grafting chains of functionalized polymers are immersed in water subphase and hence the length of backbone chain determines the parking area of a repeat unit. The repeat unit of amino modified silicone polymer chain consists of 1 unit of  $m$  per approximately 7.5  $n$  units (figure 1). Therefore the backbone length that characterizes a repeat unit is 8.5 times the length of a Si – O bond. Based on van der Waals radius

and bond lengths of Si – O, Si – C and C – H bonds, the parking area of a fully stretched chain is approximately  $136 \text{ \AA}^2$ . Molecular modeling was also performed for amino modified silicone polymer as shown in figure 4, which suggests that the repeat unit area is about  $110 \text{ \AA}^2$ . Observed surface pressure isotherms shows transition from region II to region III near about  $120 \text{ \AA}^2/\text{repeat unit}$ . While, in the case of molecular modeling, curling of amino modified silicone polymer in vacuum underestimates the length of stretched siloxane chain at air-water interface, the bond length calculation depicts ideally stretched behavior and hence overestimates the repeat unit chain length. Hence bond length calculations and molecular modeling are coherent with the observation that the chains can be in stretched conformation in region II, but have to reconform when they enter into region III. In the case of PDMS, it has been established that chains undergo stretched – helix transition from region II to region III. Work done by Lenk et al[19] have shown that the chains of end functionalized siloxane also undergo stretched – helix transition from region II to region III. But in the case of grafted chains, many functional groups will have to be pulled out of water in order to form a helix. It is not clear in this case whether the grafted silicone chains form simple loops or helices in region III.

### **Effect of functional group**

The superimposition of the isotherms of all the graft modifications (figure 3) show that the curves look almost the same down to about  $120 \text{ \AA}^2/\text{repeat unit}$  (i.e. in regions I and II), with slight differences possibly due to minor variations in the equivalent weights of respective polymers. This is proposed to be due to stretched conformation of chains in regions I and II, where only chain lengths play a governing role and not the functional groups. On further compression, between  $120 \text{ \AA}^2/\text{repeat unit}$  and  $50 \text{ \AA}^2/\text{repeat unit}$ , the chain undergoes a transition from stretched conformation to helical or loops. In this process some of the functional groups are pulled out of water. The functional group that interacts most strongly with water will offer maximum resistance to come out of water. Hence the chain having higher affinity for water undergoes higher compression and shows higher surface pressure. Based on this hypothesis, the slope of the curves in region III can be considered to be a measure of the hydrophilicity of the functional groups on the chain. It can be seen from figure 3 that according to this theory, the increasing gradation of affinity of functional groups for water is amino > quaternary amino > acid modified > unmodified. Similar trend have been reported in the past for end functionalized silicone chains[19].

### **Use of scaling theory**

When an amorphous polymer is spread on a liquid support to form a monolayer, a surface pressure exists that is analogous to the osmotic pressure characteristic of three-dimensional solutions[26]. The

present approach makes use of the scaling theory[27] to establish connection between the functional group and stability at air-water interface by making use of relationship between surface pressure and concentration. Similar works have been done in past[17, 28-31] but their work focuses mainly on finding the second virial coefficient value. Leiva[30] in his work correlated the second virial coefficient with the good or theta solvent nature of air-water interface for poly(itaconates), but their aim was not to correlate with the modifying functional groups.

According to Scaling theory, in semi-dilute concentration region, surface pressure ( $\pi$ ) obeys a power law relationship with surface concentration ( $\Gamma$ ) and is independent of molecular weight. Hence in semi-dilute regime, where the polymer chains partially penetrate the region of influence of other chains, the relation between  $\pi$  and  $\Gamma$  can be given by equation 1,

$$\pi \propto \Gamma^{d/\nu} \quad (1)$$

where  $d$  is dimensionality and  $\nu$  is characteristic critical exponent. Theoretical predictions for chains in two dimensions are that  $\nu$  is equal to 3/4, 4/7 and 1/2 for good solvent[28], theta solvent[32] and poor solvent[33] conditions respectively. At very low concentration region, surface pressure can be related to virial coefficients of surface concentration as given in equation 2.

$$\pi / \Gamma RT \propto 1/M_n \Gamma + A_2 \Gamma^2 + A_3 \Gamma^3 + \dots \quad (2)$$

where  $R$  is gas constant,  $T$  is absolute temperature,  $M_n$  is the number average molecular weight and  $A_2$  and  $A_3$  are virial coefficients in two dimensional space.

In region I of the surface pressure – area isotherm, the chains are believed to be far apart and not interact with each other. Each chain is lying separately on water surface and interacts with just water subphase. In region II the chains start touching each other and they influence the neighboring chains. Both these regions can be correlated with the dilute and semi-dilute regions mentioned above and hence the equations mentioned above can be utilized to analyze the isotherms and obtain a quantitative insight. The area per repeat unit in the Langmuir isotherms were converted to surface concentration to plot  $\pi/(\Gamma RT)$  vs  $\Gamma$  in dilute region and obtain second virial coefficient using equation 2. Similarly equation 1 can be used to plot  $\ln \pi$  vs  $\ln \Gamma$  in the semi-dilute regime and to obtain the characteristic critical exponent for given system by using equation 1. The plots of  $\pi/(\Gamma RT)$  vs  $\Gamma$  and  $\ln \pi$  vs  $\ln \Gamma$  are shown in figure 5 and 6 respectively.

Though there is some dispersion of points in figure 5 at low surface concentrations, as also seen in other works[30], there is a clear distinction between the slopes of the curves. From equation 2, the slopes of curves represent second virial coefficient. The second virial coefficient is zero for theta conditions, negative for poor solvent and positive for good solvent. Here the second virial coefficients are slightly negative for poly(dimethylsiloxane) and acid modified siloxane polymer and slightly positive for amino and quaternary

amino modified silicone chains. The observed second virial coefficient behavior supports the hypothesis that stability of various silicone chains in two-dimensions is governed by their functional groups. The absolute values of slopes obtained are shown in table 2 and the gradation in affinity for air-water interface is in the order,

$$\text{amino} > \text{quaternary amino} > \text{PDMS} > \text{acid modified}$$

The intercept of curves in figure 5 should depict the inverse of number average molecular weights of various silicone chains. But it is observed that if curves are extrapolated linearly then the intercept will be approximately  $10^{-7}$ , which will give molecular weight of millions. This contradiction can be explained on the basis of work done by Granick[18]. He showed that the reduced surface pressure value  $\pi/(\pi RT)$  descends to a considerably smaller value than  $1/M_n$  to which it must extrapolate. But under very low concentrations of the polymer, the reduced surface pressure rises again to approximately extrapolate to  $1/M_n$ . This behavior could not be verified in the current study because of the limitation of the sensitivity of the instrument.

According to equation 1, the plot of  $\ln \pi$  vs  $\ln c$  in the semidilute region should show a linear variation with slope of  $2\nu/(2\nu-1)$ . Figure 6 shows this double logarithmic plot and the values of  $\nu$  calculated from the slopes of each curves is represented in table 2. It can be observed from table 2 that amino and quaternary amino modified silicone chains have a value of close to 0.55, which indicate proximity to theta solvent conditions ( $\nu = 0.571$ ) as opposed to PDMS and acid modified silicone chains where the values are closer to poor solvent conditions ( $\nu = 0.5$ ). This observation further confirms that in semidilute conditions amino and quaternary amino modified chains are relatively more stable at air-water interface than PDMS and acid modified chains. The reason for such a behavior is not clear. The absolute values of critical exponents confirm the gradation in hydrophilicity of the functional groups studied in present work.

Both, the second virial coefficient and critical exponent, show that the air-water interface resembles close to poor solvent conditions for acid modified silicone polymer.

## CONCLUSIONS

Hydrophilically grafted silicone polymers form monolayers at air-water interface, which is stabilized by interaction of functional groups that are submerged in water subphase. Silicone chains assume a fully stretched conformation in dilute (region I) and semidilute (region II) regimes. The isotherm behavior in this region is guided mainly by the chain length and hence is independent of the nature of modification. As the surface is compressed further, the chains are forced to change their conformation. In the case of PDMS, stretched to helix conformation change is relatively easy and hence shows a plateau in the isotherm. For functional silicones the formation of helix is resisted by the interaction of functional groups with water, and

hence there is a simultaneous conformational change accompanied by compaction of the chains. This leads to differential slopes of isotherms in region III, depending on predominance of one of the two mechanisms. Higher the affinity of functional group for water, steeper is the surface pressure curve in region III. Second virial coefficients and characteristic critical exponents of excluded volume were obtained by application of scaling concepts in dilute and semi dilute regions to the isotherms. The values of virial coefficients and critical exponents further corroborate the gradation in the hydrophilicity of functional groups obtained from region III of the isotherms. They also show that while all the chains are in theta solvent conditions at air-water interface, amino and quaternary amino modified silicone chains are relative more stable than acid modified and PDMS chains.

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- Figure 1 Structural representation of modified silicone polymer. The grafting ratio is denoted by  $m:n = 1:7.5$ .
- Figure 2 Surface pressure – area isotherms of poly(dimethyl siloxane) at air-water interface, pH of water = 6, Ionic strength = 0.
- Figure 3 Surface pressure – area isotherms of all compounds at air-water interface, pH of water = 6, Ionic strength = 0. Black = PDMS, Magenta = Acid modified silicone, Blue = Quaternized amino silicone, Red = Amino silicone.
- Figure 4 Molecular modeling of amino modified silicone repeat unit in vacuum to calculate the parking area on air-water interface. Repeat unit length = 8 dimethyl siloxane and 1 grafting chain.
- Figure 5 Plot of  $\pi/RT$  vs  $\pi$  in dilute region of the surface pressure – area

isotherm to obtain the sign of second virial coefficient

Figure 6

Plot of  $\ln \eta$  vs  $\ln \gamma$  in the semi-dilute region of the surface pressure – area isotherm to obtain the characteristic critical exponent of excluded volume

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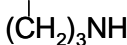
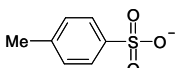
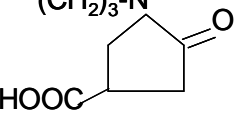
Compound	Structure	Viscosity (cps)	Amine value (mg KOH/gm)
Poly(dimethyl siloxane)	$\text{Me}_3\text{SiO}-[\text{Me}_2\text{SiO}]-\text{SiMe}_3$	50	-
Amino modified polymeric siloxane	$\text{Me}_3\text{SiO}-[\text{Me}_2\text{SiO}]_n-[\text{MeSiO}]_m-\text{SiMe}_3$ 	65	83
50% quaternization of A with methyl tosylate	$\text{Me}_3\text{SiO}-[\text{Me}_2\text{SiO}]_n-[\text{MeSiO}]_m-\text{SiMe}_3$ 	High (not analyzed)	35
50% modification of A with Itaconic acid	$\text{Me}_3\text{SiO}-[\text{Me}_2\text{SiO}]_n-[\text{MeSiO}]_m-\text{SiMe}_3$ 	Very viscous, do not flow	48.8

Table 1: Structure and properties of hydrophilically grafted silicone polymers.

Compound	2 <sup>nd</sup> virial coefficient	Critical exponent
Amino modified polymeric siloxane	Positive ( $7.727 \times 10^{-7}$ )	0.553
50% quaternization of A with methyl tosylate	Slightly positive ( $2.885 \times 10^{-7}$ )	0.544
Poly(dimethyl siloxane)	Slightly negative ( $-7.419 \times 10^{-9}$ )	0.525
50% modification of A with Itaconic acid	Slightly negative ( $-3.106 \times 10^{-8}$ )	0.524

Table 2: Second virial coefficients and characteristic critical exponent values as obtained from scaling concepts