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Physico-chemical properties of siloxane surfactants in water and their surface energy characteristics

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Abstract

A simple but efficient method has been followed for the synthesis of water soluble siloxane amphiphile by grafting poly(ethylene glycol) (PEG) onto the hydrophobic poly(hydromethyl siloxane) backbone. Systematic variations in the amount of PEG incorporations were carried out to get water soluble oligomers. The structural analysis of the systems was done by ^{1}H NMR and GPC analysis. The solution behavior of these amphiphiles was studied. The presence of nonpolar microdomains was observed at concentrations $\geq$0.01 g/dL for all the systems. Interestingly, I_3/I_1 ratio of pyrene fluoroprobe solubilised in aqueous solution of amphiphile suggests greater nonpolarity of microdomains in the system containing a higher PEG graft. The oligomers were shown to be surface active wherein, critical aggregation concentration decreased systematically with the decrease in the hydrophilic PEG substitutions. However, the system with a higher PEG substitution shows the close packed aggregates in the solution as suggested from the viscosity and fluorescence measurements. The contribution of polar and dispersion component towards the total surface energy was studied by the contact angle measurement by the sessile drop method.

Keywords: Siloxane surfactant; Surface properties; Sessile drop method

1. Introduction

The basic properties of a surfactant such as surface activity and self-assembly formation are important in polymer and surface science in addition to their practical use in medicine and surface modification applications such as paints, coatings, etc. [1,2]. The surfactants based on oligomeric or polymeric molecule have received wide attraction both at academic and industrial scale because of their unique and tailor-made properties over the conventional low molecular weight surface active agents. The oligomeric/polymeric surfactants that exhibit association and self-assembly behavior in water are basically amphiphilic in nature and consist of hydrophobic and hydrophilic moieties within the same molecule. Among various hydrophobic systems, silicon containing surface active agents are well known and applied in different fields such as polyurethane foam additives [3,4], in textile manufacture, cosmetic formulations, as agricultural adjuvants and as paint additives [5–9]. Silicone surfactants are amphiphilic materials containing methylated siloxane hydrophobe such as poly(dimethyl siloxane), trimethylsilyl groups coupled to one or more polar groups [10–12] especially polyether units, e.g. poly(ethylene oxide) (PEO) and pluronics [13,14].

The uniqueness of siloxane surfactant is that it is soluble in both water and organic liquids, thus contributing hydrophobic as well as oleophobic properties to the molecule and hence can reduce the surface tension of both water and organic liquids. This makes silicone surfactant to perform better than low molecular weight polymeric surfactants derived from long alkyl chain units, even in organic media [15]. This unusual quality of siloxane surfactant arises from two properties: one is its flexibility which enables it to acquire conformations that results in close and efficient packing at various interfaces and the other is its low cohesive energy derived from its

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greater voluminous and cross-sectional area of the siloxane unit at the interface [16]. Another interesting property of siloxane is its low T_g even for higher molecular weights, which makes it easier to perform at room temperature. Predominantly, nonionic silicone polyether copolymers are used as surfactant, which possess a maximum surface tension depression of ~21 mN/m and low critical micelle concentration (CMC) [17]. Comparing the surface activity of an amphiphile with a long methylene ($C = 11$) groups and nonionic trisiloxane surfactant with small branched hydrophobic part, the latter was found to be much effective. Roughly it is calculated that a single $SiMe_2$ unit can be compared to four CH_2 and CMe_2 can be equated only to two CH_2 groups of the alkyl chain [18]. These siloxane surfactants can self-assemble into a variety of ordered morphologies in the melt as well as in solution depending on the volume fractions of the hydrophilic units such as PEO [19]. Apart from the composition of the hydrophilic and hydrophobic units, the structural architecture of the polymer plays an important role in the self-assembling process. Though the structural variation can be brought out by various polymeric techniques (block, graft, random, co), the siloxane surfactants provide a fascinating aspect of modifying the siloxane backbone itself to form a variety of molecular architectures such as comb-like, ABC type, branched siloxanes, A–B copolymer, etc. The great popularity of PEO surfactants is driven by the unique combination of physico-chemical and biological properties as in artificial hearts, blood vessels and various catheters [20,21]. These include excellent solubility in aqueous and in most organic solutions.

Despite wide and extensive industrial usage of siloxane surfactant, the literature reveals only limited studies related to their surface active property [22,23]. Most of the studies are related to the low to medium molecular weight copolymers with comb-like and ABA type molecular structures [24]. In the case of comb-like systems, the surfactant property has been studied in aqueous solution for the surfactant system containing only one or two hydrophilic PEO units. Further, to the best of our knowledge, there are no reports on the surface energy estimation of these siloxane surfactant systems with varying hydrophilic–hydrophobic contents at solid/air interface. Here, in this report we are aiming to study the solution structure properties of water soluble comb type siloxane surfactants with varying amounts of poly(ethylene glycol) (PEG) units. The influence of the PEG units on the surfactant nature of the system was revealed using various techniques such as fluorescence and viscosity measurements. Further we attempt to study the surface energy variation at various interfaces using surface tension estimation and contact angle measurements.

2. Experimental

2.1. Materials

Polyhydromethyl siloxane (PHMS) (Mw 1902), hexachloroplatinic acid and *n*-octadecane were purchased from Lancaster and were used as received without any further purification. Monomethoxy poly(ethylene glycol) (MPEG) of molecular weight 550 obtained from Aldrich was dried over molecular sieves and used. Allyl bromide and potassium *t*-butoxide were obtained from SD Fine chemicals and used as received. Toluene was dried over calcium hydride and tetrahydrofuran (THF) was dried over potassium hydroxide. Both the solvents were freshly distilled before use.

2.2. Synthesis of allyl monomethoxy poly(ethylene glycol) (AMPEG)

AMPEG was synthesized by modifying an already reported procedure [25] shown in Scheme 1. MPEG of 10.3 g (0.018 mol) was reacted with 2.2 g (0.02 mol) of potassium *t*-butoxide in 10 mL THF by stirring for half an hour at room temperature. Allyl bromide of 3.39 g (0.028 mol) was then added dropwise and stirring was continued for another 3 h at room temperature. The product was obtained by extracting in dichloromethane after washing with water several times. A yellow liquid product was obtained by removing the solvent. Yield: 70%. The FT-IR spectrum shows a strong absorption band at 1112 cm^{-1} corresponding to the C–O–C stretch of methoxy and ethylene oxide groups. The presence of C═C due to the allyl group is confirmed by the peak at 1644 cm^{-1}.

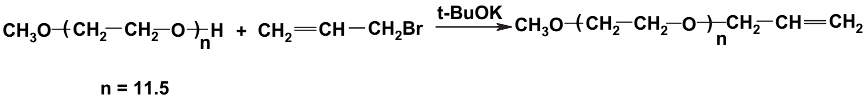
The assignments of the chemical shifts to their corresponding groups using ^1H NMR spectrum are as follows: δ 4.9 and 5.0 ppm, doublet of a doublet due to the terminal $CH_2{=}$ of the allyl group; δ 5.7 ppm, a multiplet due to the $={CH}-$ of the allyl group; δ 2.03 ppm, $-CH_2-$ of the allyl group; δ 3.43 ppm, $-(OCH_2CH_2)_n$ and δ 3.1 ppm, $-OCH_3$.

2.3. Synthesis of PHMS–AMPEG oligomer

PHMS was reacted with AMPEG by the hydrosilylation reaction [26] in the presence of hexachloroplatinic acid as a catalyst and the reaction was standardized at 110 °C for 120 h. Three sets of PHMS–AMPEG oligomer systems (Table 1) were synthesized by varying the amount of AMPEG units. The feed composition was taken so as to have 29, 20 and 10 units of PEG substitution in the systems A–C, respectively. The oligomer was purified by extracting in ether and then by extensive washing with methanol and water to ensure the removal of unreacted PHMS and AMPEG. The incorporation of PEG units was estimated from the ^1H NMR spectroscopy by employing individual characteristic integral chemical shifts of MPEG and PHMS.

Fig. 1 shows the overlapped FT-IR spectra of the oligomers A, B and C. Disappearance of alkene stretch at 1644 cm^{-1} confirms the absence of unreacted AMPEG in the systems. The gradual increase in the Si–H stretch at 2100 cm^{-1} from systems A–C confirms the incorporation of AMPEG units in the systems, which is in line with feed compositions.

The ^1H NMR spectrum of system A is shown in Fig. 2 as a demonstrative spectrum. Peak assignments for the oligomer are as follows: δ 0 ppm, $Si-CH_3$; δ 0.53 ppm, a triplet for $-CH_2-Si-$; δ 1.2 ppm, multiplet for $-CH_2-$ group in the



$$CH_3O-(CH_2-CH_2-O)_n-H + CH_2=CH-CH_2Br \xrightarrow{t\text{-}BuOK} CH_3O-(CH_2-CH_2-O)_n-CH_2-CH=CH_2$$

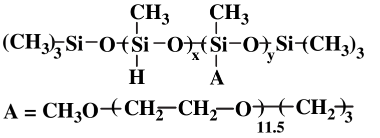
n = 11.5

Scheme 1.

Table 1
Characterization of PHMS–AMPEG oligomers: composition and molecular weight

Systems	Feed composition		Composition calculated from ^{1}H NMR		Mw (10^{-4})	PDI
	x	*y*	*x*	*y*		
A	0	29	3	26	1.7	1.2
B	9	20	12	17	1.1	1.4
C	19	10	20	9	1.3	1.9

Mw – weight average molecular weight from GPC; PDI – poly dispersity index from GPC.



$$(CH_3)_3Si-O-(\underset{H}{\overset{CH_3}{Si}}-O)_x-(\underset{A}{\overset{CH_3}{Si}}-O)_y-Si(CH_3)_3$$

$$A = CH_3O-(CH_2-CH_2-O)_{11.5}-(CH_2)_3$$

PEG moiety flanked by two other $-CH_2-$ groups; δ 3.27 ppm, $-(OCH_2CH_2)_n$ of AMPEG; δ 2.99 ppm, $-OCH_3$ of AMPEG; δ 4.6 ppm, Si–H proton. The disappearance of chemical shift at 4.5–5.5 ppm confirms the absence of unreacted AMPEG in the systems.

2.4. Characterization

All the oligomers were characterized by ^{1}H NMR using JEOL 500 MHz in $CDCl_3$ solvent without the internal standard and the reference was set with the solvent peak at 7.4 ppm. The weight average molecular weight of the oligomers was determined by gel permeation chromatography (GPC) (JASCO model MX-2080-31) with a RI detector using PL gel column in THF with a flow rate of 1 mL/min. The molecular weights were calculated with a calibration relative to polystyrene standards.

Fluorescence spectrum was recorded at ambient temperature using Varian (model Cary Eclipse) fluorescence spectrophotometer. The emission spectra were obtained by performing the experiments using slit width of 5 nm and excitation wavelength at 337 nm and emission wavelength at 354 nm. The concentration of pyrene was maintained constant (1×10^{-6} M) in all the solutions. The concentration of the oligomers studied was in the range of 1×10^{-3}–0.05 g/dL.

The viscosity of aqueous solutions of the oligomer systems was measured using 0.3 mm diameter capillary and 3.0 mL capacity Ostwald viscometer at 25 ± 1 °C. Flow through times of oligomeric solutions ranging from 2 g/dL to 15 g/dL in concentrations were determined. The intrinsic viscosity $[\eta]$ was calculated from the intercept of $[(t/t_o) - 1]/C$ versus C plots, where t is the flow time of the sample, t_o is the flow time of water and C is the concentration of the sample in g/dL.

Surface tension measurements for the three systems were done using dynamic surface tensiometer (NIMA, type DST9005 S.No. 016) using glass cover slip as the probe using Milli Q

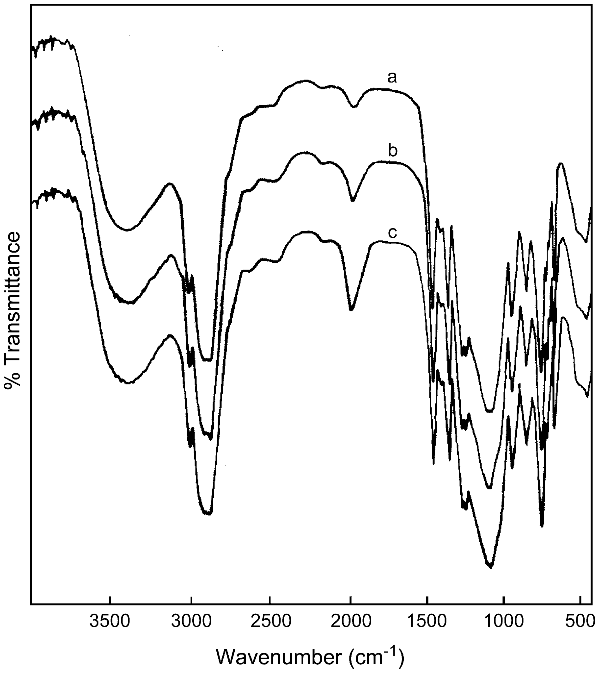


Fig. 1. Overlapped FT-IR spectra of the oligomers A, B and C.

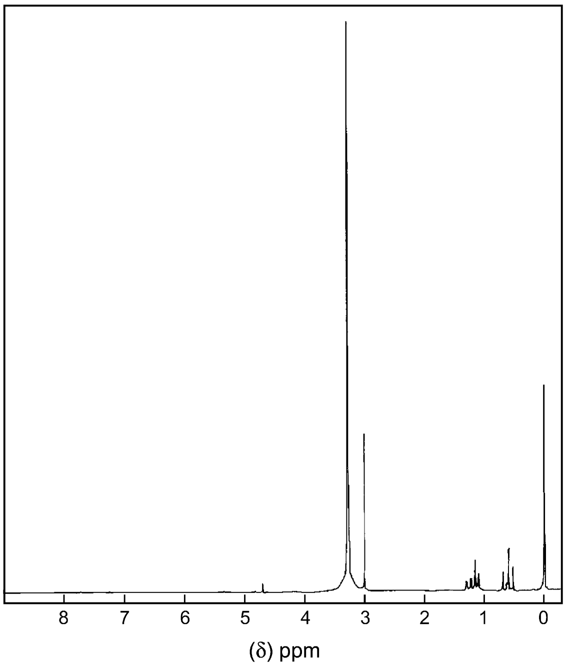


Fig. 2. ^{1}H NMR spectrum of system A.

water. The concentration of the oligomeric systems was varied from 1.5×10^{-5} M to 7.5×10^{-3} M (1×10^{-3}–0.5 g/dL).

The contact angles have been measured at ambient temperature by sessile drop method using a camera mounted on a microscope to record the drop image using Digidrop (GBX) model goniometer with Windrop software. Double distilled water and *n*-octadecane were used as solvents for the studies. The oligomer samples made from 5% (v/v) oligomer solution in water were coated by dip coating method on glass slides, followed by drying in air. Equilibrium contact angle was measured for a time period of 120 s depending on the stability of the drop. Average of the results obtained from three experiments was taken for contact angle measurements. The surface energy of the films was calculated using Young and Fowkes equation and the details of the experimental procedure are reported elsewhere [27].

3. Results and discussion

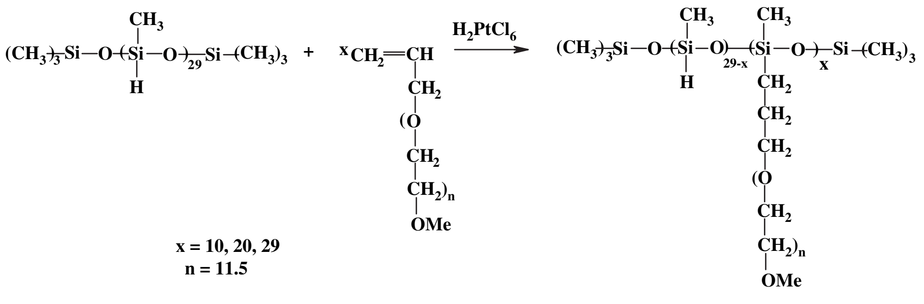
AMPEG was incorporated into PHMS by the hydrosilylation reaction to synthesise a water soluble siloxane oligomer, using platinum catalyst (Scheme 2). The amount of AMPEG was varied systematically for the hydrosilylation reaction in order to get the water soluble PHMS–AMPEG oligomers. Predictably, the solubilities of the oligomer were a function of the number of PEG units which were hydrophilic. A threshold composition for the water soluble PHMS–AMPEG oligomer was reached with the feed composition of 10 mol of AMPEG units to 1 mol of PHMS backbone below which the PHMS–AMPEG oligomer was found to be insoluble in water. Accordingly, three sets of oligomers (Table 1) have been synthesized.

The feed composition was taken so as to have 29, 20 and 10 units of PEG substitution in the systems A–C, respectively. In the oligomers, the number of incorporated PEG groups to PHMS was calculated from ^{1}H NMR using the integral ratios of the ethylene oxide protons of AMPEG at δ 3.27 ppm and methyl groups attached to siloxane of PHMS at δ 0 ppm. It could be seen from Table 1 that the incorporation of AMPEG in the oligomers is in the range of 85–90% of the feed composition. The molecular weight data of the systems obtained from GPC is in the order of 10^4. The values agree within the limits of error with the PEG incorporations as obtained from the ^{1}H NMR calculations. All the oligomers exhibit molecular weight distribution in the range of 1.2–1.9.

3.1. Investigation of the microstructural characteristics by fluorescence measurements

Emission spectra of fluorescence probes are exceptionally useful for the characterization of microheterogeneous system consisting of amphiphilic molecules such as monomeric or oligomeric surfactants, ionomers or hydrophobically modified polyelectrolytes. The formation of hydrophobic domains in solution by the self-association of the polymeric chains can be conveniently followed by pyrene probe that has longer life time in the excited singlet state [28]. From the emission spectra of pyrene in polymeric amphiphilic systems, it is possible to assess the local polarity in the probe's neighborhood, based on the intensity ratio of the third ($I_3 = 384$ nm) to the first ($I_1 = 373$ nm) emission maxima. A higher value of this polarity index is associated with nonpolar environments [29]. The chain characteristic of the polymer can also be ascertained using the excimer to monomer ratio if the probe is attached chemically to the polymer chain. Here, we are interested in only studying the presence of microheterogeneous phases in the polymeric system. So, a fixed amount of the probe [1×10^{-6} M] is physically mixed to the polymeric systems.

For the three oligomeric systems, A–C with varying amounts of PEG incorporations into the siloxane backbone, the I_3/I_1 ratio of the pyrene probe was estimated as a function of concentration and are shown in Fig. 3a–c. The variation in hydrophobic–lipophilic balance (HLB) of the oligomers afforded through the incorporation of AMPEG in the PHMS contributes to the formation of aggregated structures, which differ in micropolarity. I_3/I_1 values for the systems reach a maximum value and remain almost constant in the concentration range greater than 0.01 g/dL, which suggests that the polarity of the pyrene environment does not vary much with further increase in the concentration. All the three systems are observed to have the I_3/I_1 ratios varying from 0.93 to 1. This shows that the systems under investigation form nonpolar domains when compared to water with the I_3/I_1 ratio of 0.68. System C shows a lower ratio of 0.93 when compared to systems A and B that show a ratio of 1 and 0.97, respectively. This may be due to the fewer amounts of PEG units in system C to form nonpolar microdomains around the pyrene probe resulting in the formation of loosely coiled structure. In the case of system A with higher PEG units, higher HLB makes the surfactant more self-organized with more compactness leading to



Scheme 2.

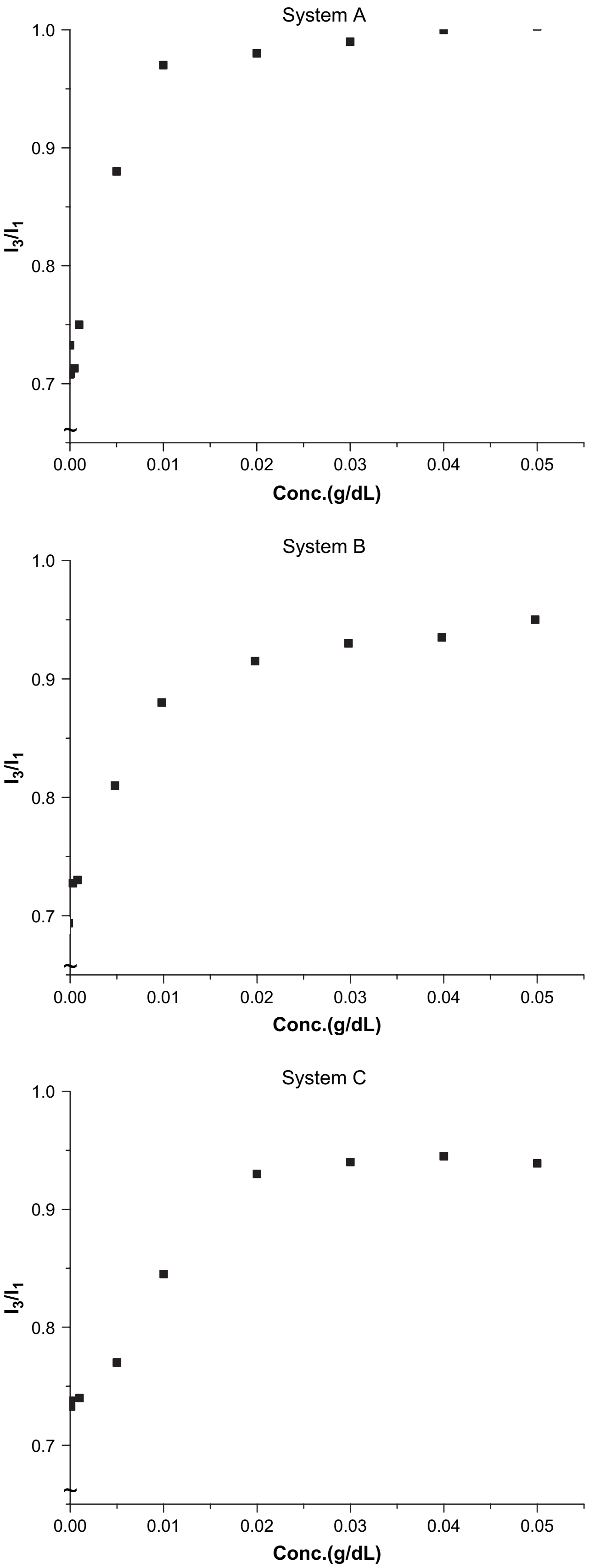


Fig. 3. I_3/I_1 emission intensity ratio of pyrene [1×10^{-6} M] for oligomers A−C as a function of concentration.

lesser exposure of pyrene to the environment. This investigation also reveals that the critical aggregation concentration (CAC) for all the three systems was almost the same with system A showing 0.0095 g/dL, system B around 0.012 g/dL and system C around 0.017 g/dL. This observation of CAC was further confirmed by the macroscopic characterization, which will be discussed further under surface tension studies.

3.2. Viscosity measurements of oligomers in aqueous solutions

In order to compare the microstructural property with the macroscopic property of the polymer solution, viscosity estimations were performed in the concentration range of 2−15 g/dL. The viscosities for all the systems were found to increase on increasing the concentration of the polymer which obeys the Huggins equation for the estimation of intrinsic viscosity by extrapolating to zero concentration. Here, in our systems, from the viscosity plots shown in Fig. 4, the intrinsic viscosity $[\eta]$ was found to increase with decreasing content of PEG units. It has been reported that for a polymeric surfactant derived from PEG units, the more compact aggregated structures were perceived by the lower intrinsic viscosity when compared to open structures [30]. A higher $[\eta]$ value of 0.034 dL/g in system C with lower PEG units indicates the presence of loosely self-assembled clusters which is in accordance with the observed lower I_3/I_1 ratio. Accordingly, systems B and A show $[\eta]$ values of 0.025 dL/g and 0.019 dL/g, respectively, suggesting the presence of more compact structures for systems B and A with increasing PEG units. This macroscopic structural assessment confirms the results observed in the microscopic investigations from fluorescence measurements.

3.3. Conformation of oligomers at air/solution interface by surface tension estimation

Surface tension method is the most versatile method used for estimating critical micelle concentration. We can also get information on the nature of adsorbed layers at the air/solution interface from the surface tension values. The higher area of the silyl group, the high flexibility and close packing arrangement of the siloxane surfactants at the air/solution interface induced us to explore the adsorption behavior of these oligomeric systems with varying HLB. The grafting of more (>10) hydrophilic PEG units onto the siloxane backbone creates an expectation in analyzing the surface tension when compared to single or double PEG units attached to trisilyl groups that show a surface tension of ∼21 mN/m. The concentration ranges employed for the surface tension estimation are 1.5×10^{-5}−7.5×10^{-3} M.

All the three systems reach an equilibrium surface tension of 50 mN/m as shown in Fig. 5, which is much higher than that of simple siloxane surfactant derived from trisilyl groups. The variation in the number of silyl units and PEG units grafted would have varied the HLB compared to trisilyl surfactant and thereby ultimately decreasing the adsorption of the oligomers to the surface of water. In spite of having similar

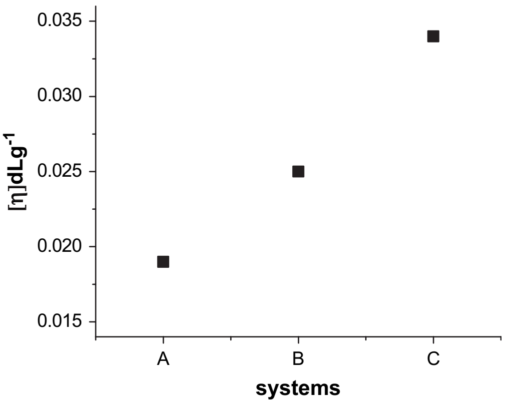


Fig. 4. Variation of [η] for oligomers A–C.

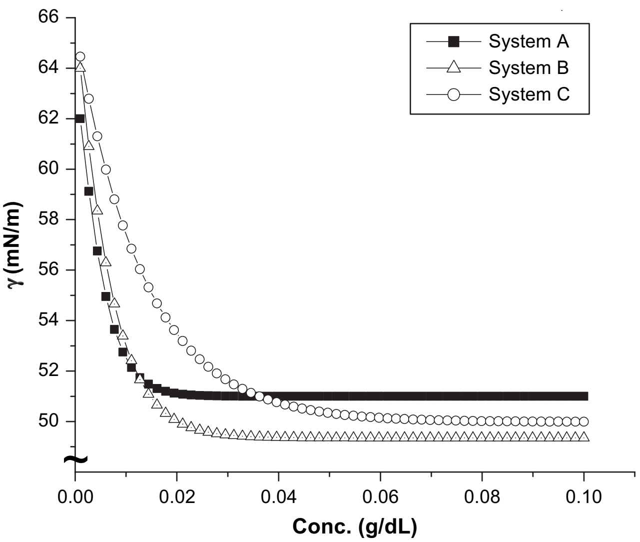


Fig. 5. Surface tension representation of the systems at the solution/air interface as a function of concentration.

equilibrium surface tension, all the three attain this equilibrium at different concentrations monitored as their CACs. System C has got a CAC of about 0.017 g/dL which is high compared to system A (0.008 g/dL). System C which has got a HLB towards hydrophobicity and loosely arranged structures as construed from the fluorescence measurements, will have to use more number of polymeric chains to form an aggregated structure, whereas system A with an optimum HLB employs minimum amount of polymeric chains to self-assemble. The length of the hydrophobic and hydrophilic moieties plays a crucial role in determining the micellar formation [31]. Since in our systems, the hydrophobic and hydrophilic chain lengths are maintained the same with the difference only in the number of incorporated hydrophilic PEG units, we could observe very close CAC values for these systems.

The packing characteristics of the groups at the interface can be inferred from the surface excess concentration Γ_2 and the area/molecule a_1^s parameters as estimated from Gibbs adsorption isotherm equation [32,33]

$$\Gamma_2 = 1/2.303RT(\delta\gamma/\delta \log C_2)_T$$

where, $R = 8.314\ \mathrm{J\,mol^{-1}\,K^{-1}}$, T = absolute temperature in K, γ = surface tension in mN/m, C_2 = concentration in M, Γ_2 is expressed in $\mathrm{mol\,cm^{-2}}$ obtained from the linear portion of the surface tension versus $\log C$ graph. From the surface excess concentration, the area/molecule at the interface in $\mathrm{\AA}^2$ is calculated using,

$$a_1^s = 10^{23}/N\Gamma_2$$

The surface excess concentration and the area/molecule values are given in Table 2. The area/molecule for all the systems is found to be around 100 $\mathrm{\AA}^2$. The dependency of the calculated surface area/molecule on the hydrophobicity of grafted siloxane surfactants is not straightforward because of the complexity and similarity of their molecular structure.

3.4. Surface energy characteristics of the oligomers by contact angle measurements

There are various other methods including microscopy, light and neutron scattering that have been extensively used to carry out the structural investigations of aggregates and gels. Contact angle is a widely accepted method to study the surface energies governed by the molecular aggregates assembled at the interface [34,35]. Contact angle is a common measure of the hydrophobicity of the surface. It can provide information about the surface energies, surface heterogeneity and surface roughness. The total surface energy for the systems was calculated from the contact angle measured by the sessile drop method employing the relationship given by Young and Fowkes equation and the results are given in Table 3. Fig. 6 shows the photographs of the water and

Table 2
Surface tension measurements at solution/air interface

Systems	$\Gamma_2 \times 10^{-10}\ \mathrm{mol\,cm^{-2}}$	a_1^s ($\mathrm{\AA}^2$)
A	1.69	98.24
B	1.64	101.23
C	1.60	103.7

Table 3
Surface energy estimations from contact angle measurements

Systems	γ_s^d	γ_s^p	γ_{SV}
A	26.51	34.97	61.48
B	26.04	46.3	72.34
C	26.77	45.51	72.28

γ_s^d = dispersion component in mN/m.
γ_s^p = polar component in mN/m.
γ_{SV} = total surface energy in mN/m.

Fig. 6. Photograph of the (a) water droplet and (b) octadecane droplet on the film of system A.

octadecane droplets on the film of system A coated on glass surface using aqueous solution of system A.

The surface energy characteristics of these systems at liquid/air interface were studied in order to know the organization behavior of these systems when coated to a solid substrate (glass). From earlier reports it is observed that the solution behavior of siloxane systems will be retained even when coated to a solid substance or when casted as a film. Before discussing the surface energy characteristics, the spreading and wetting behaviors of these films were ascertained using the kinetic plots. Fig. 7 shows the kinetic plots of the polymeric systems coated on glass substrate for water and octadecane. When a water drop is placed on the surface, system A showed an initial contact angle of 36.4°, which spreads to 28.52° and remains the same as equilibrium. System A has the maximum number of hydrophilic groups when compared to systems B and C. Therefore we expect the maximum spreading of water if all the hydrophilic groups were exposed on the surface. The initial contact angle of <40° shows that the surface is hydrophilic but the equilibrium contact angle around 28.52° reveals the non-availability of all the hydrophilic groups at the surface. Systems B and C showed increased initial spread and equilibrium contact angle when compared to system A showing the presence of more hydrophilic character at the surface. This shows that the availability of hydrophilic groups at the interface is more for systems B and C even though they have comparatively lower number of PEG groups. This observation is also supported by the spreading behavior of *n*-octadecane on the surface of these systems. The hydrophobicity at the interface is higher for system A when compared to systems B and C. System C with minimum hydrophilic groups shows the highest equilibrium contact angle confirming the highest availability of hydrophilic groups at the surface.

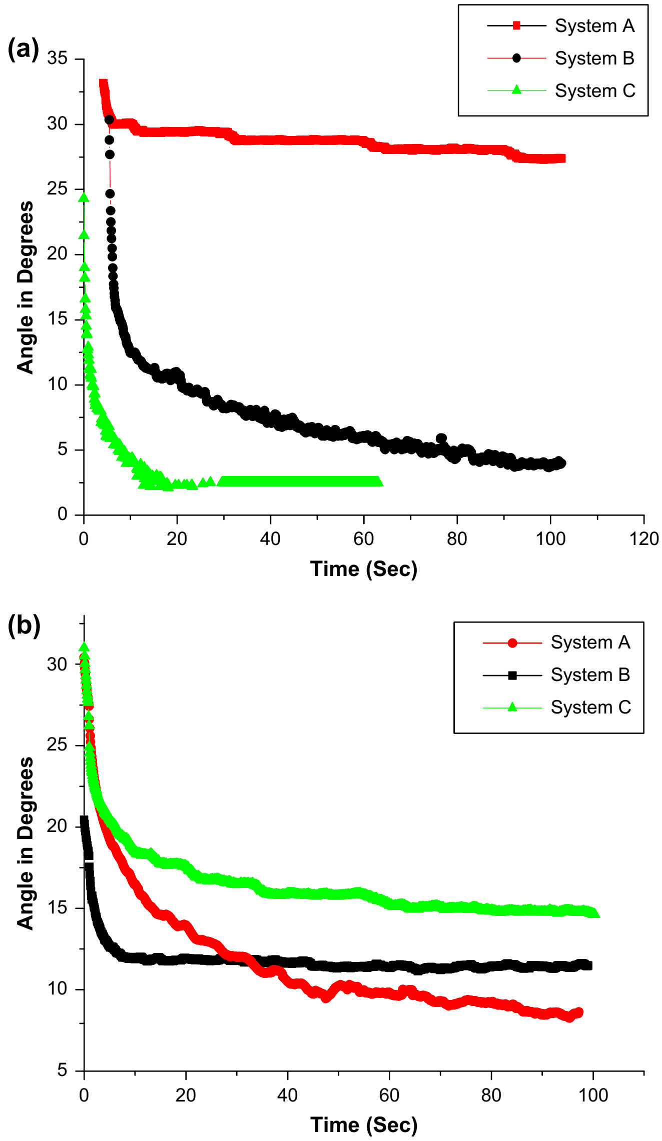


Fig. 7. Kinetic plots of the coated oligomeric systems with (a) water and (b) octadecane.

In order to determine the contribution of polar and dispersion factors towards surface energy, they were calculated using the following Young and Fowkes equation [36],

$$\gamma_{\mathrm{LV}}(1+\cos\theta)=2\left(\gamma_{\mathrm{L}}^{\mathrm{d}}\gamma_{\mathrm{s}}^{\mathrm{d}}\right)^{1/2}+2\left(\gamma_{\mathrm{L}}^{\mathrm{p}}\gamma_{\mathrm{s}}^{\mathrm{p}}\right)^{1/2}$$

where γ_{LV} is the interfacial tension at liquid/air interface, $\gamma_{\mathrm{L}}^{\mathrm{d}}$ and $\gamma_{\mathrm{s}}^{\mathrm{d}}$ are the dispersion factors for the liquid used and the sample coated substrate, $\gamma_{\mathrm{L}}^{\mathrm{p}}$ and $\gamma_{\mathrm{s}}^{\mathrm{p}}$ are the polar factors for the liquid used and the sample coated substrate, and θ is the contact angle between the coated sample and liquid/air interface. The total surface energy γ_{SV} of the samples was estimated using the following relationship,

$$\gamma_{\mathrm{SV}}=\gamma_{\mathrm{s}}^{\mathrm{d}}+\gamma_{\mathrm{s}}^{\mathrm{p}}$$

For all the three systems A–C, surface energies calculated are found to be almost similar in the range of 65–72 mN/m. However, all the systems did not show similar polar and dispersion factors. This further confirms the difference in the availability of the hydrophilic groups at the interface for these systems. For system A, the polar to dispersion ratio is less and this suggests a conformation having both hydrophilic and hydrophobic groups at the interface. Whereas, for systems B and C, the polar contribution towards total surface energy is about 63% confirming the higher hydrophilic group availability at the interface.

4. Conclusion

Hydrosilylation procedure was followed to synthesise water soluble silicone surfactants. This was achieved with the minimum incorporation of 9 PEG units to the siloxane backbone containing 29 siloxane groups. The systems with varying hydrophilic units exhibit different solution structure properties depending on the incorporation with PEG units to the hydrophobic backbone. It is understood from the fluorescence experiments that increase in the AMPEG incorporations to PHMS resulted in aggregates with more nonpolar microenvironment. The formation of aggregates in these systems with varying PEG incorporations was observed from the [η] values. An equilibrium surface tension of 50 mN/m was achieved with these systems showing almost similar CAC values. This gives the idea that the variation in the number of incorporations of equal molecular weight hydrophilic groups does not show much variation in their surface properties when compared to the chain length variation. The surface excess concentration at the air/solution interface was calculated from the surface tension experiments. The wetting behavior for the systems was also studied by the sessile drop method with water and octadecane. The contribution of the hydrophilic groups towards the total surface energy was observed in all the three systems containing different PEG (9, 17 and 26) units. The system with higher hydrophilic units shows the availability of both the hydrophobic and hydrophilic groups at the interface, whereas those with lower hydrophilic groups favour the conformation with more hydrophilic groups at the interface. The PEG incorporation has also been employed to improve solubility and to regulate membrane permeability due to the high degree of segmental flexibility for the separation of gases and liquids, which will be discussed in our future work.

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