

Studies on the Preparation of Pluronic F127 Monolayers at Air-Water Interface

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Abstract: Properties of monolayers of Pluronic F127 at air/water interface have been investigated by using Langmuir trough method. Pluronic F127 is a triblock copolymer of poly(ethyleneoxide) (PEO groups)–poly(propylene oxide) (PO groups)–poly(ethylene oxide) (PEO groups). Surface pressure versus mean molecular area isotherms is studied. The isotherm of the monolayer showed the characteristics of a pancake-to-brush transition upon compression of the monolayer. The effect of adding surfactant (SDS) to polymer and the effect of increasing loading on polymer was also studied. The effect of repeated compression and expansion cycle (or hysteresis curve) is investigated to know about stability of the film formed. Static elasticity of monolayer gives information about molecular arrangement, phase structure and phase transition.

Keywords: Surface-pressure; mean molecular area isotherms; hysteresis; static elasticity.

1. Introduction

Water-soluble triblock copolymers of Poly (ethylene oxide) (PEO) and Poly (propylene oxide) (PPO), often denoted PEO-PPO-PEO or $(EO)_{n1}(PO)_m(EO)_{n2}$, are commercially available non-ionic macromolecular surface active agents. Variation of the copolymer composition (PPO/ PEO ratio) and molecular weight (PEO and PPO block length) during synthesis leads to the production of molecules with optimum properties that meet the specific requirements in various areas of technological significance. As a result, PEO-PPO-PEO block copolymers are an important class of surfactants and have wide spread industrial applications [1, 2] in detergency, dispersion stabilization, foaming, emulsification, lubrication, and formulation of cosmetics etc.

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The PEO-PPO-PEO triblock copolymers are synthesized by the sequential addition of first propylene oxide (PO) and then ethylene oxide (EO) to a low molecular weight water-soluble propylene glycol, a poly(propylene oxide) oligomer (note that propylene glycol changes from water soluble to water insoluble as the molecular weight increases beyond about 740). The oxy alkylation steps are carried out in the presence of an alkaline catalyst, generally sodium or potassium hydroxide. The catalyst is then neutralized and removed from the final product.

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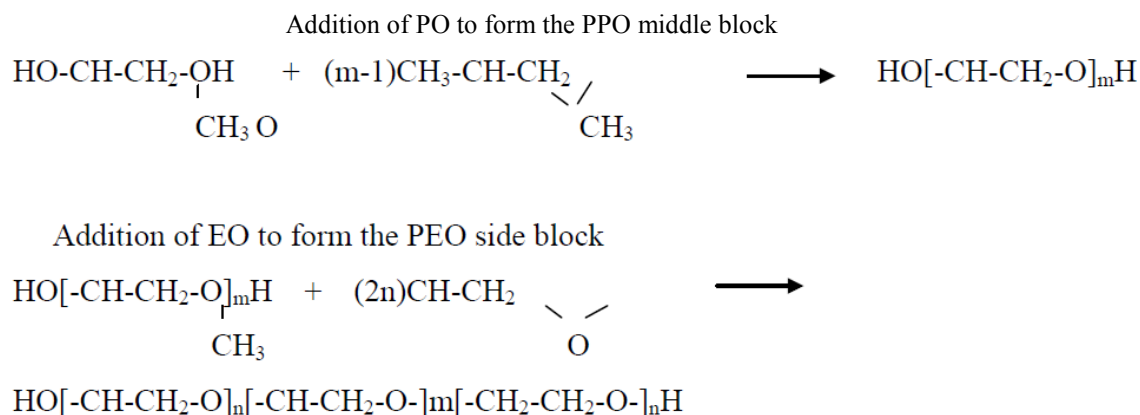


Fig. 1. Preparation of Pluronic F127

The Pluronic PEO-PPO PEO block copolymers are available in a range of molecular weights and PPO/PEO composition ratios [1-3]. The Pluronic copolymers are arranged in the so-called "Pluronic grid" [4-6]. The copolymers along the vertical lines have the same PPO/PEO composition, while the copolymers along the horizontal lines have PPO blocks of the same length. The notation for the Pluronic tri block copolymers starts with the letters L (for liquid), P (for paste), or F (for flakes). The first one or two numbers are indicative of the molecular weight of the PPO block, and the last number signifies the weight fraction of the PEO block. Cross-linking causes polymers to have a higher mechanical strength and often results in its swelling ability to be better controlled, due to its defined swelling behavior [7-9]. Such properties are important in many applications, such as in the Drug Delivery System (DDS). An example of a DDS is gels

showing a surface specificity to only a certain type of cells which are loaded with drugs. They are made to swell and release the drugs upon an external trigger, after they have reached the cells to be treated [10-14].

Cathy et al. [5] aimed to determine both the surface properties of a Pluronic F127 monolayer at the air/water interface and the effect of a surfactant to the polymer monolayer. Sodium dodecyl sulphate (SDS) was chosen as the surfactant, as its tail is sufficiently hydrophobic to allow binding to the hydrophobic groups of the polymer, but not hydrophobic enough to allow the formation of an insoluble monolayer at the air/water interface. This polymer–surfactant system therefore enabled to study the effect of a surfactant on a polymer monolayer. The isotherm of the monolayer showed the characteristics of a pancake-to-brush transition upon compression of the monolayer. Addition of ionic surfactants into a non-ionic polymer causes the polymer to crosslink at low to intermediate surfactant concentrations, and to break up the polymer at high concentrations. Cross-linking causes polymers to have a higher mechanical strength and often results in its swelling ability to be better controlled, due to its defined swelling behavior. Such properties are important in many applications, such as in the Drug Delivery System (DDS). An example of a DDS is gels showing a surface specificity to only a certain type of cells which are loaded with drugs. They are made to swell and release the drugs upon an external trigger, after they have reached the cells to be treated [15-18]. Effect of increasing loading on polymer and hysteresis cycle has not been reported. This information is useful to know about stability and porosity of film. These polymers are commercially available and are effective in sealing permeated cell membranes [18-23].

2. Experimental

Materials Used

Pluronic F127 ($M_w = 12,600$ kDa, AnaSpec, Fremont, USA) and sodium dodecyl sulphate (SDS, high purity, Wako, Japan) were used without further purification. Milli-Q water was used as the sub phase. A monolayer of F127 was spread drop wise on the pure water surface from a 12.4 M solution of F127 in chloroform (CHCl_3 , >99% purity) using a 50 μL syringe (Hamilton, Switzerland). The structures of Pluronic F127 and SDS are shown in Fig. 2.

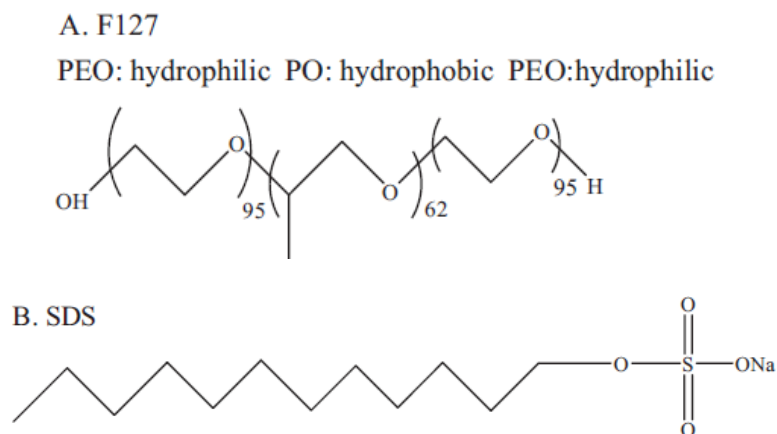


Fig. 2. Structures of A:Pluronic F127 and B: SDS

Experimental Methods

Surface pressure measurements were accomplished by the use of a Langmuir mini-trough system (KSV instruments Ltd., Finland) having trough size 324mm x 75mm. The precision in the surface pressure measurements was ± 0.02 mN.m. Milli-Q water (resistivity >18.2 M Ω .cm at 24 $^{\circ}$ C) was used as the sub phase. The surface pressure was measured using the Wilhelmy plate method. The measurements were performed at 24 $^{\circ}$ C by using a constant temperature bath. The Langmuir balance was enclosed in a box of glass in order to minimize air turbulence as well as the fallout of dust particles. Appropriate amount of the solution was spread on the water surface, and allowed to equilibrate for 20 min before starting compression. Isotherms were recorded at a compression speed of 10 mm.min $^{-1}$. The π -A curves were recorded for different loadings of di-block copolymer and during repeated compression and expansion.

The behavior of Pluronic F127 film was studied by measuring the surface pressure as a function of mean molecular area (A^2 /molecule) at the air-water. The compression rate of 10 mm.min $^{-1}$ was used. Pluronic F127 being a water soluble polymer, a part of polymer leaks into the sub phase during the compression/expansion steps. The surface pressure and mean molecular area were continuously monitored during each compression/ expansion cycle.

Number of researchers [9-13] have studied static dilatational modulus as a function of surface area and the surface dilatational modulus of the monolayer of poly(n-hexyl isocyanate) (PHIC) as a function of surface concentration at the air-water interface. Bomqvist et al. [14] have studied PEO-PPO-PEO copolymer at air-water interface. They compared surface rheological properties of Langmuir film and adsorbed film by plotting the dilatational modulus as a function of surface pressure. They compared the E- π curves for Langmuir film of P85, F88 and F127. They found similarities of the adsorbed and Langmuir layers are in

agreement with at least up to a surface pressures of 10 mN/m. Identical viscoelastic behavior in spread and adsorbed films of PEO homopolymer and PEO-PPO-PEO copolymers up to the PEO plateau surface pressure of 10 mN/m was found by other researchers also.

3. Results and Discussion

II- A Isotherms of Pluronic F127

Surfactants have been used to physically or chemically crosslink polymer gels for use in the DDS. The introduction of ionic surfactants into a non-ionic polymer has been reported to cause the polymer to crosslink at low to intermediate surfactant concentrations, and to break up the polymer at high concentrations [15-21]. The cross-links occur as a result of the binding of the surfactant molecules to the polymer chains through hydrophobic interactions [22]. In Figure 3, π -Aisotherms of the F127 monolayer on pure water and those measured after adding 10^{-5} mol SDS to the water are compared. In case of Pluronic F127 surface-pressure increases with increase in mean molecular area and pseudo plateau is obtained as polymer goes through pancake to brush transition. With Pluronic F127 maximum surface pressure that was reached was 16.70 mN/m and with addition of 10^{-5} mol of SDS maximum surface pressure increases to 24.28 mN/m. The addition of SDS also decreased the stiffness of the monolayer. This increased flexibility can be explained by (i) the more fluid nature of the SDS molecules in comparison to the polymer molecules, (ii) the electrostatic repulsion between the SDS groups in the monolayer, and/or (iii) binding between the hydrophobic PO groups and the hydrophobic tails of the SDS molecules. Similar work has been done by Cathy et al.[5]. In the literature maximum surface-pressure is 15.5 mN/m and in the present study surface-pressure of 16.70 mN/m is obtained.

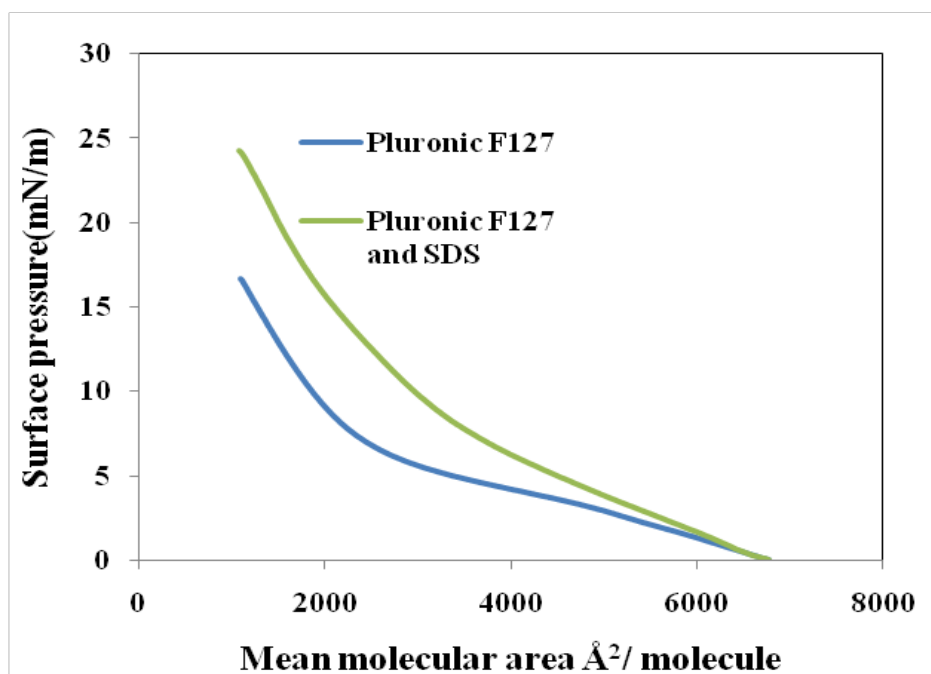


Fig. 3. Surface pressure–area isotherms. A: Blue solid line, F127 monolayer at an air/pure water sub phase. B: Green solid line, F127 monolayer with 29 μ M SDS at an air/pure water sub phase.

Effect of Repeated Compression-Expansion on Behaviour of π -A Isotherm

The surface pressure of the Langmuir film increases when the film is compressed. The highest pressure is reached when the barriers are at the closest attainable distance (40 mm). When the spread film is subjected to repeated compression-expansion sequence, initially the highest pressure increases but after reaching surface pressure = 17.41mN/m it decreases after each cycle. Figure 4 shows the highest film pressure attained during a cycle as a function of the number of cycles.

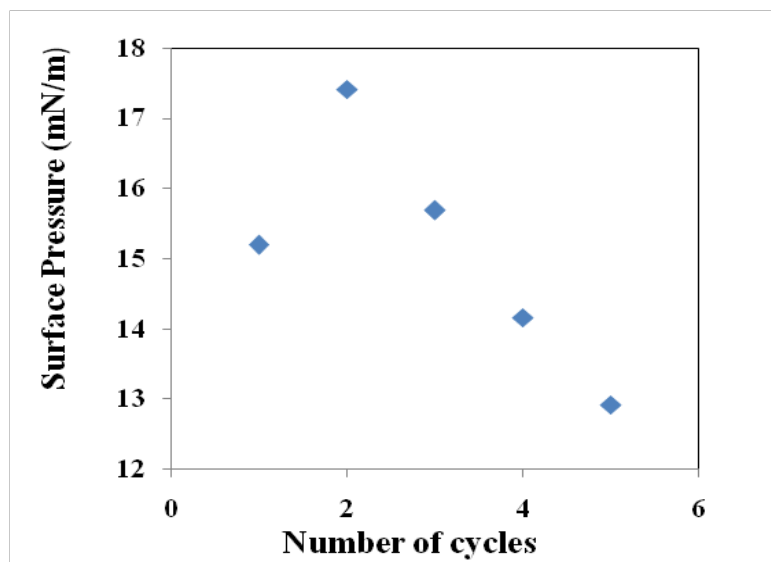


Fig. 4. Surface Pressure (π) – number of cycles plot for 12.6 kDa molecular weights of Pluronic F127 (Quantity added = 7.5 μg of Pluronic F127, Sub phase = pure water)

Hysteresis

Figure 5 shows the hysteresis in surface pressure profiles when a series of compression and expansion cycles are carried out for low loading of polymer at air - liquid interface. It is reported that the hysteresis may be because of loss of polymer to the water sub phase during the experiment. Figure shows $\pi - A$ isotherm, Pluronic F127 monolayer of loading repeated compression and expansion. A possible cause for the hysteresis in films during first compression is that compression forces some of the film into the aqueous sub phase, since isotherm Pluronic F127 is miscible with bulk water in all proportions at room temperature. The amount of loss of polymer in terms of reduction in the mean molecular area is due to dissolution into the sub phase and difficult to come back on surface as Pluronic F127 is miscible with water.

The surface pressure values recorded during expansion correspond to lower molecular areas. When a second compression is imposed, the isotherm has a similar shape and is shifted to lower molecular areas relative to the initial compression isotherm. After further compression – expansion isotherm curve shifts to lower molecular areas. Subjecting the system to repeated compression and expansion cycles causes a drift of the isotherms toward lower molecular areas, with the distance between successive compression expansion curves increasing.

Effect of Increasing Pluronic F127 Loading

We increased the total amount of polymer in the film, as it does not show a plateau of the surface pressure, indicating that there is a scope for increasing the surface pressure by compressing the film further and increasing the loading of polymer on water surface.

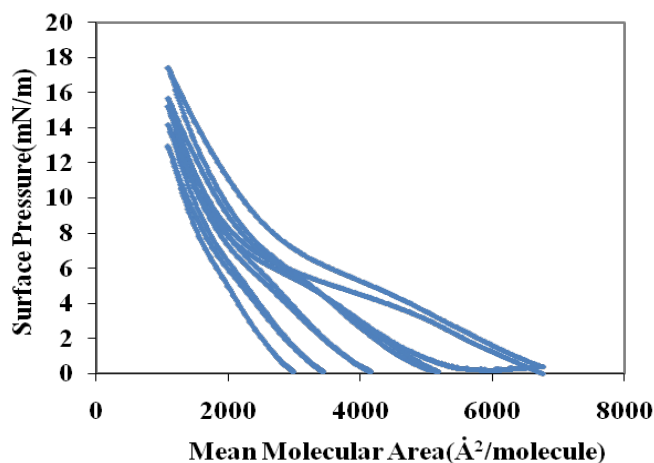


Fig. 5. Surface Pressure (π) – Mean molecular area (A) isotherms of a spread film at 24 °C obtained during repeated compression-expansion cycles.

The polymer was loaded from the dilute solutions so as to prevent clustering and forming a more coherent film. The resulting isotherms for 12.6 kDa PluronicF127 are shown in Figure 6. Moreover, the isotherm shows slow rise and then steep rise. Using loading of 7.5 μg , we have been able to achieve a maximum surface pressure of nearly $16.70 \text{ mN}\cdot\text{m}^{-1}$. In case of high loading of PluronicF127 on water surface, we obtained maximum surface pressure of $20.91 \text{ mN}/\text{m}$. Though the maximum surface pressure is increasing but the isotherm is shifting towards lower mean molecular area.

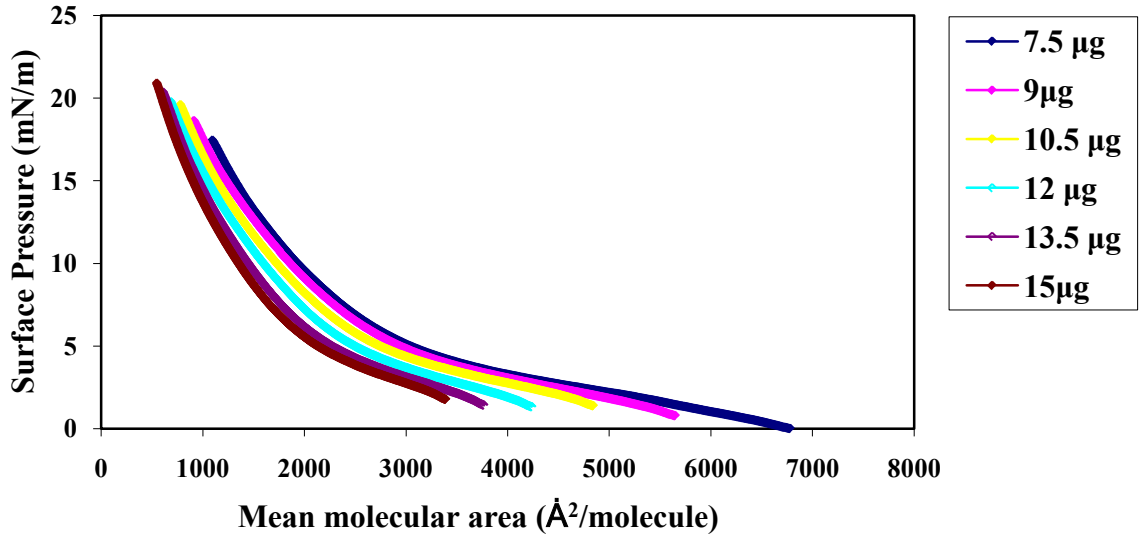


Fig. 6. Π -A isotherms of 12.6kDaPluronicF127 with increasing quantity

Static-Elasticity Measurements

An important characteristic of monolayers at air-water interface is their Gibbs elasticity, defined as the change in surface pressure ($d\pi$) caused by a change of the surface area (A), expressed as the relative area variation, dA/A [20].

$$E = A (d\gamma/dA) = (d\gamma/d \ln A) = (-d\pi/d \ln A) \quad (1)$$

In case of Langmuir films, the surface dilatational modulus is also called static dilatational modulus [21]. E can also be defined in terms of π as,

$$E = [d\pi / d \ln \Gamma] \quad (2)$$

where, Γ is surface concentration of polymer molecules at air-water interface. The unit of the E is same as the surface pressure, mN/m.

Figure 7 shows elasticity curve for compression which have similar trend as found earlier [5,6]. At low surface pressures ($\pi < 1.4$ mN/m), all blocks have an almost flat conformation without long loops and tails protruding into the water phase. At higher surface pressures beyond the first elasticity maximum, the films are no longer two-dimensional, and PEO segments begin to protrude into the sub phase, thus leading to the formation of a self-similar structure at the surface. The relaxation of surface stresses can proceed now at the expense of PEO segment exchange between the proximal, central, and distal regions of the surface layer, and

the surface elasticity decreases with increasing surface pressure. Beyond the local elasticity minimum ($\pi > 5.3$ mN/m), the PPO segments continue to have an almost flat conformation at the surface, but PEO chains extend further into the water phase. A brush structure consisting mainly of PEO segments begins to form. The interactions between the extended PEO chains, and also between PPO segments at the surface, lead to a gradual increase in the surface elasticity. Similar reasoning for elasticity has been given by earlier workers [6, 7].

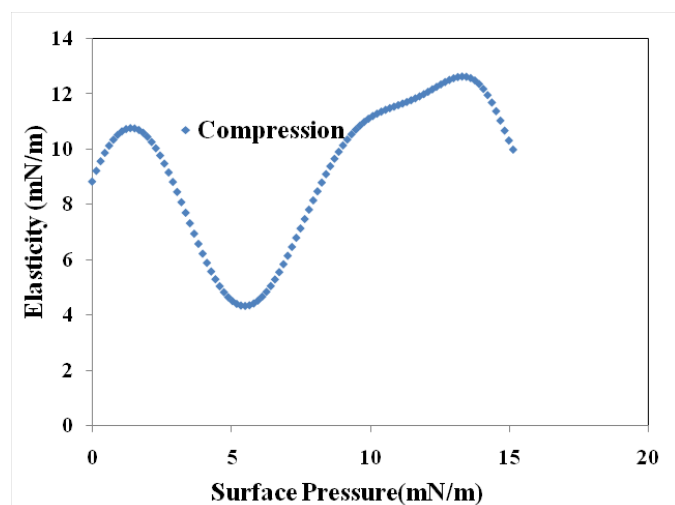


Fig. 7. Static dilatational modulus (E) vs. surface pressure (π) plot of compression(-) of Langmuir monolayer of Pluronic F127 at the air- water interface.

Fig. 8 shows compression and expansion curves of static dilatational modulus. The elasticity of spread monolayer on compression and expansion having similar curve trend reflects that film becomes cohesive and elastic in nature. Static dilatational modulus for compression is 12.64 mN/m and for expansion is 15.55mN/m. There is shift in expansion curve when the surface-pressure is between 10 mN/m to 15 mN/m because there is rapid drop in expansion curve after reaching maximum compressed state in surface-pressure vs. mean –molecular area curve.

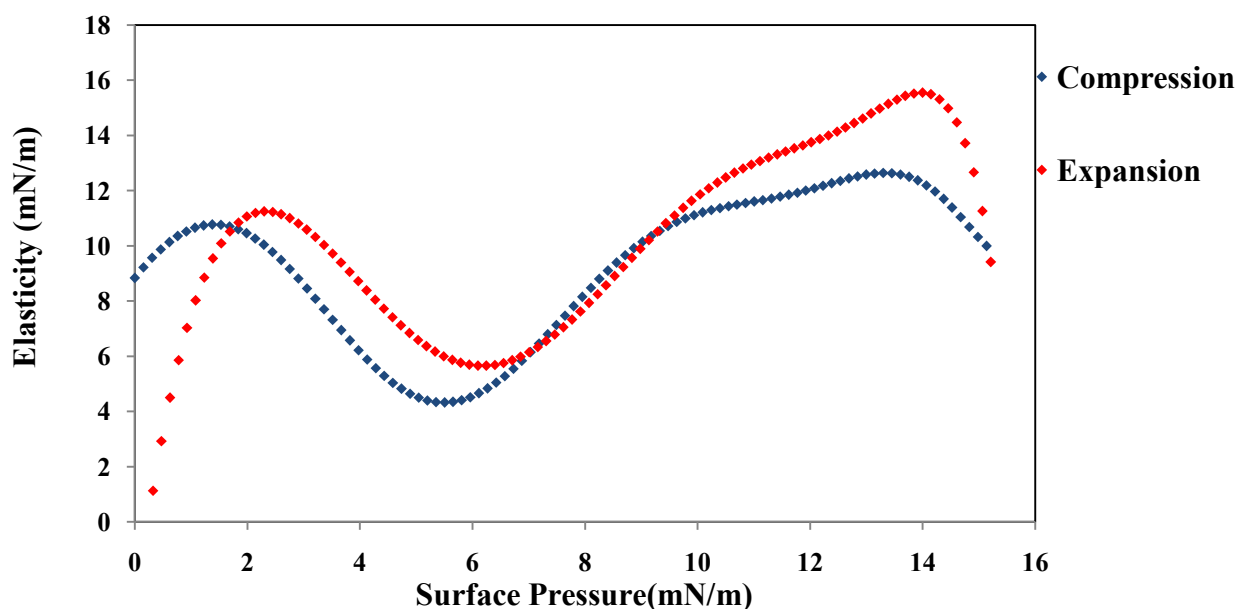


Fig. 8. Static dilatational modulus (E) vs. surface pressure (π) plot of compression (-) followed by expansion (-) of Langmuir monolayer of Pluronic F127 at the air- water interface.

4. Conclusion

The addition of SDS molecules to the aqueous sub phase caused the SDS molecules to adsorb to the F127 monolayer, either by binding to the F127 monolayer and/or forming a mixed monolayer of F127 and SDS. The presence of SDS decreased the stiffness of the monolayer, caused by (1) the inclusion of the fluid SDS molecules in the F127 monolayer, (2) the electrostatic repulsion between the negatively charged SDS groups in the monolayer, and/or (3) the changed visco-elasticity of the monolayer due to the binding between the PO groups and the hydrophobic alkyl chains of the SDS molecules. In this study also, surface-pressure vs. mean molecular area isotherms showed the characteristics of a pancake-to-brush transition upon compression of the monolayer. On adding surfactant surface-pressure increases as the introduction of ionic surfactants into a non-ionic polymer cause the polymer to crosslink at low to intermediate surfactant concentrations, and break up the polymer at high concentrations. Although much work has been reported on particular surfactant but effect of increasing loading on polymer and effect of repeated compression-expansion cycle has not been reported. Here, we have also found that for increasing the loading of polymer surface pressure increases. On performing repeated compression-expansion cycles they shifts towards lower mean molecular area in case of Pluronic F127 as it is soluble in water and film is not retained. Stability and porosity of the film is found by these experiments which is useful in drug delivery system. They are also useful in bio processing, medicine

and in sealing permeated membrane. These macromolecules adsorb at various interfaces and play a significant role in dispersion stabilization, foaming, and emulsification. Elasticity curve for compression have similar trend as found earlier [6]. In future Quartz crystal microbalance can be done to determine the areal mass density of the polymer in the film. Ellipsometry can be done to obtain the thickness of the film and atomic force measurements can be done to estimate uniformity of the film.

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