INTRODUCTION

In recent reviews1–7 various aspects of the maximum bubble pressure method (MBPM) were discussed. The physical processes taking place during the formation and growth of a bubble at the tip of a capillary and its separation, the problems of measuring bubble pressure, life time and so-called dead time were summarized in detail elsewhere5. Using this method, significant results have been obtained recently in many fields of application where dynamic surface tensions at short as well as long adsorption times are required, including industrial and biological applications.

In the present work our aim is to study the adsorption of non-ionic surfactant at the air/water interface. The adsorption properties of non-ionic surfactants have been investigated for a long time because of their importance in the fundamental surface science as well as their relevance in the efficiency of a variety of industrial formulations. The adsorption of non-ionic surfactant at the air/water interface has been intensively investigated by a verity of methods of surface tension measurement.8–10 In these studies adsorption kinetics of variety of non-ionic surfactants has been studied. In the present study the adsorption of non-ionic surfactant from dilute solution on its free aqueous interface is investigated with high precision dynamic and static surface tension measurements.

MATERIALS AND METHODS

Materials

The surfactant used in our experiment is triton x-100 (C_{14}H_{22}O (C_{2}H_{4}O)_{n}), which is a non-ionic surfactant, octylphenol polyglycol ether with 10 ethoxy groups. It has a hydrophilic polyethylene oxide group (on average it has 9.5 ethylene oxide units) and a hydrocarbon lipophilic or hydrophobic group.

Chemical structure of triton x-100

Study of adsorption of triton x-100 at air/water interface using maximum bubble pressure method

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ABSTRACT

The maximum bubble pressure method was used to measure the dynamic surface tension of triton x-100 solutions (below CMC, at the CMC, above CMC). SensaDyne surface tensiometer was used which employs maximum bubble pressure method. Wilhelmy plate method was employed to measure static surface tension. Measurements were performed at 28°C. Equilibrium surface concentration was estimated from Gibb’s adsorption equation. The Ward and Tordai equation was used to get the diffusion coefficient. The results are in agreement with the data obtained by other methods. The demicellization rate constant is obtained from the Ward and Tordai equations. It is found that the rate constant strongly depends on surfactant concentration.

Key words: Maximum bubble pressure method, critical micelle concentration, dynamic surface tension.
It was purchased from qualigens. The molecular weight of triton x-100 is 646.87. The molecular weight was accepted as claimed by manufacturer. For preparation of surfactant solution double distilled ionized water was used. Aqueous solutions were prepared and more concentrated solutions were diluted if necessary to obtain desired concentrations. The care was taken to ensure cleanness of the glassware. The glass was soaked in chromic acid and rinsed with distilled water and again with double distilled water. The same procedure was followed to clean the capillaries of the maximum bubble pressure apparatus.

Methods
Dynamic surface tension
Surface tensiometer was used for monitoring the changes in surface tension with respect to time. The maximum bubble pressure method was used to measure the dynamic surface tension of Triton X-100 solutions (below CMC, at CMC and above CMC). Readings for dynamic surface tension has been taken for the solution of Triton X-100 at different concentration by varying the bubble frequency. Before taking the readings the apparatus has been calibrated by using water as a high calibration fluid and methanol as a low calibration fluid. The accuracy and reproducibility of the surface tension values has been determined. The dynamic surface tension measurements were performed for the Triton X-100 solution of different concentration from 20-ppm to 200-ppm (C< CMC) as well as for 200 to 1000-ppm (C>C) at 28 °C.

Surface tension measurement:
Surface tension measurements were carried out by using a SensaDyne QC3000 surface tensiometer that employs maximum bubble pressure method. Figure 1 gives the details of the tensiometer and the instrumentation employed. Nitrogen gas pressurized at 50 psig is bubbled through the small and large glass orifice probes (0.5mm and 4.0 mm diameter respectively) immersed in the test fluid to produce a differential pressure signal proportional to the fluid surface tension. The presence of two probes eliminates any effect of hydrostatic head. Also, by bubbling within the body of the fluid, the system is immune to the

Fig. - 1: Functional block diagram of surface tensiometer
surface contaminants or surface foam. The temperature of the test fluid is measured using a well-calibrated thermistor attached to the orifice probes. The time interval between the newly formed interface and the point at which radius of bubble becomes equal to the capillary radius. After that dead time of the measurement starts. By altering the bubble frequencies through the probes, dynamic surface tension can be measured. In essence, the value of surface tension measured in this process is governed by the rate of diffusion of surfactant molecules toward the growing air bubble. The instrument interfaces directly with any IBM or compatible computer, and uses a Windows compatible program that allows display, storage, retrieval, and graphing of data.

Static surface tension
During static measurements the surface tension was calculated from the maximum force measured by the Wilhelmy plate method. The plate used for measurement is the platinum plate. The surface tension was accepted as an equilibrium value when it became independent of time. The time required to attain the equilibrium is nearly 10 minutes. Before taking the readings the apparatus has been calibrated. The accuracy and reproducibility of the surface tension values has been determined. The static surface tension measurements were performed for the Triton X-100 solution of different concentration from 20-ppm to 200-ppm (C< CMC) as well as for 200 to 1000-ppm (C>CMC) at 28 °C.

Theory of adsorption
Adsorption isotherm
The surface concentrations Α at the interface may be estimated from the slope of a -ln c plot at constant temperature, based on the Gibbs adsorption equation with the ideal dilute solution assumption:

\[ \Gamma = -\frac{1}{nRT} \left( \frac{\partial \gamma}{\partial \ln c} \right)_T \]

Where R is the gas constant and T is the temperature. The factor n is a constant, which depends on the number of species constituting the surfactant and adsorbing at the interface. For a non-ionic surfactant, n = 1. For an ionic surfactant, n = 2 is used.

Adsorption kinetics
Two main processes control the dynamic surface tension, the transport of surfactant to the subsurface region just below the interface and the adsorption process from the subsurface region to the interface. At concentrations below the cmc the first process is determined solely by the diffusion of the monomers in the bulk, but above the cmc the influence of the micelles begins to play a role and one needs to consider micellar diffusion and kinetics. The second process, the adsorption to the interface, is more complicated and may involve several mechanisms. In the simplest case all surfactants that reach the interface adsorb instantaneously, and hence the diffusion to the interface becomes the rate-determining factor. This is the case of diffusion-limited adsorption. Factors that may reduce the adsorption rate are, e.g., that the surfactants may need to have a certain orientation to adsorb, that the surfactants need to find an empty site to adsorb onto the site. The rate of surfactant adsorption, or the change in surface excess concentration with time Æ(t), can be calculated from surface tension by applying an appropriate isotherm. Miller, Fainerman and Makievskij derived asymptotic solutions to the Ward and Tordai equation.

At short times, t, the Ward and Tordai equation reduces to the following equation for diffusion-limited adsorption:

\[ \gamma_{t \rightarrow 0} = \gamma_0 - 2RTc\sqrt{\frac{D \gamma}{\pi}} \]

Where \( \gamma_0 \) is the surface tension of water, c is the bulk concentration (below cmc), and D is the diffusion coefficient of the surfactants. In the long-time regime the Ward and Tordai equation has been proposed is,

\[ \gamma_{t \rightarrow 0} = \frac{nRT^2}{C} \sqrt{\frac{\pi}{4Dt}} \]

where \( \gamma_0 \) is the equilibrium surface tension and other variables are same as given above.
The dynamic surface tension data above the cmc and in the long-time regime can also be analyzed by the use of the equation given below,

\[ \gamma_{t \to \infty} = \gamma_{eq} + \frac{RTT_{eq}^2}{2c_0 t} \sqrt{\frac{1}{Dk}} \]

where \( c_0 \) is the monomer concentration (= cmc), \( D \) is monomer diffusion coefficient, and \( k \) is the rate constant for demicellization. And hence the rate constant for demicellization can be obtained by fitting the surfactant diffusion data in the equation given above for surfactant solution of concentration beyond C.M.C. Experiments can be performed right at C.M.C. and dynamic surface tension data can be plotted as a function of \( t^{-1/2} \) giving a linear relationship with slope obtained by employing equation 3.

For micellar system the dynamic surface tension data can be plotted as a function of \( t^{-1} \) that gives a linear relationship with slope from equation 4.

Thus from equation 5 and equation 6 the demicellization rate constant \( k \) is obtained as,

\[ \frac{[d(\gamma_{t \to \infty} - \gamma_{eq})/dt^{1/2}]_{CT=\text{CMC}}}{[d(\gamma_{t \to \infty} - \gamma_{eq})/dt^{-1}]_{CT=\text{CMC}}} = \sqrt{\frac{k\pi}{4}} \]

RESULTS AND DISCUSSION

Static surface tension study

The surface-active additives in aqueous solution tend to diffuse towards the air /water interface and subsequently get adsorbed on it. This entire process is time dependent. And it manifests in a dynamic surface tension behavior, which eventually reduces to an equilibrium value after a sufficient long time span. Both dynamic surface tension and its approach towards equilibrium depend on additives bulk concentration, its characteristic diffusion time, ionic nature, bulk convection and mobility. This can be explained from the Fig. 2. In Fig. 2, with increasing concentration the surface tension decrease appreciably and an asymptotic limit of surface tension is obtained at the critical micelle concentration of surfactant solution, which is characterized by the formation of colloid sized clusters or aggregates of monomers called micelles and is located on the adsorption isotherm (surface tension vs. concentration plot) from the interaction of two asymptotes representing the change in slope of isotherm.

measured as a function of concentration with a GBX apparatus by using wilhelmy plate method. An abrupt slope change in the \( \tilde{\alpha} - \ln c \) curve occurs at the cmc (Fig. 3). Above the cmc, the equilibrium tensions of the solutions remain essentially constant, because only the monomeric form of the surfactant contributes to the surfactant activity and hence to the tension reduction. For
surfactant concentrations below the cmc, therefore, the surface concentrations $A$ at the interface may be estimated from the slope of a $a - \ln c$ plot at constant temperature, based on the Gibbs adsorption equation. The purpose of an adsorption isotherm is to relate the surfactant concentration in the bulk and the adsorbed amount at the interface.

In Fig. 3 the equilibrium surface tension is plotted against logarithm of concentration. Slope of this curve gives the surface excess or surface concentration of surfactant at the air/water interface. It is observed that surface excess values for triton x–100 increases with increasing concentration of surfactant and above C.M.C, surface tension remains constant which means adsorption is near to saturation.

In Fig. 4, the adsorption isotherm calculated on the basis of Gibb's equation is plotted against the concentration of surfactant solution. With increase in concentration surface excess value increases and reaches to saturation values of adsorbed amount at the point where C.M.C is achieved.

Surface age is the age of surface since its formation. In maximum bubbles pressure method this is referred as period from the beginning of the bubble formation to the point the air bubble radius is same as capillary radius. As we have discussed earlier adsorption of surfactant depends not only on concentration of surfactant but also on the characteristic diffusion time, which can be referred as surface age in this case. In fig. 5, given above dynamic surface tension normalized by static surface tension is plotted as a function of surface age for different concentration of tritonx-100 solution. From Fig.- 5, we can say that for solution of tritonx-100, surface tension decreases with increasing surface age, after a particular value of surface age of few second, slope change of these curves tend to occur. From this curve we one can observe that long time is required to attain the equilibrium surface tension. As the concentration of solution increases surface age required to attain the equilibrium surface tension decreases.

Surface age is related with the bubble frequency in such a way that with increasing bubble frequency surface age decreases. With decreasing surface age, increase in surface tension is observed because time available for surfactant molecules to diffuse from bulk to the bubble surface decreases. With increase in bubble frequency, higher values of surface tension are observed, which can be explained from the fig. 6, given below, and C.M.C. tend to shift towards higher concentration. As a result, at higher bubble frequencies, larger bulk concentrations would be needed to initiate micelle formation and C.M.C. tend to shift to the right in the plot given below.

The surface tension data from Ward and Tordai diffusion equation for adsorption at long time approximation has been plotted as function of surface age (i.e.$t^{1/2}$) for different concentration of triton x-100 solution below C.M.C. The plot clearly reveals that surface tension is linear function in $t^{1/2}$ indicating that the adsorption kinetics is only

![Fig. - 4: Adsorption isotherms of surfactant solution of different concentrations at air/water interface.](image)

![Fig. - 5: plot of ratio of dynamic surface tension to static surface tension vs. surface age for 200-ppm triton x-100 solution.](image)
diffusion controlled at long time regime below C.M.C. This proves that values of diffusion coefficient can be calculated from the equation (3) employed above.

Surfactant diffusion data obtained by using maximum bubble pressure method for adsorption of surfactant at long time regime has been presented in Fig. 7, 30 as a function of concentration. From the graph given above it is clear that the average value of diffusion coefficient \( D = 8.5 \times 10^{-11} \text{ m}^2/\text{sec} \) however error of 7-8% has been observed for few samples of surfactant solution\( ^{11, 16} \). The variation or error observed in diffusion coefficient of few samples may be due to the presence of dust particles or it may be related to the lack of experimental cleanliness. The results are in well agreement with the data obtained by other methods (oscillating jet method and inclined plate method). \( ^{15, 17} \) From the theory discussed above in section 2.3.2, surface tension plotted as function of surface age (i.e.1/t) for different concentration of triton x-100 solution above C.M.C. Also surface tension at C.M.C. plotted as a function of surface age (i.e.\( t^{-1/2} \)) shown in figure 8 below. Thus the demicellization rate constant is obtained by taking the ratio of slope of surface tension vs. surface age plot at C.M.C. to the respective values of slope of surface tension vs. surface age plot for all concentrations above C.M.C. i.e. by employing the equations 15, 16 and 17 given above in section 2.3.2.
Obtained values of demicellization rate constant with respect to all concentrations above C.M.C. are given below in table. Then demicellization rate constant is plotted as function of C.M.C. shown in Fig. 9 and it is observed that k value increased with increasing C.M.C.

In order to validate the present measurements, surface tension data given by A.V.Makievski, V.B.Fainerman and P.Joos, J. Colloid Interface Sci. 166 (1994), is compared with the surface tension data obtained by using maximum bubble pressure method and reasonable agreement between results has been observed.

REFERENCES