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Dynamic contact angles on PTFE surface by aqueous surfactants solution in absence and presence of electrolytes

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Abstract: This study presents the experimental results on dynamic contact angles of pure surfactants and surfactants with electrolyte solutions on PTFE (Teflon) surface. Dynamic advancing (θ_A) and receding (θ_R) contact angles measurements by the Wilhelmy plate technique were carried out for aqueous solution of three different surfactants TritonX–100 (TX–100), sodium dodecylbenzene sulfonate (SDBS), and cetyltrimethylammonium bromide (CTAB). The same measurements in presence of different electrolytes NaCl, Na_2SO_4, and $CaCl_2$ for ionic surfactants (SDBS and CTAB) were also carried out to see the change in contact angle and wetting behavior. The presences of electrolytes change the advancing contact angle as well as wetting properties of hydrophobic solid surface significantly even at very low surfactant concentration. Counter ion valency of the electrolyte is more important in reducing advancing contact angle on hydrophobic PTFE surface at very low concentration of ionic surfactants from CMC. Pure surfactants and ionic surfactants in presence of electrolytes show a linear relationship between the adhesional tension and surface tension at air – water interface with different slope and intercept.

Key words: Teflon, Dynamic contact angle, Wetting, Electrolyte

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1. Introduction

The wetting properties of solid materials are of both fundamental and practical importance due to its wide range of applications like detergency [1], liquid surface coating [2–4], flotation [5,6], chemical reactions at solid–liquid interface [7], agrochemicals, flows in reservoirs [8–11], mass transfer in packed column [12] etc. Understanding and characterizing the wettability of solid surfaces is thus highly essential. Proper wetting of hydrophobic solids with aqueous solutions become difficult due to low surface energy of the hydrophobic surfaces. Since water has a high surface tension (72.8 mN/m) it does not spontaneously spread over a solid which surface free energy is less than 72.8 mN/m [13]. Thus, for wetting of a solid by water having surface free energy smaller than 72.8 mN/m, we need to add surfactants to reduce the surface tension. Wettability of a liquid on a solid surface is generally depends on the physical and chemical surface characteristic of the solid, contact angle and the surface tension of the liquid.

The contact angle can be measured on a flat surface by different common methods [14,15]. The contact angle, which is measured under the condition where the three–phase contact line is moving with respect to the surface, is referred to as "dynamic contact angle" (DCA). In DCA measurement, the advancing contact angle (θ_A) can be measured during solid plate immersion, and the receding one (θ_R) during the emersion process. When $\theta_A \neq \theta_R$ the system is said to exhibit contact angle hysteresis (H), is attributed to chemical heterogeneities [16,17]) or roughness [18,19]. Miyama et al. (1997) [20] mentioned that when the hysteresis occur due to motion of the surface with respect to the water line is called "dynamic hysteresis", and due to the intrinsic change of surface configuration or surface caused by wetting of the surface by water can be termed as "intrinsic hysteresis". H can be calculated by subtracting the maximum advancing contact angle with the minimum receding contact angle ($\theta_A - \theta_R$), or in the form of ($\cos\theta_R - \cos\theta_A$). But in case of dynamic contact angle, the hysteresis value depends on the spreading velocity of the contact line (three phase line) [15] and flow flied [21,22]. If the measurement speed is very slow, dynamic values tend to equilibrium contact angle [21]. Although, the fundamental studies of equilibrium wetting and contact angle have been explored well [23–25], however, the dynamic process, which has many practical applications are not well understood [21,26]. The equilibrium contact angle is related to advancing and receding contact angle according to [20,27],

$$\theta_e = 0.5\cos\theta_A + 0.5\cos\theta_R \qquad (1)$$

The equilibrium contact angle (θ_e) is represented in terms of interfacial tensions by well known Young's equation, which is depends on liquid–air, solid–air, solid–liquid interfacial tension,

$$\gamma_{LG}\cos\theta_e = \gamma_{SG} - \gamma_{SL} \qquad (2)$$

where γ_{SL}, γ_{LG}, and γ_{SG} are the interfacial tensions between the solid – liquid, the liquid – gas, and the solid – gas, respectively.

Adsorption of surfactants at air – liquid interface reduces the liquid surface tension, which may lead to better wettability of solid surfaces by the liquid; however, adsorption of surfactants at solid – liquid interface not always reduces the solid – water interfacial tension. Therefore, it is very difficult to establish the conditions of spreading of liquid solution of the surface–active agents over the solid surface [28]. Zisman [29] showed that there is a linear relationship between the $\cos\theta$ and the surface tension for pure liquid and aqueous surfactant solutions. But, many other researchers have found there is a linear relationship between $\gamma_{LG}\cos\theta$ (adhesional tension) and surface tension of aqueous solution, γ_{LG} for hydrophobic solids [28,30–32]. They also found that the slope of the straight line is –1, implies similar adsorption density at solid –liquid and air – liquid interfaces.

Wetting behaviors of solid surfaces in presence of surfactant solution are dependent on surfactant physical chemistry, concentration at gas – liquid interfaces, and concentration along gas (or liquid) – liquid – solid contact lines [33]. Vogler (1992) found that wetting on different surfaces was highly dependent on the particular surfactant species and that both advancing and receding contact angles could either increase or decrease depending on interactions between the surfactant and the solid surface [34]. From the thermodynamic point of view when the surfactant molecules are adsorbed at the interface (gas – liquid or solid – liquid), depending on the extent of adsorption surface tension of liquid and solid – liquid interfacial tension are reduced. Which cause contact angle decrease for hydrophobic low energetic solid–solution–air systems, in the case of hydrophilic solid–solution–air systems surfactant adsorption at solid liquid interface does not always reduce the solid liquid interfacial tension [35,36].

From the literature it is very clear that the influence of surfactants on contact angle and wetting on solid–liquid system has been studied by many investigators [31,33,36], but studies on the influence of electrolytes in dilute surfactant solution are rare. We have found only one very recent literature on effect of low concentration NaCl on organic liquid (hexadecane) contact angle in ionic surfactants solutions [37]. The presences of electrolytes decrease the surface tension and CMC, as well as increase the adsorption density at both air – liquid and solid – liquid interfaces at low surfactant concentration solution. An understanding of the effect of the addition of electrolytes to aqueous surfactant solutions is of importance to a wide range of applications such as in pharmaceuticals, nonomaterials synthesis, and aqueous surface cleaning. So, it is worthy to study the effect of electrolytes on contact angle and wetting to correlate with adsorption density on both solid – liquid and air – liquid interfaces. In this investigation, we have studied dynamic contact angle of three surfactants solution (TX–100, SDBS and CTAB) on the flat hydrophobic (Teflon) surface, and influence of electrolytes (in a wide concentration range) on ionic surfactants at very low surfactant concentration (below CMC). Furthermore, mostly the reported contact angle studies on Teflon surface are static by goniometric method; we have carried out the experiments under dynamic condition by Wilhelmy balance method and compared our results with the reported studies.

2. Experimental

2.1 Materials

The surfactants TX–100 and CTAB were taken from Loba Chemie Pvt. Ltd., India, with 98% and 99.5% purity respectively. SDBS was taken from Sigma Aldrich, Germany with 99.5% purity. NaCl and $CaCl_2$ were taken from E. Merck. (India) with 99.5% purity and Na_2SO_4 was taken from Ranbaxy fine chemical Pvt. Ltd., India, with same purity. All surfactants and electrolytes were used as it is received without any further purification. Ultra pure water was used for the experiments of 18.2 mΩ resistivity and pH 6.4 – 6.5 (Sartorius, Germany). A surface tensiometer, Data Physics, Germany (DCAT–11EC) was used for measuring the surface tension and dynamic contact angle. The Teflon plate of dimension 25.192 mm × 1.0625 mm was cut from a sheet and used for dynamic contact angle measurement without any further treatment. The thickness and width of the plate was measured at four different points using a digital slide caliper and the average values taken.

2.2 Methods

The surface tension and contact angle values were measured by Wilhelmy plate technique. For surface tension and contact angle measurement, Platinum and Teflon plates were used respectively. All the measurements were repeated three to four times and their average values taken for all calculations. Due to adsorption of the surfactant on the surface of the plates, there was a fluctuation in reading between first and second measurements, to avoid that, the surface was cleaned properly after each measurement. The surface was first washed with pure water, acetone, treated with freshly prepared chromic acid, and then sonicated for 5 min. in pure water. Platinum plate was burned after acetone wash under alcohol flame to remove the adsorbed surfactants completely. All the experiments were carried out at constant temperature (28 ± 0.5 ºC). Motor speed of 1mm/sec and 0.2 mm/sec, immersion depth of the plates 3mm and 5mm were maintained respectively during the surface tension and contact angle measurements through out the experiments.

3. Results and Discussion:

3.1 Surface tension and molecular area at air – water interface: Surface tension of all the surfactants with the variation of surfactant concentration was measured to determine the critical micellar concentration (CMC) and molecular density at air – water interface. The CMC values and the molecular density at air – water interface are presented in Table 1. The minimum surface tension values, γ_{CMC} for TX–100, SDBS, and CTAB are 31.5, 33.75, 32.75 mN/m respectively. The surface excess is a useful measure of effectiveness of adsorption at the interface. The effectiveness of adsorption is an important factor for determining the properties of surfactants like wetting, contact angle, foaming, and emulsification etc. Surface excess (Γ) in mole/m^2 and surface area (A_{min}) in nm^2 for each surfactant can be calculated by using following formulae,

$$\Gamma = -\frac{1}{n \times 2.203RT}\frac{d\gamma}{d\,log\,C} \tag{3}$$

$$A_{\min} = \frac{1}{N_A \Gamma_{\max}} \tag{4}$$

Where, R is Universal Gas constant (8314 m^3.Pa/kg mole.K), T is absolute temperature, and N_A is Avogadro number (6.023 x 10^{23}). A_{min} is minimum surface area of a molecule occupied at the surface in nm^2. The value of *n* is 1 for nonionic surfactants and 2 for 1:1 ionic surfactants. Normally, Γ is measure as Γ_{max} where there is linear dependence between surface tension and log C, so that we get A_{min} for surfactant molecule. The value dγ/dlog C can be obtained from the slope of surface tension (γ) vs. log C plot at a constant temperature 28 ^{0}C. The surface excess and molecular areas for three surfactants with literature values are in given Table 1. It has been found from the literature that the reported values are of wide ranges and also difficult to get the similar temperature to compare. The values we have compared are available closed to our condition. The values available for CTAB and SDBS are close to our experimental values and measurement temperature. For TX – 100 our value is close to the value reported [35] although there is a difference in temperature.

3.2 Effect of immersion speed, surfactant concentration and type on hysteresis: During the measurement of contact angles, deviation of receding angle from advancing angle is also very important to taken into consideration. In this case, due to immersion speed and roughness of the plate, we found the receding angle is always less than the advancing angle. The hysteresis (in the form of ($\cos\theta_R - \cos\theta_A$)) values with the different immersion speed for Teflon surface is shown in Figure 1 a. Whenever the motor speed (i.e., immersion speed) is low, the contact time between the plate surface and liquid is more. Therefore, there is sufficient time available for adsorption–desorption process to reach the surface in equilibrium with the surfactant solution, ultimately the receding angle reaches to ward equilibrium contact angle. At that condition, both the angles should be very close. Hysteresis is minimum at 0.2 mm/s speed, above that there is a rise and consequently become constant with increasing immersion speed.

Hysteresis value is not only depends on the surface immersion speed, but also on the concentration of the surfactant solution. Figure 1 b shows the change in hysteresis with the variation of normalized surfactant concentrations (C_{surf}/CMC) and surfactant types (nonionic, cationic, and anionic). In presence of pure water hysteresis is may be due to the contribution of both dynamic and intrinsic factor, since the surface is hydrophobic intrinsic contribution may be smaller. With the increasing surfactant concentration hysteresis decreases and ultimately becomes constant above the CMC of the surfactant solution. With the increase in surfactant concentration of the solution, the adsorption rate of surfactant on the plate also increases; as a result, the surface becomes more heterogeneous in molecular dimension with in that limiting time. Since the surface heterogeneity changes with the change in surfactant concentration, so hysteresis value changes with the concentration change till significant adsorption is there. Thus, the effect of adsorption again support the higher hysteresis at higher motor speed since contact time is too less to reach the adsorption equilibrium at higher motor speed. In presence of surfactants both the dynamic and intrinsic hysteresis is important. Hysteresis also decreases in presence of electrolytes than the pure surfactant alone at that concentration.

3.3 Effect of surfactant concentration on contact angle and adhesion tension: The change in advancing and receding contact angles with surfactant concentration on Teflon surface is shown in Figure 2 a, b, c for TX–100, SDBS, and CTAB respectively. The advancing and receding contact angles on Teflon surface in presence of pure water are 115.3° and 45.68° respectively. The reported values of advancing angle are in the range of 108 – 116° [31] and our value is very close to the value 116° reported by Busscher et al. (1983) [36]. In presence of TX–100 θ_A decreases very sharply even at very low concentration. At 0.1 mM concentration of surfactant, advancing contact angle decreased to 85.21° and beyond this concentration contact angle is almost constant. Where as θ_R increased up to 71.8° at 0.01 mM concentration and become constant beyond that concentration. In presence of SDBS θ_A decreases gradually to a value of 87.28° at 1.5 mM concentration and above that there is no significant change in contact angle. For θ_R, just opposite trend is observed; there is an increase in contact angle up to a value of 60.63° at concentration 1.8 mM. For CTAB θ_A decreases gradually and significantly up to 0.75 mM with a value of 84.06°. This value is close to the reported value ~ 83° [13]. In case of θ_R there is a sudden increase at very low concentration (0.01 mM) to 67.15° and after that the change is not very significant. All the three surfactants show the change in θ_A is constant above the CMC, and θ_A values above the CMC are very close (within the variation of ± 3°) having highest value in SDBS. Decrease in contact angle in presence of surfactants is due to the increase in hydrophilicity of the surface since the expected orientations of the surfactants molecules are similar in nature on hydrophobic surface after the adsorption through tail groups. Since all the surfactants are having different head and tailgroups, they should show different adsorption density on the solid surface. Nonionic surfactant may have more adsorption density on PTFE surface than ionic due to absence of electrical repulsive force between headgroups, and between the ionic surfactants, CTAB may have more adsorption density due to presence of longer tail length. That may be the reason why SDBS is having little higher contact angle value than CTAB. The surface tension at air – water interface also influence the contact angle, lower surface tension gives lower contact angle. Between these three surfactants the surface tension values at CMC are also very close. Ultimately, similar adsorption pattern and close surface tension values at CMC may be the reason of not showing significant difference in contact angle. Finally, the resultant contact angle is after combining all the effects.

For the Teflon surface we have found that there is no linear relationship between $\cos\theta_A$ (cosine of advancing angle) and surface tension as shown by Bernett and Zisman (1959) [29]. Consequently, similar to other researchers [28,31,32], there is a linear relationship followed between $\gamma_{LG}\cos\theta$ (adhesion tension) and γ_{LG} according to

$$\gamma_{LG}\cos\theta = a\,\gamma_{LG} + b \qquad (5)$$

where a and b are constants. The value of a is depends on the solid surface property. Bargeman and van Voorst Vader (1973) [32] have proposed that for nonpolar solids and surfactant system the value is –1. Figure 3 shows the linear fit of all the experimental data and also there is no significant difference between three different surfactants. Table 2 shows the values of a and b for different surfactants. Our average value of a (– 0.83) that is lower than – 1, and b is also lower (31.2) than others, 46.7 [31] and 40.6 [32]. Putting the value of $\cos\theta = 1$ in the above equation we can estimate the liquid surface tension required to give zero degree contact angle or critical surface tension (γ_c), equal to 17.05 mN/m. The obtained value is lower than reported by Szymczyk et al. (2006) 23.63 mN/m [28], Bargeman and van Voorst Vader (1973) 20.3 mN/m [32] and close to that of Pyter et al. (1982) 16.5 – 19.5 [39] using hydrocarbon surfactants in water. Szymczyk et al. (2006) [28] also got different γ_c (19 mN/m) using pure alkanes than from the aqueous surfactant solution on Teflon surface. Although the reported values are in a wide range, our value also fall in that range.

3.4 Adsorption at Teflon–water and air–water interface: The change in contact angle and surface tension (γ_{LG} and γ_{SL}) at both the interfaces with the change in surfactant concentration is due to adsorption of surfactants. By combining and rearranging Young equation (Eq 2) and Gibbs surface excess equation (Eq 3) for solid – air, solid – water, and water – air interface we can write

$$\frac{\Gamma_{SG}-\Gamma_{SL}}{\Gamma_{LG}}=\frac{d(\gamma_{SV}-\gamma_{SL})}{d\gamma_{LG}}=\frac{d(\gamma_{LG}\cos\theta)}{d\gamma_{LG}} \qquad (6)$$

where Γ_{SG}, Γ_{SL}, and Γ_{LG} represents the surface excess of surfactants at respective interfaces. Assuming $\Gamma_{SG} \approx 0$ we can say the ratio of Γ_{SL} to Γ_{LG} is the slope of Equation 5. The value of slope from the fitting of experimental data is –0.83, indicates at a given bulk surfactant concentration excess concentration at solid – water interface is 0.83 times of that at water – air interface. Although several workers have found for low surface energy solids, solid – water and air – water interface surface excess are same [28,31,32,40,41], but there are also reported studies of unequal adsorption between hydrophobic solid – water and air – water interfaces like Nylon and PMMA [28,39]. It has been also mentioned that, the slope of $\gamma_{LG}\cos\theta - \gamma_{LG}$ curve equal to –1 is a necessary condition but not a sufficient condition for equal adsorption at solid – liquid and air – liquid interfaces [41,42]. Another condition, the curve of $\cos\theta - 1/\gamma_{LG}$ should be linear and intercept on the $\cos\theta$ axis equal to –1 should be fulfilled. In our study we found the curve $\cos\theta - 1/\gamma_{LG}$ is linear shown in Figure 4 with an intercept on the $\cos\theta$ axis equal to –0.77 ± 0.035. This also confirms that the adsorption at two interfaces is not equal. In further, it can be also shown that when the surface excess is equal at both the surfaces work of adhesion is independent of surfactant concentration, but when it is unequal work of adhesion will depends on surfactant concentration. Work of adhesion can be represented as

$$W_A = \gamma_{SG} - \gamma_{SL} + \gamma_{LG} \tag{7}$$

Differentiating with respect to γ_{LG} we can write:

$$\frac{dW_A}{d\gamma_{LG}} = \frac{d\gamma_{SG}}{d\gamma_{LG}} - \frac{d\gamma_{SL}}{d\gamma_{LG}} + 1 \tag{8}$$

From the Gibbs adsorption equation we can write, $d\gamma_{SG}/d\gamma_{LG} = \Gamma_{SG}/\Gamma_{LG}$ and $d\gamma_{SL}/d\gamma_{LG} = \Gamma_{SL}/\Gamma_{LG}$. Now if $\Gamma_{SG} = 0$ and $\Gamma_{SL}/\Gamma_{LG} = 1$, $dW_A/d\gamma_{LG} = 0$. So, we can say the work of adhesion will not change with the concentration of surfactant. In this study $\Gamma_{SL}/\Gamma_{LG} < 1$, and $dW_A/d\gamma_{LG} \neq 0$ shows work of adhesion well change with the concentration of surfactants.

The differences in results with others may be attributed in terms of the following reasons. In our study we have measured the advancing angle by the Wilhelmy method under dynamic condition where three phase contact line is moving but others [28,31,32,40,41] have measured by sessile drop method where three phase contact line is not moving. They have measured the contact angle after 1 to 10 minutes of (equilibrium time) the drop was settled onto the PTFE surface. In our case, for 5 mm immersion depth with 0.2 mm/s immersion speed, the maximum contact time of solid – liquid interface during advancing angle measurement is 25 sec. The contact time may be too less to achieve complete adsorption of surfactants on Teflon surface. No such reported study was found on surfactant adsorption kinetics on Teflon surface to compare, but adsorption of nonionic surfactants on a hydrophobic surface (polystyrene) shows the equilibrium time is approximately 400 sec [44]. We also did the surfactant adsorption kinetics study on PTFE powder for SDBS and TX–100. We found 5 minutes was required to reach the equilibrium for both the surfactants. Thus, it indicates our contact time is less for reaching the equilibrium. Another reason of the difference in the result may be the presence of other impurity in our Teflon surface.

3.5 Effect of surfactant concentration on work of adhesion: In further, the work of adhesion (W_A) is calculated for advancing contact angle and plotted with log C in Figure 5 using equation:

$$W_A = \gamma_{SG} - \gamma_{SL} + \gamma_{LG} = \gamma_{LG}(1 + \cos\theta_A) \tag{9}$$

where $\gamma_{SG} - \gamma_{SL} = \gamma_{LG}\cos\theta_A$. For all three surfactants, the work of adhesion decreases with increasing concentration of surfactants and the change is sharp in the low concentration. Here, as contact angle decreases in presence of surfactants wetting should increase and that should reflect in increased work of adhesion. But, initially contact angle on Teflon surface in presence of water and low surfactant concentration is above 90º, where $\cos\theta_A$ values are negative, so, $(1 + \cos\theta_A)$ term increases gradually with the decrease of contact angle, at the same time surface tension also decreases gradually. The decrease in surface tension is more than the increase in $(1 + \cos\theta_A)$ term; as a result the work of adhesion values decreases with increase in concentration. Contradictory to our results Szymczyk and Janczuk (2006, 2007, 2008) [28,30,41] found that work of adhesion is independent on the types of surfactants, their concentration, and composition in the mixture on the Teflon surface. As it is discussed before that the work of adhesion is independent of concentration when surface excess at solid–water and air–water are equal, since we got unequal surface excess on both the surfaces, the work of adhesion is dependent on surfactant concentration.

***3.6 Polar component of aqueous solution*:** According to Fowkes (1963) [44] interfacial tension can be expressed in terms of individual surface tension of the surfaces and London – van der Waals dispersion force component of the surfaces as

$$\gamma_{SL} = \gamma_{SG} + \gamma_{LG} - 2\sqrt{\gamma_L^d \gamma_S^d} \tag{10}$$

Combining this equation with equation 7 we can write

$$W_A = 2\sqrt{\gamma_S^d \gamma_L^d} \tag{11}$$

Where γ_S^d and γ_L^d are the dispersive contributions to the surface tensions of solid and liquid phases respectively. For the hydrophobic Teflon surface the polar component of surface tension is negligible and $\gamma_{SG} = \gamma_S^d = 20.24$ mN/m [31]. Now γ_L^d can be calculated from the Equation 11 and the polar component of the surface tension of surfactant solution, γ_L^p can be calculated using equation:

$$\gamma_L^p = \gamma_{LG} - \gamma_L^d \tag{12}$$

γ_{SL} calculated from equation 1 is plotted as a function of γ_L^p in Figure 6. Figure 6 shows there is a linear relationship between γ_{SL} and γ_L^p for all three surfactants,

$$\gamma_{SL} = 0.986\gamma_L^p + 0.644 \tag{13}$$

From the equation it appears that the increase in polar component of the surfactant solution will increase the solid – water interfacial tension.

3.7 Effect of electrolytes on CMC: When the ionic surfactants are adsorbed at air – liquid or solid – liquid interfaces the repulsive force exists between the headgroups of the adsorbed molecules for single surfactant solution. The presence of electrolyte reduces that repulsive interaction between the headgroups of ionic surfactant molecules at interface and also repulsive force between the charged headgroups of monomer surfactant molecules in the solution. So due to the decreased in repulsive force, CMC value of the surfactant solution also decreases in presence of electrolyte. Figure 7 shows decrease in CMC values of SDBS at different electrolyte concentration and minimum surface tension achieved (γ_{CMC}) at that concentration. Here, we found a linear correlation between log (CMC) and log (CMC + salt conc.) with slope –2.99 and intercept –6.64 for SDBS in presence of NaCl as proposed by Attwood (1969) [45]·

$$\log \mathrm{CMC} = -c - d \log (\mathrm{CMC} + C_{salt}) \tag{14}$$

where c, d are constants and C_{salt} is the salt concentration. Attwood (1969) [45] found similar linear relation ship with slope –0.54 and intercept –6.4 for other anionic surfactant (SDS) in presence of NaCl. In this section we have studied the effect of different electrolytes on surface tension, and advancing contact angle in presence of ionic surfactants. The electrolyte concentration increased gradually for a particular surfactant concentration, and the change in contact angle and surface tension was measured. When the surface tension was reached to a constant value it was assumed that CMC reached at that particular surfactant and electrolyte concentration. For SDBS three electrolytes were studied, NaCl and $CaCl_2$ to see the effect of cation valence among two electrolytes, and Na_2SO_4 for anion valence.

3.8 Effect of electrolytes on contact angle and wetting: Figure 8 shows the change in advancing contact angle with increasing NaCl concentration in presence of different initial SDBS concentration. Although there are some irregularities in the curve at low NaCl concentration for both the surfactants, still the decreasing trend is clear for advancing angle. At low surfactant concentration change is significant with the electrolyte (NaCl) concentration. The change in contact angle in presence of maximum NaCl concentration and in absence of NaCl is more when surfactant concentration is low. Specifically, at 0.05 mM SDBS concentration (~ 24 times below CMC) in presence of 200 mM NaCl advancing contact angle decreased from 100.11° to 82.31°; 0.1 mM (~ 12 times below CMC) in presence of 200 mM NaCl the change is 100.67° to 84.50°; and 0.5 mM (~ 2.4 times below CMC) in presence of 50 mM NaCl the change is 93.28° to 83.48° due to closer packing of adsorbed surfactant molecules on the Teflon – water and air – water interface. By comparing the contact angle data in absence of electrolyte it is observed that even at low surfactant concentration by adding electrolyte we can achieve similar or even lower minimum contact angle that in presence of pure surfactant with out electrolyte. From the Figure 9, it shows that the work of adhesion is decreased for all the concentrations and at high NaCl concentration it reached to a plateau. Initially the difference is more. Since for pure surfactant work of adhesion was depend on surfactant concentration and at a constant surfactant concentration by adding increasing electrolytes concentration we can see the similar effect to that of increasing surfactant concentration.

To see the effect of counter ion and co – ion valance on contact angle and wetting we have varied the concentrations of Na_2SO_4 and $CaCl_2$ at same surfactant concentration (0.05 mM). We have observed in presence of $CaCl_2$ at 1 mM concentration minimum contact angle is reached (78.43°), and in presence of 100 mM Na_2SO_4 minimum angle is 86.97° above that concentration again there is a small increase contact angle. So, it is worthy to mention that $CaCl_2$ is most effective in reducing the contact angle on Teflon surface in presence of SDBS, even at very low concentration. After comparing the effect of NaCl and Na_2SO_4 it is observed that when Na^+ concentration is same (at 100 mM Na_2SO_4 and 200 mM NaCl) Na_2SO_4 is showing little higher contact angle (86.97°) than NaCl (82.31°). So, bivalence SO_4^{2-} is probably having some negative effect on adsorption of anionic surfactant on Teflon surface, which reflect in increase in contact angle. Figure 10(a) shows there is a linear relationship between $\gamma_{LG}\cos\theta - \gamma_{LG}$ for all the initial surfactant concentrations and in presence of all the electrolytes (NaCl, Na_2SO_4, and $CaCl_2$), but the constants *a* and *b* values (in presence of electrolytes termed as a_e and b_e) are different than the pure surfactants. In presence of electrolytes, the constant values are lower than the pure surfactants, $a_e = -0.629$ and $b_e = 23.11$. The value of slope – 0.629 indicates at a given bulk surfactant concentration in presence of electrolytes the excess concentration at Teflon – water interface is 0.629 times of that at air – water interface. In presence of electrolytes, in general, surface excess of ionic surfactants at air – water interface increases due to reduction in repulsion between the surfactant headgroups [35,46]. In presence of electrolytes if Γ_{LG} increases significantly but the change is not proportionately for Γ_{SL} then the surface excess ratio $((\Gamma_{SL}/\Gamma_{LG})_e)$ will be less than that in absence of electrolyte. Since the surface is hydrophobic in nature surface charge will be close to zero the change in surface potential in presence of electrolyte will be very less, the adsorption density will increase only due to decrease in repulsion between the headgroups.

For cationic surfactant (CTAB) two electrolytes (NaCl and Na_2SO_4) was studied at 0.01 mM CTAB concentration. It is found that for both the cases contact angle is changing till 100 mM of electrolytes concentration with the values of 96.25° and 94.04° for NaCl and Na_2SO_4 respectively. The values are higher than that of pure CTAB. Both the electrolytes are showing a linear relationship of $\gamma_{LG}\cos\theta_A - \gamma_{LG}$, shows in Figure 10(b) with a different slope ($a_e = -0.467$) and intercept ($b_e = 12.43$) than in presence of SDBS. Similar to pure surfactants we have calculated polar component of the surface tension of surfactant solution in presence of electrolytes and plotted γ_{SL} vs. γ_L^p in Figure 11. The figure shows there is a linear relationship and independent of types of surfactants, and types of electrolytes. The slope and the constant value also very close to that of pure surfactant:

$$\gamma_{SL} = 0.983\gamma_L^p + 0.649 \tag{15}$$

The equation shows clearly that γ_{SL} value can be changed by changing γ_L^p and the change can be done by changing the surfactant concentration or at a particular surfactant concentration by adding electrolyte. For a particular solid in aqueous medium it follows same equation for different surfactants or surfactant in presence of electrolytes.

4. Conclusion: The results of this dynamic contact angle study can be summarized as follows:

(1) Advancing contact angle and the work of adhesion decreases with increasing the concentration of surfactants. There is a linear relationship between the adhesional tension and surface tension at air – water interface for all the three surfactants and the adsorption of surfactants at air – water interface is not equal to that of Teflon – water interface.

(2) In presence of even very dilute ionic surfactant solution similar wetting characteristics to that at high surfactant concentration in absence of electrolytes can be achieved by adding electrolytes.

(3) For ionic surfactants the valance of counter–ion is very important for reducing surface tension and contact angle at very low surfactant concentration. Like for dilute SDBS solution $CaCl_2$ is more effectively reduce the surface tension and contact angle than NaCl. Similarly, for CTAB solution Na_2SO_4 is more effective than NaCl.

(4) Similar to pure surfactants, ionic surfactants in presence of electrolytes are also show linear relationship between the adhesional tension and surface tension at air – water interface with different slope and intercept. The ratio of surface excess at solid – water and air – water interface is decreases in presence of electrolytes than that for pure surfactants for both ionic surfactants.

Finally, considering all the above points, it is concluded that for achieving a certain extent of contact angle or wetting, for different applications, low surfactant concentration in presence of electrolytes may reduce the surfactant consumption and cost of the process instead of using high concentrated surfactant solution.

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Figure Captions

Figure 1: Contact angle hysteresis on Teflon surface (a) with plate immersion speed for TX–100 solution (b) in presence of TX–100, SDBS, and CTAB with 0.2 mm/s immersion speed.

Figure 2: Advancing and receding contact angles of (a) TX–100, (b) SDBS, and (c) CTAB solutions on Teflon surface.

Figure 3: Plot of adhesional tension (γ_{LG} $\cos\theta_A$) vs. surface tension (γ_{LG}) for three different surfactants (TX–100, SDBS, CTAB) on Teflon surface.

Figure 4: Plot of $\cos\theta_A$ vs. reciprocal of surface tension ($1/\gamma_{LG}$) of aqueous surfactants solutions on Teflon surface.

Figure 5: Plot of work of adhesion (W_A) with log C for three different aqueous surfactants solutions (TX–100, SDBS, CTAB) on Teflon surface

Figure 6: Relationship between Teflon–water interfacial tension in presence of surfactants (γ_{SL}) and the polar component of the surface tension (γ_L^p).

Figure 7: The change in CMC and surface tension (γ_{CMC}) of SDBS solution in presence of NaCl.

Figure 8: Plot of advancing contact angle (θ_A) for different electrolytes (NaCl, $CaCl_2$, Na_2SO_4) in presence of SDBS and CTAB solution on the Teflon surface.

Figure 9: Plot of work of adhesion (W_A) in presence electrolytes for ionic surfactants (SDBS, CTAB) on the Teflon surface.

Figure 10: Plot of adhesional tension (γ_{LG} $\cos\theta_A$) vs. γ_{LG} on Teflon surface (a) Effect of electrolytes solution (NaCl, $CaCl_2$, Na_2SO_4) in presence of different SDBS concentration, (b) Effect of electrolytes solution (NaCl, Na_2SO_4) in presence of different CTAB concentration.

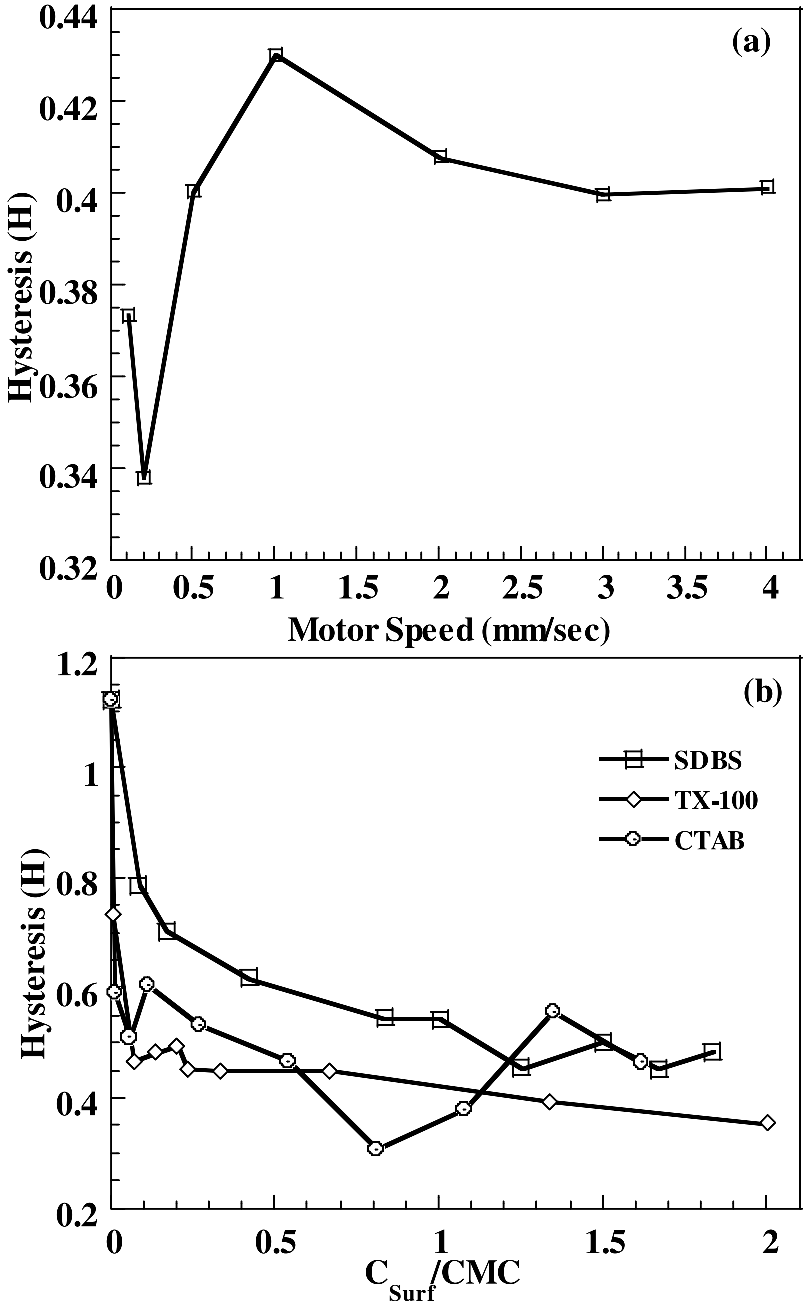
Figure 11: Relationship between Teflon–water interfacial tension in presence different electrolytes and surfactants (γ_{SL}) and the polar component of the surface tension (γ_L^p).

Table Captions

Table 1: CMC, surface tension at CMC, and comparison between experimental and literature values of surface excess and molecular area of different surfactants solution.

Table 2: Values of *a* and *b* for different pure surfactants

FIGURES:



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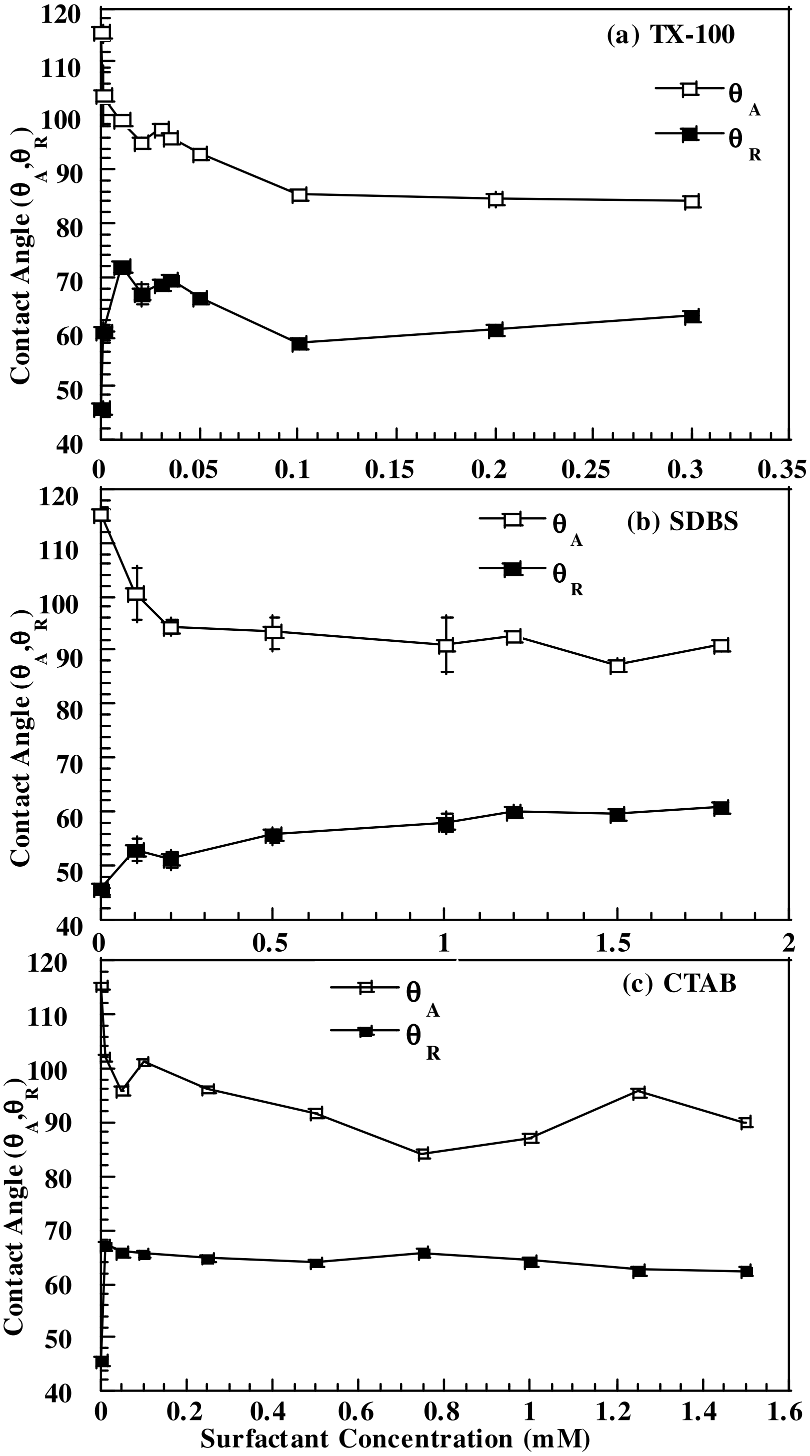

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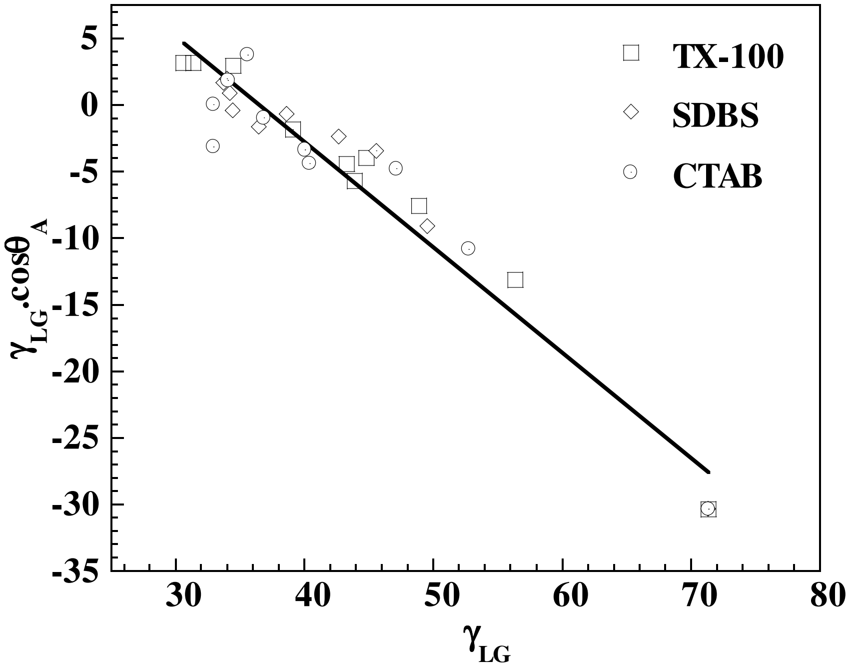

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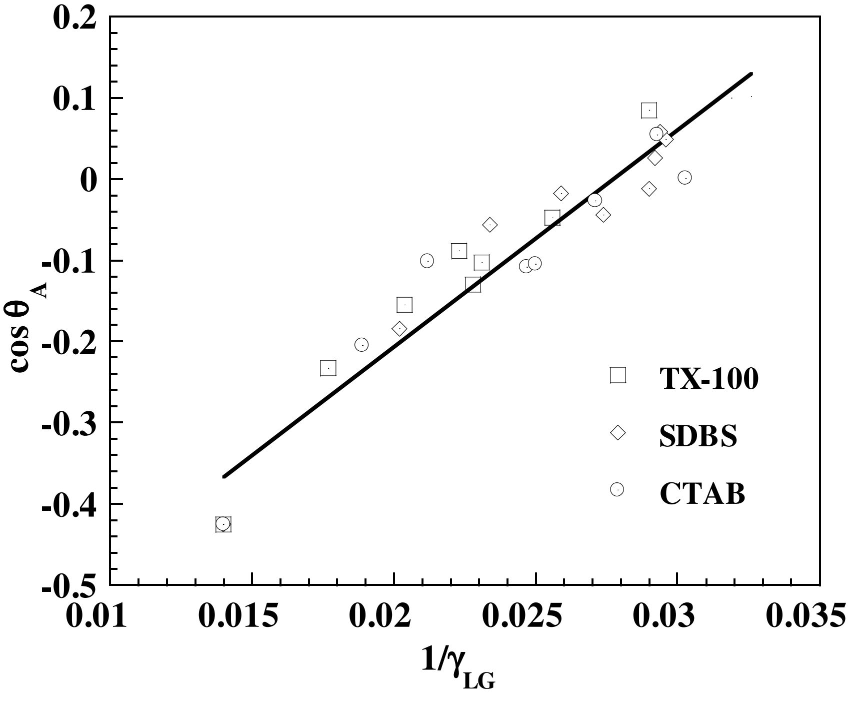

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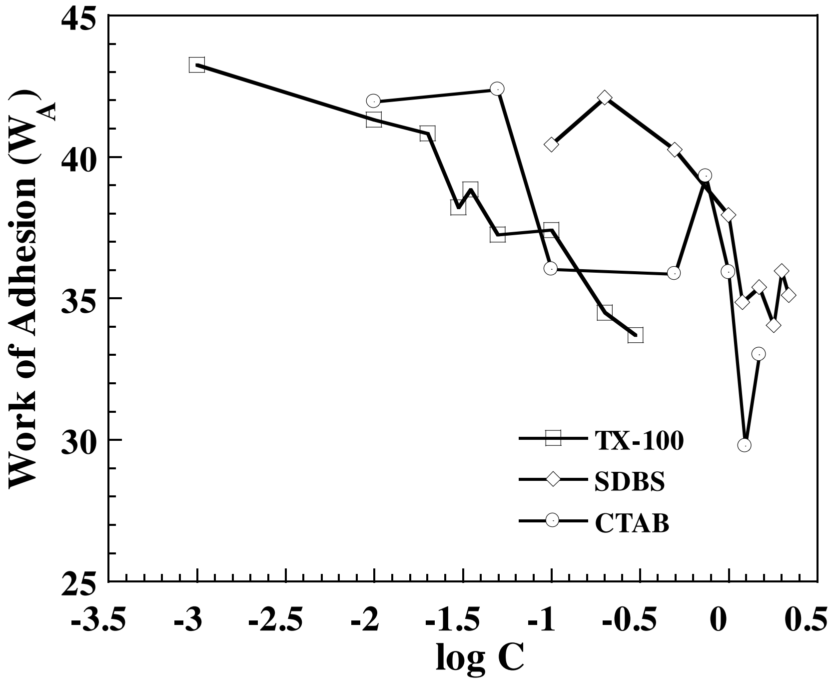

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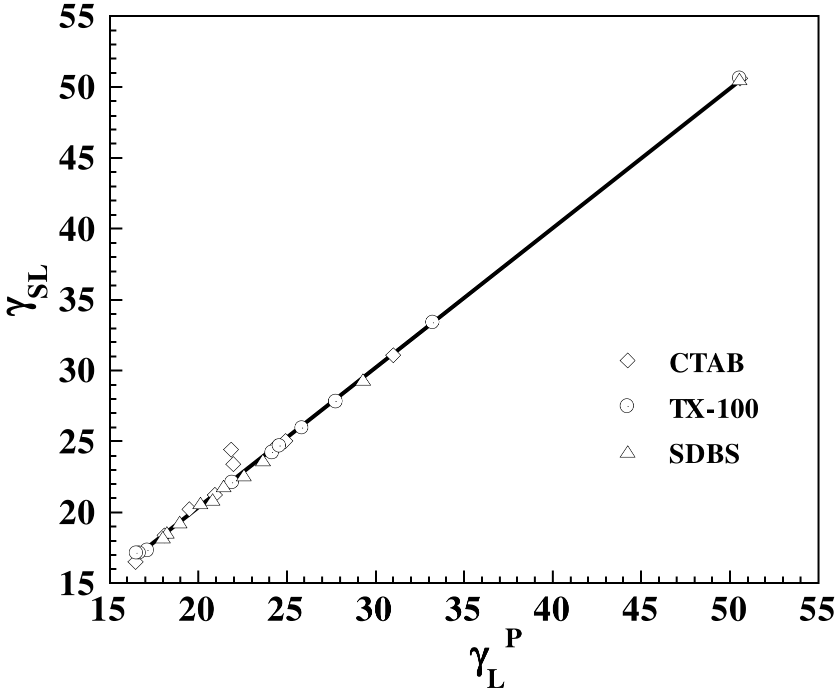

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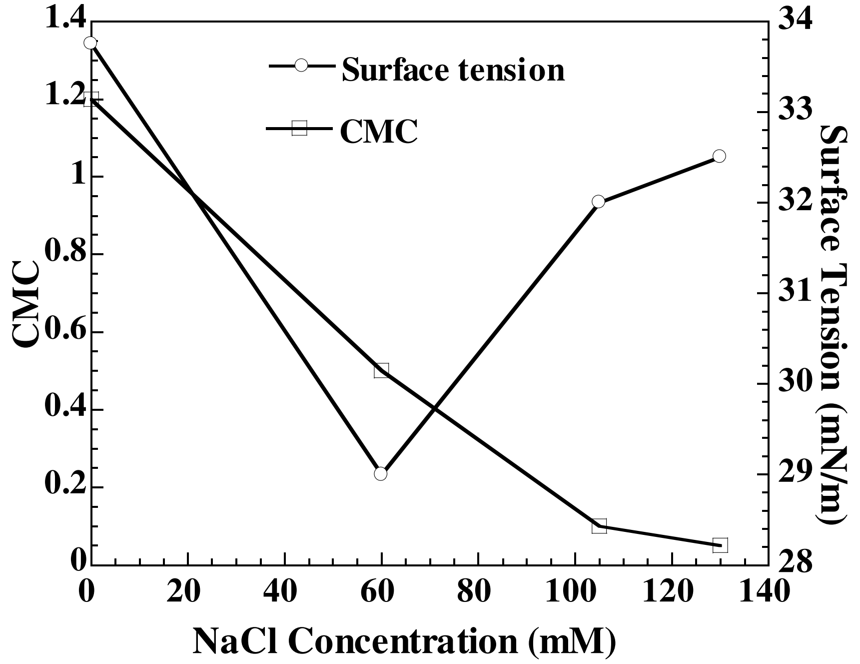

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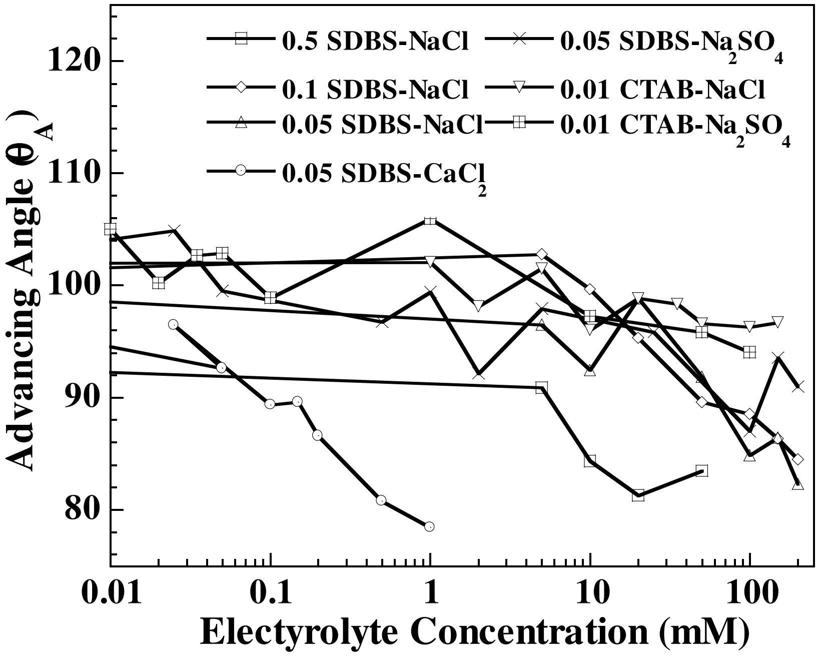

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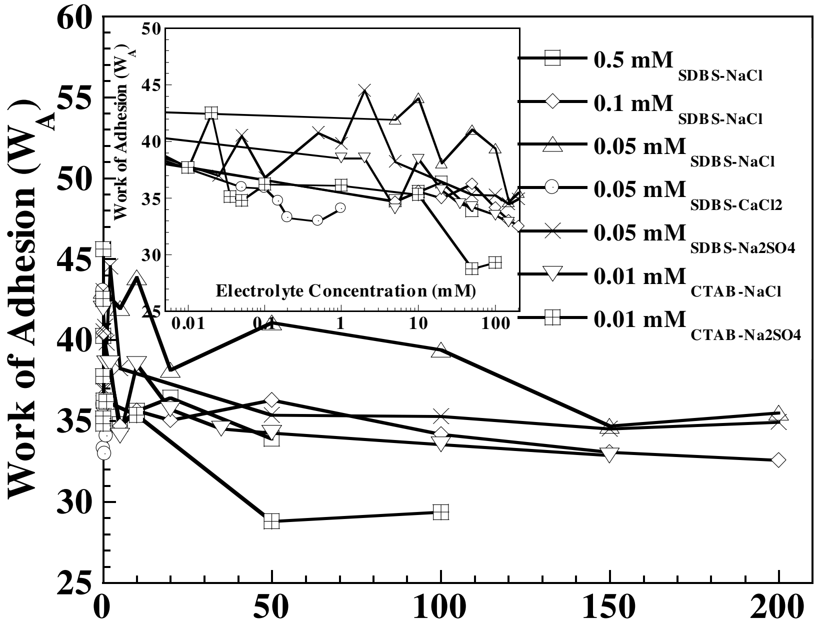

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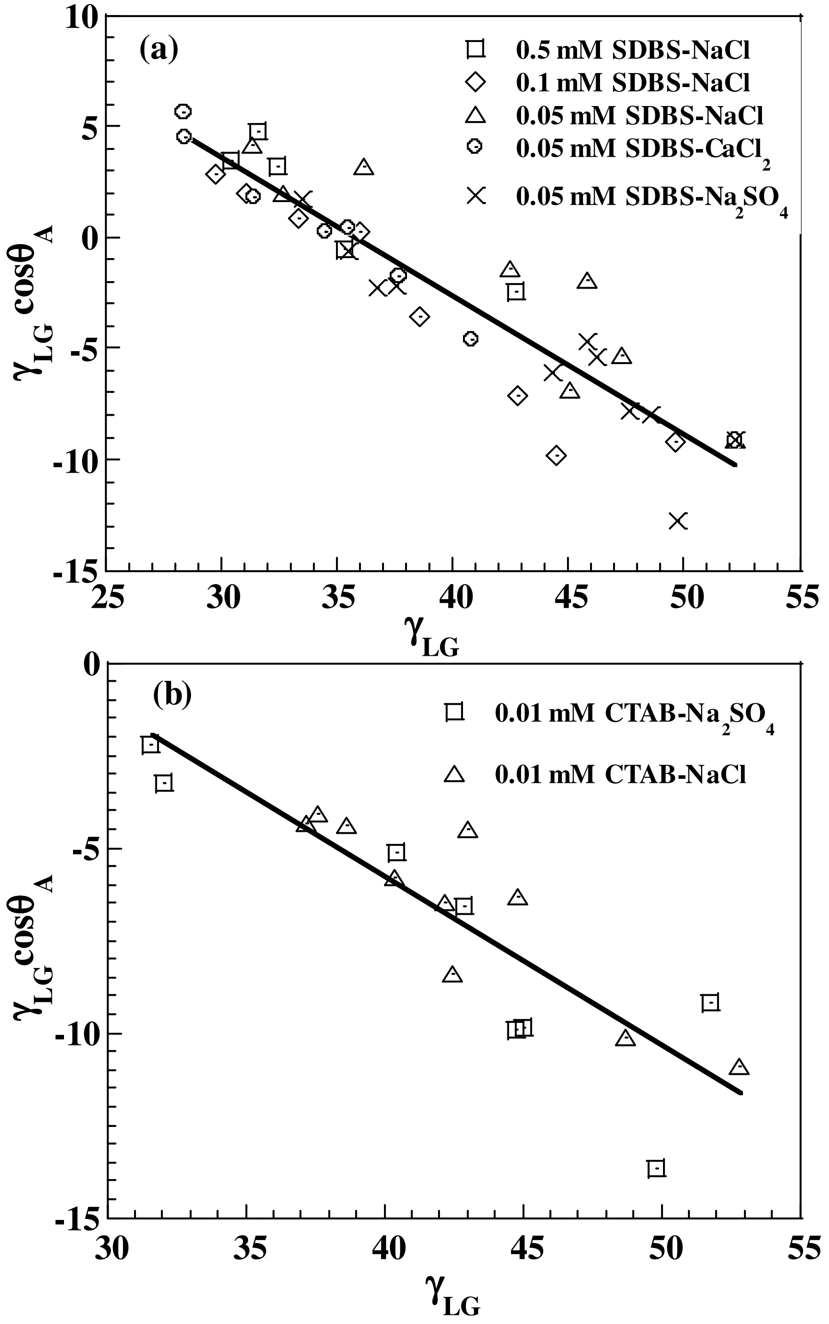

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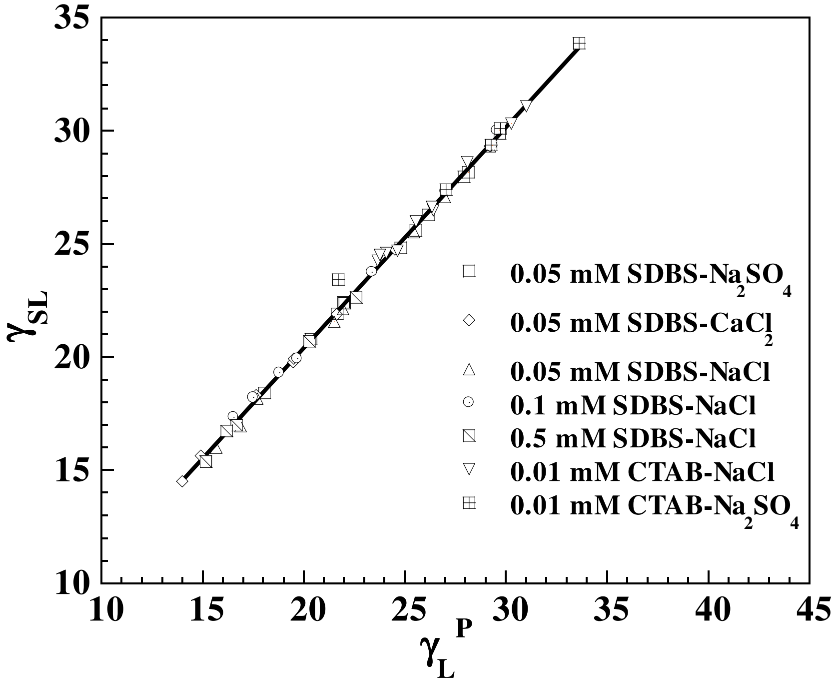

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Table 1. CMC, surface tension at CMC, and comparison between experimental and literature values of surface excess and molecular area of different surfactants solution.

Surfactant	CMC (mM)	γ_{CMC} (mN/m)	Exp. Γ_{max} (mole/m^2) x 10^6	Exp. A_{min} (nm^2)	Literature Γ_{max} (mole/m^2) x 10^6	Literature A_{min} (nm^2)
TX–100	0.15	31.5	2.444	0.68	2.8 (at 20^0C) [a]	0.61 [a]
SDBS	1.2	33.75	2.407	0.69	2.41(at 30^0C) [b]	0.69 [b]
CTAB	0.93	32.75	1.704	0.96	1.8 (at 30^0C) [a]	0.91[a]

[a] Ref. [35]

[b] Ref. [38]

Table 2. Values of *a* and *b* for different pure surfactants

Surfactant	*a*	*b*
TX–100	–0.83	31.4
SDBS	–0.82	30.3
CTAB	–0.85	31.8
Average	–0.83	31.2