Wetting of TX-100 and igepal CO-630 surfactants on a PTFE surface

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Wetting of TX-100 and Igepal CO-630 Surfactants on a PTFE Surface

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Ⓢ *Supporting Information*

ABSTRACT: Nonionic surfactants are advantageous in a diversified range of applications from household cleaners, laundry detergents, and shampoo to paints, coatings, and food emulsifiers because of their low CMC and surface tension values over the ionic surfactants. Nonionic surfactants, in general, are very useful in mixed surfactant systems because of their electrical neutrality. Among the similar class of nonionic surfactants, structural difference is important in the performance. In this study, we report on the adsorption and wetting behavior of two nonionic surfactants (TX-100 and Igepal CO-630) having the same head group but structurally different tail groups. The kinetics of adsorption follows a pseudo-second-order kinetic model and a Langmuir-type isotherm for both the surfactants. The change in contact angle with the concentration of surfactant follows a trend similar to that for adsorption onto a PTFE surface. At low surfactant concentration, Igepal CO-630 shows a slightly higher adsorption density and better wetting properties than TX-100. Both surfactants show lower adsorption densities at the PTFE—water interface than at the air—water interface.

1. INTRODUCTION

The wetting of hydrophobic surfaces by surfactant solutions is very important in surface and interface science, owing to the fact that many industrial processes and daily life applications are impossible to consider without wetting. In the wetting process, adsorption of surfactant at the solid—liquid interface and surface tension at the air—liquid interface plays an important role. Because hydrophobic surfaces have very low surface energies, wetting with a polar solvent is difficult and can be enhanced using surfactants. Surfactants having low surface tension values at the critical micellar concentration (CMC) and low solid—water interfacial tension upon the adsorption of surfactants always show better wetting properties.

In view of the widespread applications of wetting phenomena, many researchers have studied the wettability of different types of hydrophilic and hydrophobic surfaces by different single surfactants,[1,2] mixed surfactant systems,[3−5] and additives.[6,7] In mixed surfactant systems, mixtures of similar cationics[3] and nonionics[5] and dissimilar mixtures of both cationic and nonionic surfactants[4,8] have been studied. The effects of different additives such as alcohols[6,9−12] and electrolytes[7] have also been studied thoroughly.

In general, nonionic surfactants are preferable in many applications because of their biocompatibility, lower sensitivity toward electrolytes, low CMC and surface tension values compare to those of ionics, and so on. For a long time, many researchers have studied the wetting behaviors of nonionic surfactants on both hydrophilic and hydrophobic surfaces for different applications.[2,13−19] Mostly, the wetting properties increase in the presence of nonionic surfactants for both hydrophilic and hydrophobic surfaces. The wetting properties also depend on the molecular structure of the surfactant,[20] as well as the nature of hydrophilic and hydrophobic groups of different surfactants. The wetting properties of a nonionic surfactant can also be improved using alcohols of different chain lengths,[21] binary mixtures,[4,5,22,23] and ternary surfactant mixtures (two nonionic + one ionic).[24]

The present study focuses on the adsorption and wetting behaviors of two nonionic surfactants (TX-100 and Igepal CO-630) having similar head groups but dissimilar tail groups on a polytetrafluoroethylene (PTFE) surface. The surfactants have similar head groups, nine ethylene oxide groups attached to a benzene ring, but a structural difference in the tail groups. Igepal CO-630 and TX-100 contain *n*-nonyl (C_9) and an eight-carbon branched chain (C_8) hydrocarbon (1,1,3,3-tetramethylbutyl), respectively, as the tail group. The adsorption behavior of the surfactants between the PTFE—water and air—water interfaces obtained from the wetting study were also compared with the results of independent adsorption studies at those respective interfaces. To the best of our knowledge, this type of study has not been reported before. TX-100 and Igepal CO-630 were chosen because they are members of the typical alkyl polyethylene oxide category widely used in several practical applications. Moreover, from the environmental viewpoint, straight-chain hydrophobic groups are more important because of their biodegradable nature than branched chains in a nonionic surfactant.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. Polytetrafluoroethylene (PTFE) slides of dimensions 25.34 mm × 1.12 mm were cut from a sheet purchased from J. Khushal Das and Co., Mumbai, India, and the powder used for adsorption experiments was purchased from Pragati Plastics Pvt. Ltd., Delhi, India. Triton X-100 (TX-100) [*p*-(1,1,3,3-tetramethylbutyl)phenyl ether polyethylene glycol) and Igepal CO-630 (polyoxyethylene nonylphenol) were purchased from Sigma-Aldrich Gmbh, Munich, Germany (technical
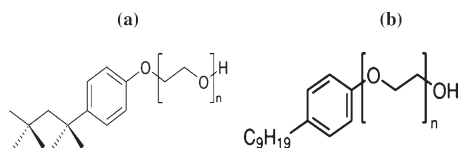
(a)   (b)

Figure 1. Structures of (a) Triton X-100 and (b) Igepal CO-630 ($n = 9$).

grade, catalog nos. 93418 and 542334) and used without any further purification. The structures of the surfactants are shown in Figure 1. Ultrapure water (Sartorius, Göttingen, Germany) of 18.20 MΩ cm resistivity, 71.50 mN/m surface tension, and 6.5–7.0 pH was used for all the experiments. The particle size of the PTFE powder was measured using a particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., Malvern, U.K.), and the average particle size was found to be 115.70 μm. The zeta potential (ζ) of PTFE powder was measured in the presence of 0.01 mol KCl solution using a Zetasizer Nano ZS instument (Malvern Instruments Ltd., Malvern, U.K.) and found to be −4.82 mV. The specific surface area [Brunauer–Emmett–Teller (BET)] of the PTFE powder was measured by N_2 adsorption–desorption studies at liquid nitrogen temperature (−195.80 °C) using an Autosorb-1 instrument (Quantachrome Instruments, Boynton Beach, FL) and found to be 4.34 m^2/g.

2.2. Measurement of Surface Tension and CMC. All surfactant solutions were prepared freshly just before the measurements. The solutions of desired concentration were prepared from a 10 mmol/L stock solution using a 100 mL volumetric flask. The surface tensions of aqueous surfactants solutions (0.0005–2 mmol/L) were measured by the Wilhelmy plate method using a surface tensiometer (DataPhysics, Filderstadt, Germany, DCAT-11EC) at 25 ± 0.5 °C, with the temperature maintained using an external constant-temperature water circulator. The motor speed was 1 mm/s, and the immersion depth of the platinum plate in the surfactant solution was maintained at 3 mm. After measurement of each concentration, the plate was cleaned with water and acetone and then burned in an alcohol flame. The CMCs of Triton X-100 (TX-100) and Igepal CO-630 were found to be 0.15 and 0.08 mmol/L, respectively, by the surface tension measurement technique.

2.3. Surfactant Adsorption Kinetics and Isotherm of on a PTFE Surface. For the adsorption experiments, a volume of 10 mL of surfactant solution having different concentrations (0.025–2 mmol/L for the isotherms and 0.05 mmol/L for kinetics) were taken in 60 mL plastic bottles, and 0.1 g of PTFE powder was added in each case. The bottles were shaken well for 2 h at 25 ± 0.5 °C on an incubator shaker. PTFE particles were separated from the mixture by centrifugation at 5000 rpm. The concentrations of the surfactant solutions before and after adsorption were determined by UV–vis spectrophotometer (UV-3600, Shimadzu, Kyoto, Japan) using their respective calibration curves (absorbance versus concentration) constructed from known concentrations. The experiments were repeated at least three times, and the average data were plotted. The amount of surfactant adsorbed was determined from the equation[25]

$$\Gamma = \frac{(C_i - C_{eq})V}{m \times 1000} \tag{1}$$

where C_i and C_{eq} are the initial and equilibrium concentrations (mmol/L), respectively; V is the volume of surfactant solution (mL); and m is the mass of adsorbent (g).
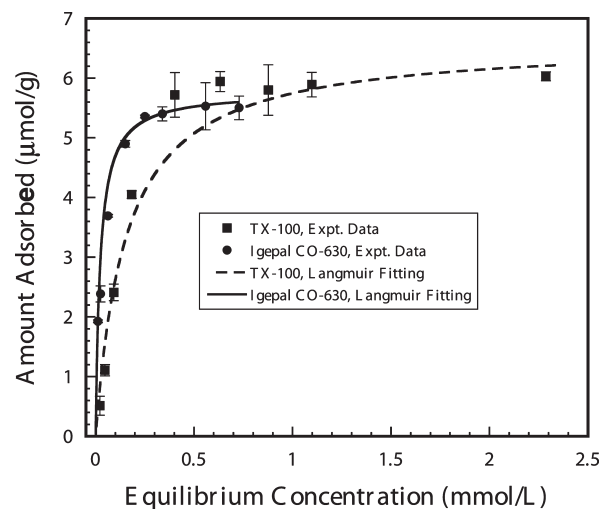

Figure 2. Adsorption isotherms of TX-100 and Igepal CO-630 on PTFE powder.

2.4. Measurement of Contact Angle. The dynamic advancing (θ_A) contact angle was measured by the Wilhelmy balance method using the above-mentioned surface tensiometer. All experiments were carried out at constant temperature (25 ± 0.5 °C). A motor speed of 0.2 mm/s and an immersion depth of the PTFE plate of 5 mm were maintained during the contact angle measurements. A good-quality PTFE plate was chosen and washed several times with first acetone and then ultrapure water to remove impurities. The plate was then dried under blowing hot air. The same procedure was repeated after the measurement of each surfactant concentration.

3. RESULTS AND DISCUSSION

3.1. Surfactant Adsorption Isotherm on a PTFE Surface. The adsorption isotherm was also determined to see the difference in amounts adsorbed at equilibrium in a range of concentrations from below to above the CMC for both surfactants. Figure 2 presents the adsorption isotherms of the two nonionic surfactants on a PTFE surface. Because of the chemical inertness of the low-energy hydrophobic solid surface, chemical interaction with the surfactant is minimal. From the figure, it is clear that the natures of the adsorption isotherms for TX-100 and Igepal CO-630 are similar and are of Langmuir type. Initially, at low equilibrium concentration, because of the presence of more free accessible sites, the isotherm rises linearly with a higher slope, whereas at higher equilibrium concentration, the formation of a plateau region indicates monolayer coverage of the surfactants on the PTFE surface because of the negligible intermolecular interaction between the adsorbed surfactant molecules. Comparison between the two isotherms shows that, at low surfactant concentrations, the amount adsorbed for Igepal CO-630 is higher than that for TX-100, which might be due to the bulkiness of the TX-100 molecule. In contrast, at the plateau level, TX-100 has a slightly higher amount adsorbed, although the change is not very significant.

Both isotherms were fitted with the Langmuir and Freundlich models, and better fits were found with the Langmuir model. The linear forms of the Langmuir and Freundlich isotherms are

Table 1. Parameters of the Langmuir and Freundlich Isotherm Models

	Langmuir			Freundlich		
surfactant	q_m (μmol g^{-1})	b (μmol^{-1})	R^2	a (μmol g^{-1})	n	R^2
TX-100	6.62	6.56	0.99	6.38	1.87	0.84
Igepal CO-630	5.78	43.25	0.99	6.99	3.70	0.92

given by[26,27]

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{2}$$

$$\log q_e = \log a + \frac{1}{n} \log C_e \tag{3}$$

respectively, where q_m is the equilibrium amount adsorbed (μmol g^{-1}), b is the adsorption constant of the Langmuir equation (μmol^{-1}), C_e is the equilibrium concentration of surfactant in solution (mmol/L), a is a constant or coefficient of the Freundlich isotherm equation representing the adsorption capacity, and n is a constant (reciprocal of the exponent of the Freundlich isotherm equation). Values for the parameters are listed in Table 1.

3.2. Surfactant Adsorption Kinetics on a PTFE Surface. Because adsorption is inherently associated with the wetting process, the adsorption kinetics was studied to determine the equilibrium time, as well as the rates of adsorption of the two different nonionic surfactants (TX-100 and Igepal CO-630) from a solution with an initial concentration of 0.05 mmol/L on a PTFE surface in a batch study. The data on the kinetics of adsorption are shown in Figure 3, from which it is clear that the rate of adsorption is very high for both surfactants, with equilibrium times of approximately 10 min for TX-100 and 5 min for Igepal CO-630 and a higher adsorption amount for Igepal CO-630. As the surface is mostly hydrophobic, adsorption of these nonionic surfactants occurs by attachment of the tail group through van der Waals forces.

Now, to calculate the rate constant of the process, the experimental results were fitted with pseudo-first-order and pseudo-second-order models, and better fits were found for the second-order model using the linear form of the equation.[25]

Pseudo-first-order kinetics can be expressed as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{4}$$

and pseudo-second-order kinetics can be expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

where q_t and q_e are the amounts (μmol/g) of surfactant adsorbed at time t and at equilibrium, respectively, and k_1 (min^{-1}) and k_2 [g/(μmol min)] are the adsorption rate constants for the pseudo-first-order and pseudo-second-order models, respectively. The adsorption rate constants of both models calculated by eqs 4 and 5 are reported in Table 2.

For both surfactants, the correlation coefficient for fitting (R^2) was found to be close to 1, with second-order adsorption rate constants of 0.91 and 2.09 g (μmol min)$^{-1}$ for TX-100 and Igepal CO-630, respectively. The high R^2 values obtained from the kinetic plots suggest that adsorption of surfactants on a PTFE surface can
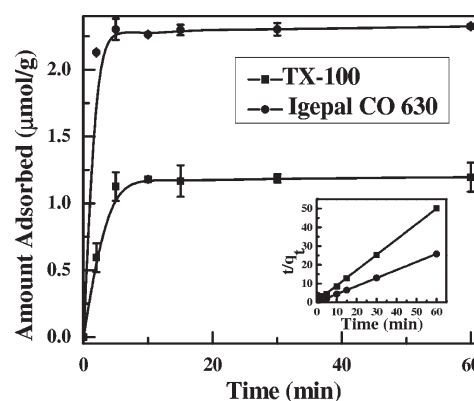
Figure 3. Adsorption kinetics of TX-100 and Igepal CO-630 on PTFE powder. Inset shows linear fitting of pseudo-second-order kinetics.

be better expressed by the pseudo-second-order model, as shown in Figure 3, having a higher R^2 value (>0.99) than the pseudo-first-order model. From the data, it is clear that, at a constant surfactant concentration, the rate of adsorption is higher for Igepal CO-630 than for TX-100, which might be due to the presence of a straight-chain hydrophobic tail group in Igepal CO-630.

3.3. Area Occupied per Surfactant Molecule at the PTFE–Water Interface. From the maximum adsorption capacity, the molecular density or the adsorption density of the surfactants can be expressed in terms of the effective area occupied per surfactant molecule at the PTFE–water interface. Assuming that monolayer adsorption occurs at the PTFE–water interface area, the occupied per molecule can be calculated as[28]

$$a_m = \frac{1}{N_A \Gamma_{SL}} \tag{6}$$

$$\Gamma_{SL} = \frac{q_m}{S_{BET} \times 10^6} \tag{7}$$

where a_m is area occupied per molecule (nm^2), Γ_{SL} is the surface excess concentration of surfactant (mol/m^2) at the PTFE–water interface, q_m is the amount of surfactant adsorbed on the PTFE surface (μmol/g) calculated from the Langmuir adsorption isotherm equation, S_{BET} is the BET surface area of the PTFE powder (m^2/g), and N_A is Avogadro's number (6.02 × 10^{23}). The values for the area occupied per molecule obtained from the above equations for TX-100 and Igepal CO-630 are 1.09 and 1.24 nm^2, respectively.

3.4. Change in Contact Angle with the Surfactant Concentration. The change in advancing contact angle on the PTFE surface was studied and is plotted in Figure 4. Figure 4 shows that there is a gradual decrease in contact angle with increasing surfactant concentration until 0.1 mmol/L (log $C = -1$) for Igepal CO-630 and 0.3 mmol/L (log $C = -0.5$) for TX-100; beyond that concentration, the contact angle remains constant. The contact angle changes from 117.14° (pure water) to 80.42° with increasing concentration of TX-100; similarly, for Igepal CO-630, the change is from 117.14° to 82.79°. Thus, for both surfactants, the contact angle decreases until close to the CMC. The contact angles are similar for the two surfactants, with a slightly lower value for Igepal CO-630 below the CMC region, although the final saturation value is ~2° lower for TX-100. Comparison of these plots with the adsorption isotherm reveals some similarities, such as that the amount of Igepal CO-630 adsorbed is also higher at low concentration and that, near the

Table 2. Pseudo-First-Order and Pseudo-Second-Order Kinetic Parameters

	pseudo-first-order kinetics			pseudo-second-order kinetics		
surfactant	k_1 (min^{-1})	q_e (μmol/g)	R^2	k_2 [g (μmol min)$^{-1}$]	q_e (μmol/g)	R^2
TX-100	0.11	0.19	0.61	0.91	1.21	0.99
Igepal CO-630	0.04	0.08	0.35	2.09	2.33	1
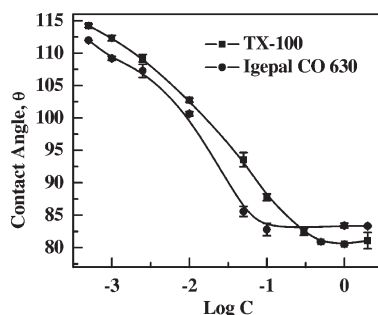
Figure 4. Change in contact angle (θ) with concentration (log C) for different surfactants.

CMC, TX-100 shows a slightly higher adsorption value at the plateau level, although the difference is not significant. This result can be explained as being due to a close relationship between the decrease in contact angle on the PTFE surface and the adsorption density. As mentioned before, this behavior might be due to the presence of the straight-chain tail in Igepal CO-630 resulting in a higher adsorption density at lower concentration as well as a greater lowering of the contact angle.

3.5. Surface Excess at the PTFE–Water and Air–Water Interfaces. Similarly to the adsorption of surfactants at the solid–liquid interface, that at the air–liquid interface is also important in the wetting process. Adsorption of a surfactant at a solid–liquid interface contributes to the wetting process by changing the hydrohilicity/hydrophobicity or the surface energy. Likewise, adsorption of a surfactant at an air–liquid interface changes the surface tension, which is similar to the surface energy at the air–liquid interface. The contact angle can be related to the surface or interfacial tensions using Young's equation as

$$\gamma_{LG} \cos \theta = \gamma_{SG} - \gamma_{SL} \qquad (8)$$

where γ_{SL}, γ_{LG}, and γ_{SG} are the interfacial tensions at the solid–liquid, air–liquid, and solid–gas interfaces, respectively. The amount adsorbed or the surface excess (Γ_{LG}) at the air–liquid interface (mol/m^2) can be calculated as

$$\Gamma_{LG} = -\frac{1}{2.303RT} \frac{d\gamma_{LG}}{d \log C} \qquad (9)$$

where R is the universal gas constant [8314 m^3 Pa/(kg mol K)], T is the absolute temperature, and N_A is Avogadro's number (6.02×10^{23}). Similarly, the surface excess at the other two interfaces (Γ_{SG} and Γ_{SL}) can also be calculated. Rearranging the surface excess equations for the three interfaces and substituting eq 8 gives the Lucassen–Reynolds equation[29,30]

$$\frac{\Gamma_{SG} - \Gamma_{SL}}{\Gamma_{LG}} = \frac{d(\gamma_{SG} - \gamma_{Sl})}{d\gamma_{LG}} = \frac{d\gamma_{LG} \cos \theta}{d\gamma_{LG}} \qquad (10)$$

The surface excess at the solid–gas interface can be assumed to be zero ($\Gamma_{SG} \approx 0$). The ratio of Γ_{SL} to Γ_{LG} can be obtained from the

slope of a plot of $\gamma_{LG} \cos \theta$ (adhesional tension) versus γ_{LG}. If the slope of the curve (Γ_{SL}/Γ_{LG}) is -1, then the surface excesses at the solid–liquid and air–liquid interfaces are equal. The plot of adhesional tension versus surface tension shows a linear relationship (Figure S1 of the Supporting Information) with a slope of -0.86 ($R^2 = 0.98$). It was also found that there was no difference between the two surfactants. This indicates that the surface excesses at the PTFE–water and air–water interfaces are not equal. To calculate the actual surface excess at the air–water interface, the surface tension of each surfactant solution was measured, and eq 6 was used to calculate the values A_{min}. The surface excess values obtained from the experimental data are also comparable with the previously reported values included in Table 3. This table shows that the values of surface excess are similar for the two surfactants. The ratios of the surface excess values between two interfaces are 0.65 and 0.58 for TX-100 and Igepal CO-630, respectively, which also confirms the inequality in surface excess at the two interfaces, in agreement with the contact angle results. The values show that there is a little difference in the Γ_{SL}/Γ_{LG} ratio between the two surfactants measured independently and that these values are lower than those obtained from the contact angle measurements. This difference can be attributed to the following causes: (i) There are differences between the different measurement techniques. (ii) The PTFE sheet and powder were obtained from different sources, which could result in variations in quality. (iii) The amounts of surfactant adsorbed on the PTFE surface are low, and the UV–vis measurement technique is not very precise, so that some experimental error could also be incurred in the adsorption experiments.

For the confirmation of equal adsorption at the solid–liquid and air–liquid interfaces, $\Gamma_{SL}/\Gamma_{LG} = -1$ is a necessary condition. At the same time, another condition should also be fulfilled: linearity of the plot of $\cos \theta$ versus $1/\gamma_{LG}$ with an intercept on the $\cos \theta$ axis equal to -1. The plot of our results (Figure S2 of the Supporting Information) shows that there is a linear relationship between $\cos \theta$ and $1/\gamma_{LG}$ with an intercept of -0.84 ($R^2 = 0.98$). Finally, it can be concluded that the surface excess concentrations at the PTFE–water and air–water interfaces are not equal in this study. In this regard, there is no general rule for predicting whether the surface excesses at the solid–liquid and air–liquid interfaces will be equal; rather, it might depend on the solid surface as well as the type of surfactant. From some previously reported studies, it appears that, for low-surface-energy solids, the surface excesses at the solid–water and air–water interfaces are same;[3,10,11,32] however, other studies have also reported unequal adsorption between hydrophobic solid–water and air–water interfaces, such as nylon and poly(methyl methacrylate) (PMMA)[3,33] and PTFE.[7]

3.6. PTFE–Water Interfacial Tension and Critical Surface Tension of Wetting. From eq 8, it is clear that the PTFE–water interfacial tension is also equally important in the wetting process as the air–water interfacial tension or surface tension. For reducing the contact angle at the PTFE–water interface, reductions in both interfacial tensions are essential. Figure 5 shows the

Table 3. CMC, Surface Tension at the CMC, Surface Excess, and Area Occupied per Molecule at the Air—Water Interface for TX-100 and Igepal CO-630

surfactant	CMC (mmol/L)	γ_{CMC} (mN/m)	exp Γ_{LG} (mol/m^2 × 10^6)	exp A_{min} (nm^2)	literature Γ_{LG} (mol/m^2 × 10^6) [A_{min} (nm^2)]
TX-100	0.15	31.01	2.36	0.70	2.5 [0.66] at 25 °C[28]
Igepal CO-630	0.08	31.02	2.31	0.71	3.25 [0.51][31]
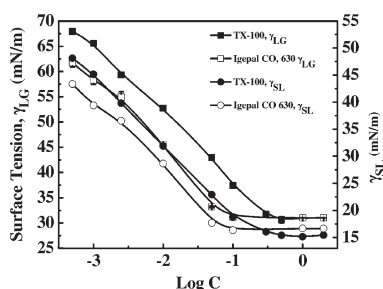
Figure 5. Change in surface tension (mN/m) and PTFE—water interfacial tension with the surfactant concentration (log C).
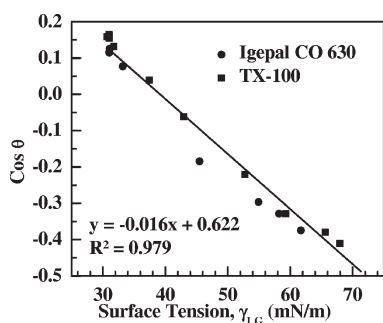
Figure 6. Plot of cos θ versus surface tension (mN/m) for different surfactants.

changes in both the interfacial tensions with log C. From the figure, it is clear that Igepal CO-630 has a slightly lower value for both the interfacial tensions than TX-100, whereas their plateau levels are almost same. The PTFE—water interfacial tension changes from 52.85 mN/m (pure water) to 15.43 and 16.36 mN/m for TX-100 and Igepal CO-630, respectively, and the surface tension value changes from 71.50 mN/m (pure water) to 31.01 and 31.02 mN/m for TX-100 and Igepal CO-630, respectively.

As in previously reported studies,[34,35] there is a linear relationship between cos θ and γ_{LG}, as shown in Figure 6. The critical surface tension (γ_C) value of 23.62 mN/m was obtained by extrapolating the curve to cos θ = 1; this value is close (23.46 mN/m) to that reported before.[5]

3.7. Work of Adhesion of Surfactant Solutions to a PTFE Surface. The work of adhesion measures the interactive force between the two different (solid and liquid) phases. The interaction between the two phases and the contact angle can be presented using the Dupree and Young—Dupree equations, respectively

$$W_a = \gamma_{LG} + \gamma_{LG} - \gamma_{SL} \quad (11)$$

$$W_a = \gamma_{LG}(1 + \cos\theta) \quad (12)$$

The work of adhesion depends on both surface tension and contact angle; for zero contact angle, $W_a = 2\gamma_{LG}$. Therefore, zero
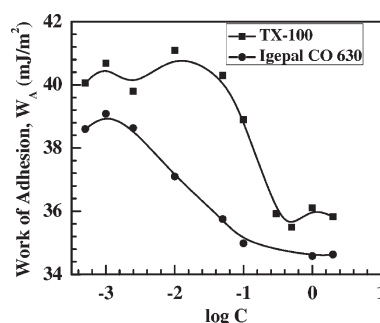
Figure 7. Change in the work of adhesion (W_a) with surfactant concentration (log C) for different surfactants.

contact angle results when the forces of attraction between liquid and solid are equal to or greater than those between liquid and liquid, and a finite contact angle results when the liquid adheres to the solid less than it coheres to itself. The values of the work of adhesion at different surfactant concentrations are plotted in Figure 7. This figure shows that the values of W_a decrease with a slight irregularity with increasing concentration of surfactant. Igepal CO-630 has lower W_a values than TX-100. The change in W_a with surfactant concentration can also be attributed to the unequal surface excesses between the air—liquid and solid—liquid interfaces. Mathematically, this can be shown as follows. The differential form of eq 11 can be written as

$$\frac{dW_a}{d\gamma_{LG}} = \frac{d\gamma_{SG}}{d\gamma_{LG}} - \frac{d\gamma_{SL}}{d\gamma_{LG}} + 1 \quad (13)$$

From the Gibbs adsorption equation, $d\gamma_{SG}/d\gamma_{LG} = \Gamma_{SG}/\Gamma_{LG}$, and $d\gamma_{SL}/d\gamma_{LG} = \Gamma_{SL}/\Gamma_{LG}$. Assuming $\Gamma_{SG} \approx 0$ when there are equal surface excesses on the two interfaces, $\Gamma_{SL}/\Gamma_{LG} = 1$, and $dW_a/\gamma_{LG} = 0$, or W_a = constant. Therefore, it can be assumed that the work of adhesion will not change with the concentration of surfactant. As shown before, for this study, $\Gamma_{SL}/\Gamma_{LG} < 1$, or $dW_a/d\gamma_{LG} \neq 0$, which indicates that the work of adhesion will change with the concentration of surfactant.

To further analyze the results for the work of adhesion, it was observed that, although the contact angle decreases in the presence of surfactant solutions, the work of adhesion also decreases simultaneously. In general, from a basic understanding, with the decrease in contact angle, the wetting property enhances; as a result, the work of adhesion increases. This result can be attributed to the fact that, initially, the contact angle on the PTFE surface in the presence of water and low surfactant concentration is above 90°, where cos θ values are negative. As a result, the (1 + cos θ) term increases gradually with the decrease in contact angle. At the same time, the surface tension also decreases gradually. The decrease in surface tension is greater than the increase in the (1 + cos θ) term; as a result, the work of adhesion values decrease with increasing concentration.

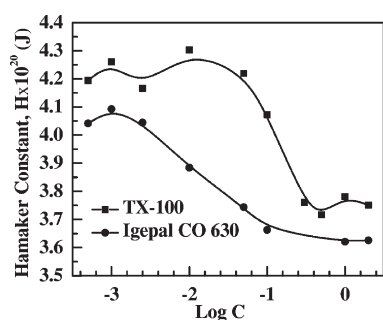**3.8. Hamaker Constant for the PTFE—Water Interaction.** The experimental determination of the Hamaker constant (A)

Figure 8. Change in the Hamaker constant (H) with concentration (log C) for different surfactants.

Figure 9. Change in the surface wetting free energy (ΔG) with concentration (log C) for different surfactants.

for a given material in surfactant solution can be useful for discussing the interaction between solid and liquid. When the Hamaker constant is positive ($A > 0$), it corresponds to an attraction between the molecules, and when it is negative ($A < 0$), it corresponds to repulsion. The constant of the PTFE−water system can be written as[36]

$$A_{PTFE-water} = 12\pi D^2 \gamma_{LG}(1 + \cos\theta) \quad (14)$$

where D is the distance between the atoms at contact. Literature values of Hamaker constant in a vacuum for water and PTFE are $A_{water} = 3.8 \times 10^{-20}$ J and $A_{PTFE} = 4.4 \times 10^{-20}$ J. Applying the Bertholet relation (geometric mean approximation), the Hamaker constant for the PTFE−water system can be calculated as $A_{PTFE-water} = (A_{water}A_{PTFE})^{1/2} = (3.8 \times 4.4)^{1/2} \times 10^{-20}$ J $= 4.08 \times 10^{-20}$ J. Using this $A_{PTFE-water}$ value, the contact angle, and the surface tension for pure water in eq 14, one obtains $D = 0.17$ nm. Further, $A_{PTFE-water}$ was calculated in the presence of surfactant solution and is presented in Figure 8. Similarly to the plot for the work of adhesion, there are slight irregularities at low surfactant concentrations, but at higher concentrations, there is a sharp decrease in Hamaker constant with increasing concentration, ultimately reaching a plateau region close to the CMC of the individual surfactants. Throughout the concentration range studied, Igepal CO-630 exhibited lower values than TX-100.

3.9. Wetting Free Energy of a PTFE Surface. As the energy of the PTFE surface is low, wetting is difficult using only water, which has a high surface energy ($\sim$71.50 mN/m). In the presence of surfactant solution, the surfactant molecules adsorb on the PTFE surface and make it hydrophilic by increasing the surface energy. In this process, knowledge of the change in wetting free energy is also very important; larger values of the negative wetting free energy are expected to enhance the wetting process. From the thermodynamic point of view, the molar wetting free energy of the solid can be calculated according to Extrand[37] as

$$\Delta G = \frac{RT}{3} \ln \frac{(1 - \cos\theta)^2 (2 + \cos\theta)}{4} \quad (15)$$

Figure 9 shows that, with the increase in surfactant concentration, the wetting free energy becomes more negative and ultimately reaches a constant value above the CMC.

3.10. Polar and Dispersion Forces of Surfactant Solutions. According to Fowkes,[38] the interfacial tension is the contribution of polar and dispersion forces. The air−water interfacial tension or surface tension can be written as

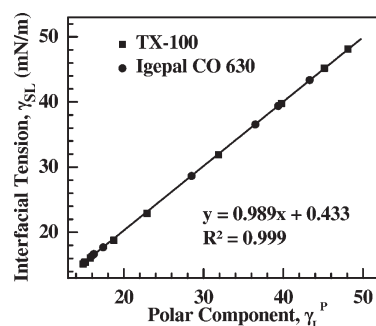$$\gamma_{LG} = \gamma_L^p + \gamma_L^d \quad (16)$$
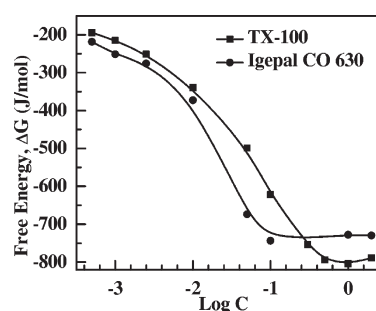
Figure 10. Plot of PTFE−water interfacial tension as a function of the polar component of the surface tension for different surfactants.

where γ_L^d is the contribution of the dispersive forces and γ_L^p is the contribution of the polar interaction term (mostly hydrogen bonding). Specifically, at the PTFE−water interface, the interfacial tension can be defined as the geometric mean of the dispersive force components

$$\gamma_{SL} = \gamma_{SG} + \gamma_{LG} - 2\sqrt{\gamma_L^d \gamma_S^d} \quad (17)$$

where γ_S^d is the contribution of the dispersive forces of PTFE. Rearranging the equation, one obtains

$$W_a = 2\sqrt{\gamma_L^d \gamma_S^d} \quad (18)$$

At the PTFE−air interface, an equation similar to eq 16 can be written by neglecting the polar component of surface tension, $\gamma_{SG} = \gamma_S^d = 20.24$ mN/m.[5] Because the work of adhesion and γ_{LG} values are known for each surfactant concentration, the γ_L^d value can be obtained from eq 16, and substituting the value into eq 16, one can calculate γ_L^p. The plot of γ_L^p versus γ_{SL} for both surfactants (Figure 10) exhibits a linear relationship: $\gamma_{SL} = 0.989\gamma_L^p + 0.433$. The direct determination of PTFE−water interfacial tension is difficult experimentally. However, there is good linear relationship between the polar component of the liquid and the solid−liquid interface, so γ_{SL} can be calculated from the polar component of the solution. It has also been observed that the relationship is independent of the type of surfactant; certain value of γ_{SL} can be obtained by maintaining a particular polar component of the liquid.

4. CONCLUSIONS

The adsorption kinetics and isotherms of TX-100 and Igepal CO-630 were found to follow pseudo-second-order kinetics and

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the Langmuir isotherm model, with a higher adsorption constant rate constant and a higher Langmuir constant for Igepal CO-630.

The decrease in contact angle with increasing surfactant concentration follows a trend similar to that of the adsorption isotherm of the respective surfactant. The free energy of wetting becomes more negative with increasing surfactant concentration, indicating that the process is spontaneous for both surfactants. The Hamaker constant and work of adhesion decrease gradually with increasing surfactant concentration and ultimately reach plateau regions above the CMC. Igepal CO-630 shows a lower work of adhesion and Hamaker constant than TX-100. The change in the polar component of the interaction term with the PTFE—water interfacial tension follows the same linear relationship for both surfactants, so the PTFE—water interfacial tension is independent of the type of surfactant.

Igepal CO-630 has a lower CMC value and better wetting properties at low concentration than TX-100, as well as comparable properties near the CMC. As a result, the use of Igepal CO-630 as a wetting agent might be more beneficial than the use of TX-100 because of lower consumption in the process and possibly higher biodegradability in nature (because of the presence of a straight-chain hydrocarbon tail).

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Plots of surface tension (mN/m) versus adhesional tension (mN/m) and cos θ versus inverse surface tension for different surfactants. This material is available free of charge via the Internet at http://pubs.acs.org.

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