Surface Tension, Adsorption, and Wetting Behaviors of Natural Surfactants on a PTFE Surface

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The adsorption kinetics and wetting behaviors of three plant-based natural surfactants (Reetha, Shikakai, and Acacia) on the polytetrafluoroethylene (PTFE) surface are reported in this study. Adsorption studies of these surfactants on PTFE surface show the equilibrium adsorption time is approximately 15 min, and Langmuir-type isotherm fits well for all three surfactants. The contact angle measurements show that the value achieved by Reetha and Acacia solutions are close (~109°), but that is low in the case of Shikakai (98.13°). Although, comparing the adsorption densities of the surfactants at PTFE–water and air–water interfaces, it has been found that adsorption densities at the PTFE–water interface are low for all three surfactants than that of air–water interface. The alcohol–Shikakai mixed solutions show nonideal behavior of surface tension reduction through a strong interaction between alcohol and Shikakai molecules, which in turn, show lower surface tension and contact angle values than that of ideal. © 2014 American Institute of Chemical Engineers *AIChE J*, 61: 655–663, 2015

Keywords: wetting, natural surfactants, Shikakai, Reetha, Acacia, synergetic effect

Introduction

Wetting of low energy solid surfaces by polar liquids is a challenging task for the researchers because of its gradual increasing practical importance in different applications.[1–6] However, because of the energy mismatch between the solid surface and the polar liquid, wetting of low energy solid surfaces is difficult. In general, different surface active agents are used to improve the wetting property. The reported studies on wetting of hydrophobic surfaces by aqueous surfactant solutions can be broadly classified into two types: (1) synthetic surfactant based, and (2) bio- or natural surfactant based. The research on synthetic surfactants are mostly concentrated on a single chain surfactants,[7–9] Gemini and double-chain surfactants,[10–13] surfactant and alcohol mixture,[14,15] surfactant and electrolyte mixture,[8] mixture of different surfactants,[16–18] and mixed surfactants in the presence of electrolytes[19] on different hydrophobic solid surfaces. The synthetic-surfactants-based studies are mostly highlighted on fundamental aspects to find the most effective surfactant for better wetting, explore the mechanism, performance enhancement, and reduction of surfactant consumption by the addition of additives or using mixed surfactant systems. In the case of industrial or domestic applications of these surfactants, especially when the consumption is more, disposal of the surfactant solutions after the application is a major environmental concern, as the synthetic surfactants are not easily biodegradable or sometimes their biodegradable products are also more harmful, so, from the environmental perspective they are not well accepted. Therefore, in the recent years, there is a gradual increasing trend on the application of environmentally friendly surfactants to reduce the environmental problems.

In spite of the fact that, there are large number of studies available on the wettability of hydrophobic surfaces by aqueous surfactant solutions but quite a few on that of environmentally friendly natural bio- or plant-based surfactants. There are only a few studies reported on rhamnolipid biosurfactants.[20,21] There might be several reasons associated behind it such as a limited number of surfactants are explored till today, performance may not be as good as that of the synthetic surfactants, limitation on bulk scale production, economically not viable, and so forth. Ishigami et al.[20] studied the wetting characteristics of rhamnolipids RB-Na (sodium salt of rhamnolipid B) and its derivative RB-Me (rhamnolipid B methyl ester) on five different types of polymer surfaces. They found when the carboxylic moiety of RB was converted to methyl ester the wetting actions of RB were significantly enhanced. Similarly, the wetting properties of anionic biosurfactant (rhamnolipids, RL) with that of anionic synthetic (sodium dodecyl sulphate) surfactant on different hydrophilic and hydrophobic surfaces were compared and found similar wettability at low concentrations, but wettability of RL was more at higher concentrations.[21] In these studies, the effect of rhamnolipid concentration on the change in wetting properties were reported, but the mechanism and the interaction of rhamnolipid molecules with the surface are not properly highlighted. So, in this study, we

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Additional Supporting Information may be found in the online version of this article.

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mainly focus on the adsorption and interaction behaviors of the plant-based natural surfactant molecules with the solid surface and as well as the synergistic effect of mixture of surfactant and coadditives (alcohol) on the wetting of hydrophobic solid surface. To the best of our knowledge, similar wetting behavior of hydrophobic surface using natural surfactant solutions was not reported before. From the application point of view, the use of plant surfactants is advantageous than that of microorganism-based biosurfactants, because the large scale production of natural surfactants is highly possible, as a result they might be economically more viable also. At the same time, the comparison of the performance of these surfactants with the conventionally used synthetic surfactants and finding the probable mechanism would be highly useful for the practical applications of natural surfactants, which in turn may reduce the surfactant-based environmental pollutions.

Experimental

Materials and methods

Polytetrafluoroethylene (PTFE) slides of dimensions $25.34 \times 1.12\ \text{mm}^2$ were cut from a sheet purchased from J. Khushal Das and Co. (India), and the PTFE powder used for adsorption experiments was purchased from Pragati Plastics Pvt. (India). Dry pods of Reetha and Shikakai were purchased from the local market, Rourkela, India and Acacia was collected from the tree. Ultrapure water of 18.2 M Ω cm resistivity, 71.5 mN/m surface tension, and 6.5–7 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 UK) and found that the average particle size was 115.7 μm. The zeta potential of PTFE powder was measured in the presence of 0.01 M KCl solution using the Zetasizer (Nano ZS, Malvern, UK) by Smoluchowski model. The zeta potential was found to be −4.82 mV. The specific surface area of the PTFE powder was measured by N_2 adsorption-desorption studies at liquid nitrogen temperature (−195.8°C) by applying Brunauer-Emmett-Teller (BET) theory using Autosorb-1 (Quantachrome) and it was $4.345\ \text{m}^2/\text{g}$. Prior to the BET analysis, the sample was degassed at 200°C.

Extraction of plant surfactants

The plant surfactants Reetha and Shikakai were extracted from the pods according to the method mentioned in our previous study.[22] Acacia was extracted first in methanol similar to those other two surfactants. The dry powder was then again extracted with a mixture of diethyl ether and methanol (5:1) to get a complete water soluble fraction.

Surface tension measurement

All the plant surfactant solutions were prepared freshly just before the measurements to avoid fungal or bacterial growth. The surface tension of aqueous surfactants solutions was measured by the Wilhelmy plate (made of Pt–Ir alloy) method using a surface tensiometer (DCAT-11EC, Data Physics, Germany) at 25 ± 0.5°C. The temperature was maintained using an external water bath circulator. A 1 mm/s motor speed and 3 mm immersion depth of the Pt-Ir plate were maintained for all experiments. After measurement of each concentration, the plate was cleaned with water, acetone, and finally burned in an alcohol flame.

Adsorption study

For the adsorption experiments, a volume of 25 mL surfactant solutions of different concentrations was taken in 60 mL plastic bottles, and 1 g of PTFE powder was used for all the experiments. The bottles were shaken well for 2 h at 25 ± 1°C in an incubator shaker. The PTFE particles were separated from the mixture by centrifugation at 6000 rpm. The concentration of the surfactant solutions before and after the adsorption was determined by the Total Organic Carbon analyzer (TOC-VCPN, Shimadzu, Japan). The experiments were repeated at least thrice and the average data were plotted. The amount of surfactant adsorbed ($\mu\text{M}/\text{m}^2$) was determined by the following equation

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

where C_i and C_eq are the initial and the equilibrium concentrations (mM/L), V, m, and SA are the volume of surfactant solution (mL), the mass of the adsorbent (g), and the surface area of the adsorbent in m^2/g, respectively.

Dynamic contact angles measurement

Dynamic advancing contact angles (θ) was measured using the Wilhelmy plate method using the surface tensiometer. All experiments were performed at a constant temperature (25 ± 0.5°C). A 0.1 mm/s motor speed and 5 mm immersion depth of the PTFE plate were maintained during the contact angle measurements. A good quality PTFE slides were chosen and washed several times with the first acetone and then ultrapure water to clean the impurity. The plate was then dried by blowing hot air. The same procedure was repeated after the individual measurement.

Results and discussion

Structure and physical properties of plant surfactants

Structures of the plant surfactants are most important before discussing the experimental results. Figure 1a shows the structure of Reetha (*Sapindus mukorossi*) with a molecular weight of 966 as proposed in our previous study.[22] Structures of Shikakai (*Acacia concinna*) and Acacia (*A. auriculiformis*) are shown in parts (b)[23,24] and (c)[25,26] of Figure 1, having the molecular weight of 1058 and 1765, respectively. The CMC value of both Reetha and Shikakai was found 0.5 mM at 25 ± 0.5°C measured by the surface tension method. The critical micellar concentration (CMC) of Acacia was found 0.39 mM at 25 ± 0.5°C. The aqueous solution of Reetha and Shikakai is slightly acidic, their pH values are 4.34 and 3.5, respectively; however, Acacia solution is neutral (pH = 6.5–7).

These surfactants are mostly nonionic in nature and they are mostly triterpenoid glycosides type.[27] The hydrophilic part mainly consists of sugars such as, D-glucose, D-xylose, L-arabinose, L-rhamnose, and glucuronic acid,[28] where as, sapindic acid and oleanolic acid are the main constituents of the hydrophobic portion.[29]

Adsorption of plant surfactants at air–water interface

The surface tension values of three plant surfactants Reetha, Acacia, and Shikakai solutions vs. logarithm of concentrations are presented in Figure 2. The figure depicts the solution behavior with the increasing surfactant concentrations is similar for all three plant surfactants studied here.

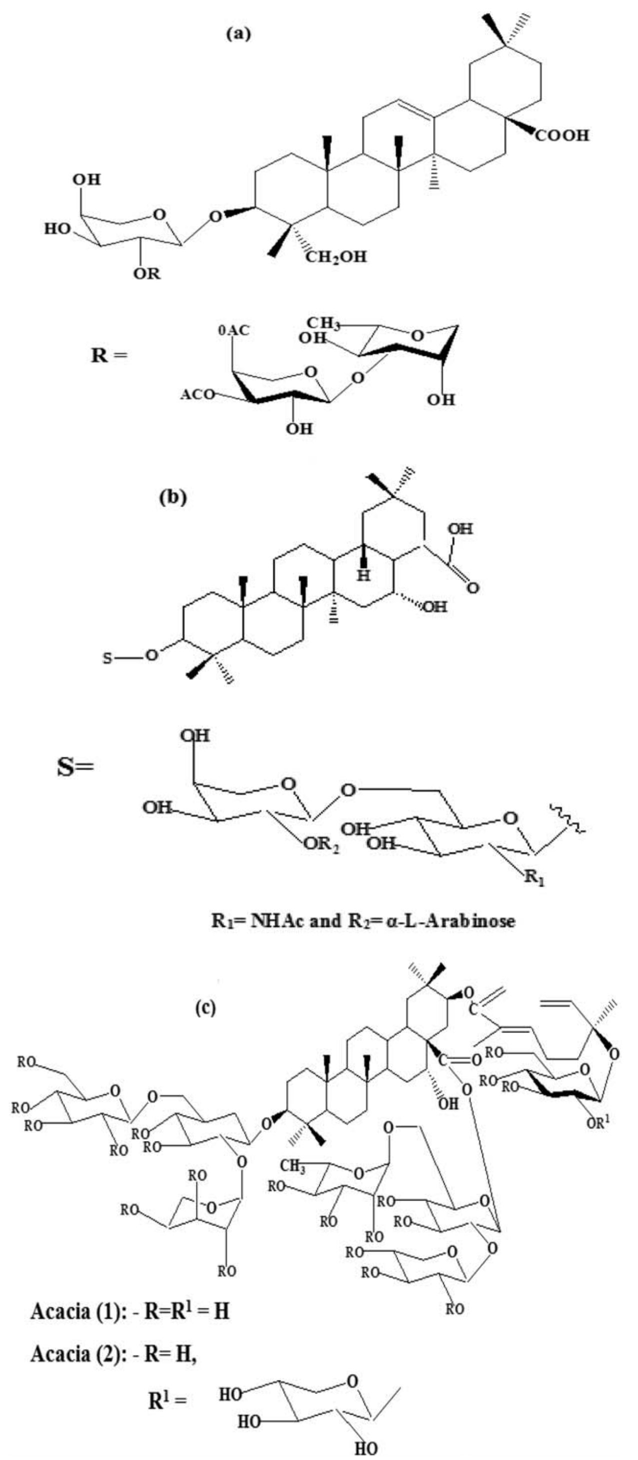

Figure 1. Structure of (a) Reetha, (b) Shikakai, and (c) Acacia.

The surface tension value decreases from 71.5 mN/m (pure water) to a minimum value near to CMC for all three individual surfactants. Minimum surface tension values of 38.29 (at 0.513 mM), 43.56 (at 0.389 mM), and 38.71 mN/m (at 0.5 mM) were achieved for Reetha, Acacia, and Shikakai, respectively.

These surface tension values are significantly higher than the conventionally used synthetic single-chain cationic (CTAB = 32.99 mN/m), anionic (SDBS = 34.22 mN/m),[8] and nonionic (TX-100 = 31.01 mN/m, Igepal CO–630 = 31.02 mN/m)[9] surfactants. The surface excess concentration at the air–water interface and area occupied per molecule for Reetha, Acacia, and Shikakai were also calculated by Gibbs adsorption Eq. 2[30] using the surface tension data below the CMC region

$$\Gamma = -\frac{1}{2.303nRT}\left(\frac{d\gamma_{\mathrm{LG}}}{d\log c}\right) \tag{2}$$

where R is universal gas constant (8.314 J mol^{-1} K^{-1}), T is absolute temperature (298 K), n is a constant equal to 1 for nonionic surfactant. The value of n is taken as 1 because all surfactants are nonionic in nature. If the surface excess concentration at the interface is maximum or at saturation ($\Gamma_{\max}$) the area occupied per surfactant molecule ($A_{\min}$) at the water–air interface in Å^2 can be calculated from the Eq. 3

$$A_{\min} = \frac{1}{N_{\mathrm{A}}\Gamma_{\max}} \tag{3}$$

where, N_{A} is the Avogadro's number (6.02 × 10^{23} mol^{-1}). The values obtained are shown in Table-S1 in Supporting Information. It can be seen that the area occupied by Reetha and Shikakai are very close, and the values are lower than Acacia. The results indicate lower surface tension values for Reetha and Shikakai than Acacia is mainly because of the close packing of the surfactant molecules at the air–water interface.

Adsorption of plant surfactants on the PTFE surface

Adsorption kinetics of three different natural surfactants Reetha, Shikakai, and Acacia of 0.05 mM initial concentration at PTFE–water interface are presented in Figure 3a. The adsorption kinetics were studied mainly to know the equilibrium time for the adsorption process. The Figure shows that the equilibrium times for all three surfactants are close to 15 min, with a slightly higher adsorption capacity for Shikakai. The adsorption isotherms were also studied for all three surfactants to know the maximum adsorption capacity, where the equilibrium time was maintained as per the kinetic data.

Figure 3b depicts the adsorption isotherms of three plant surfactants on the PTFE surface. From Figure 3b, it is clear that the nature of the isotherms is similar with a different

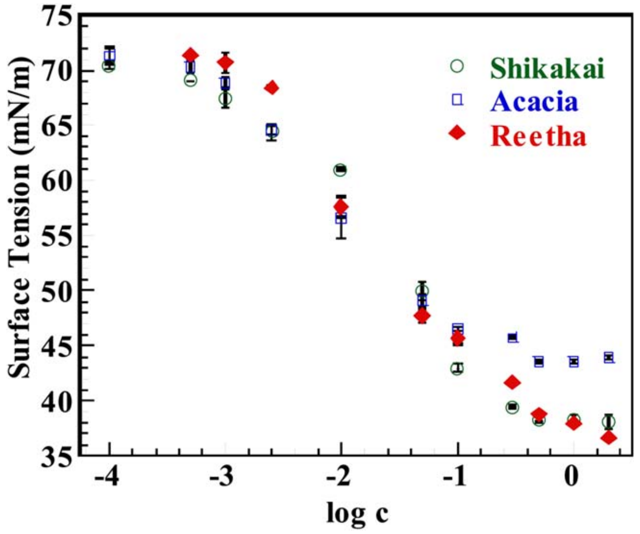

Figure 2. The change in surface tension (mN/m) with the concentration (log c) of different surfactants.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

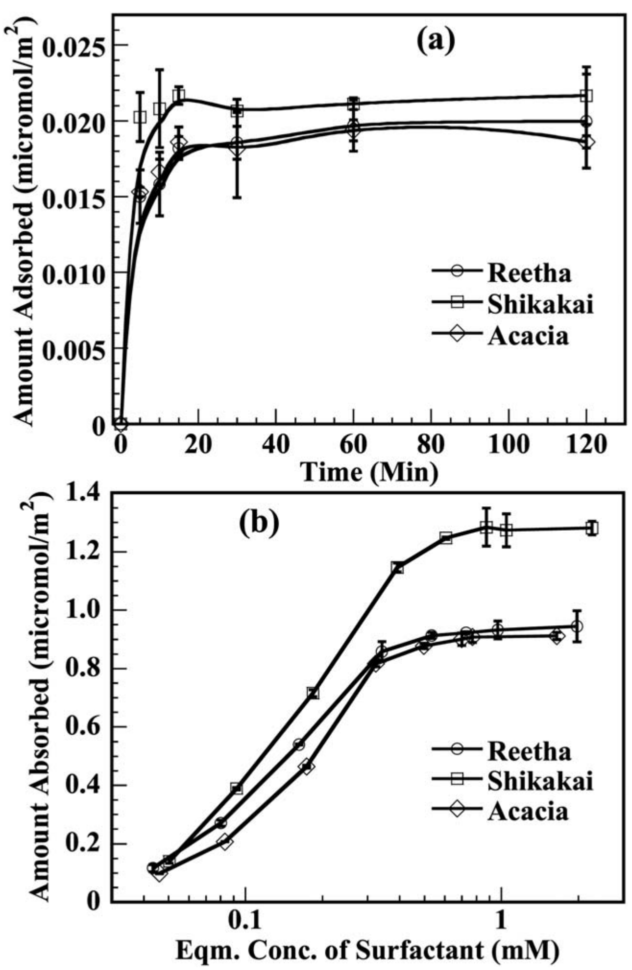

Figure 3. (a) Adsorption kinetics at 0.05 mM concentration of Reetha, Shikakai, and Acacia surfactants on the PTFE powder. (b) Adsorption isotherms of Reetha, Shikakai, and Acacia on the PTFE powder.

amount adsorbed, also noteworthy to mention that in all three cases adsorption amount is significantly low (in the range of micromol (μM)/m^2). Although comparing the isotherms of Reetha and Acacia, they are almost close to each other with a little higher adsorption capacity for Reetha; however, there is a distinct difference with Shikakai, which is having a higher adsorption capacity. The plateau level adsorption occurs just above the CMC for all three surfactants. A lower adsorption density of Reetha and Acacia compared to that of Shikakai is attributed to the presence of more hydrophilic groups which leads to make these molecules more polar.

There are several models available in the literature to fit the adsorption isotherms to know the isotherm type; however, the nature of adsorption isotherms observed for these three surfactants is very simple. So we tried to fit the isotherms with two types of simple models, Langmuir and Freundlich isotherms which are widely used in many adsorption studies at solid–liquid interfaces.

The Langmuir isotherms can be expressed as

$$\frac{C_e}{q_e}=\frac{1}{bq_m}+\frac{C_e}{q_m} \tag{4}$$

The Freundlich isotherms can be expressed as

$$\log q_e=\log a+\frac{1}{n}\log C_e \tag{5}$$

where notations used are q_m, b, C_e, a, n for equilibrium amount adsorbed (μM g^{-1}), adsorption constant of Langmuir model (mM^{-1}), the equilibrium concentration (mM), constant or coefficient of Freundlich isotherm equation representing the adsorption capacity, and a constant (reciprocal of the exponent of the Freundlich isotherm equation), respectively. When the interaction between the adsorbate molecules and surface is predominant but the intermolecular interaction between the adsorbed surfactant molecules is negligible, adsorbate forms a monolayer preferably and then Langmuir model works quite well. The Langmuir and Freundlich adsorption constants and the respective correlation coefficients (R^2) are calculated from the fitting of experimental data with Eqs. 4 and 5 and listed in Table S2 in Supporting Information.

From the Table S2 in Supporting Information, it is clear that all three plant surfactants are fitting better with the Langmuir isotherm model and forming a monolayer on the PTFE surface, because the surfactant molecules are adsorbs through the tail group on the surface. Initially, the adsorption density increases almost linearly with the equilibrium concentration, that is, follows Henry's law and ultimately reaches a plateau region. The values of b decrease for three surfactants in the following order: Shikakai > Reetha > Acacia.

From the maximum adsorption capacity, the molecular or adsorption density at the solid surface can be expressed in terms of the effective area occupied per surfactant molecule at PTFE–water interface. Assuming that monolayer adsorption occurs at PTFE–water interface, the area occupied per molecule and surface excess concentration can be calculated by Eqs. 3 and 6

$$\Gamma_{SW}=\frac{q_m}{S_{BET}\ \text{x}\ 10^6} \tag{6}$$

where Γ_{SW} is the surface excess concentration of surfactant (μM/m^2) at PTFE–water interface, q_m is the amount of surfactant adsorbed onto the PTFE surface (μM/g) calculated from the Langmuir adsorption isotherm equation, S_{BET} is the BET surface area of the PTFE powder (4.345 m^2/g). The area occupied per molecule obtained from the above equations for Reetha, Acacia, and Shikakai are 155, 146, and 112 Å^2, respectively. The obtained values clearly indicate that the adsorption density of respective surfactants at PTFE–water interface is less than that of air–water interface. Although comparing the area occupied per molecule values at air–water and PTFE–water interfaces, it can be observed that at PTFE–water interface adsorption densities of Reetha, Acacia, and Shikakai are 0.629, 0.735, and 0.866 times, respectively, to that of air–water interface.

Wettability of plant surfactant solutions on the PTFE surfaces

The advancing contact angle of three plant surfactant solutions on the PTFE surface are presented in Figure 4. Figure depicts that for these three surfactants, there is a decrease in contact angle with the increase in surfactant concentration until CMC of individual surfactant solution and above that it is almost constant. Similar to the adsorption study, Reetha and Acacia show very close change in contact angle with the

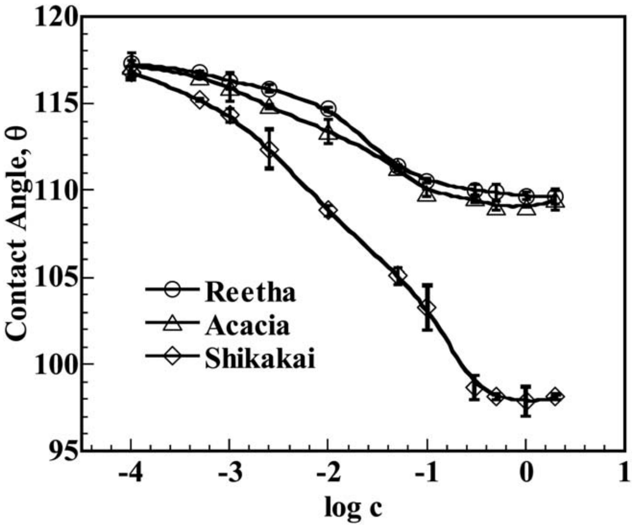

Figure 4. Relationship between the contact angle (θ) and concentration (log c) of different surfactants.

increasing concentrations, whereas, Shikakai shows much lower contact angle value compare to other two surfactants. The plateau level contact angle values for Reetha, Acacia, and Shikakai are 109.88°, 109.02°, and 98.13°, respectively, compared to 116.5° for pure water. Lower contact angle by Shikakai solutions indicates better wetting ability than the other two plant surfactants may be because of higher adsorption ability on PTFE–water and air–water interfaces as mentioned before.

Additionally, just to get an idea about the surface activity of these surfactants, contact angle values on PTFE surface is compared with the conventionally used some common surfactants. It can be clearly observed that these plant surfactants have inferior wettability compared to a different synthetic surfactants such as cationic (CTAB = 84.06°), anionic (SDBS = 86.76°),[8] and nonionic (TX-100 = 81.08°, Igepal CO-630 = 83.33°).[9] Additionally, much lower contact angle values can also be obtained using double-chain cationic (DDAB = 79°) and anionic (AOT = 78.5°) synthetic surfactants.[12]

Comparison of adsorption densities at PTFE–water and air–water interfaces

Adsorption densities of surfactants at air–water and PTFE–water interfaces are an important parameter to change the surface tension or contact angle at the respective interfaces. Adsorption densities at both interfaces are highly possible to measure independently at the equilibrium condition as presented in the previous sections. However, from the contact angle studies, a comparison of adsorption densities at both the interfaces can also be calculated indirectly under the same dynamic condition by combining Young's and Gibbs equations as presented in Eq. 7

$$\frac{d(\gamma_{\mathrm{AW}}\cos\theta)}{d(\gamma_{\mathrm{SA}})}=\frac{\Gamma_{\mathrm{SA}}-\Gamma_{\mathrm{SW}}}{\Gamma_{\mathrm{AW}}} \tag{7}$$

where Γ_{SA}, Γ_{SW}, and Γ_{AW} represent the surface excess of surfactant molecules at PTFE–air, PTFE–water, and air–water interfaces, respectively. Assuming surface excess of surfactants at PTFE–air interface is zero ($\Gamma_{\mathrm{SA}} \approx 0$), Eq. 7 can be reduced to a linear form, where the ratio of Γ_{SW} to Γ_{AW} can be calculated by plotting $\gamma_{\mathrm{AW}} \cos \theta$ vs. γ_{AW}.

From the Figure S1 (in Supporting Information), it can be seen that there are linear relationships exist between the surface (γ_{AW}) and adhesion ($\gamma_{\mathrm{AW}} \cos \theta$) tensions for all three surfactants with different slope and intersection; for all three cases slopes are less than 1 indicate unequal adsorption of surfactants at PTFE–water and air–water interfaces, with a lower adsorption density at PTFE–water interface. The negative slopes for Reetha, Acacia, and Shikakai are 0.589, 0.642, and 0.782, respectively. These values are less than that of calculated ratios from the independent adsorption studies presented previously; this can be attributed to lower contact time (~25 s) of the PTFE surface and surfactant solutions during the dynamic contact angle measurements, so the equilibrium is not reached. The work of adhesion of surfactant solutions is presented in Supporting Information.

Wetting free energy of the PTFE surface from contact angles

During the wetting process of PTFE surface in the presence of surfactant solutions, the surfactant molecules are adsorbed on the PTFE surface and make it hydrophilic; as a result, surface energy increases. In this process, the knowledge of the change in wetting free energy is very important to get an idea about the spontaneity of the wetting process. The larger value of negative wetting free energy is expected to enhance the wetting process. From the thermodynamic point of view, the molar wetting free energy of the solid can be calculated using the contact angle values[31] as

$$\Delta G=\frac{RT}{3}\ln\frac{(1-\cos\theta)^2(2+\cos\theta)}{4} \tag{8}$$

where, ΔG, R, and T are the change in surface free energy, the universal gas constant (8.314 J mol^{-1} K^{-1}), and temperature (298 K), respectively. The calculated values show the wetting free energy (ΔG) is negative over the total concentration range studied here, indicates the process is spontaneous. There is a decrease in wetting free energy with the increasing surfactant concentration, which is consistent with the decreasing contact angle values as mentioned earlier. The minimum wetting free energies of different surfactants (ΔG) on a PTFE surface are, −242.84, −247.37, and −414.44 J mol^{-1} for Reetha, Acacia, and Shikakai, respectively. These values are more negative than the pure water (−171.5 J mol^{-1}), which indicate that the PTFE surface can be wetted by these three surfactant solution more easily than pure water.

Effect of alcohols on Shikakai solutions

In most of the applications, surfactants are mainly used in the presence of additives such as, salt, alcohol, a second surfactant, and so forth to enhance the performance of pure surfactant. Electrolytes are used as an additive in the presence of ionic surfactants.[8] As plant surfactants are mostly nonionic in nature, electrolyte effect was not studied. It has been shown before that the pure natural surfactants are inferior in contact angle reduction with respect to that of synthetic surfactants; so effect of two different alcohols was studied to see the possibility of enhancement of wetting property. Further, alcohol effect was studied only on Shikakai as it acts as a better wetting agent among the three plant surfactants

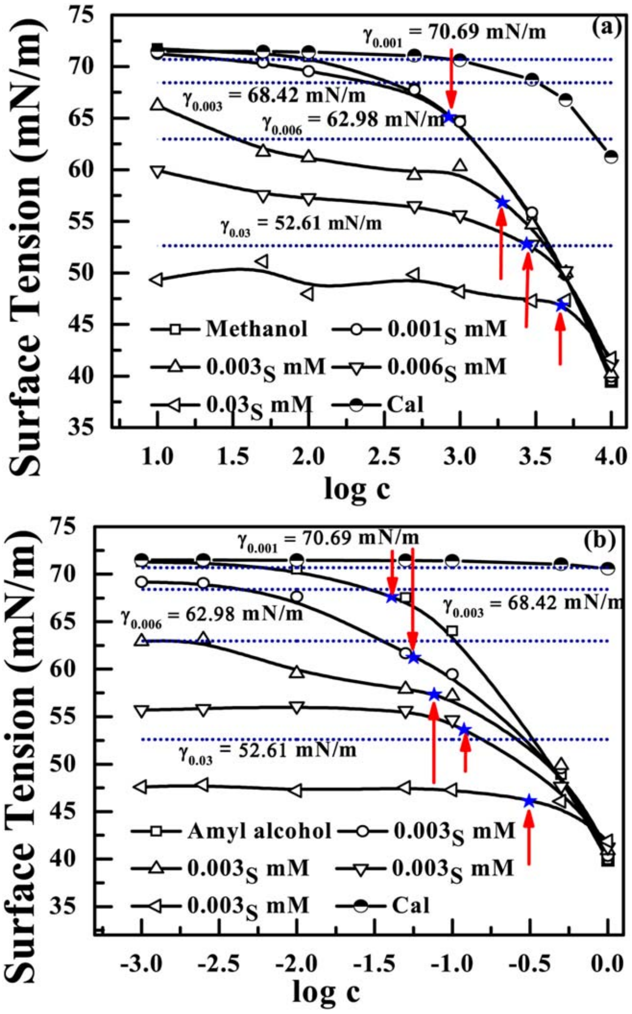

Figure 5. Relationship between the alcohol concentration (log c) and surface tension (mN/m) in the presence of constant Shikakai concentration (a) methanol, (b) amyl alcohol.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

studied here. Two different alcohols of straight chain hydrocarbon (C_1: Methanol, C_5: Amyl alcohol) were studied here.

Effect of alcohols on surface tension

The changes in surface tension as a function of alcohol concentrations at different fixed Shikakai concentrations are presented in (a) and (b) parts of Figure 5 for methanol and amyl alcohol, respectively. Both figures show that there is a gradual decrease in surface tension with the increasing concentration of pure alcohols, but the concentration of alcohol required to reduce similar surface tension for amyl alcohol is almost 10^4 times lower than methanol. More specifically, the surface tension values of 39.82 and 39.45 mN/m were achieved using 1 mM and 10 M of amyl alcohol and methanol solutions, respectively. Figure 5a shows in the presence of low surfactant concentration (0.001 mM) the change in surface tension is similar to that of pure methanol solution; however, with the increasing surfactant concentration surface tension values gradually decrease. The surface tension plots show at low alcohol concentration surface tension changes slowly and above a particular alcohol concentration there is a sharp decrease in surface tension that particular alcohol concentration is dependent on the surfactant concentration, which gradually increases with the increasing surfactant concentration. That particular point is shown by an arrow mark on the respective curves for both alcohols. Additionally, the slope of the lower alcohol concentration region decreases gradually with the increasing surfactant concentration. Similar behavior is also seen for amyl alcohol (Figure 5b), but the concentration of alcohol required is much lower than methanol.

In the case of surfactant and alcohol mixture, it is very much essential to know whether the solutions behave ideally or nonideally because of the interaction between the surfactant and alcohol molecules. Surface tension of pure water–alcohol mixtures can be calculated ideally assuming a linear function of the surface layer mole fraction

$$\gamma_{\text{w-a}} = \alpha_{\text{w}}\gamma_{\text{w}} + \alpha_{\text{a}}\gamma_{\text{a}} \tag{9}$$

where $\gamma_{\text{w-a}}$, γ_{w}, and γ_{a} are surface tensions of water–alcohol mixture, pure water, pure alcohol, respectively; and α_{w} and α_{a} are mole fraction of water and alcohol in the mixture, respectively. It can be seen from Figures 6a,b that there are deviations between the calculated surface tension values with the experimental one for alcohol–water solutions, and deviations are more in case of amyl alcohol because of the surface excess of the amyl alcohol molecules is more than methanol at the air–water interface. When surfactant–alcohol mixture is used, until a certain concentration of alcohol surface tension of water–alcohol solutions and pure surfactant are higher than surfactant–alcohol mixtures. Surface tensions of fixed concentration pure surfactant solutions are shown as dotted lines in Figures 5a,b. If surfactant–alcohol mixtures behave ideally, surface tension should be constant up to the alcohol concentration where the pure surfactant and water–alcohol surface tension lines intersect. However, all surfactant–alcohol mixtures show lower surface tension than the expected, which indicated there is a synergistic interaction between the alcohol and surfactant. The deviation of surface tension from the expected value up to the intersection point in % is calculated as

$$D = \frac{(\gamma_{\text{a-smix}} - \gamma_{\text{s}})}{\gamma_{\text{s}}} \times 100 \tag{10}$$

where, $\gamma_{\text{a-s mix}}$ and γ_{s} are the surface tension values of alcohol–surfactant mixtures and surfactant solutions, respectively. If the deviation is negative, indicates synergistic behavior and zero for an ideal. When the alcohol concentration is beyond the intersection point, then the deviation can be calculated as

$$D = \frac{[\gamma_{\text{a-smix}} - (\alpha_{\text{a}}\gamma_{\text{w-aexp}} + \alpha_{\text{s}}\gamma_{\text{s}})]}{(\alpha_{\text{a}}\gamma_{\text{w-aexp}} + \alpha_{\text{s}}\gamma_{\text{s}})} \times 100 \tag{11}$$

where α_{s} is the mole fraction of surfactant, $\gamma_{\text{w-a exp}}$ is the experimental surface tension of water–alcohol mixture.

Figures 6a,b show the negative deviations of surface tension increases with the increasing alcohol concentration and after a maximum value of negative deviation, when the alcohol concentration increases, further the negative deviation decreases toward zero. This behavior is attributed to the predominance of alcohol effect at very high alcohol concentration. Whereas, at low alcohol concentration, because of the

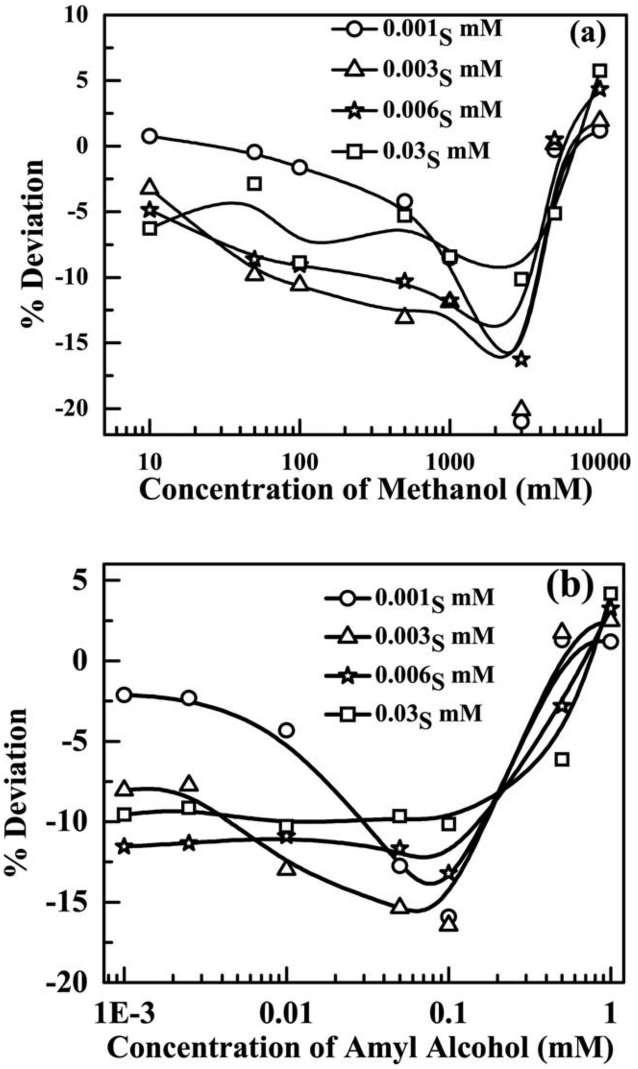

Figure 6. Relationship between the values of concentration and % deviation with varying alcohol concentration of (a) methanol and (b) amyl alcohol.

interaction between alcohol and surfactant molecules there is a sudden decrease in surface tension and gradually decreases with the increasing alcohol concentration; as more alcohol molecules interact with the surfactant molecules. The origins of molecular interactions are mainly because of polar and nonpolar moieties present in these molecules. The polar interaction is mainly because of the interaction between the hydroxyl group of alcohol and the carboxyl group of surfactant molecules; and hydrophobic interaction is between the hydrocarbon chain of alcohol and a nonpolar portion of the surfactant molecules. However, as the concentration of surfactant is constant in the solution, after a certain alcohol concentration there would not be any free surfactant molecules available to interact with the alcohol, eventually maximum deviation occurs at that point; when the concentration is beyond that surface tension of alcohol predominates in the mixture.

^{1}H-NMR (nuclear magnetic resonance) measurements of alcohol–shikakai mixture

The interaction between Shikakai and alcohol was further supported by ^{1}H-NMR spectra measurements in D_2O. ^{1}H NMR spectra of pure amyl alcohol, and their mixture of amyl alcohol–Shikakai at 50:50 molar ratio in D_2O is represented in (a) and (b) parts of Figure S3 in Supporting Information, respectively. The various protons attached to carbon atoms are labelled on the structure of amyl alcohol, and the chemical shift δ (ppm) values are presented in Supporting Information Table S3.

The ^{1}H NMR peaks of protons attached to different carbon atoms of amyl alcohol are marked from letter A to F and their corresponding δ values are identified. A triplet for protons attached to carbon B $(\delta_{CH_2}) = 3.458$–3.491 ppm, multiplets for C (δ_{CH_2}) in the range of 1.408–1.442 ppm, D (δ_{CH_2}) in the range of 1.170–1.206 ppm, and a triplet for E (δ_{CH_2}) in the range of 0.761–0.799 ppm are because of three protons. The absence of peak A can be attributed as a rapid OH exchange with the deuterium of D_2O ($ROH + D_2O \rightarrow ROD + D\text{-}O\text{-}H$). The ^{1}H NMR spectra of the mixture (1:1 molar ratio) are compared with pure alcohol, to get some idea about the interaction between the alcohol and Shikakai. The mixed solution shows upfield shifting (toward the right) of spectra for all protons of amyl alcohol presented in Supporting Information Table S3, which support interaction between amyl alcohol and Shikakai.

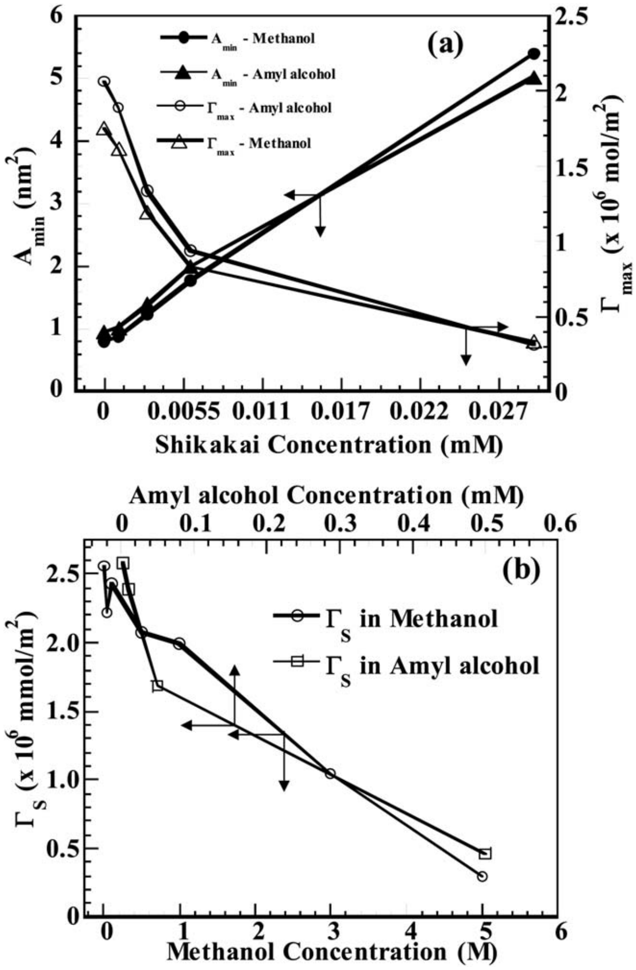

Figure 7. Relationship between the values of (a) surface excess of methanol and amyl alcohol, area per molecule with varying Shikakai concentration and (b) surface excess of Shikakai with varying methanol and amyl alcohol concentration.

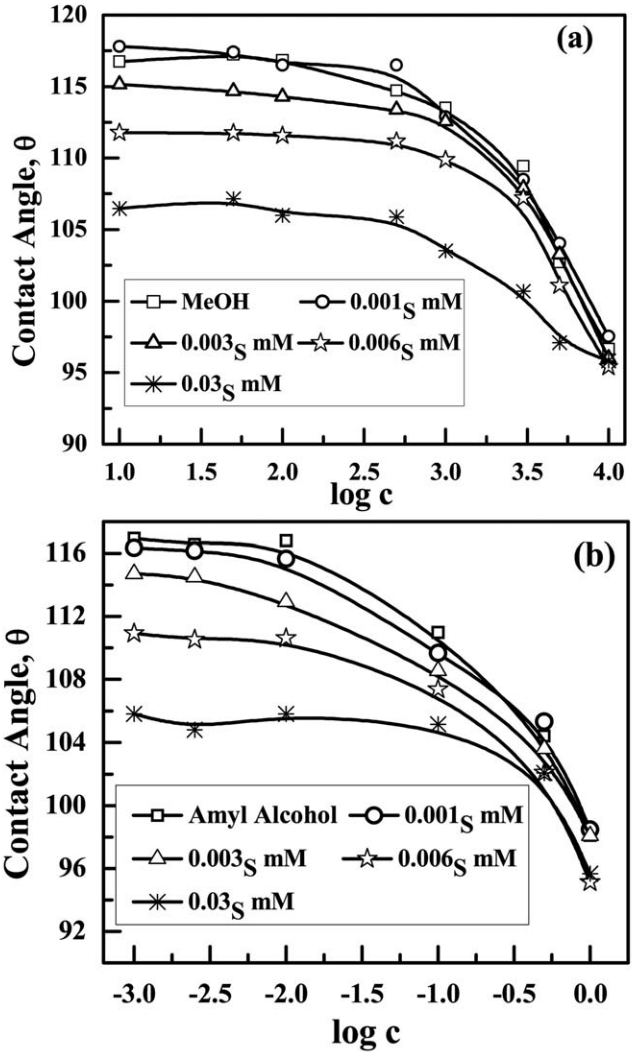

Figure 8. Relationship between the changes in contact angle with the concentrations (log c) of alcohols (a) methanol and (b) amyl alcohol in the presence of varying different Shikakai concentration.

Surface excess of amyl alcohol and methanol in the mixture

Surface excess of surface active solute molecules at the air–liquid interface is directly related to adsorption density, which in turn influences the surface tension of the liquid. The surface excess (Γ) of the surfactant and alcohols can be calculated from the plot of surface tension as a function of alcohol and surfactant concentrations using the Gibbs adsorption Eqs. 12 and 13

$$\Gamma_{\mathrm{A}}=\frac{1}{2.303nRT}\left(\frac{d\gamma_{\mathrm{LG}}}{d\log c_{\mathrm{A}}}\right)_{C_{\mathrm{S}}} \tag{12}$$

$$\Gamma_{\mathrm{S}}=\frac{1}{2.303nRT}\left(\frac{d\gamma_{\mathrm{LG}}}{d\log c_{\mathrm{S}}}\right)_{C_{\mathrm{A}}} \tag{13}$$

where n is a constant equal to one for nonionic surfactant, subscripts A and S are used for alcohol and surfactant, respectively, c is the concentration, R is universal gas constant, T is the absolute temperature (298 K), From the surface excess values, the area occupied per surfactant molecule (A_{min}) at air–water interface in $\mathrm{\AA}^2$ can be calculated from Eq. 3.

The changes of surface excess concentration of alcohols at air–water interface and area per molecule as a function of Shikakai concentration in the bulk phase presented in Figure 7a. The figure depicts surface excess of both alcohols decreases sharply with the increasing surfactant concentration may be because of higher surface activity of surfactant than the alcohols. As a result, the area occupied per molecule of alcohol also increases linearly with the increasing surfactant concentration. The changes of surface excess concentration of surfactant at air–water interface as a function of alcohol concentration presented in Figure 7b. From the figures, it is clear that the surface excess concentration of Shikakai decreases with respect to total surface excess as that of alcohol increases with the increase in alcohol concentration.

Wetting of the PTFE surface by Shikakai–alcohol mixtures

Similar to the surface tension study, contact angle measurements were done using same solutions and the contact angle values are plotted in parts (a) and (b) of Figure 8 for methanol and amyl alcohol, respectively. It has been found that the changes in contact angle values are very much similar to the surface tension results.

In the case of pure alcohol–water mixture, the contact angle reduces from pure water to 96.65° and 98.09° in the presence of 10 M and 1 mM for methanol and amyl alcohol solutions, respectively. In the presence of low surfactant concentration (0.001 mM), the change in contact angle is similar to that of pure alcohol solution for both alcohols. However, the contact angle decreases with increasing surfactant as well as alcohol concentrations. For Shikakai–alcohol mixture, at a low alcohol concentration the reduction in contact angle is more with respect to pure alcohol–water mixtures because of the synergistic interaction as mentioned earlier. These results indicate the addition of alcohol improves the wettability of natural surfactant because of the synergistic effect.

Conclusions

The major results of this study can be summarized as follows:

1. The surface tension measurements show that the surface tension values for Reetha and Shikakai at their respective CMCs are very close (~38.3 mN/m), but little higher for Acacia (~43.6 mN/m); which in turn show the surface excess values at the air–water interface for Reetha and Shikakai solutions are higher than that of Acacia.
2. The adsorption kinetics of these surfactants on the PTFE surface show adsorption is comparatively fast and approximately within ~15 min equilibrium reaches. A Langmuir-type isotherm fits well for all three surfactants studied here, similar to that of synthetic nonionic surfactants.[9] The maximum adsorption capacities of three surfactants at PTFE–water interface are found to be in the following order: Shikakai > Reetha ≈ Acacia. The comparison of adsorption densities at air–water and PTFE–water interfaces show it is more for the former case for these all surfactants.
3. The change in contact angle on the PTFE surface by the plant surfactant solutions also follow a similar trend to that of adsorption density for Reetha, Acacia, and Shikakai; the values are 109.88°, 109.02°, and 98.13°, respectively. The contact angle studies also

independently support lower adsorption density at PTFE–water interface than air–water interface for all three surfactants.

4. The addition of methanol and amyl alcohol to the Shikakai solutions show there is a synergistic interaction between the alcohol and Shikakai molecules, and that is more for amyl alcohol. As the interaction is more for amyl alcohol, consumption of alcohol is also 1000 times less than that of methanol to get the same value of surface tension reduction.

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