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Adsorption Behaviors of Novel Betaines on the Wettability of Quartz Surface

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Abstract

The contact angle measurements for the aqueous solutions of two pairs of zwitterionic on quartz surfaces have been investigated by the sessile drop analysis. The different physicochemical parameters such as critical micelle concentration (CMC), surface tension, contact angle, surface excess on air-liquid and solid-liquid interfaces and work of adhesion have been estimated. The obtained results show that the contact angle of surfactants alkyl carboxylbetaine (ACB) and ditolyl substituted alkyl carboxylbetaine (BCB) keep almost a constant value in a wide range of surfactant concentration and increase gradually above CMC, which are quite different from traditional surfactants reported in the literature. Surfactants with bigger polar group have more steric effect on the quartz surface and the contact angle remains relatively unchanged. Moreover, an increase in quartz-liquid interfacial tension (γ_{SL}) has been observed due to the adsorption of four zwitterionic surfactants. Especially for the ACB and BCB, at the surfactant concentrations higher than 5×10^{-5} mol/L, a moderate increase in the interfacial tension of the quartz-liquid is observed, which suggests that the ACB and BCB can form the saturated adsorption film briefly on the quartz surface and then adsorb again. However, the addition of alkyl sulfobetaine (ASB) and ditolyl substituted alkyl sulfobetaine (BSB) after CMC cannot adsorb on quartz surface again due to the steric effect of bigger polar group.

Keywords: Quartz; Zwitterionic surfactants; Betaine; Contact angle

1. Introduction

Wetting of solid surfaces is of special importance in surface and interface science, because many industrial processes and daily life applications are impossible to consider without this process, such as oil recovery, flotation, coating, lubrication, printing, and detergency. The extent of wettability can be modified by introducing surface active agents into the solid-liquid systems. In the wetting process of solid surfaces by surfactant solutions, the orientation of surfactant molecules in the surface layers and the amount of adsorbed surfactants at liquid-air and solid-liquid interfaces play important roles¹⁻⁴.

Quartz is a high-energy hydrophilic solid and the water should be completely spread over the quartz surface. Quartz has been used in many branches of industry due to their special properties⁵. In view of the widespread applications of wetting phenomena of quartz, many reports about the adsorption mechanism and wetting properties of different single surfactants, mixed surfactant systems, and additives on the quartz surface have been obtained in recent years^{1, 6-14}. For traditional surfactants, such as cationic, anionic and nonionic surfactants, it was appeared that the cationic surfactants can interact with quartz surface by electrostatic forces and form bilayer at the quartz-water interface; besides, the anionic and nonionic surfactants absorbed predominantly through Lifshitz-van der Waals interactions and the interaction between the water molecules and quartz surface might be stronger than those between the quartz and surfactants molecules⁶. What's more, for the above mentioned surfactant in the literatures, the CMC is an important shift point: above CMC, the saturated adsorption films at air-liquid and solid-liquid interfaces are formed and the adsorption behavior at solid-liquid interface does not change any more. In the case of mixed surfactant systems, it has been shown that the mixed surfactants exhibit strong synergistic effects in adsorption properties especially the cationic–anionic mixtures¹⁰⁻¹³, which suggested that the structure of monolayers formed in mixed systems was strongly affected by the composition of the bulk solution. The effects of different additives such as alcohols have also been studied thoroughly^{5, 9, 14}, which

indicated that the orientation of adsorbed alcohol molecules at quartz/liquid monolayer film-solution interface by -OH groups towards the solution bulk phase.

In comparison to the conventional surfactants, the zwitterionic surfactants have many advantages and have become an active research due to their high surface activities, good resistance to heat and hard water, the excellent compatibility with anionic, cationic and nonionic surfactants¹⁵. Moreover, the zwitterionic surfactants were used in enhanced oil recovery (EOR) because the IFT can be reduced to an ultra-low value by a zwitterionic surfactant alone within a wide concentration range¹⁶. It has been also reported that the zwitterionic surfactant can adsorb on the surface of reservoir rocks and change wettability of rock surfaces¹⁷. Therefore, a systematic study of wettability of solid surface in the presence of zwitterionic surfactants is important for oil exploitation. However, the studies on the problem dealing with different influences of zwitterionic surfactants on the wetting of solid surfaces are rare.

As reported in the literature⁶⁻⁹, the Lifshitz-van der Waals interactions, electrostatic interactions, hydrophobic interactions and hydrogen bonding are all the driving forces for adsorption of surfactants on quartz surface. However, there are both positively and negatively charged hydrophilic groups in the same molecule of zwitterionic surfactant, so the interaction between the surfactant and quartz surface is complicated and cannot be easily explained by a single adsorptive mechanism¹⁸. Some investigators¹⁹⁻²¹ have studied the interactions between zwitterionic surfactant molecules and quartz surfaces and got a preliminary understanding, but it is not enough to understand the mechanism responsible for the efficiency and effectiveness of zwitterionic surfactants adsorption.

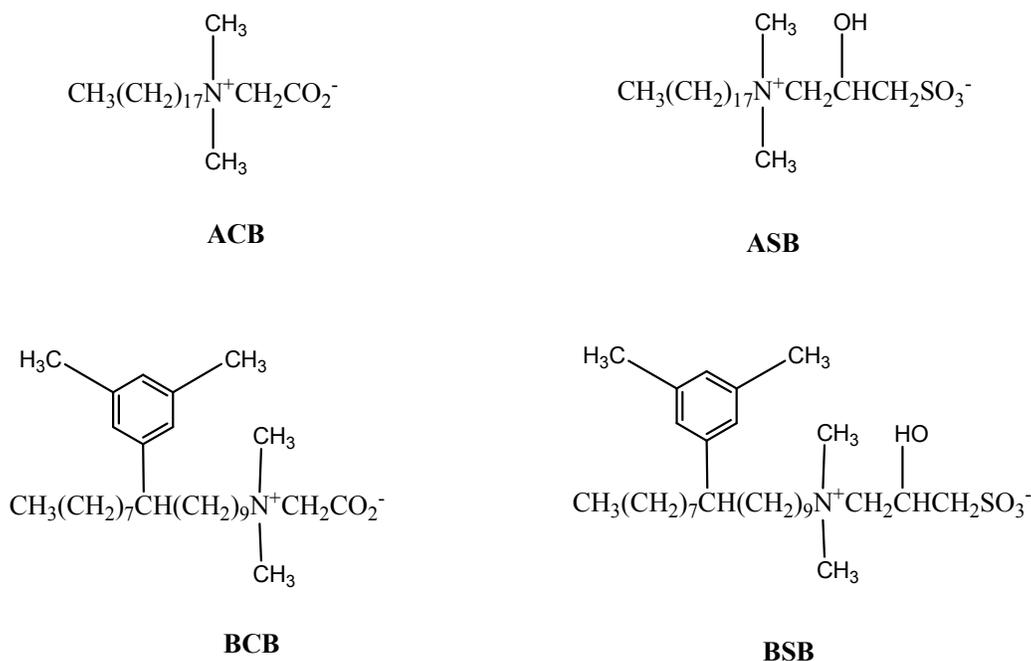
Thus, a main purpose of this paper is to determine the adsorption properties at liquid-air and quartz-liquid interfaces in relation to quartz wettability by a series of zwitterionic surfactants. Four zwitterionic surfactants are two pairs and each pair bears identical hydrophobic chain, differing by the structure of the polar groups. For this purpose the surface tension and the contact angle were measured. That is useful for us to understand the wettability alteration of the quartz surface in the

presence of zwitterionic surfactants.

2. Experimental section

2.1. Materials

Two pairs of zwitterionic surfactants, alkyl carboxylbetaine (ACB) and alkyl sulfobetaine (ASB), benzyl substituted alkyl carboxylbetaine (BCB) and benzyl substituted alkyl sulfobetaine (BSB), were synthesized in State Key Laboratory of Enhanced Oil Recovery, CNPC²². Each pair bears identical hydrophobic chain, differing by the structure of the polar groups (See Scheme 1). The purity of the compounds checked by elemental analysis and ¹H NMR spectroscopy was 99%. Ultrapure water with 18.2MΩ.cm resistivity was used for the experiment and the pH values for surfactant aqueous are approximately equal to 6.8.



Scheme 1. Formula and Abbreviations of the Surfactants

Quartz plates used for contact angle measurements were washed with pure water and acetone, and dried before being soaked in a piranha solution (a 7:3 mixture of 97% sulfuric acid and 30%

hydrogen peroxide) for at least 2 h. Caution: Piranha solution reacts violently with most organic materials and must be handled with extreme care. Once the plates had been removed from the piranha solution, they were once again rinsed with water, ethanol, and ultrapure water, in that order, and dried at 378 K for 1 h. After the plates had been cleaned, a contact angle with ultrapure water of 17° was obtained.

2.2. Surface Tension Measurements

The surface tension measurements of aqueous surfactant solutions were done by the wilhelmy plate method using a surface tensiometer (Data Physics, Germany, DCAT21), at 298 K. The platinum plate was thoroughly cleaned, and burned after under alcohol flame till red hot to remove the adsorbed surfactants completely before each measurement. Then, the vertically hung plate was dipped into the liquid to measure its surface tension. Measurements of the surface tension of pure water at 298 K were performed to calibrate the tensiometer and to check the cleanliness of the glassware. The measurements were conducted until constant surface tension values indicated that equilibrium had been reached. In all cases, more than three measurements were carried out, and the accuracy of the measurement was of the order of ± 0.2 mN/m²³⁻²⁴.

2.3. Contact Angle Measurements

The measurements of contact angles for the water and aqueous solutions of surfactants on quartz plates were carried out via the sessile drop method using the Data Physics OCA20 (DataPhysics Company, Germany), at 298 K. The measurements were repeated several times by settling other drops (2 μ l) on the new parts of the same plate. The average value from obtained at least five results was treated as the contact angle and the accuracy of the contact angle values was less than 3°. The details of the contact angle measurements were described elsewhere¹.

3. Results and discussion

3.1. Adsorption of BSB and ASB at Air-Water Interface

The surface tension value is generally considered as an indicator of the adsorption efficiency of surfactant molecules at the air-liquid interface. The surface tension values of ACB, ASB, BCB and BSB solutions versus logarithm of concentrations are presented in Figure 1.

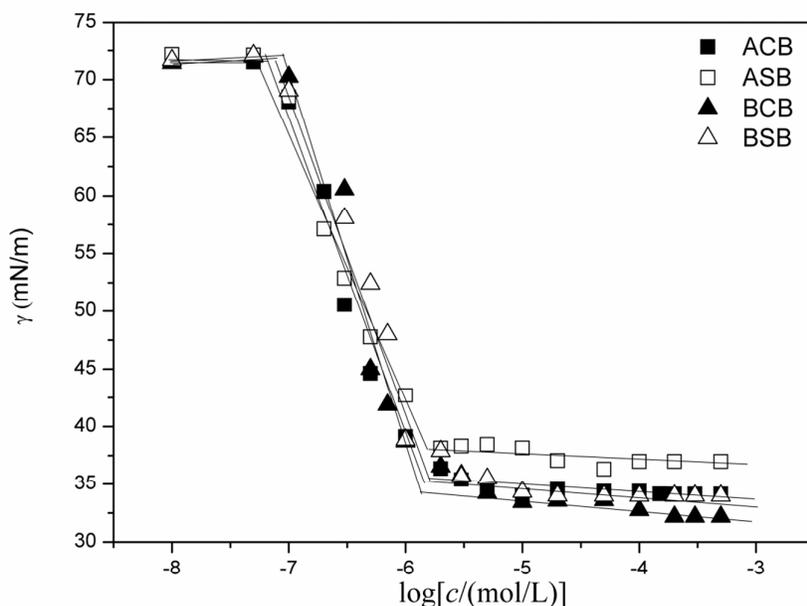


Figure 1. Surface tension (γ_{LV}) versus $\log C$ (C is the surfactant concentration) for surfactant solutions.

The figure depicts the Surface behavior with the increasing concentrations are similar for four surfactants studied here. All of them show there is a sharp decrease in surface tension until the critical micelle concentration (CMC); beyond that concentration surface tension values are almost constant, similar to the conventional single-chain surfactants²⁵.

The maximum surface excess concentration (Γ_{\max} , in $\text{mol}\cdot\text{cm}^{-2}$) at the air-water interface for ACB,

ASB, BCB and BSB can be calculated by Gibbs adsorption²⁶ using the slope from the plot of γ vs $\log C$ below the CMC region:

$$\Gamma_{max} = -\frac{1}{2.303nRT} \left(\frac{d\gamma}{d \log C} \right)_T \quad (1)$$

Where R is the gas constant ($8.31 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T is the absolute temperature and $d\gamma/d\log C$ is the slope below the CMC in the surface tension plots, n is the number of solute species whose concentration at the interface changes with variation in the value of bulk concentration. The value of n is taken as 1 for the zwitterionic surfactants because the surfactants have a net zero charge and carries no counterions²⁷. If the surface excess concentration at the interface is the maximum the adsorption density of the surfactants can be expressed in terms of the effective area occupied per surfactant molecule (A_{min}) at the air-water interface. The area occupied per molecule can be calculated as:

$$A_{min} = \frac{10^{14}}{N_A \Gamma_{max}} \quad (2)$$

In which N_A is Avogadro's number ($6.02 \times 10^{23} \text{ mol}^{-1}$).

Table 1 The interfacial active properties of surfactant solutions

Abrr.	CMC /(10^{-6} mol/L)	γ_{cmc} /(mN/m)	$10^{10}\Gamma_{max}$ /(mol/cm ²)	A_{min} /(nm ²)
ACB	1.45	35.49	2.23	0.74
ASB	1.57	38.08	1.97	0.84
BCB	1.38	34.55	2.75	0.60
BSB	1.41	35.59	2.36	0.70

The values of CMC, γ_{cmc} , Γ_{max} and A_{min} are displayed in Table 1. It can be seen that the surface tension and area occupied for BCB and BSB are lower than that of ACB and ASB. The results indicate the ditolyl may increase the hydrophobic nature and lead to the lower surface tension and area occupied for BCB and BSB. On the other hand, the values of surface tension and area occupied

are also different between the surfactants what bears identical hydrophobic chain, differing by the structure of the polar groups. Therefore, we can speculate that the polar groups also dominate the adsorption properties for our studied systems.

3.2. Wettability of Quartz

Different from the surface tension, the contact angles for aqueous solutions of zwitterionic surfactants ACB, ASB, BCB and BSB on the quartz surface follow the different trend (Figure 2). For ACB and BCB, the contact angle remains relatively unchanged in a wider range of concentration; beyond that concentration of 5×10^{-5} mol/L (about 30 times of CMC) the contact angle increases gradually and the BCB shows a lower contact angle than that of ACB, which is quite different from the zwitterionic surfactants as we reported early²⁰. However, for ASB and BSB, the contact angle remains relatively unchanged during whole experimental concentration scale.

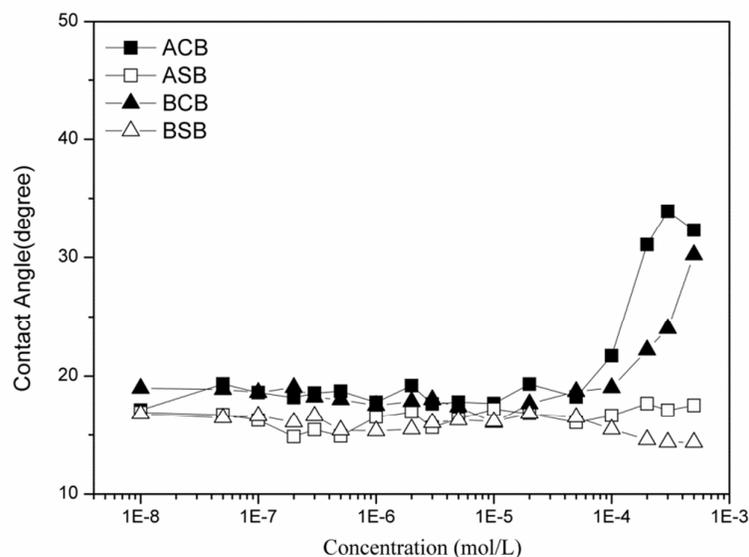


Figure 2. The effect of concentration on contact angles of surfactant solutions on quartz

Normally, the CMC is the important concentration that a sharp break in interfacial phenomena occurs at, therefore, many studies have been performed that the amount of surfactant adsorbed at the

interface no longer increases above the CMC. Anna⁶ and co-workers reported that the shapes of the $\theta - \log C$ curves for nonionic and anionic surfactants are similar to those of $\gamma_{LV} - \log C$ curves. Harkot²⁶ also suggested that the adsorption of cationic surfactants at solid-liquid interfaces share similar results. However, in this paper, the obtained results of the contact angle indicated that the continued increase took place in surfactants adsorption at solid-liquid interface for ACB and BCB while the liquid-air interface were saturated with surfactants. The responsible mechanism will be discussed later.

According to the Young equation²⁶⁻²⁹, the contact angle depends on the surface tension of solid (γ_{SV}) and liquid (γ_{LV}) as well as the solid-liquid (γ_{SL}) interface tension.

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (3)$$

So, the effects of surfactants on adhesional tensions and solid-liquid interfacial tensions of quartz should be known before discussing the adsorption mechanism in detail.

3.3. Adsorption at Quartz Surface

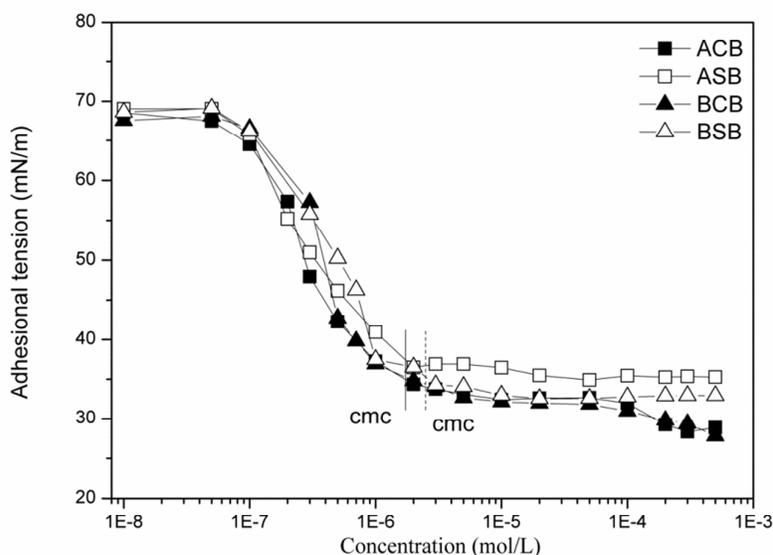


Figure 3. The effect of concentration on adhesional tension of surfactant solutions on quartz

Surface and interfacial tensions of solids are important parameters to predict the wetting properties of solid materials³⁰. The value of $\gamma_{SV} - \gamma_{SL}$ is known as the adhesional tension, which can be calculated by the values of γ_{LV} and θ . The effects of concentration on adhesional tension of ACB, ASB, BCB and BSB on quartz are presented in Figure 3.

Quartz is a high-energy hydrophilic solid, and Fowkes³¹ suggested that the quartz surface free energy is somewhat higher and is close to 76 mJ /m². In addition, on surface of such hydrophilic solids the value of γ_{SL} at quartz-water interface is very small, so the water should completely spread. For aqueous solutions of the studied surfactants, with the surfactant concentration increases, more surfactant adsorption occurs with the hydrophilic group oriented to the quartz-liquid interface, hence the surface becomes more and more hydrophobic, resulting in an increase in the γ_{SL} and decrease in the adhesional tension.

It is interesting to notice that if the surfactants concentration is higher than 5×10^{-5} mol/L, then a considerable decrease of the adhesional tensions of ACB and BCB as a function of logC are observed while those of ASB and BSB still keep almost a constant value, which indicates a continue adsorption of surfactant molecules on quartz. It may be reasonable to assume that the sulfonic group has adverse effect for zwitterionic surfactants on adsorption on quartz-liquid interface again.

To get a relationship between the adsorption of surfactant on the liquid-air and solid-liquid interfaces, a direct method to investigate relative adsorption at interfaces in wetting studies was developed by Lucassen-Reynders. By combining the Young and Gibbs equations, it is shown as follows³²:

$$\frac{d(\gamma_{LV} \cos \theta)}{d\gamma_{LV}} = \frac{\Gamma_{SV} - \Gamma_{SL}}{\Gamma_{LV}} \quad (4)$$

where Γ_{SV} , Γ_{SL} , and Γ_{LV} represent the surface excess of surfactants at the quartz-air, quartz-liquid, and liquid-air interfaces, respectively. If the surface excess at the quartz-air interface is assumed to be zero ($\Gamma_{SV}=0$, because there is no contact with the solution), the ratio of surface excess at the

quartz-liquid and liquid-air interfaces ($\frac{\Gamma_{SL}}{\Gamma_{LV}}$) can be obtained from the slope of $\gamma_{LV} \cos \theta$ versus γ_{LV} plot. The surface excess values of surfactants on the solid-liquid and liquid-air interfaces are dependent on the slope of the linear relationship; such as $\Gamma_{SL} = \Gamma_{LV}$ (slope=1), $\Gamma_{SL} > \Gamma_{LV}$ (slope>1), and $\Gamma_{SL} < \Gamma_{LV}$ (slope <1). In addition, Γ_{SL} can be obtained from the ratio and the Γ_{LV} . And then the saturated adsorption areas at the quartz-liquid interface can also be calculated by eq. (2).

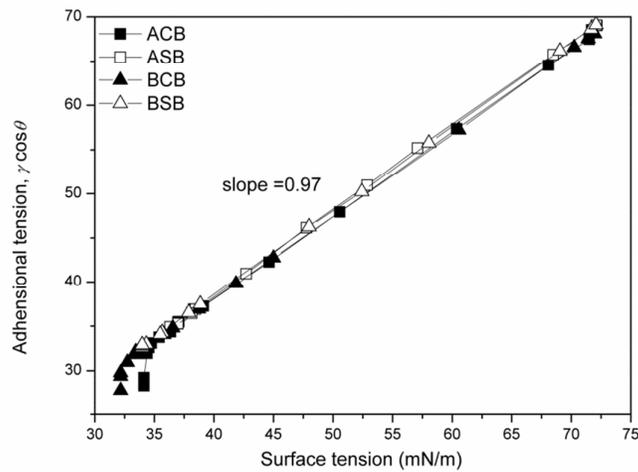


Figure 4. Dependence between the adhesional and surface tension of surfactant solutions.

The plots of adhesional tension versus surface tension for ACB, ASB, BCB and BSB show there are in general linear relationships on quartz surfaces (as shown in Fig. 4), irrespective of surfactants, with a slope very close to 1. The positive slope on quartz surface was also reported before¹. In the case of hydrophobic solids, eq. (4) is suitable because the interfacial tension of solid-liquid interface, γ_{SL} , decreases with increasing Γ_{SL} . However, in the quartz system, $\gamma_{LV} \cos \theta - \gamma_{LV}$ plots show the positive slopes, which may be result from the fact that γ_{SL} increases with increasing Γ_{SL} on quartz-liquid interface. Therefore, eq. (4) can be rewritten to the following form¹:

$$-\frac{d(\gamma_{LV} \cos \theta)}{d\gamma_{LV}} = \frac{\Gamma_{SV} - \Gamma_{SL}}{\Gamma_{LV}} \quad (5)$$

It is worth noting that at the surfactant concentrations higher than their CMC, the curves of ACB and BCB have a slight change: the adhesional tension values decrease with surfactants concentration increase even when the surface tension keeps constant. This results in the vertical phenomenon, which shared the different phenomenon with nonionic and anionic surfactants⁶.

On the other hand, the slopes for ASB and BSB are all close to 1, which qualitatively demonstrates that the surface excess on the quartz-liquid interfaces is the same as that on the liquid-air interface. The phenomena is similar to many single surfactants reported earlier^{6,33}, which means that the Lifshitz-vander Waals interactions between surfactant molecules and quartz surface may play a main role in the adsorption process. But for ACB and BCB it is impossible to describe the changes of the adhesional tension vs. surface tension by some function. Mechanism of ACB and BCB adsorption on the quartz surface is more complicated than that of ASB and BSB. The presence of inflection points on $\gamma_{LV} \cos \theta - \gamma_{LV}$ curves suggests that the mechanism of ACB and BCB adsorption on the quartz surface is changed depending on surfactants concentration in solution. To prove the suggestion is probable, the Γ_{SL} should also be calculated by Gibbs adsorption isotherm equation²⁶.

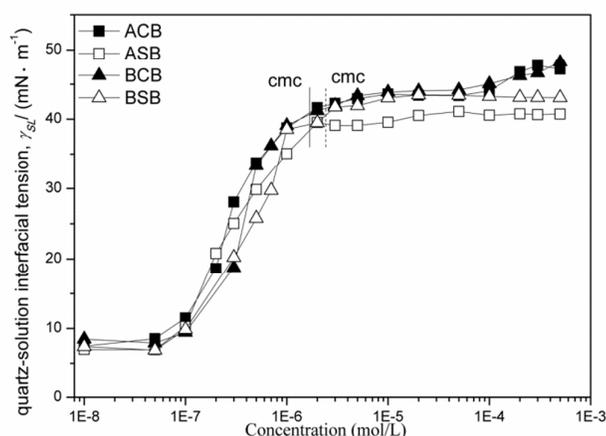


Figure 5. Effect of surfactant solutions concentrations on the quartz-solution interfacial tensions

It is well known that adsorption of surfactants on solid-liquid interface causes changes of solid-liquid interfacial tension (γ_{SL}). However, there is still no direct method to determine this value. On the other hand, if we know the value of the surface tension of a given solid (γ_{SV}), the value of the surface tension of the liquid (γ_{LV}) and the measured contact angle value (θ) of a liquid on a given surface (in the case of quartz surface) it would be possible to determine the γ_{SL} value by taking into account the Young equation (Eq. (3)). The surface tension of quartz is constant and equal to 75.34 mN/m by OWRK method³⁴. The solid-water interfacial tension values of ACB, ASB, BCB and BSB versus logarithm of concentrations are presented in Figure 5.

As described earlier in this paper, surfactant adsorption occurs with the hydrophilic group oriented to the quartz-liquid interface, the hydrophobic group pointing outwards, hence the surface becomes more and more hydrophobic, increasing the γ_{SL} . For four surfactants, in the range of surfactants concentration from 0 to CMC, the γ_{SL} values increase sharply, which results practically from the Lifshitz-van der Waals intermolecular interactions. The saturated adsorption areas of ACB, BCB, ASB and BSB on quartz-liquid interface can be calculated by Gibbs adsorption isotherm equation from Figure 5. The calculation process is the same as that at the air-water interface. The results are 0.79 nm², 0.59 nm², 0.89 nm² and 0.73 nm² at the concentrations below CMC, which are similar with calculated by eq. (5), 0.76 nm², 0.62 nm², 0.87 nm² and 0.72 nm² respectively. Comparing the results calculated by two methods can ensure the accuracy of our provided interpretation. At the surfactant concentrations higher than 5×10^{-5} mol/L, a moderate increase in the interface tension of the quartz-liquid is observed for ACB and BCB, which may result from the density of surfactant molecules on the surface changed only to a small extent. Different from the opinion of some investigators, Liu¹⁹ found that the zwitterionic surfactants hexadecylglycidyl ether glycine betaine could form a bilayer film at quartz surface and the larger molecular size shows influence on the formation of bilayer film. It means that the different structure has a great influence on the

zwitterionic molecular adsorption on quartz surface. Compared to ACB and BCB, the introduction of bigger polar group for ASB and BSB may make it difficult to adsorb again because of the steric effect, so the values of γ_{SL} keep almost a constant value at the surfactant concentrations higher than the CMC.

3.4. Work of adhesion

The adsorption of surfactants on the solid-liquid and liquid-air interfaces strongly influences the wettability of solids, which depends on the work of liquid adhesion to the solid surface (W_A)³⁵. The work of adhesion (W_A) can be calculated by using the following equation:

$$W_A = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \quad (6)$$

On the other hand, the work of adhesion fulfills the Young equation, which has the following form^{3, 36}:

$$W_A = \gamma_{LV}(\cos\theta + 1) \quad (7)$$

The adhesion work of the aqueous solutions of studied surfactants solutions to the quartz surface were calculates by putting the contact angle and surface tension values in Eq. (7) and presented in Figure 6.

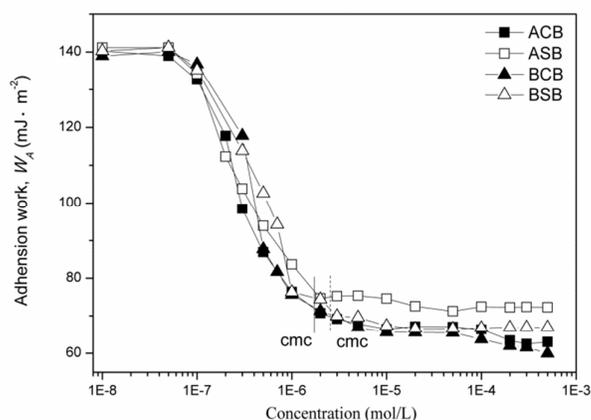
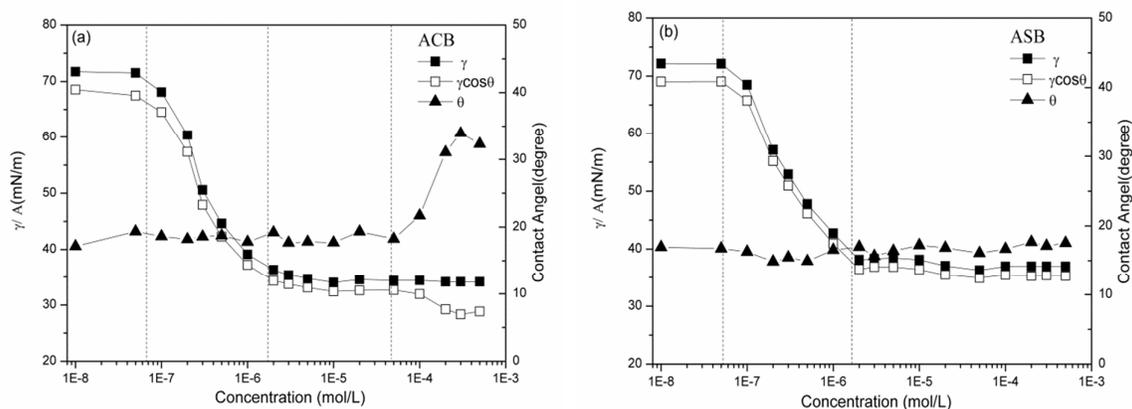


Figure 6. Effect of concentration on the adhesion work of surfactant solutions to quartz surface

From the figure it can be observed that the adhesion work of aqueous solution of all studied surfactants decreases with increase of the surfactant concentration and they are in the range of 60-141 mJ/m², which share the similar results with nonionic and anionic surfactants^{6,11}.

It is interesting that the W_A of ACB and BCB slightly decrease at concentration above 5×10^{-5} mol/L while the W_A of ASB and BSB keep constant. As reported in the literature¹, in the case of cationic surfactant there is a minimum of the W_A at concentration close to their CMC and the W_A increases at concentration above their CMC, which can be suggested that the increase of W_A corresponds to the beginning of the bilayer formation of cationic surfactant at the quartz-water interface. Therefore, the decrease of the W_A for ACB and BCB can be suggested that the adsorption of surfactant molecules on quartz surface again is still in the form of the monolayer rather than the bilayer. On the other hand, the W_A of ASB and BSB keep constant, which mean there is not adsorption on quartz surface for the surfactant molecules of ASB and BSB again at concentration above their CMC. So we can speculate that the introduction of bigger polar group has an adverse effect for the adsorption again on quartz surface.

3.5. Structural Dependence of zwitterionic surfactants on Wettability of Quartz Surface.



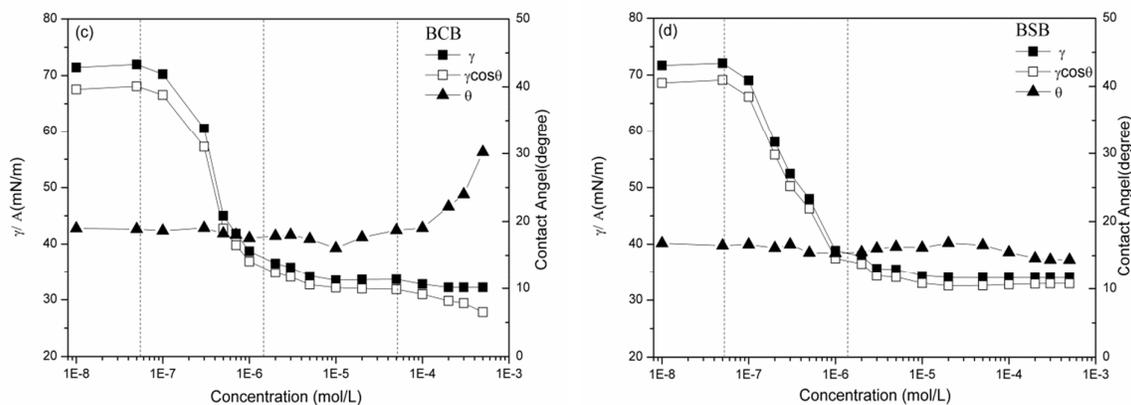


Figure 7. Concentration dependence of the adhesion data of surfactant solutions on quartz. (a: ACB, b: ASB, c: BCB, d: BSB)

In order to account for the mechanism responsible for adsorption of zwitterionic surfactants to quartz surface, the dependences of surface tension, contact angle and adhesional tension on bulk concentration have been re-plotted in Figure 7 for ACB, ASB, BCB and BSB, respectively.

As shown in Figure 7, the variations in adhesional data with increasing bulk concentration for both ACB and BCB can be divided into four stages while those of ASB and BSB can be divided into three stages. Take surfactant ACB for example, the possible schematic diagrams of the organization and structure of the adsorbed layer with the increasing concentration just as the Figure 8(a):

In stage 1 (from 1×10^{-8} to 5×10^{-8} mol/L), the bulk concentration is too low to form adsorption films on both liquid-air and quartz-liquid interfaces. As a result, the surface tension and contact angle change slightly. Adhesional tension remains almost constant.

In stage 2 (from 5×10^{-8} mol/L to CMC), there is a marked decrease in surface tension due to the increase in adsorption at liquid-air interface with the bulk concentration increases; meanwhile, surfactant molecules adsorb at the quartz surface through Lifshitz-van der Waals interactions, which will make the solid surface more hydrophobic and causes a decrease in adhesional tension. According to eq. (1), when $\theta < 90^\circ$, the decrease of surface tension can lead to the decrease of θ , and the decrease of the adhesion tension will result in the increase of θ . Therefore, the contact angle keeps almost constant at this stage because of the competition of the two factors.

In stage 3 (from CMC to 5×10^{-5} mol/L), the bulk concentrations above their CMC and saturated adsorption film has been formed at liquid-air interface, micelles forming in solution. The surface tension keeps constant. It is interesting to notice that different from cationic surfactant¹, the saturated adsorption film at quartz-liquid interfaces has been formed briefly while the adsorption of cationic surfactant is enhanced immediately. So the values of adhesional tension keep constant for ACB, which results in the constant in contact angle during whole stage 3.

In stage 4 (from 5×10^{-5} to 5×10^{-4} mol/L), as the bulk concentration further increases, surfactant molecules may adsorb on quartz surface again by the electrostatic attraction between positive sites of betaine and negative sites of the quartz surface instead of forming bilayer just as cationic surfactants. The reason may be that although there are both positively and negatively charged hydrophilic groups in the same molecule of zwitterionic surfactant, electrostatic interactions are not strong enough to form a tightness monolayer. So bilayer is not formed. Moreover, the adsorbed surfactant molecules become more vertical oriented into the solution, resulting in a larger number of active sites available for adsorption. In this situation, the increase in contact angle can be attributed only to the decrease in adhesional tension because surface tension keeps constant after CMC.

In case of ASB (Figure 7b), the stage 4 in Figure 7a has vanished, and the contact angle keeps constant; at the same time, adhesional tension also keeps constant above CMC. Quite different from ACB, the addition of surfactant molecules cannot adsorb on quartz surface again at the same bulk concentration for ASB. For ASB, according to the chemical structures in scheme 1, there are bigger polar group and -OH group. So, the adsorption characteristic of ASB at quartz-liquid interface may be complex. On one hand, the introduction of bigger polar group makes slightly variation in adsorption amount due to steric effect, which will result in weaker ability than ACB in modifying the extent of wettability of quartz. On the other hand, ASB molecules may adsorb at quartz-liquid interface via hydrogen bonding between the quartz surface and -OH group, which may cause a far stronger ability than ACB in modifying the extent of wettability of quartz. However, the

experimental results above suggest that ACB shows stronger adsorption ability than ASB on quartz. Therefore, the steric effect of bigger polar group dominates the adsorption characteristic of ASB and the molecules cannot adsorb on quartz surface again at high concentrations.

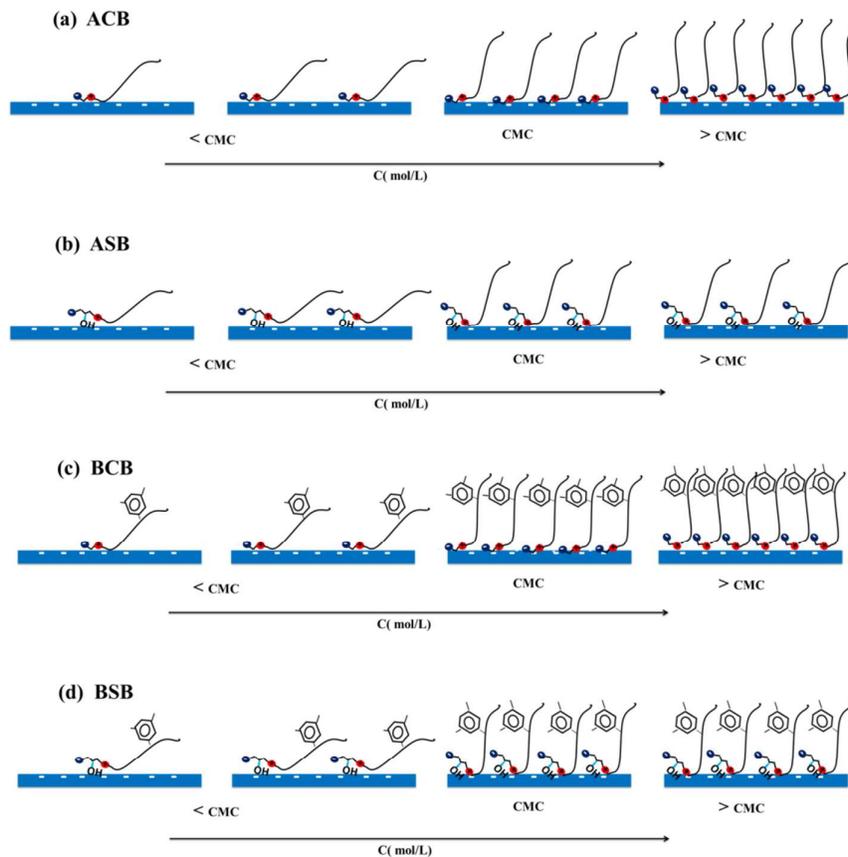


Figure 8. Schematic model of ACB, ASB, BCB and BSB molecules adsorbed on the quartz surface

BCB and BSB show similar behavior of adhesional data to ACB and ASB with the increasing bulk concentration, as shown in Figure 7c and Figure 7d. The organization and structure of the adsorbed layer with the increasing concentration are shown in Figure 8c and 8d. It's worth noting that the adsorption amount of BCB is slightly less than that of ACB at high concentrations due to the space steric of benzyl. Therefore, ACB shows stronger ability than BCB in modifying the extent of wettability of quartz.

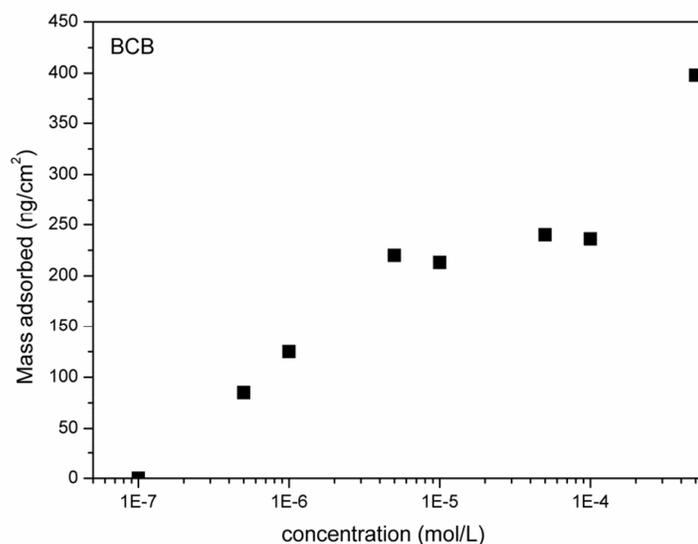


Figure 9. Mass adsorbed on quartz surface determined by QCM for BCB with concentration dependence.

In order to prove the inference of adsorption mechanisms for betaine surfactants on quartz surface, the quartz crystal microbalance (QCM) has been employed to measure the adsorption amount of BCB on the quartz and the experimental details is reported elsewhere³⁷. As shown in Figure 9, the adsorption amount of BCB on the quartz surface increases with the improvement of bulk concentration and reaches a plateau around CMC. However, when the bulk concentration is higher than 1×10^{-4} mol/L, the adsorption amount increases again, which is in accordance with the mechanism in Figure 8 perfectly.

4. Conclusion

Based on the measured values of the contact angle and their theoretical interpretation in respect to the surface tension and the adsorption parameters of quartz covered with the four zwitterionic surfactant solutions, the obtained results show that the contact angle of ACB and BCB keep almost a constant value in a wide range of surfactant concentration and increase gradually above CMC, which are quite different from traditional surfactants reported in the literature. Surfactants with bigger polar

group (ASB and BSB) have more steric effect on the quartz surface and the contact angle remains relatively unchanged. The adsorption characteristic on the quartz surface depends on the structure of surfactants. For ACB and BCB, there is a linear relationship exists between the adhesional and surface tension with a slope very close to 1 in a range of certain concentrations, and then the adhesional tension value decreases even when the surface tension keeps constant. Moreover, at the surfactant concentrations higher than 5×10^{-5} mol/L, a moderate increase in the interfacial tension of the quartz-water is observed, which suggests that the ACB and BCB can form the saturated adsorption film briefly on the quartz surface and then adsorb again through the electrostatic interaction between positive sites of betaine and negative sites of the quartz surface. However, for ASB and BSB, the values of γ_{sl} keep almost a constant value at the surfactant concentrations higher than CMC, which means the addition of ASB and BSB cannot adsorb on quartz surface again due to the steric effect of bigger polar group. On the other hand, the effect of benzyl unit incorporated in the hydrophobic group are not the same at different concentrations: compared to ACB, the lower contact angle values are observed for BCB at the concentration above CMC while a lower area occupied for BCB is obtained at the concentration below CMC.

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