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Effect of electrolytes on wettability of glass surface using anionic and cationic surfactant solutions

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ABSTRACT

Wetting behavior of a flat glass surface using pure nonionic, anionic, and cationic surfactants solutions has been studied by the dynamic contact angle (Wilhelmy plate) measurement technique. The advancing contact angle increases with the increasing concentration of surfactant and the value is maximum in the presence of cationic surfactant CTAB. The effect of different electrolytes in the presence of ionic surfactants was also studied to see the wetting behavior in the presence of electrolytes. The presence of electrolytes on ionic surfactant solutions significantly enhance the contact angle at very low concentration, which in turn lead to reduction in ionic surfactant requirement by more than 90% to achieve a particular contact angle. The effectiveness of electrolyte highly depends on the valance of counter ion. The reduction of ionic surfactant requirement is mostly useful for different applications such as flotation, and colloidal stability to reduce the production cost as well as environmental pollution.

1. Introduction

The wettability of hydrophilic solid surfaces in the presence of surfactant solutions has many practical applications such as detergency, surface cleaning, coating, adhesion, printing, colloidal stability, and flotation of minerals. Mineral beneficiation is an industrial process where wetting behavior is important to concentrated desired minerals from ore slurry, where a huge amount of surfactant is used. The efficiency of whole mineral beneficiation process largely depends of types of surfactants used [1–3]. The efficiency of all these processes generally depends on adsorption density of surfactants at solid–liquid interface as well as orientation of surfactant molecules. The surfactant adsorption density and orientation of the adsorbed surfactant molecules are mainly depends on the surface charge, surface roughness, types of surfactants, and the presence of additives in the solution. Adsorption density of a surfactant on a particular surface increases with increasing surfactant concentration and finally reaches to a plateau level. If the adsorption density can be enhanced at low surfactant concentration through the addition of low cost additives, the surfactant consumption can be reduced and which in turn may reduce the cost of the process.

During last few decades many research groups are studying the wetting properties of hydrophilic surfaces such as glass [4,5], mica [6–8], quartz [9] as well as hydrophobic surfaces such as polytetrafluoroethylene (PTFE) [10–12], and even semi-polar surface poly-

methyl methacrylate [13,14] in the presence of either pure [5,15], mixture of surfactants [10,16], surfactants in the presence of electrolyte [12,17–19] or alcohol [14,20]. The presence of electrolyte as additive on single or mixed ionic surfactants solutions affect the adsorption density of the surfactant molecules through the reduction in electrostatic repulsive force among the head groups of the surfactant molecules at air–liquid and solid–liquid interfaces, which in turn influence the surface tension of the solution as well contact angle on solid surface. The available reported studies are mostly on single surfactants (anionic or cationic) in the presence of most common salts such as NaCl, Na_2SO_4, and $CaCl_2$ either on hydrophobic (PTFE, stainless steel, methylated glass) [12,18,21] or on hydrophilic (Au) [22] surfaces. In our previous study, the effect of electrolytes such as NaCl, Na_2SO_4, and $CaCl_2$ on the wetting of hydrophobic PTFE surface in the presence low concentration of pure (SDBS and CTAB) [12] and mixed (CTAB-Igepal CO-630) [19] surfactants were studied; in both cases it was observed that the surfactant consumption (in terms of lowering of CMC) decreases in the presence of electrolytes and especially the change was maximum when higher valence counter ions are present.

In reported studies both sessile drop and dynamic contact angle techniques were used to measure the wettability of the solid surface, but dynamic angle is more important when either solid surface or liquid are in motion [23,24]. Herein we have studied the dynamic contact angle of three different pure surfactants solutions (TX-100, SDBS, and CTAB) on the flat hydrophilic (glass) surface, and as well as the influence of different electrolytes in the presence of ionic surfactants at very low surfactant concentration (below CMC). It has been found that the addition of electrolytes enhance

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adsorption density on solid surface which in turn increase the contact angle significantly. These results may be useful for flotation and other applications to reduce the surfactant consumption significantly. Reduction in surfactant consumption in a process where surfactant requirement is high directly reduces the process cost and environmental pollution where surfactant solutions are discharged to the environment.

2. Experimental

2.1. Materials

Surfactants TX-100 (98%) and CTAB (99.5%) from Loba Chemie., SDBS from Sigma Aldrich, (Technical grade, Cat No. 28995-7) were purchased for the experiments. Electrolytes NaCl (99.5%) and $CaCl_2$ (99.5%) from E. Merck.; Na_2SO_4 (99.5%) from Ranbaxy Fine Chemical were used for the experiments. All surfactants and electrolytes were used as it is received without any further purification. Ultra pure water was used for the experiments of 18.2 MΩ cm resistivity and pH 6.4–6.5 (Sartorius, Germany). The glass plate of dimension 25 mm × 1.5 mm was cut from the microscopic slide and used for dynamic contact angle measurements after cleaning with alcohol and water. The thickness and width of the plate was taken as the average values of measured value at several positions of the slides by a digital slide caliper.

2.2. Methods

All the surfactant solutions were prepared freshly just before the measurements. The surface tension measurements of aqueous surfactant solutions were done by the Wilhelmy plate method using a surface tensiometer, Data Physics, Germany (DCAT-11EC). The motor speed was 1 mm/s and the immersion depth of the platinum plate in the surfactant solution maintained was 3 mm. After the measurement of each concentration the plate was cleaned with water and acetone, and finally burned in alcohol flame till red hot. For contact angle measurements a good-quality glass plate was selected and cut from the glass slide. The plate was washed several times with first acetone and then ultrapure water to clean the surface, and the surface roughness was characterized using atomic force microscopy (Veeco). The plate was then dried by blowing hot air. The same procedure was repeated after the measurement of each surfactant concentration. The dynamic contact angle (θ) measurements were done by a surface tensiometer, Data Physics (DCAT 11EC). The contact angle was measured at motor speed rate 0.2 mm/s and the immersion depth of the plate 5 mm. All the experiments were carried out at constant temperature (28 ± 0.5 °C), repeated several times and the average of those values was taken.

3. Results and discussion

3.1. Characterization of glass surface

The solid surfaces used for this study were characterized by the atomic force microscopy to see the surface roughness and the results are shown in Fig. 1. Figure shows the surface topography of the glass plate used for this study and the surface roughness of the glass was calculated from the AFM image using SpmLab Analysis software and found to be 1.02 nm and the figure also shows height profile along the z-axis through the three different lines and the position of the lines are shown in the inset figure.
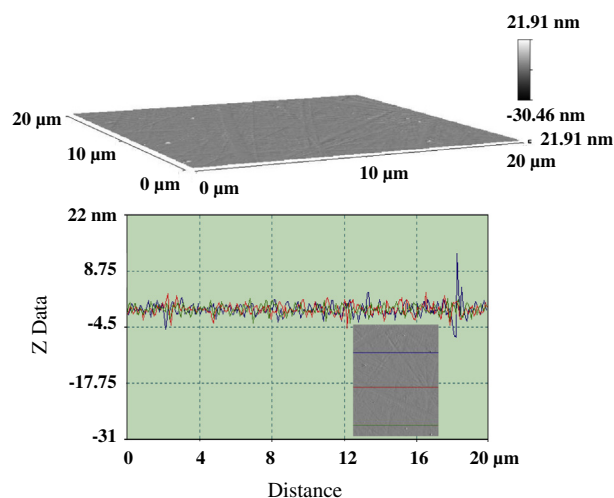

Fig. 1. AFM generated the image of surface topography of glass surface obtained from height backward mode and height profile along z-axis through three different selected lines on the surfaces. Positions of the lines are shown in inserted figure.

3.2. Effect of surfactant concentration on contact angle and adhesion tension

The change in advancing and receding contact angles with surfactant concentration on glass surface is shown in parts a, b, c of Fig. 2 for TX-100, SDBS, and CTAB respectively. The advancing and receding contact angles on glass surface in the presence of pure water are 47.87° and 0° respectively. In the presence of TX-100 θ_A increases very sharply even at very low concentration. At 0.02 mM concentration of surfactant, advancing contact angle increases to 70.08° and beyond that concentration contact angle slightly decreases and attains a plateau value 68.50° just above the CMC, whereas, θ_R increases gradually up to 65.44° at 0.30 mM TX-100 concentration. In the presence of SDBS θ_A increases gradually to a value of 74.78° at 0.50 mM concentration and above that surfactant concentration it again decreases and attain a constant value (∼66°) at higher SDBS concentration. Whereas for θ_R, the angle continuously increases up to a value of 61.86° at a concentration 1.20 mM and after that it is almost constant. Whereas for CTAB, the changes in contact angles (θ_A, θ_R) are more; the θ_A increases gradually and significantly to a value of 83.47° until 0.50 mM concentration and then the value again gradually decreases to 67.88° at 1.20 mM surfactant concentration. In case of θ_R there is a sudden increase at very low concentration (0.01 mM) to 37.70° and after that slowly increases to 65.51° at 1.25 mM concentration. All three surfactants show the constant θ_A values above the CMC, and the change is maximum for CTAB. The increase in contact angle in the presence of surfactants is because of the increase in hydrophobicity of the surface after adsorption of surfactant molecules on glass surface. The extent of final contact angle depends mainly on the orientation of the adsorbed surfactant molecules on the surface. The glass is made of silica, shows negative charge in aqueous media because of the presence of Silanol [Si(OH)] groups [25]. Therefore, CTAB molecules adsorb on the surface through the positively charged head group by strong electrostatic attraction at very low concentration (as shown in Scheme 1(c)) [26], as a result contact angle increases sharply and attend the maximum value of 83.47° at below CMC. After that with further increase in surfactant concentration the advancing angle starts to decrease because of the bi-layer adsorption (hemimicelle formation) of the surfactant molecules on the surface so that the surface properties again change from the hydrophobic to a little bit hydrophilic. Whereas, TX-100 molecules are assumed to be