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Wettability and adsorption of PTFE and paraffin surfaces by aqueous solutions of biquaternary ammonium salt Gemini surfactants with hydroxyl

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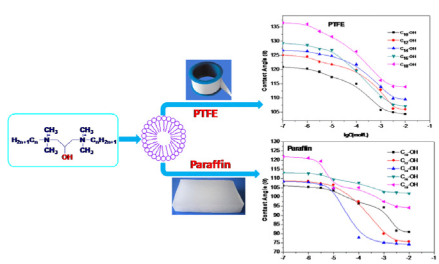
HIGHLIGHTS

- C_n-OH (n = 10,12,14,16,18)were synthesized in our laboratory.
- The spreading behavior on the surface could be divided into two processes: fast spreading and the slow spreading.
- A linear relationship exists between the adhesional and surface tension in a range of certain concentrations for PTFE.
- The wettability of C_{10}-OH solution on PTFE is best, and C_{14}-OH solution has the best wetting effect on Paraffin.

GRAPHICAL ABSTRACT



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ABSTRACT

The surface tension of five biquaternary ammonium salt Gemini surfactants with hydroxyl and the corresponding contact angles (θ) on Polytetrafluoroethylene (PTFE) and Paraffin are measured. The interfacial properties of surfactant solution in liquid-air-solid are investigated and changes in spreading coefficient (S), adhesive tension ($\gamma_{LV}\cos\theta$) and the work of adhesion (W_A) are discussed. The obtained results indicate that the surface tension decreases with the increase of surfactant concentration, and it tends to be stable when the concentration is more than CMC. The contact angle has the similar trend with surface tension. A linear relationship exists between the adhesional and surface tension in a range of certain concentrations, the slope is less than 1. It means that the adsorption amount of the surfactant solution at the liquid-air interface is larger than that at the PTFE-water interfaces. However, there is no linear relationship between the adhesional and surface tension for Paraffin-surfactant solution systems. The adhesional tension increases with the increase of concentration, and it keeps constant when the saturated adsorption film has been formed at both liquid-air and solid-liquid interfaces. The wettability of biquaternary ammonium salt Gemini surfactants with hydroxyl solutions on PTFE is poorer than that of Paraffin. The wettability of C_{10}-OH solution on PTFE surface is best, and C_{14}-OH solution has the best wetting effect on Paraffin.

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1. Introduction

Wetting solid surfaces by surfactant solutions plays an important role in many industrial processes and daily life, such as flotation, decontamination, oil recovery, paint, coating and deposition [1–6]. Therefore, it is of theoretical and practical value to study the wettability of surfactant solution on the solid surfaces. Most studies on the wettability of solid surfaces are focused on aqueous solutions of different single-chain surfactants and mixed surfactants [7–17], but are rare on Gemini surfactants. Generally, Gemini surfactants are constituted with two hydrocarbon chains on a head group or dimerized with two head groups. The reported studies showed Gemini surfactants had many superior features such as good water solubility, low critical micelle concentration (CMC), low Krafft point and excellent surface activity in aqueous solution compared with conventional single-chain surfactants [18]. Ao studied the wettability of cationic Gemini surfactant $[C_{12}$-4-$C_{12}im]Br_2$ on silica surface and showed there was a decreases in contact angle (θ) with the increasing of surfactant concentration until 5 times of CMC because of the formation of multilayer adsorption with hydrophilic head groups facing the air [19]. The studies disclosed that Gemini surfactant usually formed single film on the solid surface through direct adsorption or ion exchange adsorption at first, and then, generated double or multilayer film through the Gemini surfactant intermolecular interactions [20,21]. Positive charge of cationic Gemini surfactant interacted directly with negative charge (SiO^-) of silica surface through electrostatic interaction [22], the adsorption of MCM-41aluminum silicate surface through exchange between Gemini surfactants and H of solid surface [23]. As is known that polytetrafluoroethylene (PTFE) and Paraffin are typical representatives of hydrophobic low energetic solids, which have advantages of waterproof, corrosion resistance and so on. In recent years, the research on wettability of PTFE and Paraffin has received much attention. Janczuk studied the wettability of a series of cationic, anionic, nonionic surfactants (CTAB, SDS, TX-165, TX-100) and the mixtures on PTFE [24–30], and they found that the slope of the linear relationship between the adhesional and surface tension was equal to −1, which implied that the adsorption amount at solid-liquid and liquid-air interfaces was similar on these hydrophobic solids surfaces. The adsorption of surfactants on PTFE surface was based on hydrophobic interaction and the van der Waals force. Wang discussed the contact angle on Paraffin and found that the spreading behavior on the surface could be divided into two processes: the short time process (fast spreading) and the long time process (slow spreading) [31,32]. The former was controlled by the surface tension along the air/liquid interface, while the latter was driven by the diffusion and adsorption of surfactants on Paraffin surface. Numerous studies disclosed that the CMC was a turning point of wetting, and divided the process of surface properties of surfactants and the wettability on solid surface into different stages [33–35]. In this paper, a series of biquaternary ammonium salt Gemini surfactants with hydroxyl (C_n-OH, n = 10,12,14,16,18) were synthesized in our laboratory. On the basis of the investigation of the surface properties, and the data of the contact angle on PTFE and Paraffin measured by the sessile drop analysis, the wettability and adsorption of surfactants solutions on the solid surfaces were discussed. These results would provide theoretical basis for better understanding the wetting of the hydrophobic solids by Gemini surfactants solutions, and lay the foundation for the application of a series of Gemini surfactants.

2. Experimental

2.1. Materials

A series of biquaternary ammonium salt Gemini Surfactants with hydroxyl were synthesized in our laboratory. All the products are characterized using ^1H NMR spectra (BrukerADVANCE 600 M) in $CDCl_3$, and the final results of the analysis are as follows. The structural formula and abbreviations of surfactant are presented in Scheme 1.

C_{10}-OH($CDCl_3$, 600 MHz, ppm):δ=0.87–0.90 (t, J = 4.60, 6H); 1.25–1.37 (m, 28H); 1.74–1.86 (m, 4H); 3.40 (s, 6H); 3.43 (s, 6H); 3.50–3.54 (m, 4H); 3.61–3.66 (m, 2H); 4.31–4.34 (d, J = 8.12, 2H); 5.15–5.20 (m,1H).

C_{12}-OH($CDCl_3$, 600 MHz, ppm):δ=0.87–0.90 (t, J = 4.64, 6H); 1.25–1.36 (m, 36H); 1.74–1.86 (m,4H); 3.40(s, 6H); 3.43(s, 6H); 3.39–3.53 (m, 4H); 3.63–3.68 (m,2H); 4.33–4.36 (d, J = 8.16, 2H); 5.15–5.20 (m,1H).

C_{14}-OH($CDCl_3$, 600 MHz, ppm):δ=0.87–0.90 (t, J = 4.56, 6H); 1.25–1.36 (m, 44H); 1.74–1.87 (m, 4H); 3.39 (s, 6H); 3.42 (s, 6H); 3.47–3.50 (m, 4H); 3.64–3.69 (m, 2H); 4.38–4.41 (d, J = 8.40, 2H); 5.16–5.22 (m,1H).

C_{16}-OH($CDCl_3$, 600 MHz, ppm):δ = 0.86–0.90 (t, J = 4.56, 6H); 1.25–1.35 (m, 52H); 1.75–1.84 (m, 4H); 3.39 (s, 6H); 3.43 (s, 6H); 3.51–3.55 (m, 4H); 3.61–3.66 (m, 2H); 4.24–4.27 (d, J = 8.60, 2H); 5.14–5.19 (m,1H).

C_{18}-OH($CDCl_3$, 600 MHz, ppm):δ=0.86–0.90 (t, J = 4.6, 6H); 1.25–1.36 (m, 60H); 1.75–1.87 (m, 4H); 3.40 (s, 6H); 3.43 (s, 6H); 3.50–3.53 (m, 4H); 3.62–3.67 (m, 2H); 4.33–4.36 (d, J = 8.40, 2H); 5.15–5.20 (m,1H).

The surface tension of redistilled water is 72.5 ± 0.3 mN/m at 25 °C, which is a standard value, showed that the impurity content is lower in redistilled water, and the influence on the experiment can be neglected.

Cleaning of PTFE and Paraffin: dry the surfaces after washing with distilled water, acetone and distilled water, treated with freshly prepared chromic acid for 5 h and washed in a water ultrasonic bath for 20 min. Next, these surfaces were heated at 378 K for 2 h.

2.2. Surface tension measurements

The surface tensions of surfactant aqueous solutions were measured by the Wilhelmy ring method using a surface tension meter (JK99C, from Shanghai Zhongchen Digital Technic Apparatus CO., Ltd., China) under 298 K; the constant temperature was maintained using an external water circulator. The platinum ring was burned after washing under alcohol flame to remove the contamination and adsorbed surfactants thorough going before each experiment. The measurements were performed until constant surface tension values showed that equilibrium had been arrived. More than five continuous measurements were accomplished in all trials, and the standard deviation did not exceed 0.2 mN/m.

2.3. Contact angle measurements

The spreading ability of surfactants solution at the air/liquid/solid interface was measured by the contact angle of droplet on PTFE and Paraffin substrate using a drop shape analyzer DAS-100 (Kruss Company, Germany, accuracy ± 0.1°). The equilibrium contact time was 120 s, and the experimental temperature was controlled at 25 ± 0.5 °C. The standard deviation of the contact angle values did not exceed 2°.

3. Results and discussion

3.1. Surface properties of surfactants solutions

The surface tensions of a series of surfactant aqueous solutions measured with the Wilhelmy ring method at 25 °C are presented in Fig. 1. From Fig. 1, we can see that the surface tension decreases