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Wettability of coal pitch surface by aqueous solutions of cationic Gemini surfactants

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HIGHLIGHTS

- Series of C_n-8-C_n ($n = 8, 10, 12, 14, 16$) Gemini biquaternary ammonium salt surfactants were prepared.
- C_n-8-C_n Gemini surfactants changed their wettability on coal pitch surface by changing charge and polarity.
- The wettability of Gemini surfactants on coal pitch surface is the result of electrostatic interaction and van der Waals adsorption.

GRAPHICAL ABSTRACT
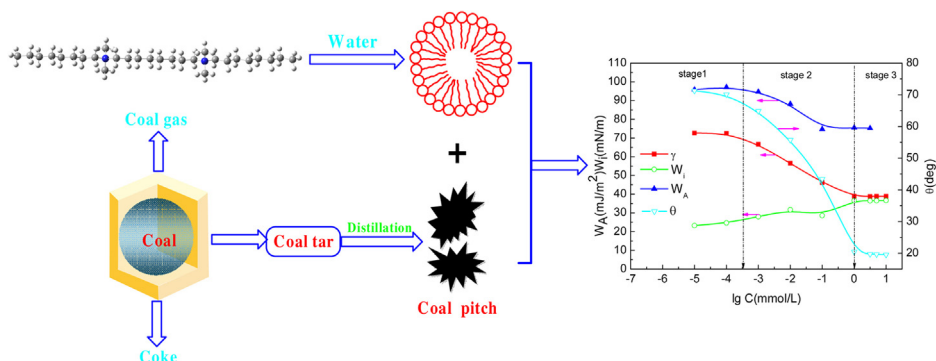
ARTICLE INFO

ABSTRACT

The purpose of this experiment is to confirm the adsorption characteristics at liquid–gas and CP–liquid interfaces in relation to CP wetting with a sequence of cationic Gemini surfactant solutions and to reduce the workload of screening of surfactant. A series of cationic Gemini surfactants with different hydrophobic chain length was synthesized (C_n-8-C_n, $n = 8, 10, 12, 14, 16$). Their wettability and adsorption mechanism for coal pitch (CP) were investigated by the sessile drop analysis and electrophoresis. Within the whole range of concentration, the Zisman theory is not in accordance with the wettability on the coal tar pitch when carbon atoms of hydrophobic chains exceed 12. Meanwhile, no liner dependence was observed between adhesion tension ($\gamma_{lg} \cos \theta$) and surface tension (γ_{lg}). In addition, with the increase of surfactant concentration, Zeta potential on the surface of the CP changed from negative to positive and finally leveled off after a certain concentration. The corresponding concentration of zero potential was at least an order of magnitude lower than CMC. C_{12}-8-C_{12} can significantly change the wettability of the CP. According to the wetting data and Zeta potential of Gemini surfactant on CP, it can be inferred that wetting was a concerted action as a result of electrostatic interaction and van der waals adsorption. Therefore, wetting process can be generally divided into three stages.

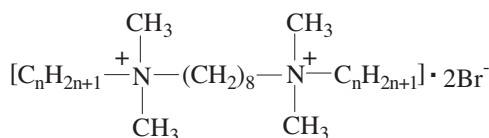© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The researches of the solid wettability with various liquids, mainly aqueous solution of surfactants, are closely related to our

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$$[C_nH_{2n+1}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{\overset{+}{N}}}-(CH_2)_8-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{\overset{+}{N}}}C_nH_{2n+1}]\cdot 2Br^-$$

Scheme 1. The structural formula of symmetrical cationic Gemini surfactants.

daily life and industrial process. Wetting is a central point for washing, oil recovering and pulping. Understanding the wetting of solid surface by the surfactants is essential for both theoretical study and practical application. Until now, mostly wettability of solid studies focused on aqueous solution of conventional single-chain surfactants [1–7] and their blend system [8–10]. Koopal presented an overview of the quantitative calculation methods on wettability of high-energy/low-energy hydrophilic solid by the surfactant aqueous solutions and the parts of organic solvent [11].

Gemini surfactants are novel type of molecules formed by two single-chain amphiphilic moieties, which are connected at the head group level through a spacer group. Commonly, the researches on Gemini surfactants are mainly focused on its solution properties, such as CMC (critical micelle concentration) values, aggregate morphology [12–14]. However, the influence of Gemini surfactants on solid surface is relatively rare, and most of the relevant researches focused on the surface of quartz, silicon slice and polymer [15–20]. The studies disclosed that Gemini surfactant usually formed single film on the solid surface through direct adsorption or ion exchange adsorption, and then, the formation of double or multilayer film through the Gemini surfactant intermolecular interactions [15,16]. Positive charge of cationic Gemini surfactant interacted directly with negative charge (SiO^-) of silica surface through electrostatic interactions [17]. In the monomer-Gemini surfactant composite system, a small amount of Gemini surfactant had a significant influence on quartz surface adsorption amount and adsorption mode [18]. The experiments of wetting on glass and mica surfaces by cationic Gemini surfactant were shown that the solid surface charge will be changed when Gemini surfactant concentration was 10 times lower than CMC [19], there is an obvious difference in wetting of PPFE and glass surface by cationic Gemini surfactant and anionic Gemini surfactant [20].

According to the preliminary reports [21,22], dispersants successfully employed in coal water slurry (CWS) were no long efficient for coal pitch water slurry (CPWS), a new-fashioned slurry fuels [23–25]. The novelty of this work is found that the dispersant of CWS and CPWS does not have commonality, and cationic Gemini surfactant is regarded as excellent dispersing agents to prepare for CPWS through the further experiments. Therefore, the objective of our study is to confirm the adsorption characteristics at liquid–gas and CP–liquid interfaces in relation to CP wetting with a sequence of cationic Gemini surfactant solutions.

2. Materials and methods

In the three flasks equipping with a stirrer, thermometer and condensing tube, the class of cationic Gemini surfactants, C_n-8-C_n (n = 8, 10, 12, 14, 16) with $(CH_2)_8$ as spacer and different length of hydrophobic chain, was synthesized by mixing 1,8-dobromooctane and N,N-dimethyl amines in ethanol solvent and refluxing for a definite time. The solvent was evaporated and the residue was recrystallized from acetone several times, and then dried under vacuum. All the products are characterized using ^1H NMR spectra (Bruker ADVANCE 600 spectrometer) in $CDCl_3$, the final results of the analysis are as follows. The structural formula and abbreviations of surfactant are presented in Scheme 1.

C_8-8-C_8, ^1H NMR (600 MHz, $CDCl_3$): δ = 0.86–0.88 (t, J = 6.48 Hz, 7.14 Hz, 6H), 1.26–1.45 (m, 28H), 1.73 (s, 4H), 1.84 (s, 4H), 3.37 (s, 12H), 3.54–3.57 (t, J = 9.48 Hz, 8.52 Hz, 4H), 3.64–3.67 (t, J = 8.34 Hz, 8.46 Hz, 4H).

C_{10}-8-C_{10}, ^1H NMR (600 MHz, $CDCl_3$): δ = 0.87–0.89 (t, J = 6.9 Hz, 7.14 Hz, 6H), 1.26–1.45 (m, 36H), 1.73 (s, 4H), 1.84 (s, 4H), 3.37 (s, 12H), 3.54–3.56 (t, J = 8.34 Hz, 8.64 Hz, 4H), 3.65–3.68 (m, 4H).

C_{12}-8-C_{12}, ^1H NMR (600 MHz, $CDCl_3$): δ = 0.87–0.89 (t, J = 6.84 Hz, 7.14 Hz, 6H), 1.25–1.46 (m, 44H), 1.72 (s, 4H) 1.85 (s, 4H), 3.36 (s, 12H), 3.50–3.53 (t, J = 8.46 Hz, 8.46 Hz, 4H), 3.67–3.70 (m, 4H).

C_{14}-8-C_{14}, ^1H NMR (600 MHz, $CDCl_3$): δ = 0.87–0.89 (t, J = 6.9 Hz, 7.14 Hz, 6H), 1.25–1.46 (m, 52H), 1.72 (s, 4H), 1.85 (s, 4H), 3.36 (s, 12H), 3.50–3.53 (t, J = 8.46 Hz, 8.46 Hz, 4H), 3.68–3.71 (m, 4H).

C_{16}-8-C_{16}, ^1H NMR (600 MHz, $CDCl_3$): δ = 0.87–0.89 (t, J = 6.84 Hz, 7.14 Hz, 6H), 1.25–1.47 (m, 60H), 1.72 (s, 4H), 1.86 (s, 4H), 3.36 (s, 12H), 3.50–3.53 (t, J = 8.34 Hz, 8.46 Hz, 4H), 3.69–3.72 (m, 4H).

The surface tension of surfactant aqueous solutions was measured by the Wilhelmy ring method using a surface tension meter with the JK99C from Shanghai Zhongchen Digital Technic Apparatus Co., Ltd., China under 293 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 thoroughgoing 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.

The contact angles for aqueous solution of surfactants and water on CP slices were achieved by the sessile drop method using the SL200B from USA Kino Industry Co., Ltd., which all experiments were achieved at constant temperature 293 K; CP slice was purged several times using first acetone and then double-distilled water to remove the impurity. Within 120 s, a certain volume of droplets was dripped on the CP slice until contact angle values remain constant. The trials were repeated four times by placing a droplet on the new parts of the slice. Then, a new slice was placed in the platform, and the above experimental operation was repeated four times. The standard deviation of the contact angle values did not exceed 2°.

Zeta potential of the surfactants aqueous solution on the CP particles was fulfilled by the electrophoresis technology with the JS94H from Shanghai Zhongchen Digital Technic Apparatus Co., Ltd., China. The aqueous solution of surfactants were mixed with the CP particles with a certain proportion (0.02 g/mL), oscillating under 293 K for half an hour. The measurements were implemented until constant Zeta potential values denoted that adsorption equilibrium had been arrived. The same procedure was repeated five times, and the average values are reported. The standard deviation of Zeta potential values did not exceed 0.5 mV.

3. Results and discussion

The surface tension values of cationic Gemini surfactant solution as a function of the logarithm of surfactant concentration are presented in Fig. 1. From Fig. 1, we can see that the surface tension decreases with the increasing concentration of cationic Gemini surfactants. Then, it remains constant until the surfactant concentration is large than the CMC. According to the theoretical assumptions, Traube's rule, it states that for every extra CH_2 group in a surfactant molecule, the surface activity approximately triples in the dilute aqueous solutions of surfactants, which means we can get away with using a much lower concentration of a longer chain length surfactant. However, according to the relevant published literature [26–28], the corresponding surface tension is not always