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Dynamic surface properties, wettability and mimic oil recovery of ethanediyl-α,β-bis(cetyldimethylammonium bromide) on dodecane modified silica powder

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In order to increase petroleum oil recovery, the wettability of the interface between flooding aqueous solution and oil reservior plays an important role. A surfactant dissolved in the flooding solution can be adsorbed on the reservior surface and then the wettability of the interface can be changed. For the purpose of mimic oil recovery, a cationic gemini surfactant, ethanediyl-α,β-bis(cetyldimethylammonium bromide) (**16-2-16**), was synthesized and characterized. The dynamic surface and interface tensions have been measured using pendant drop method at the air-water surface and dodecane-water interface, and experimental curve is close to orientation model and interaction model of surface equations of state. Compared with conventional cationic surfactants, cetyldimethylammonium bromide (CTAB), **16-2-16** has very low *cmc* value (1.8×10^{-5} mol/L to 1.0×10^{-3} mol/L). The most hydrophilic condition between the surfactant aqueous solution and the silica powder surface appears near the cmc for both **16-2-16** and CTAB. The best mimic oil recovery is also reached around the cmc for the two surfactants, but the efficiency for the former (68%) is higher than the one for the latter (63%).

1. Introduction

Chemical flooding is one of the important methods in enhanced oil recovery (EOR). During the process, surfactants are usually added into the flooding solution and the adsorption of surfactants at the reservior surface can lead to change of wettability of the interface and then oil will be replaced. The recent synthesis of so-called "gemini" or dimeric surfactants has provided a new method of controlling surfactant properties. Some of these molecules have been shown to be superior to the analogous monomeric surfactants in depressing surface tension and also tend to micellize at 1/10–1/100 lower concentrations [1, 2]. The synthesis of cationic Geminis is relatively easy, their cmc is low as mentioned above, and the adsorption amount is lower than that of their monomeric counterparts [3], as well as their Krafft temperatures (soluble at oil reservoir temperature). Besides these, the cationic Geminis exhibit viscoelastic behavior at low concentration [2]. All of these indicate extensive applicable potential in enhanced oil recovery.

In the past, properties of cationic Gemini surfactant have been much investigated [3–12]. But most of the studies were related to Alkanediyl-α,ω-bis(Dodecyldimethylammonium bromide) series (Herein referred to as m-s-m, where m is the length of hydrophobic moiety, s is the length of spacer, here referred to as 12-s-12), whereas 16-s-16 has been very little investigated so far. The investigation of 16-s-16 concentrated on measurement of *cmc* [5], phase behavior [6]. No consideration is given to the surface and interface properties of **16-2-16**, especially dynamic surface properties. As we know, some of potential applications of cationic surfactants, such as disinfection and antistatic effect are related to dynamic adsorption. In this study, the dynamic surface tension of **16-2-16** was investigated by means of pendent drop method with *n*-dodecane as oil phase, the dynamic adsorption of 16-2-16 was also studied at dodecane/water interface.

We had tried to use a series of sodium dodecyl benzene sulfonate (SDBS) aqueous solutions as mimic flooding solution; it was found that good residual oil recovery was achieved by surface wettability changes of silica gel powders [13]. Normally, the surface of silica gel powders was negatively charged. Comparing to an anionic surfactant SDBS, cationic surfactants CTAB and 16-2-16 may have advantages to be adsorbed at the

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negatively charged surfaces. In this paper, both dilute CTAB and **16-2-16** aqueous solutions are used as mimic flooding solution. The most hydrophilic condition between the surfactant aqueous solutions and the silica powder surfaces appears at the cmc for both **16-2-16** (cmc $= 1.8 \times 10^{-5}$ mol $\cdot$ L^{-1}) and CTAB (cmc $= 1.0 \times 10^{-3}$ mol $\cdot$ L^{-1}). The best mimic oil recovery is also reached around the cmc for the two surfactants, but the efficiency for the former (68%) is higher than the one for the latter (63%). At that situation, the concentration ratio of **16-2-16** to CTAB is only about one fiftieth.

2. Experimental procedure

2.1. Chemicals

N, N, N′, N′-tetramethylethylenediamine was from Beijing Chemical Reagent Company. 1-bromohexadecane, ethanol, *n*-hexane and cetyltrimethylammonium bromide (CTAB) were from Beijing Chemicals Factory. Dodecane was from Shanghai Chemical Reagent Company. All chemical reagents were analytical grade and used without further purification. Silica gel powder, H-60, is from E. Merck, Darmstadt. Its specific surface area is 48 m$^2 \cdot$ g^{-1} measured by BET gas adsorption. Deionised water was used with electric conductance between 1.3–1.5 μS $\cdot$ cm^{-1}.

2.2. Surface and interfacial tension measurement

Dynamic surface and interfacial tension were measured with JC2000A POWEREACH (made by Shanghai Powereach Digital Equipment Company) using pendent drop method. The principal of this method has been expatiated in related reference [14]. The apparatus was calibrated with the surface tension of deionised water, pure ethanol, and the interfacial tension of water-isoamyl alcohol system. The measured values were 72.2, 22.4 and 4.7 mN/m, respectively, which are in agreement with values from references.

As the equilibration time for the experiment is long, the effect of evaporation of the liquid drop on results can not be neglected. Therefore, deionised water was added in the cuvette for measurement and a sealed membrane was used to cover the cuvette. The measurements were carried out after water vapor equilibration had been attained. The loss of liquid drop caused by evaporation was found less than 4% after 4 h of suspension, which could satisfy the experimental need under normal time and accuracy of measurement.

Equilibration values of surface tension were taken at least 30 min until measured values were constant, and those of interfacial tension received at 10–15 min intervals.

2.3. Synthesis

The surfactant was synthesized by using N,N,N′,N′-tetramethylethylenediamine with 1-bromohexadecane. Reaction was performed as reference [5]. The structure and purity of the compound were confirmed with elemental analysis and ^{1}H NMR spectrum. Anal. cacld. For $C_{38}H_{82}N_2Br_2$:C 62.79, H 11.37, N 3.86, Br 21.99; found C 62.39, H 11.56, N 3.67, Br 22.47; ^{1}H NMR (MHz, solvent, temperature. TMS): $\delta = 0.87$ (t, 6H), 1.24–1.37 (m, 52H), 1.82 (m, 4H), 3.70–3.69 (m, 4H), 3.50 (s, 12H), 4.73 (s, 4H) ppm. As shown by the data of elemental analysis and ^{1}H NMR, the synthesized product is in good agreement with theoretic value, and there is no monoquaternization product occurred. In addition, the surface tension-concentration curve performing the absence of a minimum value shows the purity of product can conform to the experimentation.

2.4. Wettability measurements of silica gel powder

Capillary penetration (rising) method was used in the wettability investigation. This approach is based on measurement of the height of a penetrating liquid through a packed bed of powder contained in a capillary tube as a function of time. The relationship between parameters can be expressed by improved Washburn equation [13]:

$$H^2 2\eta\gamma^{-1} = (cR)t \cos\theta = H'^2 \qquad (1)$$

where H is the penetration height, η is the liquid viscosity, γ is the surface tension of the liquid, c is the calibration factor for the irregular orientation of capillaries in the powder bed, and R is average radius of the capillary tube, t is the time, θ is the contact angle; $\cos\theta$ can be determined from the slope of the straight line fit by H'^2-t diagram. In the experimentation, for each series of solutions, the solution which had the fastest penetration rate was selected as the standard, and assumed its θ value on the surface of powder to be zero. Then the (cR) in the equation can be calculated. Relative contact angles of the other solutions, in turn, were obtained. This processing can investigate the relative wettability of a series of surfactant solutions on solid powders. Washburn tube, diameter 0.8 cm, length 15 cm, is used to measure the wettability of both 16-2-16 and CTAB aqueous solutions on silica gel powder surface.

2.5. Surface modification of silica gel powder by oil and mimic oil recovery in lab

After weightting, the solid powder was soaked with *n*-dodecane and let it stay over night, then filtrated and dried with an infra-red lamp, keeping the temperature on the surface of powder at about 60°C. The processed powder did not agglomerate, and continued to be dried until the weight became constant. According to the oil (*n*-dodecane) content adsorbed and the specific surface area of the powder, the average oil film thickness on the powder surface can be calculated. For example, a modified silica gel powder containing oil content 27.7% (mass fraction), with the specific surface area 48 m$^2 \cdot$ g^{-1}, gives rise to an average oil film thickness calculated to be 11.2 nm. The mimic oil recovery in lab was conducted as mentioned in reference [13].

TABLE I Some thermodynamic parameters of 16-2-16 and CTAB

surfactant	*cmc* (mol · L^{-1})	γ_{cmc} (mN · m^{-1})	$(d\gamma/d\lg C)_T^a$	$10^6\Gamma_{\max}$ (mol · m^{-2})	$10^{20}A_m$ (m^2)	ΔG_m (kJ · mol^{-1})
16-2-16	1.8×10^{-5}	40.4	−32.0	1.9	87	−70.1
CTAB	1.0×10^{-3}	34.9	−29.3	2.6	64	−34

[a] Calculated by the least-squares fits.

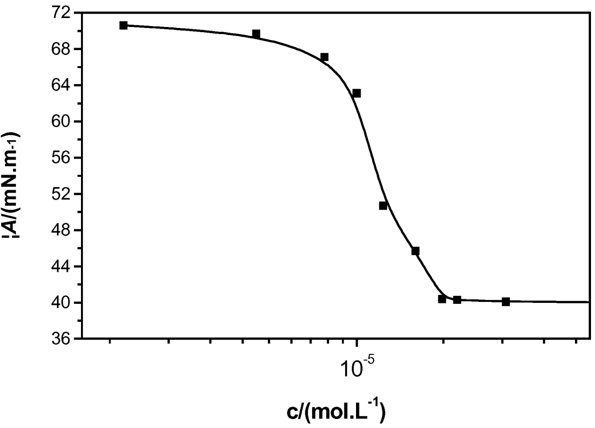

Figure 1 Surface tension as a function of concentrations of **16-2-16**.

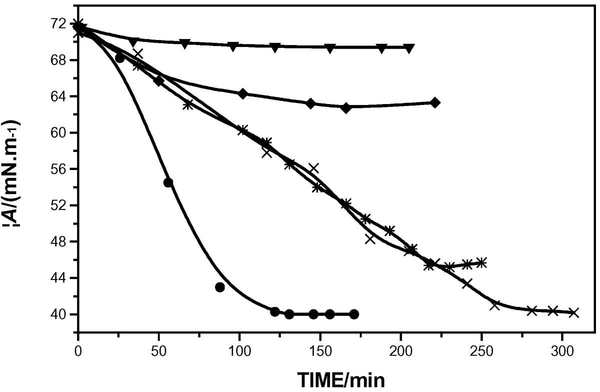

Figure 2 Dynamic surface tension of 16-2-16 aqueous solution: – ▼– 0.5×10^{-5} mol/L – ♦– 1.0×10^{-5} mol/L – ∗ – 1.5×10^{-5} mol/L; – × – 2.0×10^{-5} mol/L, – ●– 1.0×10^{-4} mol/L.

3. Results and discussion

3.1. The aggregation of 16-2-16

The *cmc* was determined by surface tension versus concentrations (see Fig. 1). From Fig. 1, we derived the *cmc* and γ_{cmc} of 16-2-16 as 1.8×10^{-5} mol/L and 40.4 mN/m. Using *cmc* and γ_{cmc}, some thermodynamic parameters of surfactant in aqueous solution can be calculated. By Gibbs adsorption equation and some references [7, 15], the maximum surface excess, surface area and free energy of micelle formation are calculated. The results are listed in Table I, where the values of Cetyltrimethylammonium Bromide (CTAB) are also included in order to compare with the adsorption of monoquaternary ammonium surfactant with the same chain length.

As can be seen from Table I, the *cmc* of **16-2-16** is 50 times smaller than that of CTAB. The surface excess ($\Gamma_{\max}$) of **16-2-16** is smaller and the surface area (A_m) of **16-2-16** is larger than those of CTAB, however, the surface area of **16-2-16** per head group is smaller than that of CTAB if compared to the numbers of head group. This indicates that head groups of Gemini surfactants are closer to each other at the air-water interface, with limit of spacer reducing the effect of electrostatic. In comparison with homologous **12-2-12**, the surface area of **16-2-16** is also smaller [7, 11], which demonstrates the length of the hydrophobic moiety affects the adsorption of cationic Geminis. In addition, the free energy of micelle formation (ΔG_m) of **16-2-16** is about two times of CTAB, showing every carbon atom in the hydrophobic chains having the same contribution to the energy of micelle formation in aqueous solution.

3.2. Dynamic surface adsorption of ***16-2-16***

Usually, the adsorption of a surfactant at the liquid/fluid interface is very fast and its dynamics is basically described by diffusion-controlled process [16, 17]. However, for some surfactants, the adsorption rate can be reduced in the presence of the orientation [17], electrostatic repulsion [18], interaction between hydrophobic chains and desorption of adsorption molecules [16, 19], resulting in other adsorption mechanisms.

Fig. 2 shows the dynamic surface tension of **16-2-16** aqueous solution as a function of time. As shown in Fig. 2, the time **16-2-16** achieving equilibrium is much longer than general surfactants at air-water interface, with 3–4 h around *cmc*. This phenomenon occurred is correlative with the unique structure and size of **16-2-16**. Zana confirmed that the arrangement of m-s-m will adopt the mode at air-water interface which the spacer is in contact with water and lies more or less stretched at the interface with the two hydrophobic chains erecting on the water when the distance between spacers is less than that of equilibrium of electrostatic repulsion [7]. Because of the rigidity of the spacer, more time is needed for the arrangement and reorientation of the two hydrophobic chains of m-s-m. Fig. 3 is some possible arranging and orientating processes of **16-2-16** at the air-water interface. As can be seen from this figure, molecules of **16-2-16** could lie on the water surface, or erect on the water, and the reorientation between lying and erecting is correlated with the flexibility of spacer.

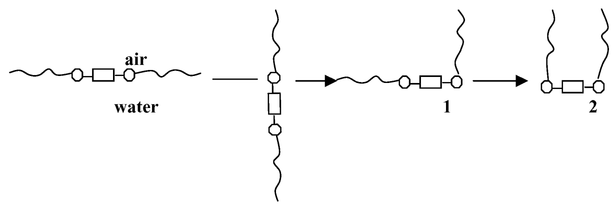

Figure 3 Possible orientations of **16-2-16** at the air-water interface.

In addition to orientation, larger molecular weight and size of **16-2-16** make its diffusion slower. Dam *et al.* [15] measured the surface tension of **12-s-12** homologue surfactants by means of maximum bubble pressure method. By the same way, however, they met difficulty in determining the *cmc* of **14-2-14**. The surface tensions obtained were around 70 mN/m when the concentrations are much higher than *cmc*, and *cmc* fail to be given by this method. The explanation given is viscoelastic behavior of **14-2-14**. From our experiment, it is evident that the adsorption rate of surfactant is low at the new emerging interface, which results in high surface tension within short time interval.

The adsorption of surfactants at surface can be described by surface equation of state. When there is no interaction between the adsorbed monomers, with low surface concentrations, the Henry equation

$$\Pi = \gamma_o - \gamma = nRT\Gamma \tag{2}$$

can be used. And with large surface concentrations, the Szyszkowski-Langmuir equation

$$\Pi = \gamma_o - \gamma = -nRT\Gamma_\infty \ln(1 - \Gamma/\Gamma_\infty) \tag{3}$$

can be used. If there is interaction between the adsorbed molecules, Frumkin equation [20]

$$\begin{aligned}\Pi = \gamma_o - \gamma = -nRT\Gamma_\infty[\ln(1 - \Gamma/\Gamma_\infty)\\ + a(\Gamma/\Gamma_\infty)^2]\end{aligned} \tag{4}$$

is often used. Where Π is the surface pressure, γ_0 and γ are the surface tensions of the solvent and the solution, respectively, Γ is surface excess concentration Γ_∞ is the maximum surface excess concentration a is the intermolecular interaction constant. For the case of electrostatic repulsion, Bonfillon *et al.* [18] proposed a simple model to explain the electrostatic interaction between active ions at adsorbed monolayer based on Langmuir equation.

$$\Pi = \gamma_o - \gamma = -\frac{n}{2}RT\Gamma_\infty \ln(1 - \Gamma/\Gamma_\infty) + nRT\Gamma \tag{5}$$

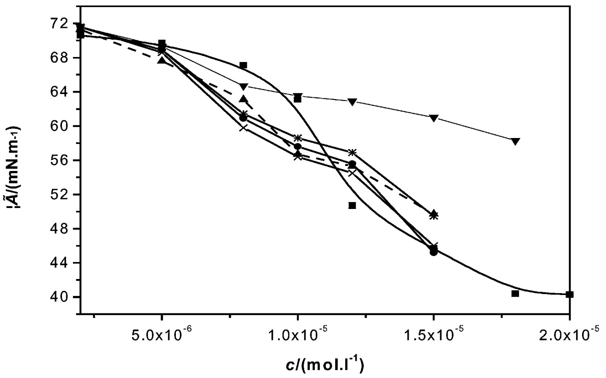

Figure 4 Surface tension isotherm for 16-2-16: – ■– experimental isotherm – ▼– Henry model – ∗– Langmuir model – ×– Frumkin model ($a = -0.4$) – ●– orientation model (with $A_\Sigma = 5.8 \times 10^5$ m$^2 \cdot$ mol^{-1} – ▲– electrostatic interaction mode.

The meanings of the symbols used in Equation 5 are the same as in Equation 1–4. With regard to molecular orientation of surfactants at absorbed monolayer, Fainerman *et al.* [20] suggested a model of molecular orientation as a controlling process in adsorption dynamics. They postulated that adsorbed surfactant molecules can exist in two states 1 and 2 (see Fig. 3), characterized by different values of the partial molar area A: A1 > A2, with the adsorption activity of surfactant molecules in state 1 being larger than in state 2. Because of larger surface activity of state 2, state 1 can transit to state 2, i.e. molecular orientation. The orientation process within the surface layer requires some time, and results in deceleration of the surface tension decrease. The surface equation of state provided is defined as

$$\begin{aligned}\Pi = \gamma_o - \gamma &= -\frac{nRT}{A_\Sigma}\ln(1 - \Gamma_1 A_1 - \Gamma_2 A_2)\\ &= -\frac{nRT}{A_\Sigma}\ln(1 - \Gamma A_\Sigma)\end{aligned} \tag{6}$$

where A_Σ is the mean partial molar area of adsorbed surfactant molecule. Taking $n = 3$ [7, 15], the data of surface adsorption can be treated with the surface equation of state. The result is plotted in Fig. 4. Each c in Fig. 4 corresponds with each Γ in the equation at equilibration time. Γ was obtained from the experimental isotherm, then each equation was calculated and plotted as π vs. c.

As shown in Fig. 4, the calculated curves of five surface equation of state can not be in good agreement with the experimental curve. The results of orientation model and Frumkin model are closer to the experimental results comparatively. It indicates that the adsorption of **16-2-16** can not only be described by single interaction simply, which is the comprehension of multiple interactions. Among these, the orientation and intermolecular interaction of surface active ions at surface may be major factors of low adsorption rate.

As the concentrations increase in the bulk, the orientation of adsorbed ions of **16-2-16** at adsorbed layer becomes more difficult, and the interaction of adsorbed ions increases accordingly. Therefore, the time of equilibration prolongs, and reaches maximum around *cmc*. If the concentrations are higher than *cmc*, however, because of large concentration just below the interface (interchange between micelle and monomer molecules is fast [8]) which reduces the diffusive time significantly, the final equilibration time reduces conversely.

3.3. Interfacial adsorption of **16-2-16** at dodecane-water interface

The variations of the interfacial tension with concentrations of **16-2-16** at dodecane-water interface are shown in Fig. 5. We can see that the curve also has a break point that corresponds to 1.5×10^{-5} mol $\cdot$ L^{-1}. This phenomenon can be explained by dodecane inserting itself into the adsorbed layer of surfactant at interface,

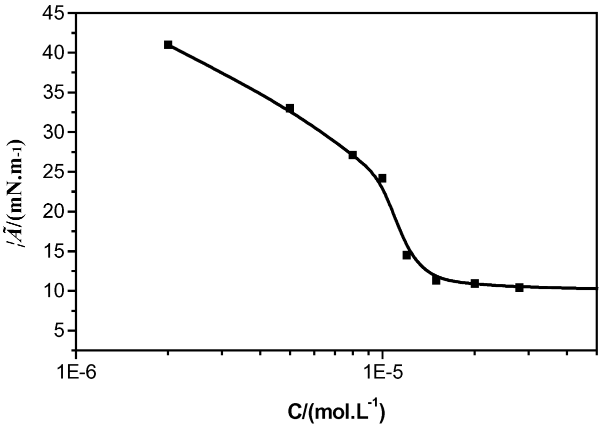

Figure 5 Variation of the interfacial tension with the concentrations of **16-2-16**.

which results in an equilibration value of interfacial tension attained at a lower concentration. In addition, the stable interfacial tension values can not be obtained at larger concentrations with long time intervals, which results from the trace amount of impurities [18, 21]. The values were taken at 10–15 min intervals until measured values were constant during experimentation.

The tendency of dynamic interfacial tension between dodecane and **16-2-16** aqueous solution interface is similar to that of dynamic surface tension of **16-2-16**. But the equilibration time of interfacial tension is shorter than that of surface tension. For instance, the equilibration time of surface tension is 280 min at 1.5 $\times$ 10^{-5} $\text{mol}\cdot\text{L}^{-1}$, whereas the equilibration time of interfacial tension is 120 min for dodecane-water interface. The interfacial tension shown in Fig. 5 is the data after the equilibration time. This is due to high adsorption activity at oil-water interface of **16-2-16**, and the interaction between hydrophobic chain and dodecane reducing the free energy of system [21]. In addition, dodecane inserting adsorption layer reduces the electrostatic repulsion of **16-2-16** head group ions. The two factors shorten the equilibration time of interfacial tension.

3.4. The wettability alterations and mimic oil recovery of modified silica gel by CATB aqueous solutions

The wettability data measured were listed in Table II. After modified and adhering a dodecane oil film, the silica gel became more hydrophobic (dodecane oil film adsorbed and/or adhered on the powder surface). In this time, the adsorption of surfactant on the powder surface is lined with the concentration of the surfactant. The higher concentration, the smaller contact angle, i.e. the more hydrophilic surface. This conformed to the hydrophilic group of the surfactant molecules toward the water phase. And the adsorption was in agreement with the first step of adsorption. But while the concentration of CTAB is larger than 6.0 $\times$ 10^{-4} $\text{mol}\cdot\text{L}^{-1}$, there were some aggregations on the solid surface giving rise to the increase of the contact angles and the weakness of the surface hydrophilicity. At that time, the adsorption was in agreement with the second step of adsorption [22].

TABLE II Surface tension (γ), Contact angle (θ) and mimic oil recovery of CTAB aqueous solutions on modified silica gel H* (20°C)

CTAB concentration $C(\text{mol}\cdot\text{L}^{-1})$	Surface tension $\gamma(\text{mN}\cdot\text{m}^{-1})$	Contact angle $\theta(°)$	Oil recovery (%)
0	72.9	65	29
1.0×10^{-6}	71.3	59	42
1.0×10^{-5}	68.1	57	44
1.0×10^{-4}	62.6	55	50
2.0×10^{-4}	56.4	49	52
5.0×10^{-4}	43.4	43	54
6.0×10^{-4}	39.3	0	63
1.0×10^{-3}	34.9	23	63

*Oil content of the modified silica gel was 27.7% (mass fraction).

An interesting phenomenon was also observed. When CTAB dilute aqueous solutions were used to penetrate and move up into the modified silica gel bed, the oil attached on the silica gel surface can be replaced. In the end, almost all of the oil can be displaced and converge on the top of the silica gel powder bed. Finally an oil column on it was formed. We can read the volume of the oil column, and calculate the oil recovery. As shown in Table II, water was able to displace the oil, too, but the surfactant solution had much higher efficiency of oil recovery. The best efficiency of oil recovery appear at the concentration around *cmc*. There was no emulsification occurred in the flooding. The phenomenon was that the surfactant absorbed on the solid surface leading to the change of the wettability of powder surfaces, and oil film ruptured and was displaced.

3.5. The wettability alterations and mimic oil recovery of modified silica gel by **16-2-16** aqueous solutions

The data available were listed in Table III. Similarly, as the aqueous solution penetrated up in the bed, the oil film adhered on the silica gel surface was displaced and moved up. Finally, it can transcend powder bed, and formed an oil column on the top. We can read the volume of the oil column, and calculate the oil recovery. The best efficiency of mimic oil recovery appears at the concentration around *cmc* (Fig. 6). At that time, the interfacial tension (around 10 $\text{mN}\cdot\text{m}^{-1}$, refer to Fig. 5) is far from ultra low general referred to as $10^{-3}\text{mN}\cdot\text{m}^{-1}$order of magnitude, no emulsification of the oil can occur. Compared with conventional cationic surfactants CTAB, **16-2-16** has very low *cmc* value

TABLE III Surface tension (γ), Contact angle (θ) and mimic oil recovery of **16-2-16** aqueous solutions on modified silica gel *H** (20°C)

16-2-16 concentration $C(\text{mol}\cdot\text{L}^{-1})$	Surface tension $\gamma(\text{mN}\cdot\text{m}^{-1})$	Contact angle $\theta(°)$	Oil recovery (%)
0	72.9	65	29
1.8×10^{-6}	70.0	29	52
6.3×10^{-6}	68.0	18	60
1.8×10^{-5}	43.0	0	68
6.3×10^{-5}	40.0	16	65
1.8×10^{-4}	40.0	22	63

*Oil content of the modified silica gel was 27.7% (mass fraction).

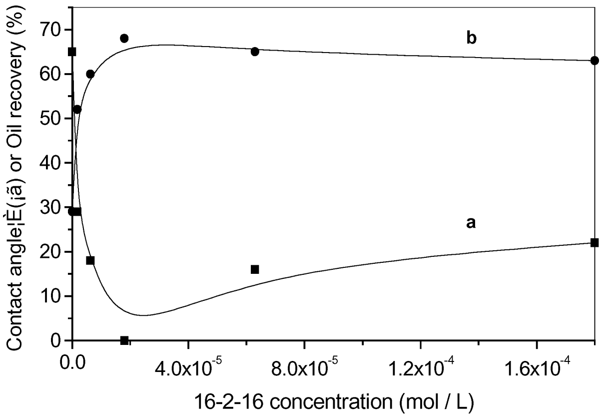

Figure 6 Contact angle (a) and oil recovery (b) of **16-2-16** aqueous solutions on modified silica gel.

(1.8×10^{-5}mol · L^{-1} to 1.0×10^{-3} mol · L^{-1}). The most hydrophilic condition between the surfactant aqueous solutions and the silica gel powder surfaces appears near the *cmc* for both **16-2-16** and CTAB. The best mimic oil recovery is also reached around the *cmc* for the two surfactants, but the efficiency for the former (68%) is higher than the one for the latter (63%).

4. Conclusions

It is shown in this study that the adsorption rate of **16-2-16** is slow at liquid/fluid interface, whereas the adsorption at air-water is much slower than that at oil-aqueous solution. This is attributed to the unique molecular structure and size of **16-2-16**. In this paper, the *cmc* for **16-2-16** is only about one fiftieth of that for CTAB. The most hydrophilic condition between the surfactant aqueous solutions and the silica powder surfaces appears near the *cmc* for both **16-2-16** and CTAB. The best mimic oil recovery is also reached around the cmc for the two surfactants, but the efficiency for the former (68%) is higher than the one for the latter (63%). Because of its small *cmc*, low Krafft temperature (measured as 44°C) and lower amount of adsorption at solid surface, **16-2-16** may have a broad applicable potential in Enhanced Oil Recovery (EOR) in the future.

Acknowledgements

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References

1. F. M. MENGER and C. A. LITTAU, *J. Am. Chem. Soc.* **113** (1991) 1451.
2. M. J. ROSEN, *Chemtech.* **3** (1993) 30.
3. K. ESUMI, M. GOINO and Y. KOIDE, *J. Colloid Interf. Sci.* **183** (1996) 539.
4. C. A. BUNTON, L. ROBINSON, J. SCHAAK and M. F. STAM, *J. Org. Chem.* **36** (1971) 2346.
5. R. ZANA, M. BENRRAOU and R. RUEFF, *Langmuir* **7** (1991) 1072.
6. E. ALAMI, H. LEVY, R. ZANA and A. SKOULIOS, *ibid.* **9** (1993) 940.
7. E. ALAMI, G. BEINERT, P. MARIE and R. ZANA, *ibid.* **9** (1993) 1465.
8. M. FRINDI, B. MICHELS, H. LEVY and R. ZANA, *ibid.* **10** (1994) 1140.
9. D. DANINO, Y. TALMON and R. ZANA, *ibid.* **11** (1995) 1448.
10. R. ZANA and H. LEVY, *Colloids Surf. A: Physicochem. Eng. Asp.* **127** (1997) 229.
11. F. DEVINSKY, I. LACKO, F. BITTEREROVA and K. TOMECKOVA, *J. Colloid Interf. Sci.* **114** (1986) 314.
12. C. CHORRO, M. CHORRO, O. DOLLADILLE, S. PARTYKA and R. ZANA, *ibid.* **199** (1998) 169.
13. Z. C. BI, F. XU, P. H. YANG, J. Y. YU and J. B. LI, *Colloids Surf. A*: *Physicochem. Eng. Asp.* **180** (2001) 235.
14. S. LAHOOTI, O. I. DEL RIO, A. W. NEUMANN and P. CHENG, Axisymmetric Drop Shape Analysis (ADSA) in "Apllied Surface Thermodynamics", edited by A. W. Neumann and Jan K. Spelt (Marcel Dekker, New York, 1996).
15. T. DAM, J. B. ENGBERTS, J. KARTHAUSER and S. KARABORNI, *Colloids Surf. A: Physicochem. Eng. Asp.* **118** (1996) 41.
16. J. EASTOE and J. S. DALTON, *Adv. Colloid Interf. Sci.* **85** (2000) 103.
17. F. RAVERA, L. LIGGIERI and R. MILLER, *Colloids and Surf. A: Physicochem. Eng. Asp.* **175** (2000) 51.
18. A. BONFILLON, F. SICOLI and D. LANGEVIN, *J. Colloid Interf. Sci.* **168** (1994) 497.
19. V. B. FAINERMAN, R. MILLER and E. V. AKSENENKO, *Adv. Colloid Interf. Sci.* **86** (2000) 83.
20. V. B. FAINERMAN, R. MILLER, R. MUSTNECK and A. V. MAKIEVSKI, *J. Phys. Chem.* **100** (1996) 7669.
21. R. MILLER, E. V. A KSENENKO and L. LIGGIERI, *Langmuir* **15** (1999) 1328.
22. B. ZU and T. GU, *Ad. Colloid Interf. Sci.* **37** (1991) 1.