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Synthesis and Viscoelastic Behavior of an Anionic Gemini Surfactant in Aqueous Solution

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A novel anionic Gemini surfactant, sodium dialkylbenzene disulfonate with spacer of -C_3H_6-, was synthesized and confirmed by ^{1}HNMR, MS and IR. Such Gemini surfactant in dilute aqueous solution without additives was researched by rotational rheometer and exhibited special viscoelastic behaviors and shear-thinning properties like entangled polymer solution. The influence of concentration and shear rate on viscosity and shear modulus has been studied and the reason of enhancing viscosity has also been discussed.

1. Introduction

Gemini surfactants, made of two conventional surfactants units connected with a spacer group on or near hydrophilic groups, exhibit many special properties, compared to single chain conventional surfactants [1,2]. Anionic Gemini surfactants solutions with high viscosity are rarely researched, especially for the solutions at low concentration without any additives, although much more attention has been paid to cationic Gemini surfactants with short spacers, which make the solution systems express high viscosity [3–5]. The anionic Gemini surfactant we studied is dialkylbenzene disulfonate, in which two single-chain alkylbenzene sulfonate surfacants ($C_nH_{2n+1}C_6H_5SO_3^-Na^+$) are linked near the benzene groups by -C_mH_{2m}-, marked as n-m-n, Fig. 1. Parts of this kind Gemini surfactants with n = 6, 8, 10, 12, 14, m = 4, 6 have been synthesized and reported before in our former work [6], but surfactants with m < 4 can not be synthesized by the

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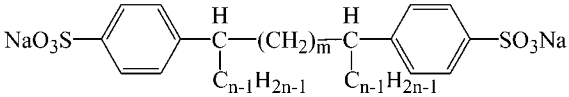


Fig. 1. Chemical structure of the studied anionic Gemini surfactant n–m–n.

same synthesis route [6]. Therefore, another new synthesis route was designed to synthesize sulfonate Gemini surfactants with spacer group length $m < 4$. And, in this article Gemini surfactant with shorter spacer $m = 3$ and alkyl chain length $n = 15$ (15–3–15) was synthesized by this new optimized synthesis route, shown in Scheme 1. Viscoelastic behavior was observed when it solved in aqueous solution, and rheological properties of the solution at different concentrations were studied by rotational rheometer at steady shear model and oscillating shear model, in comparison with polymer aqueous solution.

2. Experiment and method

2.1. Synthesis of alkylbenzene sulfonate Gemini surfactant 15–3–15

The structure and synthesis method of sodium dipentadecyl dibenzene disulfonate with $n = 15$, $m = 3$, marked 15–3–15, are showed in Scheme 1. The main resultants through the synthesis are confirmed by ^{1}HNMR and MS, such as 1, 5-Diphenyl-1, 5-pentanedione, dipentadecyldibenzene, and the final products 15–3–15 (IR: 3040.23 cm^{-1}(Ar-H); 2919.36, 2851.24 cm^{-1}(-CH_2-, -CH_3); 1601.54, 1580.00, 1496.01, 1467.13 cm^{-1}(Ar-C); 1194.34, 1130.90, 1042.36 cm^{-1}(S = O); 832.45 cm^{-1}(p-Ar). ^{1}HNMR (400MHz, D_2O, δ in ppm): 7.60 (d, 4H), 7.00 (d, 4H), 2.30 (m, 2H), 1.14–1.80 (m, 58H), 0.92 (t, 6H). ESI-MS (negative): $m/z = 775.6$ $[M\text{-}2Na+H]^-$, $m/z = 797.6$ $[M\text{-}Na]^-$.).

2.2. Viscoelastic property measurement

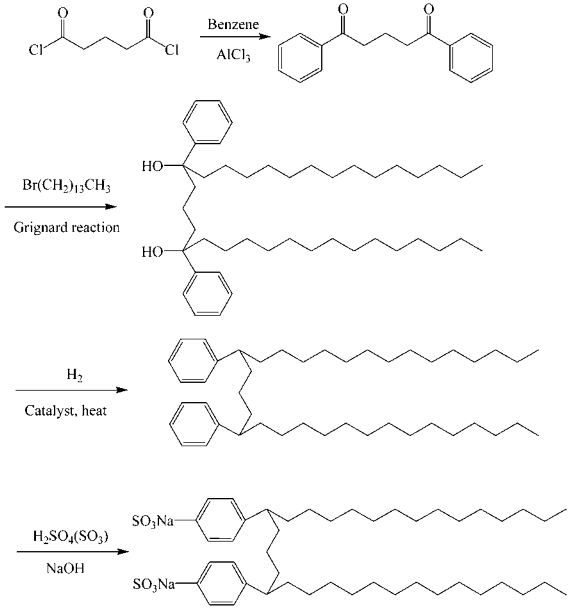
At first, transparent Gemini surfactant 15–3–15 solutions at different concentrations and 0.25 wt% HPAM (Hydrolytic polyacrylamide, molecular weight of 1.2×10^7) solution were prepared in triply distilled water by warmly heating.

2.2.1 Shear-thinning measurements

The steady shear viscosity of 0.01 mol/L 15–3–15 solution and 0.25 wt% HPAM solution were measured at different shear rate by using concentric cylinder rotational rheometer, Brookfield R/S plus Rheometer (rotor of CC 48) , with shear rate control state at room temperature about 30 °C.

2.2.2 Oscillating shear measurements

The oscillating rheological measurements on 15–3–15 solution were carried out on a stress-controlled cone-plate rheometer (Haake MARS II). The cone and



Scheme 1. Synthesis route of dipentadecyldibenzene disulfonate surfactant 15–3–15.

plate are made of Titan steel with a diameter of 60 mm and a cone angle of 1°. The gap between the center of the cone and plate is 0.045 mm and 1 mL sample is needed for a test. The temperature was kept at 30 °C throughout the experiments.

3. Result and discussion

3.1. Viscoelastic behavior

"Weissenberg effect"(the climbing of a viscoelastic liquid up a rotating rod) was observed when stirring at 800 rpm, compared with distilled water at the same rotate speed, which fell down the rotating rod, white arrow in Fig. 2. "Weissenberg effect" is a common phenomenon that occurs in polymer aqueous solution or liquid polymer. The reason for this behavior is that the stresses in the direction of the streamlines and in a direction normal to the streamlines is not equal. The difference between these stresses causes the Gemini micelle solution to climb the rotating rod. "Weissenberg effect" phenomenon was observed before in few mixture surfactants system such as cetyltrimethyl ammonium hydroxide and 2-hydroxy-1-naphthoic acid solution where rod-like micelles were forming [7], this special phenomenon of pure dilute Gemini surfactant was scarcely studied.

Fig. 2. "Weissenberg effect" 0.01 mol/L Gemini surfactant 15–3–15 aqueous solution (right), compared with distilled water (left) at 800 rpm stirring at the room temperature about 30 °C.

"Weissenberg effect" of surfactant 15–3–15 solution indicates its viscoelastic property like polymer aqueous solution.

Different from conventional single chain alkylbenzene sulfonate surfactant solutions with viscosity like water, Gemini surfactant 15–3–15 with short spacer of -C_3H_6- solutions show high viscosity at low concentrations like polymer solutions. According to former research of some conventional single chain cationic surfactant systems mixed with salt [8,9] or some cationic Gemini surfactants with short spacer group [3–5], the viscoelastic behavior of solution is contributed to wormlike micelles formed and entangled in solutions. The molecular packing parameter P is often used to predict shape of aggregate of the surfactant in solution [10,11]. When P = 1/3–1/2, wormlike micelles or entangled micelles are formed. For Gemini surfactant, shorter spacer groups induce P to satisfy proper value and make wormlike micelles form in solution without any other additive. Wormlike micelles can be observed and confirmed by TEM or cryo-TEM [12–15]. The high viscosity of studied alkylbenzene sulfonate Gemini surfactant solution system is also probably due to entangled wormlike or netlike micelles formed in solution system.

3.2 Shear-thinning behaviour

The viscosity of Gemini solution and polymer solution depending on shear rate is show in Fig. 3. Unlike water, the viscosity of both solutions decreases rapidly along with increasing of shear rate in log axis. Fluid model equation

$$\eta = K\gamma^{n-1} \tag{1}$$

where η is apparent viscosity and γ is shear rate, and its transformation

$$\lg\eta = \lg K + (n-1)\lg\gamma \tag{2}$$

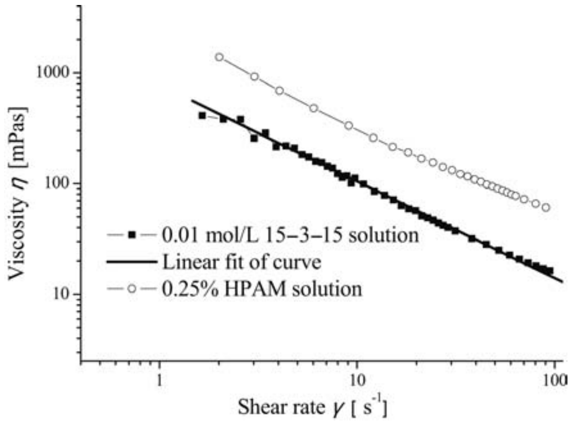


Fig. 3. Dependence of viscosity on shear rate at temperature of 30°C.

can be used to character this non-Newton fluid behavior. Both anionic Gemini surfactant and polymer solution can fit this formula, so we can calculator the constant value of $K = 734.01$, n = 0.184 for 15–3–15, and $K = 2084.49$, n = 0.199 for polymer solution. K indicates how viscous the solution is and n indicates the fluid property. Higher K value means higher viscosity, and the more deviation of n from 1 (value of water) means stronger non-Newton fluid behavior of the solution. The shear-thinning behavior may results from the microstructure change of micelles in this anionic Gemini surfactant solution.

3.4. Oscillating shear measurements

A strain sweep was performed at a frequency of 1Hz (6.28 rad s^{-1}) before the test to make sure that the sample was in the linear viscoelastic region during oscillatory measurements. There is no linear viscoelastic region for the solutions until the concentration reaches 0.0025 mol/L, above which the stress is constant at 0.1 Pa during the oscillating measurements.

Elastic modulus *G'* (storage modulus) and viscous modulus *G"* (loss modulus) of 15–3–15 solutions at different concentrations are shown in Fig. 4. Both modulus increase with increasing concentrations, and for the 15–3–15 solution at 0.0025 mol/L, the viscous modulus *G"* is always above the elastic modulus *G'* in the examined frequencies range, while *G"* is always below *G'* for the solution at 0.05 mol/L, which shows very strong elastic behavior. The two modulus cross in the case of 0.005 and 0.01 mol/L solutions, and the sample exhibits

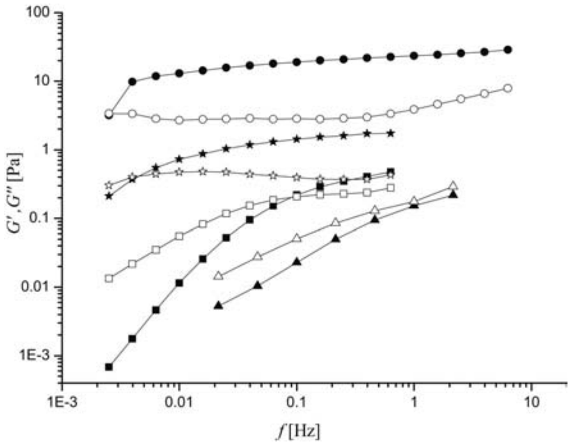


Fig. 4. Variations of *G'* (filled symbols) and *G"* (open symbols) with frequency *f* in 15–3–15 solutions at different concentrations. The symbols represent 0.0025 mol/L (triangles), 0.005 mol/L (rectangles), 0.01 mol/L (pentacle) and 0.05 mol/L (circle), respectively.

elastic behavior at high frequency *f* , whereas at low *f* the sample shows a viscous behavior (*G"* exceeds *G'*).

Besides, the complex viscosity $|\eta^*|$ for surfactant solutions can also be measured simultaneously, shown in Fig. 5. Almost all the studied solutions fit Maxwell fluid model [16–17]. $|\eta^*|$ decreases rapidly at high frequency, and reaches a plateau value at low frequency. Thus the zero-shear viscosity η_0 can be obtained by extrapolating f to the ordinate at $f = 0$ ($\omega = 2\pi f = 0$) [17]. With the increasing concentrations of 15–3–15 solutions, Zero-shear viscosity η_0 increase slowly at first and then rapidly, which is shown in Fig. 6. The increasing viscosity of solution is contributed to more and more wormlike micelles formed and entangled in solutions, but this surfactant won't dissolve well above concentration of 0.05 mol/L at 30 °C.

4. Conclusions

The novel anionic Gemini surfactant with shorter spacer group (-C_3H_6-) was synthesized by a new method and confirmed by IR, ^{1}HNMR and ESI-MS. This anionic Gemini surfactant exhibits special viscoelastic property in dilute solution without additives like polymer aqueous solution. "Weissenberg effect" is observed, which indicates the viscoelastic property of the system. The steady shear viscosity and zero-shear viscosity of solution increase with the concentration growing up and the shear-thinning curves can fit non-Newton fluid model. The 15–3–15 solutions exhibit higher elastic or storage modulus at high concentration at high frequency than viscous or loss modulus, or vice versa.

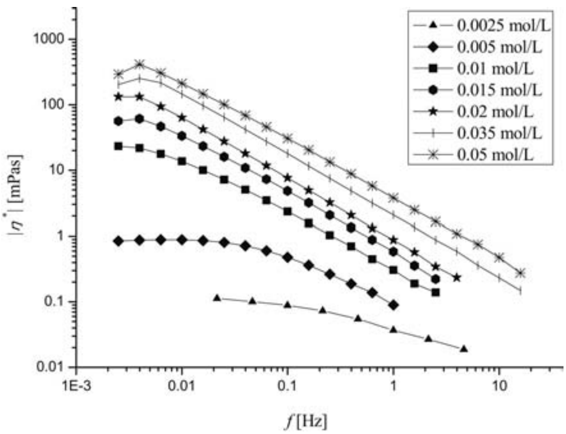


Fig. 5. The complex viscosity $|\eta^*|$ as a function of frequency f for 15–3–15 solutions at different concentrations.

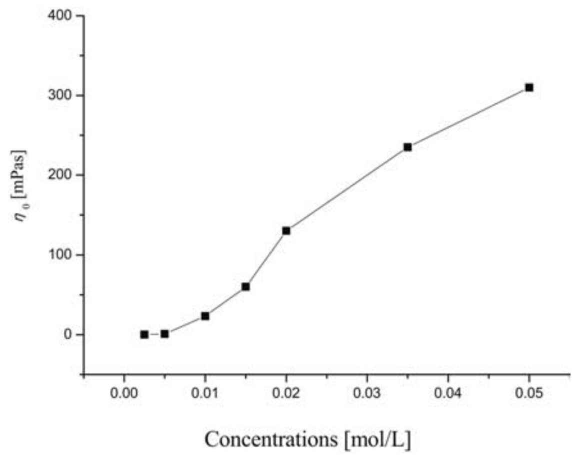


Fig. 6. Zero-shear viscosity η_0 as a function of concentration of 15–3–15 aqueous solution.

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