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ORIGINAL ARTICLE

Synthesis and Properties of 4,4′-Di(*n*-Tetradecyl) Diphenyl Methane Disulfonate Salt

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Abstract The gemini surfactant, sodium 4,4′-di(*n*-tetradecyl) diphenyl methane disulfonate, has been synthesized in four steps with high yield and only one isomer. The structures of intermediate products were analyzed by ^{1}H-NMR spectrometry and elemental analysis. Mass spectrometry was applied to the analysis of the final product. The Krafft point, surface tension, and critical micelle concentration of the aqueous solution and the oil–water interfacial tension were measured. The results indicate that the gemini surfactant exhibits an ultra-low interfacial tension of 7.22×10^{-3} mN/m, which shows potential applications for enhanced oil recovery.

Keywords Gemini surfactant · Clemmensen reduction · Double straight-chain alkyl diphenyl methane · Enhanced oil recovery · Oil–water interfacial tension

Introduction

The typical difference between a gemini surfactant and a traditional surfactant is that a gemini surfactant has two hydrophilic groups and two lipophilic groups, and the amphiphilic groups are linked by spacer chain, while a traditional surfactant only has one hydrophilic group and one lipophilic group. Precisely because of its special structure, gemini surfactants possess some special properties, which make them a hot topic in the field of surfactants in recent years [1–7]. Surfactants flooding began in the 1930s, and they was widely used all over the world because of low investment costs and high returns [8–14].

A gemini surfactant has significantly lower critical micelle concentration (CMC) value and higher surface activity, and it requires lower concentration to form ultra-low interfacial tension, so it is possible to reduce the oil–water interfacial tension efficiently. It also has good solubilization and complexation. There is a great prospect for gemini surfactants in chemically enhanced oil recovery (EOR). Wang et al. [15] reported that gemini surfactants, which have excellent rheological and interfacial properties are expected to replace the alkali in the alkali/surfactant/polymer (ASP) flooding system and reduce the amount or replace the polymer in the system. Zhou et al. [16] mentioned that anionic sulfonate gemini surfactants are widely used in EOR. Anionic sulfonate gemini surfactants not only have the advantage of high cloud point, less adsorption on sandstone surface, high interfacial activity, and good heat resistance, but also optimal economic benefit due to lower costs. Gemini surfactants not only share the properties of polymers in oil flooding, but also the property of traditional surfactant flooding agent, so it has great potential in the field of EOR [17–21].

However, the presence of positional isomers in 4,4′-di(alkyl) diphenyl methane disulfonate salt synthesized by the conventional alkylation reaction results in problems of high interfacial tension and poor surface activity [22, 23]. To identify the relationship between the surfactant structure and properties, a single component product was synthesized using the Clemmensen reduction reaction. The

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pure 4,4′-di(*n*-tetradecyl) diphenyl methane disulfonate salt obtained showed ultra-low interfacial tension.

Experimental Procedures

Materials

Tetradecanoic acid was purchased from Cognis Chemicals (China) Co., Ltd. and purified to greater than 98 %. Diphenyl methane was obtained from Jintan Huakang Fine Chemical Plant and purified to greater than 98 %. Nitromethane, aluminium trichloride, and hydrochloric acid was purchased from Sinopharm Chemical Reagent Co., Ltd. and their purity are all greater than 95 %. Thionyl chloride, zinc, mercuric chloride, and chlorosulfonic acid of analytical grade was purchased from Sinopharm Chemical Reagent Co., Ltd. Chloroform of analytical grade was purchased from Shanghai Reagent Factory. Sodium hydroxide, methyl alcohol, and calcium chloride of analytical grade were purchased from Shanghai Chemical Reagent Co., Ltd. Crude oil having a viscosity of 87.5 mPa S and a density of 0.9342 g cm^{-3} at room temperature was obtained from Shengli Oilfield Gudao Oil Production Plant.

Synthetic Routes and Methods

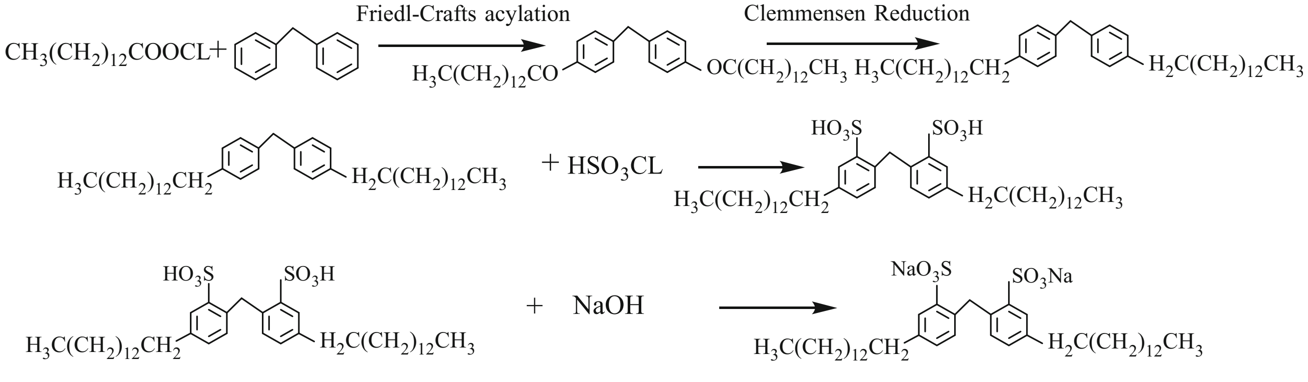
Firstly, tetradecanoyl chloride was synthesized using tetradecanoic acid and thionyl chloride. Then 4,4′-di(*n*-tetradecanoyl) diphenyl methane was produced using diphenyl methane and tetradecanoyl chloride via Friedel–Crafts acylation reaction. After that, by means of Clemmensen reduction [24], sulfonation with chlorosulfonic acid and neutralization with NaOH aqueous solution, the final product was synthesized. The overall synthetic route is shown in Scheme 1.

Synthesis of 4,4′-Di(*n*-Tetradecanoyl) Diphenyl Methane

The reaction was run in a 250 mL three-necked flask with a stirrer, a condenser, and a dropping funnel. A tube containing calcium chloride was connected to the condenser, and the gas absorption device was connected to the tube. Tetradecanoyl chloride used in the experiments was prepared in previous work.

A certain amount of diphenyl methane was weighed quickly and added into the three-necked flask, then an appropriate amount of aluminum chloride was added. A certain amount of tetradecanoyl chloride was added dropwise with the dropping funnel under stirring. The molar ratio of diphenyl methane, tetradecanoyl chloride, anhydrous aluminum chloride, and nitromethane was l:2.5:3.2:6.5. At the beginning, the reaction flask was immersed in an ice bath to ensure the reaction temperature was about 0 °C. The color of reaction liquid changed from colorless to yellow, and aluminum trichloride was gradually dissolved with HCl gas escaping. After the addition of tetradecanoyl chloride was completed (approximately 30 min), the reaction was continued in the ice bath for 20 min. Then, the bath was heated to room temperature, and the reaction was carried out for 24 h. Next, the bath was heated to 70 °C and the reaction continued for 6 h until no additional HCl gas escaped. At this time, the color of reaction liquid became dark green. The reaction liquid was poured into the ice water, which was treated with dilute hydrochloric acid under constantly stirring until the ice was completely dissolved. After the reaction liquid stratified completely, the organic layer was gathered and washed with distilled water several times until pH was about 7. The product yield was 93.4 %.

Purification of the 4,4′-di(*n*-tetradecanoyl) diphenyl methane: The raw product was soaked in ethanol and heated to just boiling. Then, it was concentrated and the



Scheme 1 Schematic for the synthetic preparation of 4,4′-di(*n*-tetradecyl) diphenyl methane disulfonate salt

product was precipitated after the mixture cooled. Afterwards, the product was removed by filtration and treated by vacuum drying (50–60 °C, 0.1 MPa). The purpose was to remove unreacted tetradecanoyl chloride, diphenyl methane, and nitromethane.

Synthesis of 4,4′-Di(*n*-Tetradecyl) Diphenyl Methane

Step 1: Synthesis of zinc amalgam: 50 mL dilute hydrochloric acid solution and 0.85 g mercuric chloride were added to a 200 mL three-necked flask. After the mercuric chloride dissolved completely, 12.2 g zinc was added into the flask under magnetic stirring. The water was removed by filtration after 5 min of stirring.

Step 2: Method of Clemmensen reduction reaction: Clemmensen reduction is a chemical reaction described as a reduction of ketones (or aldehydes) to alkanes using zinc amalgam and hydrochloric acid. The synthetic route is shown in Scheme 2.

Twenty grams of 4,4′-di(*n*-tetradecanoyl) diphenyl methane was added to a 250 mL three-necked flask that was equipped with a mechanical stirrer and a reflux apparatus. An appropriate amount of zinc amalgam prepared in advance and 37.65 mL of hydrochloric acid were then added. The flask was heated until the contents boiled and reacted for 8 h (hydrochloric acid was supplemented several times during the process of the reaction). After cooling overnight, the paraffin-like supernatant was taken out and dried. Finally 4,4′-di(*n*-tetradecyl) diphenyl methane was obtained and the product yield was 91 %.

Purification of the 4,4′-di(*n*-tetradecyl) diphenyl methane: the mixture was extracted with petroleum ether because the product after reduction was soluble. In this way, we removed unreacted 4,4′-di(*n*-tetradecanoyl) diphenyl methane.

Synthesis of 4,4′-Di(*n*-Tetradecyl) Diphenyl Methane Disulfonate Salt

Seventeen grams of 4,4′-di(*n*-tetradecyl) diphenyl methane and 51 g chloroform were added to a 250 mL three-necked flask equipped with a mechanical stirrer and a reflux apparatus. Chlorosulfonic acid (7.07 g) was then added slowly at room temperature, and the reaction lasted for 6 h after the addition was complete [25]. The appropriate amount of NaOH solution (10 %) was added in order to adjust the pH to 9–10 and the product was distilled at atmospheric pressure to remove the solvent and water. The mass fraction of active matter was 90 % after it was dried.

Characterization of the Product

Analysis and Characterization of 4,4′-Di(n-Tetradecyl) Diphenyl Methane

The resulting product was subjected to elemental analysis using an Elementar Vario ELIII elemental analyzer (two main elements are hydrogen and carbon). The results were compared with the theoretical value to ascertain whether the desired product was obtained. ^{1}H-NMR spectra was recorded on a Bruker 400 MHz instrument with $CDCl_3$ as solvent.

Analysis and Characterization of 4,4′-Di(n-Tetradecyl) Diphenyl Methane Disulfonate Salt

Mass spectral peak of the sample was measured via an electron impact (EI) method with water as substrate. The equipment used was a Waters Platform ZMD 4000 mass spectrometer.

Surface Properties

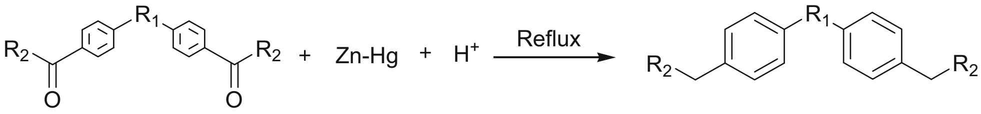
Measurement of Krafft Point (T_k)

The T_k of the gemini surfactant was measured using the electrical conductivity method. A 0.1 g sample was charged to a 20 mL bottle and dissolved in 9.9 g ultrapure water to prepare a 1 wt % solution. The solution was placed in a refrigerator in a sealed bottle and the temperature maintained at about 1 °C. Once the solution appeared cloudy, the solution was left refrigerated for more than 1 day. The solution containing precipitate was placed in a cold water bath and the initial temperature was set at 0–2 °C. After the temperature of the bath stabilized, it was heated up at intervals of 2 °C until the solution became clear and transparent, and the conductance (K) was determined during the progress [26].

Measurement of Surface Tension

A series of concentrations of 4,4′-di(*n*-tetradecyl) diphenyl methane disulfonate salt aqueous solutions were prepared with ultrapure water [27]. The surface tension was measured

Scheme 2 Schematic for the Clemmensen reduction



with a DCA-315 Automatic Interfacial Tension Meter (Thermo Cahn Co., USA) by the pendant drop method at 45 °C. CMC of the product was obtained by means of surface tension method.

Measurement of Interfacial Tension

The interfacial tension of the sample solution was measured using a Dataphysics SVT20N Spinning Drop Interface Tensiometer [28]. The spinning drop method is based on a balance of centrifugal and interfacial tension forces. It has a wide range of measurement, 1 × 10^{-6}–2 × 10^{3} mN/m. Aqueous phase: the sample aqueous solution of 0.3 % mass fraction with 300 mg/L hard water and 6 g/L salinity was prepared. Hydrocarbon phase: crude oil.

Results and Discussion

Characterization of the Product

Analysis and Characterization of 4,4′-Di(n-Tetradecyl) Diphenyl Methane

The ^{1}H-NMR spectra is shown in Fig. 1 (400 MHz,$CDCl_3$). δ 7.07–7.24 (m, 8 H, hydrogen of benzene), 3.90 (s, 2 H, hydrogen of benzene), 2.52–2.58 (t, $J = 7.6$ Hz, 4 H, hydrogen of carbon chain benzyl), 1.55–1.60 (m, $J = 7.3$ Hz, 4 H, β hydrocarbon of carbon chain), 1.25–1.30 (br, 44 H, long chain hydrocarbon), 0.85–0.90 (t, $J = 6.9$ Hz, 6 H, terminal hydrogen of long carbon chain) [29]. The spectra are consistent with the structure 4,4′-di(*n*-tetradecyl) diphenyl methane.

The molecular formula of the alkylated product is $C_{45}H_{76}$. The experimental value and (theoretical value) of the elemental analysis are: C 87.58 (87.66); H 12.34 (12.44). The data show that the C and H percentages are close to the theoretical values, thus we can further confirm that the product is 4,4′-di(*n*-tetradecyl) diphenyl methane.

Analysis and Characterization of 4,4′-Di(n-Tetradecyl) Diphenyl Methane Disulfonate Salt

Figure 2 is the mass spectrum analysis of 4,4′-di(*n*-tetradecyl) diphenyl methane disulfonate salt. From Fig. 2, $m/z = 741.29$ $[M\text{-}Na]^-$ is evidence for the existence of disubstituted monosodium salt; $m/z = 359.14$ $[M\text{-}2Na]^{2-}$, $m/z = 639.37$ $[M\text{-}SO_3Na_2]^-$ suggest the disubstituted disodium salt. Thus, we can conclude that the main product is disulfonate salt after sulfonating.

Surface Chemical Properties

Krafft point (T_k) is the temperature (more precisely, narrow temperature range) above which the solubility of a surfactant rises sharply. At this temperature the solubility of the surfactant is equal to the critical micelle concentration. It is best determined by locating the abrupt change in slope

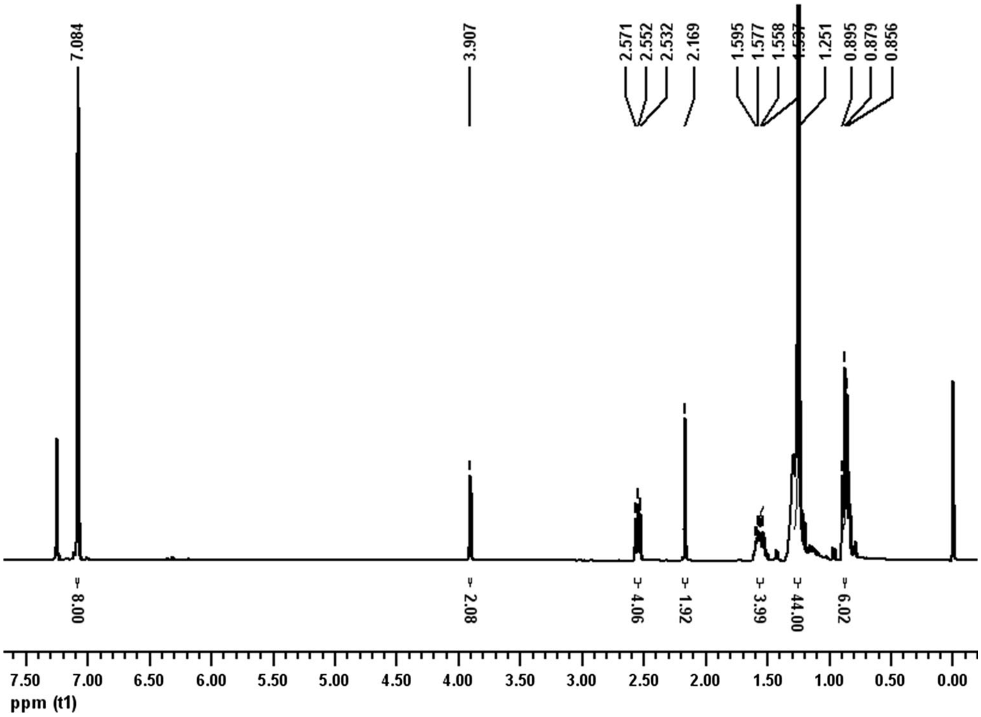


Fig. 1 ^{1}H-NMR of 4,4′-di(*n*-tetradecyl) diphenyl methane

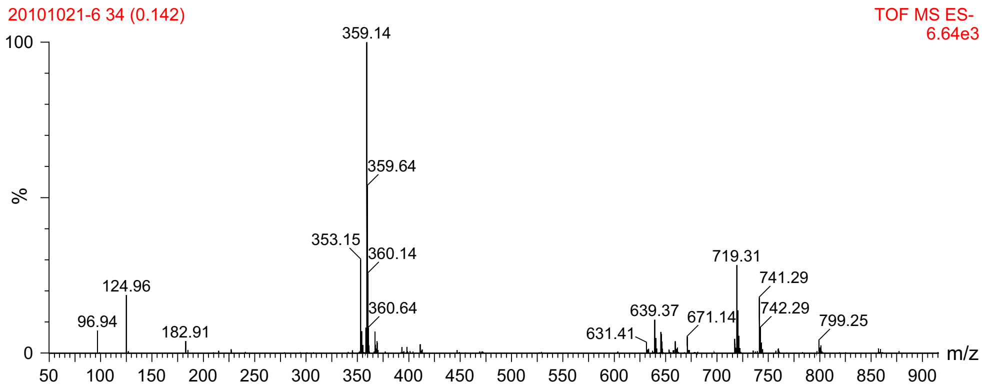


Fig. 2 MS of 4,4′-di(*n*-tetradecyl) diphenyl methane disulfonate salt

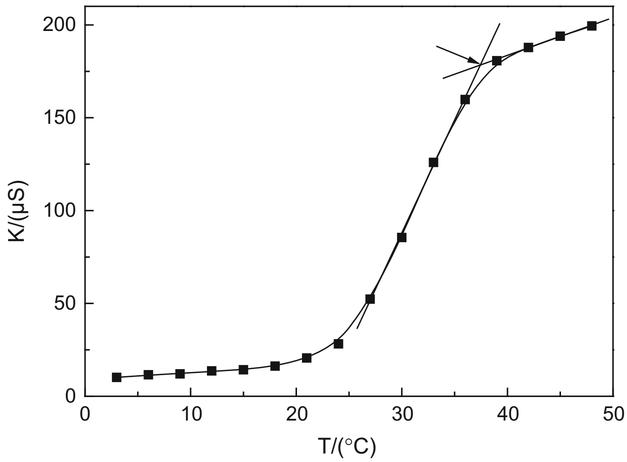


Fig. 3 Determination of the Krafft point of C_{14}-DSDM

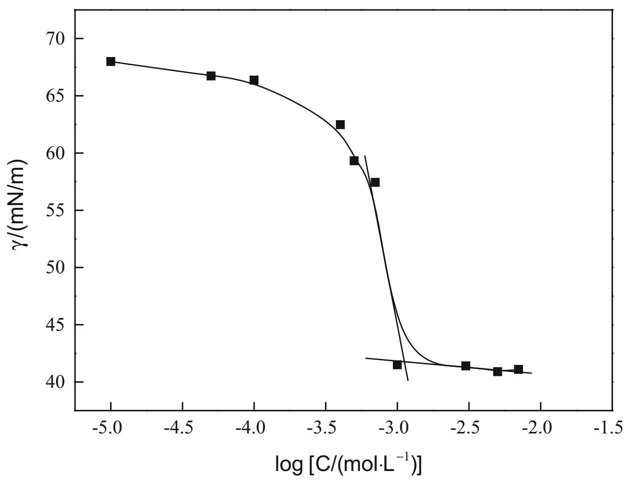


Fig. 4 Surface tensions of C_{14}-DSDM aqueous solutions at different concentrations at 45 °C

from a graph of the conductance *K* against *T*. Figure 3 shows the conductance *K* versus *T* plot of 1 wt % C_{14}-DSDM aqueous solution. We can see an obvious break, which usually coincides with the temperature of full clarification of the system, and the temperature corresponding to the break is the value of T_k. As shown in Fig. 3, the Krafft point of C_{14}-DSDM (4,4′-di(*n*-tetradecyl) diphenyl methane disulfonate salt) is found to be 37.6 °C.

Surface Tension and CMC

The surface tension of C_{14}-DSDM was measured with a DCA-315 Automatic interfacial tension meter by the pendant drop method at 45 °C. γ versus log *C* curves are shown in Fig. 4.

The surface adsorption on the surfactant aqueous solution is essentially the change of chemical composition on the outermost surface of the solution, and it is a process of water molecules that have a strong force gradually being replaced by non-polar groups. When the concentration of the solution increases, the surface adsorption also increases on the surfactant aqueous solution, and the space occupied by non-polar groups on the surface also increases. Therefore, the surface tension of aqueous solution gradually reduces when concentration increases. The chemical composition on the outermost surface of the solution no longer changes when concentration increases to a certain value, at this time, surface tension of the solution no longer changes [30]. CMC and the surface tension at the CMC (γ_{cmc}) are two major parameters to characterize the surface activity of a surfactant and they are determined from the breakpoint of the surface tension isotherm. As is shown in Fig. 4, the CMC of C_{14}-DSDM at 45 °C is 1.00×10^{-3} mol/L, which is much smaller than that of sodium dodecyl sulfate (SDS) 8.7×10^{-3} mol/L. The surface tension of C_{14}-DSDM at the CMC is 41.4 mN/m which is high compared to SDS [31].

Interfacial Tension

Surfactant molecules easily gather at the water–oil interface. When the concentration of surfactant on the interface

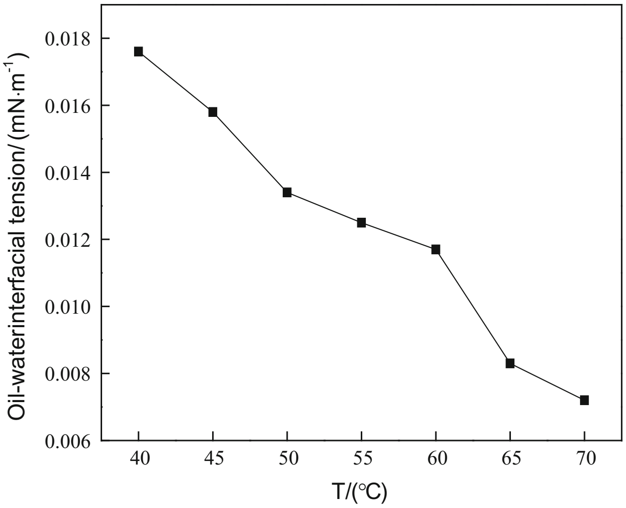


Fig. 5 Oil–water interfacial tension of C_{14}-DSDM at different temperature

is very small, the molecules can lie flat on the interface [32]. The decrease of interfacial tension is caused by the adsorption of surfactant molecules at the water/oil interface. It usually takes time for surfactant molecules to diffuse and adsorb at the interface. Therefore, the dynamic interfacial tension will change over time [33]. Dynamic interfacial tension often shows the lowest point corresponding to the maximum amount of interfacial adsorption.

Aqueous samples of C_{14}-DSDM gemini surfactant were prepared in 300 mg/L hard water and 6 g/L salinity base solution. The interfacial tensions between the solution and crude oil were measured over a range of temperatures. The most important thing worth attention here is that the solution had an extremely high salinity (6 g/L) and a high degree of mineralization (300 mg/L). Even under this extreme condition, no precipitation or phase separation happened for any of the test temperatures. In contrast, conventional (monomeric) surfactants used in the petroleum industry today generally show poor aqueous solubility/stability under such harsh conditions (high mineralized degree or salinity). Thus, complex surfactant formulations are studied in which a co-surfactant and/or co-solvent are added to enhance the solubility [34]. This unfortunately generates a lot of issues, including design complexity, elevated cost, and chromatographic separation [35].

The gemini surfactants synthesized in the current study have shown extraordinary tolerance to salinity and degree of mineralization. The interfacial tension (IFT) versus temperature plot for the gemini surfactants are shown in Fig. 5. As shown in Fig. 5, interfacial tension decreases with increasing temperature, and the interfacial tension of C_{14}-DSDM can reach as low as 7.22×10^{-3} mN/m at 70 °C, which indicates that the novel gemini surfactants are capable of reducing the interfacial tension to ultra-low levels even at extremely high salinity and high degree of mineralization, and it promises the basis for future exploitation of oil fields.

Conclusion

4,4′-Di(*n*-tetradecanoyl) diphenyl methane was produced by using diphenyl methane and tetradecanoyl chloride as raw materials by a Friedel–Crafts acylation reaction. Then by means of the Clemmensen reduction, sulfonation with chlorosulfonic acid and neutralization with NaOH aqueous solution, the final product was synthesized.

The CMC of 4,4′-di(*n*-tetradecyl) diphenyl methane disulfonate salt aqueous solution is 1.00×10^{-3} mol/L, and its surface activity is good enough. The interfacial tension of 4,4′-di(*n*-tetradecyl) diphenyl methane disulfonate salt aqueous solution reaches ultra-low values suggesting t is a suitable surfactant for EOR applications.

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References

1. Zhu YP, Masuyamarn A, Kobata Y (1993) Double-chain surfactants with two carboxylate groups and their relation to similar double-chain compounds. J Colloid Interf Sci 158:40–45
2. Zhang YM, Zhu H, Xia JH (2007) Synthesis of sulfonate gemini surfactant and its application in tertiary oil recovery. J Beijing Jiaotong Univ 31:101–103
3. Wang LY, Liu J, Huo SC (2014) Synthesis and surface properties of novel gemini imidazolium surfactants. J Surfactants Deterg 17:1107–1116
4. Kumar N, Tyagi R (2015) Synthesis and surface studies of anionic gemini surfactant in the different counter-ions. Int J Ind Chem 6:59–66
5. Zhuang LH, Yu KH, Wang GW (2013) Synthesis and properties of novel ester-containing gemini imidazolium surfactants. J Colloid Interf Sci 408:94–100
6. Lai L, Mei P, Wu XM (2014) Micellization of anionic gemini surfactants and their interaction with polyacrylamide. Colloid Polym Sci 292:2821–2830
7. Tiwari AK, Sonu Sowmiya M (2012) Micellization behavior of gemini surfactants with hydroxyl substituted spacers in water and water-organic solvent mixed media: the spacer effect. J Mol Liq 167:18–27
8. Shah DO (1981) Surface phenomena in enhanced oil recovery. Springer, New York
9. Xu HJ, Ye ZW, Lv CX (2004) Synthesis and properties of a kind of anionic gemini surfactant. J East China Univ Sci Technol 22:33–37
10. Ahmadi MA, Zendehboudi S, Shafiei A (2012) Nonionic surfactant for enhanced oil recovery from carbonates: adsorption kinetics and equilibrium. Ind Eng Chem Res 51:9894–9905

11. Kamal MS, Sultan AD, Al-Mubaiyedh UA (2014) Evaluation of rheological and thermal properties of a new fluorocarbon surfactant-polymer system for EOR applications in high-temperature and high-salinity oil reservoirs. J Surfactants Deterg 17:985–993
12. Zhou M, Zhao JZ, Wang X (2013) Research on surfactant flooding in high-temperature and high-salinity reservoir for enhanced oil recovery. Tenside Surfactants Deterg 50:175–181
13. Ahmadi MA, Arabsahebi Y, Shadizadeh SR (2014) Preliminary evaluation of mulberry leaf-derived surfactant on interfacial tension in an oil-aqueous system: EOR application. Fuel 117:749–755
14. Ma BD, Gao BY, Zhang L (2014) Influence of polymer on dynamic interfacial tensions of EOR surfactant solutions. J Appl Polym Sci 131:40562
15. Wang HF, Yang Y, Zhang GY (2003) Application prospect of novel gemini surfactants in tertiary oil recovery. Pet Geol Recovery Effic 10:59–61
16. Zhou YW, Han F, Xu BC (2010) Research progress of anionic gemini surfactant. Chemical World 6:375–379
17. Benko M, Puskas S, Kiraly Z (2013) Application of mass spectrometry for study of the adsorption of multicomponent surfactant mixtures at the solid/solution interface. Adsorption 19:71–76
18. Guo YJ, Liu JX, Zhang XM (2012) Solution property investigation of combination flooding systems consisting of gemini-nonionic mixed surfactant and hydrophobically associating polyacrylamide for enhanced oil recovery. Energ Fuel 26:2116–2123
19. Gao B, Sharma MM (2013) A family of alkyl sulfate gemini surfactants. 2. Water–oil interfacial tension reduction. J Colloid Interf Sci 407:375–381
20. Zhang R, Zhou JW, Peng L (2013) The wettability alteration behavior of cationic gemini surfactants on oil-aged mica mineral surfaces. Tenside Surfactants Deterg 50:214–218
21. Wei H, Wei L, Yin JH (2010) Fractal applications in fluid mechanics of enhancing oil recovery from low-permeability oil reservoirs by gemini surfactant flooding. Appl Mech Mater 29–32:163–169
22. Alul HR, Clark SG and Mcewan GJ (1967) Alkyl aryl process. US Patent 3,349,144
23. Alul HR (1968) Control of isomer distribution of straight-chain alkylbenzenes. Ind Eng Chem Prod Res Dev 7:7–11
24. Zhang X, Ma GW, Chen T (2007) Preparation of 2,7-dibromo fluorene by reduction of 2,7-dibromo fluorenone with zinc amalgam and hydrochloric acid. Fine Chem 10:932–935
25. Yu T, Hu LJ, Ding W (2004) A new surfactant-synthesis and properties of dialkyl disulfonate diphenyl dethane. J Daqing Pet Inst 28:35–38
26. Zana R (2002) Alkanediyl-α, ω-bis(dimethylalkylammonium bromide) surfactants: II. Krafft temperature and melting temperature. J Colloid Interface Sci 252:259–261
27. Rosen MJ (1993) Gemini: a new generation of surfactants. Chemtech 23:30–34
28. Vonnegut B (1942) Rotating bubble method for the determination of surface and interfacial tensions. Rev Sci Instrum 13:6–9
29. Huang H, Mao SC (2007) Fine chemicals commonly used instrument analysis. South China Univ Technol Press, Guangzhou
30. Szyszkowski BV (1908) Surface tension of the aqueous surfactant solution. Z Phys Chem 64:385
31. Evans HC (1956) Critical micelle concentrations of the sodium salts. J Chem Soc 80:579–586
32. Aguiar HB, Strader ML, Beer AGF (2011) Surface structure of sodium dodecyl sulfate surfactant and oil at the oil-in-water droplet liquid/liquid interface: a manifestation of a nonequilibrium surface state. J Phys Chem B 115:2970–2978
33. Yuan QS (2003) Study of dynamic interfacial tension characteristic and its influencing factors. Pet Geol Recovery Effic 10:60–61
34. Liu S, Zhang DL, Yan W (2008) Favorable attributes of alkaline surfactant polymer flooding. SPE J 13:2–6
35. Hirasaki G, Miller CA, Puerto M (2008) Recent advances in surfactant EOR. SPE J 16:889–907

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