

# Cleaning Oil-Based Drilling Cuttings with Synthetic Gemini Surfactants

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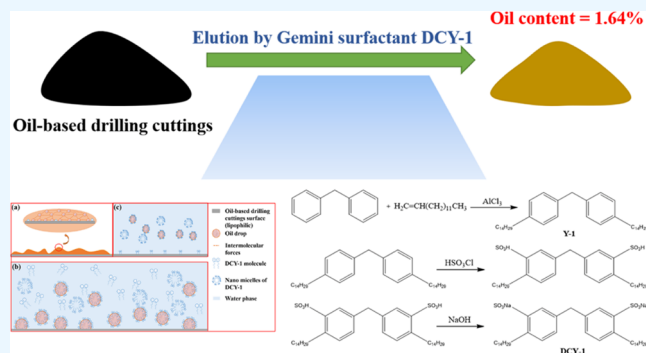
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**ABSTRACT:** The chemical cleaning method is the simplest approach for degreasing oil-based drilling cuttings (ODCs), with the effectiveness of the treatment relying mainly on the selection of the surfactant and the cleaning conditions. However, achieving the standard treatment of ODCs directly using conventional surfactants proves challenging. In light of this, this study introduces a synthesized and purified Gemini surfactant named DCY-1. The structure of DCY-1 was confirmed through Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) analyses. The characterization in this article encompasses the use of an interface tension meter, nanoparticle size analysis, scanning electron microscopy, and infrared oil measurement. The critical micelle concentration (CMC) of DCY-1 was determined to be  $3.37 \times 10^{-3}$  mol/L, with a corresponding  $\gamma_{\text{cmc}}$  value of 37.97 mN/m. In comparison to conventional surfactants, DCY-1 exhibited a larger micelle size of 4.52 nm, approximately 24.52% larger than that of SDS. Moreover, the residual oil rate of 3.96% achieved by DCY-1 was the lowest among the chemical cleaning experimental results. Through a single-factor experiment, the optimal cleaning ability of DCY-1 for ODCs was determined as follows: a surfactant concentration of 3 mmol/L, a temperature of 60 °C, an ODC/liquid mass ratio of 1:4, a cleaning duration of 40 min, and a stirring speed of 1000 rad/min. Under these optimal conditions and after merely two cleaning procedures, the residual oil content of ODCs was reduced to 1.64%, accompanied by a smooth and loose surface structure.



## 1. INTRODUCTION

Compared to conventional oil and gas resources, shale gas is set to assume a pivotal role in the energy transition, owing to its wide distribution and comparatively cleaner nature.<sup>1</sup> To increase production from shale gas reservoirs, a combination of fracturing technology and horizontal wells is commonly utilized,<sup>2,3</sup> with the extensive use of oil-based drilling fluids due to their exceptional stability.<sup>4</sup> As shale gas extraction is expanding, the volume of oil-based drilling cuttings (ODCs) generated during drilling operations is also escalating.<sup>5</sup> Presently, the generation of ODCs has evolved into an environmental concern encountered by oilfields worldwide. Improper management of ODCs not only leads to resource wastage but also poses a severe threat to the ecological environment.<sup>6–8</sup> Chemical cleaning has emerged as a favored and widely acknowledged method for treating an ODC, primarily due to its simplicity, minimal equipment requirements, and cost-effectiveness. The efficacy of the surfactant and the establishment of appropriate washing conditions significantly impact the ultimate oil removal effectiveness in the chemical cleaning treatment of ODCs.

As the chemical cleaning method serves as an oil removal technique, it is crucial to characterize the oil-based drill chips,

including their oil and water contents as well as their structure. Additionally, evaluating surfactant properties such as the critical micelle concentration (CMC), emulsification capacity, and micelle size is crucial.<sup>9</sup> Notably, surfactants that exhibit a greater ability to reduce interfacial tension tend to enhance oil removal efficiency.<sup>10</sup> Moreover, a higher surface activity is directly associated with higher oil recovery rates.<sup>11</sup>

The removal of oil from the surface of drilling cuttings through surfactant action involves diffusion and solubilization processes. First, when the concentration of the surfactant is lower than the CMC, the surfactant exists in the form of a monomer. Surfactants are amphiphilic molecules, and this dual nature causes surfactants to adsorb at the oil–water interface, thereby reducing the oil–water interfacial tension.<sup>12</sup> Surfactant molecules penetrate into the junction of drilling cuttings and

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oil, destroying the mutual bonding between drilling cuttings and oil, achieving the purpose of oil and drilling cutting separation. Second, the concentration of the free monomer no longer increases and a large number of micelles are produced when the surfactant concentration is above the CMC. These micelles will encapsulate the oil droplets that enter the aqueous phase.<sup>13</sup>

Conventional surfactants consist of one terminal hydrophilic group and one hydrophobic group.<sup>14</sup> Gemini (or dimeric) surfactants are a relatively novel class of surfactants, which consist of more than one intermediate polarity group (as a spacer chain) chemically connected between two basic surfactant entities consisting of a hydrophobic tail and a hydrophilic head.<sup>15–17</sup> The spacer may be short or long, rigid or flexible; and the two nonpolar tails may be short or long. The polar head groups can be cationic, anionic, nonionic, or zwitterionic, depending on the nature of the corresponding single-chain surfactant(s).<sup>18</sup> Unlike conventional surfactants, which form spherical micelles in bulk solution, Gemini surfactants are capable of forming threadlike (short-spacer) or rodlike (long-spacer) micelles. The presence of two hydrophobic tail groups and two hydrophilic polar heads confers enhanced surface-active properties and the ability to self-aggregate at low concentrations.<sup>19,20</sup> The CMC of Gemini surfactants is 1–2 orders of magnitude lower than that of analogous surfactants. In addition, Gemini surfactants exhibit better rheology and a low concentration requirement in comparison to conventional monomeric surfactants. Since Gemini surfactants have two hydrophilic groups, they often show increased water solubility and they are salt-resistant.<sup>21</sup> The molecular weight of Gemini surfactants falls between those of traditional and polymeric surfactants.<sup>22</sup> Gemini surfactants have been generating increasing interest owing to their tunable molecular geometry and their excellent performance in applications.<sup>23</sup> They are expected to become widely used in the 21st century.<sup>24,25</sup>

In summary, the distinctive molecular structure of Gemini surfactants imparts notable stability, hydrophobic (oil-absorbing) properties, and a superior emulsification performance when compared with conventional surfactants. As a result, Gemini surfactants exhibit significant potential for enhancing the cleaning of ODCs. However, their widespread utilization is hindered by challenges related to commercial availability, limited entrepreneurial efforts, and a relatively short industry experience, particularly concerning chemical cleaning treatments for ODCs.

To enhance the effectiveness of chemical cleaning methods, an anionic Gemini surfactant was synthesized and purified using diphenylmethane and 1-tetradecene as primary raw materials for ODC treatment. Compared to conventional surfactants, the synthesized surfactant demonstrated a superior cleaning performance, showcasing promising practical applications. This work meticulously investigates the influence of various conditions on the ODC cleaning efficiency of the DCY-1 surfactant. The results indicate that DCY-1 effectively meets the relevant standards for the ODC disposal. This study contributes to a deeper understanding of the Gemini surfactant performance, offering theoretical guidance for their practical application.

## 2. MATERIALS AND METHODS

**2.1. Materials.** The ODCs in this study were collected from the shale gas exploitation base in Sichuan Province.

ODCs consisted of 10.69 wt % oil, 8.86 wt % water, and 80.45 wt % solids.

Diphenylmethane, chlorosulfonic acid, anhydrous calcium chloride, anhydrous sodium sulfate, potassium bromide, and deuterated chloroform were obtained from Aladdin. 1-Tetradecene, anhydrous aluminum trichloride, Tween 80, and tetrachloroethylene were obtained from Macklin. Trichloromethane and Triton X-100 were obtained from Sinopharm Group Chemical Reagent Co., Ltd. NaCl, H<sub>2</sub>SO<sub>4</sub>, NaOH, KMnO<sub>4</sub>, sodium dodecylbenzenesulfonate (SDBS), sodium dodecyl sulfate (SDS), fatty alcohol polyoxyethylene ether (AEO-9), and OP-10 were supplied by Kelong Chemical Co., Ltd., Chengdu, China.

**2.2. Apparatus.** The WQF-520 FTIR spectrometer was used to preliminarily characterize the structure of the synthesized products according to the characteristic absorption peaks of different groups. The scanning range was 4000–440 cm<sup>-1</sup>, and the number of scans was 16 times. The NMR spectrometer was used to determine the molecular structure. Deuterated chloroform was used as the solvent. The synthesized product was characterized by <sup>1</sup>H NMR spectroscopy. The integrated interface parameter measurement system was mainly used to evaluate the performance of DCY-1. The size of the micelles was determined by measuring the hydrodynamic diameter by dynamic light scattering (DLS). A freeze-dryer was used to dry the ODCs. An infrared oil meter was used to determine the oil content of the ODCs. A magnetic stirring water bath was used to clean the ODCs. Scanning electron microscopy (SEM) was used to observe the microstructure and outer surface of the ODCs.

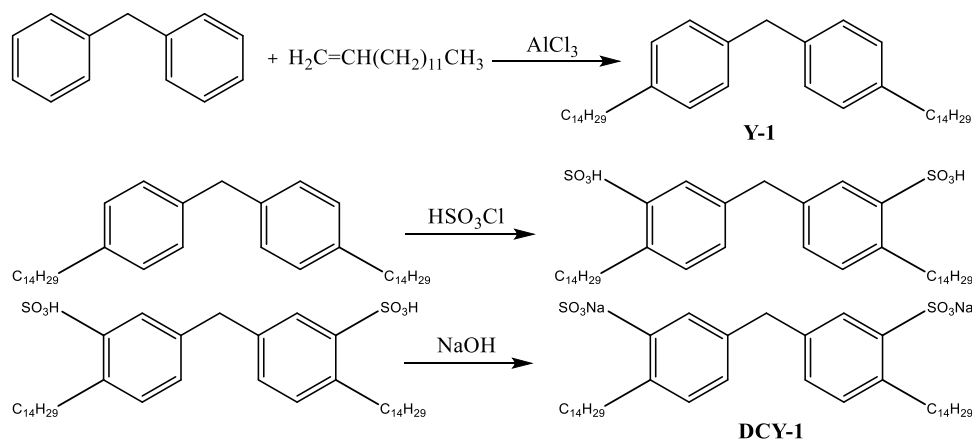
**2.3. Synthesis of DCY-1.** **2.3.1. Preparation of the Intermediate Product.** Diphenylmethane (0.1 mol) was added to the flask, and then anhydrous aluminum trichloride (0.01 mol) was rapidly added as a catalyst; the mixture was fully stirred in a water bath (45 °C). 1-Tetradecene (0.2 mol) was continued to be slowly added dropwise to the flask for about 30 min. After the dropwise addition, the reaction was carried out in a water bath (80 °C) for 6 h. After the reaction, the product was transferred to a 500 mL separatory funnel and washed repeatedly with pure water until neutral, the lower water layer was released, and the upper oil phase was the target product called Y-1.

**2.3.2. Preparation of the DCY-1 Surfactant.** Y-1 (0.1 mol) and chloroform (0.2 mol) were added to the three-necked flask and stirred well in a water bath (20 °C). Chlorosulfonic acid (0.4 mol) was continued to be slowly added dropwise to the three-necked flask for about 30 min. After the dropwise addition, the reaction was continued for 4 h. After the reaction, 20% NaOH solution was slowly added dropwise until the pH value of the reaction system was about 8 to obtain the target product DCY-1.

**2.3.2.1. Purification.** Dichloromethane was used to dissolve the product. The dissolved product was transferred to a separatory funnel, washed with saturated sodium chloride solution many times, and the lower water layer was discharged. After the sample was cleaned, anhydrous sodium sulfate was added to remove water. After the water was removed, the product was suction-filtered and put into a chicken heart bottle, and then the organic solvent was removed using a rotary evaporator. After taking it out, it was dried in a vacuum desiccator at 50 °C for 24 h to obtain the purified surfactant product.

The primary reaction process is depicted in [Scheme 1](#).

Scheme 1. Systematic Diagram for DCY-1



**2.4. Performance Characterization.** **2.4.1. Determination of the CMC.** The surface tension  $\gamma$  and the CMC were measured by the hanging drop method and the interface parameter integrated measurement system.

Values of the surface tension per concentration were the weighted averages of three different means measured in 10 s time-lapses. After plotting the relationship between surface tension and surfactant concentration, two regression lines were obtained, which were the regression line of decreasing surface tension before the CMC and the regression line of stable surface tension after the CMC. The CMC was determined by obtaining the intercept point between the two regression lines.<sup>26</sup>

**2.4.2. Determination of Emulsifying Ability.** The emulsifying force was measured by the graduated cylinder method. The experimental temperature was controlled at 25 °C, taking an appropriate amount of the surfactant and pure water to prepare a 0.1% surfactant solution. 20 mL of surfactant solution was transferred to a 100 mL stoppered measuring cylinder, and then 20 mL of diesel oil was pipeted into the stoppered measuring cylinder. After the stoppered measuring cylinder was squeezed tightly with the glass stopper, the measuring cylinder was vigorously vibrated up and down five times and then allowed to stand for 1 min after the last vibration. The above operation was repeated five times, and timing was started after the last vibration. The emulsion was observed, at which point the oil and water gradually separated. When the water phase increased to 10 mL, it could be regarded as the end point of the experiment; the timing was stopped, the time was recorded, and the measurement was done three times to get the average value.

**2.4.3. Determination of Surfactant Micelle Size.** The size of the micelles was determined by measuring the hydrodynamic diameter by DLS (Malvern Zetasizer Nano ZS90, Malvern Instruments Limited, U.K.). The surfactant concentrations used were higher than the CMC to ensure monodispersity of the sample (i.e., the homogeneous presence of micelles after the CMC). After the size of the micelles was determined, the polydispersity index, PDI (a dimensionless width parameter of the size distribution of the micelle sizes), was obtained per sample.

**2.4.4. Experiment of the Chemical Cleaning Method.** An appropriate amount of surfactant was weighed in a beaker, and quantitative pure water was added. The ODCs were treated

with the formulated surfactant solution, and each set of experiments was set up in 3 parallels.

10 g of ODCs was weighed into a 100 mL beaker, the ODC/liquid mass ratio was set to 1:5, with a cleaning temperature of 50 °C, and cleaning under magnetic stirring was performed for 30 min at a stirring speed of 1000 rad/min with a magnetic stirring water bath. After cleaning, the rotor was taken out, allowed to stand for 1 h, and then a plastic dropper was used to suck out the upper layer of the liquid. After that, the drilling cutting residue and cleaning water were separated by the centrifugation process with a high-speed centrifuge. After that, the residue of the drilling cuttings was processed by a freeze-dryer to reach a constant weight, and the oil content was measured using an automatic infrared oil spectrometer.

**2.4.5. Analysis of Cleaning Ability.** The ODCs were treated by the chemical cleaning method. The mixture was stirred in a constant temperature shaker at different speeds and constant temperatures for a period of time.

After each cleaning, the conical flask was allowed to stand for 1 h. The upper oil layer was then recovered, and the cleaning water was removed from the conical flask. Then, the drilling cutting residue and cleaning water were separated by the centrifugation process with a high-speed centrifuge. After that, the residue of the drilling cuttings was processed by a freeze-dryer to reach a constant weight, and the oil content was measured using an automatic infrared oil spectrometer. This value was the residual oil rate of the ODCs after treatment.

The oil removal rate was estimated, as represented in eq 1:

$$\text{oil removal rate} = \frac{w_1 - w_2}{w_1} \times 100\% \quad (1)$$

Here,  $w_1$  (%) was the oil rate of the original ODC sample and  $w_2$  (%) was the oil rate of the residual drilling cutting sample after cleaning.

**2.5. Analytical Method.** The morphology and the outer surface of solid particles were observed using the scanning electron microscopy (SEM) method. The ODCs were plated with gold in a vacuum chamber before SEM.

## 3. RESULTS AND DISCUSSION

### 3.1. Structural Characterization. 3.1.1. FTIR Spectrum.

In order to explore the structural changes of the synthesized products, FTIR spectroscopy was used for characterization, and the results are shown in Figure 1.

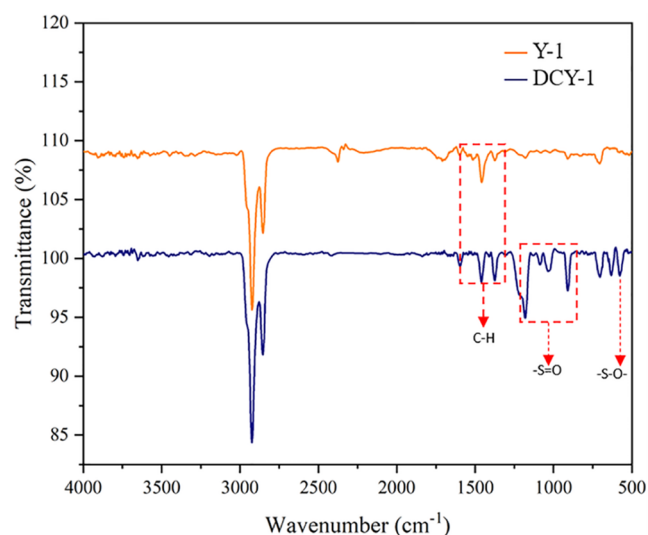


Figure 1. FTIR spectrum of DCY-1.

It can be seen that the strong absorption peaks of Y-1 at wave numbers 2924 and 2854  $\text{cm}^{-1}$  are C–H stretching vibration peaks, the absorption peaks at wavenumber 1460  $\text{cm}^{-1}$  are C–H vibrational absorption peaks on the aromatic ring, and the absorption peaks at wavenumber 1380  $\text{cm}^{-1}$  are methyl bending vibration peaks. The absorption peak at wavenumber 707  $\text{cm}^{-1}$  is the absorption peak of the para-substituted group of the aromatic ring. From the spectrum, it is clear that the alkylation reaction of diphenylmethane with 1-

tetradecene resulted in the addition of long alkyl chains to the para-aryl-ring methylene to produce Y-1, which is consistent with the expected intermediate product.

In comparison with the spectrum of Y-1, DCY-1 has an additional C–H vibrational absorption peak at a wavelength of 1600  $\text{cm}^{-1}$  on the aromatic ring. The absorption peaks of DCY-1 at 1181, 1086, and 1040  $\text{cm}^{-1}$  are –S=O stretching vibrational absorption peaks, the absorption peaks at wave numbers 909 and 707  $\text{cm}^{-1}$  are characteristic peaks of the benzene ring adjacent to the para-position, and the absorption peak at wavenumber 630  $\text{cm}^{-1}$  is a vibrational absorption peak of –S–O–. The spectrum reveals the outcome of the reaction, wherein a long alkyl chain is added to the aromatic ring and the sulfonic acid group attaches to the adjacent position of the alkyl chain. These findings collectively indicate the congruence of the synthesized product with the target compound DCY-1.

**3.1.2.  $^1\text{H}$  NMR Spectrometry.** The hydrogen nuclear magnetic resonance spectrum of synthesized Y-1 is shown in Figure 2, and the proton hydrogen nuclear magnetic resonance spectrum of synthesized DCY-1 is illustrated in Figure 3.

It can be seen that  $\delta = 0.89$  (6H, hydrogen at the end of the long carbon chain).  $\delta = 1.26$  (52H, hydrogen on the long carbon chain).  $\delta = 7.06$ – $7.30$  (6H, hydrogen on the benzene ring). Through  $^1\text{H}$  NMR analysis, successful addition of the long-chain alkane to the benzene ring is confirmed, thereby establishing the identified product as the target compound Y-1.

It can be seen that  $\delta = 0.89$  (6H, hydrogen at the end of the long carbon chain).  $\delta = 1.26$  (52H, hydrogen on the long carbon chain).  $\delta = 3.81$ – $3.85$  (2H, linking group hydrogen on the benzene ring).  $\delta = 7.36$ – $7.79$  (6H, hydrogen on the

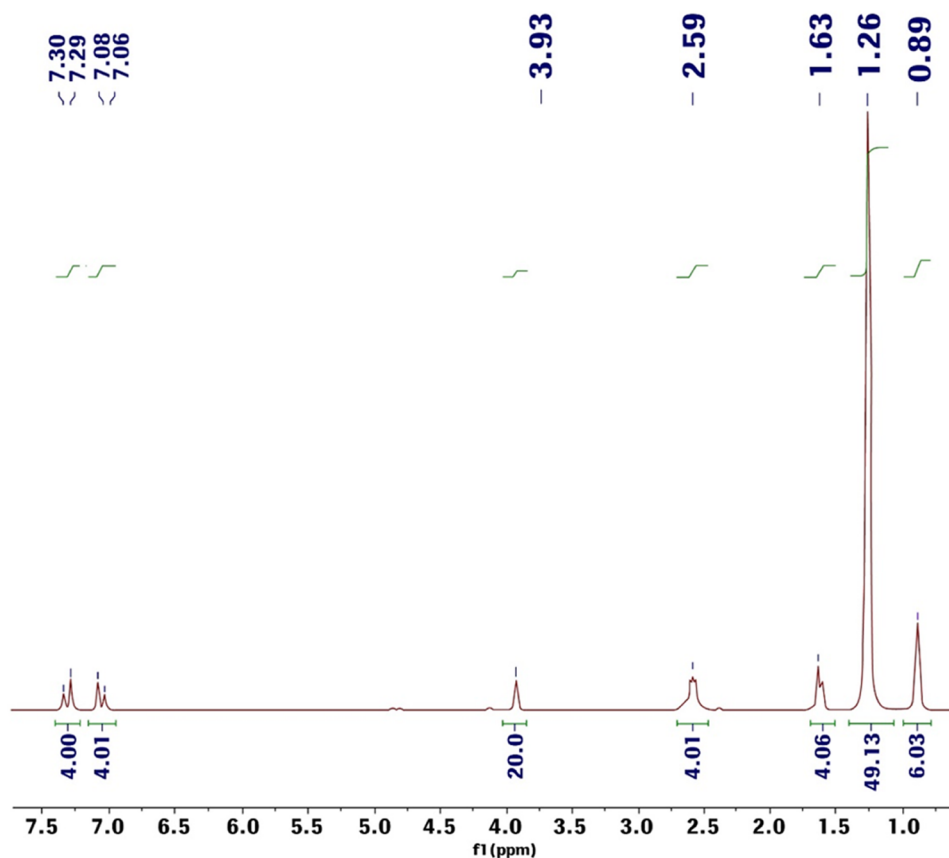


Figure 2.  $^1\text{H}$  NMR spectra of Y-1.



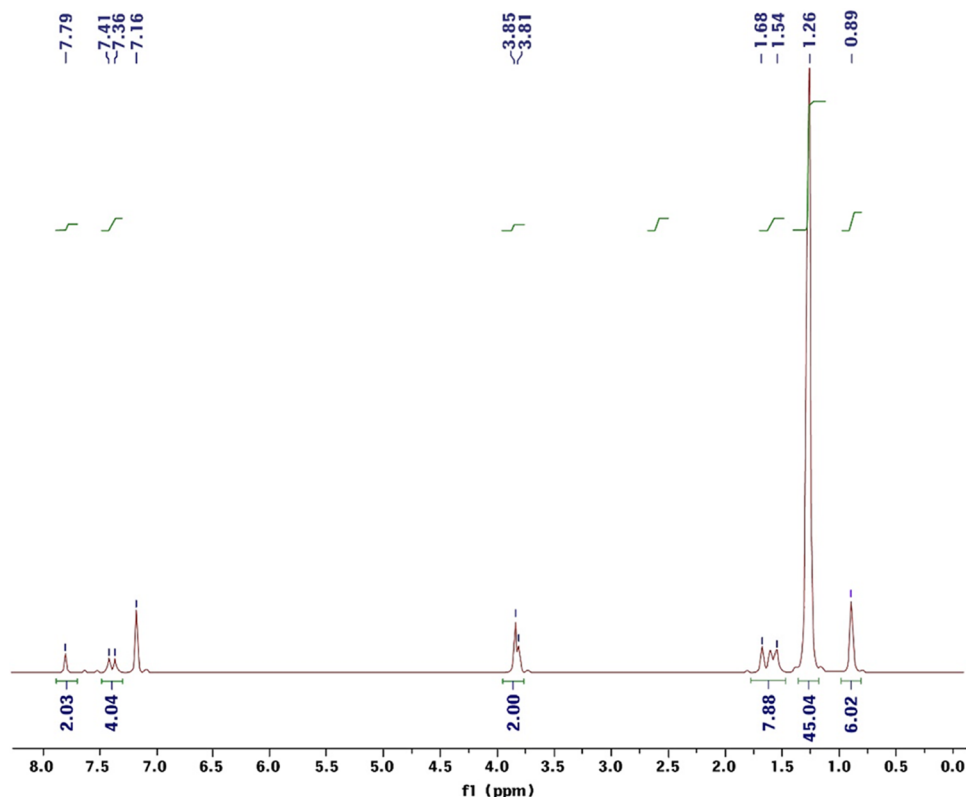


Figure 3.  $^1\text{H}$  NMR spectra of DCY-1.

benzene ring). In addition,  $\delta = 7.16$  is the proton peak of the deuterated chloroform solvent. After  $^1\text{H}$  NMR measurement, it was proved that the obtained product was the target product.

**3.2. Determination of the CMC.** According to the  $\gamma$ -lgC curve of DCY-1 based on the data measured by the pendant drop method, as shown in Figure 4, the CMC was determined, and the corresponding surface tension was  $\gamma_{\text{cmc}}$ .

It can be seen from Figure 4 that the experimentally measured surfactant DCY-1 has a CMC of  $3.37 \times 10^{-3}$  mol/L and a  $\gamma_{\text{cmc}}$  of 37.97 mN/m, indicating that the surfactant has a strong surface activity.

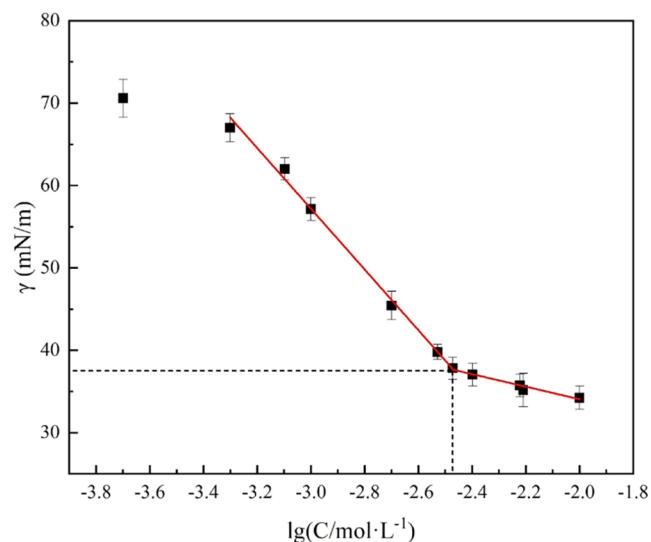


Figure 4. Surface tension–concentration curves of DCY-1.

**3.3. Determination of the Size of the Micelles.** As shown in Figure 5a, the micelles of anionic Gemini surfactants

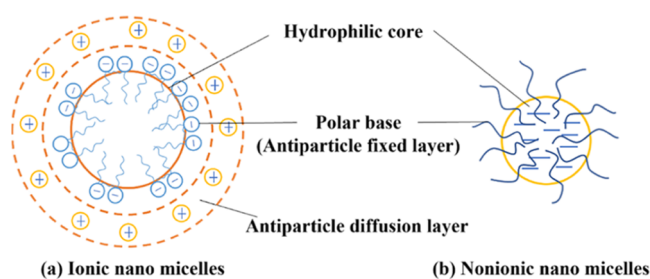


Figure 5. Schematic diagram of the micelle structure.

are composed of hydrophobic hydrocarbon chains, similar to the core of liquid hydrocarbons, and they also have a shell called the micelle water “interface” or surface phase. In order to maintain its electrical neutrality, there is also a diffusion double electric layer composed of counterions outside the micelles. As shown in Figure 5b, the micelles of nonionic surfactants have a core composed of hydrophobic hydrocarbon chains and a shell composed of polyoxyethylene chains and water combined with ether bond atoms. In a recent study, super affinity nanoparticles were found to modify shale surface wettability.<sup>27</sup> Compared with nonionic surfactants, the application of anionic surfactants is more extensive. This is due to drilling cuttings and sediment particles often having negative charges.<sup>28</sup> These negative charges form a repulsive effect with the negative charges carried by the hydrophilic groups on the oil–water interface, which will accelerate the stripping of oil from the surface of drilling cuttings into the aqueous solution and form negatively charged micelles. In the aqueous solution, the

polarity of surfactant micelles varies from the shell to the core. This microenvironment with different polarities provides a suitable dissolution environment for oil. This phenomenon of greatly improving oil solubility due to the formation of micelles is called solubilization. In particular, it is pointed out that solubilization is the solubilized matter entering the micelles rather than improving the solubility of the solubilized matter in the solvent, so it is not dissolution in the general sense.

Table 1 shows the hydrodynamic diameters of the micelle sizes of the surfactants. There are four surfactants shown in

**Table 1. Micelle Sizes (Hydrodynamic Diameters) of the Surfactants Measured by DLS**

| surfactant   | concentration (mM) | micelle size (nm) | PDI                |
|--------------|--------------------|-------------------|--------------------|
| DCY-1        | 4                  | 4.52( $\pm$ 0.07) | 0.12( $\pm$ 0.01)  |
| SDS          | 14                 | 3.63( $\pm$ 0.05) | 0.19( $\pm$ 0.001) |
| Tween 80     | 3                  | 11.1( $\pm$ 0.18) | 0.18( $\pm$ 0.003) |
| Triton X-100 | 1                  | 7.56( $\pm$ 0.06) | 0.13( $\pm$ 0.03)  |

Table 1, among which DCY-1 and SDS are anionic surfactants and Tween 80 and Triton X-100 are nonionic surfactants. In general, nonionic surfactants have larger micelles because the micelle shell formed by the polar groups of nonionic surfactants occupies a considerable volume of micelles. Hydrophilic polyoxyethylene and its associated water molecules make the outer layer of this micelle more bulky. However, in the oil removal process of cleaning ODCs, the oil solubilization mainly occurs in the core of micelles, and the oil is completely in a nonpolar environment. Compared with SDS with the same anionic surfactant, DCY-1 has longer and more hydrophobic carbon chains, its CMC value decreases, the aggregation number of micelles increases, and the micelle size increases. Therefore, the micelle size of DCY-1 is larger than that of SDS, so it has a better solubilization effect on oil and a better cleaning effect on ODCs. In addition, the smaller the PDI value, the more homogeneous is the sample size.

As shown in Figure 6a, oil droplets adhere to the surface of oil-bearing cuttings and are surrounded by other oil droplets in the initial state. The interaction between them is mainly the intermolecular force between nonpolar oils. When the oily cuttings enter the water, they are incompatible with water as a

solid phase, and the surface of the cuttings will show the same hydrophobicity as the oil phase.

Figure 6b shows that when using DCY-1 for chemical cleaning of the ODCs, DCY-1 molecules will be adsorbed on the oil–water interface due to its hydrophilicity and hydrophobicity in the transition state, which will first reduce the interfacial tension. Second, due to the negative charge on the surface of drilling cuttings, it will form a repulsive force with the negatively charged hydrophilic group exposed outside the oil–water interface, which will accelerate the falling off of oil droplets from the ODC surface. The oil droplets entering the aqueous phase will be wrapped by the micelles formed by DCY-1.

As can be seen from Figure 6c, DCY-1 forms a large number of micelles in water in the final state, a small part of free DCY-1 monomer molecules will be adsorbed on the surface of the ODCs due to the hydrophobic effect, and the exposed hydrophilic groups will change the surface of the ODCs from hydrophobic to hydrophilic.

**3.4. Determination of Emulsifying Ability.** The results of the emulsifying abilities of DCY-1, SDBS, and SDS are shown in Table 2.

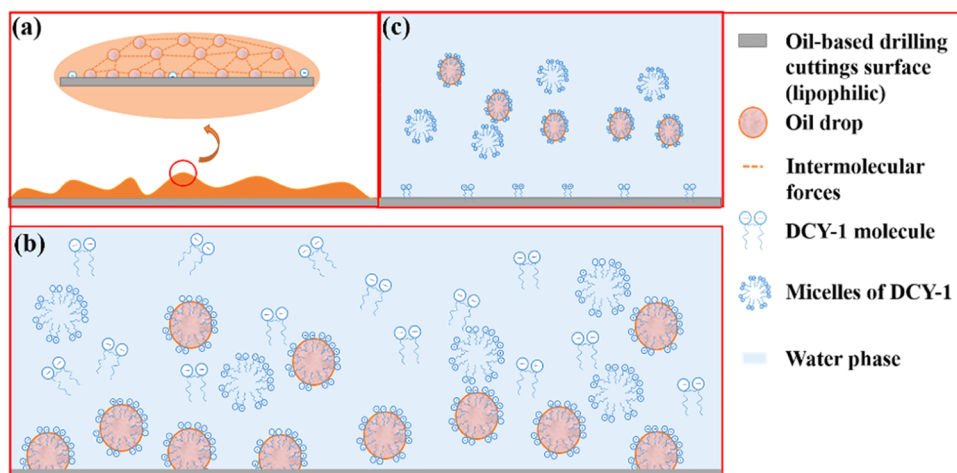
**Table 2. Determination of the Emulsifying Ability of the Surfactant**

| surfactant | water splitting time |
|------------|----------------------|
| DCY-1      | 14'35"               |
| SDBS       | 11'47"               |
| SDS        | 9'50"                |

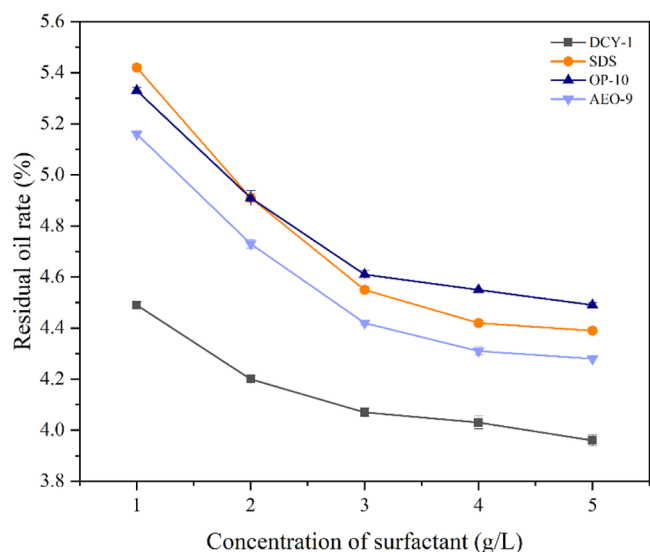
As can be seen from Table 2, there are some differences in the emulsification abilities of different types of surfactants for diesel fuel at the same mass fraction concentration. Compared with the conventional anionic surfactants SDBS and SDS, the water–oil separation time of DCY-1 was longer, indicating its stronger emulsification ability.

**3.5. Comparison of Cleaning Effects.** The chemical cleaning effects of different types of surfactants on the ODCs at different concentrations are shown in Figure 7.

It can be seen from Figure 7 that the heat cleaning effect of synthetic DCY-1 on oil-bearing drilling cuttings is better than that of these surfactants, and the oil content of the treated



**Figure 6.** Oil removal process of DCY-1 micelles acting on ODCs. (a) Initial state. (b) Degreasing process. (c) End state.

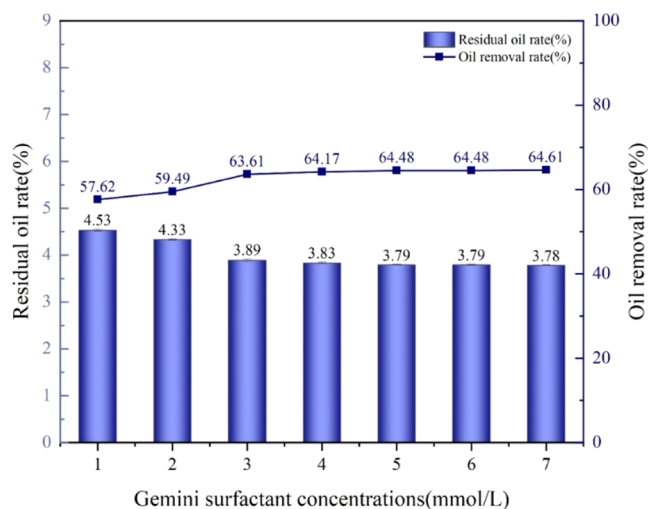


**Figure 7.** Cleaning effects of different types of surfactants at different concentrations.

drilling cuttings is lower, up to 3.96%. This is because the unique structure of the Gemini surfactant makes it easier to form micelles and has high interfacial activity. Moreover, the longer lipophilic chain of surfactant molecules also makes the CMC smaller, which makes it have the characteristics of high surface activity, strong wettability, emulsification, and dispersion and makes it achieve a good oil removal effect.

### 3.6. Optimization of the Cleaning Process Condition.

**3.6.1. Effect of DCY-1 Concentration.** The impact of the concentrations of the surfactant on the oil removal rate for the treatment of ODCs was conducted, and the result is shown in Figure 8.



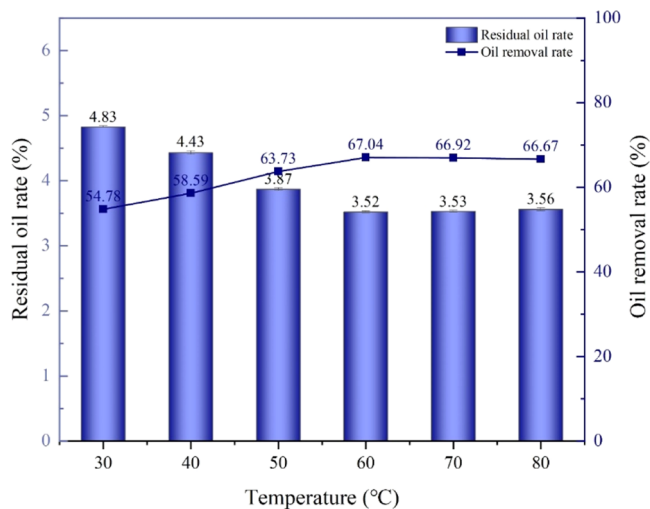
**Figure 8.** Cleaning effects of DCY-1 at different concentrations.

It can be seen from Figure 8 that the oil content of the ODCs decreased continuously with the increase of the surfactant concentration. After the surfactant concentration was increased to 3 mmol/L, the oil content of ODCs decreased less and could be as low as 3.79%. It was found that the oil content of ODCs continued to decrease after the concentration of DCY-1 reached the CMC. This is because when the concentration of the surfactant solution reaches the

CMC, the molecular monomers of the surfactant will associate in water to form micelles. These micelles have a solubilizing effect and are able to solubilize oil molecules into the micelles. This phenomenon can further increase the cleaning and degreasing effect.

To sum up, when the concentration of the surfactant is higher than the CMC, the oil removal rate can reach the maximum value. However, for the consideration of economic cost, the optimal concentration of the DCY-1 solution is 3 mmol/L.

**3.6.2. Effect of Cleaning Temperature.** The impact of the cleaning temperature on the oil removal rate for the treated ODCs was conducted, and the result is shown in Figure 9.

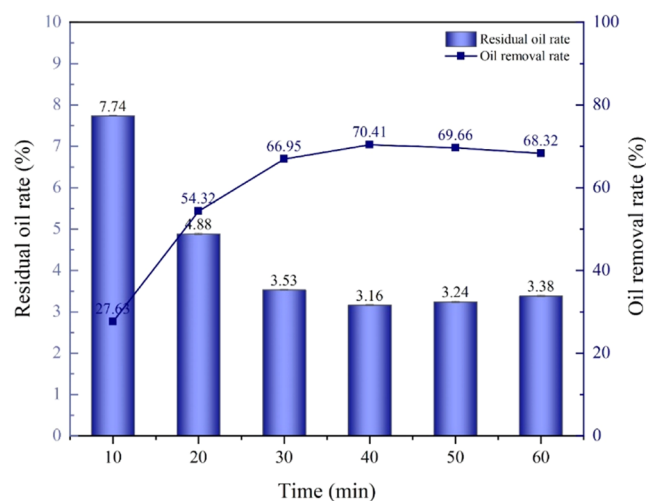


**Figure 9.** Cleaning effects of DCY-1 at different cleaning temperatures.

As can be seen from Figure 9, with the gradual increase of the cleaning temperature, the oil content of the ODCs decreases rapidly and then tends to be stable. When the cleaning temperature increases from 30 to 60 °C, the cleaning efficiency is continuously improved. At the temperature of 60 °C, the oil content is reduced to a minimum of 3.52%. Increasing the cleaning temperature is conducive to accelerating the reaction speed, reducing the viscosity of crude oil, reducing the adhesion of crude oil, and achieving a better oil removal effect. When the cleaning temperature reaches more than 70 °C, long-term high-temperature stirring will lead to rapid evaporation of water. A large amount of water loss is not conducive to chemical cleaning. In addition, the higher the cleaning temperature, the greater is the energy consumption of the system. In conclusion, the best cleaning temperature is 60 °C.

**3.6.3. Effect of Cleaning Time.** The impact of the cleaning time on the oil removal rate for the treated ODCs was conducted, and the result is shown in Figure 10.

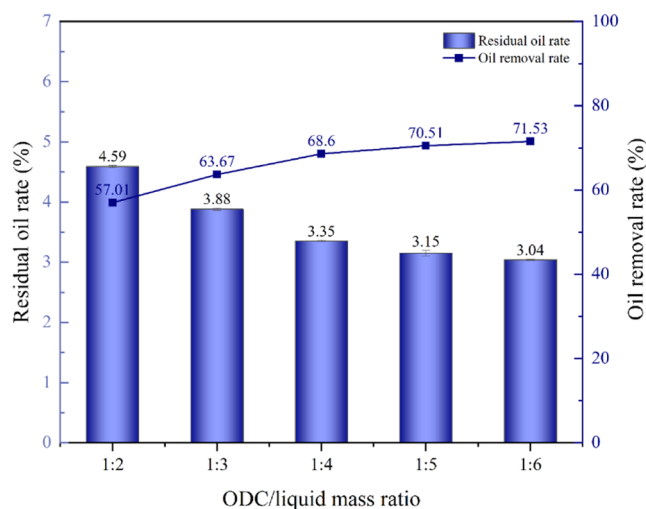
It can be seen from Figure 10 that the oil content of oil-based cuttings first decreased rapidly with the increase of the cleaning time and then increased slightly. When the hot-cleaning time increased from 10 to 40 min, the cleaning efficiency continued to increase. The oil content of oil-based cuttings was 40 min after the cleaning time and it dropped to a minimum of 3.16%. This is because the cleaning time is short, due to which the surfactant and the oil cannot be fully contacted on the surface of the drill cuttings. Thus, it is difficult



**Figure 10.** Cleaning effects of DCY-1 at different cleaning times.

to achieve a good oil removal effect. As the cleaning time increases, the surfactant and the drill cutting particles are fully contacted, and the oil phase is gradually dispersed and dissolved into the surfactant solution, which accelerates the separation of the oil originally adhering to the surface of the drill cuttings. After the cleaning time is longer than 40 min, a large amount of water evaporates and loses, which increases the emulsification of the oil and reduces the oil removal effect slightly. At the same time, the prolongation of the cleaning time also increases the energy consumption of the system, so the optimal cleaning time is determined to be 40 min.

**3.6.4. Effect of ODC/Liquid Mass Ratio.** The impact of the ODC/liquid mass ratio on the oil removal rate for the treated ODCs was conducted, and the result is shown in Figure 11.

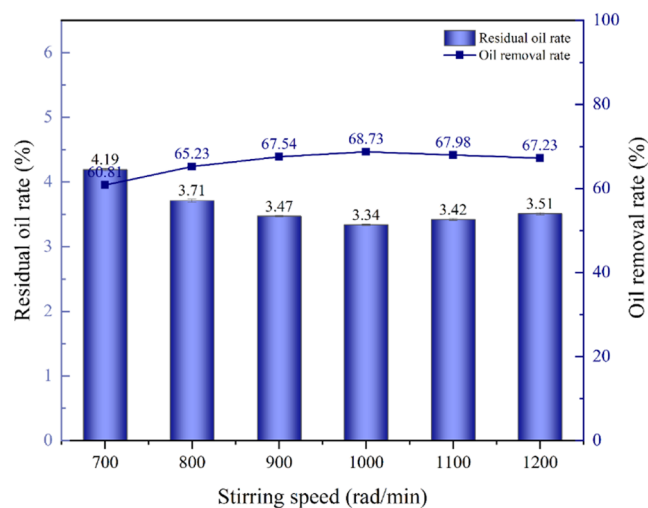


**Figure 11.** Cleaning effects of DCY-1 at different ODC/liquid mass ratios.

It can be seen from Figure 11 that with the increase of surfactant solution addition in oil-based rock chips, the residual oil rate of oil-based rock chips gradually decreased. When the the ODC/liquid mass ratio was 1:4, the residual oil rate of the ODCs decreased to a lower level of 3.35%, and when the amount of surfactant solution continued to increase, the residual oil rate of the ODCs did not change much. This is

because sufficient surfactant solution can be added to ensure full contact between the ODCs and the surfactant and improve the cleaning efficiency. If the amount of surfactant solution added is too large, it will increase the difficulty of subsequent treatment of oil-containing wastewater and the cost of pharmaceuticals. Combined with the above factor analysis, the ODC/liquid mass ratio is 1:4.

**3.6.5. Effect of Stirring Speed.** The impact of the stirring speed on the oil removal rate for the treated ODCs was conducted, and the result is shown in Figure 12.



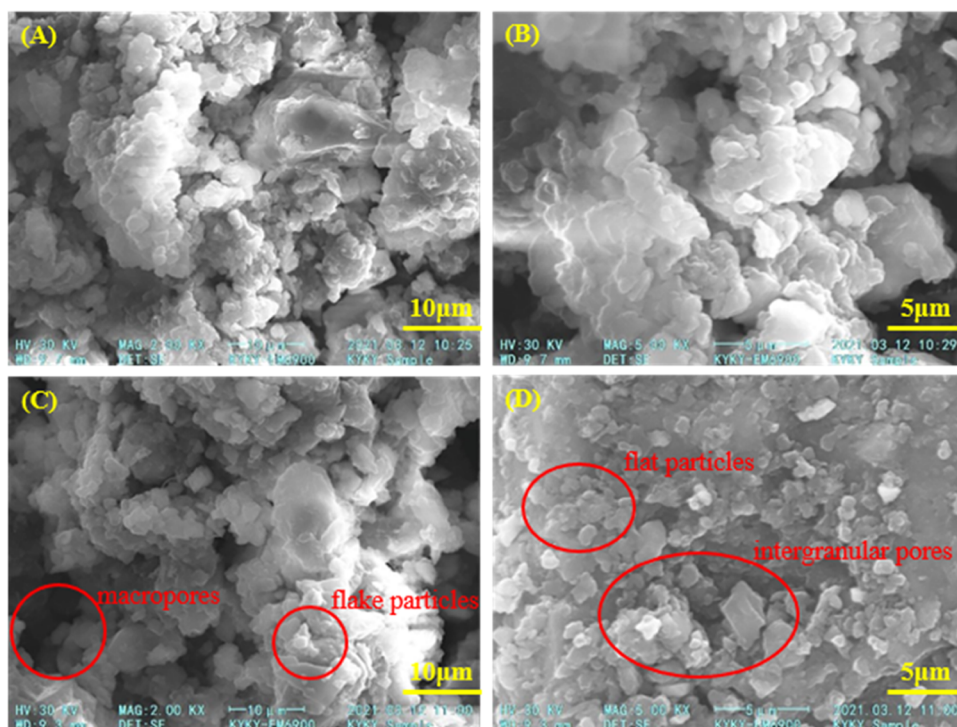
**Figure 12.** Cleaning effects of DCY-1 at different stirring speeds.

It can be seen from Figure 12 that with the increase of the stirring speed, the residual oil rate of oil-based rock cuttings gradually decreases to 3.34%, and then the residual oil rate gradually increases. This is because a reasonable stirring speed is conducive to accelerating the separation of oil, drilling cuttings, and water. When the mixing speed is too high, the emulsification between oil and water increases, which makes it difficult to separate oil and water and affects the cleaning effect of drilling cuttings. Therefore, the mixing speed should be 1000 rad/min.

**3.7. SEM Characterization Analysis of ODCs after Chemical Treatment.** The mechanical behavior of the soil was the external reflection of its internal microstructure. Therefore, the microstructure of the ODC sample was highly significant for the removal of crude oil.

As shown in Figure 13, the microstructure characteristics were described by SEM including the morphology of the solid particle and pore characteristics. From the morphology of the skeleton particles of drilled cuttings, the solid particle units of the sample showed a variety of structures, mainly flat and flaky particles. The diameter of the particle unit varied from 1 to 10  $\mu\text{m}$ . For pristine ODCs, Figure 13 illustrates that a substantial quantity of petroleum hydrocarbons adheres to the surface of the ODCs prior to treatment. The rock chips exhibit a denser and relatively compact structure attributable to the adhesion of petroleum hydrocarbons. However, Figure 13C,D reveals that the surface of the ODCs becomes smooth and flat after chemical cleaning treatment. Macropores and intergranular pore structures emerge, and flake particles and flat particles become distinctly separated. This transformation is attributed to the decrease in the petroleum hydrocarbon content in the





**Figure 13.** SEM images of (A, B) pristine ODCs and (C, D) ODCs treated by DCY-1.

oil-based rock chips, leading to reduced adhesion and increased porosity, resulting in a loose structure.

#### 4. CONCLUSIONS

A Gemini surfactant, DCY-1, was synthesized in the laboratory. The synthesis of DCY-1 yielded a critical micelle concentration (CMC) of  $3.37 \times 10^{-3}$  mol/L and a  $\gamma_{\text{cmc}}$  of 37.97 mN/m, underscoring its robust surface activity. Comparative analysis revealed that DCY-1 exhibits superior emulsifying capabilities compared to common surfactants such as SDBS and SDS. The oil removal mechanism of DCY-1 micelles on ODCs was scrutinized using a microscale approach. Due to its larger micelle size in comparison to SDS, the optimal chemical cleaning scheme involves a surfactant concentration of 3 mmol/L, a cleaning temperature set at 60 °C, a cleaning time of 40 min, an ODC/liquid mass ratio of 1:4, a stirring speed of 1000 rad/min, and a two-step cleaning process. Under these conditions, the oil removal rate of the ODCs reached 84.66%, with the oil content reduced to a mere 1.64%. The ODCs, post chemical cleaning, adhere to pertinent pollution control standards, demonstrating the efficacy of the cleaning process. The DCY-1 Gemini surfactant exhibits promising applications in the realm of oilfield environmental protection.

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X.Y.: investigation, methodology, and roles/writing—original draft; Y.L.: conceptualization; Z.H.: project administration; L.Y.: resources; J.Y.: writing—review and editing; and W.D.: formal analysis.

##### Notes

The authors declare no competing financial interest.

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##### REFERENCES

- Vidic, R. D.; Brantley, S. L.; Vandenbossche, J. M.; Yoxtheimer, D.; Abad, J. D. Impact of Shale Gas Development on Regional Water

- Quality. *Science* **2013**, *340* (6134), No. 1235009, DOI: 10.1126/science.1235009.
- (2) Wu, L.; Hou, Z.; Luo, Z.; Xiong, Y.; Zhang, N.; Luo, J.; Fang, Y.; Chen, Q.; Wu, X. Numerical simulations of supercritical carbon dioxide fracturing: A review. *J. Rock Mech. Geotech. Eng.* **2023**, *15* (7), 1895–1910.
- (3) Lei, Q.; Yun, X.; Bo, C.; Baoshan, G.; Xin, W.; Guoqiang, B. L.; Hui, L. I.; Shuai, L. I.; Bin, D.; Haifeng, F. U. Progress and prospects of horizontal well fracturing technology for shale oil and gas reservoirs. *Pet. Explor. Dev.* **2022**, *49*, 191–199, DOI: 10.1016/S1876-3804(22)60015-6.
- (4) Xu, P.; Xu, M. Damage Mechanism of Oil-Based Drilling Fluid Flow in Seepage Channels for Fractured Tight Sandstone Gas Reservoirs. *Geofluids* **2019**, *2019*, 2672695.
- (5) Leonard, S. A.; Stegemann, J. A. Stabilization/solidification of petroleum drill cuttings. *J. Hazard. Mater.* **2010**, *174*, 484–491, DOI: 10.1016/j.jhazmat.2009.09.078.
- (6) Gordalla, B. C.; Ewers, U.; Frimmel, F. H. Hydraulic fracturing: a toxicological threat for groundwater and drinking-water? *Environ. Earth Sci.* **2013**, *70* (8), 3875–3893.
- (7) Soeder, D. J.; Sharma, S.; Pekney, N.; Hopkinson, L.; Capo, R.; et al. An approach for assessing engineering risk from shale gas wells in the United States. *Int. J. Coal Geol.* **2014**, *126* (2), 4–19.
- (8) Vengosh, A.; Jackson, R. B.; Warner, N.; Darrah, T. H.; Kondash, A. A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. *Environ. Sci. Technol.* **2014**, *48* (15), 8334–8348.
- (9) Bera, A.; Mandal, A.; Belhaj, H.; Kumar, T. Enhanced oil recovery by nonionic surfactants considering micellization, surface, and foaming properties. *Pet. Sci.* **2017**, *14* (2), 362–371.
- (10) Seo, S.; Mastiani, M.; Mosavati, B.; Peters, D. M.; Mandin, P.; Kim, M. Performance evaluation of environmentally benign nonionic biosurfactant for enhanced oil recovery. *Fuel* **2018**, *234*, 48–55.
- (11) Yao, E.; Liang, T.; Li, Y.; Sun, J.; Zhou, F. Development of a New Multifunctional Cationic Surfactant System with Corrosion Inhibiting Ability. *Geofluids* **2017**, *2017*, 2849356.
- (12) Deshpande, S.; Shiau, B. J.; Wade, D.; Sabatini, D. A.; Harwell, J. H. Surfactant Selection for Enhancing ex-Situ Soil Washing. *Water Res.* **1999**, *33* (2), 351–360.
- (13) Moud, A. A. Rheology and microscopy analysis of polymer-surfactant complexes. *Colloid Polym. Sci.* **2022**, *300*, 733.
- (14) Deng, X.; Yang, Y.; Ma, Y.; Sun, X.; Zhou, G.; Wu, H.; Lu, G. Self-assembled structure of sulfonic gemini surfactant solution. *AIP Adv.* **2018**, *8* (7), No. 075003, DOI: 10.1063/1.5040684.
- (15) Menger, F. M.; Littau, C. A. Gemini-surfactants: synthesis and properties. *J. Am. Chem. Soc.* **1991**, *113* (4), 1451–1452.
- (16) Menger, F. M.; Littau, C. A. Gemini surfactants: a new class of self-assembling molecules. *J. Am. Chem. Soc.* **1993**, *115* (22), 10083–10090.
- (17) Zana, R.; Xia, J. *Gemini Surfactants: Synthesis, Interfacial and Solution-Phase Behavior, and Applications*; Routledge, 2004.
- (18) Pal, N.; Hoteit, H.; Mandal, A. Structural aspects, mechanisms and emerging prospects of Gemini surfactant-based alternative Enhanced Oil Recovery technology: A review. *J. Mol. Liq.* **2021**, *339* (8), No. 116811.
- (19) Zana, R. A.; Talmon, Y. Dependence of aggregate morphology on structure of dimeric surfactants. *Nature* **1993**, *362*, 228–230, DOI: 10.1038/362228a0.
- (20) Zana, R. Dimeric and oligomeric surfactants. Behavior at interfaces and in aqueous solution: a review. *Adv. Colloid Interface Sci.* **2002**, *97*, 205–253, DOI: 10.1016/S0001-8686(01)00069-0.
- (21) Kabir-ud-Din; Koya, P. A. Micellar Properties and Related Thermodynamic Parameters of the 14–6-14, 2Br Gemini Surfactant in Water + Organic Solvent Mixed Media. *J. Chem. Eng. Data* **2010**, *55* (5), 1921–1929.
- (22) Yang, X.; Mao, J.; Zhang, Z.; Zhang, H.; Heng, B.; Yang, B.; Zhao, J. Rheology of Quaternary Ammonium Gemini Surfactant Solutions: Effects of Surfactant Concentration and Counterions. *J. Surfactants Deterg.* **2018**, *21* (4), 467–474.
- (23) Zhou, M.; Chen, Y.; Zou, J.; Bu, J. Recent Advances in the Synthesis of Sulfonate Gemini Surfactants. *J. Surfactants Deterg.* **2018**, *21*, 443–453, DOI: 10.1002/jsde.12046.
- (24) Zhou, M.; Zhang, Z.; Xu, D.; Hou, L.; Zhao, W.; Nie, X.; Zhou, L.; Zhao, J. Synthesis of three gemini betaine surfactants and their surface active properties. *J. Taiwan Inst. Chem. Eng.* **2017**, *74*, 7–13, DOI: 10.1016/j.jtice.2016.10.012.
- (25) Zhou, M.; Zhao, J.; Hu, X. Synthesis of Bis[N,N'-(alkylamideethyl)ethyl] Triethylenediamine Bromide Surfactants and Their Oilfield Application Investigation. *J. Surfactants Deterg.* **2012**, *15* (3), 309–315.
- (26) Yuan, X.; Ren, F.; Zeng, G.; Zhong, H.; Fu, H.; Liu, J.; Xu, X. Adsorption of surfactants on a *Pseudomonas aeruginosa* strain and the effect on cell surface hydrophobicity. *Appl. Microbiol. Biotechnol.* **2007**, *76* (5), 1189–1198.
- (27) Luo, X.; Jiang, G.; Wang, G.; Yang, L.; He, Y.; Cui, K.; Yang, J. Novel approach to improve shale stability using super-amphiphobic nanoscale materials in water-based drilling fluids and its field application. *Rev. Adv. Mater. Sci.* **2022**, *61* (1), 41–54.
- (28) Mao, X.; Jiang, R.; Xiao, W.; Yu, J. Use of surfactants for the remediation of contaminated soils: A review. *J. Hazard. Mater.* **2015**, *285*, 419–435.