Research Article

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Application of Thermal Resistant Gemini Surfactants in Highly Thixotropic Water-in-oil Drilling Fluid System

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Abstract: Traditional water-in-oil drilling fluids are limited by their shear thinning behavior. In this article, we propose the synthesis of a thermal resistant quaternary ammonium salt gemini surfactant DQGE-I. This surfactant was synthesized using monomers such as N,N-dimethyl-1,3-propanediamine, organic acids and epichlorohydrin, as well as blocking groups such as N-vinylpyrrolidone (NVP). The prepared surfactant exhibited various advantages over traditional surfactants, including excellent thermal stability, good emulsifying and wetting capability. The use of these surfactants was shown to improve the compactness of emulsifier molecules at the oil/water interface, as well as the overall emulsification effect. Laboratory studies revealed that water-in-oil emulsions prepared using DQGE-I showed high emulsion breaking voltage, low liquid precipitation and small and uniformly distributed emulsion drops. Highly thixotropic water-in-oil drilling fluids based on DQGE-I showed low viscosity, high shear rate and thermal tolerance up to 260°C. Additionally, the proposed fluid was applied in 16 wells (including WS1-H2, GS3 and XS1-H8) in the Daqing Oilfield. Testing showed that DQGE-I exhibited excellent rheological behavior and wall-building capability. The emulsion breaking voltage exceeded 1500 V, and the yield point/plastic viscosity ratio exceeded 0.4. The use of this surfactant can help to solve problems such as high formation temperature and poor well wall stability.

Keywords: Gemini surfactants; water-in-oil emulsifier; oil-based drilling fluid.

1 Introduction

Developed countries have surpassed China in the development of emulsifiers for water-in-oil drilling fluids. In fact, China's progress is approximately equivalent to other countries in the 1980s. Currently, emulsifiers commonly use include oleic acid, stearic acid, fatty acid amide, esters (span-80), etc. Most of these emulsifiers are single chain or single adsorption group surfactants, which require a high in-situ quantity and frequent maintenance, and show poor emulsification as well as poor thermal resistance. Previous studies revealed two disadvantages of conventional emulsifiers. Firstly, emulsifiers based on fatty acid amide, esters and oleic acid were readily subjected to hydrolysis and saponification, resulting in degraded interfacial activity and emulsifying capability. Secondly, the emulsifying capability of these emulsifiers was poor due to the simple molecular structure and few adsorption groups. As a result, water-in-oil drilling fluids that used these emulsifiers exhibited poor stability, high viscosity and low shearing force. Additionally, the efficiency of borehole cleaning was low, and cutting beds were commonly observed. Therefore, these water-in-oil drilling fluids are not suitable for long horizontal wells and other complicated structures [1-15]. This article proposes an intensive study of emulsifiers from the view of molecular structure. A highly thixotropic water-in-oil drilling fluid system is also designed. The proposed system was applied in 16 wells (including WS1-H2, GS3 and XS1-H8) in the Daqing Oilfield to solve common problems such as high formation temperature, formation of cutting beds and poor well wall stability.

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2 Experimental

2.1 Materials

N,N-dimethyl-1,3-propanediamine, 4-dodecylaniline, ethylenediamin, epichlorohydrin, absolute ethanol, NVP, organic acids (including ricinoleic acid, aromatic acid, oxalic acid, oleic acid, palmitic acid, stearic acid, lauric acid, 13-docosenoic acid), KOH, 2-butoxyethanol, and ethyl acetate were utilized. All of these chemicals are analytical reagents.

2.2 Instruments

The instruments used included a magnetic stirrer, a four-neck flask, a thermostatic oil-bath pot, a high-speed electrical stirrer, a six speed rotating viscometer, an electrical stability tester, a high-temperature roller furnace, a high-temperature/high-pressure filtrate loss analyzer, an opto-digital microscope (Olympus DSX500), FTIR spectrometer, NMR spectrometer, thermal-gravity analyzer (TGA), etc.

2.3 Methods

2.3.1 Preparation of quaternary ammonium salt gemini surfactants

Organic acids (ricinoleic acid, aromatic acid, oxalic acid, oleic acid, palmitic acid, stearic acid, lauric acid, 13-docosenoic acid, or a mixture of all), N,N-dimethyl-1,3-propanediamine and NVP were mixed at a fixed mass ratio and added into a four-neck flask. The mixture was stirred in N₂ at a refluxing temperature for 12 h to obtain intermediate I. 4-dodecylaniline was added into a flask with absolute ethanol, which acted as a solvent. Epichlorohydrin was added in slowly with a separation funnel. After 12 h, the excess naphthenic acid amide and ethanol were removed by vacuum distillation, and intermediate II was obtained. The intermediates I and II were mixed at a mass ratio of 1:3 to allow quaternary amination, with 2-butoxyethanol as a solvent. DQGE-I, which is a quaternary ammonium salt gemini surfactant, was obtained after rinsing. The chemical equations involved are as follows:

2.3.2 Preparation of emulsion

DQGE-1 and naphthenic acid amide were added into 5# technical white oil and stirred at 12000 r/min for 10 min. 20% CaCl₂ solution was added until the oil/water ratio was 80:20. The mixture was stirred for another 60 min to obtain the water-in-oil emulsion.

2.3.3 Evaluation of emulsion stability

Electrical stability evaluation: $n = 3$, relative error < 5%, the probe should not touch the bottom of the container. Centrifugation evaluation: 10 mL of the emulsion was added into a scaled centrifuge tube and stirred at 2000 r/min for 5 min. A small supernatant volume (liquid precipitation, ΔV) indicated a stabilized emulsion. Microscope evaluation: the size and distribution of an emulsion drop was investigated using a microscope.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

We propose a new emulsifier with a unique molecular structure to reduce the limitations of drilling fluids using conventional emulsifiers: (1) gemini structure, which has a compacted arrangement on the oil/water interfacial membrane, thus improving surface activity and membrane strength; (2) presence of an acylamino group (strong hydration group), resulting in enhanced emulsifier adsorption; (3) presence of a five-membered ring group with significant steric effect, resulting in improved high-temperature behavior; (4) Optimized HLB value (4-6) with precise control of hydrophilic/hydrophobic ratio.

3.1 Structure of DQGE-I

Figures 1 and 2 show the FTIR spectrum and TGA results of DQGE-I. As shown in Figure 1, peaks at following positions were observed: 3400 cm^{-1} , corresponding to absorption peak of bonded water molecules; 1270 cm^{-1} , corresponding to stretching vibration of C-N bonds; 1690 cm^{-1} , corresponding to strong absorption peak of C-N bonds; 3300 and 1700 cm^{-1} , corresponding to stretching vibration absorption peak of secondary amides; 1100 cm^{-1} , corresponding to stretching vibration absorption peak of secondary alcohol; 1480 cm^{-1} , corresponding to out-of-plane bending vibration absorption peak of -NH groups; 2900 , 1400 and 710 cm^{-1} , corresponding to bending vibration absorption peak of methyl group/methylene. The presence of these peaks indicated the consistency of the product structure and the designed structure. Additionally, TGA results (Figure 2) revealed that the mass loss of DQGE-1 was 5% at 260°C and 14% at 300°C . There was negligible mass loss at temperatures below 200°C . This demonstrated the excellent thermal stability of DQGE-1.

3.2 Properties of DQGE-I

The stability of DQGE-I and the naphthenic acid amide water-in-oil (white oil base) emulsion was evaluated. The results of this evaluation are shown in Table 1.

As shown, DQGE-I that was re-mixed with naphthenic acid amide, exhibited a high emulsion breaking voltage and low liquid precipitation, indicating an excellent emulsification performance and good stability. The optimal emulsion stability was achieved when quantities of DQGE-1 and naphthenic acid amide were 3.0-3.5% and 1.0-1.2%. In this case, the emulsion breaking voltage and liquid precipitation of the emulsion, which was heated at 260°C for 16 h, were above 500 V and 0.5 mL, respectively.

The size and morphology of emulsion drops were investigated using an optical microscope. The emulsions were compared with those prepared using span-80. Figure 3 and 4 show the different emulsions before and after heating.

Note: The water/oil ratio was 20:80, a mixture of 20% CaCl_2 , 4% span, 3% oleic acid and 3% naphthenic acid amide was used in a, while a mixture of 20% CaCl_2 , 3% DQGE-I and 1% naphthenic acid amide was used in b. The hot rolling conditions were 260°C and 16 h.

Emulsions prepared using DQGE-I had a smaller size and a more uniform distribution compared with those prepared using span-80. Additionally, no significant

Figure 1: FTIR spectrum of DQGE-I.

Figure 2: TGA results of DQGE-I.

Table 1: The emulsification performance of DQGE-I remixed with naphthenic acid amide.

DQGE-I /%	Naphthenic acid amide /%	Emulsion breaking voltage ES/V		Liquid precipitation /mL	
		Before aging	After aging	Before aging	After aging
2.5	0.8	468	438	0.6	0.8
3.0	1.0	546	521	0.4	0.5
3.5	1.2	564	517	0.4	0.5

Note: The water/oil ratio was 20:80, CaCl_2 concentration was 20% and the hot rolling conditions were 260°C and 16 h.

Figure 3: Emulsions before heating (a) Emulsion prepared using span-80; (b) Emulsion prepared using DQGE-I.

Figure 4: Emulsions after heating (a) Emulsion prepared using span-80; (b) Emulsion prepared using DQGE-I.

changes were observed in the size and distribution of emulsions after heating, while emulsions prepared using span-80 tend to show enlarged drops and degraded distribution uniformity after heating [16,17]. This serves as an indicator that DQGE-I has strong emulsification capabilities, and the emulsions prepared using DQGE-I showed improved stability over emulsions prepared using span-80.

3.3 Development and evaluation of highly thixotropic oil-based drilling fluids

A highly thixotropic water-in-oil drilling fluid system was developed using DQGE-I and other additives, including a precipitation reducing agent, organic soil and a wetting agent. The density and thermal resistance limit of the

products were 1.2-2.0 g/cm³ and 260°C, respectively. The properties of the products are shown in Table 2. The water/oil ratio used ranged from 25:75 to 10:90. 20% CaCl₂ was mixed with 3.0-3.5% DQGE-I, 1.0-1.2% naphthenic acid amide, 3-5% organic soil and 1.5% CaO, 3-5% precipitation reducing agent, 2-4% wetting agent and a certain amount of barite powder.

3.3.1 Overall evaluation

DQGE-I is a quaternary ammonium salt gemini surfactant with dual adsorption groups. Results of experiments have indicated that DQGE-I could be effective in improving the compactness of emulsifier molecules at the water/oil interface, which results in enhanced emulsion stability. Emulsions prepared using DQGE-I exhibited a

Table 2: Overall performance evaluation of highly thixotropic water-in-oil drilling fluid system (FL_{HTHP} was measured at 200°C and 3.5. MPa).

Experimental parameters	AV (mPa·s)	PV (mPa·s)	YP (Pa)	Gel (Pa/Pa)	YP (PV)	ES (V)	FL_{HTHP} (mL)
Before aging	26	18	8	3.5/5.0	0.44	1653	/
260°C, 16 h	27	19	8	4.0/6.5	0.42	1644	8.2
260°C, 48 h	29	20	9	4.0/6.5	0.45	1613	8.4
260°C, 72 h	30	21	9	3.5/6.0	0.43	1548	8.4

Table 3: Anti-contamination capability of highly thixotropic water-in-oil drilling fluid system (FL_{HTHP} was measured at 200°C and 3.5 MPa and all values were obtained after aging at 260°C for 16 h).

Contaminants	AV (mPa·s)	PV (mPa·s)	YP (Pa)	Gel (Pa/Pa)	ES (V)	FL_{HTHP} (mL)
Blank	27	19	8	4.0/6.5	1644	8.2
5% debris	29	20	9	4.5/7.0	1605	8.4
10% debris	32	21	10	5.0/7.5	1543	8.4
15% debris	35	24	11	5.5/8.5	1509	8.6
5% water	30	21	9	4.5/6.0	1536	8.4
10% water	33	23	10	4.5/5.0	1458	8.6
15% water	36	25	11	5.0/6.0	1402	8.4
20% water	40	27	13	5.0/7.0	1397	8.4

reduced size but an increased quantity of emulsion drops compared to those that were prepared using conventional water-in-oil drilling fluids. Additionally, the VDW force between emulsions and solid particles (e.g. organic soil) was enhanced, and a 3D ‘organic soil-emulsion drop-other solid particle’ network was developed, resulting in increased gel strength and suspension behavior. Due to the low strength of VDW interactions, the rupture of the network could be triggered by a relatively low shearing rate, indicating that the system obtained was highly thixotropic (low viscosity and high shearing force, as shown in Table 2). Meanwhile, DQGE-I exhibited excellent emulsifying and wetting capabilities, as well as good stability. These characteristics can be attributed to the high surface activity and low CMC of the emulsions. The system showed 15% anti-debris and 20% anti-water, indicating a good anti-contamination capability (Table 3).

3.3.2 Field application

The DQGE-based drilling fluids obtained in this study were tested in six fields, including WS1-H2, GS3, and XS1-H8. Issues such as side-wall exfoliation, side-wall coring and retardation were not observed during the drilling

processes. The absence of these problems indicated that the proposed drilling fluid was a significant improvement over the previous fluid.

The designed and total depths of WS1-H2 were 4820.5 m and 4821 m, respectively. Made up of a Denglouku Formation (with large sections of mudstone and mudstone/siltstone interbed) and a Yingcheng Formation (made up of volcanic rock and rhyolite, crack-growing and highly sensitive to moisture), the three-open section of this well was continually subject to leakage and side-wall exfoliation. By using the proposed drilling fluid, drilling in the three-open section was both smooth and rapid. The electrical stability (emulsion breaking voltage > 1500 V), filtration and wall-building capability were good, the yield point/plastic viscosity ratio was larger than 0.4 and initial and final shearing pressure were 3-6 Pa and 5-15 Pa. The drilling speed was 1.8 m/h in the horizontal section, and the total drilling length was 1704.35 m, which is the highest value that has ever been reported.

The other key well in this study was the GS3 well. Located in the Gulong depression Aonan pit, this well is a high-temperature, high-risk well with a design depth of 4920 m. Drillings in the vicinity have revealed that the well has a high geothermal gradient (4.07°C/100 m) and a final temperature of 200°C. During the drilling of other wells

Table 4: Drilling fluid properties vs. well depth in the case of WS1-H2 well.

Well depth (m)	ρ (g/cm ³)	FV (s)	PV (mPa·s)	YP (Pa)	YP (PV)	Gel (Pa/Pa)	ES (V)	FL _{HTHP} (mL)
3773	1.20	50	18	8	0.44	5/13	1553	7.0
4039	1.20	56	28	12	0.43	5.5/13.5	1574	6.8
4325	1.20	62	32	14	0.41	6/14	1608	7.0
4570	1.20	67	32	15	0.46	6/14.5	1624	7.2
4760	1.20	67	32	14	0.43	6.5/15	1638	7.4
4821	1.20	69	35	14	0.40	6/15	1643	7.0

Table 5: Drilling fluid properties vs. depth of the GS3 well.

Well depth (m)	Temperature (°C)	ρ (g/cm ³)	FV (s)	PV (mPa·s)	YP (Pa)	YP (PV)	ES (V)	FL _{HTHP} (mL)
4482	182.4	1.16	53	25	11	0.44	1742	7.2
4576	186.2	1.20	56	28	12	0.43	1655	7.4
4689	190.8	1.30	57	31	13	0.42	1608	7.4
4774	194.3	1.30	62	32	13	0.41	1571	7.2
4880	198.6	1.30	65	34	14	0.41	1538	7.2
4920	200.2	1.30	65	35	14	0.40	1569	7.4

in this area, retardation and exfoliation were observed due to the significantly degraded rheological behavior of the drilling fluids used. Therefore, the developed thermal resistant and highly thixotropic water-in-oil drilling fluid system was used in the drilling of the three-open section. The system showed good rheological behavior, electrical stability and filtration, and wall-building capability. The average uniform change of the well diameter was 5.83%, enabling successive works.

4 Conclusions

(1) The gemini surfactant (DQGE- I) synthesized exhibited high surface activity due to the multiple adsorption functional groups. An acylamino group (strong hydration group) and an NVP (protection group) were introduced to enhance the adsorption capability and thermal resistance of the surfactant, which resulted in enhanced emulsifier adsorption. An optimized HLB value was achieved with a suitable hydrophilic/hydrophobic ratio.

(2) Compared to conventional water-in-oil drilling fluids, emulsions prepared using DQGE-I exhibited smaller drop size and more uniform distribution. The VDW force between emulsions and solid particles (e.g. organic

soil) was enhanced, resulting in increased gel strength and suspension behavior. A network rupture could be triggered by a relatively low shearing rate, indicating that the system was highly thixotropic.

(3) A highly thixotropic water-in-oil drilling fluid system was developed using DQGE-I and additives such as a precipitation reducing agent, organic soil and a wetting agent. The density and thermal resistance limit of the products were 1.2-2.0 g/cm³ and 260°C, respectively. Additionally, the proposed system showed 15% anti-debris and 20% anti-water, indicating a good anti-contamination capability.

(4) In virtue of its excellent rheological behavior, thermal resistance and stability, the drilling fluid prepared was successfully applied in six wells in the Daqing Oilfield. During these tests, no accidents occurred. The fluid was successful in complicated drilling formations, such as wells within enlarged cracks, hard and brittle mudstone, and volcanic wells. The longest deep horizontal well (1704.35 m) and the highest well temperature (200 °C) were achieved in WS1-H2 and GS3, respectively.

Conflict of interest: Authors declare no conflict of interest.

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