

# Solution Property Investigation of Combination Flooding Systems Consisting of Gemini–Non-ionic Mixed Surfactant and Hydrophobically Associating Polyacrylamide for Enhanced Oil Recovery

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**ABSTRACT:** The aim of this work was to investigate the solution properties of a new polymer–surfactant (SP) flooding system, including hydrophobically associating polyacrylamide (HAPAM) and mixed surfactant [mixture of fatty acid disulfonate anionic gemini surfactant (DMES) and non-ionic surfactant Triton X-100 (TX-100)]. The critical micelle concentrations (cmc's) of four gemini surfactants were smaller than 100 mg L<sup>-1</sup>. Furthermore, their interfacial tensions (IFTs) could reach an ultralow value with Bohai oil at lower concentrations. Through optimized formulation, we found that DMES-14 had better properties and was selected as the major component of the surfactant. We designed an optimal formulation of the SP system with 1750 mg L<sup>-1</sup> HAPAM and 3000 mg L<sup>-1</sup> mixed surfactant (the mass ratios of DMES-14 and TX-100 are from 4:1 to 5:1). The SP system (ratio of 4:1) with a very small surfactant concentration could reach ultralow IFT with different crude oils, which proved that the simpler component surfactant had better reservoir compatibility. TX-100 could widen the “window” of increasing viscosity and weaken the disadvantage of the interaction between HAPAM and the surfactant. The stability of this SP system was evaluated by the temperature, mineralized degree, shearing, aging time, adsorption, and chromatographic separation. All of experiments showed that it still keeps higher viscosity and ultralow IFT with different evaluation conditions; therefore, it is feasible to use as a SP combination flooding system for enhanced oil recovery (EOR).

## 1. INTRODUCTION

The chemical flooding technologies for enhanced oil recovery (EOR), such as polymer flooding and alkali surfactant polymer (ASP) flooding, have been applied successfully worldwide.<sup>1–5</sup> Although many laboratory tests and oil field applications have confirmed that the ASP flooding can increase oil recovery more notably than water flooding and polymer flooding,<sup>3,6–9</sup> alkali could react with an acid substance to produce an *in situ* surfactant and emulsify crude oil to increase recovery.<sup>1,10,11</sup> However, the presence of a high concentration of alkali may cause some disadvantages. First, the alkali could react with divalent ions, such as Ca<sup>2+</sup> and Mg<sup>2+</sup>, to scale on pipe and equipment.<sup>12</sup> Second, it could react with polymer, which contains acrylamide monomer to degrade it.<sup>12,13</sup> Third, it could react with metal ions in clay to decrease formation permeability.<sup>12</sup> Therefore, the polymer–surfactant (SP) flooding system without alkali received more attention. At present, the SP combination flooding system has already been applied in the Shengli oilfield in China.<sup>14</sup>

In chemical flooding systems, the partially hydrolyzed polyacrylamide (HPAM) was widely used as a thickener. The viscosity of the HPAM solution increases as its molecular weight increases, but a higher molecular weight HPAM could be degraded irreversibly at a higher shear rate; therefore, it easily lost viscosity in its application.<sup>15,16</sup> However, for the associating polymers, such as hydrophobically associating

polyacrylamide (HAPAM), which were different from HPAM that contains a small number of hydrophobic groups [less than 1% (mol/mol)], the intermolecular association between different hydrophobic groups could build a reversible supermolecular network structure to increase solution viscosity. Furthermore, it showed excellent shearing, temperature, and salinity stability.<sup>17</sup> At present, the HAPAM has been successfully applied as a mobility control agent to EOR.<sup>4</sup>

The surfactant, which was used in the chemical flooding system, played an important role to decrease oil/water interfacial tension (IFT) and wettability modification. The petroleum sulfonate, as a high oil/water interfacial activity surfactant, was often used in ASP or SP flooding systems,<sup>8,18,19</sup> but because of the composite difference of raw materials and complication of producing technology, it was difficult to obtain a stable quality of industrial products to adapt to different crude oil.<sup>20</sup> Furthermore, most of them showed higher interfacial activity, which must cooperate with a high concentration of alkali;<sup>10</sup> therefore, the developed new surfactants with higher interfacial activity and wider suitability were an important target to realize the SP flooding system in practical application. The gemini surfactant or other two-tail surfactant that contains two

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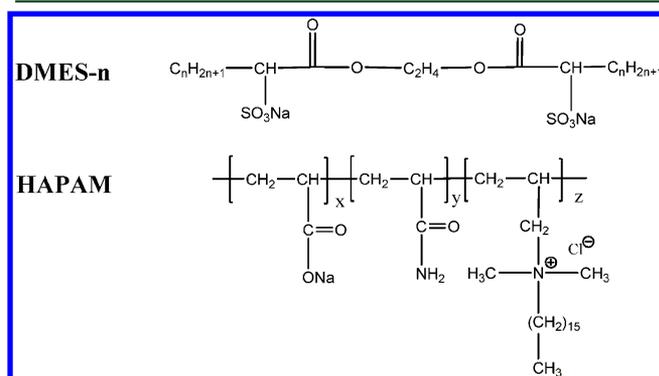
hydrophobic groups showed higher interfacial activity on gas/water and oil/water interfaces at much lower concentrations than a conventional single-chain surfactant.<sup>21,22</sup> Therefore, on the basis of the associating polymer and gemini surfactant, it is possible to form a new combination flooding system with excellent properties for EOR.

However, the interaction of the hydrophobically modified and unmodified water-soluble polymer with the surfactant showed different characteristics, especially in the rheology of SP solution.<sup>23–25</sup> Generally, the former solution viscosity increased at a low level of the surfactant concentration, but the viscosity decreased dramatically with the surfactant concentration increasing. Some studies found that the mixed surfactants could tune the SP solution properties; for example, a certain surfactant with the appropriate hydrophilic–lipophilic balance (HLB), such as nonylphenol ethoxylates, could weaken the disadvantage effect.<sup>26,27</sup>

In this paper, the surface activities and interfacial activities of disulfonate anionic gemini surfactant (DMES)-*n* were measured. Furthermore, on the basis of DMES as the major surfactant, authors formed and optimized the formulation of the SP flooding system, which was composed of the mixed surfactant and hydrophobically associating polymer; subsequently, its IFT and viscosity under reservoir conditions have been investigated to confirm the possibility of application in the Bohai offshore oilfield.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Anionic gemini surfactants DMES-*n* were synthesized according to a patent.<sup>28</sup> HAPAM was synthesized according to the literature.<sup>29</sup> [intrinsic viscosity, 2624.9 mL g<sup>-1</sup>; hydrolysis degree, 23% (w/w); and hydrophobic monomer content, 0.5% (mol/mol)]. Their molecular structures were illustrated in Figure 1.



**Figure 1.** Structures of DMES-*n* gemini surfactants (*n* = 12, 14, 16, and 18) and HAPAM.

The petroleum sulfonate (ORS-41, Witco, Avoca, MI) was obtained from the Daqing oilfield. HPAM (MO4000) was purchased from Japan [molecular weight, 25 000 kg mol<sup>-1</sup>; hydrolysis degree, 17.6% (w/w)]. Sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS) were purchased from Aldrich. They were dissolved in hot ethanol, under stirring, filtered, and then precipitated with cold acetone. Non-ionic surfactant TX-100 and other reagents were purchased from Chengdu Kelong Chemical Reagents Corporation (China) and used as received without further purification. Distilled water was used to prepare formation water in all experiments.

The different dehydrated crude oils were obtained from the Bohai offshore oilfield (density of 0.95 g/cm<sup>3</sup>), Daqing oilfield (density of 0.85 g/cm<sup>3</sup>), and Shengli offshore oilfield (density of 0.95 g/cm<sup>3</sup>).

Inorganic salts were added to distilled water to simulate the injected water in the pilot that was used for solution property experiments, and no precipitate was present in any formation water. Its composition and salinity are given in Table 1.

**Table 1. Composition of the Injected Water**

ion style	ion concentration (mg L <sup>-1</sup> )		
	Bohai offshore oilfield	Daqing oilfield	Shengli offshore oilfield
K <sup>+</sup> and Na <sup>+</sup>	3085.61	1044.74	7404.10
Ca <sup>2+</sup>	275.55	56.5	299.01
Mg <sup>2+</sup>	154.50	26.14	779.06
CO <sub>3</sub> <sup>2-</sup>	14.18	0	0
HCO <sub>3</sub> <sup>-</sup>	311.52	2352.02	264.12
SO <sub>4</sub> <sup>2-</sup>	85.25	148.15	706.28
Cl <sup>-</sup>	5439.06	255.97	13545.41
total dissolved substance (TDS)	9365.66	3883.52	22997.96
temperature (°C)	65	45	65

**2.2. Methods.** **2.2.1. Solution Preparation.** The surfactants or polymer stock solution of 5000 mg L<sup>-1</sup> was prepared by dissolving surfactants or polymer in pure water or formation water. The dilute surfactant–polymer solution was prepared by mixing their stock solution in formation water to obtain the desired surfactant and polymer concentrations. In the SP flooding system, the polymer concentration was 1750 mg L<sup>-1</sup> and the total surfactant concentration was 3000 mg L<sup>-1</sup>.

**2.2.2. Measurement of Surface Activity.** The equilibrium surface tensions of different concentration solutions in pure water were measured using the Wilhemy circle method on a JYW-200A tensionmeter (China) at 25 °C. Equilibrium surface tension data were reproducible within 0.02 mN m<sup>-1</sup>. The critical micelle concentration (cmc) and the concentration that reduces the surface tension by 20 mN m<sup>-1</sup> (C<sub>20</sub>) were determined from the plot of the surface tension versus the logarithmic molar surfactant concentration in water.

**2.2.3. Measurement of the Krafft Point Temperature.** The conductivities of 1% surfactant solution under different temperatures were measured by an EC-215 conductivity meter (HANNA, Woonsocket, RI). The Krafft point temperatures (T<sub>K</sub>) were taken as the temperature where the conductivity versus temperature plot showed a break.

**2.2.4. Measurement of Aggregation Numbers.** The aggregation numbers of surfactants were determined with a steady-state fluorescence quenching technique (SSFQ).<sup>30</sup> The fluorescence spectra were recorded on a F-4500 fluorescence spectrophotometer (Japan, Hitachi) at 25 °C using pyrene as the fluorescence probe and cetyl pyridinium chloride (CPC) as the quencher. The concentration of surfactant was 10 cmc, and the concentration of pyrene probe was 1.6 μM. The excitation wavelength was 335 nm. The fluorescence spectrum of pyrene was measured, and its third vibronic peak (383 nm) was used for the analysis.

**2.2.5. Measurement of Oil/Water IFT.** The oil/water IFTs between solution and crude oil were measured using a TX-500C spinning drop tensionmeter (Bowing, Stafford, TX) to last 30 min at the prescribed temperature. The instrument could automatically record the IFT with an image pick-up device and image acquisition software.

**2.2.6. Measurement of Viscosity.** The viscosity of solution was measured using a DV-III viscometer (Brookfield, Middleboro, MA) with a shear rate of 7.34 s<sup>-1</sup> at 65 °C.

**2.2.7. Stability of the SP Flooding System.** **2.2.7.1. Shear Degradation.** The experimental instrument was a seven-speed blender (Waring blender, Torrington, CT). A total of 400 mL of SP solution was poured into the cup and stirred at 3500 rpm for 10 s to simulate the solution shearing process, while it was injected into the floor. The origin and final IFTs and viscosities were measured.

**2.2.7.2. Aging Stability.** A total of 30 mL of SP solution was injected into eight ampules. They were degassed with a performing vacuum-injected nitrogen cycle 3 times to replace the oxygen in bottles. The ampules were sealed under vacuum, and then they were placed in an oven at 65 °C. At a prescribed time, one bottle was taken out to measure IFT and viscosity of solution.

**2.2.7.3. Salinity Stability.** The salinity of Bohai formation water was defined as 1.0 TDS. The salinity and composition were varied multiples of Bohai formation water to prepare formation water with different salinity, and then the SP solution was made up with it. Finally, IFT and viscosity of solution were measured.

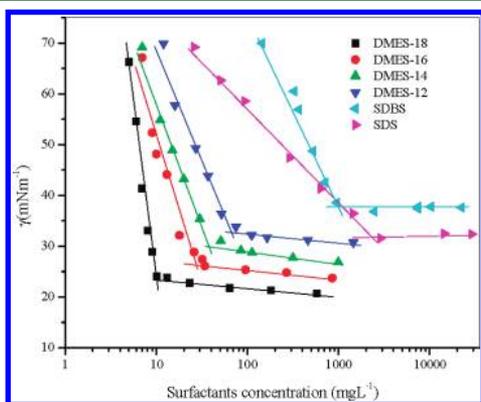
**2.2.7.4. Adsorption Isotherm.** A total of 10 g of clear and dried quartz sand were mixed with 50 g of SP solution in a ground-pyramid flask after pumping into nitrogen to last 15 min. The sealed flasks were placed on a water bath vibrator and shaken for 24 h at a constant temperature of 65 °C. The upper layer solution in the flask was poured out and centrifuged at 2000 rpm for 30 min to separate the sand. Then, the upper clear solution was added again to adsorb with fresh quartz sand by the former method to last 5 times. The IFTs and viscosities of every separated upper layer clear solution were measured.

**2.2.8. Chromatographic Separation.** The sand of 60–100 mesh was added to the tube of 100 cm length and compacted with a pressure beyond 10 MPa, and its dry weight and size were measured. In the next step, the formation water was injected at a constant velocity of 1.0 mL/min until the pressure was steady, and the water permeability and porosity were calculated on the basis of Darcy's law.

With the continued injection of SP solution, the outlet solution was collected every 5 mL (approximately 0.15 pore volume). The concentrations of every component were analyzed. The DMES concentration was measured by two-phase titration with cationic surfactant cetyltrimethylammonium bromide (CTMAB) and indicator (Thymol blue). The HAPAM concentration was determined by iodine–starch colorimetric analysis.<sup>31</sup> The normalized concentrations were calculated with the ratio of the outlet solution concentration/inlet solution concentration.

### 3. RESULTS AND DISCUSSION

**3.1. Surface Activity.** The equilibrium surface tensions of gemini surfactant DMES-*n* (*n* = 12, 14, 16, and 18) and conventional single-chain surfactant (SDS and SDBS) aqueous solutions at different surfactant concentrations were measured and shown in Figure 2. Clearly, the surface tension of all



**Figure 2.** Equilibrium surface tensions versus the surfactant concentration in pure water.

surfactants decreases with an increasing concentration until cmc. Above the cmc, the surface tension became steady.

Generally, the gemini surfactant in water gave smaller cmc's and greater efficiency in lowering the surface tension than the single-chain surfactant.<sup>32</sup> The surface activity and micellization data of all surfactants were summarized and shown in Table 2

**Table 2.** Surface Activity and Micellization Data of Surfactants in Pure Water Solution

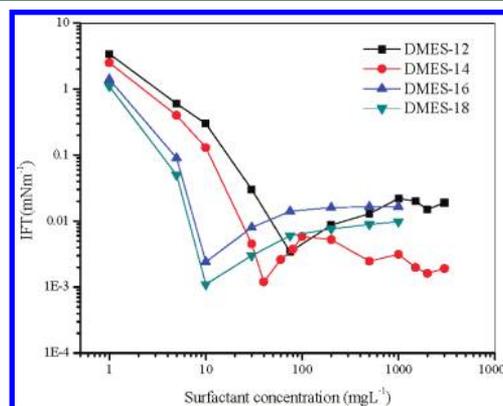
surfactant	cmc (mg L <sup>-1</sup> )	$\gamma_{cmc}$ (mN m <sup>-1</sup> )	C <sub>20</sub> (mg L <sup>-1</sup> )	cmc/C <sub>20</sub>	aggregation numbers	T <sub>K</sub> (°C)
DMES-18	10.31	23.2	6.25	1.64	19	46.2
DMES-16	27.45	26.2	9.68	3.54	28	42.7
DMES-14	38.04	29.9	12.98	4.32	35	34.2
DMES-12	66.29	32.8	24.89	3.03	43	29.1
SDBS	1044.24	38.0	401.94	2.60	77 <sup>a</sup>	31.5 <sup>a</sup>
SDS	2413.60	31.9	178.19	13.55	80 <sup>a</sup>	16.0 <sup>a</sup>

<sup>a</sup>From ref 33.

(part of the data come from the literature<sup>33</sup>). It could be found that DMES-*n* in water gave smaller cmc's and greater efficiency in lowering the surface tension than SDS and SDBS. The surface tensions at cmc ( $\gamma_{cmc}$ ) of DMES-*n* were similar to single-chain surfactants. However, the cmc's and C<sub>20</sub> of DMES-*n* in water were 1 or 2 orders of magnitude smaller than that of single-chain surfactants. Furthermore, the aggregation numbers were smaller than single-chain surfactants. It suggested better micelle-forming ability of gemini surfactants in water. Owing to the contribution of the alkyl chain to the surface activity, the cmc's and aggregation numbers of DMES-*n* decreased with an increasing alkyl chain length under common spacer length.

**3.2. IFTs between Surfactants and Crude Oil.** In the procedure of oil displacement, before the residual oil drop in holes and rocks was collected to form oil bands, it must overcome the capillary forces with the oil/water IFT. Ultralow IFT (<1.0 × 10<sup>-2</sup> mN m<sup>-1</sup>) means a larger capillary number to mobilize the oil drop easily.<sup>34</sup> Furthermore, the chemical flooding with surfactants was needed to lower the concentration to reduce the expensive cost of the surfactant.

The equilibrium IFTs between surfactant solution with Bohai formation water and crude oil were measured and shown in Figure 3. Below the cmc's, the surfactant started to adsorb at

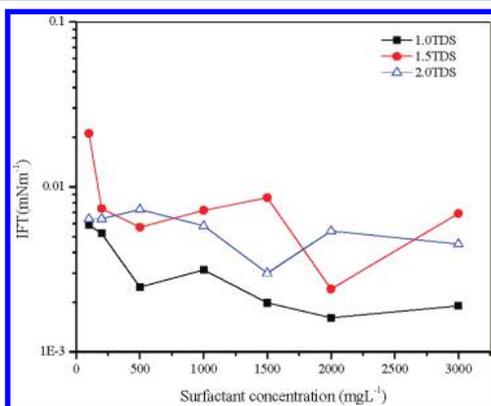


**Figure 3.** IFTs versus the surfactant concentration for different alkyl chain lengths (65 °C, Bohai formation water, and Bohai oil).

the oil/water interface; therefore, the oil/water IFTs decreased dramatically with an increasing surfactant concentration. Owing to the effect of salinity on interfacial activity, all of the four DMES gemini surfactants could reach a minimum and realize ultralow IFT quickly. Above this concentration, the IFTs increased steadily with an increasing surfactant concentration and finally reached 0.1–0.001 mN m<sup>-1</sup>. However, the solutions of DMES-16 and DMES-18 were turbid when their concentrations were beyond 1000 mg L<sup>-1</sup>, although they

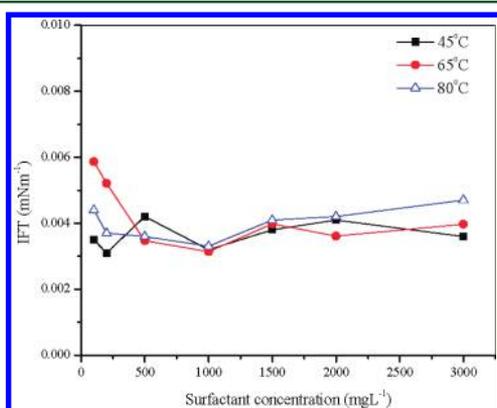
exhibited better oil/water interfacial activity at lower concentrations than DMES-12 and DMES-14.

**3.3. Formulation of the SP Flooding System.** **3.3.1. Selection of the Major Surfactant.** Generally, the displacement system is prepared with injected water in the oilfield application. However, the lower temperature of water may lead to the decrease of the solubility of the surfactant, and the aggregation behavior of surfactants and distribution in the oil and water phase could change because of salt effects. Besides, some surfactants could react with bivalent ion (for example,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) to precipitate.<sup>12</sup> Through lots of compatibility experiments, we found that DMES-16 and DMES-18 solutions with a higher concentration surfactant may precipitate at a lower temperature and higher salinity, although they had better interfacial activity (Figure 3). In addition, DMES-12 could not reach ultralow IFT, despite better solubility. We measured the IFTs of DMES-14 with different ratios of formation water from 1.0 to 2.0, in contrast with the salinity of Bohai formation water (Figure 4) and different temperatures from 45 to 80 °C



**Figure 4.** IFTs versus the DMES-14 concentration for different mineralized degree formation water (65 °C and Bohai oil).

(Figure 5). At higher salinities, bivalent ion concentration, and different temperatures, we found that DMES-14 could still keep

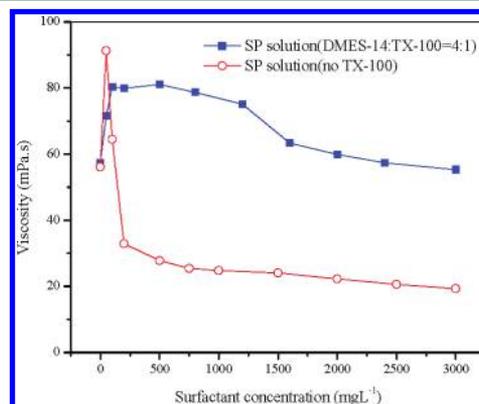


**Figure 5.** IFTs versus the DMES-14 concentration at different temperatures (Bohai formation water and Bohai oil).

ultralow IFT. Moreover, the solution did not appear cloudy under all experiments. Therefore, DMES-14 was selected as the major component of the surfactant.

**3.3.2. Effect of the Non-ionic Surfactant on IFT and Viscosity.** In evaluating criteria of chemical flooding, viscosity was another important parameter affecting displacement

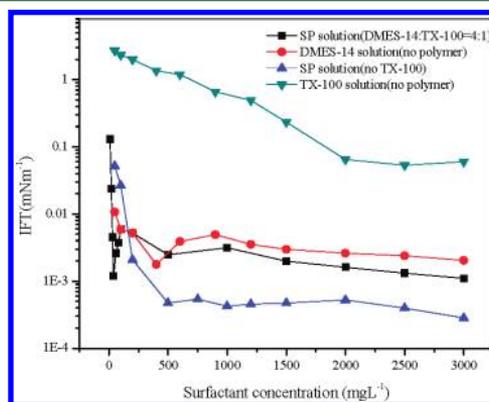
efficiency, except IFT, because the polymer solution could reduce the water/oil mobility ratio and improve sweep efficiency.<sup>17</sup> Therefore, both viscosity and IFT should be concerned in the SP flooding system. As Figure 6 illustrated,



**Figure 6.** Viscosity of the SP system versus the DMES-14 concentration for TX-100 present ( $C_{\text{HAPAM}}$  of 1750  $\text{mg L}^{-1}$ , 65 °C, and Bohai formation water).

although the DMES-14/HAPAM system without the non-ionic surfactant could obtain ultralow IFT, however, because of the interaction of the surfactant and associating polymer,<sup>25</sup> the viscosity of the polymer solution increased sharply below 100  $\text{mg L}^{-1}$ , subsequently decreasing dramatically with the surfactant concentration increasing. In some literature, a certain non-ionic surfactant significantly increased the viscosity and weakened the disadvantage effect, especially at high overall surfactant concentrations.<sup>26,27</sup> Through an attempt with different non-ionic surfactants, we found that terocetylphenoxy polyoxyethanol (TX-100) could slow the declining tendency of viscosity and widen the surfactant concentration “window” of increasing viscosity (Figure 6). The addition of TX-100 to anionic surfactant micellar solutions increased the microviscosity of the micellar interface. It implied that TX-100 molecules tend to penetrate the DMES-14 micelles, which decreased the micellar charge density and resulted in a closer arrangement between long hydrophobic chains.<sup>35</sup>

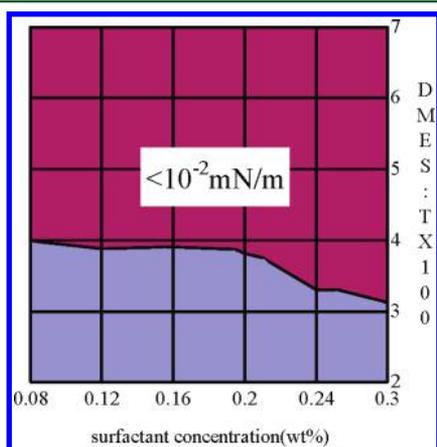
Furthermore, in this experiment, we contrasted the IFTs of four systems (Figure 7). We found an interesting phenomenon that the SP system has a lower IFT than single DMES-14 solution, but we did not find that the HAPAM solution without



**Figure 7.** IFTs of the SP system versus the surfactant concentration for TX-100 present ( $C_{\text{HAPAM}}$  of 1750  $\text{mg L}^{-1}$ , 65 °C, Bohai formation water, and Bohai oil).

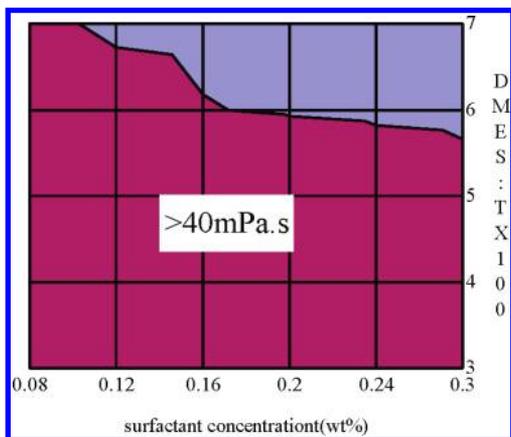
the surfactant could decrease IFT obviously. Namely, DMES-14 and HAPAM had a synergism effect on the reduction of IFT, perhaps owing to the fact that HAPAM could stabilize oil-in-water (O/W) emulsion.<sup>36,37</sup> The three-dimensional networks formed by HAPAM play a vital role in this SP system. The strong network structure of HAPAM is able to hold oil particles, including the lipophilic surfactant, without the occurrence of phase inversion. However, unhydrophobically modified polymers were unable to form O/W emulsions with lipophilic surfactants because their network structures and viscoelastic properties were not sufficient to hold oil particles in a stable fashion.<sup>36</sup> Although the IFTs of solution increased with the addition of TX-100, it still made the IFT of the solution reach an ultralow value.

**3.3.3. Formulation Optimized for the SP System.** On the basis of the cost of HAPAM, in all of our experiments, the concentration was  $1750 \text{ mg L}^{-1}$ . The mixed surfactant and HAPAM formulation was optimized adding different proportions of DMES-14 and TX-100 from 2:1 to 7:1 (w/w). In the IFT graph (Figure 8), the SP system could reach an ultralow



**Figure 8.** IFT versus the surfactant concentration with different proportions of DMES-14 and TX-100 ( $C_{\text{HAPAM}}$  of  $1750 \text{ mg L}^{-1}$ ,  $65^\circ\text{C}$ , Bohai formation water, and Bohai oil).

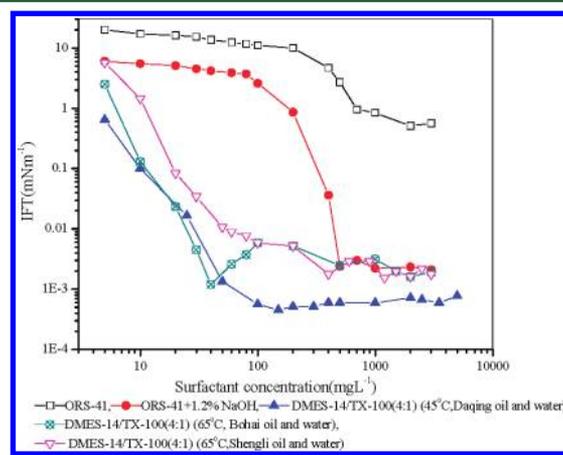
IFT when the proportion was more than 4:1. Moreover, in the viscosity graph (Figure 9), the SP system could go beyond  $40 \text{ mPa s}$  when the proportion was less than 6:1, because the viscosity played a more important role during displacement<sup>38</sup>



**Figure 9.** Viscosity versus the surfactant concentration with different proportions of DMES-14 and TX-100 ( $C_{\text{HAPAM}}$  of  $1750 \text{ mg L}^{-1}$ ,  $65^\circ\text{C}$ , and Bohai formation water).

and higher proportions of DMES-14 implied higher costs of the SP flooding system. Therefore, we choose the ratios of 4:1 and 5:1 as the mixed surfactant formulation for EOR.

**3.3.4. Compatibility of the Mixed Surfactant to the Reservoir Condition.** Most of the petroleum sulfonate sources of light oil, which are multi-component mixtures, were difficultly compatible with different petroleum; therefore, we thought whether the surfactants with simpler components can adapt to various crude oils. Therefore, we prepared the surfactant solution with different formation waters (Table 1) and compared interfacial activity under three reservoir conditions (Bohai offshore oilfield, Daqing oilfield, and Shengli offshore oilfield). Here, the petroleum sulfonate, ORS-41, is an effective surfactant of ASP, which was already used successfully in the Daqing oilfield. As Figure 10 showed, ORS-41 could not



**Figure 10.** IFTs versus the surfactant concentration under different reservoir conditions.

decrease IFT to an ultralow value, except mixed with 1.2% NaOH. However, this mixed surfactant could realize the goal without alkali. It exhibited wide adaptability to different crude oils and formation waters. It means that it is possible to apply this mixed surfactant in different oilfields. Therefore, it is a feasible method with simpler component surfactants to replace the petroleum sulfonate for EOR.

**3.4. Stability of the SP Flooding System under Bohai Reservoir Conditions.** **3.4.1. Mineralized Degree and Temperature Stability.** Owing to the complexity of reservoir conditions, the displacement flooding system had to be investigated for different mineralized degrees and temperatures. We prepared the SP solution with different salinity levels from  $3800$  to  $23\,000 \text{ mg L}^{-1}$ . Similar to Figure 4, the DMES-14 surfactant showed excellent mineralized degree stability. In Figures 11 and 12, IFTs of the SP system still kept an ultralow value. It showed better mineralized degree and temperature stability, but the viscosity of the SP system decreased dramatically because of two reasons. First, the polymer chain could coil in high-salinity water;<sup>17</sup> furthermore, the polymer could degrade by reacting with dissolved oxygen at higher temperatures.<sup>39</sup> When the mineralized degree was lower than  $14\,000 \text{ mg L}^{-1}$  and the temperature was lower than  $85^\circ\text{C}$ , the SP system viscosity still reached  $40 \text{ mPa s}$ , which means that it could satisfy the condition of Bohai offshore reservoirs.

**3.4.2. Shear Stability.** The polyacrylamide is sensitive to shear degradation because of its chain flexibility, when the polymer or SP solution was applied for EOR. The shearing can

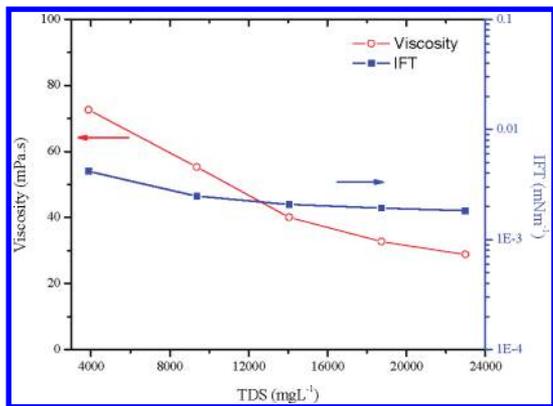


Figure 11. Viscosity and IFT of the SP system versus the total dissolved substance [ $C_{\text{HAPAM}}$  of  $1750 \text{ mg L}^{-1}$ ,  $C_S$  of  $3000 \text{ mg L}^{-1}$  (4:1 DMES-14/TX-100),  $65 \text{ }^\circ\text{C}$ , Bohai formation water, and Bohai oil].

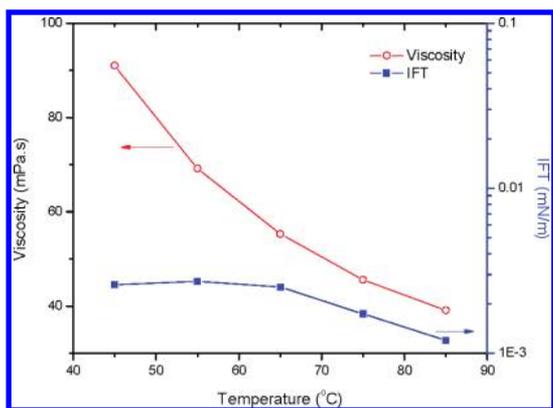


Figure 12. Viscosity and IFT of the SP system versus the test temperature [ $C_{\text{HAPAM}}$  of  $1750 \text{ mg L}^{-1}$ ,  $C_S$  of  $3000 \text{ mg L}^{-1}$  (4:1 DMES-14/TX-100),  $65 \text{ }^\circ\text{C}$ , Bohai formation water, and Bohai oil].

occur at different stages of handling and injection processes, such as dissolution in injected water, recirculation with centrifugal pump, flow-through chokes, down-hole valves, and perforations at high pressure and high flow rate.<sup>40</sup> Violently shear effects made the solution viscosity decrease, so that mobility control ability was weakened.

The hydrophobically associative polymer can build reversible supermolecular networks to improve solution viscosity with an associative effect.<sup>17</sup> Therefore, the flooding system with HAPAM may obtain better shear stability.

As Table 3 showed, after violent shearing, the IFT of the SP solution was kept steady and the two formulations of SP solution with HAPAM obtained a higher viscosity residual rate above 60%, whereas the HPAM lost most of the viscosity. The

Table 3. Shearing Stability of the SP Flooding System [ $C_{\text{HAPAM}}$  of  $1750 \text{ mg L}^{-1}$ ,  $C_{\text{HPAM}}$  of  $2750 \text{ mg L}^{-1}$ ,  $C_S$  of  $3000 \text{ mg L}^{-1}$  (4:1 DMES-14/TX-100),  $65 \text{ }^\circ\text{C}$ , Bohai Formation Water, and Bohai Oil]

DMES-14/TX-100 (w/w)	viscosity (mPa s)		IFT (mN m <sup>-1</sup> )	
	before shearing	after shearing	before shearing	after shearing
4:1	57.4	36.1	0.00278	0.00281
5:1	47.2	30.2	0.00085	0.00094
4:1 <sup>a</sup>	47.5	8.3	0.00257	0.00287

<sup>a</sup>The polymer is HPAM (MO4000).

results showed that HAPAM could improve the shear stability of the SP flooding system, while IFT kept an ultralow value.

3.4.3. *Aging Stability.* Dependent upon the injection rate, formation permeability, and well spacing, the SP flooding system often stays in the floor to last several months or years during the displacement process. The dissolved oxygen, metals, and free-radical generators in solution could promote the polymer degradation.<sup>39</sup> Therefore, its aging stability is very important to the pilot application. We investigate the aging stability for 90 days. As Figure 13 showed, under reservoir

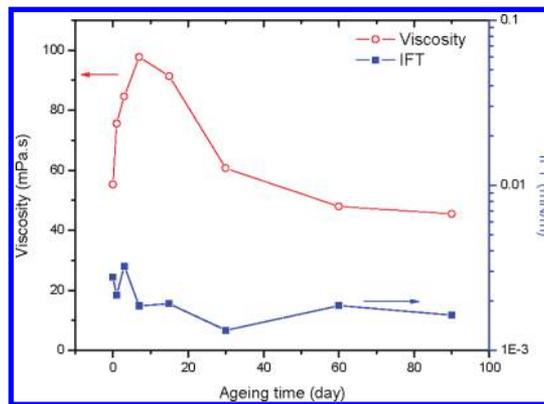


Figure 13. Viscosity and IFT of the SP system versus the aging time [ $C_{\text{HAPAM}}$  of  $1750 \text{ mg L}^{-1}$ ,  $C_S$  of  $3000 \text{ mg L}^{-1}$  (4:1 DMES-14/TX-100),  $65 \text{ }^\circ\text{C}$ , Bohai formation water, and Bohai oil].

conditions, the viscosity increased to a maximum because the polymer dissolved fully in 7 days and then decreased steady because of degradation; meanwhile, IFT changed very little, and the system did not appear to phase separate. It illustrated that the SP system properties could be kept steady during the displacing period.

3.4.4. *Adsorption Property.* It has been reported that the adsorption loss in reservoir rocks is a major factor for displacement efficiency and cost-effectiveness.<sup>8</sup> Therefore, the SP flooding system must determine the adsorption loss effect on IFT and viscosity. It was a simple method that determines the IFT and viscosity of the SP solution through adsorption for several times by fresh quartz sand. As Figure 14 showed, after

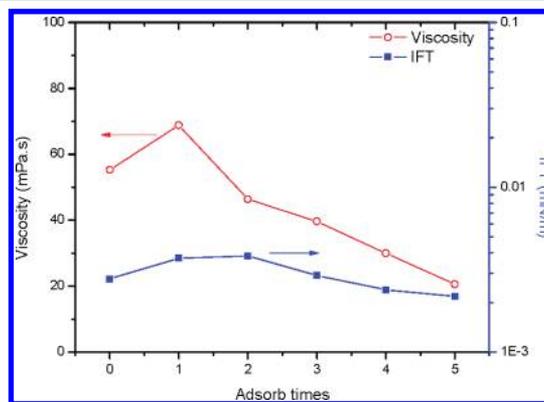


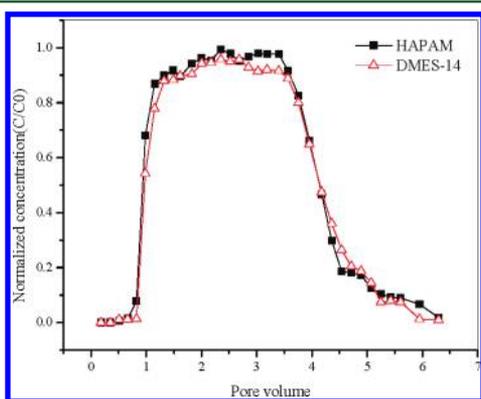
Figure 14. Viscosity and IFT of the SP system versus the adsorption time [ $C_{\text{HAPAM}}$  of  $1750 \text{ mg L}^{-1}$ ,  $C_S$  of  $3000 \text{ mg L}^{-1}$  (4:1 DMES-14/TX-100),  $65 \text{ }^\circ\text{C}$ , Bohai formation water, and Bohai oil].

adsorption for 5 times, although the cationic hydrophobical group increased the adsorption, the viscosity still held 20 mPa s

because the hydrophobically associative effect could decrease the loss.<sup>31</sup> The anionic surfactant DMES-14 has less adsorption in quartz sand, owing to its negative surface. Therefore, the IFT of the SP system could keep an ultralow value.

**3.4.5. Chromatographic Separation Property.** During the process in which the displacement fluid flows from the injected well to the produced well, the reservoir can be regarded as a large chromatographic column. The various chemical agents can be selectively adsorbed in the surface of the rock, because of the different properties of every component. The adsorption and retention are different. Therefore, the composition of the SP flooding system may change during flowing in the reservoir. Because every component can play an important role in incremental oil recovery, the miniature chromatographic separation effect is very important to realize higher displacement effectively.<sup>41</sup>

In Figure 15, the changes of normalized concentration curves of DMES-14 and HAPAM in effluent solution showed that the



**Figure 15.** Normalized concentration of DMES-14 and HAPAM versus the injected pore volume [ $K_w$  of  $0.351 \mu\text{m}^2$ ,  $C_{\text{HAPAM}}$  of  $1750 \text{ mg L}^{-1}$ ,  $C_s$  of  $3000 \text{ mg L}^{-1}$  (4:1 DMES-14/TX-100),  $65 \text{ }^\circ\text{C}$ , and Bohai formation water].

surfactant concentration was behind HAPAM with very little injected volume. During the total flooding process, the formulation was kept stable, owing to the weak chromatographic separation effect. We thought that the SP system could form a “polymer–surfactant complex” because of the strong interaction. It illustrated that the flooding system could work effectively to displace oil.

#### 4. CONCLUSION

The air/water and oil/water interfacial activities of DMES- $n$  were investigated. The results showed that the gemini surfactants were excellent surfactants that could decrease oil/water IFT to an ultralow value. Through optimized formulation, the optimum composition is  $1750 \text{ mg L}^{-1}$  HAPAM and  $3000 \text{ mg L}^{-1}$  mixed surfactant and the optimum proportion of DMES-14 and TX-100 is from 4:1 to 5:1 (w/w). It could reach an ultralow IFT with different crude oils at very small concentrations and proved that the simpler component surfactant was better for reservoir compatibility. The non-ionic surfactant TX-100 could widen the “window” of increasing viscosity and weaken the disadvantage of the interaction between HAPAM and the surfactant, and HAPAM could stabilize the oil/water emulsion to decrease IFT.

The viscosity and IFT stability of this combination flooding system were investigated, such as the mineralized degree,

temperature, shearing, aging time, and adsorption in quartz sand. Under wide Bohai offshore oilfield reservoir conditions, this system can reach an ultralow IFT and a higher viscosity beyond  $40 \text{ mPa s}$ . The sandpack test showed that the formulation could be kept stable, owing to the weak chromatographic separation effect in the flooding process. All of experiments showed that it still kept a higher viscosity and an ultralow IFT with different evaluation conditions; therefore, this system is feasible to use as a SP combination flooding system without alkali in the Bohai offshore oilfield for EOR. Subsequently, we will carry out core experiments to confirm its recovery.

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##### Notes

The authors declare no competing financial interest.

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