

# Effective Synergistic Action of Benzimidazolium Nano Gemini Ionic Liquid and Conventional Surfactant for Chemical Enhanced Oil Recovery

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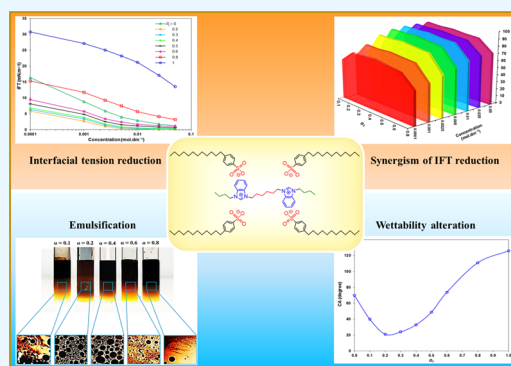
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**ABSTRACT:** Blends of newly developed Gemini surface-active ionic liquids (GSAILs) and conventional surfactants offer significant enhancements to the interfacial properties between crude oil and water, providing economic benefits in chemically enhanced oil recovery. In this study, the mixtures of a benzimidazolium cationic GSAIL,  $[C_4\text{benzim}-C_6\text{-benzim}C_4][Br_2]$ , and sodium dodecyl benzenesulfonate (SDBS) were successfully utilized for improving crude oil–water interfacial properties. The research revealed synergistic effects of up to 99.6% in reducing interfacial tension (IFT), achieving a low IFT value of  $0.04 \text{ mN m}^{-1}$  corresponding to an optimal GSAIL mole fraction of 0.2 for the mixture of surfactants. Additionally, significant synergies of 53.4 and 74% were observed in oil–water emulsification and in surface wettability when using a GSAIL mole fraction of 0.2. These results showcase the importance of the dominant interaction between the opposite-charged surfactants. The Frumkin isotherm and the Rosen model were employed for the theoretical study of adsorption behavior of individual surfactants and their mixture at the interface, demonstrating reasonable parameter variations. The overall findings emphasize the potential of utilizing these unique blends to enhance oil recovery processes through tailored interfacial properties.



## 1. INTRODUCTION

Oil plays an increasingly important role in life and industry, whereas a high percentage of crude oil still remains unavailable despite primary and secondary recoveries.<sup>1</sup> Thus, it is essential to explore efficient and feasible methods for chemical enhanced oil recovery (CEOR) by using a new generation of surfactants.<sup>2,3</sup> Conventional surfactants have limitations in use because of being sensitive to high salinity and temperature, dominant in oil reservoirs.<sup>4</sup> In contrast, surface-active ionic liquids (SAILs) are known as promising materials due to their resistance against harsh reservoir conditions, activity, recyclability, and desired environmental properties.<sup>5</sup> However, synthesis of SAILs is still in its infancy and their production could be rather expensive.<sup>6,7</sup>

For precise CEOR, the crude oil–water interfacial tension (IFT) needs to be decreased to very low values; hence, use of SAILs could not be adequate, whereas blends of an SAIL and a conventional surfactant can bring about significant synergy in IFT reduction and interesting outcomes economy. In this regard, the (toluene + *n*-decane)–water system was reported with high reduction in IFT by using surfactant mixtures.<sup>8</sup> It was also demonstrated that different mixtures of a single-chain SAIL with a conventional surfactant could remarkably improve the interfacial properties of the crude oil–water system, making oil recoveries highly efficient.<sup>9</sup>

As a subset of SAILs, Gemini SAILs (GSAILs), consisting of two hydrophilic head and hydrophobic chain groups linked by a hydrocarbon spacer, have recently received much attention. Desired properties and environmentally friendly nature have been specifically reported for GSAILs, with high interfacial activity.<sup>10,11</sup> Of note, among various imidazolium, benzimidazolium, pyrrolidinium, morpholinium, and pyridinium types, imidazolium and benzimidazolium GSAILs demonstrate greater activity.<sup>12</sup> Meanwhile, the nanosize nature, associated with GSAILs even in solutions, improves their surface/interface activity.<sup>13,14</sup>

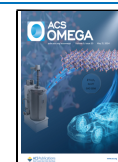
Continuing our studies on basic concepts of CEOR,<sup>15–17</sup> this study was devoted to the mixtures of the benzimidazolium cationic GSAIL,  $[C_4\text{benzim}-C_6\text{-benzim}C_4][Br_2]$  and the conventional sodium dodecyl benzenesulfonate (SDBS) anionic surfactant. The mixtures can give a solution to the high price of GSAIL, particularly if a synergy being appeared. Aspects of IFT reduction, critical micelle concentration

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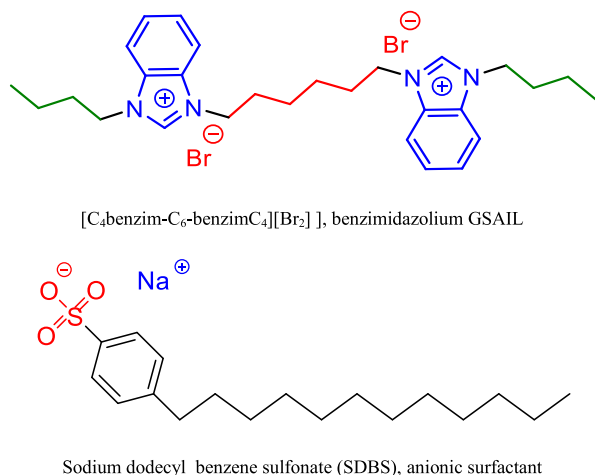


(CMC), ease of emulsion formation, and surface wettability alteration are investigated for the crude oil–water system. Considering that most CEOR studies are concerned with using single-chain SAILs, use of mixtures of a GSAIL and SDBS can give a new endeavor. Briefly, the following major objectives are sought:

1. Impact of the individual GSAIL and SDBS components.
2. Degree of synergism in IFT and CMC reductions.
3. Theoretical inspection based on the Frumkin isotherm and the Rosen nonideal interactions in binary mixtures (NIBM) model.
4. Performance of mixtures in emulsification and surface wettability.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** The synthesized nanosized benzimidazolium cationic GSAIL comprised four carbon atoms alkyl chains and six methylene in the spacer as well as two bromine anions, denoted as [3,3'-(hexane-1,6-diyl)bis(1-butyl-1*H*-benzo[*d*]-imidazol-3-ium) bromide], briefly [C<sub>4</sub>benzim-C<sub>6</sub>-benzimC<sub>4</sub>]-[Br<sub>2</sub>]. The synthesis of the product was according to the previously reported methods.<sup>17,18</sup> For better understanding, the chemical structure of the benzimidazolium GSAIL and SDBS surfactant is illustrated in Figure 1. To ascertain quality,



**Figure 1.** Used GSAIL and the conventional surfactant.

FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, dynamic light scattering (DLS), and scanning electron microscopy (SEM) analyses were performed. Corresponding results are presented in Figures S1 to S5 (Supporting Information). The purity of the products was proved by specific peaks of the benzimidazolium GSAIL and no obvious signal of the reagent/byproduct in the NMR spectra. The hydrodynamic and micelle sizes of the as-prepared products were examined via SEM and DLS methods, as outlined in Table 1. It is important to note that the obtained size in DLS as “hydrodynamic size” belongs to the GSAIL particles in aqueous solution which is different from that of particle size observed in SEM. The 99% pure SDBS surfactant

was from Sigma-Aldrich. For conducting experiments, crude oil was supplied from the Ahwaz oil field in south Iran. The major specifications are listed in Table 2. High-quality distilled water was used for preparing solutions.

**Table 2. Most Important Crude Oil Specifications**

specification/composition	value
°API	20.7
saturated (wt %)	54.0
aromatic (wt %)	22.3
resin (wt %)	6.7
asphalt (wt %)	7.7
acidity number (mg KOH g <sup>-1</sup> )	0.09
sulfur content (wt %)	1.63
salt content (lb per 1000 bbls)	4
water content (wt %)	nil
density at 20 °C (g cm <sup>-3</sup> )	0.915
viscosity at 70 °F (cP)	55
viscosity at 100 °F (cP)	44
kinematic viscosity at 70 °F (cSt)	60
pour point (°F)	10
flashpoint (°F)	70
reid vapor pressure (psi)	12.1
loss at 200 °C (wt %)	9.3

**2.2. Instruments and Procedures.** The measurement of the IFT and contact angle (CA) was performed by means of a pendant drop tensiometer (CA-ES10, Fars EOR Technology). The crude oil was conducted to the tip of a precise stainless steel needle, which was submerged in the aqueous bulk solution. The experimental setup and methodology have been systematically detailed in previous publications.<sup>19,20</sup> The IFT ( $\gamma$ ) was detected several times based on the geometry of shape of the formed pendant drop and processing the image via a software.<sup>21</sup> Through this technique, to measure the IFT of crude oil–pure water, it took about 25 min to find a stable value; however, measurement was continued for 1 h to record minor changes and reach equilibrium. Each measurement was conducted thrice. Thus, the IFT of the system was stabilized at 32.9 mN m<sup>-1</sup>, indicating attainment of equilibrium IFT for the crude oil–pure water system at 298.2 K. Further, the surface tension of water (in contact with air) was 71.9 mN m<sup>-1</sup> at the same temperature, remarkably close to the literature-reported value of 72.0 mN m<sup>-1</sup>.<sup>22</sup> The experiments were conducted under the ambient pressure and temperature of 298.2 K, which were maintained constant by a thermostat (uncertainty of 0.1 K).

The surfactants (individually and in mixtures) were utilized within a concentration range of (1.0 × 10<sup>-4</sup>–1.25) mol dm<sup>-3</sup>, which were prepared by mass. The mixing of components was based on the mole fraction of GSAIL as  $\alpha_1 = C_1/C_{12}$ , where C<sub>1</sub> represents the molar bulk concentrations of the GSAIL and of SDBS, and C<sub>12</sub> = C<sub>1</sub> + C<sub>2</sub> represents the molar bulk concentration of the mixture, all in the aqueous phase. The proper range of mole fraction ( $\alpha_1$ ) was considered. Meanwhile,

**Table 1. Pure GSAIL Particle Size Obtained by SEM and Those Obtained by DLS Analysis**

GSAIL	SEM (nm)	DLS (nm)	
		hydrodynamic	micelle
[C <sub>4</sub> benzim-C <sub>6</sub> -benzimC <sub>4</sub> ][Br <sub>2</sub> ]	103.0–529.1	2.1–13.5	220.2–712.3

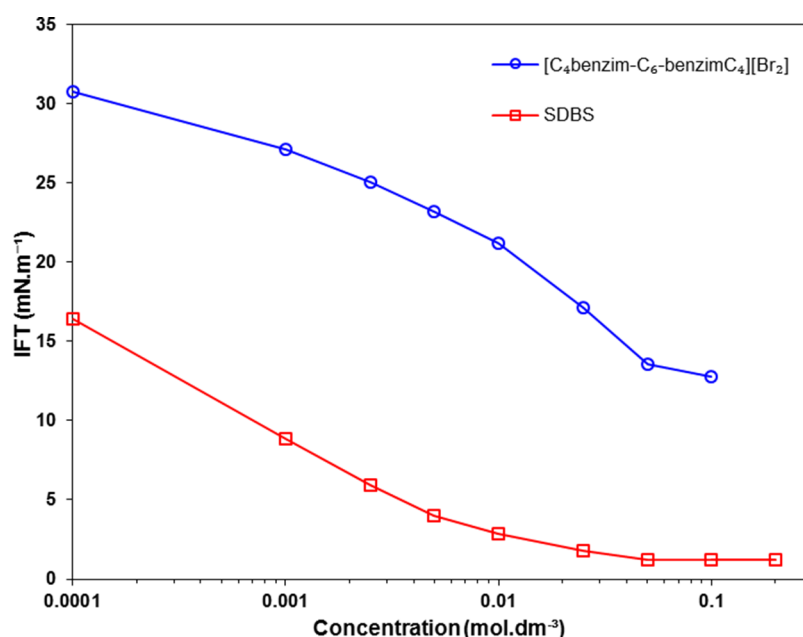


Figure 2. IFT variation of the crude oil–water system vs concentration surfactants.

an Anton Paar oscillating densitometer (DMA 4500, Austria) was used for measuring the density of solutions, as an essential parameter in IFT measuring. The uncertainty of the densitometer was  $1.0 \times 10^{-4} \text{ g cm}^{-3}$ . To determine CMCs, the corresponding concentration at the intersection of tangent lines to the upper and lower regions of the IFT variations versus the surfactant concentration was determined.

Emulsion formation was performed with equal volumes of either of the aqueous/oil phases. Here, the aqueous phase concentration was  $0.05 \text{ mol dm}^{-3}$  having a significant influence. Samples were transferred to a scaled glass vial and sonicated in an ultrasound bath (40 kHz, 305 W) for 30 min and then were allowed to rest at 298.2 K over 1 day and 1 week. After that, the formed emulsion volume ( $V_e$ ) was measured, and the emulsion index (in percentage) was calculated from  $V_e/V_t \times 100$ , where  $V_e$  and  $V_t$  stand for the emulsion and the total sample volumes, respectively.<sup>23</sup>

For wettability alteration, measuring CA on a quartz plate was the basis. Accordingly, to simulate aging, the plate was maintained in crude oil for 15 to 20 h. Then, injection of crude oil into aqueous phase was done via a vertical stainless steel needle to create a released drop to attach the upper quartz plate.<sup>24</sup> After allowing the drop to settle over a minimum of 1 h time, images were captured and the CA was obtained as an average of the right and left sides of the hemispherical drop. A constant  $0.05 \text{ mol dm}^{-3}$  concentration corresponding to different mole fractions of mixtures was considered.

### 3. RESULTS AND DISCUSSION

**3.1. Interfacial Tension in the Presence of Individual Surfactants.** Figure 2 illustrates the variation of IFT in the presence of individual surfactants. A significant IFT reduction is observed up to CMC. In the presence of benzimidazolium GSAIL and SDBS, the initial IFT value of  $32.9 \text{ mN m}^{-1}$  reached to, respectively, 12.8 and  $1.2 \text{ mN m}^{-1}$ . The corresponding CMCs appeared at 0.025 and  $0.03 \text{ mol dm}^{-3}$  (Table 3).

Comparing GSAIL with SDBS reveals that the long alkyl chain 12 C atom conventional surfactant gives an edge over the

Table 3. CMC and IFT at CMC and Minimum Achieved Value for the Individual Used Surfactants

surfactant	CMC (mol dm <sup>-3</sup> )	$\gamma_{\text{CMC}}$ (mN m <sup>-1</sup> )	$\gamma_{\text{min}}$ (mN m <sup>-1</sup> )	maximum IFT reduction (%)
[C <sub>4</sub> benzim-C <sub>6</sub> -benzimC <sub>4</sub> ][Br <sub>2</sub> ]	0.03	17.0	12.8	61.1
SDBS	0.03	1.9	1.2	96.2

4 C atom short-chain GSAIL. The maximum IFT reduction of more than 95% with the conventional surfactant could be compared to about 61% reductions with the benzimidazolium GSAIL.

The Frumkin adsorption isotherm, which takes into account the nonideal interaction among adsorbed species, gives a satisfactory explanation of IFT variations with individual surfactants. Considering the charged rings in the GSAIL structure and in SDBS, one can confirm certain interactions among their own molecules in solutions and in the adsorbed layer.

The Frumkin adsorption model and the isotherm are as<sup>25</sup>

$$\Pi = -2RT\Gamma_{m,F}[\ln(1 - \theta) + \beta\theta^2] \quad (1)$$

$$b_{\text{E}\pm}f_{\pm}[C(C + C_{\text{electrolyte}})]^{1/2} = \frac{\theta}{1 - \theta} \exp(-n\beta\theta) \quad (2)$$

where  $\Pi = \gamma_0 - \gamma$  represents the interfacial pressure, and  $\gamma_0$  and  $\gamma$  are, respectively, the pure and the reached IFT values under specified conditions. Also,  $\theta = \Gamma/\Gamma_{m,F}$  represents the fraction of interface coverage, corresponding to  $\Gamma$  and  $\Gamma_{m,F}$  (the Frumkin maximum interface excess concentrations). Also parameters  $b_{\text{E}\pm}$ ,  $\beta$ , and  $f_{\pm}$  are, respectively, the Frumkin adsorption constant, the van der Waals molecular interaction, the activity coefficient of ions, and the number of cations and anions. The accuracy of fittings was based on achieving the lowest value for an objective function (OF) using the IsoFit software.<sup>26</sup> The parameters obtained from fitting to experimental data and the OF values are listed in Table 4. Evidently, the data can precisely fit the Frumkin adsorption isotherm.

**Table 4. Frumkin and Thermodynamic Parameters and the OF Values in Accordance with the Frumkin Isotherm**

surfactant	$\Gamma_{m,F} \times 10^6$ (mol m <sup>-2</sup> )	$A_m \times 10^{36}$ (m <sup>2</sup> )	$\beta$	$b_F$ (dm <sup>3</sup> mol <sup>-1</sup> )	OF	$\Delta G_{ads}^o$ (kJ mol <sup>-1</sup> )	$\Delta G_{mic}^o$ (kJ mol <sup>-1</sup> )
[C <sub>4</sub> benzim-C <sub>6</sub> -benzimC <sub>4</sub> ][Br <sub>2</sub> ]	0.69	24.07	-3.9	$2.69 \times 10^2$	0.035	-44.18	-9.82
SDBS	0.83	13.97	-2.5	$6.47 \times 10^4$	0.391	-105.58	-8.69

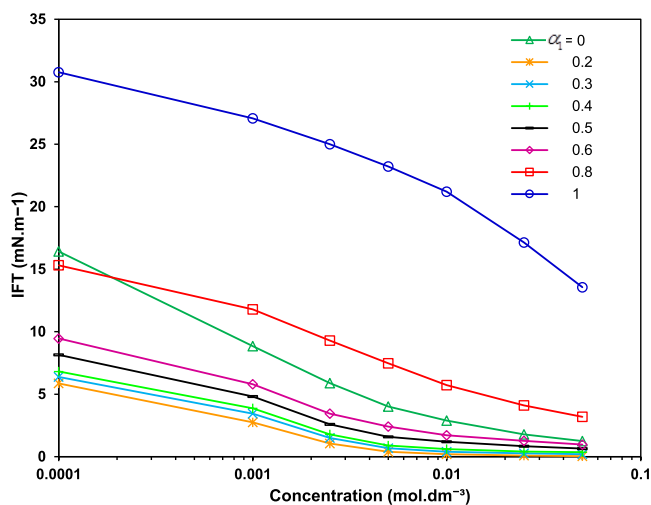
Results indicate that  $\Gamma_{m,F}$  values for SDBS, with long 12 carbon chains, are greater than those of GSAIL (4 carbon chain) in agreement with to previous studies.<sup>27,28</sup> Relatedly, the minimum occupied interface area per adsorbed molecule ( $A_m = 1/\Gamma_{m,F}N_{Av}$ , where  $N_{Av}$  is the Avogadro number) is consistent. As expected, SDBS finds a more compact orientation at the interface and, thus, low interfacial area per each molecule. Also, negative values of the molecular interaction parameter  $\beta$  prove intermolecular repulsions. Moreover, the  $b_F$  value is greater for the conventional surfactant, indicating its superior hydrophobicity and greater adsorption tendency. Consistently, the adsorption and micellization Gibbs free energies are ascertained considering the  $\rho' = \rho/18$  for the water molar concentration as<sup>29</sup>

$$\Delta G_{ads}^o = -2RT \ln \frac{b_F \rho'}{2} \quad (3)$$

$$\Delta G_{mic}^o = RT \ln CMC \quad (4)$$

The negative values for the Gibbs free energies (Table 4) confirm both the GSAIL and the SDBS tendencies to adsorb and form micelle spontaneously. Indeed, the strong hydrophobic nature accompanied with the low electrostatic repulsion provides more adsorption capability for the conventional surfactant. Furthermore, higher absolute values of  $\Delta G_{ads}^o$  imply a tendency to adsorb rather than to form micelles.

### 3.2. Interfacial Tension in the Presence of Surfactant Mixtures. Figure 3 illustrates the IFT variations versus



**Figure 3.** Variation of the crude oil–water IFT vs concentration of individual and mixture of surfactants for different mole fractions.

mixture concentration for different benzimidazolium GSAIL mole fractions ( $\alpha_1$ ). It is evident that for all the mole fractions, the IFT consistently decreases with the concentration of surfactants, and facile adsorption at low concentrations gives more pronounced slope of IFT variation, leading to extremely low IFTs of about 0.04 mN m<sup>-1</sup>. Notably, low IFTs are comparable with high capillary number in oil reservoirs.<sup>12,30</sup> It

is also evident that the IFT decreases with  $\alpha_1$  and then rises toward the corresponding IFT with just the GSAIL.

The synergistic action of surfactants could be quantified by comparing the dominant IFT with that corresponding to the linear contribution of the GSAIL and SDBS (i.e., no synergism) under a specific concentration. Based on this, the percentage of synergy in IFT reduction versus  $\alpha_1$  is depicted in Figure 4 for typical concentrations. It is evident that the percentage of synergy experiences a remarkable surge at low concentrations, stabilizes with minor variations after 0.01 mol dm<sup>-3</sup>, and then remains almost constant at around 99%. At low concentrations, positive and negative charged molecules are regularly positioned in proximity, neutralizing the electrostatic repulsion; thereby, giving high synergies. At high concentrations, on the other hand, the close arrangement of the adsorbed molecules gives no sensible change in the synergy. In comparison to previous investigations reported for blends of cationic and anionic surfactants<sup>9,31</sup> and also single-chain SAILs and surfactants,<sup>32,33</sup> the much higher degree of synergy in this study proves the strong actions of the benzimidazolium GSAIL and SDBS mixtures.

As a distinct GSAIL mole fraction, it is evident from Figure 4 that the highest degree of synergy (established with the lowest IFTs) corresponds to  $\alpha_1 = 0.2$ . Also, the most appropriate 99.6% synergy was with 0.04 mol dm<sup>-3</sup> of the mixture. With respect to the structure of the surfactants (see Figure 1), it is evident that a proximal orientation at the interface is plausible because of the attractive forces between the surfactants. Notably, owing to the impact of the single negative charge of SDBS and the two positive charge rings of the GSAIL, it is likely that the maximum synergy to be associated with a GSAIL:SDBS molar ratio of 1:2. However, this ratio has appeared with the best results as 1:4 (i.e.,  $\alpha_1 = 0.2$ ). Figure 5 depicts the most possible assembly of the considered surfactant molecules and their arrangement at the interface of the crude oil–water system. This finding is remarkable since an optimal mixture of such a low GSAIL contribution is so effective. The reason can be attributed to the bulky GSAIL head groups and the fact that GSAIL molecules can expand at the interface, enabling the attraction of four SDBS molecules to each GSAIL.

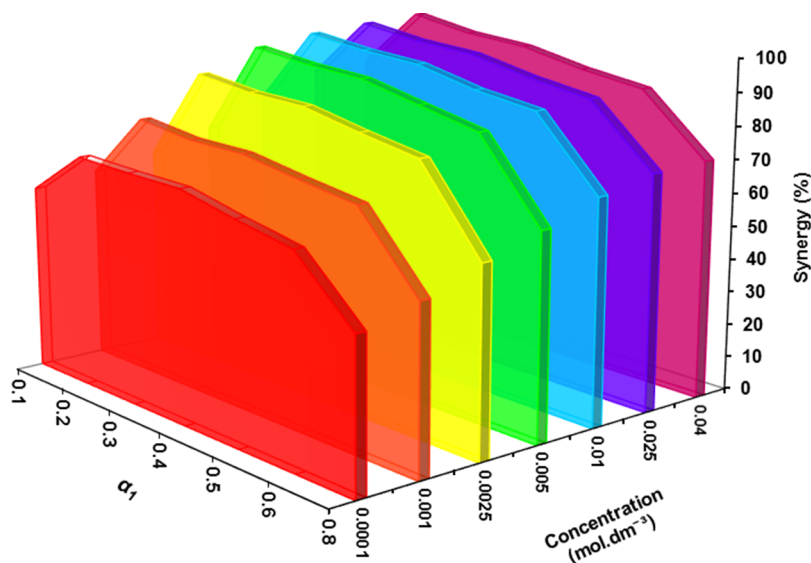
A comparable mechanism could also be attributed to micelle formation. The CMC falls to an exceptionally small value of 0.005 mol dm<sup>-3</sup> coincident with 82.8% synergy (compared to linear contribution of surfactants in mixture) at  $\alpha_1 = 0.2$ . It has to emphasize that a low CMC is always desirable in CEOR due to the transport of oil droplets via surfactant flooding.<sup>6</sup>

The NIBM theory<sup>4</sup> was employed to ascertain the obtained results and to determine the adsorbed GSAIL mole fraction ( $X_1$ ) and the parameter of adsorbed molecular interaction ( $\beta$ ), as included in the following equations<sup>4</sup>:

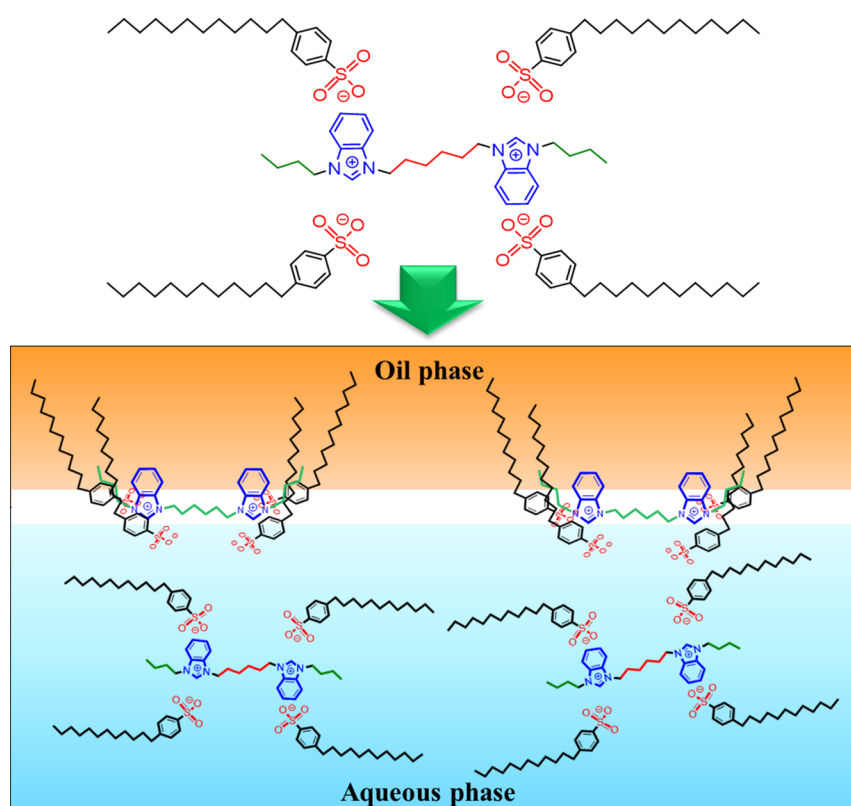
$$\frac{(X_1)^2 \ln(C_{12}\alpha_1/C_1^0 X_1)}{(1 - X_1)^2 \ln[C_{12}(1 - \alpha_1)/C_2^0(1 - X_1)]} = 1 \quad (5)$$

$$\beta = \frac{\ln(C_{12}\alpha_1/C_1^0 X_1)}{(1 - X_1)^2} \quad (6)$$





**Figure 4.** Synergy percentage in IFT reduction vs GSAIL mole fraction,  $\alpha_1$ , and mixture concentration.



**Figure 5.** Assembly of the GSAIL and SDBS molecules and their arrangement at the interface of the crude oil–water system.

where  $C_1^0$ ,  $C_2^0$ , and  $C_{12}^0$  denote the bulk concentration of the GSAIL, SDBS, and their mixture, respectively, all corresponding to a certain IFT. These concentrations were derived from IFT variations versus individual surfactant concentration and their mixture for a particular  $\alpha_1$  value (see Figure 3). Consequently, accurate values of  $X_1$  and  $\beta$  were calculated from eqs 5 and 6 using an iteration method.<sup>34</sup>

Here, negative  $\beta$  values validate an attractive molecular interaction, while positive values validate a repulsive one. Figure 6a shows that the maximum  $X_1$  values are corresponding to  $\alpha_1 = 0.2$  with the highest degree of synergy.

Moreover, as indicated by negative  $\beta$  values (Figure 6b), it becomes clear that despite self-repulsions among adsorbed individual surfactant molecules, an attractive interaction is dominant for surfactants in mixtures. High absolute  $\beta$  values, in other words, indicate a strong synergistic effect.<sup>35</sup> Furthermore, the highest absolute interactions are evident at  $\alpha_1 = 0.2$ , aligning with the previously described outcomes.

**3.3. Emulsifying Behavior.** Transferring surfactants to low-permeable zones and dissolution of crude oils through oil-in-water (O/W) emulsions are the important states in CEOR. This decreases the crude oil adsorption on reservoir

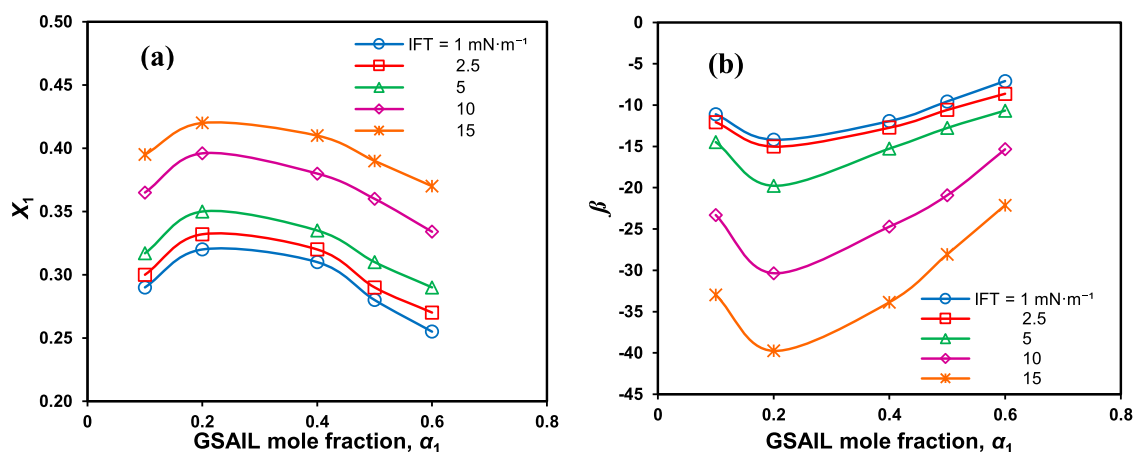


Figure 6. Interface mole fraction (a) and interaction parameter (b) vs mole fraction for various IFTs.

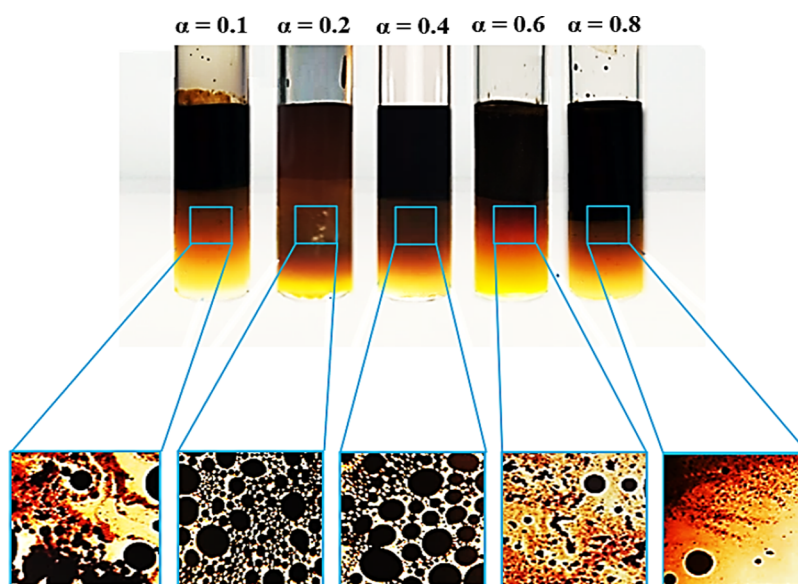


Figure 7. Crude oil–water emulsions under different mole fractions with  $0.05 \text{ mol dm}^{-3}$  of mixtures after 1 day.

rocks and gives rise to residual crude oil flow<sup>36</sup> and mobility and sweeping efficiency of injection fluids in nonswept areas.<sup>37,38</sup> Indeed, achieving low IFT values is vital for the creation of stable emulsions.

Figure 7 depicts different emulsion images achieved with various mixtures under a typical  $0.05 \text{ mol dm}^{-3}$  mixture concentration (significant synergy with this concentration, Figure 4). The role of surfactant mixture in producing emulsions is evident. Dependably, microscopic images demonstrate that the uniform O/W emulsions are formed with surfactant mixture. Further, Figure 8 shows the variation of emulsion indices versus GSAIL mole fractions after 1 day and 1 week. Once more, the highest emulsification appears at a mole fraction of  $\alpha_1 = 0.2$ , bringing about 89 and 85% emulsion indices after 1 day and after 1 week, respectively. These are relevant to 47.2 and 53.4% synergy compared to the linear contribution of components. Meanwhile, monitoring emulsions, after 2 months, showed no significant reduction in the emulsion volumes, i.e., consistent stability. This is a result of surfactants' regular orientation at the interface of drops, creating hydrophilic protective layers.<sup>39</sup> Notably, achieving stable emulsions with conventional surfactants necessitates

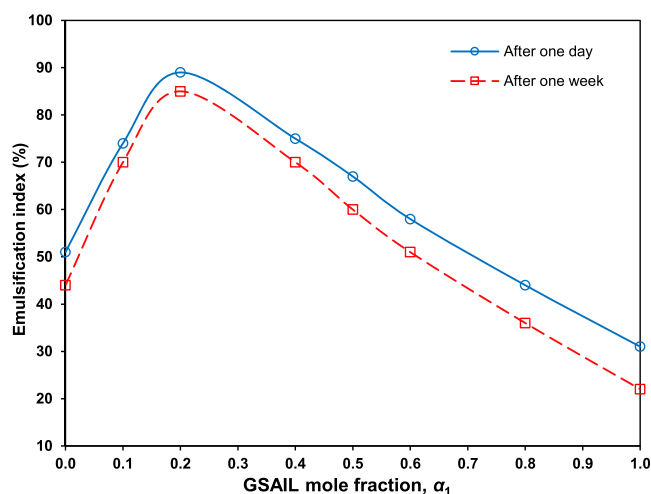
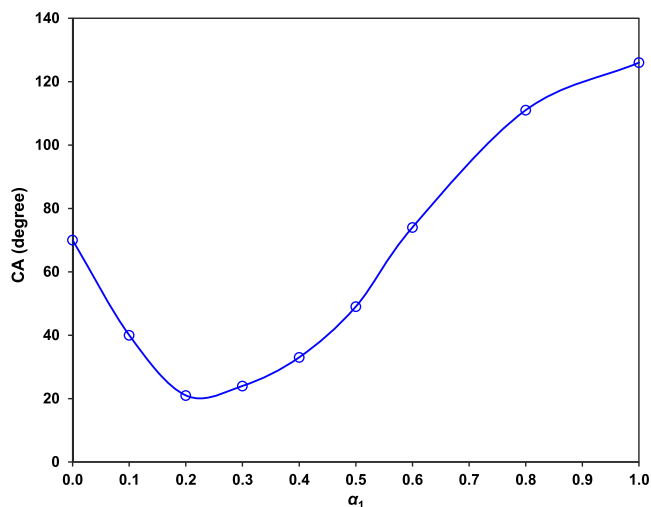


Figure 8. Emulsification index as a function of the GSAIL mole fraction with  $0.05 \text{ mol dm}^{-3}$  of mixtures.

regular use of cosurfactants that are volatile and environmentally hazardous<sup>6</sup>; however, no cosurfactant was used here.

**3.4. Wettability Alteration.** Wettability is crucial for reservoir rocks since a shift of wettability from oil-wet to water-wet results in detachment of residual oil from rocks and improves the crude oil flow. Based on CA measurements, reservoir rocks are categorized as hydrophilic (water-wet, CA ranging from 0 to 80°), moderate (CA from 80 to 100°), and hydrophobic (oil-wet, CA from 100 to 180°).<sup>40</sup>

The measured CAs and the wettability state and the corresponding shapes with 0.05 mol dm<sup>-3</sup> mixture concentration are presented in Figure 9 and Table 5. Notably, CAs of



**Figure 9.** Variation of contact angle vs the GSAIL mole fraction under a mixture concentration of 0.05 mol dm<sup>-3</sup>.

126° and 70° with the GSAIL and SDBS highly decrease to about 21° with the same mixture mole fraction of  $\alpha_1 = 0.2$ . This, in turn, results in a maximum degree of synergism of 74.1%. Thus, shifting wettability is from oil-wet to water-wet. These outcomes could be attributed to the surfactants' capability to accumulate on the solid surfaces, pointing their alkyl chains toward the solid surface while the polar parts toward the aqueous solution.

#### 4. CONCLUSIONS

The performance of mixtures of a benzimidazolium nanosize GSAIL and the conventional anionic SDBS surfactant on the crude oil–water system was studied. Primary experiments confirmed the effectiveness of individual surfactants in IFT reduction and in theoretical agreement with the Frumkin isotherm. The adapting charge interactions between surfactants enables the mixtures to drastically reduce the IFT, up to 99.6% stronger than that that could be achieved with the linear contribution of the individuals. The mixtures find the best performance at the GSAIL optimum mole fraction of only 0.2 under which extremely low IFT of 0.04 mN·m<sup>-1</sup> was achieved. The IFT variations were consistent with the NIBM model while exhibiting reasonable parameters of mole fraction at the interface and the interaction between adsorbed molecules. Emulsion formations confirmed stable crude oil in water dispersions based on the criterion of emulsion index and are still more effective under the same optimum mole fraction. Consistently, surface wettability showed a transition from oil-wet to water-wet due to reducing the contact angle, which was attributed to the low adhesion of crude oil drops to the surface in the presence of mixtures.

**Table 5.** Shape and CA of Crude Oil Drops on a Quartz Surface with 0.05 mol dm<sup>-3</sup> of Individual Surfactants and Mixtures

Mole fraction	Image	Contact angle	Wettability state
Pure water		CA = 158°	oil-wet
$\alpha_1 = 0$		CA = 70°	intermediate-wet
$\alpha_1 = 0.1$		CA = 40°	water-wet
$\alpha_1 = 0.2$		CA = 21°	water-wet
$\alpha_1 = 0.5$		CA = 49°	intermediate-wet
$\alpha_1 = 0.6$		CA = 74°	oil-wet
$\alpha_1 = 0.8$		CA = 111°	oil-wet
$\alpha_1 = 1$		CA = 126°	oil-wet

In summary, applications of the mixture of GSAILS and conventional surfactants in CEOR are highlighted. To ensure the huge application prospects, more studies are required for environmental adaptability, e.g., under high salinity and pressure/temperature conditions.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c01768>.

FT-IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra of the prepared GSAIL and plots of DLS analyses as well as SEM images of the GSAIL (PDF)

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## Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Tamayo-mas, E.; Mustapha, H.; Dimitrakopoulos, R. Testing geological heterogeneity representations for enhanced oil recovery techniques. *J. Pet. Sci. Eng.* **2016**, *146*, 222–240.
- (2) Painter, P.; Williams, P.; Lupinsky, A. Recovery of bitumen from Utah tar sands using ionic liquids. *Energy Fuels* **2010**, *24*, 5081–5088.
- (3) Chowdhury, S.; Shrivastava, S.; Kakati, A.; Sangwai, J. S. Comprehensive review on the role of surfactants in the chemical enhanced oil recovery process. *Ind. Eng. Chem. Res.* **2022**, *61*, 21–64.
- (4) Rosen, M. J.; *Surfactants and Interfacial Phenomena*; 3rd ed.; John Wiley and Sons, 2012.
- (5) Hajjaji, F. E.; Salim, R.; Taleb, M.; Benhiba, F.; Rezki, N.; Chauhan, D. S.; Quraishi, M. Pyridinium-based ionic liquids as novel eco-friendly corrosion inhibitors for mild steel in molar hydrochloric acid: Experimental and computational approach. *Surf. Interfaces* **2021**, *22*, No. 100881.
- (6) Nasirpour, N.; Mohammadpourfard, M.; Heris, S. Z. Ionic liquids: Promising compounds for sustainable chemical processes and applications. *Chem. Eng. Res. Des.* **2020**, *160*, 264–300.
- (7) Lebedeva, O.; Kultin, D.; Zakharov, A.; Kustov, L. Advances in application of ionic liquids: Fabrication of surface nanoscale oxide structures by anodization of metals and alloys. *Surf. Interfaces* **2022**, *34*, No. 102345.
- (8) Jia, H.; Leng, X.; Hu, M.; Song, Y.; Wu, H.; Lian, P.; Liang, Y.; Zhu, Y.; Liu, J.; Zhou, H. Systematic investigation of the effects of mixed cationic/anionic surfactants on the interfacial tension of a water/model oil system and their application to enhance crude oil recovery. *Colloids Surf. A Physicochem. Eng. Asp.* **2017**, *529*, 621–627.
- (9) Xu, Y.; Wang, T.; Zhang, L.; Tang, Y.; Huang, W.; Jia, H. Investigation on the effects of cationic surface active ionic liquid/anionic surfactant mixtures on the interfacial tension of water/crude oil system and their application in enhancing crude oil recovery. *J. Dispers. Sci. Technol.* **2023**, *44*, 214–224.
- (10) Ezzat, A.; Ayman, O.; Atta, M.; Al-lohedan, H. A. Demulsification of stable seawater/arabian heavy crude oil emulsions using star-like tricationic pyridinium ionic liquids. *Fuel* **2021**, *304*, No. 121436.
- (11) Saien, J.; Eghtenaie, A.; Kharazi, M. Synergistic performance of a gemini ionic liquid and sodium dodecyl sulfate surfactants at the crude oil–water interface. *Arab. J. Chem.* **2023**, *16*, No. 105329.
- (12) Pillai, P.; Kumar, A.; Mandal, A. Mechanistic studies of enhanced oil recovery by imidazolium-based ionic liquids as novel surfactants. *J. Ind. Eng. Chem.* **2018**, *63*, 262–274.
- (13) Kharazi, M.; Saien, J. Mechanism responsible altering in interfacial tension and emulsification of the crude oil–water system with nano Gemini surface active ionic liquids, salts and pH. *J. Pet. Sci. Eng.* **2022**, *219*, No. 111090.
- (14) Liu, D.; Zhang, X.; Tian, F.; Liu, X.; Yuan, J.; Huang, B. Review on nanoparticle-surfactant nanofluids: Formula fabrication and applications in enhanced oil recovery. *J. Dispers. Sci. Technol.* **2022**, *43*, 745–759.
- (15) Kharazi, M.; Saien, J.; Yarie, M.; Zolfigol, M. A. Promoting activity of gemini ionic liquids surfactant at the interface of crude oil–water. *Pet. Res.* **2021**, *117*, 113–123.
- (16) Kharazi, M.; Saien, J. Upgrading the properties of the crude oil–water system for eor with simultaneous effects of a homologous series of nanogemini surface-active ionic liquids, electrolytes, and pH. *ACS Omega* **2022**, *7*, 40042–40053.
- (17) Saien, J.; Kharazi, M.; Shokri, B.; Torabi, M.; Zolfigol, M. A. A Comparative study on the design and application of new nano benzimidazolium gemini ionic liquids for curing interfacial properties of the crude oil–water system. *RSC Adv.* **2023**, *13*, 15747–15761.
- (18) Kharazi, M.; Saien, J.; Yarie, M.; Zolfigol, M. A. Different spacer homologs of Gemini imidazolium ionic liquid surfactants at the interface of crude oil–water. *J. Mol. Liq.* **2019**, *296*, No. 111748.
- (19) Saien, J.; Shokri, B.; Kharazi, M. Synergism in mixtures of nano benzimidazolium Gemini ionic liquid and sodium dodecyl sulfate surfactants in tuning interfacial properties of crude oil–water system. *J. Mol. Liq.* **2023**, *391*, No. 123280.
- (20) Kharazi, M.; Saien, J.; Torabi, M.; Zolfigol, M. A. Molecular design and applications of a nanostructure green tripodal surface active ionic liquid in enhanced oil recovery: Interfacial tension reduction, wettability alteration and emulsification. *Pet. Sci.* **2023**, *20*, 3530–3539.
- (21) Stauffer, C. E. The measurement of surface tension by the pendant drop technique. *J. Phys. Chem.* **1965**, *69*, 1933–1938.
- (22) Lan, M.; Wang, X.; Chen, P.; Zhao, X. Effects of surface tension and wood surface roughness on impact splash of a pure and multi-component water drop. *Case Stud. Therm. Eng.* **2016**, *8*, 218–225.
- (23) Taisne, L.; Walstra, P.; Cabane, B. Transfer of oil between emulsion droplets. *J. Colloid Interface Sci.* **1996**, *184*, 378–390.
- (24) Kharazi, M.; Saien, J.; Torabi, M.; Zolfigol, M. A. Green nano multicationic ionic liquid based surfactants for enhanced oil recovery: A comparative study on design and applications. *J. Mol. Liq.* **2023**, *383*, No. 122090.
- (25) Stubenrauch, C.; Fainerman, V. B.; Aksenenko, E. V.; Miller, R. Adsorption behavior and dilational rheology of the cationic alkyl trimethylammonium bromides at the water/air interface. *J. Phys. Chem. B* **2005**, *109*, 1505–1509.
- (26) Möbius, D.; Miller, R.; Fainerman, V. B.; *Surfactants: Chemistry, Interfacial Properties, Applications*; Elsevier, 2001.
- (27) Xu, J.; Zhang, Y.; Chen, H.; Wang, P.; Xie, Z.; Yao, Y.; Yan, Y.; Zhang, J. Effect of surfactant headgroups on the oil/water interface: An interfacial tension measurement and simulation study. *J. Mol. Liq.* **2013**, *1052*, 50–56.
- (28) Zhong, Q. L.; Zhou, Z. H.; Zhang, Q.; Ma, D. S.; Luan, H. X.; Zhang, L.; Ma, G. Y.; Zhang, L. Studies on interfacial tensions of ionic surfactant and alkyl sulfobetaine mixed solutions. *Energy Fuels* **2018**, *32*, 8202–8209.
- (29) Liu, G.; Gu, D.; Liu, H.; Ding, W.; Luan, H.; Lou, Y. Thermodynamic properties of micellization of sulfobetaine-type zwitterionic gemini surfactants in aqueous solutions—A free energy perturbation study. *J. Colloid Interface Sci.* **2012**, *375*, 148–153.
- (30) Zhang, L.; Geng, Y.; Duan, W.; Wang, D.; Fu, M.; Wang, X. Ionic liquid-based ultrasound-assisted extraction of fangchinoline and tetrandrine from *stephaniae tetrandrae*. *J. Sep. Sci.* **2009**, *32*, 3550–3554.
- (31) Kumari, R.; Kakati, A.; Nagarajan, R.; Sangwai, J. S. Synergistic effect of mixed anionic and cationic surfactant systems on the interfacial tension of crude oil–water and enhanced oil recovery. *J. Dispers. Sci. Technol.* **2018**, *40*, 969–981.
- (32) Kumar, H.; Kaur, G. Scrutinizing self-assembly, surface activity and aggregation behavior of mixtures of imidazolium based ionic liquids and surfactants: A comprehensive review. *Front. Chem.* **2021**, *9*, No. 667941.
- (33) Nabipour, M.; Ayatollahi, S.; Keshavarz, P. Application of different novel and newly designed commercial ionic liquids and surfactants for more oil recovery from an iranian oil field. *J. Mol. Liq.* **2017**, *230*, 579–588.



(34) Saien, J.; Asadabadi, S. Synergistic adsorption of triton x-100 and ctab surfactants at the toluene + water interface. *Fluid Phase Equilib.* **2011**, *307*, 16–23.

(35) Olea, A.; Gamboa, C. Synergism in mixtures of cationic surfactant and anionic copolymers. *J. Colloid Interface Sci.* **2003**, *257*, 321–326.

(36) Guang, Z. H.; Caili, D. A.; Qing, Y. O. Characteristics and displacement mechanisms of the dispersed particle gel soft heterogeneous compound flooding system. *Pet. Explor. Dev.* **2018**, *45*, 481–490.

(37) Yazhou, Z.; Demin, W.; Zhipeng, W.; Rui, C. The Formation and viscoelasticity of pore-throat scale emulsion in porous media. *Pet. Explor. Dev.* **2017**, *44*, 111–118.

(38) Mandal, A.; Samanta, A.; Bera, A.; Ojha, K. Characterization of oil–water emulsion and its use in enhanced oil recovery. *Ind. Eng. Chem. Res.* **2010**, *49*, 12756–12761.

(39) Gao, B.; Sharma, M. M. A family of alkyl sulfate gemini surfactants. I. characterization of surface properties. *J. Colloid Interface Sci.* **2013**, *404*, 80–84.

(40) He, L.; Lin, F.; Li, X.; Sui, H.; Xu, Z. Interfacial sciences in unconventional petroleum production: from fundamentals to applications. *Chem. Soc. Rev.* **2015**, *44*, 5446–5494.