

# Interaction between Zwitterionic Surface Activity Ionic Liquid and Anionic Surfactant: Na<sup>+</sup>-Driven Wormlike Micelles

Xiaoqing Wang,<sup>†</sup> Ruitao Wang,<sup>‡</sup> Yan Zheng,<sup>†</sup> Limei Sun,<sup>§</sup> Li Yu,<sup>\*,†</sup> Jingjing Jiao,<sup>†</sup> and Rui Wang<sup>†</sup>

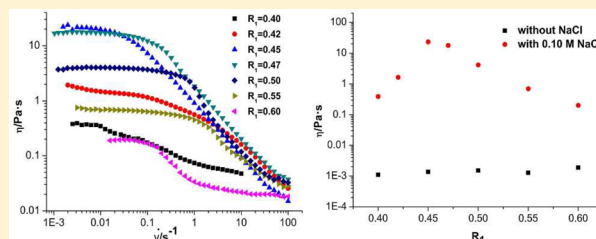
<sup>†</sup>Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan, 250100, PR China

<sup>‡</sup>China Research Institute of Daily Chemical Industry, Taiyuan, 030001, PR China

<sup>§</sup>Working station for postdoctoral scientific research in Shengli Oilfield, Dongying, 257002, PR China

## S Supporting Information

**ABSTRACT:** The physicochemical properties of the mixed zwitterionic surface activity ionic liquid/anionic surfactant (*N*-alkyl-*N'*-carboxymethyl imidazolium inner salts/sodium dodecyl sulfate, [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS) at various molar ratios ( $R_1 = C_{[N-C_{12}, N'-CO_2-Im]}/(C_{[N-C_{12}, N'-CO_2-Im]} + C_{SDS})$ ) were investigated by surface tension and steady-state fluorescence measurements. The results show that the mixed [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS system has a much lower cmc value and higher surface activity than individual surfactant. Compared with the mixed zwitterionic betaine surfactant/SDS system, the mixture studied exhibits a stronger synergism, i.e., more negative interaction parameters ( $\beta^m$  and  $\beta^o$ ). Through addition of NaCl, the wormlike micelles (WMs) could be formed in a [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS system. Steady and dynamic rheology was employed to characterize the WMs with different surfactant ratio ( $R_1$ ), NaCl concentration, and temperature. An optimal composition, viz.,  $C_T = 60$  mM,  $R_1 = 0.45$ , and  $C_{NaCl} = 0.10$  M, was detected to form the strongest and longest wormlike micelles. Compared with the WMs formed by a traditional zwitterionic C<sub>12</sub> betaine/anionic surfactant mixture (e.g., laurylamidopropyl betaine/SDS), the WMs studied have a stronger network structure, which is expected to have potential applications in some fields, such as in nanomaterials synthesis, personal care products, and flooding liquid for tertiary oil recovery.



## 1. INTRODUCTION

Surfactant mixtures are commonly preferred in medicinal and pharmaceutical formulations and industrial preparations due to the purpose of suspension, solubilization, and dispersion.<sup>1–4</sup> Compared with a single surfactant, the mixed surfactants exhibit superior interfacial properties, such as higher surface activity and lower critical micelle concentration (cmc), which is known as synergism. Many different combinations of mixed surfactant systems have been studied, including nonionic/nonionic,<sup>5</sup> anionic/nonionic,<sup>6</sup> cationic/cationic,<sup>7,8</sup> and cationic/non-ionic<sup>8,9</sup> surfactant systems. Recently, mixtures containing anionic and zwitterionic surfactants have been a research focus, due to their easy biodegradability, mildness to eyes and skin, high foam stability, and outstanding salt tolerance, making them widely used in household cleaning and personal care products.<sup>10</sup>

It is well-known that mixtures of anionic and zwitterionic surfactants show significant synergism in aqueous solution.<sup>11–14</sup> Thus, they can self-assemble to form various supramolecular structures above the cmc in aqueous solution, such as spherical micelle, wormlike micelle, vesicle, and laminar structure. From a fundamental perspective, wormlike micelles (WMs) have attracted extensive interest over the past years because of their various industrial applications as drag-reduction agents, rheology modifiers, and personal care products.<sup>15,16</sup> WMs often show highly viscoelastic properties that can be broken

down and reformed, which is different from polymer solutions. They are also called “living polymers”.<sup>17–20</sup> It is common that viscoelastic WMs can be induced by adding an inorganic salt to cationic surfactant solutions, where micelle growth occurs by screening the electrostatic repulsion between charged head groups.<sup>21–23</sup> In addition, mixtures of oppositely charged surfactants can form WMs due to charged neutralization.<sup>24,25</sup> In the recent years, a few studies have revealed that blends of anionic and zwitterionic surfactants can also form MWs.<sup>13,26–28</sup> Erick and David<sup>28</sup> reported the MW solution made of zwitterionic surfactant *N*-tetradecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate (TDPS), sodium dodecyl sulfate (SDS), and salty water. Additionally, Qiao et al.<sup>27</sup> researched the metal-driven WMs in anionic and zwitterionic surfactant mixtures, and they found the efficiency of metal ions at inducing MWs was related to the valence state of metal ions and the order was trivalent > bivalent > monovalent metal ions. However, the studies on the WM solution made of anionic-zwitterionic surfactants are still lacking.

Ionic liquids (ILs) have generated intense scientific and industrial interest due to their special physicochemical properties.<sup>29–31</sup> ILs with long-chain alkyl groups, emerging as

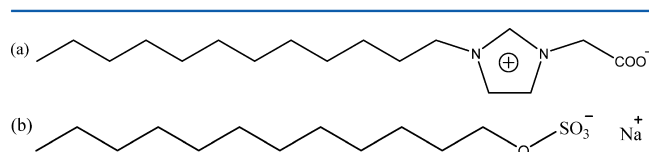
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novel surfactants, are of inherent amphiphilic nature and named surface active ionic liquids (SAILs). The great advantage of SAILs is that their physicochemical properties can be designed by reasonable selection of cations, anions, and substituents. Therefore, the self-aggregation behavior of SAILs in aqueous solution has attracted a considerable amount of attention of researchers, including our group.<sup>32–36</sup> In the recent years, we have investigated the aggregation behavior of imidazolium-based cationic SAILs, 1-alkyl-3-methylimidazolium bromide ( $[C_n\text{mim}]\text{Br}$ ,  $n = 12, 14, 16$ )<sup>35</sup> and imidazolium-based anionic SAILs, 1-butyl-3-methylimidazolium dodecylsulfate ( $[C_4\text{mim}][C_{12}\text{SO}_4]$ ) and *N*-butyl-*N*-methylpyrrolidinium dodecylsulfate ( $[C_4\text{MP}][C_{12}\text{SO}_4]$ )<sup>36</sup> in aqueous solution and discovered that imidazolium-based SAILs exhibit superior surface activity. However, so far most studies in the field of colloid and interface chemistry are related to the cationic or anionic SAILs. Only a few studies on the zwitterionic SAILs have been reported, although they are of practical interest.<sup>37,38</sup> Joseph et al.<sup>39</sup> reported sequential formation of carboxylic acid functionalized ionic, zwitterionic, acid-zwitterionic, and lithium salt-zwitterionic liquid crystals (LCs), in which the zwitterion and acid-zwitterion adducts represent two new classes of imidazolium based LCs. Tondo and his co-workers<sup>40</sup> synthesized an imidazolium-based zwitterionic SAIL, 3-(1-tetradecyl-3-imidazolio)propane-sulfonate (ImS3-14), and evaluated the chameleon-like behavior of zwitterionic micelles. These reports reveal that zwitterionic SAILs have superior surface activity and can form self-aggregates in aqueous solution. However, to the best of our knowledge, no report on the WMs containing zwitterionic SAILs has appeared so far.

Herein, we report a detailed study of the synergetic behavior of zwitterionic SAILs, *N*-alkyl-*N*'-carboxymethyl imidazolium inner salts ( $[N-C_{12}, N'-CO_2\text{-Im}]$ ), and anionic surfactant, sodium dodecyl sulfate (SDS), in aqueous solution. Figure 1



**Figure 1.** Chemical structures of (a)  $[N-C_{12}, N'-CO_2\text{-Im}]$  and (b) SDS.

represents their chemical structures. It is found that the WMs could be formed through addition of inorganic salt (NaCl) to the mixed system. The  $[N-C_{12}, N'-CO_2\text{-Im}]/\text{SDS}$  mixture was characterized by various measurements, including surface tension, fluorescence, and rheological methods.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** The zwitterionic SAIL,  $[N-C_{12}, N'-CO_2\text{-Im}]$ , was prepared and purified as described elsewhere.<sup>41</sup> SDS (99.9%) was achieved from Alfa Aesar. NaCl (analytical grade) was purchased from Tianjin Experimental Reagent Co. Ltd. of China. In steady-state fluorescence measurements, pyrene (99%), obtained from Alfa Aesar, was used as a fluorescent probe. All the above reagents were used without further purification. Triply distilled water was used for solution preparation.

**2.2. Sample Preparation.** The mixed surfactants with desired molar ratios  $R_1$  of  $[N-C_{12}, N'-CO_2\text{-Im}]$  ( $R_1 = C_{[N-C_{12}, N'-CO_2\text{-Im}]} / (C_{[N-C_{12}, N'-CO_2\text{-Im}]} + C_{\text{SDS}})$ ) were prepared by

mixing the individual surfactant solution directly. The samples for surface tension and fluorescence measurements were prepared by diluting the mixed surfactant solution. The WM samples were induced to form by adding the appropriate quantity of NaCl to the mixed surfactants. After sealing, they were handled by mild heat at 40–50 °C for half an hour to ensure the added NaCl solid completely dissolved. The total concentration of surfactants ( $C_T$ ) was kept constant at 60 mM. All the WM samples were prepared and left at the experimental temperature for at least 1 week prior to measurements to keep equilibrium.

**2.3. Surface Tension Measurements.** Surface tension was measured with a Krüss-K12 tensiometer (Hamburg, Germany, accuracy  $\pm 0.01 \text{ mN}\cdot\text{m}^{-1}$ ) using the ring method. The temperature was controlled using a HAAKE DC 30 thermostatic bath (Karlsruhe, Germany) within  $\pm 0.1$  °C. The surface tension was determined with a single measurement method. All measurements were repeated until the difference between two values was less than  $0.2 \text{ mN}\cdot\text{m}^{-1}$ .

**2.4. Steady-State Fluorescence Measurements.** Steady-state fluorescence measurements were performed using a PerkinElmer LS-55 spectrofluorometer (PE Company, U.K.) at  $25 \pm 0.1$  °C. The pyrene-containing solution was collected with a  $1 \text{ cm}^2$  quartz cuvette. Although imidazolium-based ionic liquid is verified to have weak fluorescence, the absorption is negligible as compared to pyrene.<sup>42,43</sup> Excitation and emission bands were fixed at 2.5 and 10 nm, respectively. The sample containing pyrene was excited at 335 nm, and the range of emission spectra wavelengths was from 350 to 450 nm. The ratio of  $I_{373}/I_{384}$  depends on the polarity of the environment, which can be analyzed to obtain the cmc.<sup>44</sup> The pyrene concentration was kept at  $1 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$  in all the samples to avoid excimer formation.<sup>45–48</sup>

**2.5. Rheological Measurements.** Rheological measurements were carried out on a HAAKE RS6000 Rheometer with a coaxial cylinder sensor system (A41Ti). The experimental temperature was controlled by a cyclic water bath (Phoenix) within  $\pm 0.1$  °C. The sample thickness in the middle of the cylinder sensor was 3.0 mm. Frequency spectra were conducted in the linear viscoelastic regions, obtained by the dynamic strain sweep measurements. The range of shear rate was from 0.001 to  $1000 \text{ s}^{-1}$  in the steady-shear measurements. The zero-shear viscosity for samples was obtained by extrapolation of the viscosity curve to the vertical coordinates. All the samples were equilibrated at the experimental temperature for at least 5 min prior to measurements.

**2.6. Cryogenic Transmission Electron Microscopy (Cryo-TEM).** The WMs were observed by cryogenic transmission electron microscopy (cryo-TEM). The sample was prepared in a controlled-environment vitrification system (Cryoplunge3, Gatan, USA) at 25 °C. A  $1 \mu\text{L}$  portion of solution was placed on a copper grid coated with carbon film, and the redundant liquid was blotted with filter paper. The thin film was produced. Then, the thin film was quickly plunged into liquid ethane cooled by liquid nitrogen. The vitrified sample was placed in a cryogenic specimen holder and examined with a JEOL JEM 1400 TEM operated at 120 KV.

## 3. RESULTS AND DISCUSSION

**3.1. Surface Tension Measurements.** Figure S1 (Supporting Information) depicts the variation of surface tension ( $\gamma$ ) as a function of the concentration ( $C$ ) for the pure and binary surfactant mixtures ( $[N-C_{12}, N'-CO_2\text{-Im}]/\text{SDS}$ ) in

aqueous solution at 25 °C. The break point of curves corresponds to the cmc value. The values of cmc and surface tension at cmc ( $\gamma_{\text{cmc}}$ ) are listed in Table 1. It is obvious that the

**Table 1. Values of cmc,  $\gamma_{\text{cmc}}$ ,  $\Pi_{\text{cmc}}$ ,  $pC_{20}$ , and  $I_1/I_3$  for Different Molar Fractions ( $R_1$ ) of the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS System in Aqueous Solution, at 25 °C**

$R_1$	cmc <sup>a</sup> (mol·L <sup>-1</sup> )	cmc <sup>b</sup> (mol·L <sup>-1</sup> )	$\gamma_{\text{cmc}}$ (mN·m <sup>-1</sup> )	$\Pi_{\text{cmc}}$ (mN·m <sup>-1</sup> )	$pC_{20}$	$I_1/I_3$
0	7.73	6.66	37.7	35.3	3.46	1.21
0.1	1.83	1.21	25.8	47.2	4.02	1.22
0.3	1.09	0.710	26.2	46.8	4.11	1.25
0.5	0.808	0.568	27.0	46.0	4.22	1.11
0.7	0.604	0.454	27.5	45.5	4.34	1.26
0.9	0.686	0.535	28.3	44.7	4.22	1.28
1.0	1.30	1.06	35.4	37.6	3.77	1.32

<sup>a</sup>From surface tension measurements. <sup>b</sup>From steady-state fluorescence measurements.

$\gamma_{\text{cmc}}$  value of the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS mixed systems is much lower than that of a single surfactant. Surface activity expresses that a compound has the capacity to reduce the surface tension of solution. The lower cmc and  $\gamma_{\text{cmc}}$  values indicate that the binary surfactant mixture has superior surface activity. Evidently, for the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS mixed system, the synergistic effects occur easily due to the strong electrostatic attraction between the imidazolium cationic portion of [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im] and the SO<sub>3</sub><sup>-</sup> group of SDS. Similar behavior has been reported for some other zwitterionic/anionic surfactant systems.<sup>11,12,14</sup> The  $\gamma_{\text{cmc}}$  value decreases upon increasing the mole ratio of [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im], reaching a minimum value (25.8 mN·m<sup>-1</sup>) at  $R_1 = 0.1$ . Furthermore, the mixed systems have a much lower cmc value compared with pure SDS. Generally, the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS mixed systems exhibit better surface activity than SDS. As is well-known to all, the surfactant mixture usually forms mixed micelles in aqueous medium. The formation of mixed micelles mainly depends on two factors, i.e., the interaction between the charged head groups of individual surfactant and the hydrophobic interaction among hydrocarbon chains. For the binary system of [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im] and SDS, a pseudo-double-chain surfactant is formed due to the strong electrostatic interaction between the imidazolium cationic portion of [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im] and the SO<sub>3</sub><sup>-</sup> group of SDS. There also exists an enhanced hydrophobic interaction between the hydrocarbon chains, which favors the mixed micelle formation and decreases the cmc.<sup>27,11,49</sup> As shown in Table 1, the cmc value diminishes with the increase of the  $R_1$  value and shows a minimum at  $R_1 = 0.7$ . The initial decrease of cmc value with the increase of  $R_1$  can be attributed to the part neutralization of charges on the SO<sub>3</sub><sup>-</sup> group of SDS, which favors the formation of micelles. However, when  $R_1$  is larger than 0.7, the mole ratio of [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im] substantially exceeds that of SDS, and the self-interaction of the individual surfactant gradually dominates the formation of micelles. Thus, it causes an increase of the cmc.

On the basis of the surface tension plots, two micellization parameters, the adsorption efficiency ( $pC_{20}$ ) and the effectiveness of surfactant to decrease the surface tension of solvent ( $\Pi_{\text{cmc}}$ ), have been estimated (Table 1).  $pC_{20}$  is the negative logarithm of  $C_{20}$ , which is the concentration of surfactant causing the surface tension of solvent to decrease by 20 mN·m<sup>-1</sup>. The larger the  $pC_{20}$  value, the higher the adsorption

efficiency of surfactant molecules is. The  $\Pi_{\text{cmc}}$  value is the maximum reduction of surface tension of solvent. The larger the  $\Pi_{\text{cmc}}$  value, the higher the effectiveness of surfactant to decrease the surface tension of solvent is. As presented in Table 1, both the  $pC_{20}$  and  $\Pi_{\text{cmc}}$  values of the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS mixed system are larger than those of two pure surfactants. This further manifests that the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS mixed system has a higher surface activity than an individual surfactant.

**3.2. The Synergism of Surfactants.** According to regular solution theory,<sup>50</sup> the strength of interaction between two surfactants in solution can be measured by the interaction parameter  $\beta$ , which mainly reflects the interaction between the head groups of two surfactants. Commonly, the interaction parameter of mixed micelles ( $\beta^m$ ) and mixed monolayer formation ( $\beta^\sigma$ ) can be obtained. The more negative the  $\beta$  value, the stronger the attractive interaction of two surfactants is.

The interaction between [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im] and SDS surfactants in the mixed monolayer and micelle can be measured by the parameter  $\beta$  obtained from Rubingh's theory of nonideal mixing.<sup>51</sup> According to Rubingh's theory of nonideal mixing, the cmc values of nonideal mixed surfactant systems ( $C_{12}^m$ ) are given as follows:

$$C = R_1 f_1^m C_1^m = R_1 \cdot C_{12}^m \quad (1)$$

where  $C$  is the concentration of surfactant 1 ([N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]) in solution,  $R_1^m$  and  $R_1$  are the molar ratios of surfactant 1 in the mixed micelle and in solution, respectively,  $C_1^m$  and  $C_{12}^m$  are the cmc values of surfactant 1 and binary mixture, respectively, and  $f_1^m$  is the activity coefficient of surfactant 1 in mixed micelles.

The activity coefficients of [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im] ( $f_1^m$ ) and SDS ( $f_2^m$ ) in mixed micelles are related to the  $\beta^m$  parameter, which are given as follows

$$\ln f_1^m = \beta^m (1 - R_1^m)^2 \quad (2)$$

$$\ln f_2^m = \beta^m (R_1^m)^2 \quad (3)$$

Since  $f_1^m = [R_1 C_{12}^m / R_1^m C_1^m]$  and  $f_2^m = [C_{12}^m (1 - R_1) / C_2^m (1 - R_1^m)]$ , the following equation can be derived from eq 2:<sup>50,52</sup>

$$\frac{R_1^m \ln(C_{12}^m R_1 / C_1^m R_1^m)}{(1 - R_1^m)^2 \ln[C_{12}^m (1 - R_1) / C_2^m (1 - R_1^m)]} = 1 \quad (4)$$

where  $C_2^m$  is the cmc of surfactant 2 (SDS).  $R_1^m$  can be calculated from eq 3 iteratively. Then, the micellar interaction parameter  $\beta^m$  can be evaluated using the following equation:

$$\beta^m = \frac{\ln(C_{12}^m R_1 / C_1^m R_1^m)}{(1 - R_1^m)^2} \quad (5)$$

Similarly, the interaction parameter of the mixed monolayer ( $\beta^\sigma$ ) can be calculated by the equations derived using Rubingh's equation.

$$\frac{(R_1^\sigma) \ln(R_1 C_{12}^\sigma / R_1^\sigma C_1^\sigma)}{(1 - R_1^\sigma)^2 \ln[(1 - R_1) C_{12}^\sigma / (1 - R_1^\sigma) C_2^\sigma]} = 1 \quad (6)$$

$$\beta^\sigma = \frac{\ln(R_1 C_{12}^\sigma / R_1^\sigma C_1^\sigma)}{(1 - R_1^\sigma)^2} \quad (7)$$

where  $R_1^\sigma$  is the mole ratio of surfactant 1 in mixed monolayer,  $C_1^\sigma$ ,  $C_2^\sigma$ , and  $C_{12}^\sigma$  are the concentrations of surfactant 1, surfactant



**Table 2.** Interaction Parameters ( $\beta^\sigma$ ,  $\beta^m$ ), Interfacial Compositions ( $R_1^\sigma$ ), Micellar Compositions ( $R_1^m$ ), and Activity Coefficients ( $f_1^\sigma$ ,  $f_2^\sigma$ ,  $f_1^m$ ,  $f_2^m$ ) for the Binary Mixture of [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS in Aqueous Solution at 25 °C

$R_1$	$f_1^m$	$f_1^\sigma$	$f_2^m$	$f_2^\sigma$	$R_1^m$	$R_1^\sigma$	$\beta^m$	$\beta^\sigma$
0.1	0.302	0.118	0.396	0.194	0.468	0.467	-4.23	-7.53
0.3	0.439	0.191	0.227	0.110	0.573	0.536	-4.52	-7.68
0.5	0.496	0.252	0.138	0.0724	0.627	0.580	-5.04	-7.80
0.7	0.492	0.278	0.0675	0.0394	0.661	0.614	-6.17	-8.58
0.9	0.646	0.426	0.0333	0.0204	0.736	0.681	-6.28	-8.39

2, and surfactant mixture ([N-C<sub>m</sub>, N'-CO<sub>2</sub>-Im]/SDS) in solution when the surface tension of the solution reaches 42 mN·m<sup>-1</sup>. The activity coefficients of [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im] ( $f_1^\sigma$ ) and SDS ( $f_2^\sigma$ ) in a mixed monolayer can be calculated from the interaction parameter of the mixed monolayer ( $\beta^\sigma$ ).

On the basis of the cmc,  $C_1^*$ ,  $C_2^*$ , and  $C_{12}^*$  values obtained by surface tension measurements, a series of parameters, including  $R_1^m$ ,  $R_1^\sigma$ ,  $\beta^m$ ,  $\beta^\sigma$ ,  $f_1^m$ ,  $f_2^m$ ,  $f_1^\sigma$ ,  $f_2^\sigma$ , have been calculated according to eqs 2–7 and listed in Table 2. It should be noted that both the  $\beta^m$  and  $\beta^\sigma$  values for the binary surfactant mixtures are negative, which indicates that the interaction between [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im] and SDS in the mixed micelles and mixed monolayer is stronger than the self-interaction of the individual surfactant before mixing. Compared with  $\beta^m$ , the more negative  $\beta^\sigma$  values indicate the stronger interaction at the air/liquid interface. As shown in Table 2, there exists a minimum  $\beta^\sigma$  value at  $R_1 = 0.7$ , where the corresponding  $pC_{20}$  value is the largest and the cmc value is minimum, i.e., the adsorption efficiency is the highest. It can be explained that the stronger interaction between [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im] molecules at the air/liquid interface causes a higher adsorption efficiency.

In addition, the value of  $|\beta^m|$  is higher than that of  $|\ln(C_1^m/C_2^m)|$  (~1.8), which further supports the conclusion that there exists a synergistic interaction between [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im] and SDS molecules. The  $|\beta^m|$  value increases with the  $R_1$  value, suggesting a stronger synergism. Compared with the mixture of betaine-type zwitterionic and anionic surfactants, such as *N*-dodecyl-*N,N*-dimethylbetaine (DNB)/SDS,<sup>53</sup> and *N*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate (ZW3-12)/SDS,<sup>54</sup> the mixed system of zwitterionic SAIL and anionic surfactant studied in this work has a higher  $|\beta^m|$  value, indicating the stronger interaction between [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im] and SDS. The data in Table 2 also shows that the activity coefficients ( $f_1^m$  and  $f_2^m$ ) are less than unity, indicating that the interaction between [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im] and SDS presents a nonideal behavior. However, compared with the mixture of cationic SAIL and anionic surfactant, such as 1-decyl-3-methylimidazolium bromide/sodium dodecyl sulfate (C<sub>12</sub>mimBr/SDS) system ( $\beta^m = -21.6$ ),<sup>55</sup> the  $|\beta^m|$  value for the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS system is lower, which indicates that the mixture of [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im] and SDS has a weaker synergistic interaction. It is due to the stronger electrostatic interaction between the imidazolium cationic headgroup of C<sub>12</sub>mimBr and the SO<sub>3</sub><sup>-</sup> group of SDS.

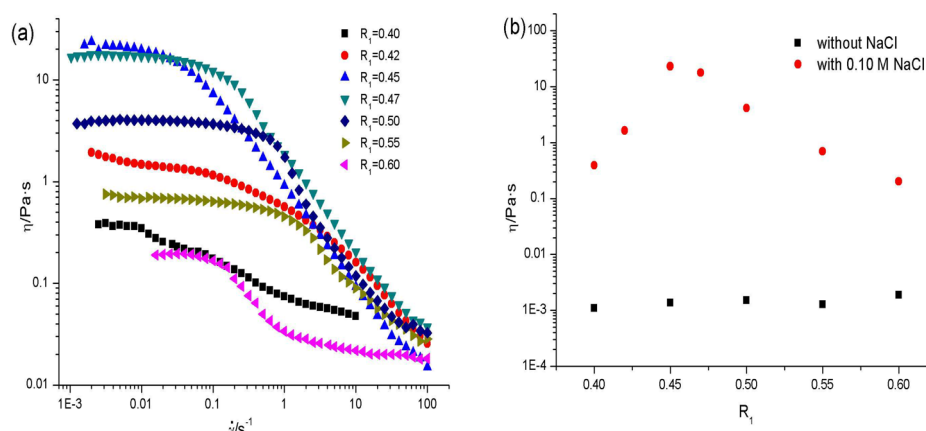
**3.3. Steady-State Fluorescence Measurements.** Fluorescence measurements using pyrene as a probe are also a widely used method for studying the aggregation of surfactants. In the region of 370–400 nm, the fluorescence emission spectrum of pyrene exhibits a character of five bands. The intensity ratio of the first to the third band ( $I_1/I_3$ ) can be considered as a function of monitoring the polarity of the microenvironment, and it decreases with the increasing polarity of solvent.

Figure S2 (Supporting Information) shows the  $I_1/I_3$  ratio versus the concentration of the pure and binary mixed surfactant systems ([N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS) in aqueous solution at 25 °C. There is an abrupt change of the  $I_1/I_3$  value, which is due to the change of the microenvironmental polarity, where the pyrene molecules are solubilized. The cmc values correspond to the inflection point of the curves, which are provided in Table 1. Obviously, the cmc values for [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS mixtures with various compositions obtained from fluorescence measurements are in accordance with those determined by the surface tension technique.

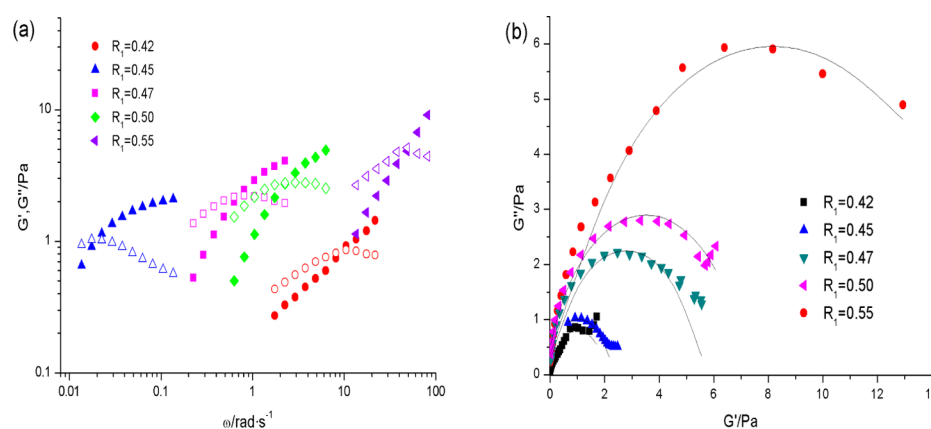
As shown in Figure S2 (Supporting Information), above the cmc, the  $I_1/I_3$  values for the most binary surfactant mixed system are higher than that for pure SDS. It was reported that the  $I_1/I_3$  values indicated the degree of water molecule penetration into micelles.<sup>44</sup> The more compactly the surfactant molecules arrange in the micelles, the more difficultly water molecules have penetrating into micelles. Thus, higher  $I_1/I_3$  values for the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS mixtures indicate that the polarity of the microenvironment for the pyrene probe increases and the surfactant molecules in most mixed micelles arrange more loosely compared with the self-aggregates of anionic surfactant SDS. It is possible due to the stronger steric hindrance of the bulky imidazolium cationic headgroup in the mixed micelles. The similar behavior has been shown for the other zwitterionic/anionic surfactant mixed systems, such as dodecyl dimethyl ammoniumpropane sulfonate/sodium dodecyl sulfate (DDPS/SDS) and 3-(*N,N*-dimethyl)dodecylammonio)propane sulfonate/dioctyl sulphosuccinate sodium salt (DPS/AOT).<sup>11,56</sup> However, the  $I_1/I_3$  value at  $R_1 = 0.5$  is lower than the individual surfactant, which can be ascribed to the stronger electrostatic interaction between the head groups of the interacting species.

**3.4. Na<sup>+</sup>-Driven Viscoelastic Wormlike Micelle in the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS System.** It is observed that the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS solution ( $C_T = 60$  mM) showed a low viscosity at various molar ratios, while it displayed a high viscosity upon addition of NaCl. It indicates that the viscoelastic fluid was induced to be formed in the presence of NaCl. However, when some other inorganic salts (e.g., MgCl<sub>2</sub>, CaCl<sub>2</sub>, and AlCl<sub>3</sub>) were added to the waterlike solution, the viscosity of solution could not change obviously. This behavior is likely to be the result of stronger binding of multivalent ions to dodecyl sulfate ions, compared to Na<sup>+</sup>.<sup>57</sup> These anionic surfactants with multivalent ions might coordinate with the single-chain zwitterionic SAIL, [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]. The coordination compounds formed may have very low solubility, which decreases the concentration of surfactants in solution.<sup>58–61</sup>

The effect of molar ratio ( $R_1$ ) on the flow properties of the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS/NaCl solution ( $C_T = 60$  mM,  $C_{NaCl} = 0.10$  M) was investigated by steady and dynamic rheological measurements at 25 °C. Figure 2a shows the variation of steady



**Figure 2.** Effect of  $[N-C_{12}, N'-CO_2-Im]$  molar ratio on the steady rheological properties of the  $[N-C_{12}, N'-CO_2-Im]/SDS/NaCl$  system ( $C_T = 60$  mM,  $C_{NaCl} = 0.10$  M) at  $25^\circ C$ . (a) Steady shear viscosity curve. (b) Zero-shear viscosity profile.



**Figure 3.** Effect of  $[N-C_{12}, N'-CO_2-Im]$  molar percentage on the dynamic rheological properties of the  $[N-C_{12}, N'-CO_2-Im]/SDS/NaCl$  system ( $C_T = 60$  mM,  $C_{NaCl} = 0.10$  M) at  $25^\circ C$ . (a) Elastic modulus  $G'$  and viscous modulus  $G''$  as a function of angular frequency  $\omega$ . (b) Cole–Cole plots for the WMs (solid lines indicate the best fitting of the Maxwell model).

shear viscosity as a function of shear rate for the  $[N-C_{12}, N'-CO_2-Im]/SDS/NaCl$  system. It is clear that all the samples studied exhibit a constant viscosity at low shear rate and shear-thinning behavior at high shear rate, which corresponds to the typical non-Newtonian flow behavior. It also suggests the formation of a viscoelastic wormlike micelle.<sup>27,62,63</sup> The zero-shear viscosity ( $\eta_0$ ) values for the mixed system with and without NaCl are presented in Figure 2b. In the presence of 0.1 M NaCl, the viscosity of  $[N-C_{12}, N'-CO_2-Im]/SDS$  solution ( $C_T = 60$  mM) with various molar ratios ( $R_1$ ) is enhanced remarkably. As shown in Figure 2b, the  $\eta_0$  value sharply rises initially as  $R_1$  increases, presenting a maximum value (23.1 Pa·s) at  $R_1 = 0.45$ . It suggests that there exists an optimal composition ( $R_1 = 0.45$ ) where the solution exhibits a maximum viscosity and the micelles reach the maximum growth. The dynamic viscoelastic properties for the  $[N-C_{12}, N'-CO_2-Im]/SDS/NaCl$  system are depicted in Figure 3a. The elastic modulus ( $G'$ ) is less than the viscous modulus ( $G''$ ) (i.e., the samples show liquidlike behavior) at low frequency region, and  $G'$  is higher than  $G''$  (i.e., the samples manifest solidlike behavior) at high  $\omega$ . The crossover frequency corresponds to  $\omega_{co}$ , where the crossover modulus corresponds to  $G_{co}$ . The  $G'$  and  $G''$  values are fitted as the equations<sup>63</sup>

$$G' = G_0(\omega\tau)^2/[1 + (\omega\tau)^2] \quad (8)$$

$$G'' = G_0\omega\tau/[1 + (\omega\tau)^2] \quad (9)$$

where  $G_0$  is the plateau modulus of  $G'$  and  $\tau$  is the stress relaxation time.  $G_0$  and  $\tau$  can be calculated from the following equations, respectively

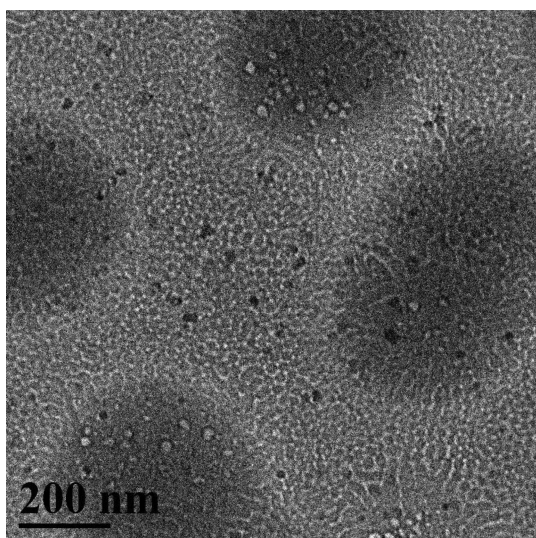
$$G_0 = 2G_{co} \quad (10)$$

$$\tau = 1/\omega_{co} \quad (11)$$

Furthermore, the Cole–Cole plots of  $G''$  against  $G'$  are demonstrated in Figure 3b, showing a semicircle expected for Maxwell fluid. It is obvious that all the experimental points appropriately follow the Maxwell fluid at low frequencies, while there exists deviations from the Cole–Cole plots at high frequencies. This result reveals that the solution behaves as a Maxwell fluid at low frequencies, testifying the formation of entangled WMs in the solution.<sup>13,64,65</sup> Herein, it is necessary to mention that, for  $R_1 < 0.40$ , the  $[N-C_{12}, N'-CO_2-Im]/SDS$  solution ( $C_T = 60$  mM,  $C_{NaCl} = 0.10$  M) has no viscoelastic response. For  $R_1 > 0.60$ , a rapid reduction in the viscosity of solution is observed, indicating the destruction of WMs. Moreover, as shown in Figure 3b, the samples in the molar ratio range of  $0.42 \leq R_1 \leq 0.60$  fit the Maxwellian Cole–Cole semicircle. Therefore, these samples have been chosen to be studied systematically in this work.

Figure S3 (Supporting Information) presents the  $G_0$  and  $\tau$  values for the WMs as a function of  $R_1$ . As shown in Figure S3a (Supporting Information),  $G_0$  increases slightly with  $R_1$ , reaching a small maximum at  $R_1 = 0.55$ . However, when  $R_1 \leq 0.45$ , the  $G_0$  values for various  $R_1$  value have little change. It has been reported that  $G_0$  is inversely proportional to the network mesh size.<sup>13</sup> Thus, this result indicates that the mesh size of the WM solutions is not particularly affected by  $R_1$  when  $R_1 \leq 0.45$ . The plot of  $\tau$  versus  $R_1$  shows a pronounced peak ( $\tau \sim 51$  s) at  $R_1 = 0.45$ . The  $\tau$  value is directly proportional to the average contour length of micelles.<sup>18</sup> This suggests that the average contour length of WM reaches the maximum and the network structure at  $R_1 = 0.45$  is the strongest, which is in accordance with the result obtained from the steady rheological measurements. Moreover, the WMs studied here have a much larger  $\tau$  value in comparison with the WMs formed by the traditional zwitterionic/anionic surfactant with the same hydrophobic alkyl chain, e.g., for laurylamidopropyl betaine and SDS mixture,  $\tau \sim 0.55$  s,<sup>26</sup> which indicates a stronger network structure of the WMs studied.

Rheological results indicated that the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS solution exhibits many features of wormlike micelles. In addition, cryo-TEM was employed to visualize the micelle morphology. As shown in Figure 4, many elongated flexible



**Figure 4.** Cryo-TEM image of WMs in the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS/NaCl system ( $C_T = 60$  mM,  $R_1 = 0.45$ ,  $C_{NaCl} = 0.10$  M) at 25 °C.

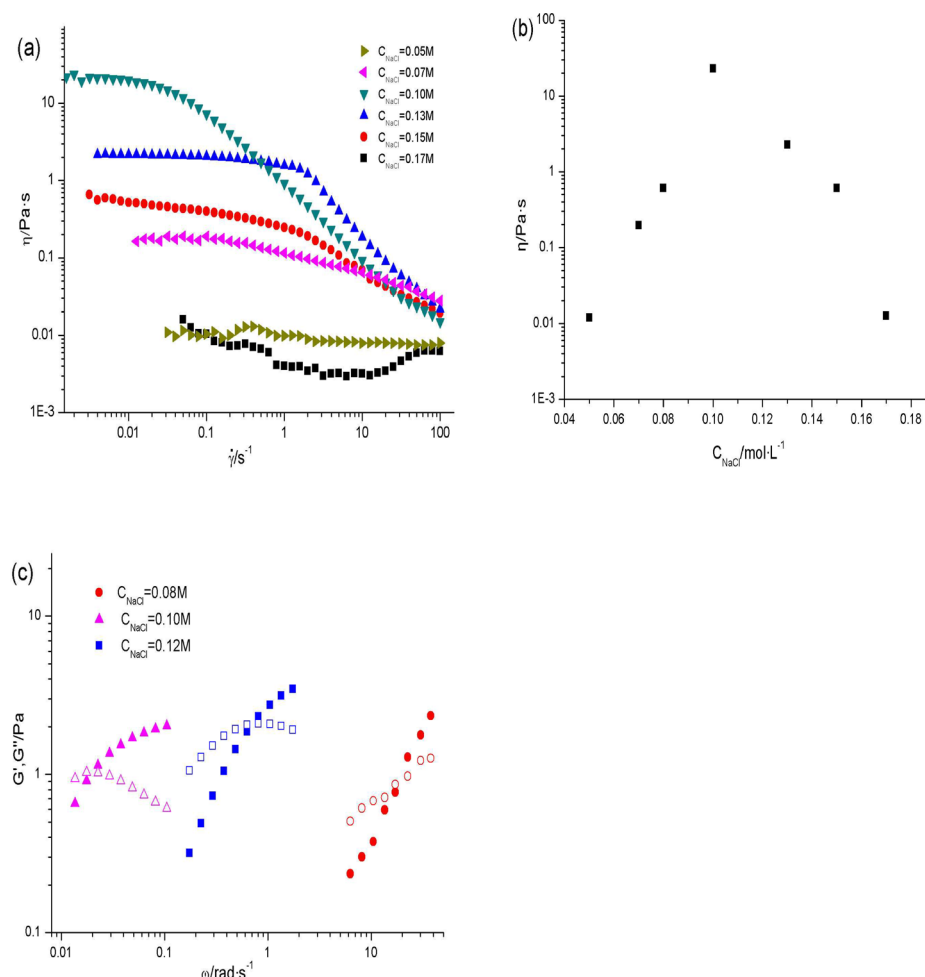
wormlike micelles were determined in [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS solution in the presence of 0.1 M NaCl. The micelles were over 100 nm, and they overlapped with each other and formed 3D network structures. Thus, the cryo-TEM image directly demonstrated the formation of the WMs in the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS solution.

Mulqueen and Blankshtein<sup>66</sup> proposed a mode of how C<sub>12</sub> betaine and SDS molecules were adsorbed at the air/liquid interface. Qiao et al.<sup>27</sup> explained the WM formation mechanism in the tetradecyldimethylammoniumpropanesulfonate (TPS)/SDS/Ca(NO<sub>3</sub>)<sub>2</sub> system by a schematic. According to the previous reports as above and the results of this work, a possible formation mechanism of WMs can be obtained in [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS/NaCl solution. It is well-known that the phase transition is dependent on the packing parameter  $p$ ,<sup>67</sup>  $p = \nu/(la_0)$ , where  $\nu$  and  $l$  are the volume and length of the

hydrophobic alkyl chain, respectively, and  $a_0$  is the area of the hydrophilic headgroup of surfactant. The value of  $p$  can be used to monitor the category of aggregates formed in surfactant solution. Examples are as follows: global micelles ( $p \leq 1/3$ ), wormlike micelles ( $1/3 < p \leq 1/2$ ), bilayers ( $1/2 < p \leq 1$ ), and reverse structures ( $p > 1$ ). Without Na<sup>+</sup>, the electrostatic repulsion between the charged head groups in the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS system leads to a loose packing of surfactant molecules, although there exists a synergic interaction between [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im] and SDS molecules, where the  $p$  value is below 1/3. This factor prevents the formation of WMs. With the addition of Na<sup>+</sup>, the electrostatic repulsion is reduced, resulting in the growth of micelles. Meanwhile, Na<sup>+</sup> associates with the SO<sub>3</sub><sup>-</sup> group of SDS strongly due to electrostatic attraction, which increases the  $p$  value ( $1/3 < p \leq 1/2$ ). These factors induce the formation of WMs in the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS/NaCl system. It is different from the ionic/ionic surfactant systems, such as 1-butyl-3-methylimidazolium octyl sulfate/3-methyl-1-octylimidazolium chloride ([C<sub>4</sub>mim]-[C<sub>8</sub>OSO<sub>3</sub>]/[C<sub>8</sub>mim][Cl])<sup>68</sup> and 1-dodecyl-3-methylimidazolium bromide/sodium dodecyl sulfate (C<sub>12</sub>mimBr/SDS).<sup>69</sup> In the ionic/ionic surfactant aqueous solution, vesicle structure is apt to form due to both electrostatic and hydrophobic interactions. First, the oppositely charged head groups can form ion pairs and lead to a lower  $a_0$  (the area of the hydrophilic headgroup of surfactant) because of the stronger electrostatic interaction. Then, the ion pairs form aggregates that usually grow into vesicles via hydrophobic interactions. On the basis of the above mode, the relationship between  $\eta_0$  and  $R_1$  can be interpreted. When  $R_1 < 0.45$ , the viscosity of the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS/NaCl system increases with  $R_1$  (Figure 2). In the region, the net negative charges of mixed micelles cannot be completely neutralized by 0.1 M NaCl. As  $R_1$  increases, the net negative charges of mixed micelles gradually are reduced and the electrostatic repulsion in the mixed micelles is weakened, leading to the growth of micelles. At  $R_1 = 0.45$ , the system exhibits a maximum viscosity in the profile, where the net negative charges of mixed micelles are neutralized completely and the micellar network behaves as a classic linear micellar system (viz., WMs). However, when  $R_1$  is higher than 0.45, the predominant zwitterionic SAIL [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im] may restrict the surfactants to pack closely and lower the  $p$  value.<sup>70</sup> Thus, here the viscosity of solution decreases as  $R_1$  increases (Figure 2).

**3.5. The Effect of NaCl Concentration on the Rheological Properties of the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS System.** The effect of NaCl concentration on the flow properties of [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS solution ( $C_T = 60$  mM,  $R_1 = 0.45$ ) was studied by steady and dynamic rheological measurements at 25 °C. As indicated in Figure 5a, the samples display a shear thinning behavior, except for those at 0.05 and 0.17 M NaCl, which suggests the formation of WMs at 0.07 M  $\leq C_{NaCl} \leq 0.15$  M. The  $\eta_0$  values are presented as a function of NaCl concentration in Figure 5b. It is clear that the  $\eta_0$  values rise with the increase of  $C_{NaCl}$ , followed by a decrease. There exists a maximum  $\eta_0$  value at  $C_{NaCl} = 0.10$  M, evidencing the maximum growth of WMs. When the NaCl concentration is lower than 0.1 M, the addition of NaCl can screen electrostatic repulsion between surfactants gradually, which favors the growth of micelles. As a result, the solution viscosity increases with the addition of NaCl. However, at higher NaCl concentration, the WMs cannot grow further and even break into several pieces.<sup>26,63</sup> Hence, the viscosity decreases.





**Figure 5.** Effect of NaCl concentration on the rheological properties of the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS system ( $C_T = 60$  mM,  $R_1 = 0.45$ ) at 25 °C. (a) Steady shear viscosity curve. (b) Zero-shear viscosity profile. (c) Elastic modulus ( $G'$ ) and viscous modulus ( $G''$ ) as functions of the angular frequency.

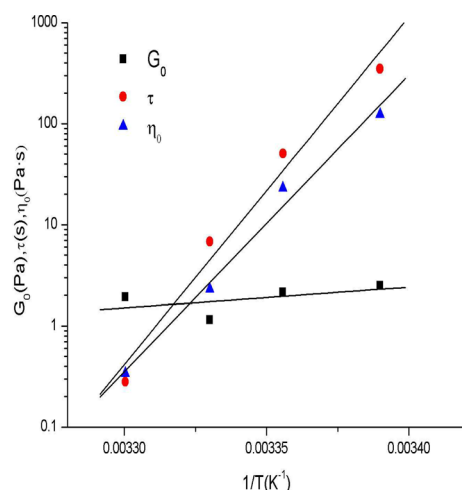
The dynamic viscoelastic curves for the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS solution are illustrated in Figure 5c in the presence of different NaCl concentrations. These curves conform to eqs 8 and 9, and the samples behave as a simple Maxwell fluid at low frequencies. The  $G_0$  and  $\tau$  values for the samples can be obtained from eqs 10 and 11. Figure S4 (Supporting Information) shows the graphs of  $G_0$  and  $\tau$  for the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS systems upon addition of various concentrations of NaCl. Both  $G_0$  and  $\tau$  values do not increase continuously with the increasing concentration of NaCl.  $G_0$  keeps almost constant with the addition of NaCl when  $C_{\text{NaCl}} \leq 0.10$  M, followed by an increase (Figure S4a, Supporting Information), while the  $\tau$  value passes through a maximum at  $C_{\text{NaCl}} = 0.10$  M and then decreases (Figure S4b, Supporting Information). It suggests that the salt-induced WMs formed by [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS systems at  $C_{\text{NaCl}} = 0.10$  M have the strongest network structure, which is in agreement with the results obtained from the steady rheological measurements. It is known that  $G_0$  is inversely proportional to the network mesh size and  $\tau$  is directly proportional to the average contour length of micelles. At  $C_{\text{NaCl}} < 0.10$  M, the addition of NaCl causes the screening effect of electrostatic repulsions, which mainly promotes an increase in the average contour length of micelles and cannot modify the network mesh size. Thus, the  $G_0$  value increases slightly, while the  $\tau$  value rises as  $C_{\text{NaCl}}$  increases.

When  $C_{\text{NaCl}}$  is higher than 0.10 M, the WMs may break into several pieces, leading to a reduction in the network mesh size. Consequently, the  $G_0$  value rises and the  $\tau$  value decreases. A similar trend has been reported for the WM systems formed by anionic/zwitterionic surfactant systems, e.g., *N*-tetradecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate (TDPS)/SDS and laurylamidopropyl betaine and SDS mixtures.<sup>26,28</sup>

### 3.6. The Temperature Effect on the Rheological Properties of the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS/NaCl System.

The temperature dependence of the flow curves for WMs formed by the [N-C<sub>12</sub>, N'-CO<sub>2</sub>-Im]/SDS/NaCl system ( $C_T = 60$  mM,  $R_1 = 0.45$ ,  $C_{\text{NaCl}} = 0.10$  M) was also investigated (Figure S5, Supporting Information). The  $G_0$ ,  $\eta_0$ , and  $\tau$  values as a function of  $1/T$  are shown in Figure 6. It is found that  $\tau$  decreases while  $G_0$  keeps approximately constant with the increasing temperature. This indicates that the micellar contour length decreases with temperature, whereas the network mesh size is independent of temperature. In addition, the solution viscosity decreases with temperature, which can be attributed to the shortening of WMs.

In the case,  $\tau$  fits Arrhenius' law,<sup>71,72</sup>  $\tau = Ae^{E_a/RT}$ . Here,  $A$  is a constant,  $R$  is the gas constant,  $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ , and  $E_a$  is the flow activation energy, which describes the energy for the reversible scission mechanism of the micelles and the end-cap energy. The decay of viscosity with temperature also



**Figure 6.** Semilog plots of  $G_0$ ,  $\eta_0$ , and  $\tau$  versus  $1/T$  for the  $[\text{N-C}_{12}, \text{N}'\text{-CO}_2\text{-Im}]/\text{SDS}/\text{NaCl}$  system ( $C_T = 60 \text{ mM}$ ,  $R_1 = 0.45$ ,  $C_{\text{NaCl}} = 0.10 \text{ M}$ ).

approximately follows Arrhenius' law,  $\eta_0 = G_0 A e^{E_a/RT}$ . The  $E_a$  value calculated from the slope of the  $\tau$  versus  $1/T$  curve is  $658 \text{ kJ}\cdot\text{mol}^{-1}$ , close to that obtained from a plot of  $\eta_0$  versus  $1/T$ ,  $561 \text{ kJ}\cdot\text{mol}^{-1}$ .

#### 4. CONCLUSIONS

The interaction between a novel zwitterionic SAIL,  $[\text{N-C}_{12}, \text{N}'\text{-CO}_2\text{-Im}]$ , and a traditional anionic surfactant, SDS, in aqueous solution was studied for the first time in this work. It is found that the mixed  $[\text{N-C}_{12}, \text{N}'\text{-CO}_2\text{-Im}]/\text{SDS}$  system has a much lower cmc and better surface activity than an individual surfactant. Compared with the zwitterionic  $\text{C}_{12}$  betaine surfactant/SDS system, the mixture studied exhibits a stronger synergism, which can be ascribed to the stronger electrostatic interaction between the imidazolium cationic moiety of  $[\text{N-C}_{12}, \text{N}'\text{-CO}_2\text{-Im}]$  and the  $\text{SO}_3^-$  group of SDS. Interestingly, the rheological results show that, through the addition of NaCl, the waterlike solution of the mixed  $[\text{N-C}_{12}, \text{N}'\text{-CO}_2\text{-Im}]/\text{SDS}$  system can turn into WMs. It is proposed that, upon addition of NaCl, the screening effect of the electrostatic repulsion between charged groups of  $[\text{N-C}_{12}, \text{N}'\text{-CO}_2\text{-Im}]$  and SDS molecules promotes the growth of micelles. It is found there exists an optimal composition at  $C_T = 60 \text{ mM}$ ,  $R_1 = 0.45$ , and  $C_{\text{NaCl}} = 0.10 \text{ M}$ , where the network structure of WMs is the strongest. This work not only advances our understanding of the formation of wormlike micelles but also enriches the possible application fields of zwitterionic SAIL.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

Details of surface tension, steady-State fluorescence, rheological parameters, and the effect of temperature on the rheological properties are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### ■ AUTHOR INFORMATION

##### Corresponding Author

\*Phone: +86-531-88364807. Fax: +86-531-88564750. E-mail: [ymlt@sdu.edu.cn](mailto:ymlt@sdu.edu.cn).

##### Notes

The authors declare no competing financial interest.

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