

# Development of a High Efficient Compound Surfactant for Foam Drainage in Gas Wells

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**Abstract**—In this study, the foaming properties of a compound surfactant formula containing cetyltrimethylammonium chloride (CTAC), cocamidopropyl betaine (CDAB), fatty alcohol polyoxyethylene ether-7 (AEO7) and sodium alpha-olefin sulfonate (AOST) were evaluated to meet the application requirements for foam generation and foam drainage in gas wells. The results exhibited that the foaming volume and the half-life of the compound surfactant solution (0.05 wt % CTAC + 0.7 wt % CDAB + 0.6 wt % AEO7 + 0.05 wt % AOST) can reach the values of 550 mL and 23 min, respectively, which suggested that the foaming ability and stability were improved in comparison with each solution containing a single surfactant. It showed that the surface tension can be lowered to 22.4 mN/m with the presence of the compound surfactants. Simultaneously, the microstructure of the foam was observed using a polarizing microscope, and it was found that there were almost no polyhedron structures in the foam within a certain range of formula concentrations. The results of the experiments also clarify that the formula has well properties of temperature resistance and salt resistance (measured using a high-speed agitator).

**Keywords:** foaming agent, foaming stability, surface tension, microstructure, salt resistance

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## INTRODUCTION

Since their inexpensive and high performance, surfactants are widely used in various areas including chemistry, cosmetics, textile, food industries and water treatment [1–3]. Besides, surfactants play a crucial role in the area of oilfield chemistry [4, 5]. With the continuous exploitation of gas fields, a large amount of liquids would possibly flow into the gas wells and accumulate at the bottom of the wells, which would certainly reduce the production efficiency of the natural gas from the reservoirs [6, 7]. In order to remove the accumulated liquid in gas wells, foam drainage technology was widely used and considered as a promising method to solve the loading liquids in wells [8–10].

Anionic surfactants are the most commonly used surfactants for gas well deliquification due to their high foamability and low absorbability [11]. Among the other anionic foaming surfactants, AOST exhibits relatively higher foaming ability under high salinity and temperature conditions. Moreover, the AOST also exhibits good compatibility with other co-surfactants [12, 13]. Zwitterionic surfactants were often used to enhance the stability of the foam generated by anionic surfactants [14, 15] due to the zwitterionic surfactants' high performance in harsh conditions (e.g., high temperature, wide pH range and high amount of divalent ions, etc.). Roncorni et al. [15] confirmed the synergy effects between AOST and a zwitterionic surfactant (cocamidopropyl hydroxysultaine) in foam generation and stability.

Quaternary ammonium salts with certain structures can also be used as foaming agents for unloading the liquid in the gas wells [16, 17]. It also should be noted that large amounts of salts dissolved in the formation water would certainly reduce the performance of the foaming agents being injected into the gas wells [9, 18]. For the sake of carrying out the foam deliquification treatment under harsh conditions, foaming agents containing compound surfactants are usually required to achieve a better synergistic effect [19].

When the surfactant solution was injected into the gas wells, it would be mixed with the bottom liquids by the agitation of flowing natural gas, which would facilitate the formation of large amounts of foams [20]. Furthermore, the foams would be lifted to the ground by the flows of natural gas. During the process of foam formation and flowing back to the ground, the accumulated liquids would be lifted to the grounds [21]. Hence, the combinations of proper surfactants can generate a stable foam and herein carry a large number of accumulated liquids in the gas wells, and further promote natural gas recovery [22]. The key to foam drainage technology is the performance of the foaming agents. The foaming agents should perform well under the crucial conditions of high water, salinity, and methanol content (used to inhibit the formation of gas hydrate if required) and high formation temperature [23]. In this study, CTAC and CDAB were used in combination with AEO7 and AOST to achieve high foaming performance. Besides, the effects of several conditions (high temperature, salt content and methanol content) on the interfacial properties of surfactants were studied. The performance of the optimized foaming agents in this paper is higher than that of Gao's (0.05 wt % CTAC+0.7 wt % CDAB) [24].

## EXPERIMENTAL

**Materials.** CTAC (98%) was purchased from Cologne Chemical Reagent Factory (Chengdu, China). CDAB (85%) was purchased from Huazhiguang Chemical Co., Ltd. (Guangzhou, China). AEO7 (99%) was purchased from Youso Chemical Technology Co. Ltd. (Shandong, China). AOST (92%) was purchased from Lusen Chemical Co., Ltd. (Linyi, China). Methanol and petroleum ether were purchased from Fuyu Fine Chemical Co., Ltd. (Tianjin, China). All products were used as received without further purification.

**Surface tension measurement.** The surface tension of each solution was measured by the hanging-ring method

at room temperature. Before the measurements, the tensiometer (Kruss K 100, Germany) was used to test the surface tension of a distilled water sample to confirm the accurateness of the instrument [25], the surface tension of distilled water was measured in this manner was 72.65 mN/m. Each measurement was repeated at least three times and reported as the average.

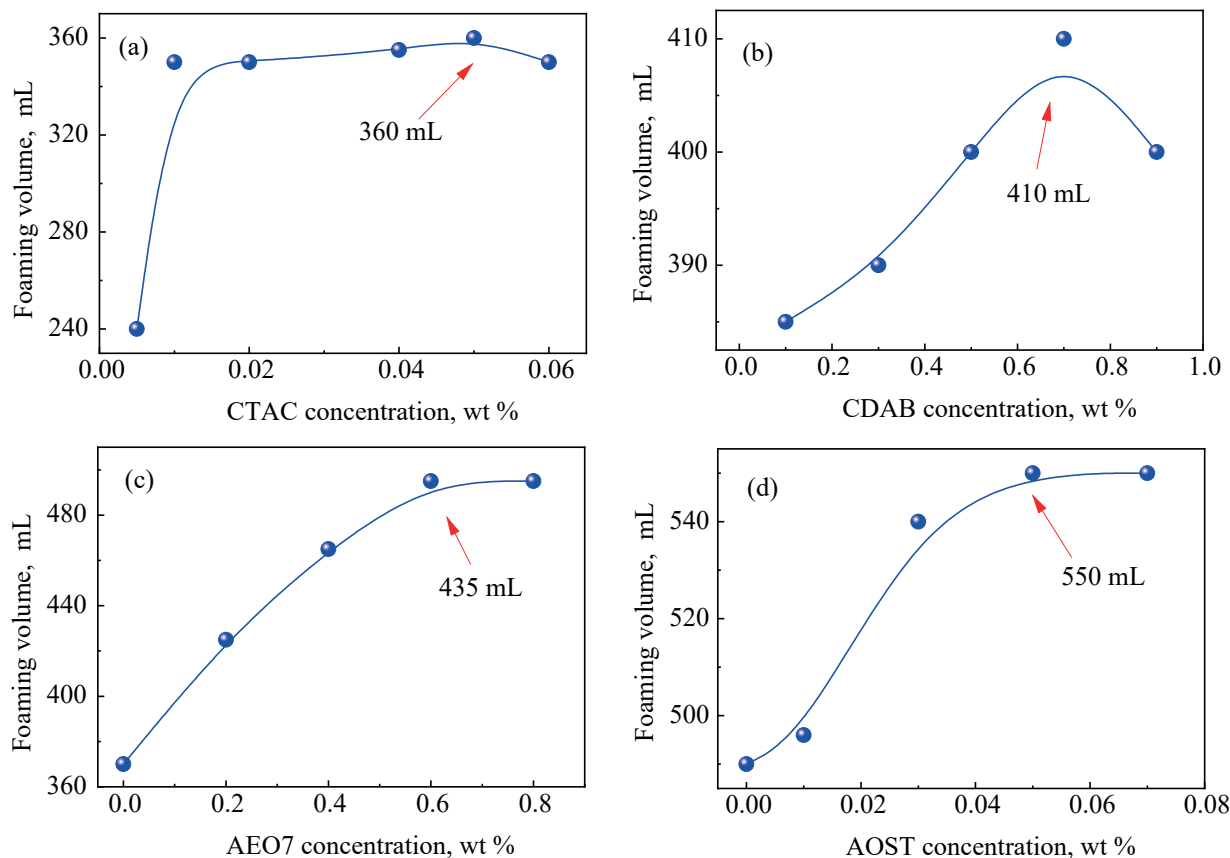
**Foaming capacity evaluation.** A high-speed agitation method was used to generate foams using a high-speed mixer (GJ-3S, Qingdao Haitongda Special Instrument Co., Ltd.). In each test, 100 mL surfactant solution was agitated at 7000 r/min for 3 min at ambient conditions. After the foam preparation, the foam was transferred into a graduated cylinder immediately. The volume and half-life time (the time that 50 mL free water phase accumulated at the bottom of the cylinder) of the foam were recorded. Each test was repeated in triplicate. All measurements were performed at 25°C and atmospheric pressure.

**Salt resistance evaluation.** Generally, the salinity of formation water has a strong adverse effect on the generation of foam [26]. To study the effect of concentration and species of inorganic ions on the foaming ability and related foaming stability of the surfactants, surfactant solutions with different salt concentrations (NaCl, KCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>) were prepared.

**Temperature resistance.** The temperature in a well has a significant effect on the performance of foaming agents. Therefore, the Ross–Miles method was used to measure the foaming capacity and stability of the formula at temperatures ranging from 30 to 70°C [27]. Each test was repeated three times.

**Foam microstructure observation.** A polarized optical microscope (DM4500P LFD, Germany) was used to observe the microstructure of foam under static conditions, after the preparation of foam using the optimized foaming agents (agitated at 7000 r/min for 30 min).

**Methanol effect evaluation.** During gas production, methanol was usually used to prevent the formation of gas hydrate [24]. However, the presence of methanol may also retard the performance of foaming agents. Therefore, it is necessary to check the methanol's influence on the foaming ability of the optimized foaming agents. In this section, the foaming performance of optimized surfactant solution with 0, 5, 10, and 15% methanol was tested in a temperature range of 40 to 70°C using the Ross–Miles method.



**Fig. 1.** Foaming ability of: (a) CTAC; (b) 0.05 wt % CTAC + CDAB; (c) 0.05 wt % CTAC + 0.7 wt % CDAB + AEO7; (d) 0.05 wt % CTAC + 0.7 wt % CDAB + 0.6 wt % AEO7 + AOST.

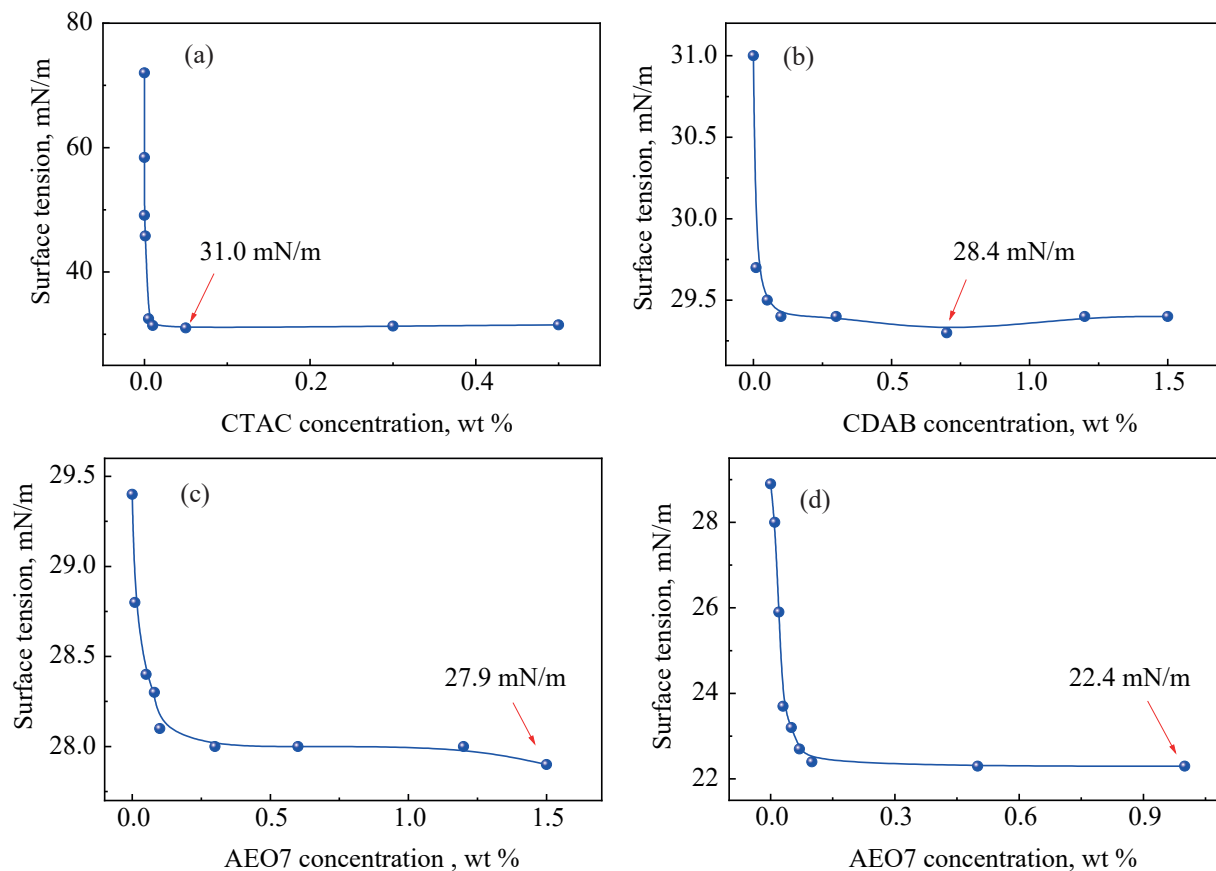
## RESULTS AND DISCUSSION

**Foaming ability.** The variation in foaming properties of surfactant aqueous solutions versus concentration is shown in Fig. 1. In our study, initial foam height was gradually increased with the increase of the surfactant dosage before 0.05 wt %. Fig. 1a presented that CTAC concentration at 0.05 wt % produced the highest initial volume, which implied that the optimized concentration of CTAC was 0.05 wt %. The effect of CDAB's concentration on its foaming ability was shown in Fig. 1b. It can be drawn from Fig. 1 that 0.7 wt % CDAB + 0.05 wt % CTAC produced more foam than that of 0.05 wt % CTAC. Similarly, Fig. 1c indicated that the optimized dosage of AEO7 was 0.6 wt % in the presence of 0.7 wt % CDAB + 0.05 wt % CTAC, while in Fig. 1d it can be found that the introduction of 0.05 wt % AOST into the solution containing

0.7 wt % CDAB + 0.05 wt % CTAC + 0.6 wt % AEO7 could generate the highest amount of foam.

**Measurement of surface tension.** The change in surface tension of solution as a function of surfactant's concentration is shown in Fig. 2. As shown in Fig. 2, the surface tension could be rapidly reduced after the addition of surfactant. For each solution, the surface tension of which gradually decreased with the increasing content and then remained stable (CMC was reached). Furthermore, the surface tension of compound surfactant was lower than that of CTAC alone. The optimized formula turned out to be 0.05 wt % CTAC + 0.7 wt % CDAB + 0.6 wt % AEO7 + 0.05 wt % AOST.

**Mineral content impact test.** In this section, NaCl, KCl, MgCl<sub>2</sub> and CaCl<sub>2</sub> with various dosages was dissolved in the solution containing optimized surfactant formula to measure the formula's foaming ability against salt. The foaming ability of the formula was evaluated by



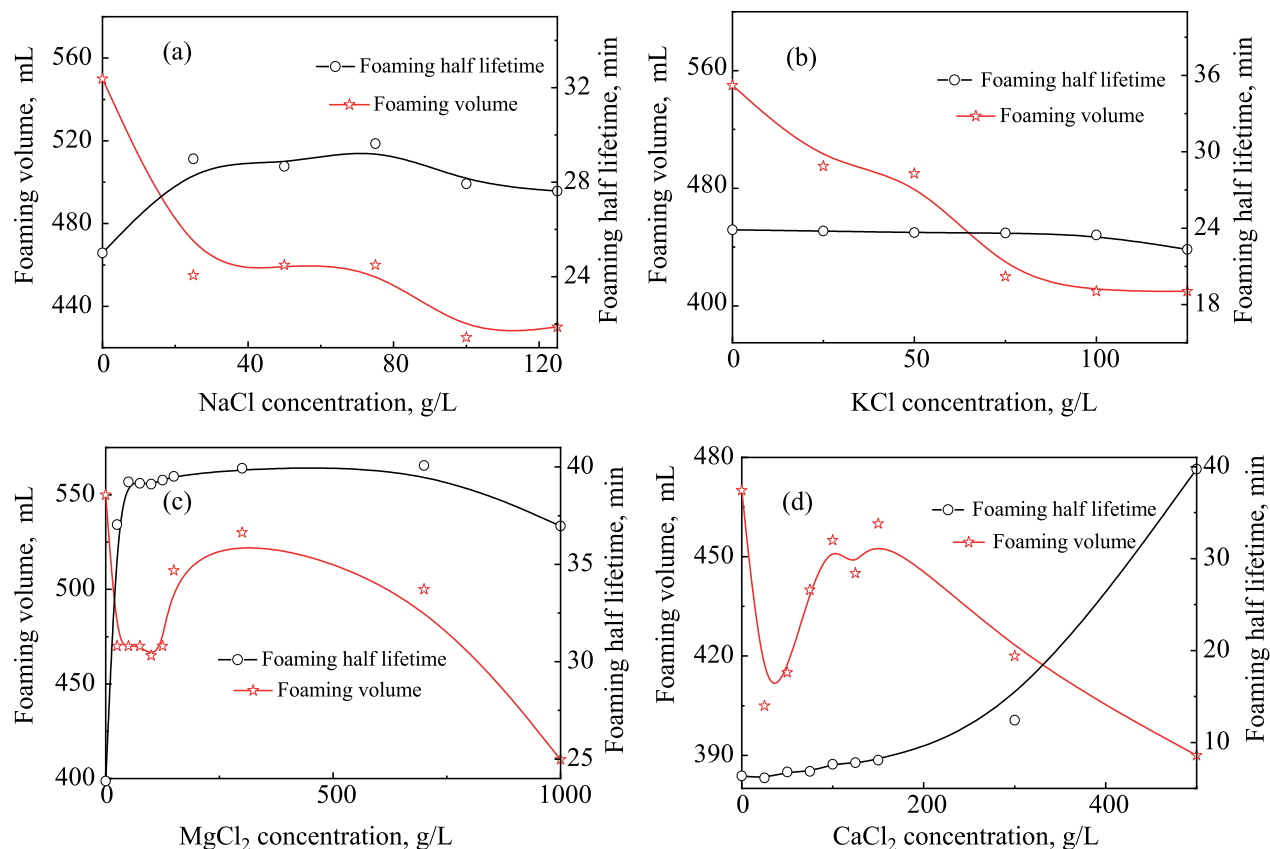
**Fig. 2.** Surface tension of: (a) CTAC; (b) 0.05 wt % CTAC + CDAB; (c) 0.05 wt % CTAC + 0.7 wt % CDAB + AEO7; (d) 0.05 wt % CTAC + 0.7 wt % CDAB + 0.6 wt % AEO7 + AOST.

the initial volume of the foam produced by mechanical stirring at 7000 r/min for 3 mins. The experiment was repeated three times to avoid errors.

The influence of salt on foamability is ambiguous. Figure 3 showed that the foam volume generated by the optimized formula decreased with the increase of NaCl and KCl concentration. The negative effect of NaCl and KCl on the foaming ability of the formula may be ascribed to the retarded electrostatic repulsion among the charged bubble surfaces and therefore reduces foamability [26]. It should be noted that the impact of NaCl and KCl on the formula's foaming ability was limited. However, Fig. 3 showed that in a certain concentration range of MgCl<sub>2</sub> and CaCl<sub>2</sub> the foam volume could be increased by the salts, which may be due to the compressed diffusion electric double layer of the surfactant molecule caused by the Ca<sup>2+</sup> and Mg<sup>2+</sup> ions that facilitate the formation of adsorption layer with high packing density and herein reduce of

surface tension of the solution [28, 29]. As the CaCl<sub>2</sub> concentration continues to increase, a gradual decrease in the foam volume was observed, while a limited increase in the half lifetime was observed. This is because the addition of CaCl<sub>2</sub> would increase the concentration of counter ions (Cl<sup>-</sup>), which would compress the hydrophilic electric double layer of the surfactant and screen the electrostatic repulsion. Under these conditions, the formation of micelles would be promoted and herein lower the critical micelle concentration and surface tension, which contributes to the stability of the formula [1]. As described in Fig. 3, the maximum concentrations of NaCl, KCl, MgCl<sub>2</sub> and CaCl<sub>2</sub> that the formula can resistant were 75, 50, 300 and 150 g/L, respectively.

**Temperature resistance evaluation.** In this section, 300 mL surfactant solution was prepared and kept at 30°C in a water bath. The Ross–Miles method was used to evaluate the temperature-tolerance property. The foam



**Fig. 3.** Effects of different salt concentrations on the formula (0.05 wt % CTAC + 0.7 wt % CDAB + 0.6 wt % AEO7 + 0.05 wt % AOST): (a) NaCl; (b) KCl; (c) MgCl<sub>2</sub>; (d) CaCl<sub>2</sub>.

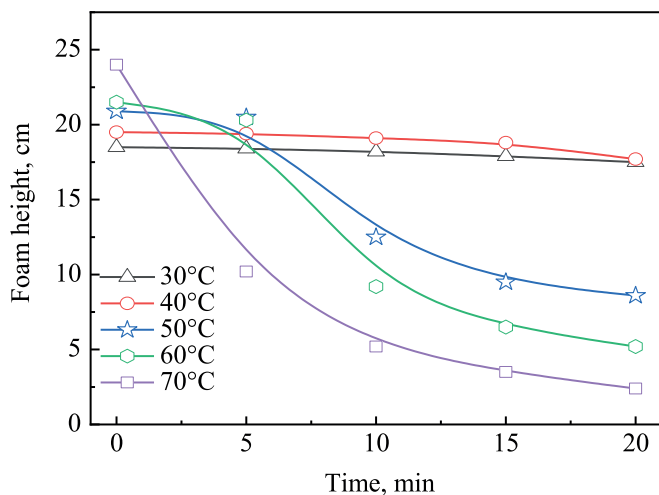
height can be observed and recorded at 0, 5, 10, 15, and 20 min after the formation of the foam. As shown in Fig. 4, the foam heights at 30 and 40°C were almost equal to each other. When the temperature was kept higher than 50°C, the height of the foam was found to decrease obviously with the increase of temperature, which may be caused by the increased liquid loss rate of the foam film at higher temperatures, leading to the gradual decrease in the liquid films thickness and deterioration of stability [30].

**Analysis of foam microstructure.** An optical microscope was used to characterize the microstructure of the foam produced at different concentrations after being stirred at 7000 r/min for 3 min. As shown in Fig. 5, the formula not only had good stability at the optimized concentration (0.05 wt % CTAC + 0.7 wt % CDAB + 0.6 wt % AEO7 + 0.05 wt % AOST) but also had good stability after reducing and increasing the concentration of the formula (for example: 0.5, 1.5, and 2 times of the whole formula). When molecules were adsorbed at

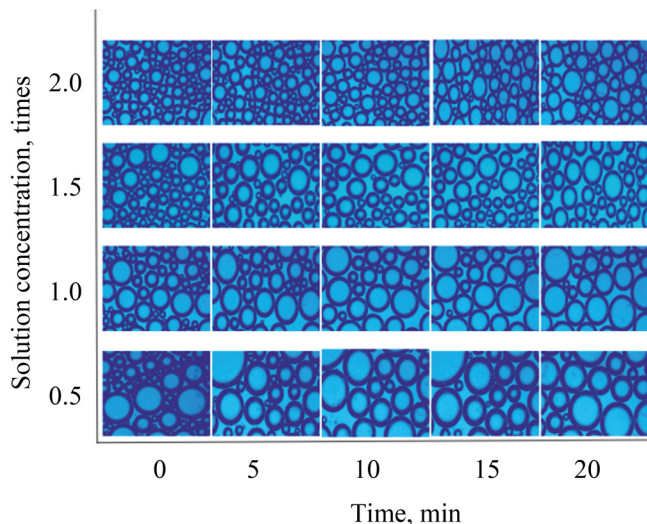
the gas-liquid interface, the molecules in the liquid film can entangle with each other because of the hydrogen-bonded between them, thereby providing higher foaming ability and stability. Foam microstructure was observed as described in Fig. 5. The average size of the bubbles at higher concentrations was smaller than that at lower surfactant concentrations. Moreover, with the increase of concentration, the number of small foam increases significantly, which may contribute to the stability of the foam.

**Methanol resistance test.** The influence of methanol on the formula's foaming ability is shown in Fig. 6. With the presence of 5% methanol, the foam height was higher than that without methanol, which may be caused by the lowered surface tension contributed by a certain amount of methanol. As the content of methanol continues to increase, the polarity of the solution will be reduced and herein promote the solubilization of surfactants in the aqueous phase, which would decrease the number of





**Fig. 4.** The formula's foaming properties and stability at different temperatures (0.05 wt % CTAC + 0.7 wt % CDAB + 0.6 wt % AEO7 + 0.05 wt % AOST).

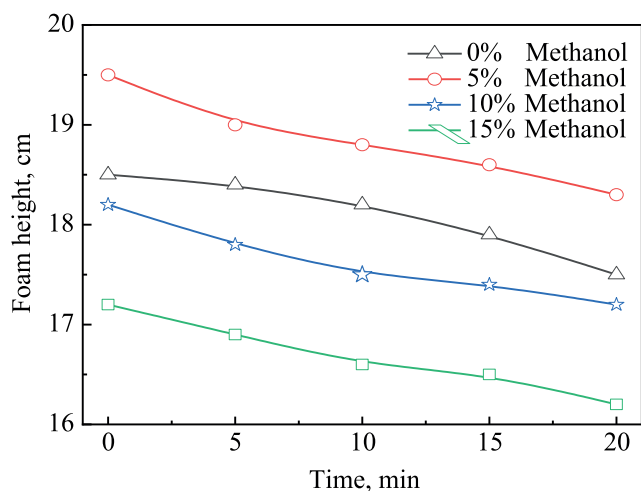


**Fig. 5.** Foam microstructure at different formula's concentrations (0.05 wt % CTAC + 0.7 wt % CDAB + 0.6 wt % AEO7 + 0.05 wt % AOST).

surfactants staying at the water-air interface and lower the stability of the liquid film.

### CONCLUSIONS

In conclusion, a novel surfactant formula (0.05 wt % CTAC + 0.7 wt % CDAB + 0.6 wt % AEO7 + 0.05 wt % AOST) that has excellent foaming ability and stability was developed in this study, which is expected



**Fig. 6.** The formula's effect of different reaction conditions on methanol resistance (0.05 wt % CTAC + 0.7 wt % CDAB + 0.6 wt % AEO7 + 0.05 wt % AOST).

to be an important reference for foam drainage in gas wells. The results showed that the foaming ability of the optimized formula was higher than that of a single surfactant included in the formula, it also had good salt tolerance (the influence of NaCl, KCl, MgCl<sub>2</sub> and CaCl<sub>2</sub> on the formula is weak in a certain range of concentration). The formula could lower the surface tension of a solution rapidly. This formula had a certain temperature resistance, a little amount of methanol will increase the foaming ability of the formula. Moreover, the microstructure of the foam also verified the good stability of the formula and it is still a spherical structure in the foam was observed within 20 min after foam generation. All the results showed that there is a synergistic effect between surfactants, the overall performance of formula is more effective than that of each surfactant, which exhibited a promising application potential in gas well deliquification.

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#### CONFLICT OF INTEREST

The authors declare no conflict of interest requiring disclosure in this article.

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