Synthesis and surface activity evaluation of new surfactants derived from cetyl betaine

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Abstract. Because the surface tension, foaming ability, high temperature resistance, methanol resistance, salt resistance and foam shape of the single cetyltrimethylammonium chloride and cetyltrimethylammonium chloride reaction with formaldehyde are not very significant. Therefore, the product HM-CTAC and cetyl betaine were selected to optimize the compound ratio and further evaluate the performance of the compound product. The foam volume decreases gradually with the increase of temperature; in the aspect of methanol resistance: the foam volume of the compound surfactant disappears slowly under the same methanol concentration; in the aspect of salt resistance: the foam height is more stable with the increase of salt concentration in the system, and the half-life decreases gradually; the surface tension and foam microscopic: the surface tension of the compound system decreases.

Keywords: Synthesis, High temperature resistance, Methanol resistance, Salt resistance.

1. Introduction
In the process of gas field development, gas wells will be flooded by edge water, bottom water or external water ahead of time because of the heterogeneous performance of gas bearing reservoir on the plane and nonuniform distribution of gas production well yield on gas reservoir plane; Longitudinal inhomogeneity in air layer and gas production inhomogeneity in different small layers will also cause edge water, bottom water or external water to burst into high permeability zone, crack and high production gas layer, which will further cause gas wells to be flooded prematurely. After the gas well produces water, the resistance of the seepage into the well and the loss of the total energy of the gas stream in the gas phase increase, gas wells are shut down even because of serious fluid accumulation at the bottom of the well [1-3]. In order to ensure the normal gas production of the gas wells with liquid accumulation, and to slow down the gas production and increase the oil recovery, drainage and gas recovery are required. At present, a variety of drainage and gas recovery technologies have been formed, among which foam drainage is a simple and cost-effective drainage and gas recovery technology [4]. Foam drainage and gas recovery technology has the advantages of low cost, quick effect and simple operation, so it does not affect the daily gas production of gas wells [5]. This technology adapts to
various environments and the condition of gas wells. It is one of the most effective methods to increase gas well production and extend gas production cycle at home and abroad [6]. In addition to the lack of energy in the gas well formation, the difficulty in restricting the implementation of the foam drainage and gas production process is that the foaming agent is not adaptable to the condensate oil and high salinity of the gas well formation water, resulting in foaming capacity and liquid carrying capacity, which leads to inadequate foaming capacity and liquid carrying capacity [7,8]. In this paper, cetyl betaine and HM-CTAC were selected as raw materials, and formaldehyde was used as assistant synthetics to prepare different multifunctional surfactants. The high temperature resistance, methanol resistance and salt resistance of these surfactants were evaluated.

2. Experimental

2.1. Materials
Formaldehyde was supplied from Mulan Town Industrial Development Zone, Chengdu. Cetyltrimethyl ammonium chloride was purchased from Tianjin Hedong District Hongyan Reagent Factory. Cetyl betaine were purchased from Shanghai Reagent Factory, China. Methanol, Sodium chloride and Calcium chloride were purchased from Tianjin Chemical Reagent Co., Ltd.

2.2. Preparation of surfactant
Cetyl betaine was modified by the Aldol reaction with formaldehyde according in methanol. The reactants was dissolved in methanol with different ratio, and the mixture was heated under refluxing for 4h. After cool to room temperature, methanol was removed by distillation. The residue was re-crystalized in acetone to give the product. The reactants and the products' name was listed in Table 1.

| Reactant A               | Reactant B            | The molar ratio | Solvent | Names             |
|-------------------------|-----------------------|-----------------|---------|-------------------|
| Cetyl betaine           | CTAC                  | 0:40            | Methanol| CTAC              |
| Cetyl betaine           | CTAC                  | 16:24           | Methanol| R0                |
| Cetyl betaine           | CTAC                  | 40:0            | Methanol| CEB               |
| Cetyl betaine           | HM-CTAC(1:1)          | 0:40            | Methanol| HM-CTAC(1:1)      |
| Cetyl betaine           | HM-CTAC(1:1)          | 16:24           | Methanol| R1                |
| Cetyl betaine           | HM-CTAC(1:1)          | 40:0            | Methanol| CEB               |
| Cetyl betaine           | HM-CTAC(1:2)          | 0:40            | Methanol| HM-CTAC(1:2)      |
| Cetyl betaine           | HM-CTAC(1:2)          | 16:24           | Methanol| R2                |
| Cetyl betaine           | HM-CTAC(1:2)          | 40:0            | Methanol| CEB               |
| Cetyl betaine           | HM-CTAC(1:3)          | 0:40            | Methanol| HM-CTAC(1:3)      |
| Cetyl betaine           | HM-CTAC(1:3)          | 16:24           | Methanol| R3                |
| Cetyl betaine           | HM-CTAC(1:3)          | 40:0            | Methanol| CEB               |
| Cetyl betaine           | HM-CTAC(1:4)          | 0:40            | Methanol| HM-CTAC(1:4)      |
| Cetyl betaine           | HM-CTAC(1:4)          | 16:24           | Methanol| R4                |
| Cetyl betaine           | HM-CTAC(1:4)          | 40:0            | Methanol| CEB               |

2.3. Foaming ability and stability evaluation
In this paper, the optimum foaming concentration of surfactant was determined by measuring the foaming volume and half-time of surfactant by the Waring Blender method [7-9]. The surfactants with 100 mL content of different concentrations were prepared and placed in a digital high-speed mixer. The adjusting speed is 7000 revolution per minute, and the time is 180 seconds. When it is no longer stirring, the foam and solution generated in the process will immediately be poured into the measuring cylinder of 500mL. At the same time, the volume of the foam will be read by pressing the stopwatch. When the 50 mL solution is precipitated, the time displayed on the stopwatch is read, and the time at this time is the half-time of the surfactant [10].
2.4. High temperature resistance evaluation

In order to evaluate the temperature resistance of surfactants, the foam volume of surfactants at different temperatures was measured. The optimum concentration of surfactant was determined by comprehensive analysis of foaming volume and half-time [9], and surfactant solution of the optimum concentration of 300 mL was prepared. Foaming volume at 30°C, 40°C, 50°C, 60°C and 70°C is measured using a special ROSS-Miles water bath [10]. The foaming volume was recorded at different temperatures for 5 min, 10 min, 15 min and 20 min, which was taken as an index to evaluate its high temperature resistance.

2.5. Methanol resistance evaluation

When methanol is injected into gas wells, it can not only prevent freezing, but also prevent plugging of wellbore string. However, the addition of methanol will greatly affect the stability of foam. Therefore, the foaming properties of foaming agents containing different proportions of methanol were tested. The temperature of the special water bath of ROSS-Miles was controlled to 50°C. At the optimum concentration of surfactant, the surfactant solution containing 10%, 20% and 30% methanol was prepared, and the volume of the solution was 300 mL. The foaming volume was recorded at 0 min, 5 min, 10 min, 15 min and 20 min under different methanol content, which was taken as an index to evaluate its methanol resistance [11].

2.6. Salt resistance evaluation

At the optimum surfactant concentration, 100 mL solution containing 50 g/L, 100 g/L, 150 g/L, 200 g/L and 250 g/L salinity (\(m_{CaCl_2} : m_{NaCl} = 1:4\)) was prepared, respectively. The prepared solution was placed in a high speed mixer at 7000 r·min\(^{-1}\) for 180 seconds. When the agitation was stopped, the foam and solution produced during the process were immediately injected into a 500 mL measuring cylinder. At the same time, the foaming volume was read by pressing the stopwatch. When 50 mL of solution precipitated, the time shown on the stopwatch is the half-time of the surfactant. The salt resistance of surfactants was evaluated by the above two measurements.

2.7. Micro-structure of foams

The micro-structures of foam produced by the surfactant solution and their change with time were studied. The studied structures were inspected by optical microscopy in polarized light in order to observe the size distribution of particles. The optical microscope equipped with a digital camera and automated stage and focusing movement, controlled by software that also handles the analysis of the images collected was used [20].

3. Results and discussion

3.1. Foaming ability and stability

The optimum concentration of cetyltrimethylammonium chloride, HM-CTAC(1:1), HM-CTAC(1:2), HM-CTAC(1:3) and HM-CTAC(1:4) all were 0.4%. The above five substances were mixed with Cetyl betaine the ratio of 0:40, 16:24, 40:0. The foaming volume and half-time of the foams were measured by the Waring Blender method, and the results was listed in Table 2. Among them, R1 has better foaming property, the highest foaming volume can reach 480mL. The foam stability of R4 is better than others, and the half time of the foam can reach 6.59 min. The foaming volume and half-time of surfactants were considered synthetically, R2 had a great influence on foaming volume and half-time. Finally, compared with single surfactant, it can be concluded that the introduction of methylol groups improves the performance of the prepared new surfactants in certain properties.
### Table 2. Names of the synthesized product

| Surfactant                | Foam volume (mL) | Half-life (min) |
|---------------------------|------------------|-----------------|
| CTAC                      | 385              | 5.06            |
| R0                        | 400              | 5.35            |
| CEB                       | 365              | 4.56            |
| HM-CTAC (1:1)             | 450              | 5.45            |
| R1                        | 480              | 6.02            |
| CEB                       | 365              | 4.56            |
| HM-CTAC (1:2)             | 450              | 6.34            |
| R2                        | 475              | 6.52            |
| CEB                       | 365              | 4.56            |
| HM-CTAC (1:3)             | 440              | 6.20            |
| R3                        | 420              | 6.08            |
| CEB                       | 365              | 4.56            |
| HM-CTAC (1:4)             | 430              | 6.31            |
| R4                        | 450              | 6.59            |
| CEB                       | 365              | 4.56            |

#### 3.2. High temperature resistance

The foaming volume of surfactant at different temperatures was determined by the ROSS-Miles at the optimum concentration. The results are shown in Fig 1, with the increase of temperature, the defoaming velocity of surfactant R0-R4 increases and the volume of initial foam increases. This is because when the temperature is low, liquid drainage reduces the thickness of foam wall, but the defoaming speed is not fast at this time. And when the temperature becomes higher, the diffusion of gas will increase, and many bubbles will form together to form big bubbles [12,13]. Overall, R2 has a better high temperature resistance.
3.3. Methanol resistance

The foaming ability of surfactants with different methanol content was tested. It can be seen from Fig 2 that as the methanol content increases, the foaming volume of the surfactant decreases, and the rate of decline becomes faster and faster. This is because methanol weakens the solubilization of surfactants and increases the resistance to aggregation, thus reducing the strength of the foam film formed by surfactants [14]. When the methanol content is 30 mL and 60 mL, R0 has the fastest defoaming speed and poor stability, and R3 has better methanol resistance. When the methanol content is 90 mL, R3 has the strongest methanol resistance.
3.4. Salt resistance

The foaming volume and half-time of surfactants with different salinity (\( m_{CaCl_2} : m_{NaCl} = 1:4 \)) were measured. As can be seen from Table 3, the foaming volume of R1, R2 and R4 increases first and then decreases. However, the foaming volume of R2 tend to remain unchanged. Generally speaking, the addition of salt in surfactant can change the surface charge of surfactant, accelerate the drainage process, and reduce the intensity of liquid film, which is the reason that the foaming volume increases first and then decreases [14-16]. Among all the surfactants synthesized, R2 has the best salt resistance.

| Table 3. Salt resistance of different surfactants |
|---------------------------------------------|
| Salinity | Surfactant | 50g/L | 100g/L | 150g/L | 200g/L | 250g/L |
|----------|------------|-------|--------|--------|--------|--------|
|          | R0         | 390   | 390    | 415    | 290    | 235    |
|          | R1         | 425   | 420    | 420    | 350    | 345    |
|          | R2         | 380   | 445    | 425    | 385    | 350    |
|          | R3         | 430   | 430    | 385    | 380    | 325    |
|          | R4         | 415   | 415    | 415    | 365    | 305    |
| Foaming volume/mL | R0 | 5.85 | 6.15 | 7.37 | 3.10 | 1.10 |
|          | R1         | 5.45 | 7.45 | 8.90 | 7.25 | 3.35 |
|          | R2         | 6.10 | 7.15 | 9.12 | 8.35 | 4.20 |
|          | R3         | 6.10 | 7.25 | 8.35 | 8.45 | 3.15 |
|          | R4         | 6.20 | 7.10 | 8.75 | 8.60 | 3.85 |
| Half-time/min | R0 |       |       |       |       |       |
|          | R1         |       |       |       |       |       |
|          | R2         |       |       |       |       |       |
|          | R3         |       |       |       |       |       |
|          | R4         |       |       |       |       |       |
3.5. Micro-structure of foam

The microstructure of the surfactant (R0, R1, R2, R3, R4) at the same concentrations of 4 min was observed with a polarizing microscope. As shown in Figure 3, there are some differences in the foam microstructure of different surfactants. The more stable the foam formed by the surfactant, the thicker the foam wall [13]. From the Figure 3, the shape of the R2 and R4 foam becomes an irregular polygon. This phenomenon indicates that the foam of R2 and R4 is unstable and the water loss rate is faster, which is consistent with the bubble half-life rule. Among the newly synthesized surfactants, the foam stability of R0 is more prominent.

Figure 3. Foam microstructure of different surfactants

4. Conclusion

A series of new surfactants were prepared by from HM-CTAC and cetyl betaine, and their properties were evaluated. The foaming volume and half-time of surfactants were considered synthetically, R2 had a great influence on foaming volume and half-time. With the increase of temperature, the defoaming velocity of surfactant R0-R4 increases and the volume of initial foam increases. Overall, R2 has a better high temperature resistance. When the methanol content is 30 mL and 60 mL, R0 has the fastest defoaming speed and poor stability, and R3 has better methanol resistance. When the methanol content is 90 mL, R3 has the strongest methanol resistance. Among all the surfactants synthesized, R2 has the best salt resistance. The results show that among the newly synthesized surfactants, the foam stability of R0 is more prominent.
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