The CO\textsubscript{2} foam stabilized with the mixture of CO\textsubscript{2}-soluble surfactants

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Abstract. The CO\textsubscript{2}-soluble surfactants have been studied extensively for their ability to reduce gas mobility and provide the essential mobility control in CO\textsubscript{2}-EOR in recent years. In this paper, the synergism of the mixture was investigated. It was conducted that the cloud pressure points of surfactants mixture were located in the middle of single component. However, the synergism of viscosity was positive absolutely, where the apparent foam viscosity of mixture in sand-pack could increase 22.3\% and 8.5\% separately, comparing with C\textsubscript{12-14}NEO\textsubscript{2} and C\textsubscript{16-18}NEO\textsubscript{5}. Anyway, adding the C\textsubscript{16-18}NEO\textsubscript{x} to C\textsubscript{12-14}NEO\textsubscript{2} makes the CO\textsubscript{2} foam more stable and viscous and CO\textsubscript{2} mobility in reservoir was reduced efficiently.

1. Introduction
Carbon dioxide (CO\textsubscript{2}) is inexpensive, volatile, nonflammable, and environmental benign gas\cite{1} and CO\textsubscript{2} flooding has grown significantly over the past 50 years\cite{2}. However, the CO\textsubscript{2} trends to pass through in high permeability zones, named as viscous fingering and gravity override. CO\textsubscript{2} foam is a promising method to reduce CO\textsubscript{2} mobility of in porous media by trapping or resisting the bubbles movement\cite{3}. In recent years, some surfactants that can be dissolved in CO\textsubscript{2} are investigated to stabilize foam, and many following advantages are presented in recent years, such as lower adsorption on reservoir rock surface, in-situ foam with formation brine and high injection ability in ultra-low permeability field. The switchable surfactant composed of 2 ethoxylated amine headgroups with cocoalkyl tails (C\textsubscript{12}NEO\textsubscript{2}) was proved to be good candidate as CO\textsubscript{2}-soluble foam agents\cite{4}, even at high temperature and in high salinity brine, but the surfactant of ethoxylated amine headgroups with longer chain tallow-tails (C\textsubscript{16-18}NEO\textsubscript{x}) could enhance the foam stability further\cite{5}.

Many papers studied the synergism of mixing surfactants system, but few of them focused on the surfactants with different alkyl chain but same head group\cite{6}. In this paper, the interaction and the synergism effect on foam stability of the two surfactants with different alkyl carbon chain were investigated when the C\textsubscript{16-18}NEO\textsubscript{x} was added into C\textsubscript{12}NEO\textsubscript{2} solutions.

2. Experimental methods

2.1. Materials and experimental apparatus
All the surfactants were gifted from Haian Petro-chemical Company and used as received. The surfactants, C\textsubscript{12}NEO\textsubscript{2}, C\textsubscript{16-18}N(EO)\textsubscript{5}, C\textsubscript{16-18}N(EO)\textsubscript{10}, have a dodecyl or tallow alkyl chain and tertiary amine, but different ethoxylation units (EO number) and usually, they were named as 1202, 1805, 1810.
The CO$_2$ gas was purchased from Qingdao Tianyuan Gas Manufacturing Co., Ltd with 99.9% and it can be pressed to 25-30MPa with a gas compression pump in laboratory, which is deposited in accumulator. The visual cell with variable-volume was used to evaluate the surfactant solubility and that with the constant volume of 800ml was used to generate foam with stirring method. The sand-pack used in foam flooding experiments are prepared with dolomite powder (100-120 meshes), where the permeability is around 1.5 Darcy and porosity is 38%.

2.2. Surfactant solubility in CO$_2$
A visual variable-volume cell with 150-350 ml was used to evaluate the surfactants solubility at various pressures and temperatures where the cell volume could change with the screw position. During the experiments, 0.2wt% surfactant was placed on the platform in the visual chamber and then CO$_2$ was charged up to the designated pressure at constant temperature. After stirring 6 h with about 500 r/min, if the surfactant on the platform is disappeared, we expand chamber slowly at same temperature to test the cloud pressure point, and if it couldn’t dissolve absolutely, the pressure was increased with reducing the volume, then repeat above procedure.

2.3. Bulk foam stability
At the bottom of the visual cell, the mixing blades rotates along with magnet outside of the instrument, so that it could bear high pressure. After stirring 150ml surfactant solution with CO$_2$ for 3min at 1000r/m, foam initial height and dynamic foam height with time are measured to evaluate foam stability[7].

2.4. Foam behavior in porous media
The pressure drop along the sand-pack was measured by differential pressure transducers (HP series, Guangzhou Senex Instrument LTD) along with the error ±5 kPa, which was collected by computer in real time. The porosity of the sandpack was around 35% and the permeability was 1.5 Darcy conducting with brine for above 20 total pore volume (PV). Firstly, the system was pressurized to high pressure at given temperature, then the foam were generated by co-injection with various gas ratios (v/v) until the pressure drop came to relative equilibrium and the foam apparent viscosity ($\mu_{app}$) was calculated using Darcy’s Law[8]

$$\mu_{app} = \frac{kA\Delta P}{qL}$$

where $k$ is the permeability of the porous media, $q$ is the volumetric flow rate, $L$ is the length of the sand pack and $A$ is the cross-sectional area.

3. Results and discussion
3.1. Surfactant Solubility in CO$_2$
During the process of decreasing the pressure of CO$_2$ after the surfactants was dissolved, the bulk phase changed to cloudy from clear one phase at certain pressure value, which means that the surfactants could not dissolved absolutely in CO$_2$ once the pressure is lower than the cloud pressure point. Same with previous studies, the 1805 was harder to dissolve in CO$_2$ phase with higher cloud pressure points at any temperature due to the long alky chain. In the Fig.1, when adding the 1805 or 1810 to 1202 system, the cloud pressure point increased as predicted easily. However, it was found that when the 1202 was dominant in the mixture, as the molar ratio 2:1 (1202:1805), the increasing cloud pressure points was not so much. For example, in the mixture 2:1 (1202:1805) at 110 ℃, the cloud pressure point increased only 5%, from 17.6 to 18.5MPa. But for the ratio 1:1, it increased 21%. In order to keep the similar solubility in CO$_2$, the 2:1 mixture of 1202 and 1805 was mainly used to investigate for foam stability.
3.2. Bulk Foam Stability

The foam decay process was recorded after foam generation at 50°C and 15 MPa. From the Fig.2, the foam stabilized with 180X destroyed slowly than 1202, while the initial foam height was lower slightly. Interestingly, the initial foam heights were not influenced after adding the 180X to 1202 solutions, which demonstrated that the foaming ability was dominate by 1202. Besides, in the experiments, we can see that the foam generated with short stirring time, about 20 seconds for 1202 solution, but near 1.5 minutes for 1805 solution. In the mixture with 2:1 of 1202 and 1805, it was shown that the foam height increased from 14 to 17 cm at 50 min, which shown that the 1805 could enhance the foam stability with some extent. Even the foam could be more stable with higher ratio of 1805 or replaced by 1810, the hard solubility in CO₂ make it be not good foam agent candidate. Further, we can consider that the long carbon chain can account for the influence on better foam stability. Foam stability depends on the lamella stability and the surfactants adsorbed layer at the gas-liquid surface decides the lamella stability. Even in this paper, the dilatational modulus at high temperature and high pressure were not shown, it is deduced that the surface dilatational modulus increased with higher alky carbon chain and higher EO number based on previous studies[9]. When the CO₂-soluble surfactant adsorbed at the surface, the carbon chain tail could insert into CO₂ phase and decrease the surface tension efficiently. Once the surface area changed, the 180x was harder to desorb from surface than 1202, then they can resist the deformation of foam.

3.3. Foam viscosity in porous media

The bulk foam stability is easy method to evaluate the foam properties, but the foam behavior in porous media is more reliable to guide the engineering application in reservoir. In this part, the foam apparent viscosity (μ_app) was investigated as function of foam quality and injection volume. From the Fig.3, μ_app increased with higher foam quality up to 90%, then the μ_app was not stable and decreased to 20-40 mPa·s. It’s the most essential to conclude that the μ_app of mixture were higher than that of any single component.
and when the mole ratio was 1:1, the $\mu_{\text{app}}$ value was largest and increased 22.3% and 8.5% separately, comparing with 1202 and 1805. With larger foam quality below 90%, the increasing bubble amount brought much resistance along the flowing direction, thus the $\mu_{\text{app}}$ increased. However, once the foam quality was higher than 90%, the fast decrease of $\mu_{\text{app}}$ can be explained with foam fast rupture, because the disjoining pressure between the adjacent bubbles could not resist the high capillary pressure.

The Fig.4 showed the pressure drop between the inlet and outlet of sand-pack. Obviously, it was positive synergism of mixture for producing high pressure drop, which represents that the CO$_2$ mobility decreases much in porous media after enough injection volume. Besides, with adding 1805 to the solutions, the foam generation needs more injection volume, while the foam achieved to the steady state with injecting 1PV 1202 solutions. The minimum pressure gradient (MPG) could account for this phenomena and Rossen et al. discussed the influence of MPG on foam generation and lamellae mobilization in detail[10]. Here, the strong and stable foam generation needs higher MPG when stabilized with 1805 comparing with 1202, so it took longer injection time or injection volume to achieve the MPG for strong foam generation.

**Figure 3.** The foam apparent viscosity with different foam qualities at 50°C and 15MPa

**Figure 4.** The pressure drop along the sand-pack when injecting surfactant solutions at 50°C and 15MPa

4. **Conclusion**

The influence of mixing two surfactants on solubility in CO$_2$ and foam stability were investigated in this paper. Adding surfactant with long EO length leads to the mixture was hard to dissolve in CO$_2$, while the influence could be neglected when the 1805 ratio was lower than 33%. The mixture with 1805 enhanced the foam stability on the premise that it does not affect the foam initial volume. Most of all, from the results of foam apparent viscosity in porous media, it was shown clearly that the positive synergism generated after mixing 1202 and 1805.
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