Experimental Curriculum Reform of Applied Chemistry in Petroleum Colleges and Universities

-- An example of surfactant evaluation for drainage and gas recovery

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Abstract. In order to further improve the comprehensive experimental skills of undergraduates, understand the performance of different surfactants, and understand the working principles and evaluation methods of drainage gas recovery more effectively, a comprehensive experiment of foam draining agents were designed using four different kinds of surfactants. The surface tension, foaming ability and stability were evaluated. The students can further comprehend the investigative background and applicative field of the foam drainage agent as well as deepen the understanding of mechanization of foaming ability and stability through the design of this experiment. This experiment combines chemicals theory and experimental technology, which can improve students' professional test skills, skills of analysis and problem-solving.

Keywords: Comprehensive experiment; Foam drainage agent; Foaming ability; Foaming stability.

1. Introduction

Applied Chemistry in Oil and Gas Fields is an important specialized course in petroleum colleges and universities, which covers drilling and completion fluids, oil well cement, fracture acidizing, water shut-off and profile control, oil and gas field wastewater treatment, crude oil demulsification and paraffin, crude oil coagulation and viscosity reduction and chemical oil displacement. Students are required to grasp the basic theory of oilfield chemistry and develop their analytical and problem-solving skills by combining indoor experiments and on-site practice. With the diversification and innovation of talent training mode in colleges and universities, comprehensive experiments are increasingly applied to the scientific and technological quality training of science-technology students. Especially for petroleum colleges and universities, comprehensive experiments are indispensable for experimental teaching and are needed to cultivate high-quality talents with modern thinking. Allow the undergraduates in the direction of oilfield chemistry of applied chemistry design comprehensive experiments of oilfield chemistry, so that they can have systematic training of scientific research quality in a short period through the training of procedures such as literature research, experimental design, data processing, result discussion and experimental reports writing.

Many gas wells in China's gas fields that have entered the late stage of extraction have experienced bottom hole liquid loading, which has dramatically reduced gas production or even drowned the gas wells [1]. In order to further improve the recovery ratio of gas fields, various methods are used to eliminate the bottom hole liquid loading, mainly including foam drainage gas recovery, downhole throttle drainage gas recovery, continuous gas lift drainage gas recovery, and jet pump drainage gas recovery [2-3]. Among them, foam drainage gas recovery has become an effective measure to improve the recovery rate of water-bearing gas reservoirs in the late stage of gas well extraction due to its superior performance such as low cost, quick effect, and simple operation process [4-5]. Foam drainage gas recovery is the injection of different foam agents from the wellhead with poor liquid-carrying capacity into the bottom of the well. Under the continuous agitation of the natural gas flow, the foam agent solution can be in full contact with the liquid loading at the bottom of the well, which further generates a large amount of water-containing foam and reduces the amount of gas slip, making

the gas-liquid mixture less dense in order to substantially reduce the friction loss in the tube of the flowing well and the gravity gradient in the well, as shown in Figure 1. When no surfactant is added, the water liquid drops are larger, and when surfactant is added, the water liquid drops and the surfactant form foam liquid drops that are carried from the bottom of the well to the ground with the gas flow [6].

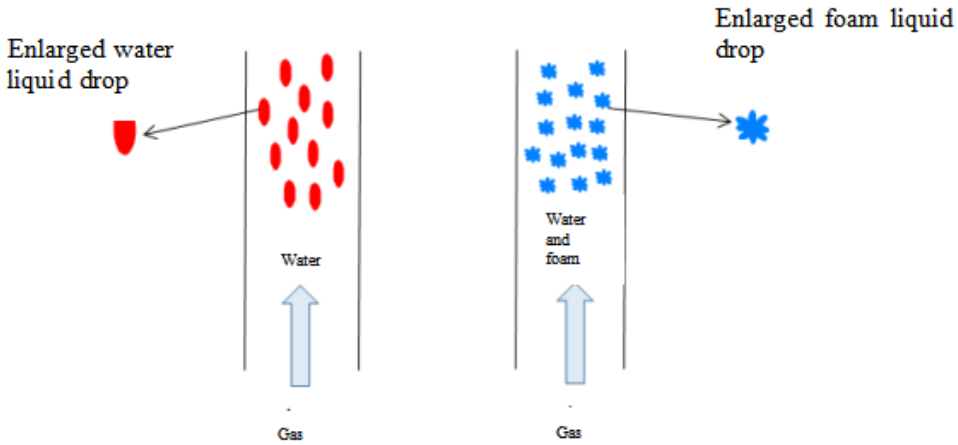


Figure 1. Working Principle of Foam Agent

However, the key to the foam drainage technique depends on the performance of the foam agent. The foam agent used in the foam drainage technique is usually a single surfactant or a combination of surfactants. In general, surfactants used in foam drainage can be divided into solids and liquids, among which liquid surfactants are mainly classified as anionic, cationic, nonionic, amphoteric, etc.

(1) Anionic: typical anionic surfactants include alkyl sulfonates, alkyl sulfates, and alkyl benzene sulfonates[7], which have the advantages of good foaming performance, wide sources, low cost, and resistance to total mineralization of formation water <60g/L; the disadvantage is that because the molecular structure contains anionic groups such as SO42-, it produces precipitation with cations such as Ca2+ and Mg2+, thus causing the poor foaming ability [8];

(2) Cationic: typical anionic surfactants include tertiary amine oxide and organic ammonium salts [9], which have the advantages of strong anti-electrolyte resistance and resistance to total mineralization of formation water <250g/L; the disadvantage is that they are seldom used for economic reasons due to the few source and high price;

(3) Nonionic: typical nonionic surfactants include alkylphenol ethoxylates, fatty acid alcohol amides, and alkyl glycosides [10-11], which have the advantages of small adsorption loss and strong foaming ability due to the presence of ether functional groups between hydrophilic and lipophilic bonds, and the disadvantages of which are resistance to total mineralization of formation water <120g/L and the range of use is often affected by turbidity point [12];

(4) Amphoteric: typical nonionic surfactants include betaine, imidazoline, β-aminocarboxylic acid, α-imino acid, and alkylamine oxide [13], which have the advantages of good foaming performance, low toxicity, certain biodegradability, and resistance to total mineralization of formation water <250g/L; which have the disadvantages of high cost and less use [14].

The group combined the teaching needs of applied chemistry majors and the current development of the oil and gas industry to apply scientific research results to experimental teaching and design comprehensive drilling fluid experiments [15]. In order to further improve the comprehensive experimental skills of undergraduates, to understand the performance differences of different surfactants, and to practically understand the working principles and evaluation methods of drainage and gas recovery, a comprehensive experiment using foam agent evaluation was designed.

2. Experimental Purpose

(1) Understand the theoretical knowledge related to natural gas well drainage and gas recovery, and to understand the mechanism of foam generation and stabilization through literature research;

(2) Master the use of the main instruments such as surface tension meter, digital high-speed mixer, and Ross-Miles;

(3) Understand the conditions of use of different types of surfactants as foam agents;

(4) Learn to analyze the causes of the changes in the performance of surfactants as foam agents by means of experimental data and data review.

3. Experimental Principle

The foam is a system in which many bubbles are separated by liquids and is a dispersion system. Foam is a dispersed system of gas dispersed into the liquid, the gas is the dispersed phase (discontinuous phase), and the liquid is the dispersed medium (continuous phase). Because of the difference in density between the gas and the liquid, bubbles in the liquid can always quickly rise to the surface, and form a bubble polymer with a liquid film consisting of a small amount of liquids separating the gas, which is commonly referred to as foam. Foam formation in pure water is very difficult, and even if formed, it will immediately break. The process of bubbles in pure water is shown in Figure 2.

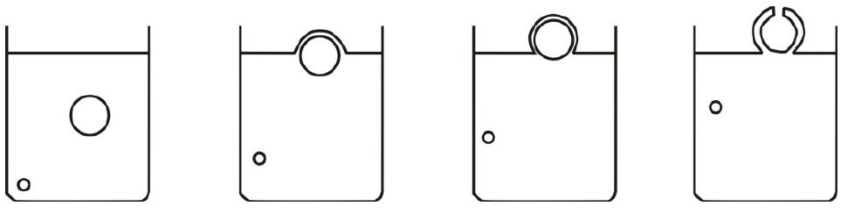


Figure 2. Diagram of the Rising Process of Bubble in Pure Water

In thermodynamics, foams are defined as unstable. To make the foam more stable, the conditions of foam formation must be changed, for example, surfactants can be added. The process of foam generation in foam agents is shown in Figure 3.

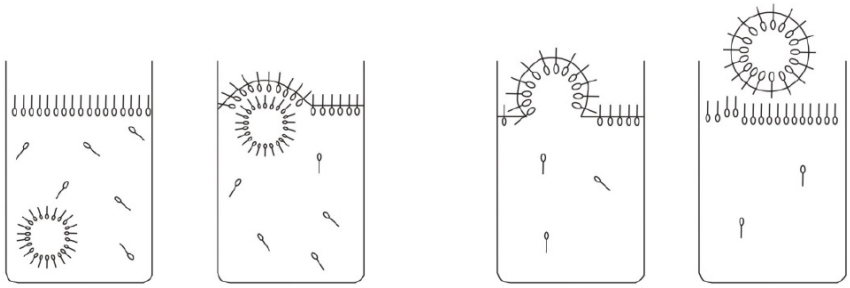


Figure 3. Diagram of the Rising Process of Bubble in Surfactant Solution

3.1 Foam generation mechanism

Gas-liquid contact with each other is a condition for foam generation, and another necessary condition is to pass the gas into the solution so that foam is generated. Foam rupture occurs throughout the foam generation process, but the addition of surfactant makes the foam generation rate greater than the foam rupture rate, thus obtaining the stable foam. The surfactant molecule is not only hydrophilic but also lipophilic, which is called amphiphilic, that is, the hydrophobic group of the foam agent molecule extends inward into the bubble, while the hydrophilic group inserts outward into the liquid solution, forming a unique directionally arranged single molecule film on the surface of the bubble. As the bubble will keep rising to reveal the liquid surface and contact with air, the surfactant molecules will be oriented on both the inner and outer sides of the liquid film, and form a bubble with a certain thickness of both inner and outer bimolecular liquid film. Surfactants can also substantially reduce the surface tension of water, and the lower the surface tension, the easier it is to generate foam in solutions. The foaming performance of surfactants is influenced by the molecular

structure, type, concentration, temperature, mineralization, and condensate of surfactants. When the concentration of surfactant solution is less than the critical micelle concentration, the increase of its concentration makes more and more surfactant molecules arranged on the liquid film and more and more regular, so that the surface tension of liquid and the surface energy of the system is getting lower and lower, and the amount of foam generated will increase until the concentration of the foam agent reaches the critical value.

3.2 Foam decay mechanism

It is generally accepted that the foam decay mechanism is: (1) Loss of fluid in the foam, (2) Diffusion of gas through the liquid film. Both are directly related to the nature of the foam and the interaction between the liquid film and the Plateau boundary [15].

3.2.1 Drainage of liquid

The loss of liquid in the foam is caused by the mutual squeezing of bubbles and gravity. The squeezing of the bubbles mainly originates from the surface pressure. Figure 4 represents the junction of the liquid film of the three bubbles, which is the so-called Plateau boundary. According to the Laplace equation, it is not difficult to derive:

$$P_A - P_B = \frac{\delta}{R}$$

Where: PA is the liquid pressure at A in Figure 4;

PB is the liquid pressure at B in Figure 4;

R is the radius of the three gases (assuming the foaming size is the same);

δ is the surface tension.

The equation shows that the liquid pressure at A is less than that at B. Under this pressure difference, the liquid in the foam automatically flows from B to A and makes the liquid film thinner, which eventually leads to rupture. From the surface pressure, when the angle between the films is 120°, the pressure difference between B and A is the smallest, and the foam is the most stable, so the foam is mostly hexagonal.

Another drainage process is due to the thinning of the film by gravity, but it only has a significant effect when the film is thick.

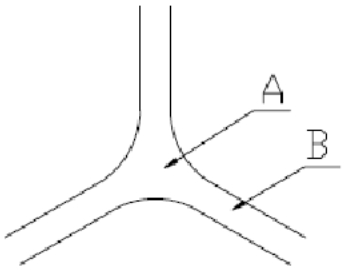


Figure 4. Boundary of the Foam Liquid Film Plateau

3.2.2 Gas diffusion through liquid film

No matter what method is used to produce the bubble, its size is always uneven. According to Laplace's equation, the gas pressure inside the small bubble is higher than that of the large bubble, so the gas inside the small bubble will diffuse into the large bubble through the liquid film, which causes the small bubble to become smaller and the large bubble to become larger, and eventually both tend to burst.

De Vries has studied the diffusion process of gas in foam in detail and found that when small bubbles are surrounded by large bubbles, the square of the radius of small bubbles decreases linearly with time; the total number of bubbles decreases with the increase of the inverse of the square of time. This inhomogeneous phenomenon of bubbles is similar to the aging of suspensions, and the driving

force of the process of material transfer from smaller to larger volumes is the reduction of surface energy of the material. Thus, the bubble growth law is proposed as follows:

$$\frac{dr_i}{dt} = K\left[\frac{1}{r_{21}} - \frac{1}{r_i}\right]$$

Where: ri is the radius of the bubble i;

t refers to the time;

r21 is the instantaneous average radius (bubbles with ri greater than r21 will grow larger and those with ri less than r21 will become smaller)

K is the set of various parameters suitable for the transfer of substances.

4. Experimental Procedure

4.1 Instruments and reagents

GJ-3S high-speed mixer, Qingdao Haitongda Special Instrument Co., Ltd.; 2151 Ross-Miles, Shanghai Longtuo Instrument Co., Ltd.; lauryl sodium sulfate, analytical reagent, Shanghai Keda Reagent Co., Ltd.; cetyl trimethyl ammonium chloride, analytical reagent, Chengdu Kelong Chemical Reagent Factory; nonylphenol polyoxyethylene ether, analytical reagent, Chengdu Kelong Chemical Reagent Factory; octadecyl betaine, analytical reagent, Tianjin Hedong District Hongyan Reagent Factory; sodium chloride, analytical reagent, Tianjin Kemiou Chemical Reagent Co., Ltd.; anhydrous calcium chloride, analytical reagent, Chengdu Kelong Chemical Reagent Factory; anhydrous methanol, analytical reagent, Linyi Zhongtong Technology Co., Ltd.

4.2 Evaluation of surface tension of different surfactant solutions

4.2.1. Preparation of sample solutions

0.0001%, 0.001%, 0.01%, 0.03%, 0.05%, 0.1%, 0.3%, 0.5% (mass fraction) of surfactant solutions were prepared with distilled water, and the surface tension of different surfactant solutions was determined using the Du Nouy Ring method.

4.2.2. Determination of surface tension

(1) Turn on the instrument: turn on the power of the surface tension meter and press the "On/Off" button to warm up for 30 minutes.

(2) In the first use or after using a period of time, perform a full range calibration of the surface tension meter:

a. Hang the hook and platinum plate;

b. Press the "Tare" button, the instrument can display "0.0";

c. Press the "Calibration" button, "CAL" will be displayed, and the standard code of 400mN (or 200mN) will be attached;

d."400.0" (or "0.00") mN will be displayed after about 5 seconds, and the calibration will be completed when the "beep" sound is heard.

(3) Remove the cleaned platinum plate with tweezers. Burn the platinum plate with an alcohol lamp, generally at an angle of 45 degrees to the horizontal, until the platinum plate becomes red, with 20-30 seconds. Hang the platinum plate and cover the lid of the alcohol lamp.

(4) Hang the burned platinum plate on the hook and press the "Tare" button, the instrument can display zero.

(5) Add the surfactant solution to be measured in the sample pan and place the sample to be measured on the sample table. Be sure to visually check the height of the platinum plate before placing it, and press the "Down" button to lower the sample table if it may submerge the sample.

(6) After the sample is placed, start timing for five minutes to read a value, and then press the "Down" button to lower the sample table, separate the platinum plate from the measured sample, and then press the "Up" button to repeat the operation twice each for five minutes to take the value. Then

add up the three values read to get the average value, and the average value is the surface tension of surfactant solution.

(7) Use tweezers to pick up the platinum plate, and rinse with running water, pay attention to keep a certain angle with the water flow, try to let the water flow to clean the surface of the platinum plate and not let the water flow make the platinum plate deformation; then dry the surface of the plate with alcohol lamp hanging on the hook, cover the lid of the alcohol lamp, close the door.

4.2.3 Creation of surface tension-mass concentration curve

Based on the prepared surfactant concentration and the corresponding surface tension, a surface tension-concentration curve is created in Origin 8.5. The critical micelle concentration and the minimum surface tension can be obtained in the figure.

4.3 Evaluation of foaming ability of different surfactant solutions

A series of surfactant solutions with concentration (mass fraction) gradients of 0.02%, 0.04%, 0.06%, 0.08%, 0.1%, 0.2%, 0.3%, 0.4% and 0.5% were configured with distilled water before and after the critical micelle concentration of the surfactant solutions, and the optimal foaming concentrations of different surfactant solutions were determined by the stirring method. The volume of the solution was 100 mL, the stirring time was 7000r/min, and the stirring time was 3min. The foam formed by high-speed stirring was poured into a 500mL measuring cylinder immediately when the stirring stopped and started timing with a stopwatch, and the starting volume of the foam reached in the cylinder and the half-life period of the foam (time to precipitate 50mL of water) were recorded.

4.3.1 Evaluation of foaming ability of surfactant solutions at different temperatures

Prepare a certain concentration of solution with distilled water (the concentration is the best for testing by stirring method) and place it in a water bath at 30±0.5℃ to be used, inject the configured sample solution slowly along the inner wall of the burette to 200mL with a syringe, avoid the formation of foam on the surface of the sample, and measure the foam height at 30℃, 40℃, 50℃, 60℃ and 70℃ for 5min, 10 min, 15min and 20min to record the foam height.

4.3.1.1 Diagram of Ross-Miles

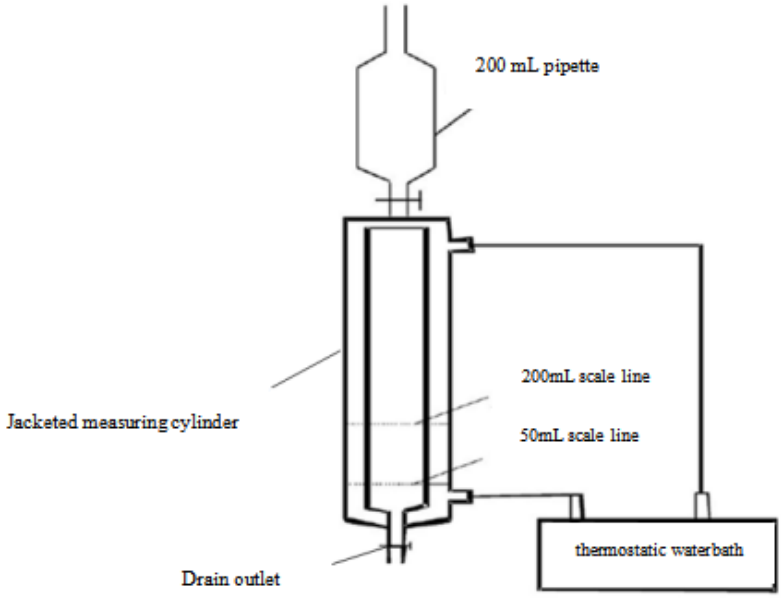


Figure 5. Diagram of Ross-Miles

4.3.1.2 How to use Ross-Miles

(1) Turn on the thermostat, turn on the pump when the thermostat reaches a certain temperature, keep the temperature of the water bath of the graduated tube, and make it stable at 30±0.5℃.

(2) Completely rinse the inner wall of the graduated tube with distilled water, and then rinse the wall of the tube with test solution, which must also be completely rinsed.

(3) Close the piston of the graduated tube, use another dropping pipette to inject 50mL of test solution to the 50mL scale, and then fill the dropping pipette with 200mL of test solution.

(4) Place the dropping pipette on the holder and the cross section of the graduated tube into a vertical shape, so that the sample solution flows to the center of the graduated tube, and the outlet of the dropping pipette should be placed on the 900mm scale.

(5) Open the piston of the graduated tube and let the sample solution flow down. When the sample solution in the dropping pipette flows out, immediately turn on the stopwatch for timing and measure the foam height, and then record the foam height after 5min, 10min, 15min and 20min.

(6) Repeat the above experiment twice to three times, and the wall of the Ross-Miles must be cleaned before each experiment.

5. Data Processing

The experimental data in Experiment 3.2 were recorded to derive the critical micelle concentration and minimum surface tension for different surfactant solutions. A series of surfactant solutions with concentration gradients were prepared before and after the critical micelle concentrations, and the stirring method was used to determine the optimal foaming concentrations. At the optimal foaming concentration, the foam heights at different temperatures were determined using the Ross-Miles, and the effects of different temperatures on the foaming ability of different surfactant solutions and the reasons for these effects were analyzed.

6. Questions

(1) Why is it necessary to evaluate the foaming performance and foam stabilization performance of surfactants? What factors are related to foaming performance and foam stabilization performance respectively?

(2) What factors may cause errors in the determination of surface tension during the experiment and why?

(3) What have the students learned from this experiment?

7. Conclusion

The design of this experiment mainly uses the knowledge of surface and colloid chemistry and oilfield chemistry to further evaluate the surface tension, foaming ability and foam stabilization ability of different foam agents by mastering the use of digital display high-speed mixer and Ross-Miles with cationic, anionic, nonionic and amphoteric surfactants as foam agents respectively. Students can fully grasp the methods of evaluating the performance of the foam agent in the process of experiment, which is helpful for students to understand the specific application of foam agents in the process of gas extraction, and lay a foundation for the work after graduation. By reviewing the Chinese and foreign literature, students can deepen their understanding of the background of foam agent study, and also improve their ability to analyze and solve problems. The experimental design is close to the site of gas field extraction and is rich in content, which requires students to collaborate with each other, and is conducive to enhancing students' collaboration ability and team spirit.

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