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Comprehensive Experimental Design for Evaluation of Surfactants Used in Oilfield

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Abstract: The performance evaluation experiment of common surfactants in oil field is designed, and the evaluation principle used in the evaluation process is discussed. The Krafft point, surface tension, interfacial tension, foaming property and emulsification ability of surfactants were evaluated. The experimental content can be closely combined with the basic theory knowledge of applied chemistry in oil field, and can be applied to field practice. It is helpful for students to deepen their understanding of surfactants, and to obtain the comprehensive training of related experimental skills and the cultivation of analytical ability and innovative ability.

1. Introduction

No matter what kind of surfactants, their molecular structure is composed of two parts, namely, hydrophilic polar group and hydrophobic non-polar group (Fig. 1), sometimes also known as hydrophobic group or vividly called hydrophilic head. This unique structure of surfactants is usually called "amphiphilic structure", surfactants molecules are therefore also called "parental molecules". Based on this special structure, surfactants are widely used in petroleum [1], textile, pesticide, mining, food, civil washing and other fields, with wetting, emulsification, washing, foaming, dispersion, coagulation, sterilization and other important functions [2]. At the same time, surfactants are widely used in petroleum exploitation, transportation and processing. Therefore, it is of great significance to cultivate the students of oilfield chemistry to grasp the evaluation methods of surfactants' properties used in oilfield [3].

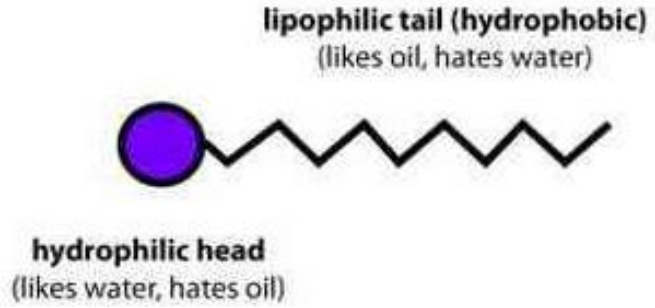

Fig.1 The structure of surfactant

2. Design of the Experiment

2.1. Purpose

(1) Understand a method for the determination of the surfactants Krafft point.

(2) Master the principle and method of measuring the surface tension of the surfactant and the principle and method of calculating the critical micelle concentration (cmc) by surface tension.

(3) Master the principle and method of measuring the interfacial tension between surfactants solution and diesel oil.

(4) Master the use method of high speed agitator and be used to determine the foaming performance of surfactants.

(5) Learn to observe the emulsification of surfactant solution mixed with crude oil.

2.2. Principle

When the oil well goes through some operations, it may lead to the decrease of reservoir permeability, the result is that it is difficult to produce oil and the fracturing cost is increased. This phenomenon is called reservoir damage. Surfactants can effectively prevent the damage that may be caused to oil wells in the construction stage [4]. At the same time, in the course of the exploitation, the gas well will produce a bottom hole, which can cause the production of the gas well to be reduced or even cut off, and the surfactant can discharge the bottom hole by foaming, and the surfactant is also called a foaming agent [5]. Due to the variety of surface activity, its classification is widely accepted according to the dissociation properties of polar groups. According to this classification, surfactants can be divided into four types: anionic type, cationic type, z-ionic type and non-ionic type. All the surfactants have a current property of aggregation to small micelle under above a certain concentration (as shown in Fig. 2), which is named as critical micelle concentration (cmc). Different types of surfactants have different effects and effects, therefore, it is very important to select suitable surfactants to treat the hazard of oil layer and gas well accumulation [6].

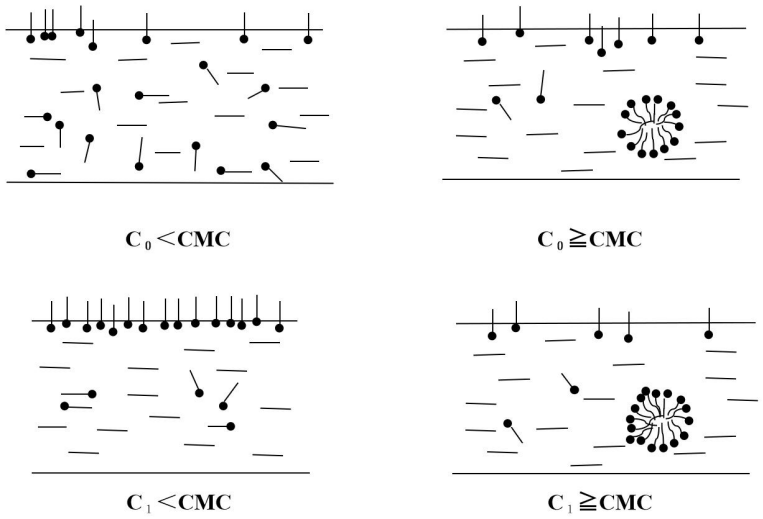

Fig. 2 The aggregation state of surfactants under different concentration

2.3. Materials and Instruments

Sodium lauryl sulfate(SDS) was purchased from China Pharmaceutical Group Chemical Reagent Co., Ltd., cetyl trimethyl ammonium chloride (CTAC) was purchased from Tianjin Jindong Tianzheng Fine Chemical Reagent Factory, cetyl betaine (CTBT) was purchased from the market and used without further purification. Table 1 shows the main instruments, and the surface tension measurement and Du Nuoy ring tensiometer were shown in Fig.3.

Table 1 The main instruments of the experiment

Instrument	Instrument model
electronic balance	TP-520H
surface tension instrument	QBZY
digital display high-frequency stirrer	GJ-3S
interfacial tension instrument	XZD5
water-bath	DK-97-IIA

Fig. 3 Surface tension measurement (left) and Du Nuoy ring tensiometer (right)

3. Methods

3.1. Krafft Point

Weighing a certain amount of SDS CTAC, CTBT, respectively, prepared into 1% aqueous solution, poured into a large test tube, heated and stirred in a water bath. After the solution was transparent and clarified, the cold water bath stirred down the temperature until there were crystals precipitated in the solution, repeated several times, and recorded the temperature.

3.2. Surface Tension

The mass fraction is 0.0001%, 0.001%, 0.01%, 0.03%, 0.05%, 0.1%, 0.3%, 0.5% of SDS, CTAC and CTBT. They are used to measure the surface tension, respectively. The surface tension of distilled water was measured by platinum sheet method and the instrument was calibrated. Then the surface tension of the solution was measured from low concentration to high concentration. The surface tension-concentration curve is made, and the inflection point is cmc value. If you want to measure the value accurately, it can be realized by adding a few measuring points at the inflection point. The average value of each point is determined three times. The steps for determining the surface tension of surfactants solution by platinum sheet method are as follows:

(1) Place the instrument in a place free from vibration and stability, adjust the screws below the instrument and adjust the instrument to a horizontal state. Wash platinum tablets and glassware with distilled water and dry them. Platinum chips and platinum wires should be very smooth and should not be touched by hand after washing.

(2) Start up and warm up for 30min.

(3) Click the "ON/OFF" button to open the display screen.

(4) Add a certain amount of distilled water into the glassware used for testing, hang the platinum sheet, close the instrument door, and prevent the external environment from affecting the platinum sheet, resulting in inaccurate data.

(5) After the platinum sheet is stable, click the "Tare" button, and the display screen interface is in "0.00".

(6) Click the "up" button, and the lifting platform rises gradually. When the platinum sheet is in contact with the liquid level, click the "stop" button and record the data after the reading is stable. The surface tension of distilled water is 72 mN/m. If the measured data deviate from 72mN/m, the platinum sheet needs to be re-cleaned and then treated at high temperature on the alcohol lamp in order to completely remove the impurities on the platinum sheet. Repeat step (6) until the surface tension of distilled water is about 72 mN/m.

(7) After the instrument is calibrated, the sample is measured, the glassware is wetted with the solution mentioned above two to three times, and the surface tension of the solution is measured by repeated step (6), and the data are recorded.

(8) After the determination of surface tension, clean platinum sheets and glassware and put them back where they were.

(9) After the surface tension measurement is over, press the "ON/OFF" button.

3.3. Interfacial Tension

The mass fraction of the surfactants solution was 0.0001%, 0.001%, 0.01%, 0.03%, 0.05%, 0.1%, 0.3%, and 0.5%, respectively. (the concentration of the solution can be adjusted according to the measured results). The steps for determining the interfacial tension of surfactants solution by interfacial tension instrument are as follows:

(1) Turn on the power supply of the instrument, open the instrument, and adjust the temperature to 60℃(the instrument needs to be preheated for about 30min before use).

(2) The glass centrifuge tubes used in the experiment were pre-treated. washing with non-polar organic solvent, washing with distilled water, and washing with surfactant solution sample to be tested.

(3) After preheating, the sample is injected according to the use method of XZD5- rotating droplet interface tension instrument.

(4) The centrifugal tube is loaded into the rotating shaft of the instrument, the compression cap is tightened, and the speed control is started.

(5) Adjusting the rotating speed, observing the change of oil droplets and adjusting the instrument, so that the oil droplets are basically in the middle position of the centrifugal tube, and when the ratio of length to width is greater than or equal to 4, recorded data.

(6) After completing the experiment, decelerate step by step, after the instrument stops automatically, take out the centrifugal tube, and clean in the same step (3).

(7) The interfacial tension of each surfactants at different concentrations was measured according to (1)-(7) steps.

3.4. Foaming Ability of Surfactants

(1) The mass fraction was 0.02%, 0.04%, 0.06%, 0.08%, 0.1%, 0.2%, 0.3%, 0.4%, 0.5% and they were used to measure the foaming ability.

(2) Adjust the speed control knob to the display to be 700, adjust the time knob and display the display screen as 180s.

(3) Pour the sample into the liquid cup and pack it. Press the speed control knob, the "run" indicator light is on and the instrument starts to work.

(4) After the stirring stops, the foam in the liquid cup is poured into the 500ml measuring tube immediately and the foam volume is recorded with a stopwatch when the first drop of foam falls.

(5) The half-life time $t_{1/2}$ of the foam is recorded when the volume of the liquid from the bottom of the measuring cylinder is 50 ml.

3.5. Emulsifying Ability of Surfactants

(1) Preparation of a series of concentrations of SDS, CTAC, CTBT, the prepared aqueous solution and crude oil were mixed in 25ml plug cylinder at 1:1.

(2) Place the measuring tube in a constant temperature water bath pot at 60 ℃ for 30 min, then shake it up and down for five times, then put it back in the water bath pot for one minute and repeat it five times.

(3) The treated samples were placed in a constant temperature water bath at 60 ℃. The volume of water in the oil-water mixture system was recorded with a stopwatch until the oil-water system was stable and the water evolution rate was calculated.

4. Data Processing

When the speed R is large enough, the drop can be regarded as a cylinder with two semicircular bases. The diameter of the vertical direction after a stretching is D/mm, the maximum length in the horizontal direction is L/mm (when L/D =4, the test is considered successful and the data is meaningful), and the data is recorded. The calculation formula for interfacial tension is as follows:

$$\gamma=1.223\times10^{3}\times(\rho_A-\rho_B)\times(K\times D)^{3}\times(60000/R)^{-2}$$

In formula:
K-amplification factor, 0.24;
D-droplet diameter, mm;
R-instrument rotational speed, r/min;
ρ_A, ρ_B-liquid A, B density.

5. Questions and Exercises

(1) Why is the Krafft point present in the ionic surfactant? How should these features be considered in practical applications?

(2) What are the basic conditions of emulsifying crude oil with surfactants and through what principle does emulsification improve formation recovery?

(3) What is the range of the ultra-low oil-water interface tension of the surfactant and the crude oil, what kind of principle is used as improving the recovery of the formation crude oil through reducing the interfacial tension?

6. Conclusion

This experiment is simple and involves a wide range of knowledge. It is necessary for students to master the use of the instruments used in the evaluation of surfactants and some commonly used evaluation indexes of surfactants. The students should master the calculation method of surface tension, cmc value, interfacial tension and water evolution rate. At the same time, there is a need for a comprehensive understanding of some basic evaluation principles. The experiment also trained the students' ability to follow-up analysis of the data. In the course of consulting and completing the experiment, the students must have a certain ability to analyze the problems and solve the problems, so as to promote the students' innovative consciousness and improve the scientific research potential. This experiment is comprehensive and multi-content, and needs to be completed by several students, which can improve the cooperative ability and mutual communication and learning ability of students.

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