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Standards for Selection of Surfactant Compositions used in Completion and Stimulation Fluids

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ABSTRACT

The growing need of the population for energy and hydrocarbon fuel, leads to an accelerated pace of development of the oil industry. In this regard, there is a need to develop new or renew the development of old oil fields. Among a range of existing EOR methods, the use of surfactants is considered as one of the main options aimed for both raising oil production and improving oil recovery. In this work, a study was carried out to define the characteristics and criteria for selection of an effective surfactants which are used in the tertiary scheme of recovery (IOR or EOR) from reservoir formations and especually during Enhanced Oil Recovery (EOR) flooding system. Three cationic surfactants with specific trade names were used in this study. It has been revealed that addition of surfactants positively affects inhibition of clay issues even in a more efficient manner than potassium chloride as one of the most widespread used clay inhibitors. At the end, a comprehensive discussion and suggestions are provided on the importance of temperature, concentration and bottom-hole conditions that affect selection of an optimum surfactant.

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1. INTRODUCTION

Surfactants, well-known substances are used to reduce surface tension on liquid and solid interfaces, are mainly consist of non-polar and polar components. They are widely used in industrial processes, especially, to increase oil recovery factor from depleted reservoir rocks. They own a specific capability to reduce interfacial tension at the "oil-water" interface that is crucial for increasing the efficiency of residual oil displacement [1, 2].

Surfactants have hyrophobic and hydrophilic properties that provide the capability to bind in water and aggregate at the boundary of immiscible phases. The former property belongs to a range of compositional characteristics, such as presence of long-chain hydrocarbon, fluorocarbon, siloxane or short polymer chain [3, 4]. Hydrophilic groups have been classified into anionic (nonpolar lipophilic), cationic (polar hydrophilic), nonionic and zwitterionic (amphoteric) surfactants by Green and Willhite [5].

Polymer flooding by addition of surfactants, as one of the main subgroups of chemical flooding methods, is an effective method of enhanced oil recovery (EOR), which can be applied with a high level of efficiency in both carbonate and terrigenous reservoirs.

Previous review work have identified main criteria according to which a surfactant can be considered effective including capability to:
- dissolve in formation water
- reduce interfacial tension at the oil-water interface
- minimal adsorption
- maintain activity when in contact with fluids
- prevent inhibition of clayey rocks as a part of reservoir
- economically accessible and environmentally safe.

Nonionic surfactants that meet all the above criteria are widely used in the field practice of waterflooding of reservoirs by surface-active substances. Besides using surfactants in waterflooding, they have an impact on rheological and filtration characteristics of process fluids during primary and secondary recovery. Also, the use of surfactants during drilling process is recommmended to

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reduce the negative impact of fluid filtrate on permeability of the drilled interval, reduce the hardness of rocks, increase the lubricating properties and prevent clay mud thickening, as well as to emulsify oil and aerate the drilling fluids.

First of all, it is necessary for a surfactant-based mud to have an effect on reservoir rock wetting and to have oil-washing properties. In order to fulfill these conditions the surfactant must take part in dispersion of heterogeneous systems, in the processes of formation or separation of hydrophobic films and have stabilizing properties [6]. To assess these properties it is necessary to take into account the following physico-chemical parameters, such as, change in surface tension, critical concentration of micelle formation and the value of the boundary wetting angle.

Rock wettability controls the movement of fluids in the porous medium during drilling and production stages [6, 7]. For example, hydrophilic rock has low relative permeability to water, and oil cannot be extracted efficiently from hydrophobic skeleton of a porous medium. Thus, a change in the surface wettability of rocks by drilling fluid filtrate during drilling can have a positive or negative effect on reservoir recovery at least in near-wellbore region.

Note that sometimes surfactants become more hydrophobic due to shielding of electrostatic repulsion between the end groups (heads) of surfactants by dissolved electrolytes [8].

Mud invasion can also activate smectite/illite clays and cause further permeability reduction and formation damage. The process of changing wettability is more common at carbonate reservoirs where change of wettability towards more "water-wet" means reduction in the residual oil saturation and increasing water absorption.

It has been suggested that cationic surfactants work efficiently for the case of clay-rich terrigenous reservoirs in which carry negative surface charges [9]. In models of relative permeability and capillary pressure as a result of changes in wettability were proposed and the effects of different mechanisms in oil recovery associated with surfactants are compaired as well. In particular, the effect of changes in wettability and reduction of the wetting angle were compared. Numerical simulation results showed that change in wettability plays an important role when the marginal angle is high, and it is effective in early times. The marginal angle plays a very important role with or without the change in wettability and is effective throughout the EOR process.

It is important to have a precise study for optimization of the concentration of surfactant that specially affect the critical concentration in surfactant micelle formation (CCM) in which significantly decreases with the addition of salt [10].

Determination of inhibitory capacity is also important. Clays are negatively charged aluminosilicates, blocks of which are weakly held together by electrostatic forces of attraction due to cations (Na^+, Ca^{2+}, Mg^{2+}, K^+) [11].

When clays come into contact with water, water molecules are adsorbed on positively charged cations by weak forces (i.e. Van der Waals forces) [12, 13]. The surface of the shale minerals becomes hydrophilic, and the incoming water molecules begin to disturb the internal structure of the shale environment. When the clay particles are finally dispersed in the aqueous phase, electrostatic interaction leads to the formation of a double layer [14, 15].

In addition to the electrostatic forces between water molecules and cations, osmotic swelling promotes the penetration of freely moving water molecules into the clay pores, depending on the concentration gradient [16]. All of these processes lead to the initiation of the swelling process. For this purpose, it is necessary to conduct a test for linear swelling of the clay material.

2. METHODOLOGY AND MATERIALS

To determine surface wettability, edge angle measurements are made using the Kruss droplet shape analyzer shown in Figure 1. The wetting angle is a parameter that determines the wettability of a solid surface with water or another liquid.The wetting angle is influenced by adhesion and cohesion. The ratio of the two determines the shape of the droplet and the extent to which it spreads over the solid. A distinction is made between hydrophilic and hydrophobic surfaces depending on the value of the wetting angle.

If the wetting angle is less than 90°, the surface is called hydrophilic. Liquids will spread widely over such a surface. And angles up to 60° can be called superhydrophilic, where water spreads completely over the surface. The presence of a certain amount of

Figure 1. Device for measuring the edge angle of wetting Easydrop (compiled by the authors)

surfactant in the process liquid can change the value of the wetting angle from a hydrophilic to a hydrophobic.

During this study, according to the experience and knowledge described above, two basic instruments were used to select the optimum surfactant for the process liquids including:

1. EasyDrop DSA 100 tensiometer
2. An instrument for measuring the linear swelling of clays.

In order to investigate the effectiveness of non-inogenic surfactants, five samples of each surfactant were prepared in 0.05, 0.1, 0.25, 0.5 and 1 wt% concentrations. Next, the study was carried out on a tensiometer, the principle of which is schematically shown in Figure 2 [17]. First, the effect of surfactant on wettability was evaluated, the study was conducted as follows:

1. The sample under study was drawn into a syringe.
2. After the syringe is inserted, the needle is dipped into the cuvette, where the medium is isooctane.
3. The scale was set through the software so that the outline of the drop at the bottom of the cuvette was clearly visible.
4. The wetting angle is automatically calculated for the lying droplet.
5. Three measurements are taken in order to get a more accurate value.

After 3 measurements have been made, the cuvette should be washed and dried and degreased with isopropyl alcohol to prevent deliberately false readings. While the wetting-angle cuvette is being prepared, a new isooctane cuvette is placed on the moving stage. The interfacial tension is then measured:

1. The interfacial tension measurement is performed on a hanging drop, so a program change is necessary.
2. The needle is not lowered to the bottom of the cuvette, as space is needed for the hanging drop.
3. Video recording starts automatically when the drops are squeezed out.
4. The values calculated directly before the drop is detached from the syringe are recorded.
5. Three measurements are taken in order to get a more accurate value. Avarge values were reported. In this way a total of at least 6 measurements were performed for each sample. It is possible to take more measurements to reduce the error, but less is not recommended.

After conducting a tensiometer study, there is data on how effectively surfactants reduce interfacial tension and change the wettability of the fluid. Since these reagents will be used in drilling fluids, it is necessary to evaluate their effectiveness in the composition of the process fluid on the rock. For this purpose, an instrument for measuring linear swelling of clays LSM 2100 is used (Figure 3). The study is carried out as follows:

1. On the compactor tablets are made - compressed rock, in the form of a cylinder.
2. This tablet is installed in a container under the measuring device.
3. We carried out calibration, according to instructions LSM 2100.
4. The test liquid is poured into the container.
5. The study was carried out from 6 to 48 hours, depending on the regulations.
6. After a certain time, the program stops the test.
7. The meters are lifted and the tablets are taken out for visual analysis.

Thus, at the end of the test there are the following data: csv file with the measurements of the device, a graph of swelling over time: the change in percentage and absolute value. On the basis of visual inspection it is possible to estimate the depth of penetration of liquid, to see violation of tablet integrity, if the liquid contained colmatant then there is a possibility to see a filtration crust.

According to the methodology described above, samples of an aqueous surfactant solution in 5 concentrations were prepared first. Next, a minimum of 3 measurements of each sample were taken to reduce

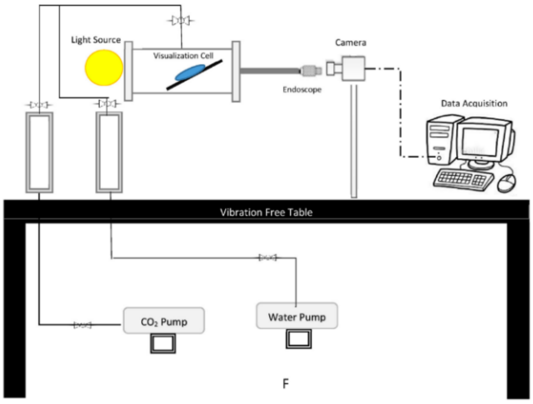


Figure 2. Schematic of the principle of operation of the tensiometer used to measure the wetting angle and surface tension [17]

Figure 3. Linear clay swelling tester LSM 2100 (compiled by the authors)

measurement error. Figure 4 shows examples of lying droplets, from which the edge wetting angle is calculated, and hanging droplets, from which the interfacial tension forces are determined.

Based on the results of the studies, the data obtained is sufficient to make the primary choice of surfactant for the process fluid.

3. RESULTS

After obtaining all the values, it is necessary to calculate the average value of the indicators for each sample [18]. The calculated values of interfacial tension for each surfactant are summarized in a table, and the results of studies on the tensiometer are presented as graphs, for ease of analysis (Figures 5 and 6).

Based on the data obtained, it is possible to assess the effect of each surfactant on the interfacial tension and wetting properties of the liquid [19]. It is known that there is a critical concentration above which it is not practical to introduce surfactants into the system, as it does not affect the change in the properties of the liquid. This concentration can be determined in the graphs. If after adding 0.05 and 0.1% of surfactant there is a sharp decrease in the force of interfacial tension and the angle becomes more obtuse, then at a concentration above 0.5% the effect decreases and the line becomes more straight. Thus, we can say that the optimal surfactant concentration for solutions is 0.25%. The force of interphase tension of distilled water at the boundary with isooctane is 73 mN/m, so it follows from the obtained data that surfactant 2 is the most effective reagent. This is confirmed by the fact that the interfacial tension force at a concentration of 0.05% was reduced almost by 15-fold. The contact angle has also increased up to 105 degrees, which indicates hydrofibbing of the surface by the liquid treated with this surfactant. The process fluid with these values will prevent the negative effect of the fluid on reservoir properties, and during waterflooding will provide an increase in the oil recovery. These effects are achieved because the surfactants in the solution hydrophobize the rock surface and provide a better yield for hydrocarbons [20, 21].

Figure 4. View of lying and hanging droplets from which the edge wetting angle and interfacial tension forces are determined (compiled by the authors)

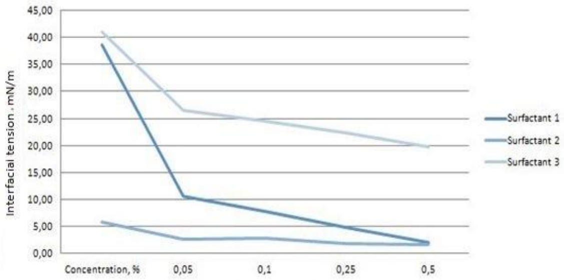


Figure 5. Dependency of interfacial tension on natural logarithm of surfactant concentration (compiled by the authors)

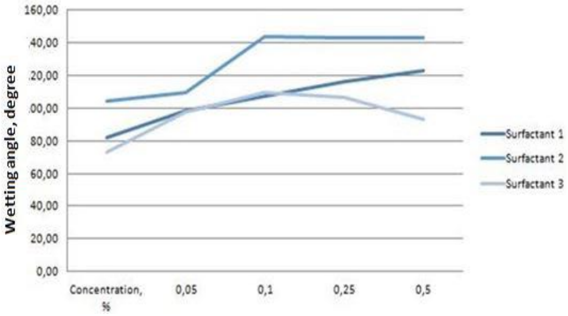
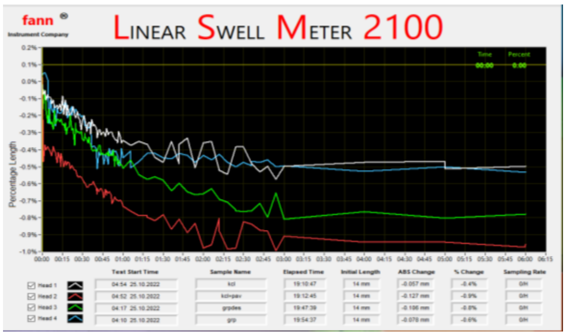


Figure 6. Dependency of boundary wetting angle on natural logarithm of the surfactant (compiled by the authors)

The use of surfactants in process fluids can also ensure the integrity of the rock skeleton. This is achieved due to the fact that the filtrate will penetrate less into the rock, thereby preventing swelling and cracking of the rock mass. It is possible to check this hypothesis thanks to a device for measuring linear swelling of clays LSM 2100. A comparative study was performed with 4 samples: 2% KCl solution and 3 samples with 0.25% surfactant added. The results are shown in Figure 7.



	Test Start Time	Sample Name	Elapsed Time	Initial Length	ABS Change	% Change	Sampling Rate
☑ Head 1	04:54 25.10.2022	kcl	19:10:47	14 mm	-0.057 mm	-0.4%	[illegible]
☑ Head 2	04:52 25.10.2022	kcl+pav	19:12:45	14 mm	-0.127 mm	-0.9%	[illegible]
☑ Head 3	04:17 25.10.2022	grpdes	19:47:39	14 mm	-0.106 mm	-0.8%	[illegible]
☑ Head 4	04:10 25.10.2022	grp	19:54:37	14 mm	-0.078 mm	-0.6%	[illegible]

Figure 7. Results obtained from the clay swelling analyzer (compiled by the authors)

4. CONCLUSIONS

It can be concluded that the addition of surfactants has a positive effect on rock inhibition, and that some are better than potassium chloride, which is the most widely used inhibitor of clay. Taken together, these studies allow us to make an initial selection of surfactants for IOR and EOR. The importance of this study is that the LSM2100 test results and the information on the interaction of the system with the surfactant and the rock are sufficient to recommend the use of the surfactant in EOR. It should be noted that the tests carried out are not fundamental to a decision on the choice of surfactant for drilling conditions. For example, when drilling salt formations, it is necessary to evaluate surfactants in a highly mineralized environment, as it is known that mineralization affects surfactant efficiency and may result in the need to increase surfactant concentration to achieve the required performance. Another important factor is temperature, which affects the value of the critical concentration for micellar formation; hence, the need for refinement studies to determine the need to increase or decrease the surfactant concentration in solution. The use of a scanning electron microscope is a promising tool for the study of surfactants, allowing the behaviour of the surfactant in solution to be assessed, as well as its interaction with other chemical reagents present in the dispersion medium. Overall, the results of our study, based on laboratory tests, show that among the three surfactants used in this work, OLBECK (trade name of a cationic surfactant) at a concentration of 0.25 wt% is the most optimal choice.

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Persian Abstract

چکیده

نیاز روزافزون جمعیت به انرژی و سوخت هیدروکربنی، سرعت توسعه صنعت نفت را تسریع می کند. در این راستا نیاز به توسعه جدید یا تجدید توسعه میادین نفتی قدیمی وجود دارد. در میان طیف وسیعی از روش‌های EOR موجود، استفاده از سورفکتانت‌ها به عنوان یکی از گزینه‌های اصلی برای افزایش تولید نفت و بهبود بازیافت نفت در نظر گرفته می‌شود. در این کار، مطالعه‌ای برای تعریف ویژگی‌ها و معیارهای انتخاب یک سورفکتانت مؤثر که در طرح سوم بازیابی (IOR یا EOR) از سازندهای مخازن و به‌ویژه در سیستم سیل‌آیی بهبود یافته بازیابی نفت (EOR) استفاده می‌شود، انجام گردید. در این مطالعه از سه سورفکتانت کاتیونی با نام تجاری خاص استفاده شد. مشخص شده است که افزودن سورفکتانت ها به طور مثبتی بر مهار مسائل خاک رس حتی به شیوه ای کارآمدتر از کلرید پتاسیم به عنوان یکی از رایج ترین بازدارنده های خاک رس تأثیر می گذارد. در پایان، بحث و پیشنهادات جامعی در مورد اهمیت دما، غلظت و شرایط سوراخ پایین که بر انتخاب یک سورفکتانت بهینه تأثیر می‌گذارد، ارائه شده است.