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INVESTIGATION OF THE SURFACTANT ADSORPTION ON THE	NGHIÊN CỨU QUÁ TRÌNH HẤP THỤ CÁC CHẤT HOẠT ĐỘNG BỀ MẶT CỦA
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DRAGON SOUTH-EASTERN
(DSE) DIORITE QUARTZ
SURFACE

ABSTRACT

The success of surfactant flooding process for enhanced oil recovery depends on: creating low interfacial tension between oil-water phase, changing in rock wettability, minimizing loss of surfactant and thereby increasing the displacement residual oil efficiency.

Surfactants adsorbed onto diorite quartz resulted in reducing the oil recovery. Adsorption is determined mainly by the surfactants structure, rock surface properties, oil composition, reservoir fluids and other conditions such as salinity, pH and temperature. In this paper, the adsorption of varying anionic and nonionic surfactants such as: alkoxyated sulfate, alpha olefin sulfonate and alkylphenol ethoxylate was investigated.

Adsorption experiments were carried out with surfactant solution at concentration of 500ppm and aging temperature of 910C using UV analytical method to measure amount of surfactant adsorbing onto diorite quartz surface.

The testing results indicated

DIORITE THẠCH ANH
THUỘC MỎ RỒNG Ở VÙNG
ĐÔNG NAM BỘ

TÓM TẮT

Sự thành công của phương pháp bơm chất hoạt động bề mặt phụ thuộc vào: việc tạo sức căng bề mặt thấp giữa pha dầu-nước, sự thay đổi khả năng thấm ướt của đá, giảm thiểu tổn hao của chất hoạt động bề mặt và qua đó tăng hiệu suất dịch chuyển của dầu cặn. Các chất hoạt động bề mặt được hấp thụ trên diorite thạch anh dẫn đến giảm hiệu suất thu hồi dầu. Mức độ hấp thụ chủ yếu được xác định qua cấu trúc của chất hoạt động bề mặt, các tính chất của bề mặt đá, thành phần dầu, chất lưu trong vỉa chứa và các điều kiện khác chẳng hạn như độ mặn, độ pH và nhiệt độ. Trong bài báo này, chúng tôi tiến hành nghiên cứu khả năng hấp thụ của các chất hoạt động bề mặt anion (chất hoạt động bề mặt mang điện tích âm) và chất hoạt động bề mặt không mang điện tích khác nhau chẳng hạn như alkoxyated sulfate, alpha olefin sulfonate và alkylphenol ethoxylate. Thí nghiệm về khả năng hấp thụ được tiến hành với dung dịch chất hoạt động bề mặt ở nồng độ 500ppm và nhiệt độ lão hóa 910C dùng phương pháp phân tích UV để đo lượng chất hấp thụ bề mặt trên bề mặt diorite thạch anh.

Kết quả thử nghiệm cho thấy

that the alkylphenol ethoxylate has the highest adsorption; and alkoxylated sulfate is reverse. The sharp reduction of surfactant adsorption was obtained after addition of Ethylene glycol monobutyl ether (EGBE) as a scarified agent into surfactant solution and it can be a remedy to cut down surfactant loss during injection.

Addition of EGBE as a scarified agent, a co surfactant that it is able to keep surfactant molecules from overcrowding the interface, spreading their effect over a larger surface area while, achieving ultra low IFT and adsorption with diluted concentrations.

INTRODUCTION

Among the methods used in the advanced recovery of petroleum are the chemical methods, which the surfactant flooding is a part of. The surfactant flooding seeks to reduce the interfacial tensions between the oil and the water, increasing the displacement efficiency [1,2]. The surfactant flooding is considered a method of additional recovery of oil of reservoirs partially depleted. The mechanism of action of the surfactant in a

rằng alkylphenol ethoxylate có khả năng hấp thụ cao nhất; và alkoxylated sulfate có khả năng hấp thụ thấp nhất. Khi thêm Ethylene glycol monobutyl ether (EGBE) với vai trò là chất khử vào dung dịch chất hoạt động bề mặt thì chúng tôi nhận thấy sự hấp thụ chất hoạt động bề mặt giảm đáng kể và đây có thể là giải pháp để giảm sự tổn hao chất hoạt động bề mặt trong quá trình tiêm (bơm).

Việc thêm EGBE với vai trò là chất khử, chất đồng hoạt động bề mặt có thể giữ cho các phân tử của chất hoạt động bề mặt không tụ tập nhiều ở bề mặt phân cách, mở rộng khả năng ảnh hưởng của chúng trên diện tích bề mặt lớn hơn trong khi đó vẫn đạt được IFT và khả năng hấp thụ cực thấp ở các nồng độ loãng.



porous media, filled partially with oil and brine, is still not very well understood. In water wet systems, for example, the oil in place, after water flooding, consists mainly of isolated oil drops within the pores. In order to mobilize residual oil trapped by capillary forces in oil reservoirs, many enhanced oil recovery (EOR) methods rely on reducing the oil-water interfacial tension (IFT) to extremely low values, often to 10^{-2} dyne/cm or less [3]. Therefore, it is important to keep low interfacial tensions for large periods of time. The complexity of the system increases with the effects of other parameters, such as: heterogeneity of the rock, the charge on the rock surface [4,5], interaction of the surfactants with reservoir fluids, coalescence of the oil drops and surfactant adsorption. The surfactant flooding process, however, encounters problems due to loss of high cost surfactant in the form of adsorption and retention in the porous media.

The adsorption of surfactant solutions on to surfaces of reservoir rock is one of very important factors in EOR because surfactant loss due to adsorption on the reservoir rocks weakens the

effectiveness of the injected chemical slug in reducing oil-water tension (IFT) and makes the process uneconomical.

In this paper, the adsorption of nonionic surfactant (SN1) and three anionic surfactants (AS1, AS2 and AS3) on to DSE diorite quartz surface had been investigated.

EXPERIMENTAL

Chemicals

- NS1: Alkyl Phenol Ethoxylate, 8 -10 Ethoxylate groups(Taiwan);
 - AS1: Anionic surfactant of sulfate family, 4 Propoxylate groups, C14-15 (Sassol,USA);
 - AS2: Anionic surfactant of sulfate family, 3 Ethoxylate groups, C8-12 (Stepan,USA);
 - AS3: Alpha Olefin Sulfonate, C12-16 (Stepan, USA);
 - Brine from DSC oilfield (table 1).
 - Kerosene was used in interfacial tension measurements.
 - Diorite quartz from DSC oilfield (table2).
- ### Equipments
- OCA 20 Tensionmeter, Dataphysis, German;

- Heat and pressure resistant Ampul (Pyrex, USA)
- Oven Heating Shellox(USA).
- UV/VIS spectrophotometer (Jasco,Japan)
- AR60

pH/mV/°C/DO/ISE/Conductivity Meter (Fisher Scientific,USA)

Preparation of DSE diorite quartz sample

The diorite quartz sample from the DSE basement was washed with distilled water, dried at 800C, ground in 30 minutes with 300 rpm spinning speech. To have same size particles, about 80µm, the following procedure was applied: the very fine particles were added to a bottle of double distilled water, settling for 1 hour. The suspension was then shaken vigorously and allowed to settle during 20 seconds. Subsequently the unsettled suspension of fines was removed. Fresh water was added and the procedure was repeated until water above remained clear. The cleaned suspension was then put in a furnace at 400oC in order to dry for 4 hours.

Surfactant adsorption on to diorite quartz

The stock solutions of high



concentration of surfactant were prepared and diluted to obtain the designed concentrations. The sample solutions with concentration range between 50ppm to 500ppm were prepared by diluting 5% surfactant solution with brine. UV absorption indexes obtained for NS1 solution at wavelength 237nm and for AS1, AS2, AS3 solutions at wavelength 224nm. The values were used to construct the calibration curve for testing.

For adsorption experiments, all of samples were diluted at concentration of 500ppm. The tests were conducted with a weight ratio of liquid/solid of 20 in heat and pressure resistant ampoules. The ampoules were corked and gently shaken so that the diorite quartz powder comes into contact with the surfactant solution thoroughly. The solutions were allowed to equilibrate with diorite quartz powder for 48 hours at 91°C subject to gentle periodic shakings. The slurry was then centrifuged at 1200 rpm for 20 minutes to separate the solid particles from the liquid solution. The supernatant was carefully pipetted out to avoid the solid particles. The supernatant was then

centrifuged again for 20 minutes to obtain particle free supernatant. UV spectrometry was used to determine the residual surfactant concentration in the supernatant liquid [6]. The adsorbed surfactant concentration was calculated through the calibration curves.

The above procedure was used for testing SN1, AS1, AS2 and AS3 solutions. These similar tests were conducted with solutions added 250ppm EGBE.

Interfacial Tension Measurement

For this study, the IFT measurement technique should be able to use in a liquid-liquid system at high temperature and high pressure.

Fig. 1 - Definition of dimensions and coordinates describing the sessile drop

The pendant drop method is the best one suited for this study. Commercial software, so called Drop Shape Analysis for IFT calculation, is introduced as figure 1 The drop shape is a function of γ and other parameters and is easily to be measured, as showing in the following Young-Laplace equation:

where γ is IFT, R1 and R2 are the radii of the surface at point

P of height Z, C is the pressure difference across the interphase in $Z = 0$, g is the gravity acceleration, and $\Delta\rho$ is the density difference between the drop and the surrounding fluid [7]. This method was used to measure the IFT of initial and after aging with diorite quartz powdersurfactants

RESULTS ANDDISCUSSION

There are several mechanisms which are responsible for surfactant adsorption. The main mechanisms include: (1) electrostatic interactions, (2) Vander Waal's interactions, (3) non-polar chain-solid interactions, (4) covalent bonding and hydrogen bonding, (5) solvating and desolvating of adsorbate and adsorbent, (6) salt formation at the solid/liquid interface, (7) surfactant precipitation at the solid interface. In petroleum recovery, surfactant adsorption from solution onto solid surfaces most commonly occurs in porous media. This adsorption is also of considerable scientific interest because the surfactant can adsorb as individual molecules or as surfactant aggregates of various types. Ionic surfactants tend to adsorb onto opposite-charged solid surfaces due to electrostatic interactions, most mineral surfaces in aqueous

solution being charged. For example, positive charged cationic surfactant will be attracted to negative charged surfaces, while negative charged anionic surfactants will be attracted to positive charged surfaces. Adsorption of ionic surfactants on a like-charged substrate is less understood, but can occur via hydrogen bonding or attractive dispersion forces.

Figures 3,4,5,6 show calibration curves and their normal equations.

Adsorption of surfactants has been measured on the diorite quartz powders, Figure 7 shows the adsorption densities of NS1 - nonionic surfactant is the highest, about 80 %. This result can be explained as for the non-ionic surfactant, adsorption seems to be physically rather electrostatically or chemisorbed [8]. Beside that, it is different from anionic surfactant in that, just quite small changes in temperature, high salinity of the medium can cause a large effect on the adsorption process. This is due to adsorbate-adsorbate and adsorbate-solvent interactions, which causes surfactant

aggregation in bulk solution and which leads to change in orientation and packing of surfactant at the surface (figure 9). On the other hand, increasing temperature increases the enthalpy of the system. If the adsorption is enthalpy driven as is the case with surfactants with low density of adsorption, then increasing temperature increases the adsorption density.[9].

Conversely, the concentration of the anionic surfactants in the supernatant after adsorption was found to be higher than the initial concentration before adsorption and hence a negative adsorption density (figure 7). This kind of behavior was also observed for some electrolyte concentrations as DSC brine (high salinity, high pH). This causes the surface to acquire negative charge of diorite quartz (SiO^-) and repel the like charged anionic polar head group of the surfactant. It is reasoned that the surfactant molecules were repelled from the interfacial region of the diorite quartz particles and got concentrated in the upper part of the vial, from which supernatant was removed, causing an apparent 'negative adsorption'.

Figure 7 and table 3 show that

the surfactant AS1 has also a negative adsorption. However, Figure 8 displays reverse results, the IFT values of the initial and after aging (with diorite quartz powders) AS1 solutions increase from 1.5 dynes/cm to 6.68 dynes/cm. Obviously that due to high temperature and salinity condition of aging, the hydrolyze reaction has taken place and as a result, a part of sulfate groups has been separated from AS1 molecules and surfactant effectiveness in IFT reduction has sharply decreased.

The addition of EGBE as a co surfactant or a sacrificed agent that it is able to keep surfactant molecules from overcrowding the interface, spreading their effect over a larger strongly surface area while, achieving low IFT and adsorption, reduced a negative effect of high temperature. All it makes surfactant adsorption reduced, especially for NS1 adsorption became 20% less than the initial (Figure 7,8).

CONCLUSIONS

1. In the high temperature and salinity condition of aging process the adsorption of nonionic surfactant (NS1) on to DSE diorite quartz increases,

up to 80%.

2. Anionic propoxylate surfactant AS1 is unstable at high temperature and salinity conditions.

3. Addition of EGBE decreases well adsorption of the surfactant samples, especially of NS1.

4. Anionic ethoxylate AS2 and sulfonate AS3 surfactants are thermo and high salinity stable. They have also low adsorption capacity on to DSE diorite quartz

5. The combining method of interfacial tension and adsorption measurement in this study could help to get a more correct and comprehensive observation of the role of the medium during injecting surfactant solution into reservoirs.

