



Effect of organic alkali on interfacial tensions of surfactant solutions against crude oils



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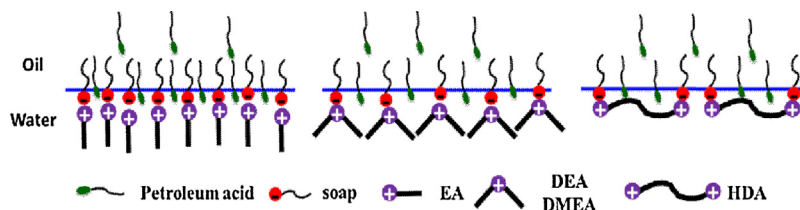
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HIGHLIGHTS

- The ultralow IFTs can be reached at optimum conditions for organic alkaline and crude oil interfaces.
- The content and structure of petroleum acid are important factors to control IFTs.
- The increase of molecular size of organic counter ion will result in the increment of IFT.
- The ultralow IFTs can be easily reached by adding petroleum sulfonate to organic alkaline solutions.

GRAPHICAL ABSTRACT



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ABSTRACT

The dynamic interfacial tensions (IFTs) of petroleum sulfonate and organic alkali combined solutions against crude oils with different acid numbers have been investigated by a spinning-drop interfacial tensiometer. The influences of surfactant concentration, organic structure and concentration on the IFTs were expounded. The experimental results show that the petroleum acids can react with the organic alkalis and produce the surface-active soaps at the interface in situ. Both the ultralow transient and equilibrium IFTs can be reached at optimum conditions. The structures and contents of petroleum acids play important roles in controlling IFTs between the crude oils and the organic alkaline solutions. It is believable that fatty acids contribute to the lower transient IFT in short time and aromatic acids with condensed ring determine the equilibrium IFTs. The crude oil with higher acid number usually shows lower IFT values, however the structures of petroleum acids are more crucial factors and the crude oils with similar acid numbers may behave quite different dynamic IFT behaviors. The concentrations and structures of organic alkalis also strongly affect the IFTs of crude oil–alkaline solution systems. An obvious IFT minimum appears as a function of organic alkali concentration and the increase of molecular size of the organic counterion results in a loosely packed film and an increment of IFT. By adding petroleum sulfonate to organic alkaline solutions, the IFTs may be easily reduced to an ultralow value through the formation of close-packed mixed adsorption film containing surfactant, petroleum acid and soap molecules. For organic alkalis with larger molecular size, the loose mixed adsorption film is beneficial for the synergistic effect among petroleum acids, soaps and surfactant molecules, which can enlarge the applying reservoirs of organic alkali.

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1. Introduction

There are still about two-thirds of the crude oils left in the oil reservoir after primary and secondary oil recovery. Therefore, the technique named tertiary recovery, which mainly employs chemical agents such as alkalis, polymers and surfactants, has been widely applied in oilfields for enhanced oil recovery (EOR). Theoretical and experimental researches show that the residual oil trapped in the reservoir could be displaced by increasing the capillary number, N_c , which determines the microscopic displacement efficiency of oil. One of the most effective ways to improve the N_c value is to reduce the value of interfacial tension (IFT) between the crude oil and the chemical flooding because the N_c value can be improved by several orders of magnitude using surfactants. As a result, the efficiency of oil recovery will increase remarkably if the IFT value is lower than 10^{-2} mN/m (ultralow IFT) [1,2].

It has long been known that the IFT is reduced between an acidic crude oil and an alkaline aqueous phase by the in situ produced soap through chemical reaction between petroleum acid and alkali [3]. A transient ultralow IFT value of crude oil can be easily obtained by adding alkali with adequate concentration [4,5]. Therefore, inorganic alkalis, such as NaOH, NaHCO₃ and Na₂CO₃, had been employed in EOR for several decades. After that, numerous reports involving the mechanisms responsible for the IFT behavior between acidic oil and alkaline solution have been published [6–12].

The IFT value of the crude oil can also be reduced dramatically by the application of an appropriate surfactant. Anionic surfactants (such as petroleum sulfonate and alkyl benzene sulfonate) and nonionic surfactants (such as Triton X-100) have been widely used in EOR due to their high interfacial activity, extensive source and lower cost [13]. However it is difficult to reach ultralow IFT by using surfactant alone. On the other hand, it is more difficult to obtain equilibrium ultralow IFT by alkaline solution alone due to the partitioning of soaps from the interface into the aqueous. Therefore, Reisburg and Doscher firstly combined surfactants with crude oil/alkali systems in 1956 and developed surfactant enhanced alkaline flooding [14]. The researches on interfacial interactions among EOR surfactants, petroleum acids and soaps and the mechanisms responsible for reducing the IFT is not only of great significance in theory but is believed to have good prospect of application [15–21]. Rudin et al. found that a synergism between the added surfactant, ionized acids, and un-ionized acids in forming mixed micelles and a mixed adsorbed interfacial layer at low pH, which results in a large decrease of the IFT; however, the synergistic effect with the acid is totally lost at high pH, since all of the acid is ionized [16]. Argillier et al. investigated the surfactant-enhanced alkaline/diluted heavy oil systems. They found the ultra-low IFT could be eased in the presence of indigenous surfactants contained in a reactive crude oil and imply not only a suitable choice of surfactant type and concentration but also optimization of salinity and pH [21].

Unfortunately, the using of inorganic alkali will bring birth some serious shortcomings, such as scale-buildup and clay swell, and cause irreversible formation damage, which results in the rarely application of inorganic alkali in oilfields nowadays. The organic alkalis have been proposed by Berger to displace inorganic alkali in EOR because the organic alkalis can play the same role in reducing IFT like inorganic without formation damage [22]. Therefore, the application of organic alkali for chemical flooding and the IFT behavior of crude oil–organic alkali systems are drawing more and more attention recently [23–27]. The ultralow IFT values have been reported for EOR surfactant solutions containing some organic alkali at proper concentration. Bai et al. investigated the oil/water IFT of ethanolamine (ETA)/surfactant solution and Gudong oil. The results indicate that the oil/water IFT can be reduced by 2 orders of magnitude, the oil can be emulsified and dispersed more easily [27]. However, the interactions between the organic soaps and

the surfactants in reducing IFT are still not clear, and the effects of organic alkali structure and the property of crude oil on ultralow IFT have not been explored systematically.

In this paper, four organic alkalis with different molecular sizes, four kinds of crude oils with different acidic values and EOR surfactants with high interfacial activity (petroleum sulfonate) were employed to study the interfacial interactions among surfactant, organic alkali and acidic crude oil and to detect the real mechanisms controlling the IFT behavior. Based on our experimental results, the molecular size of organic alkali plays the same important role as pH. Our findings are very important for the design of organic alkali formula of ASP flooding.

2. Materials and methods

2.1. Materials

Organic alkalis ethanolamine (EA), N,N-dimethyl ethanolamine (DMEA), dimethylamine (DMA) and 1,6-hexylenediamine (HDA) were used as the analytical reagent. Four different crude oils, two from Gudong block (GD1# and GD2#) and two from Shengtuo block (ST1# and ST2#), were all collected from Shengli oilfield, China. The properties of four crude oils are listed in Table 1. Petroleum sulfonate (SLPS, R-SO₃Na (R = C₂₃–C₃₁)) with a purity of over 82.0 wt% was provided by Shengli oilfield. NaCl was analytical reagent.

2.2. Interfacial tension measurements

The dynamic interfacial tensions were measured by Texas-500C spinning drop interfacial tensiometer (CNG USA CO.). The surfactant solution as outer phase was injected into the glass tube and about 2 μ L alkanes as an inner phase was put into the middle of the tube. In all case, the measurements of the interfacial tension are at a rotating velocity of 5000 rpm.

When the IFT is not low enough and the length of the oil drop (L , mm) is smaller than 4 times its diameter (D , mm), IFT is calculated according to following equation:

$$\gamma = 2.74156 \times \exp(-3) \frac{(\rho_h - \rho_d)\omega^2}{C} \quad L/D < 4 \quad (1)$$

where ρ_h is the density of heavy (outer) phase (mg L^{-1}), ρ_d is the density of light (drop) phase (mg L^{-1}), ω is the rotational velocity in rpm, and C is a coefficient determined by the ratio of the length to the width of the oil drop.

For low IFT systems, where the length of the oil drop (L) in the spinning tube is greater than 4 times its diameter (D), IFT is calculated with a built-in software system according to the following equation:

$$\gamma = 3.42694 \times 10^{-7} (\rho_h - \rho_d)\omega^2 D^2 L/D \geq 4 \quad (2)$$

The volumetric ratio of water to oil in the spinning drop tensiometer is about 200. Samples were assumed to be equilibrated when measured values of IFT remained unchanged for half an hour. All experiments were performed at 70.0 ± 0.5 °C.

3. Results and discussion

3.1. The effect of organic alkali on dynamic IFTs of SLPS solutions against kerosene

The applications of surfactants for EOR were mainly based on their strong ability to adsorb onto interface and reduce the IFT values between the crude oils and the chemical flooding. The dissimilarity between the oil side and the water side of the interface will be weakened when surfactant molecules adsorb at the interface. To reach an ultralow IFT (10^{-3} mN/m) means that the nature

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