Influence of Polymer on Dynamic Interfacial Tensions of EOR Surfactant Solutions

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ABSTRACT: The effects of different types of polymers, partially hydrolyzed polyacrylamide (HPAM) and hydrophobically modified polyacrylamide (HMPAM), on dynamic interfacial tensions (IFTs) of surfactant/model oil systems have been investigated by the spinning drop method in this article. Two anionic surfactants, 1,2-dihexyl-4-propylbenzene sulfonate (366), 1,4-dibutyl-2-nonylbenzene sulfonate (494) and an anionic–nonionic surfactant octyl-[ω-alkyloxy-poly(oxyethylene)]yl-benzene sulfonates (828) with high purity were selected as model surfactants. The influences of polymer concentration on IFT were expounded. It was found that the addition of polymer mostly results in increasing IFT because the interfacial molecular arrangement is modified owing to the interaction between polymer and surfactants. For HPAM, the polymer chains will enter the surfactant adsorption layer to form mixed-adsorption layer. Therefore, HPAM shows strong effect on surfactant molecules with large size, such as 366. Conversely, surfactants can interact with the hydrophobic blocks of HMPAM and form mixed micelle-like associations at interface. As a result, HMPAM shows more impact on IFT of 494 due to small steric hindrance for the formation of interfacial associations. This mechanism has been ensured by 828 molecules with two long alkyl chains. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40562.

INTRODUCTION

Many researchers have focused on the studies of tertiary oil recovery to enhance oil recovery (EOR) and stabilize oil production as approximately two-thirds of the oil is left in the reservoir after primary and secondary (water flooding) production.[1] Abundant researches indicate that larger the capillary number Nc, higher the oil recovery efficiency.[2] It was found that Nc is directly proportional to the viscosity of the displacement fluid, and varies inversely with the interfacial tension (IFT) between the displacement fluid and crude oil. That is to say, the effective way to the enhancement of Nc is reducing the oil/water IFT and improving the fluidity of displaced liquid. Therefore, surfactants have been used in EOR.[3–13] Alkaline surfactant polymer (ASP) flooding is an effective technique proposed in 1980s. Although ASP flooding can increase oil production more observably than water flooding, it is also faced with many problems, such as the corrosion of the oil production equipments and damage of the stratum.[14,15] Therefore, the complex surfactant systems without alkali have received more attention.[16–18]

One of the most widely used polymers in oil field is partially hydrolyzed polyacrylamide (HPAM), which is used as thickener or modifier in the areas of tertiary oil recovery, drilling fluids, hydraulic fracturing, and drag reduction.[19,20] With development of oil fields, the temperature and the mineralized degree of water in oil pool are both becoming higher, which put forward much higher requirements for polymer. Polyacrylamides modified with relatively low amounts of hydrophobic comonomers (hydrophobically modified polyacrylamide [HMPAM]) using as aqueous viscosity modifiers have become the subject of extensively research due to their interesting solution behaviour.[21] However, the studies related to IFT for EOR surfactant and HMPAM systems are relatively less.[22,23]

The surfactants which have been studied most are the anionic surfactants such as petroleum sulfonate and sodium alkyl benzene sulfonates. Sodium alkyl benzene sulfonates are the most commonly used synthetic anionic surfactant class, which have attracted multitudinous attention because of their well-known physicochemical characteristics and numerous industrial
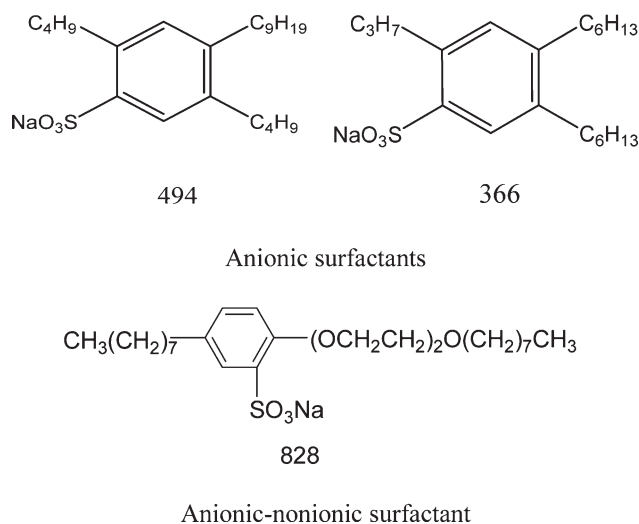
Figure 1. Structures of model surfactants in this article.

Figure 2. Effect of HPAM concentration on the dynamic interfacial tension between 494 solution and nonane.

applications.[3] In this article, the effect of two types of polymers (HPAM and HMPAM) on the IFT of three sodium alkyl benzene sulfonates has been investigated. The results show that the different interactions among surfactants and polymers can induce great differences in IFT, which are useful for the design of EOR formulation.

EXPERIMENTAL

Materials

In this study, two anionic surfactants, 1,2-dihexyl-4-propylbenzene sulfonate (366), 1,4-dibutyl-2-nonylbenzene sulfonate (494) and an anionic–nonionic surfactant octyl-[ω-alkyloxy-poly(oxyethylene)]yl-benzene sulfonates (828) were synthesized in our laboratory (Figure 1).[24,25] The purities of the synthesized surfactants were more than 99.0%. Partly HPAM, Mo-4000, was supplied by Mitsubishi Corporation (Japan), with 25.0% degree of hydrolysis. Its viscosity-average molecular weight is about 2.2×10^7. Hydrophobically modified partially hydrolyzed polyacrylamide (HMPAM with viscosity average molecular weight of about $4 \times 10^6 - 5 \times 10^6$ was obtained from Shengli Oilfield. The hydrocarbons were of 99+ mol % purity. Sodium chloride used was of analytical purity. Double-distilled water was used in the preparation of the aqueous solutions.

Apparatus and Methods

The spinning drop technique was used to measure dynamic IFTs. The standard spinning-drop tensiometer had been modified by the addition of video equipment and an interface to a personal computer. The computer had been fitted with a special video board and a menu-driven image enhancement and analysis program. The video board can "capture" a droplet image for immediate analysis. Analysis usually consists of measurement of drop length and drop width.

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. The experiments of model surfactants were performed at 30.0 ± 0.5°C.
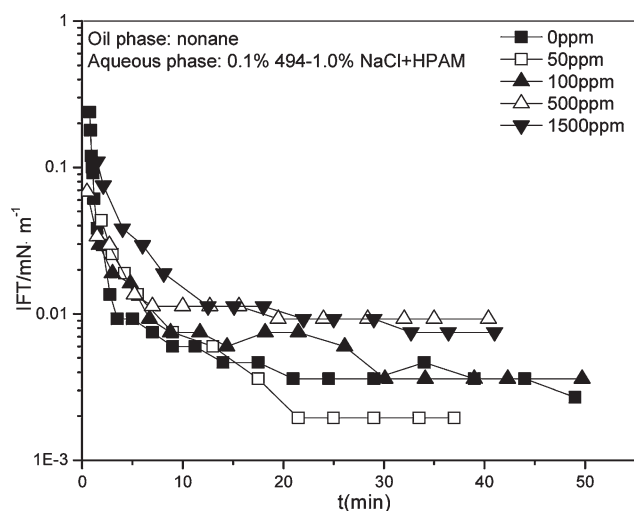
RESULTS AND DISCUSSION

Effect of Interaction between HPAM and Alkyl benzene Sulfonates on Dynamic IFT

Two alkyl benzene sulfonates, 494 and 366, have been used to investigate the dynamic IFT of surfactant–polymer system. As known, each surfactant, or surfactant mixture, may produce a minimum IFT when measuring the IFTs against a homologous series of n-alkane. The alkane carbon number for the minimum IFT is called n_{min} for this surfactant solution. For a surfactant or surfactant mixture, the n_{min} value can represent its hydrophilic–lipophilic balance (HLB): the higher its n_{min} value is, the lower its HLB is.[26] As we measured before,[27] both two sulfonates can produce minimal IFT against nonane under our experimental conditions (0.1% sulfonates and 1.0% NaCl). Compounds 494 and 366 show similar interfacial activity and the same n_{min} value, while the molecular size of 366 is believed to be larger than that of 494. Therefore, they are appropriate model surfactants to investigate interaction between surfactant and polymer responsible for IFT behavior.
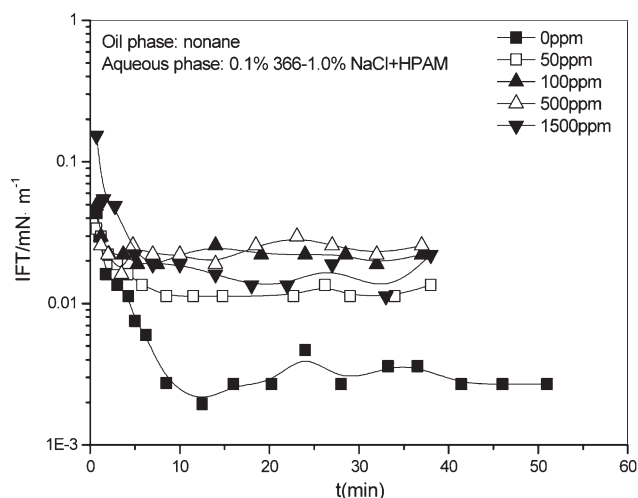

Figure 3. Effect of HPAM concentration on the dynamic interfacial tension between 366 solutions and nonane.
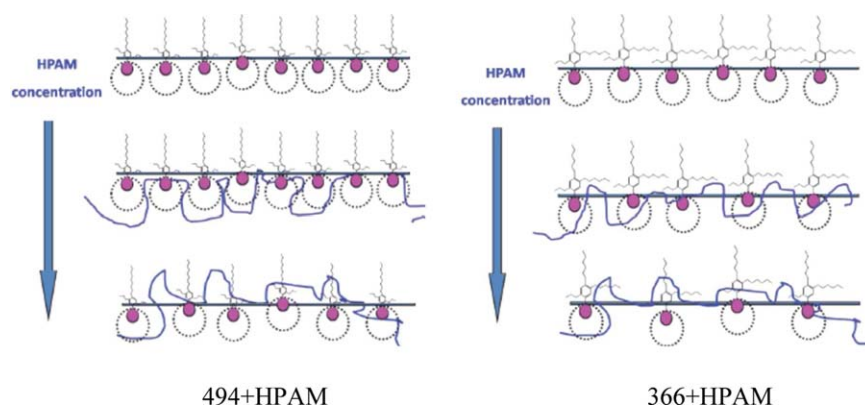
Figure 4. Schematic illustration of polymer and surfactant molecules at interface. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The effect of HPAM concentration on dynamic IFT between 494 solution and nonane is shown in Figure 2. As can be seen from Figure 2, the effect of different HPAM concentration on the stable value of dynamic IFT of 494 solution is a little different: for the system with 50 ppm HPAM, the stable value has a slight decrease; for the system with 100 ppm HPAM, there is no great difference in the stable value; for the system with other concentration, the stable value has a slight increase. The possible reasons for this are as follows: for anionic surfactant, larger vacancies between surfactant molecules exist at the interface due to strong electrostatic interaction, so the chain of polymer molecules may enter these vacancies and form a mixed-adsorption layer with surfactant molecules, which influences the interfacial molecular arrangement and results in a decrease in IFT at low polymer concentration. As polymer concentration increases, interfacial 494 molecules may decrease because of the insertion of polymer chains, which leads to the increasing IFT value.[28]

The effect of the HPAM concentration on dynamic IFT between 366 solution and nonane is shown in Figure 3. It can be seen that the stable value of IFT for the system in presence of polymer are all obvious higher than that of single 366. Moreover, the stable value increases slightly with increasing polymer con-

centration. In a word, HPAM shows stronger effect on IFT of 366 solutions than that of 494.

The schematic illustrations of polymer and surfactant molecules at interface are shown in Figure 4. One can easily see that it is difficult to form mixed adsorption film and the insertion of polymer chains into interfacial film has more impact on the arrangement of surfactant molecules for HPAM and 366 systems due to the larger size of hydrophobic part of 366, which can explain the difference of IFT results between Figures 2 and 3 very well.

Effect of Interaction Between HMPAM and Alkyl benzene Sulfonates on Dynamic IFT

Figure 5 shows the effect of HMPAM concentration on dynamic IFT between 494 solution and nonane. We can see from Figure 5 that the stable value of IFT increases sharply, when HMPAM is added. Moreover, the stable value between nonane and 494 solutions in the presence of HMPAM during concentrations range from 50 to 1500 ppm is basically the same (about 0.2 mN/m). For 494 solutions, the observed effect rule in presence of HMPAM is completely different from that of HPAM.

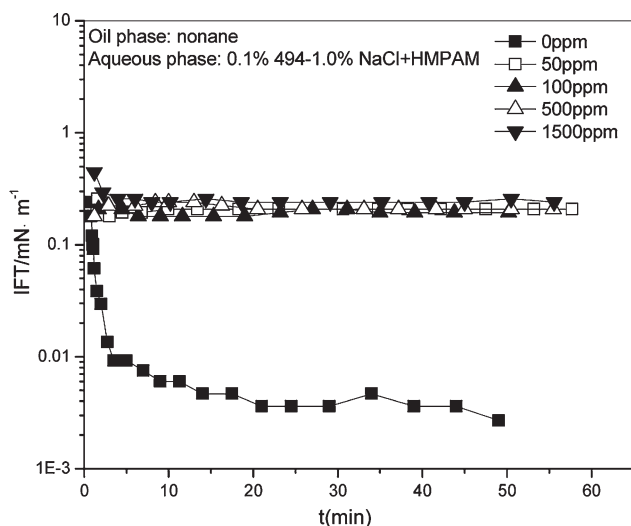Figure 6 shows the effect of the HMPAM concentration on dynamic IFT between 366 solution and nonane. It can be seen

Figure 5. Effect of HMPAM concentration on the dynamic interfacial tension between 494 solutions and nonane.
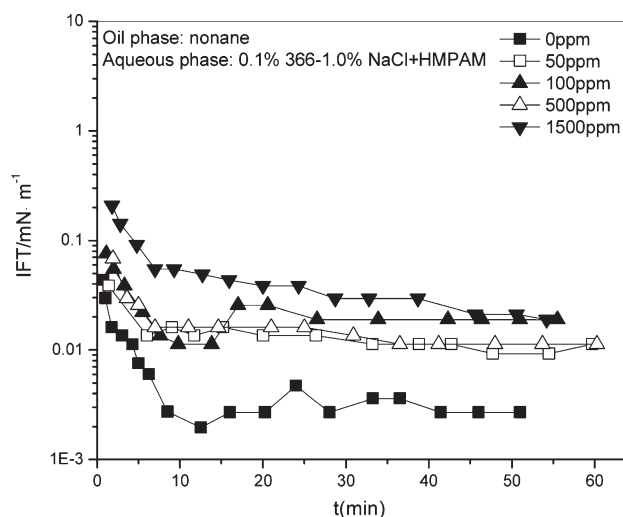

Figure 6. Effect of HMPAM concentration on the dynamic interfacial tension between 366 solutions and nonane.
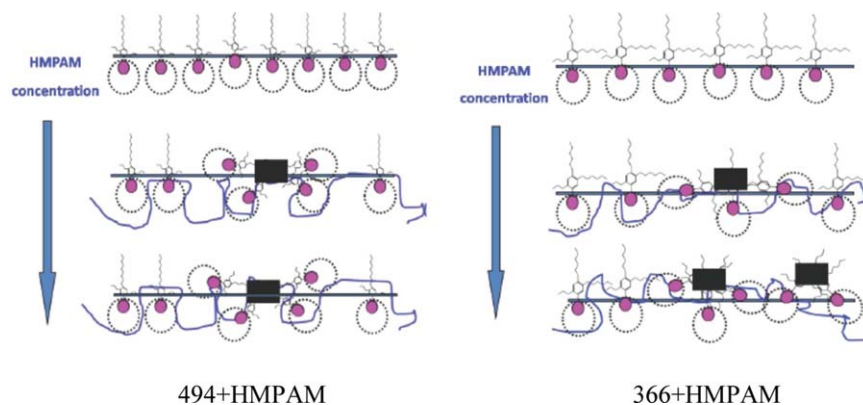
Figure 7. Schematic illustration of the mixed association formed by surfactant molecules and hydrophobic blocks at interface. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that the stable values of IFT are all higher than that without HMPAM, increasing from the order of magnitude of 0.001 to 0.01 mN/m, and change little with increasing polymer concentration.

It is very interesting to point out that HMPAM has a stronger impact on IFT of 494, while HPAM shows more effect on IFT of 366. The special influence of HMPAM on IFT has its inherent rationality. The interaction between HMPAM and surfactant molecules at the interface is diagrammatically shown in Figure 7. In previous studies, it has been found that when the HMPAM are dissolved in aqueous solution, the hydrophobic groups tend to favor intrapolymer and interpolymer associations to minimize their exposure to water. Small molecule surfactants, when added to such a system, can interact with these hydrophobic blocks through hydrophobic interaction leading to the formation of mixed micelle-like associations.[29–32] The numbers of surfactant molecule in the mixed associations plays the crucial role in controlling IFT. The interfacial free surfactant molecules will decrease with the increase of surfactant molecules in associations, which results in the improvement of IFT value.

The molecule 494 has symmetric structure, and its steric hindrance is smaller than that of 366. We have previously investigated, the

adsorption of 366 and 494 at water–nonane interface in 0.17 M NaCl (1 wt %) at 30°C, and the A_{min} values of 366 and 494 are 0.57 and 0.30 nm^2, respectively. The occupied molecular area of 366 is larger than that of 494 at interface for brine solutions, which is probably due to the longer chain at metaposition to the sulfonate group.[24] Therefore, it is easy for 494 molecules to form mixed associations with hydrophobic blocks of HMPAM. Therefore, the HMPAM has more significant influence on IFT of 494. As a result, a little HMPAM (50 ppm) can enhance the stable IFT value dramatically and the further increase of polymer concentration from 50 to 1500 ppm shows no impact on IFT for 494.

Effect of Interaction Between HPAM/HMPAM and Anionic–Nonionic Surfactants on Dynamic IFT

To verify the above proposed mechanism, we investigated the dynamic IFT of anionic–nonionic surfactant 828 containing the two long alkyl chains in surfactant molecules, as 366 has. The effects of HPAM and HMPAM on dynamic IFT between 828 solutions and decane are shown in Figures 8 and 9, respectively. It can be seen from the above figures that 828 solution can reduce the IFTs to the order of magnitude 10^{-2} mN/m, which indicates 828 has a high interfacial activity. Obviously, the addition of
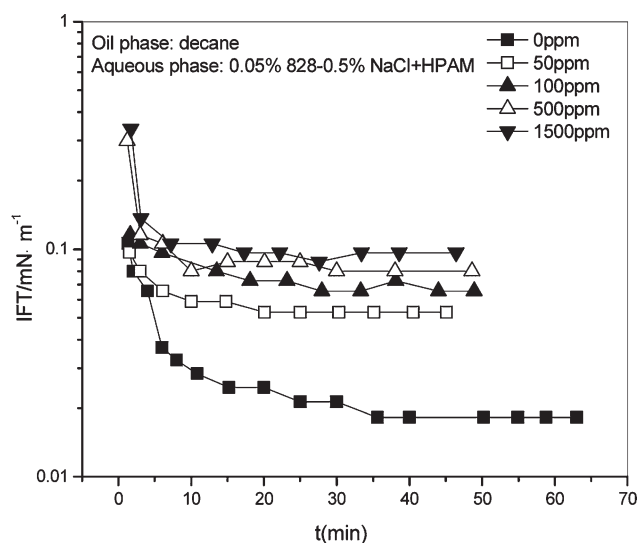

Figure 8. Effect of HPAM concentration on the dynamic interfacial tension between 828 solutions and decane.
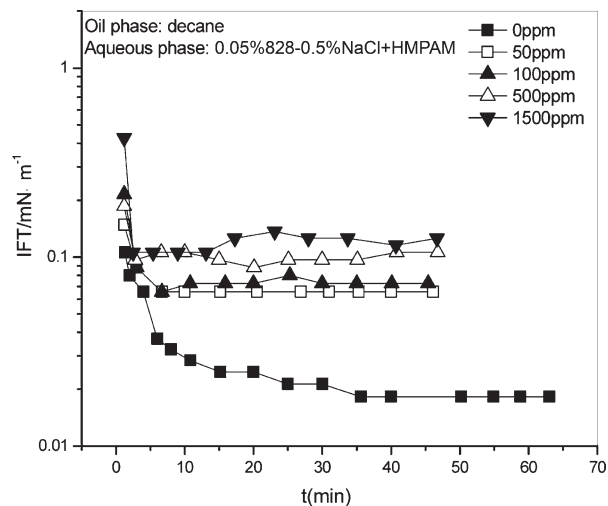

Figure 9. Effect of HMPAM concentration on the dynamic interfacial tension between 828 solutions and decane.

HPAM and HMPAM may increase the stable value of dynamic IFT between 828 solutions and decane. Moreover, the stable value increases with an increase in both the polymer concentrations, which displays basically similar variation trend as that of 366.

It must be pointed out that the molecular weight of polymer plays another important role in affecting IFT, especially for the same series of polymer. However, in this article, the structural difference of polymer between different series is the main decisive factor for IFT. We will focus on the effect of polymer molecular weight on IFT in the future works.

CONCLUSIONS

In this article, we have investigated dynamic IFT between hydrocarbons and model EOR surfactants with different structures. The effects of HPAM and HMPAM concentration on dynamic IFTs of above systems were studied in detail. For single surfactant systems, all the model surfactants show high interfacial activity. It was found that the addition of polymer results in increasing IFT, except for 50 ppm HPAM+494 solution. This is because that the interfacial molecular arrangement is modified owing to the interaction between polymer and surfactants. For HPAM, the chain of polymer molecules may enter the vacancies between adjoining surfactant molecules and form a compact mixed-adsorption layer at low polymer concentration, which may reduce IFT. However, with the increasing HPAM, the insertion of polymer chains leads to the decrease of interfacial surfactant molecules and a loose adsorption film. Therefore, the IFT increases. In the presence of HMPAM, surfactants can interact with the hydrophobic blocks of HMPAM and form mixed micelle-like associations. These mixed micelle-like associations with low interfacial activity induce an obvious increase of IFT. Interestingly, 494 molecule with small steric hindrance is easier to form mixed associations with the hydrophobic blocks of HMPAM; therefore, HMPAM shows more impact on IFT of 494. This mechanism has been ensured by 828 containing the two long alkyl chains.

ACKNOWLEDGMENTS

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