



Interfacial tensions upon the addition of alcohols to phenylalkane sulfonate monoisomer systems

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Abstract

The effects of *n*-pentanol and *n*-octanol on the interfacial tensions of phenylalkane sulfonate monoisomer systems against *n*-alkanes were investigated for elucidating the mechanism of ultra-low interfacial tensions related to enhanced oil recovery. The addition of *n*-pentanol to phenylalkane sulfonate monoisomer systems had little effect on the interfacial tensions of 1-phenylalkane sulfonate systems, whereas *n*-octanol could lower their interfacial tensions up to 1–2 orders for some *n*-alkanes. *n*-Pentanol could lower the interfacial tensions of 3-phenyltetradecane sulfonate against *n*-hexane, *n*-heptane and *n*-octane, but *n*-octanol had little effect on the interfacial tensions of 3-phenyltetradecane sulfonate. The interfacial tensions of 5-phenyltetradecane sulfonate could be lowered by the addition of *n*-pentanol, but increased upon the addition of *n*-octanol. The effects of alcohol concentration and time on interfacial tensions were also researched to show that interfacial tensions of 5-phenyltetradecane sulfonate solution increased with time at whether lower (0.04%, vol%) or higher (0.4%, vol%) *n*-octanol concentrations.

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1. Introduction

Producing ultra-low interfacial tensions is one of the most important mechanisms for oil recovery with respect to surfactant flooding. Many papers focus on the study of interfacial tensions between surfactant systems and crude oils for the reason of practical application [1,2]. Crude oils, however, are the most complicated mixtures with thousands of compositions which are distinct from one well to another. We are often frustrated attempting to clarify the reason of producing low interfacial tensions during theoretical study. So the concept of equivalent alkane carbon number was introduced by Cayias [3] and some papers studied the interfacial tensions of surfactant systems against *n*-alkanes [4–6].

Interfacial tensions related to enhanced oil recovery depend on a lot of variables among which molecular weights of surfactants, concentrations of surfactants,

electrolytes, and alkali have been extensively studied. Alcohols play a very important role in microemulsions which can produce ultra-low interfacial tensions, and also in low concentration surfactant systems which may be of more important significance with respect to surfactant flooding. Therefore, some papers [7,8] studied the effects of alcohols on interfacial tensions. These papers, however, are not as profound as the studies about other variables. What is more, only short chain alcohols (usually *n*-butanol) were researched. We have studied the interfacial tension behavior of 1-phenylalkane sulfonates against crude oil and *n*-alkanes, and interfacial tension behavior of 1-phenyltetradecane sulfonate, 3-phenyltetradecane sulfonate and 5-phenyltetradecane sulfonate against *n*-alkanes [9]. In this paper the effects of short chain alcohol (*n*-pentanol) and long chain alcohol (*n*-octanol) on the interfacial tensions of phenylalkane sulfonate monoisomer systems were studied. All percentages in this article are by weight, unless otherwise indicated, and all surfactants used are sodium sulfonates.

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2. Experimental

2.1. Materials

1-Phenyldodecane sulfonate, 1-phenyltetradecane sulfonate, 1-phenylhexadecane sulfonate, 3-phenyltetradecane sulfonate, and 5-phenyltetradecane sulfonate were prepared as our previous papers [9 and work in publication]. *n*-Pentanol, *n*-octanol and *n*-alkanes (6–13C) are of analytical purity.

2.2. The measurement of interfacial tensions

Interfacial tensions between aqueous solutions containing surfactants and *n*-alkanes were measured at 45 °C using the spinning drop interfacial tensiometer of Texas-500.

3. Results and discussion

3.1. Interfacial tension behavior of phenylalkane sulfonates upon the addition of *n*-pentanol and *n*-octanol

On the basis of our previous study [9] the interfacial tensions of 1-phenylalkane sulfonates upon the addition of *n*-pentanol and *n*-octanol are further researched and the results are shown in Figs. 1–3 with 1-phenyldodecane sulfonate, 1-phenyltetradecane sulfonate and 1-phenylhexadecane sulfonate being used, respectively. The concentrations of surfactants, NaOH, and alcohols used in this section are kept constant at 0.005 g/l, 0.12 (g/l) and 0.2% (vol%), respectively. According to the three figures the addition of *n*-pentanol has little effect on the interfacial tensions of 1-phenylalkane sulfonate systems, whereas the addition of *n*-octanol can lower their interfacial tensions up to 1–2 orders for some alkanes.

The effects of the addition of *n*-pentanol and *n*-octanol on the interfacial tensions of 3-phenyltetradecane sulfonate and 5-phenyltetradecane sulfonate are shown with Figs. 4 and 5, respectively. *n*-Pentanol can lower the interfacial tensions of

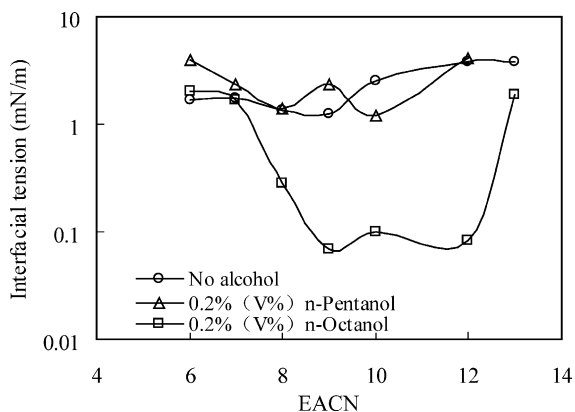


Fig. 1. Interfacial tensions upon the addition of *n*-pentanol and *n*-octanol to 1-phenyldodecane sulfonate system.

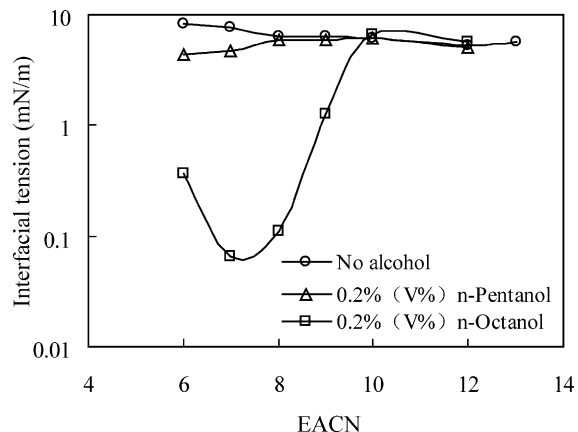


Fig. 2. Interfacial tensions upon the addition of *n*-pentanol and *n*-octanol to 1-phenyltetradecane sulfonate system.

3-phenyltetradecane sulfonate against *n*-hexane, *n*-heptane and *n*-octane, while the interfacial tensions of other *n*-alkanes maintain unchanged. *n*-Octanol, however, has little effect on the interfacial tensions of 3-phenyltetradecane sulfonate against all *n*-alkanes measured. Interfacial tensions of nearly all *n*-alkanes except heptane can be lowered by the addition of *n*-pentanol to 5-phenyltetradecane sulfonate solution, but the addition of *n*-octanol shows adverse influence on lowering interfacial tensions, namely, interfacial tensions increase upon the addition of *n*-octanol.

The results discussed above are summarized in Table 1 which shows that with benzene ring moving from end to middle positions of carbon chains in phenylalkane sulfonate isomers the addition of *n*-pentanol increases interfacial activity of these surfactants, nevertheless, the addition of *n*-octanol decrease their interfacial activity. (The interfacial activity of a surfactant decreases, as its interfacial tensions increase.) So *n*-pentanol and *n*-octanol have opposite effects on the change trend of interfacial tensions of surfactants researched.

Surfactants can lower interfacial tensions due to their amphiphilic nature which makes surfactants tend to separate

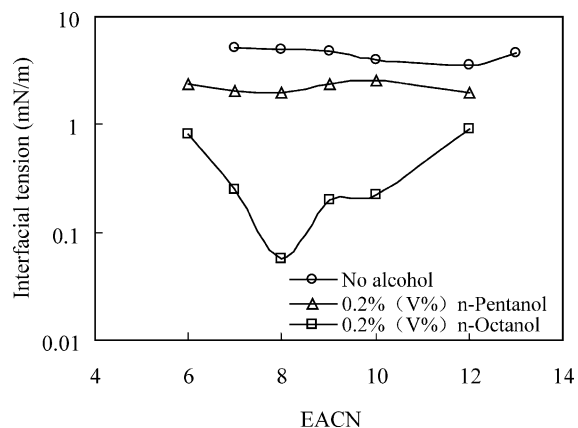


Fig. 3. Interfacial tensions upon the addition of *n*-pentanol and *n*-octanol to 1-phenylhexadecane sulfonate system.

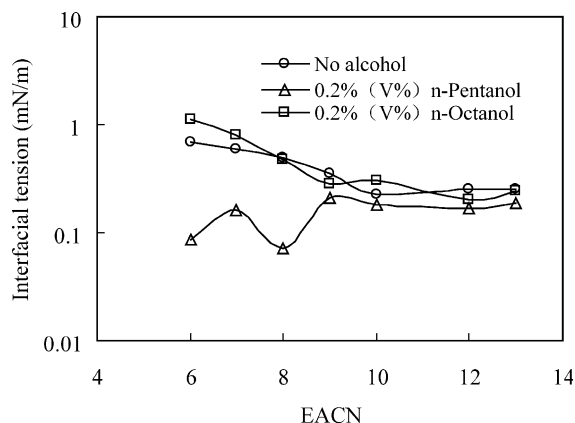


Fig. 4. Interfacial tensions upon the addition of *n*-pentanol and *n*-octanol to 3-phenyltetradecane sulfonate system.

out from the aqueous phase and to be adsorbed into interface. The lipophilic groups of surfactants are arranged toward oil phase, hydrophilic groups toward aqueous solution and interfacial tensions are related to interfacial energy [10]. The interfacial energy of CH₃ group is smaller than that of CH₂ group. If more CH₃ groups of a surfactant are present in the interface, the interfacial tension of the surfactant aqueous solution will be lower. After the addition of alcohols, molecules of *n*-pentanol and *n*-octanol insert among surfactant molecules which are loosely arranged in interface through hydrophobic effect and ion–dipole interaction [10]. If the carbon chains of alcohols added are much shorter than that of surfactants, alcohols may be shielded by chains of surfactants, so the function of alcohol CH₃ groups may be reduced. As *n*-pentanol is compared with *n*-octanol, the chance of carbon chains covered by chains of surfactants is greater than that of *n*-octanol. Therefore, the addition of *n*-pentanol does not change interfacial tensions of 1-phenylalkane sulfonate much. *n*-Octanol is longer than *n*-pentanol, more CH₃ groups may play a role to lower the interfacial tensions of 1-phenylalkane sulfonate systems.

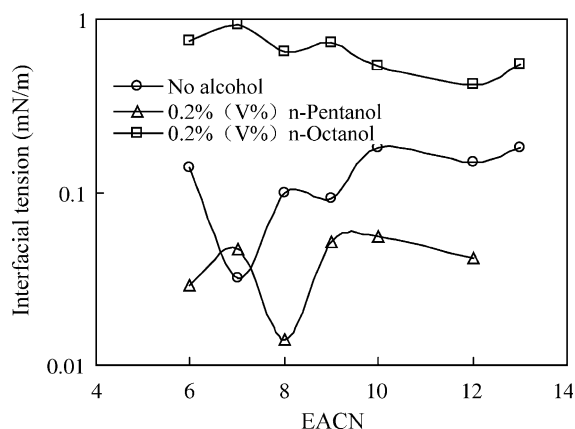


Fig. 5. Interfacial tensions upon the addition of *n*-pentanol and *n*-octanol to 5-phenyltetradecane sulfonate system.

Table 1

The dependence of interfacial activity on the addition of *n*-pentanol and *n*-octanol

Surfactants	Activity with no alcohol	Activity upon addition of <i>n</i> -pentanol	Activity upon addition of <i>n</i> -octanol
1-Phenyldodecane sulfonate	Low	Unchanged	Increased
1-Phenylhexadecane sulfonate	Low	Unchanged	Increased
1-Phenyltetradecane sulfonate	Low	Unchanged	Increased
3-Phenyltetradecane sulfonate	Middle	Increased for some <i>n</i> -alkanes	Unchanged
5-Phenyltetradecane sulfonate	High	Increased	Decreased

The chain length of *n*-pentanol is comparable with the short chain of 3-phenyltetradecane sulfonate, that ensures the CH₃ groups of *n*-pentanol may have more chance to contact with oil phase, then interfacial energy of interface decreases with the addition of *n*-pentanol. So the addition of *n*-pentanol increases the interfacial activity of 3-phenyltetradecane sulfonate system. It may sound seemingly that *n*-octanol plays the same role as *n*-pentanol does. It is so, but we must consider the other factor that affects interfacial tensions. That is the stability of *n*-octanol and 3-phenyltetradecane sulfonate molecules in interface. Since 3-phenyltetradecane is more soluble in water than 1-phenylalkane sulfonate, the molecules of 3-isomer may not be as stable as 1-isomer for staying in interface. Compared to *n*-pentanol, *n*-octanol is more stable in interface (as *n*-octanol may enhance surface activity of surfactants), so more molecules of 3-phenyltetradecane sulfonate are pushed into the bulk solution by *n*-octanol molecules. Taking into this consideration, the interfacial tensions of 3-phenyltetradecane sulfonate with the addition of *n*-octanol may go up. To combine the effects of this two factors on interfacial tensions, the addition of *n*-octanol to 3-phenyltetradecane sulfonate solution does not change the interfacial tensions much.

The chain length of *n*-pentanol is also comparable with the short chain of 5-phenyltetradecane sulfonate, and the stability of *n*-pentanol molecules in interface is not so good, then the addition of *n*-pentanol improves the interfacial activity of 5-phenyltetradecane sulfonate as it does for 3-phenyltetradecane sulfonate. Compared to 1-isomer and 3-isomer, 5-phenyltetradecane sulfonate is more soluble in water, so the addition of *n*-octanol decreases the concentration of 5-phenyltetradecane sulfonate the most among the three surfactants in interface. What is more, in our previous article (in publication), it had been proved that 5-phenyltetradecane sulfonate was most interface-active in the three isomers. Therefore, the replacement of 5-phenyltetradecane sulfonate molecules by *n*-octanol molecules makes the interfacial tensions of 5-phenyltetradecane sulfonate go up greatly.

For giving evidence of the above interpretation, the effects of alcohol concentration on interfacial tensions, and dynamic interfacial tensions are discussed in the following sections.

3.2. The effect of alcohol concentration on interfacial tensions

In the above study the concentration of alcohols was kept constant, the effect of alcohol concentration on interfacial tensions of 5-phenyltetradecane sulfonate against *n*-octane is shown in Fig. 6. With the increase of *n*-pentanol concentration the interfacial tension of 5-phenyltetradecane sulfonate reaches minimum at 0.2% (vol%). If the concentrations of alcohols are lower than 0.2% (vol%), *n*-pentanol enhances the activity of 5-phenyltetradecane sulfonate as depicted above. When the concentrations are higher than 0.2% (vol%), much more *n*-pentanol molecules adsorb into the interface, then the concentration of 5-phenyltetradecane sulfonate in interface go down, so interfacial tensions begin to increase. At the concentration of 0.2% (vol%) a good balance is gained, the interfacial tension is lowest as 10^{-2} mN/m.

No minimum of interfacial tensions, however, is observed for *n*-octanol in Fig. 6. With the increase of *n*-octanol concentration, interfacial tensions increase steadily to a constant value as *n*-octanol concentration higher than 0.4% (vol%). In the alcohol concentration range measured *n*-octanol molecules inhibit the adsorption of 5-phenyltetradecane sulfonate molecules into interface, so the addition of alcohols lowers the interfacial activity. From the above discussion it is concluded that the competition of adsorption of alcohols with surfactants also control the interfacial tensions of aqueous solution and *n*-alkanes. This conclusion will be further proved from the discussion of dynamic interfacial tensions.

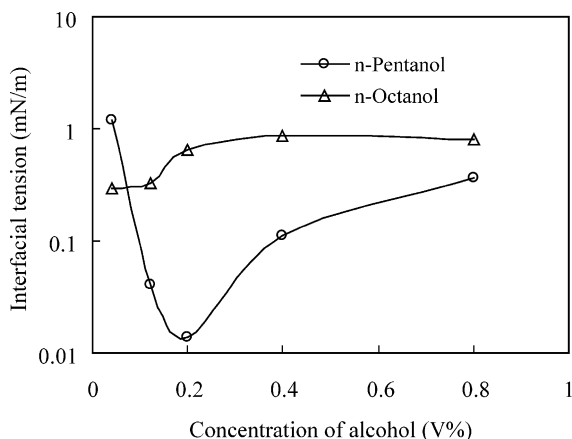


Fig. 6. The effect of concentration of alcohol on interfacial tensions.

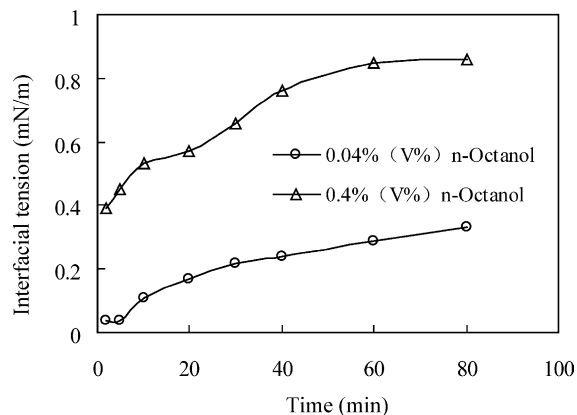


Fig. 7. The dynamic interfacial tensions upon the addition of *n*-octanol.

3.3. A study on dynamic interfacial tensions of 5-phenyltetradecane sulfonate

The dynamic interfacial tension behavior of 5-phenyltetradecane sulfonate upon the addition of *n*-octanol was investigated to elucidate the effect of *n*-octanol on the interfacial activity of 5-phenyltetradecane sulfonate. Two concentrations of *n*-octanol were studied as shown with Fig. 7 in which both of curves increase with time.

As oil phase contacts with surfactants solutions, both of 5-phenyltetradecane sulfonate and *n*-octanol adsorb into the interface, they together contribute to lowering the interfacial tensions. This step is speed-controlled, that is the one adsorbing faster contributes more to lowering the interfacial tensions. At low *n*-octanol concentration the molecules of 5-phenyltetradecane sulfonate adsorb faster to produce lower initial interfacial tensions compared to at higher *n*-octanol concentration. As the adsorption process continues, speed-controlled step gradually transfers to balance-controlled step. The one staying more stable in interface contributes more to lowering the interfacial tensions. Since *n*-octanol is more stable in the interface compared to 5-phenyltetradecane sulfonate, the concentration of *n*-octanol in interface increases with time. This explains the reason that interfacial tensions increase with time at whether lower or higher *n*-octanol concentrations.

4. Conclusion

Through the study of the effects of the addition of *n*-pentanol and *n*-octanol to phenylalkane sulfonate mono-isomer systems on interfacial tension behavior, the effects of concentration of alcohols on interfacial tensions and dynamic interfacial tensions of 5-phenyltetradecane sulfonate, the following conclusion could be obtained. *n*-Pentanol and *n*-octanol showed opposite effects on

the change trend of interfacial tensions of phenylalkane sulfonate monoisomer systems. The interfacial energy and the competition of adsorption of alcohols with surfactants play very crucial roles in controlling the interfacial tensions between these surfactant solutions and *n*-alkanes. If right formulations of surfactants are chosen ultra-low interfacial tensions could be gotten. Through this work the reasons of producing ultra-low interfacial tensions related to enhanced oil recovery could be obtained. This work may be helpful for designing practical formulations used for enhanced oil recovery and for further theoretical research.

Acknowledgements

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