



## Dynamic interfacial tensions of binary nonionic–anionic and nonionic surfactant mixtures at water–alkane interfaces



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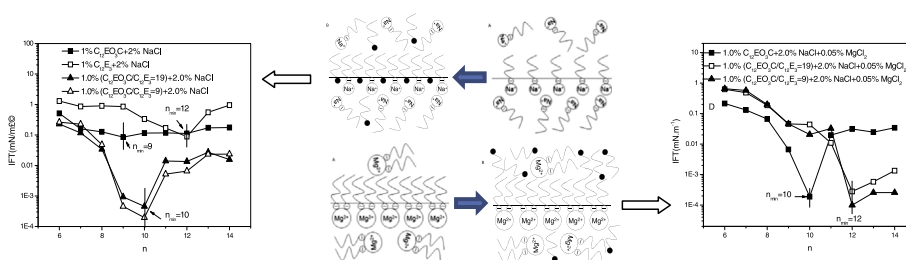
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### HIGHLIGHTS

- $C_{12}E_3$  will reduce IFT to ultralow value for  $C_{12}EO_3C$  solution with  $Na^+$ .
- Both synergism and antagonism can be observed in mixed solutions with  $Mg^{2+}$ .
- The effect of  $Ca^{2+}$  on IFTs is similar to that of  $Mg^{2+}$ .
- The hydrophilic–lipophilic balance plays the dominate role for compact adsorption films.
- The mixed adsorption mainly controls the nature of loose interfacial films.

### GRAPHICAL ABSTRACT

Different mechanisms are responsible for the variations of IFTs of mixed surfactant solutions with  $Na^+$  and  $Mg^{2+}$  respectively.



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### ABSTRACT

The influences of nonionic surfactant on interfacial properties of anionic–nonionic surfactant against alkanes are studied by measuring the dynamic interfacial tension (IFT). The surfactants chosen are fatty alcohol polyoxyethylene carboxylate ( $C_{12}EO_3C$ ) and fatty alcohol polyoxyethylene ( $C_{12}E_3$ ) with various counterions,  $Na^+$ ,  $Mg^{2+}$ , and  $Ca^{2+}$ . On the basis of our experimental results, one can find that the addition of nonionic surfactants  $C_{12}E_3$  could achieve an ultralow IFT value at some specific alkane carbon numbers under  $NaCl$  condition and the obvious synergistic effect on reducing IFT can be observed during all experimental alkane carbon numbers. However, for  $MgCl_2$  systems, the ultralow IFT values can be achieved by pure  $C_{12}EO_3C$  solutions and one can observe synergistic effect and antagonistic effect on IFTs at higher and lower alkane carbon numbers respectively by adding nonionic surfactant. On the other hand, for  $CaCl_2$  systems, the addition of 0.05%  $C_{12}E_3$  shows the same influence on the IFTs as that of  $NaCl$  systems, while the similar effect as that of  $MgCl_2$  systems will be observed when adding 0.1%  $C_{12}E_3$ . An interfacial model combined two mechanisms, controlling hydrophilic–lipophilic balance and forming mixed adsorption film, responsible for varying IFT has been provided based on the difference of ion radius. By adding nonionic surfactant, the mechanisms of forming mixed adsorption film and controlling hydrophilic–lipophilic balance play crucial roles in effecting IFTs for  $NaCl$  systems and  $MgCl_2$  systems, respectively. Moreover, for  $CaCl_2$  systems, the responsible mechanism of forming mixed adsorption film will change into controlling hydrophilic–lipophilic balance with the increase of nonionic surfactant concentration.

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## 1. Introduction

Surfactant enhanced oil recovery (EOR) has been investigated for many years. It is well-known that interfacial tension (IFT) is of fundamental importance in determining the capillary forces acting on trapped oil within porous media [1]. Reservoirs have different characteristics (crude oil type, temperature, and water composition), and the structures of the added surfactants have to be tailored to these conditions to achieve an ultralow IFT, especially the reservoir is of a high temperature and a high salinity. Therefore, new types of surfactants that possess several hydrophobic and hydrophilic moieties in the same molecule have attracted considerable interest because they exhibit extraordinary surface activity [2–7]. At the moment, attention has mostly been focused on nonionic–anionic surfactants, such as alkyl polyoxypropoxylated surfactants having an anionic head at the end of the molecule [8].

Zeng et al. [9] investigated sodium fatty alcohol polyoxypropylene ether sulfates and sodium fatty alcohol polyoxyethylene ether sulfates. They found that when surfactant is unaltered, the lowest equilibrium IFT of system decreases when alkane carbon number (ACN) of oil increases, and when model oil is the same, with a rise of the number of PO units in surfactants, the lowest equilibrium IFT decreases while the optimal salinity and breadth of low IFT region increase.

Salager and Manchego [10–12] found there existed optimum formulation as follows for commercial ethoxylated surfactants systems.

$$C1 + C2 \text{ SACN} - \text{EON} - k\text{ACN} + c_T(T - T_{ref}) = 0$$

where C1 depends on the surfactant hydrophobe structure, SACN is the surfactant *n*-alkyl carbon number, EON the number or average number of ethylene oxide groups in the head group, and *T* is the temperature. Constants  $c_T$  depend on the system type.

Witthayapanyanon et al. investigated that the introduction of additional PO and EO groups in the extended surfactant yielded lower IFT and lower optimum salinity, both of which are desirable in most formulations [13].

Clint [14] reported that the anionic surfactant has a stronger repulsive electrostatic nature of the polar group than the static hydration requirement of the ethylene oxides in a nonionic–anionic surfactant moiety.

Most surfactants used in practical applications are mixtures. Hence, understanding both the structure and properties of mixed anionic–nonionic surfactants is essential for many industrial uses of surfactants [15]. Because of their tendency to efficiently solubilize hydrophobic compounds, anionic and nonionic surfactant mixtures result in their outstanding interfacial properties [16], which has attracted many scientists' interests, and many papers about such surfactant mixtures have been reported [17–19].

Al-Sabagh and Azzam [4] investigated mixed solutions of ethoxylated alkyl sulfosuccinate surfactants. They supposed that the ethylene oxide chain in the molecule to coil around the sulfonic group of the anionic surfactant may reduce its polar electrostatic repulsive force.

Zhang et al. [19] investigated the dynamic IFT in hydrocarbons/binary anionic and nonionic surfactant mixtures systems. They found that the synergism/antagonism for lowering IFT in these systems depended on the factors that can change the surfactant partition coefficients, such as the hydrophilic–lipophilic ability of the surfactant, the salinity, and the alkane carbon number of the oil phase.

Before, the influence of counter ions and temperature on dynamic IFTs of alkyl ether carboxylate ( $C_{12}EO_3C$ ) against alkanes had been studied [20]. We had found that the NaCl concentration

had little effect on the IFT, while divalent ions could reduce the IFT to an ultralow value. With the increase of  $CaCl_2$  or  $MgCl_2$  concentration, dynamic IFT passed through a minimum at a particular salt concentration (“V” shape). Moreover, the stable value of IFT achieves an ultralow value and also passed through a minimum at the same salt concentration.  $MgCl_2$  had a stronger tendency to achieve ultralow IFT than that of  $CaCl_2$ , while the addition of  $CaCl_2$  had a stronger tendency to partition surfactant molecules to the oil phase.

However, commercially used surfactants are invariably mixtures of different surface-active compounds, and most surfactant-related products are complex formulations involving two or more surfactants. Therefore, the influence of counterions in surfactant mixtures systems should be taken into account. In this paper, we investigated the interfacial properties of electrolyte solutions in alkanes/binary surfactant mixtures of alkyl ether carboxylate ( $C_{12}EO_3C$ ) and alkyl ether ( $C_{12}E_3$ ) systems. On the basis of our experimental results, we found that mixed anionic–nonionic surfactants for lowering IFT in these systems depended on the factors that can change the surfactant partition coefficients, such as the ionic type, the alkane carbon number of the oil phase and the proportion of anionic and nonionic surfactants. The molecular mechanism for achieving ultralow IFT was also studied for these systems. It has a great important guidance for EOR of high-temperature and high-salinity oil reservoirs.

## 2. Experimental section

For all of the systems studied, the nonionic–anionic surfactant used was alkyl ether carboxylate  $C_{12}EO_3C$ , and the nonionic surfactant used was  $C_{12}E_3$ . Surfactant was synthesized in our laboratory, which has a purity of about 90% (Scheme 1). The oils used in this study were a homologous series of alkanes with chain lengths from  $C_6$  to  $C_{14}$  with 99 + mol% purity. All inorganic reagents used were analytical-grade. Double-distilled water was used in the preparation of the aqueous solutions.

The Texas-500C spinning drop technique (CNG USA CO) was employed 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 the measurement of the drop length and drop width.

The volumetric ratio of water/oil in the spinning drop tensiometer is about 200. Samples were assumed to be equilibrated when measured values of IFT remained unchanged for 30 min. The IFT measurements were performed at  $85.0 \pm 0.5$  °C.

## 3. Results and discussion

### 3.1. Synergistic effect of anionic–nonionic and nonionic surfactant mixtures on dynamic IFT

The tension across the interface is significantly reduced by the adsorption of surfactant molecules because these interactions are much stronger than the original interaction between the oil and water molecules. For a given surfactant, the greater the concentration of surfactant molecules at the interface, the larger number of surfactant molecules replaced oil and water molecules on the interface, which results in a lower IFT. The interfacial surfactant concentration depends on the desorption energy of surfactant molecule. The greater the energy of desorption is, the higher the interfacial surfactant concentration is [8,21]. Therefore, the extent of lowering the IFT is related to the properties of the surfactant

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