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Effect of inorganic alkalis on interfacial tensions of novel betaine solutions against crude oil

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ABSTRACT

The effects of inorganic alkalis on the dynamic interfacial tensions (IFTs) of three betaine surfactants with different structures against daqing crude oil and model oils containing crude oil fractions, such as saturate, aromatic, resin, asphaltene and acidic fractions, have been studied by spinning drop tensiometer. The influences of pH value (alkali concentration and types) have been investigated. On the basis of the experimental results, one can find that it is difficult to reach the ultralow IFT value for all betaine solutions because of the mismatching of the hydrophilic head and hydrophobic tail. The unsaturated and branched alkyl chain can enlarge the size of hydrophobic part and reduce the equilibrium IFTs. By adding alkali, the IFTs are controlled by the mixed adsorptions of the petroleum acids, produced soaps and betaine molecules. For betaines with small hydrophobic part, 18C and 22C, the mixed adsorption films are compact than those of pure betaine films, which results in the decrease of IFT. On the other hand, the petroleum acids and soaps adsorb competitively with betaine molecules, due to the tighter packing of 26C molecules at the interface, the equilibrium IFT values of 26C increase with an increase in pH value. The stronger the alkali is, the better the synergism or antagonism is. The effects of pH on the IFTs of betaine solutions against model oils containing crude oil fractions agree with those against crude oil. For all betaines, the order of the ability of affecting IFT is acidic fractions > resin > asphaltene > aromatic > saturate in general.

1. Introduction

The crude oil is very important for the energy supply of the world among various sources of energy. However, after primary (relying on the original reservoir energy) and secondary (through water supplement energy) oil recovery, there are about two-thirds of the oils still left in the oil reservoir (Shah, 1981). Therefore, new methods of tertiary oil recovery came into being and then have been widely applied in oil fields for enhanced oil recovery (EOR), which mainly employs chemical agents such as alkalis, polymers and surfactants. Experimental results show that the residual oil trapped in the reservoir pore structure could be displaced by increasing the capillary number, *Nc*, which determines the microscopic displacement efficiency of oil, and the most effective way to improve *Nc* value is to reduce the oil/water interfacial tension (IFT). If the IFT value between the aqueous phase and the oil phase reaches ultralow level (10^{-3} mN/m or lower), the efficiency of oil recovery will be remarkably improved (Wilson, 1976; Zhang et al., 2008; Kumar and Mandal, 2016; Mandal and Kar, 2016).

The IFT between crude oil and aqueous solution can be reduced to an ultralow level by the employment of an appropriate surfactant in the EOR process. However, for high-temperature and high-salinity oil reservoirs, traditional surfactants for EOR, such as petroleum sulfonates and alkylbenzene sulfonates, will lost their interfacial activity, which results in low oil recovery (Zhang et al., 2008). Therefore, zwitterionic surfactants with both cationic and anionic centers attached to the same molecule gradually appeared in public, due to their special molecular structures those show many unique properties such as high foam stability, low toxicity, temperature resistance and salt tolerance. Moreover, temperature, pH and added electrolyte have little effects on properties of zwitterionic surfactants, which make zwitterionic surfactants as one of the handful surfactants type applied to high-temperature and high-salinity reservoir (FernLey, 1978; Ghosh and Moulik, 1998; Tsubone et al., 1990; Kumar et al., 2003; Yoshimura et al., 2006; Zhou et al., 2014). Betaine is an important kind of zwitterionic

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surfactant, the synergism between crude oil systems and novel betaines can reduce IFT greatly, so it has been widely applied to EOR recently. Yoshimura and Zhou have researched the dynamic IFTs between betaine surfactants and crude oils from Shengli Oilfield. The results showed that at optimum conditions the IFT value becomes ultralow and it is well matched the screening criteria of surfactants used in EOR (Zhou et al., 2015; Song et al., 2014; Zhang et al., 2015; Xue et al., 2011; Zhao et al., 2007).

It is well known that the composition of crude oil is very complex and there exist different kinds of natural active components, such as asphaltene, resin, wax, aromatic, saturate, hydroxybenzene and ester etc (Riazi, 2005). The interfacial properties of these fractions play important roles in the stabilization of crude/water emulsions and the reduction of IFT. Alkali added to crude oil/ surfactants systems may produce ultra-low IFT, one of the reasons is that acidic fractions present in the crude oil react with the alkaline solution to produce in situ surfactant (soap) as nature surfactants, which lowers the oil-water IFT; (Li et al., 2000, 2008) the other is the synergistic effect between surfactant and in situ soap (Zhang et al., 2003; Touhami et al., 1998a, b; Rudin et al., 1994; Bera et al., 2014; Mandal et al., 2016). The ionized acid (soap) is very active, which has a trend to partition into the aqueous phase and changes the surfactant partition coefficients (Zhao et al., 2010; Li et al., 2015).

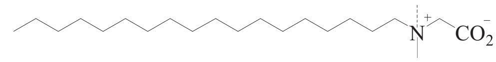
Though many attempts have been made to elucidate the physicochemical mechanisms responsible for lowering IFT in betaines/oil systems, (Zhou et al., 2014, 2015; Song et al., 2014; Zhang et al., 2015; Xue et al., 2011; Zhao et al., 2007) however, the interactions between the inorganic alkali and betaines in reducing IFT are still extremely rare, and the effects of betaine structure on ultralow IFT have not been explored systematically.

In earlier research some authors found acidic fractions with different molecular weight had shown different interfacial activities with alkaline solutions, depending on the rates of production and desorption of interfacial ionized acids (Acvdeeo et al., 1999). The acidic fractions with lower molecular weight can produce a close packing of polar heads, leading to IFT values significantly lower than the acidic fractions with high molecular weight. The acid number of crude oil can also strongly affect the IFTs of crude oils/inorganic alkaline solutions and there exists an optimum concentration with respect of surfactant and alkali in a certain acid number, at which the IFT is the lowest. The higher acid number of crude oil is, the higher optimum concentration of inorganic alkali. In this article, three kinds of inorganic alkalis (NaOH, $NaHCO_3$ and Na_2CO_3) and three kinds of betaines were employed to detect the effects of inorganic alkali on IFT of crude oil against betaine solutions. According to the experimental results, it is demonstrated that the pH of inorganic alkali and the molecular structure of betaine play important roles on the IFTs of alkali/betaine/acidic oil systems. Our findings are very important to the design of formula of betaine flooding systems for EOR.

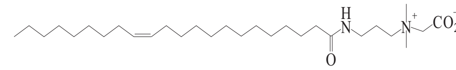
2. Experimental section

2.1. Materials

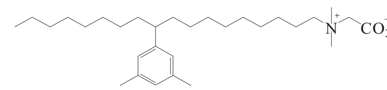
Carboxyl betaines 18C, 22C, 26C employed in this paper were obtained from our laboratory and the molecular structures are listed in Scheme 1. They were named as betaine 18C、22C、26C according to their carbon atom number in the hydrophobic chains. For these three betaines, the introducing of benzene ring and double bond makes them novelty. The purity of the three betaines checked by elemental analysis and ^{1}H nuclear magnetic resonance (NMR) spectroscopy was above 95 mol%. The crude oil was from Daqing oil field with a density of 0.850 g/cm^3 at 45 °C and the acid number of 0.05 mg KOH/g (Daqing, China). The asphaltene, saturate, aromatic, resin and acidic fractions were separated from crude oil as described in our early work (Zhou et al., 2015). NaOH, $NaHCO_3$ and Na_2CO_3 (AR) were used to prepare a series of alkali and NaCl (AR) mixed solutions with different NaCl/alkali ratios, and the pH of the mixed solution were listed in Table 1. The alkanes (> 99 mol%) have chain lengths from C_6 to C_{14}. Kerosene was further purified by glass chromatography column filled with the silica gel layer until the IFT value is stabilized at about 40 mN/m against pure water. Double-distilled water was used in the preparation of the aqueous solution.



18C



22C



26C

Scheme 1. Structures and abbreviations of carboxyl betaines.

Table 1
pH values of all experimental solutions.

	Alkail	NaCl: Alkail				
		10:0	**9:1**	**5:5**	**1:9**	**0:10**
	$NaHCO_3$	7.53	8.76	9.20	9.32	9.36
Betaine	**Na_2CO_3**	7.53	10.48	11.18	11.30	11.33
	NaOH	7.53	11.93	13.18	13.72	13.81

2.2. Apparatus and methods

The dynamic interfacial tensions were measured by a J2000BW spinning drop interfacial tensiometer (DT Shanghai CO.). The standard spinning-drop tensiometer had been modified by the addition of video equipment and an interface to a personal computer. The surfactant solution as an outer phase (ca. 0.27 mL) was injected into the glass tube, and about 2 μL of oil as an inner phase was put into the middle of the tube. 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. Samples were assumed to be equilibrated when measured values of IFT remained unchanged for half an hour (Zhou et al., 2014). In all cases, the measurements of the interfacial tension were performed at a rotating velocity 5000 rpm and 45 ± 0.5 °C. In all cases, the standard deviation did not exceed ± 5%.

3. Results and discussion

3.1. The Effect of surfactant concentration on the dynamic IFTs between betaine solutions and n-decane

As we all know, the comprehensive applications of surfactants for EOR are mainly based on their strong ability to adsorb onto interface and reduce the IFT value between the crude oil and chemical flooding. With the addition of a surfactant in bulk aqueous, the dissimilarity between the oil side and the water side of the interface will be weakened more or less when surfactant molecules adsorb at the interface (Rosen and Rosen, 1989). In order to reach an ultralow IFT