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Dilational rheological properties of sulphobetaines at the water–decane interface: Effect of hydrophobic group

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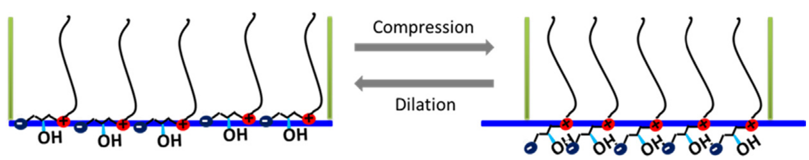
HIGHLIGHTS

- The benzyl substituted alkyl sulphobetaine occupies larger interfacial area than that of linear sulphobetaine.
- The sulphobetaines can form more compact adsorption films with higher moduli than traditional surfactants.
- The benzyl substituted alkyl sulphobetaine shows more elastic nature due to the rigidity of benzene ring.
- The electrolyte NaCl has little effect on interfacial tension but can reduce interfacial modulus.

GRAPHICAL ABSTRACT

The whole hydrophilic part, sulfonic group, hydroxyl and ammonium group, can response to the area variations by change the orientation between parallel to the interface and introduce to the aqueous instead of diffusion-exchange process, which can enhance the elasticity of film.



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ABSTRACT

The interfacial tensions and dilational properties of adsorbed films of two zwitterionic surfactants with different hydrophobic groups, alkyl sulphobetaine (ASB) and benzyl substituted alkyl sulphobetaine (BSB), at the decane–water interface have been investigated by the drop shape analysis method. The influences of dilational frequency and bulk concentration on the interfacial dilational modulus and phase angle were expounded. The effects of electrolyte NaCl on the interfacial tensions and dilational properties have also been researched. The experimental results show that the similar CMC and IFT_{CMC} values for ASB and BSB indicate their similar interfacial activity. The A_{min} value of BSB is larger than that of ASB, which is due to the steric effect of benzene ring in BSB molecule. The dilational data show that betaines can form compact adsorption films due to their electric neutrality in experimental condition, which results in the higher maximum values of dilational moduli for both BSB and ASB than those of common surfactants. Moreover, the whole hydrophilic part, sulfonic group, hydroxyl and ammonium group, can response to the area variations by change the orientation between parallel to the interface and introduce to the aqueous instead of diffusion-exchange process, which can enhance the elasticity of the film. The electrolyte NaCl has a function of accelerating the diffusion-exchange process of surfactant molecules. As a result, the dynamic interfacial properties such as dilational properties show obvious variations, while the static interfacial property such as interfacial tension has little change after the addition of 1% NaCl.

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1. Introduction

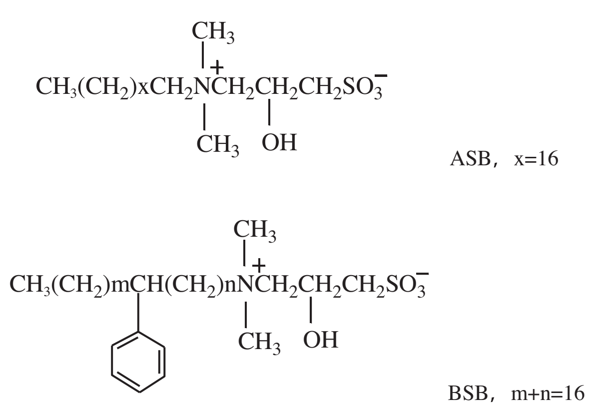
It is well recognized that producing ultralow interfacial tension (IFT) between the flooding solution and crude oil is one of the most important mechanisms for oil recovery with respect to chemical flooding, such as alkaline water flooding, surfactant flooding, surfactant–polymer flooding and alkali–surfactant–polymer flooding. In the so-called primary oil recovery process (natural flow), the yield is generally only 10–20% of the original oil in place (OOIP). By application of the secondary oil recovery method, such as water flooding, the yield can be increased to 20–30% OOIP. At the end of water flooding, almost 65–70% of OOIP is left in the reservoirs, which is believed to be in the form of ganglia and trapped in the pore structure of the rock by capillary forces. In order to recover additional oil by a chemical flooding process, the capillary number, which determines the microscopic displacement efficiency of oil, should be increased by 3–4 orders of magnitude through reducing the IFT of oil ganglia from its value of 20–30 mN/m to 10^{-3} mN/m [1,2].

Using an appropriate surfactant system, the IFT between crude oil and chemical flooding solutions can be reduced to lower than 10^{-2} mN/m. Anionic surfactants, such as petroleum sulfonate and alkylbenzene sulfonate, with extensive source and lower cost advantage, have been widely employed in enhanced Oil Recovery (EOR) [3]. However, anionic surfactants have high krafft point and poor salt tolerance which restricts their application scope for high salinity reservoirs. Zwitterionic surfactants have both cationic and anionic centers attached to the same molecule, they exists as Zwitterions over a wide pH range. Compared with those of the conventional anionic, cationic and nonionic surfactants, zwitterionic surfactants are interesting molecules because of their many unique properties. In general, they display excellent water solubility, high foam stability, low toxicity, and the advantages of temperature resistance, salt tolerance and biodegradation. Also, changes in temperature, pH, and added electrolyte have been found to have minimal effects on zwitterionic surfactants [4–7]. Hence, researches about zwitterionic surfactants for oil extraction field with high temperature and salinity have been reported in recent years.

Betaines are an important kind of zwitterionic surfactants and have wide applications [8]. The synthesis and interfacial properties of betaine applied to EOR have been reported recently [9–11]. However, the nature of adsorption film by betaine molecules is still unclear due to the limit of IFT measurement, which cannot reflect the information of film structure and in-film interactions.

Rheological properties are the main characteristics of the dynamic properties of a film. There are two rheological properties of the interfacial films: interfacial shear and dilational viscoelasticity. It is beneficial to better understand the microcosmic properties of interfacial film through the research of dilational viscoelasticity. Moreover, the measurements of dilational properties can provide more information about the arrangement of adsorption layers, which is helpful to speculate the possible schematic diagrams of adsorbed molecules at the interface [12–14]. However, the studies of the dilational viscoelasticity are very scarce for zwitterionic surfactants, especially for betaines [15].

In this paper, we designed and synthesized two zwitterionic surfactants with different hydrophobic parts, alkyl sulphobetaine and benzyl substituted alkyl sulphobetaine, and investigated their dynamic interfacial tensions and dilational properties by the drop shape analysis method. It may be useful for us to understand the influence of hydrophobic parts on the interfacial behavior of zwitterionic surfactants.



Scheme 1. Structures of alkyl sulphobetaine and benzyl substituted alkyl sulphobetaine.

2. Theoretical background

The Gibbs interfacial dilational modulus is defined by the surface tension increase after a small increase in area of a surface element

$$\varepsilon = \frac{d\gamma}{d\ln A} \quad (1)$$

It gives a measure of the interfacial resistance to changes in area. Where ε is the dilational modulus, γ is the interfacial tension and A is the interfacial area. When the interfacial area is subjected to periodic compressions and expansions at a given frequency, relaxation processes such as diffusion exchange between the surface layer and the bulk solution or molecular rearrangements within the layer may cause a phase difference (measured by the phase angle θ) between the applied area variation and the surface tension response. In that case ε is a complex number and can be decoupled into real and imaginary components, respectively [16,17].

$$\varepsilon = \varepsilon_d + i\omega\eta_d \quad (2)$$

where ε_d is the dilational elasticity or storage modulus and $\varepsilon_\eta = \omega\eta_d$ the dilational viscous component or loss modulus that represents a combination of internal relaxation processes and relaxation due to transport of matter between the surface and the bulk.

Phase angle θ is calculated according to

$$\tan\theta = \frac{\varepsilon_\eta}{\varepsilon_d} \quad (3)$$

In the absence of relaxation processes affecting the surface dilational modulus, the phase angle θ is equal to 0 and the surface layer behaves as a purely elastic body.

3. Materials and methods

3.1. Materials

Two zwitterionic surfactants, alkyl sulphobetaine (ASB) and benzyl substituted alkyl sulphobetaine (BSB) were synthesized in our laboratory. The structures and abbreviations are listed in Scheme 1. The purity of the compounds checked by elemental analysis and ^{1}H NMR spectroscopy was 99 mass%. The solutions were prepared with deionized water (resistivity >18.2 MΩ cm^{-1}), which were distilled two times from potassium permanganate solution.

3.2. Interfacial tension and interfacial dilational rheological measurements

Interfacial rheological measurements were performed using an oscillating bubble/drop tensiometer (Tracker, IT Concept, France). Details of the instrumentation together with the corresponding experimental procedure were described in detail elsewhere [18], and will be covered here only briefly. The main elements of the