



## Dilational rheological properties of novel zwitterionic surfactants containing benzene ring and polyoxyethylene group at water–decane interface



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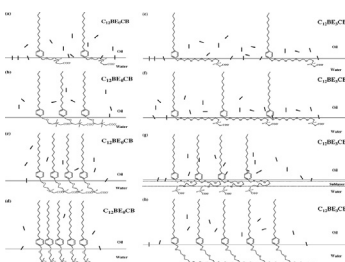
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### HIGHLIGHTS

- The dynamic phase angle of  $C_{12}BE_xCB$  film decreases with ageing time.
- The dilational modulus passes through a plateau value with the increasing concentration.
- The exchange between the interface and the sub-layer plays a crucial role for  $C_{12}BE_xCB$  film.
- The interfacial viscoelasticity of  $C_yBE_2CB$  film with different alkyl chain can support above mechanism strongly.

### GRAPHICAL ABSTRACT

The exchange of ethylene oxide groups between the interface and the sub-layer plays a crucial role for the nature of  $C_{12}BE_xCB$  film.



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### ABSTRACT

The interfacial dilational rheological behaviors of four zwitterionic surfactants with benzene ring and polyoxyethylene group, *p*-(*n*-lauryl)-benzyl polyoxyethylene ether carboxybetaine  $C_{12}BE_xCB$  ( $x=0, 1, 2, 3$ ), were investigated via the drop shape analysis method. The influences of time, oscillating frequency and bulk concentration on dilational properties were explored. The experimental results show that the number of ethylene oxide groups is one of the principal factors to control the interfacial film. The dilational properties of  $C_{12}BE_xCB$  are quite different from those of common surfactants: the phase angle decreases with aging time, the slope of the  $\log \varepsilon - \log \omega$  curve and phase angle of  $C_{12}BE_xCB$  decrease in a wide concentration range, and the dilational modulus of  $C_{12}BE_xCB$  passes through a plateau value with the increasing concentration for surfactant with more ethylene oxide groups. These phenomena become more and more apparent with increasing ethylene oxide groups and it cannot be attributed to the diffusion-exchange process between the bulk and the interface. It is reasonable to consider that ethylene oxide groups are flexible and can be compressed and expanded, just like a spring. The compression and expansion of the ethylene oxide groups in the interfacial layer and the exchange between interface and sub-layer play a crucial role for  $C_{12}BE_xCB$ . Possible schematic diagrams of adsorbed molecules with time and concentration at the water–decane interface are proposed. The results of static modulus measurements and dynamic interfacial viscoelasticity for  $C_yBE_2CB$  ( $y=8, 10, 12$ ) with different length of hydrophobic chain can support our provided mechanism strongly.

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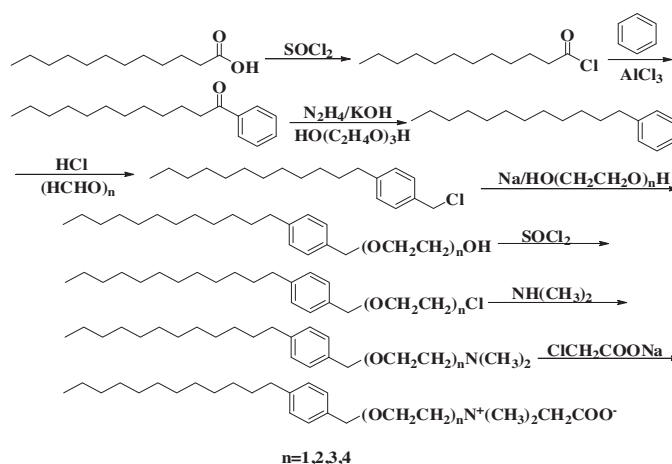
## 1. Introduction

The dilational viscoelasticity plays a significant role in many fields, such as foam and emulsion stability [1–3]. Its microcosmic basis is relaxation process at the interface and near the interface [4,5]. 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. Therefore, many reviews about dilational viscoelasticity have been reported in recent years [6–10]. However, the studies of the dilational viscoelasticity are very scarce for zwitterionic surfactants. Feng et al. [11] studied the dilational viscoelasticity of the zwitterionic gemini surfactants ( $C_8E_xNC_{12}$ ) with polyoxyethylene spacers at the water–decane and water–air interfaces, and found the dilational viscoelasticity at the water–decane is close to that at the water–air interface on the whole.

The hydrophilic polyoxyethylene group is an important factor which influences interfacial layer [12–21]. Zhang et al. [16] studied the dilational viscoelasticity of nonylphenol polyoxyethylene ethers solutions and found surface dilational elasticity and viscosity passed through the distinctive maximum with the increase of bulk concentration and changed little with the increase of the number of polyoxyethylene groups from 8 to 12. Fainerman et al. [17] studied the dilational viscoelasticity of TX45, TX100, TX165 and TX405 surfactants at water–air interface, and found with an increase of ethylene oxide groups the dilational modulus of TX100, TX165 and TX405 show two maxima by increasing bulk concentration. The first maximum is caused by the transition of the expanded state of the adsorbed Triton molecules in the surface layer (ethylene oxide groups are adsorbed at the interface) to a more compact state (increase in surface pressure leads to desorption of the ethylene oxide groups from the interface). The existence of the second maximum is caused by the internal compressibility of Triton molecules at higher surface pressure. Feng et al. [4] studied the dilational properties of anionic gemini surfactants (oligooxa)- $\alpha$ ,  $\omega$ -bis(*m*-octylbenzene sulfonate) ( $C_8E_xC_8$ ) with polyoxyethylene spacers at the water–air and water–decane interfaces, and found with an increase of ethylene oxide groups, the dilational modulus of  $C_8E_8C_8$  shows two maxima with the increasing concentration, furthermore, the dilational modulus at the water–decane interface is close to that at the water–air interface for  $C_8E_8C_8$ .

Zwitterionic surfactants have both cationic and anionic centers attached to the same molecules, they exist as “Zwitterions” over a wide pH range [22]. Compared with those of conventional anionic, cationic and nonionic surfactants, zwitterionic surfactants are interesting molecules because of their many unique properties. In general, they are mild to the skin and eyes, exhibit low toxicity, display excellent water solubility, broad isoelectric ranges, high foam stability, and resistance to hard water and to degradation by oxidizing and reducing agents [23,24]. Also, changes in temperature, pH, and added electrolyte have been found to have minimal effects on zwitterionic surfactants. They are used as promising surfactants in many industrial, biological, and daily processes [25–28].

Betaines are an important kind of zwitterionic surfactants and can reduce the irritation action of the surfactants on the eyes and skin [29]. Moreover, they are widely used as boosters because they stabilize foams against the antifoaming action of the oil droplets contained in commercial hair conditioners or shampoos [30]. In spite of the wide applications of betaine surfactants and their increasing commercial use, it is clear from the literature that their theoretical aspects have received far less attention than those of nonionic or ionic surfactants, especially the studies of betaine



**Fig. 1.** Synthetic scheme used to prepare *p*-(*n*-lauryl)-benzyl polyoxyethylene ether carboxybetaine  $C_{12}BE_xCB$  ( $x=0, C_{12}BE_0CB$ ;  $x=1, C_{12}BE_1CB$ ;  $x=2, C_{12}BE_2CB$ ;  $x=3, C_{12}BE_3CB$ ).

surfactants with benzene ring and polyoxyethylene spacers have not been reported systematically.

In earlier works we synthesized and studied the surface behaviors of four zwitterionic surfactants with benzene ring and polyoxyethylene group, *p*-(*n*-lauryl)-benzyl polyoxyethylene ether carboxybetaine  $C_{12}BE_xCB$  ( $x=0, 1, 2, 3$ ) [31]. To detect the nature of adsorption films formed by these specific molecules, the dilational viscoelastic properties at the water–*n*-decane interface have been investigated by a drop shape analysis method in this paper. It may be useful for us to understand the influence of polyoxyethylene spacers on the interfacial behavior of zwitterionic surfactants.

## 2. Experimental

### 2.1. Materials

The novel zwitterionic surfactants, *p*-(*n*-lauryl)-benzyl polyoxyethylene ether carboxybetaine  $C_{12}BE_xCB$  ( $x=0, 1, 2, 3$ ), with different numbers of ethylene oxide groups were synthesized from lauric acid, benzene and polyethylene glycol through several processes, including Friedel–Crafts acylation, Huang–Minlon reduction, chloromethylation, Williamson reaction, halogenation and quaternization reaction. The purity of the compounds was above 98% and checked by FTIR,  $^1H$ NMR, and ESI-MS [31]. The series of zwitterionic surfactants have the same structure except for the spacer length of polyoxyethylene chain. The synthetic scheme of  $C_{12}BE_xCB$  ( $x=0, 1, 2, 3$ ) is shown in Fig. 1. The solutions were prepared with ultrapure water (resistivity > 18.2 M $\Omega$  cm). *n*-decane was obtained from Beijing Xingjin Chemical Co., Ltd., China and used as oil phase, which was purified by further distillation. The value of interfacial tension of *n*-decane against pure water is about 51 mN/m.

### 2.2. Small-amplitude oscillation drop method

In this study, the interfacial dilational viscoelasticity meter DataPhysics OCA20 (DataPhysics Company, Germany) was employed. The working principle is similar to that of Lucassen and Giles [32]. The main elements of the method are dosing system, light source, CCD camera, frame grabber, cuvette with needle for bubble formation. In this device, the interface was created by injecting a known volume of *n*-decane into an inverted stainless steel needle attached to a gastight syringe. The tip of the bent needle is immersed in quartz cuvette containing the surfactant solution. The image of

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