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Surface dilational rheological and foam properties of aromatic side chained N-acyltaurate amphiphiles

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ABSTRACT

The surface dilational rheological behaviors of two anionic surfactants with aromatic group in branch, sodium N-2-(phenoxy)-tetradecanolytaurinate (12+B-T) and sodium N-2-(2-naphthoxy)-tetradecanolytaurinate (12+N-T), were expounded by oscillating bubble method and interfacial tension relaxation method. The foam properties of both surfactants were also investigated by air flowing method. The results show that the adsorption layers of both surfactants behave elastic in nature at low bulk concentration. With increasing concentration, the dilational modulus becomes more frequency dependent and reaches a maximum value. The diffusion-exchange process controls the dynamic dilational properties with increasing bulk concentration for 12+N-T, but not 12+B-T. The possible mechanism has been elucidated and confirmed by the high-frequency-limit value of surface dilational elasticity. The foam stability of 12+N-T is stronger than that of 12+B-T, which indicates that the low frequency elasticity plays a positive effect on foam stability for present systems.

1. Introduction

The interfacial properties of adsorption layer formed by surfactant molecules play a crucial role in several technological processes such as flotation, microfluidics, food production and processing, high-speed coating, *etc.* since they are key factors to determine the stability of foams and emulsions [1–4]. Therefore, understanding and tuning the interfacial properties of a fluid with the aid of soluble amphiphiles is very important [5,6]. The spontaneous adsorption of amphiphiles at the air–water or oil–water interface reduces the surface tension and modifies the interfacial rheology [7]. Dilational rheology based on the thermodynamics and kinetics of the respective adsorption layers is a complementary method to describe a surfactant adsorption layer quantitatively [3]. By employing this method, the dilational properties of surfactant layers have been comprehensively investigated in recent years [8–31], and some focuses were on the correlation between the stability of foam films and surface rheological parameters [16,18,32]. Rao and co-workers studied the effect of binding of sodium dodecyl sulfate (SDS) and oligomeric cationic fluorooxetane surfactants on the dynamic surface tension and dilational rheological properties of adsorbed gelatin-surfactant complexes [8,14]. Bos's group presented an overview of interfacial properties of proteins at mesoscopic scale and the effect of low molecular weight (LMW) surfactants (emulsifiers) on them [2]. Stubenrauch and Miller studied the dilational surface elasticity and viscosity of two nonionic surfactants β-$C_{12}G_2$ and $C_{10}E_4$, and investigated the correlation between the stability of the film and the surface dilational rheological properties of the respective monolayer [18].

As illustrated in the aforementioned literatures, the measurement of dynamic dilational behavior of surface-active molecules adsorbed at the interface had been shown to be a powerful technique to probe interfacial structure of adsorption layer formed by many kinds of protein molecules [33–41]. However, this technique has not been used extensively in LMW surfactant systems due to the dominant fast molecular exchange process between the bulk and the interface for normal surfactant systems [42].

The aromatic side chained amphiphiles have received much attention in recent years because of their high surface activities and good aggregation behaviors. Gin and co-workers studied the lyotropic liquid-crystalline behavior of aromatic side chain-functionalized long chain acid salts and taurine salts [43,44]. However, the dilational properties of such kind of surfactants have not been investigated as far as we know. As illustrated,

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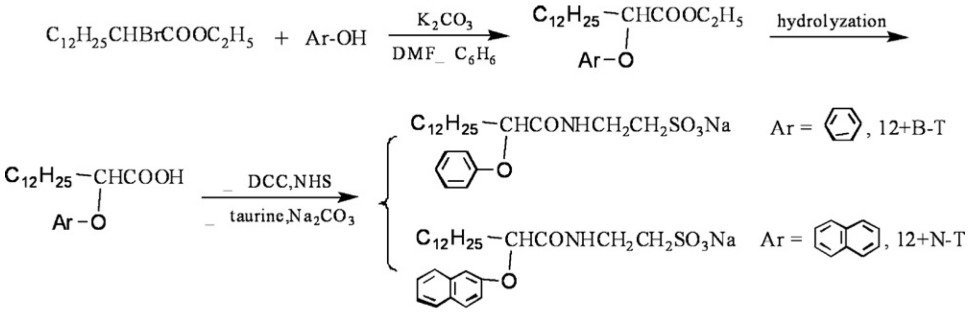

Scheme 1. Synthetic scheme used to prepare 12+B-T and 12+N-T.

monolayers of double-chain surfactants, such as synthetic glycolipids [37] and phospholipids have exhibited strong viscoelastic effects [45] which can be attributed to side-chain condensation in many cases. Therefore, it is expected that surfactants with aromatic nucleus in branches will show stronger surface viscoelastic effects.

In this paper, we presented two novel aromatic side chained N-acyltaurate amphiphiles, sodium N-2-(phenoxy)-tetradecanolytaurinate (12+B-T) and sodium N-2-(2-naphthoxy)-tetradecanolytaurinate (12+N-T) and investigated their dynamic surface tensions and dilational properties by oscillating drop/bubble method. The correlation between the foam properties and surface rheological parameters was discussed. The introducing of aromatic ring to the branches may result in particular adsorption state of surfactant molecule at air–solution interface, which may be useful for our understanding of interfacial behavior of surfactants.

2. Experimental

2.1. Synthesis of 12+B-T and 12+N-T

Two novel aromatic side chained N-acyltaurates were synthesized from ethyl 2-bromomyristate, phenol (or 2-naphthol), and taurine through three processes, Williamson reaction, hydrolyzation and acylation. The synthetic scheme was shown in Scheme 1. The structures and purities were characterized by ^{1}H NMR, ESI-MS and elemental analysis. The contents of the surfactant in the respective products, determined by two-phase titration [46] were above 99%.

2.2. Surface tension and surface dilational rheological measurements

Equilibrium surface tensions were obtained by the Wilhelmy-plate method using a Powereach JK99A tensiometer (Shanghai Zhongchen Digital Technic Apparatus Co. Ltd., China) at 30 °C. Dynamic surface tensions and surface rheological measurements were performed using a commercial bubble tensiometer (The Tracker, IT Concept, France) also at 30 °C. This technique has been outlined elsewhere [47,48].

The air–solution interface was created by injecting a known volume (5 μL) of air into an inverted stainless steel needle attached to an airtight syringe. The tip of the bent needle is immersed in quartz cuvette containing the surfactant solution. A computer-controlled dosing system generates periodical oscillations of the bubble volume at chosen amplitude ($\Delta A/A$). The image of the drop formed at the tip of the needle was captured by a charge-coupled device (CCD) camera and transferred to the data acquisition computer where it was digitized and analyzed by software employing the Laplace equation [7] to obtain the surface tension at the air–solution interface. For dynamic surface tension measurements, the surface tension was monitored as a function of time and the interface was assumed to be equilibrated when the surface tension did not change with time. For surface rheological measurements, the bubble was oscillated with a maximum change of 10% of the original drop volume and the change in the surface was measured as a function of the change in the surface area. The frequency of volumetric oscillations varied from 0.005 to 0.1 Hz and was achieved by translating the piston of the airtight syringe. The four rheological parameters, dilational modulus, phase angle, elasticity and viscosity, of the interfacial layer are obtained from a Fourier analysis of the measured signals.

As originally proposed by Gibbs, the dilational modulus was defined as

$$\varepsilon = \frac{d\gamma}{d\ \ln A} \tag{1}$$

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. Dilational modulus can also be expressed as a complex number and incorporates a real part (storage modulus) representing the elastic energy stored in the interface and an imaginary part (loss modulus) arising from the transport of molecules between the bulk and the interface, which corresponds to the elasticity ε_d and viscosity $\varepsilon_\eta = \omega\eta_d$, respectively [49].

$$\varepsilon = \varepsilon_d + i\omega\eta_d \tag{2}$$

Phase angle θ, describing the phase difference between dynamic interfacial tension variation and interfacial area variation, is calculated according to [16]

$$\tan\theta = \frac{\varepsilon_\eta}{\varepsilon_d} \tag{3}$$

2.3. Interfacial tension relaxation measurements

Interfacial tension relaxation experiments are a reliable way to obtain surface dilational parameters [50]. In this method, the equilibrium of a surface layer is rapidly disturbed by a sudden expansion or compression of the axisymmetric drop area. The adsorption layer was expanded about 10% in area by a sudden expand in 1 s in this paper. This causes an interfacial tension jump and then the interfacial tension will decay to the equilibrium again.

For an instantaneous area change rising from $\Delta A(t) = 0$ for $t \le 0$ to $\Delta A(t) = \Delta A$ for $t > 0$, the values of ε are obtained as a function of the frequency by Fourier transformation (FT) of the interfacial