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Dilational Properties of *N*-Acyltaurates with Aromatic Side Chains at Water−Air and Water−Decane Interfaces

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ABSTRACT: A series of novel surfactants, sodium *N*-2-(alkylphenoxy)-tetradecanolytaurinates (12 + *n*B-T, where 12 means the carbon number of alkyl chain in the main chain and *n* is the carbon number of alkyl chains in the side chain attached to the phenoxyl group, *n* = 0, 2, 6) bearing identical polar groups, were designed and synthesized. The dilational properties of the three surfactants at the water−air and water−decane interfaces were investigated by drop shape analysis. The influences of oscillating frequency and bulk concentration on dilational properties were explored, and the effect of alkyl chain length in the side chain on interfacial behavior has been expounded. The longer alkyl chains in the side chains lead to a higher surface dilational elasticity at low bulk concentrations, owing to strong interaction among the longer hydrophobic alkyl chains. However, at high bulk concentrations, the longer the hydrophobic alkyl chain is, the easier the diffusion-exchange between the bulk and the surface becomes. As a result, the surface dilational elasticity of surfactant with the shortest chain is the highest at a corresponding concentration range. The insertion of oil molecules will reduce interfacial molecular interactions and ease down the diffusion exchange process. Consequently, dilational elasticity decreases at low concentrations and increases at high bulk concentrations, respectively. Moreover, the maximum of dilational viscous components at two types of interfaces is approximately equal for all three surfactants, which may be attributed to the offset between the variation of interfacial molecular interaction and diffusion exchange process.

1. INTRODUCTION

Surfactants with an amphiphilic structure play a crucial role in many technological processes since they can manifest remarkable interfacial activity at air−water or oil−water interfaces. The relationship between the structures and the properties of surfactants is very important for understanding the mechanism of these processes. Most of the studies on surfactant systems aim to understand their adsorption and aggregation behaviors. Equilibrium adsorption data can provide a kind of baseline for the interfacial behavior of a surfactant only; however, the dilational rheology, resulting from the derivative of interfacial tension over adsorption, and this in turn from the derivative of interfacial tension over bulk concentration, is extremely sensitive even to small changes in adsorption layer behavior.

The microcosmic basis of the dilational rheology is a relaxation process at the interface and near the interface. It is conducive to understanding the microcosmic properties of adsorption layer through the research of dilational viscoelasticity. The measurement of interfacial dilational properties is a powerful tool to probe the structure of adsorption film.[1−8] Recently, interfacial dilational properties have been studied extensively due to the availability of commercial instruments.

Since they are quite different from polymers and proteins, traditional surfactants with low molecular weights can exchange between the bulk and the interface easily; therefore, values of the interfacial dilational parameters of surfactants are usually low and can provide little information about the interfacial structure of the film. However, interfacial interactions among surfactant molecules with special structures will be reflected clearly in their dilational properties. For examples, Huang et al. found that the dynamic dilational modulus passed through an obvious maximum with time for hydroxy-substituted alkyl benzene sulfonate solution due to the arrangement of adsorption film.[9] Zhao's group presented the effect of the intermolecular hydrogen bonding on the adsorption and the association by comparing the interfacial rheological behavior of 12-3-12 and 12-3(OH)-12.[10]Zhang and co-workers investigated the anionic gemini $C_8E_xC_8$ and found that the structure of the adsorption sublayer at the aqueous side played a more important role.[11]

N-Acyltaurate surfactants based on taurine have been used in a wide range of surfactant applications, for example, detergents, dishwashing/cleaning products, and cosmetics. They have shown improved performance, favorable ecotoxicological properties, reduced environmental impact, and potential applications in pharmaceutical and biochemical fields.[12−14] During the past several decades, investigations of *N*-acyltaurate surfactants were mainly focused on two typical anionic surfactants: sodium taurocholate (NaTC) series[15,16] and straight-chain sodium-*N*-acyl-*N*-methyl taurate series.[17] However, *N*-acyltaurates with side chains, especially the side chain containing aromatic nucleus homologous ones, have received less attention.[18]

It is very important to study the interfacial dilational properties of surfactants with special structures for our understanding of the nature of interfacial adsorption film. In this paper, dilational viscoelastic properties of a series of sodium *N*-acyltaurate surfactants with aromatic side chains containing alkyl chains with different lengths at air−water and decane−water interfaces were measured by drop-shape analysis of a sessile bubble/drop,

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respectively. The length effect from the alkyl chain of aromatic side chains on the interfacial behavior of this kind of surfactants was investigated and discussed. Being different from traditional surfactants, hydrophobic interactions between the adjoining aromatic side chains from conformational constraints may be a crucial factor in interfacial behaviors for the sodium *N*-2-(alkylphenoxy)-tetradecanolytaurinate (12 + *n*B-T, where 12 means the carbon number of alkyl chain in the main chain and *n* is the carbon number of alkyl chains in the side chain attached to the phenoxyl group, *n* = 0, 2, 6) system. The results derived from this paper may be useful for the understanding of the effect of variations in aromatic side chains on the interfacial behavior of this kind of surfactants and benefit us to better utilize these surfactants in applications.

2. THEORETICAL BACKGROUND

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

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

It gives a measurement 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.[19,20]

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

where ε_d is the dilational elasticity or storage modulus accounting for the recoverable energy stored in the interface and $\varepsilon_\eta = \omega\eta_d$ (ω is the oscillating frequency, η_d is the dilational viscosity) is the dilational viscous component or loss modulus reflecting the loss of energy through any relaxation processes occurring at or near the interface.

The phase angle θ is calculated according to

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

The phase angle reflects the relaxation processes affecting the interfacial dilational modulus, which means that the dilational elasticity ε_d and the dilational viscous component ε_η can also be written as:

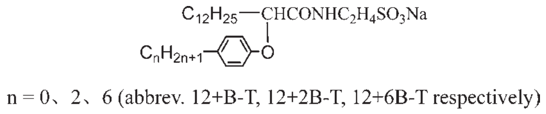
$$\varepsilon_d = |\varepsilon|\cos\theta \tag{4}$$

$$\varepsilon_\eta = |\varepsilon|\sin\theta \tag{5}$$

3. EXPERIMENTAL SECTION

3.1. Materials. Three novel sodium *N*-2-(alkylphenoxy)-tetradecanolytaurinates were a series of homologues, which were synthesized in our laboratory.[21] This series of surfactants bear identical polar groups, differing only by the length in the branched chain (see Scheme 1). The structures and purities were characterized by ^{1}H NMR, electrospray ionization mass spectrometry (ESI-MS), and elemental analysis. The contents of the surfactant in the respective products were determined by two-phase titration and were above 0.99 mass fraction.[22] The critical micelle concentrations (CMCs) of 12 + B-T, 12 + 2B-T, and 12 + 6B-T are $7.4 \cdot 10^{-5}$ mol·L^{-1}, $5.4 \cdot 10^{-5}$ mol·L^{-1}, and $1.5 \cdot 10^{-6}$ mol·L^{-1} at 303 K, respectively. The water used in the experiments was distilled twice from potassium permanganate solution.

Scheme 1. Sodium *N*-2-(Alkylphenoxy)-tetradecanolytaurinates with Different Structures



n = 0, 2, 6 (abbrev. 12 + B-T, 12 + 2B-T, and 2 + 6B-T, respectively).

3.2. 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 elsewhere[9,11] and will be covered here only briefly. The main elements of the method are a dosing system, light source, charge-coupled device (CCD) camera, frame grabber, and cuvette with a needle for bubble formation. The bubble (air or *n*-decane) was formed at the tip of a bent stainless steel needle immersed in a quartz cuvette containing the aqueous surfactant solution to produce the interface. A computer-controlled dosing system allows periodical oscillations of the bubble volume (5 μL) at a chosen amplitude ($\Delta A/A$, 10 %). For dynamic measurements, the surface tension, the modulus, and the viscous phase angle were monitored as a function of time with an oscillating frequency of 0.1 Hz, and the interface was assumed to be equilibrated when the surface tension and the dilational moduli are little changed with time. Then, interfacial rheological measurements were performed with frequency between (0.005 and 0.1) Hz. The measurements of the interfacial tension and the rheological measurements are based on the digital profile of the drop image and the solution of the Gauss–Laplace equation. In the surface tension and interfacial tension ranges of the studied systems, the accuracy of the measurements is of the order of ± 0.1 mN·m^{-1}. The reproducibility of dilational data is ± 1 mN·m^{-1}. All experiments were carried out at 303 ± 0.1 K.

4. RESULTS AND DISCUSSION

4.1. Surface Tension and Interfacial Tension of *N*-Acyltaurates. The surface tension and interfacial tension of sodium *N*-2-(alkylphenoxy)-tetradecanolytaurinates are listed in Table 1. We can see from the table that both the surface tension and the interfacial tension decrease with the increasing bulk concentration and the length of alkyl chain.

4.2. Dilational Properties of 12 + *n*B-Ts at the Air–Water Interface. Dilational rheological properties are the main characteristics of the dynamic properties of an interfacial film or surface. In surfactant systems, when the interface is perturbed, different processes occur, which contribute to the re-equilibration of the system, that is, to the adsorption dynamics. Among

Table 1. Surface Tension and Interfacial Tension of Sodium *N*-2-(Alkylphenoxy)-tetradecanolytaurinates

12 + B-T		12 + 2B-T		12 + 6B-T	
concentration	tension	concentration	tension	concentration	tension
$\text{mol}\cdot\text{L}^{-1}$	$\text{mN}\cdot\text{m}^{-1}$	$\text{mol}\cdot\text{L}^{-1}$	$\text{mN}\cdot\text{m}^{-1}$	$\text{mol}\cdot\text{L}^{-1}$	$\text{mN}\cdot\text{m}^{-1}$
		Surface			
$1\cdot10^{-7}$	61.0	$1\cdot10^{-7}$	62.9	$1\cdot10^{-7}$	59.1
$5\cdot10^{-7}$	64.1	$5\cdot10^{-7}$	62.2	$5\cdot10^{-7}$	53.0
$1\cdot10^{-6}$	61.0	$1\cdot10^{-6}$	60.4	$1\cdot10^{-6}$	45.7
$5\cdot10^{-6}$	61.4	$5\cdot10^{-6}$	52. 3	$5\cdot10^{-6}$	36.6
$1\cdot10^{-5}$	57.6	$1\cdot10^{-5}$	49.3	$1\cdot10^{-5}$	30.7
$5\cdot10^{-5}$	46.2	$5\cdot10^{-5}$	35.9	$3\cdot10^{-5}$	30.8
$7.4\cdot10^{-5}$	40.5				
		Interface			
$1\cdot10^{-7}$	34.7	$1\cdot10^{-7}$	33.3	$1\cdot10^{-7}$	27.7
$5\cdot10^{-7}$	35.2	$5\cdot10^{-7}$	30.0	$5\cdot10^{-7}$	22.3
$1\cdot10^{-6}$	33.0	$1\cdot10^{-6}$	27.4	$1\cdot10^{-6}$	17.1
$5\cdot10^{-6}$	27.7	$5\cdot10^{-6}$	20.7	$5\cdot10^{-6}$	7.9
$1\cdot10^{-5}$	23.6	$1\cdot10^{-5}$	17.3	$1\cdot10^{-5}$	4.5
$5\cdot10^{-5}$	13.4	$5\cdot10^{-5}$	6.3		
$7.4\cdot10^{-5}$	8.2				

the mechanisms involved in the adsorption dynamics, there are diffusions in the bulk phases and kinetic processes inside the adsorbed layer, such as reorientation, aggregation, and other rearrangements of the layer or of the molecular structure.[23] The dilational elasticity originated from the variety of interfacial intermolecular interactions by the change of interfacial area, and the dilational viscous component directly relates to the relaxation processes.

4.2.1. Influence of the Oscillating Frequency on the Dilational Properties of 12 + nB-Ts at the Air—Water Interface. The variation of dilational viscoelasticity with oscillating frequency could reflect the dynamic properties of interfacial adsorption film. To investigate the dependence of the surface dilational properties on frequency, measurements in a range from (0.005 to 0.1) Hz have been carried out. For the sake of brevity, only 12 + B-T surfactant will be discussed; similar behaviors are found for the other surfactants investigated. In Figure 1, data of the dilational elasticity for 12 + B-T solutions at air—water interface are presented. As seen from Figure 1, the dilational elasticity shows almost no frequency dependence at low concentrations, which indicates that the adsorbed layer is predominantly elastic in nature. However, the dilational elasticity increases gradually with increasing dilational frequency at higher bulk concentrations, which means that the dilational properties of the adsorbed layer may be dominated by the exchange of the molecules between the bulk and the interface over the frequency range examined. At low frequencies, the surfactant has enough time to respond to the change in area. Hence, relaxation processes may occur within the layer, and the dilational elasticity becomes small. As the oscillating frequency increases, the restoration of interfacial tension becomes slower as compared with the quick change of interfacial area, leading to a higher interfacial tension gradient. Specifically, the elastic component of the layer increases.[24]

It is generally believed that the dilational viscous component reflects the summation of the various microscopic relaxation processes at and near the interface and different relaxation processes have different characteristic frequencies. The frequency dependence of the dilational viscous component for 12 + B-T solutions at the air—water interface is shown in Figure 2.

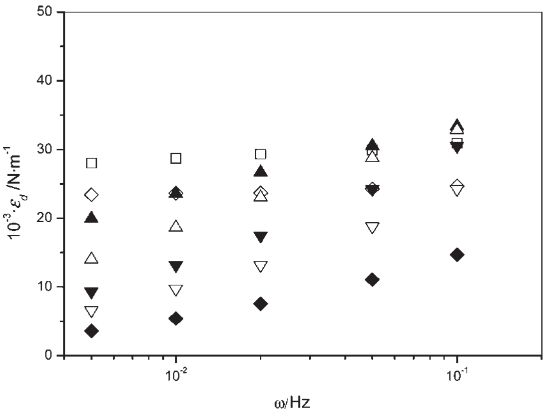


Figure 1. Influence of the oscillating frequency on the dilational elasticity of 12 + B-T at the air—water interface. ($C/\text{mol}\cdot\text{kg}^{-1}$: ■, $5\cdot10^{-7}$; □, $1\cdot10^{-6}$; ▲, $5\cdot10^{-6}$; △, $1\cdot10^{-5}$; ▼, $5\cdot10^{-5}$; ▽, $7.4\cdot10^{-5}$; ◆, $1.5\cdot10^{-4}$).

As can be seen from Figure 2, an obvious difference arises between the different concentration regions: at low concentrations, the dilational viscous component decreases monotonically with frequency, whereas the opposite tendency is observed at high concentrations. At low concentrations, it is likely that the relaxation processes detected at this point are related to the in-interface slow relaxation process, such as molecular rearrangements involving the whole interfacial film. Thus, the experimental frequencies may be higher than the characteristic frequency of the relaxation processes; that is to say, the maximum of the dilational viscous component with frequency should occur at a lower frequency than the experimental frequencies. A further

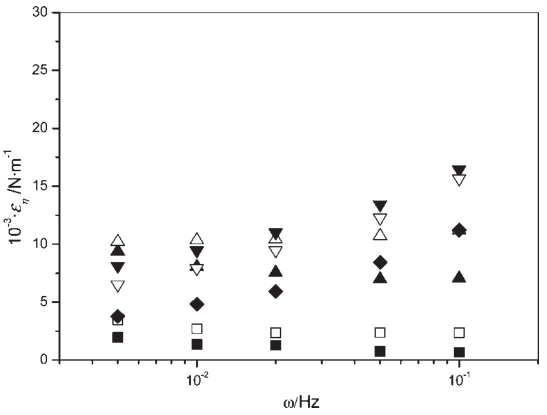


Figure 2. Influence of the oscillating frequency on the dilational viscous component of 12 + B-T at the air–water interface (C/mol·kg^{-1}: ■, $5\cdot10^{-7}$; □, $1\cdot10^{-6}$; ▲, $5\cdot10^{-6}$; △, $1\cdot10^{-5}$; ▼, $5\cdot10^{-5}$; △, $7.4\cdot10^{-5}$; ◆, $1.5\cdot10^{-4}$).

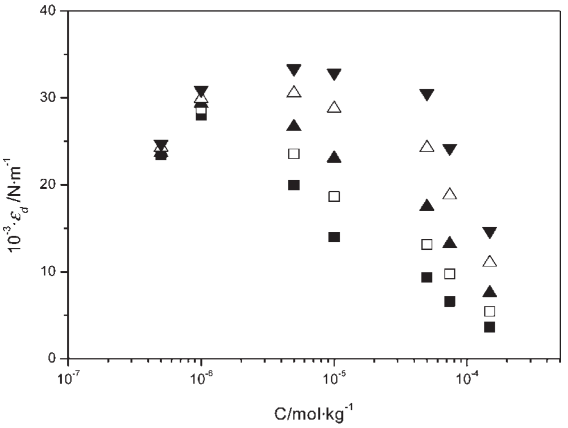


Figure 3. Influence of bulk concentration on the dilational elasticity of 12 + B-T at the air–water interface (frequency/Hz: ■, $5\cdot10^{-3}$; □, $1\cdot10^{-2}$; ▲, $2\cdot10^{-2}$; △, $5\cdot10^{-2}$; ▼, $1\cdot10^{-1}$).

increase in the concentration causes the enhancement of molecular exchange between the bulk and the surface. The characteristic frequencies of the relaxation processes are expected to be higher than the maximum frequency accessible in our lab.

4.2.2. Influence of the Bulk Concentration on the Dilational Properties of 12 + nB-Ts at the Air–Water Interface. The concentration dependency of dilational elasticity for 12 + B-T solutions at the air–water interface is presented in Figure 3. The surface dilational elasticity runs through a maximum with increasing concentration for all surfactant solutions.

In general, an increase of the surface concentration would lead to strong intermolecular interactions, which result in an increase in the dilational elasticity. At the same time, an increase of bulk concentration would produce an increase in the molecular exchange between the bulk and the surface. With the diffusion of surfactant molecules from the bulk to the interface, the interfacial tension gradient can go down, which creates a decrease in the dilational elasticity. Thus, it is the increasing surface concentration at low surfactant concentrations, while it is the molecular exchange at high surfactant concentrations that may play a dominant role in determining the ε_d. This "crossover" is mirrored in a maximum of the ε_d (c) curve.[25] Moreover, at high concentrations the surface tension gradient is evened out immediately, especially when the micelles exist in the layer close to the interface, which makes the dilational elasticity decrease significantly.

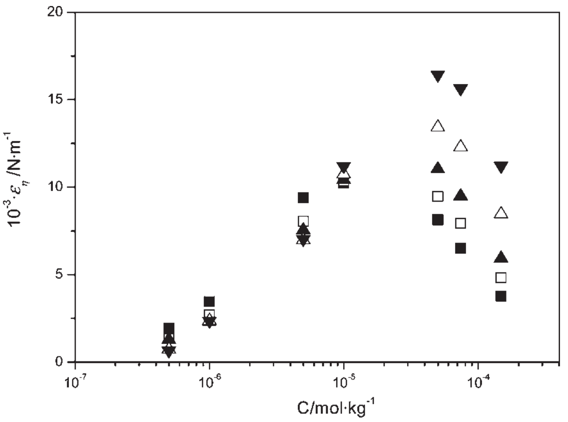


Figure 4. Influence of bulk concentration on the dilational viscous component of 12 + B-T at the air–water interface (frequency/Hz: ■, $5\cdot10^{-3}$; □, $1\cdot10^{-2}$; ▲, $2\cdot10^{-2}$; △, $5\cdot10^{-2}$; ▼, $1\cdot10^{-1}$).

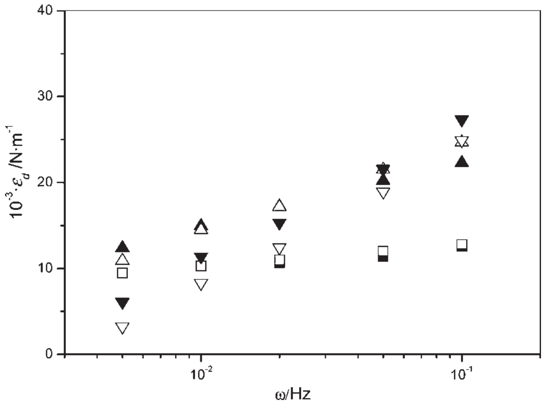


Figure 5. Influence of the oscillating frequency on the dilational elasticity of 12 + B-T at the decane–water interface (C/mol·kg^{-1}: ■, $5\cdot10^{-7}$; □, $1\cdot10^{-6}$; ▲, $5\cdot10^{-6}$; △, $1\cdot10^{-5}$; ▼, $5\cdot10^{-5}$; ▽, $7.4\cdot10^{-5}$).

Similarly, the dilational viscous component of the layer formed at the air–water interface also reaches a maximum. This phenomenon can be explained through two aspects from the analysis of the influence of surfactant bulk concentration on the dilational viscous component (see Figure 4). On one hand, the surface concentration increases with an increase of the bulk concentration, which, in turn, leads to a higher dilational viscous component and the more relaxation processes. On the other hand, an increase in the bulk concentration gives rise to a decrease in the interfacial tension gradient, which may cause a decrease in the total dilational modulus and in the dilational viscous component. As the surfactant concentration increases up to a certain extent, the number of microscopic relaxation processes remains stable, and their contributions to dilational viscous component do not increase remarkably. Therefore, the dilational viscous component may reach a maximum with increasing concentration.

4.3. Dilational Properties of 12 + *n*B-Ts at the Decane–Water Interface. *4.3.1. Influence of the Oscillating Frequency on Dilational Properties of 12 + nB-Ts at the Decane–Water Interface.* We also investigated the influence of oscillating frequency

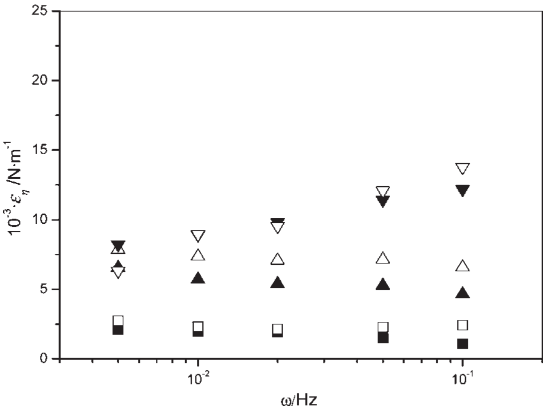


Figure 6. Influence of the oscillating frequency on the dilational viscous component of 12 + B-T at the decane−water interface (C/mol·kg^{-1}: ■, 5·10^{-7}; □, 1·10^{-6}; ▲, 5·10^{-6}; △, 1·10^{-5}; ▼, 5·10^{-5}; ▽, 7.4·10^{-5}).

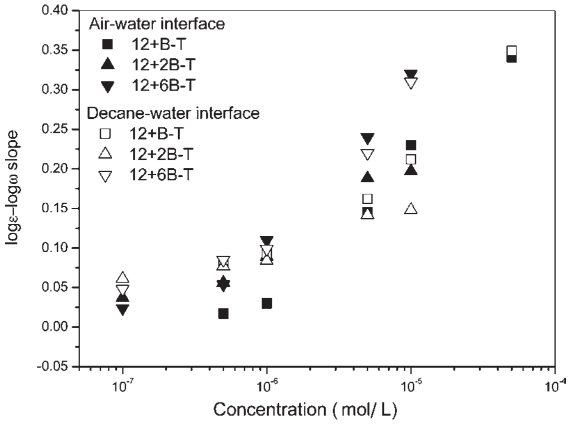


Figure 7. Influence of bulk concentration on the slope of log ε versus log ω at air−water and decane−water interfaces (air−water interface: ■, 12 + B-T; ▲, 12 + 2B-T; ▼, 12 + 6B-T; decane−water interface: □, 12 + B-T; △, 12 + 2B-T; ▽, 12 + 6B-T).

on the interfacial dilational properties of 12 + nB-Ts at the decane−water interface, and the results of 12 + B-T are summarized in Figures 5 and 6, respectively. The frequency dependency of 12 + nB-Ts at the decane−water interface is similar to that of the air−water interface. At first sight, the dilational properties of 12 + B-T show the same general trend in its frequency dependence at both interfaces. However, there are differences owing to the nature of the adhering phases.

As is known, if the characteristic frequency of the relaxation process at the interfacial layer exceeds the highest oscillating frequency used in this experiment, the curves of log ε versus log ω are almost quasi-linear, and the lower the slope is, the more elastic the film appears. For comparison, the influence of bulk concentration on the slope of log ε versus log ω at the air−water and decane−water interfaces is shown in Figure 7. At low concentrations, the slopes of decane−water interfaces are apparently higher than those of air−water interfaces for all three surfactants. However, the slopes of decane−water interfaces are almost equal to or slightly lower than those of air−water interfaces at high concentration. We will come back to this point in Section 4.4.

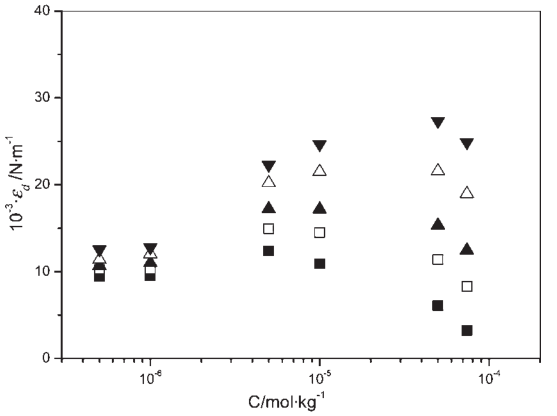


Figure 8. Influence of bulk concentration on the dilational elasticity of 12 + B-T at the decane−water interface (frequency/Hz: ■, 5·10^{-3}; □, 1·10^{-2}; ▲, 2·10^{-2}; △, 5·10^{-2}; ▼, 1·10^{-1}).

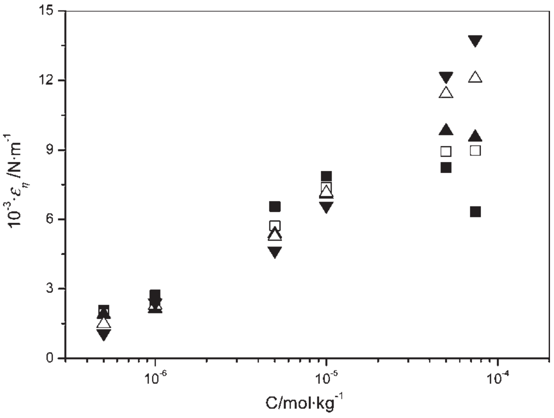


Figure 9. Influence of bulk concentration on the dilational viscous component of 12 + B-T at the decane−water interface (grequency/Hz: ■, 5·10^{-3}; □, 1·10^{-2}; ▲, 2·10^{-2}; △, 5·10^{-2}; ▼, 1·10^{-1}).

4.3.2. Influence of the Bulk Concentration on the Dilational Properties of 12 + nB-Ts at the Decane−Water Interface. Figures 8 and 9 illustrate the influence of bulk concentration on the dilational properties of 12 + B-Ts at the decane−water interface. The concentration dependency of dilational elasticity at the decane−water interface is similar to the air−water interface, which runs through a maximum with increasing concentration (Figure 8). The dilational viscous component at the decane−water interface increases monotonously with increasing concentration, except at 0.005 Hz, due to the narrow experimental concentration range (Figure 9).

4.4. Comparison of the Dilational Properties for 12 + *n*B-Ts between the Air−Water Interface and the Decane−Water Interface. To clarify the differences between dilational properties at the air−water and decane−water interfaces, the concentration dependence of dilational properties at both interfaces has been replotted in Figures 10 and 11.

We will first address the elastic behavior of the interfacial layer. The surface dilational elasticity of a surfactant with a long branched-chain is larger than that with a shorter branched-chain at low concentrations, whereas the tendency is opposite at high surfactant concentrations (see Figure 10A). For 12 + nB-Ts, the hydrophilic groups (−CONHC$_2$H$_4$SO$_3$) intervene the aqueous

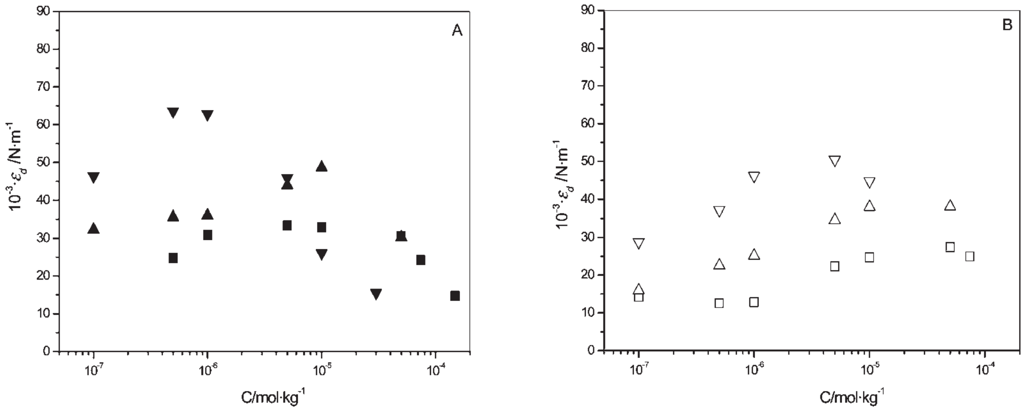


Figure 10. Dependence of dilational elasticity on the bulk concentration at a fixed oscillating frequency of 0.1 Hz (air—water interface: ■, 12 + B-T; ▲, 12 + 2B-T; ▼, 12 + 6B-T; decane—water interface: □, 12 + B-T; △, 12 + 2B-T; ▽, 12 + 6B-T).

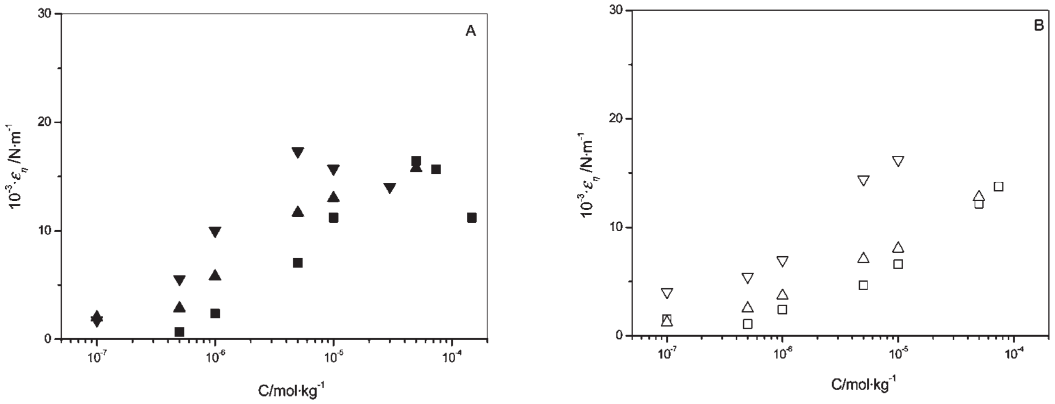


Figure 11. Dependence of dilational viscous component on the bulk concentration at a fixed oscillating frequency of 0.1 Hz (air—water interface: ■, 12 + B-T; ▲, 12 + 2B-T; ▼, 12 + 6B-T; decane—water interface: □, 12 + B-T; △, 12 + 2B-T; ▽, 12 + 6B-T).

bulk and long-alkyl ($-C_{12}H_{25}$) and phenyls ($-C_6H_4-O-C_nH_{2n+1}$) orient predominantly toward the air. At low concentrations, the dilational elasticity depends on the intermolecular interactions owing to the surfactant molecules distributed loosely on the surface. The dilational elasticity increases because of the enhancement of hydrophobic interaction with increasing hydrophobic chain length. Upon increasing the concentration, the surfactant molecules would pack more closely at surface and result in the increase of molecular exchange between the bulk and the surface. Surfactants with longer hydrophobic chains form a more compact state of the hydrophobic chains at the surface, which is more difficult to resist surface deformation by contracting/stretching themselves at the surface. That is to say, at high concentrations, the surfactant with longer hydrophobic chains desorbs from the surface more easily upon compressions. The longer the hydrophobic chain is, the easier the diffusion-exchange becomes, leading to an obvious decrease in the dilational elasticity. Consequently, at high concentrations, the dilational elasticity of the 12 + B-T layer is the highest, while that of 12 + 6B-T is the lowest.

Comparing the data of the dilational elasticity at the two interfaces, it can be found that the dilational elasticity at the decane—water interface is smaller than that at the air—water interface. Moreover, it is very interesting that the maximum of the $\varepsilon_d(c)$ curve is slightly shifted toward higher concentrations at the decane—water interface. This is due to the fact that the hydrophobic chains and the oil molecules have a similar nature. The hydrophobic chains can penetrate into the oil phase and result in the decrease of occupied surface area by surfactant molecules themselves and the van der Waals interactions.[26] In the case of low concentrations, the dilational property is mainly controlled by the interactions between hydrophobic alkyl chains of adsorbed molecules. The insertion of oil molecules will weaken the intermolecular interactions dramatically and speed up the diffusion exchange process between the bulk and the interface. That is the reason that dilational elasticity and the dependence of frequency go up as the results of slope of log ε versus log ω in Figure 7. However, at high concentrations, the film formed at the decane—water interface appears more resistant than that at the air—water interface. This could be related to the presence of relative stronger interactions between the hydrophobic chains and the oil phase than those with air, which leads to the tendency of staying at the interface for surfactant molecules and the slower diffusion-exchange process. Within this region, the molecular exchange determines the dilational properties. Accordingly, the dilational elasticity will increase, and the slope of log ε versus log ω will also grow slightly when the water—oil interface displaces the air—water interface.

Let us now discuss the viscosity of the interfacial layers formed at the air—water and decane-—water interfaces shown in Figure 11. It goes without saying that experiments at higher concentrations are needed to complete the picture. Note that obvious differences arise between the dilational elasticity and the dilational viscous component. The maximum of dilational elasticity increases with increasing hydrophobic chain length at air—water and decane—water interfaces, while similar maximum values of the dilational viscous component can be observed at both interfaces for three surfactants. At low concentrations, the dilational viscous component increases with increasing hydrophobic chain length originating from the contribution of molecular rearrangement to viscosity due to the enhanced reorientation change of the hydrophobic chains. However, in the case of high concentrations, an increased diffusion exchange process may offset the abovementioned interactions for longer hydrophobic chains. In similar cases, the insertion of oil molecules into the interfacial adsorption layer will induce the decrease of contribution of molecular rearrangement to viscosity, which may be offset by the easedown of diffusion exchange process. As a result, the maximum of the dilational viscous component at two types of interfaces are approximately equal. Moreover, the maximum of the ε_η curve slightly shifts toward higher concentrations at the decane—water interface, which indicates that the existence of oil phase reduces the diffusion-exchange process as outlined above.

5. CONCLUSIONS

In this paper, the dilational properties of a series of novel surfactants, sodium *N*-2-(alkylphenoxy)-tetradecanolytaurinates, at the water—air and water—decane interfaces were investigated by drop-shape analysis. For the air—water interface, the dilational elasticity of 12 + *n*B-Ts increases dramatically with increasing the length of hydrophobic chain at low bulk concentrations, owing to strong interactions among the longer hydrophobic chains. However, the opposite trend was observed at high surfactant concentrations. The longer the hydrophobic chain is, the easier the diffusion-exchange becomes, which leads to the highest dilational elasticity for the 12 + B-T layer. At the decane—water interface, the insertion of oil molecules has an obvious effect on interfacial molecular interactions; therefore, the dilational elasticity of 12 + *n*B-Ts is characterized by lower values. On the other hand, the maximum of the dilational viscous component at two types of interfaces is approximately equal for all three surfactants, which may be attributed to the offset between the variation of interfacial molecular interaction and diffusion exchange process. Moreover, the maxima of the ε_d and ε_η curves are slightly shifted toward higher concentrations at the decane—water interface compared with the water—air interface. This could be related to the presence of relative stronger interactions between the hydrophobic chains and the oil phase than those with air and consequently a slower diffusion-exchange process. By comparing the dilational properties at the air—water and decane—water interfaces, we can obviously find that the presence of the aromatic side chains plays different roles in affecting the nature of adsorption film depending on the interfacial concentration and oil phase. This can be useful for our understanding of interfacial behavior of surfactant adsorption film, allowing the development of specific applications in future.

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