

Dynamic Interfacial Dilational Properties of Hydroxy-Substituted Alkyl Benzenesulfonates

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Synthesis, characterization, and interfacial properties of hydroxy-substituted alkyl benzenesulfonates, sodium 2-hydroxy-3-decyl-5-octylbenzenesulfonate ($C_{10}C_8OHphSO_3Na$) and 2-hydroxy-3-octyl-5-decylbenzenesulfonate ($C_8C_{10}OHphSO_3Na$), are reported. The dynamic dilational properties of the surfactants are expounded by means of oscillating the bubble/drop method at both water–air and water–decane interfaces. The distinct maxima appear in dilational modulus vs time curves in some cases, which is believed to be attributed to the change of surfactant conformation and the arrangement of surface layer. Our results show that the measurement of dynamic interfacial dilational properties is a powerful tool to probe the structure of the surfactant adsorption film.

1. Introduction

The interfacial properties of the adsorption film formed by surfactant molecules, which are very important for controlling the stability of foams and emulsions, play a crucial role in several technological processes, such as flotation, food production and processing, detergency, etc.^{1,2} The rheological interfacial properties of surfactant solution can provide more accurate information about the structure of adsorption layers. While shear rheology yields only qualitative structure information, dilational rheology is based on the thermodynamics and kinetics of the respective adsorption layers and is hence a complementary method to describe a surfactant adsorption layer quantitatively.³ Therefore, the dynamic dilational properties of surfactant layers have been comprehensively investigated in recent years.^{4–27} However, our knowledge about the interfacial behavior of surfactant molecules is still limited especially at liquid–liquid interface due to the lack of both research methods and experimental data.

By employing modern video recording equipment and automated image-analysis software, pendant-drop dynamic tensiometry is now a robust and routine technique capable of researching dynamic dilational properties starting a few seconds after drop formation.^{21,28–30} Dilational measurements can be performed both during the adsorption process at a given concentration, i.e., the modulus was measured as a function of the interfacial age, and on equilibrated solutions at various concentrations.

The measurement of dynamic dilational behavior of surface-active molecules adsorbed at the interface has been proven to be a powerful technique to probe the interfacial structure of film formed by many kinds of protein molecules;^{31–39} however, this technique has not been employed to surfactant systems extensively due to the lack of characteristic dynamic dilational behavior for normal surfactant molecules.⁴⁰ In this paper, we

design and synthesize two novel hydroxy-substituted alkyl benzenesulfonates, sodium 2-hydroxy-3-octyl-5-decylbenzenesulfonate ($C_8C_{10}OHphSO_3Na$) and sodium 2-hydroxy-3-decyl-5-octylbenzenesulfonate ($C_{10}C_8OHphSO_3Na$), and investigate their dynamic interfacial tension and dilatational properties by using the oscillating bubble/drop method. The introduction of hydroxy to the alkyl benzenesulfonate molecule results in a particular adsorption state of the surfactant molecule at both gas–water and decane–water interfaces, which may be useful for our understanding of the interfacial behavior of surfactants.

2. Experimental Section

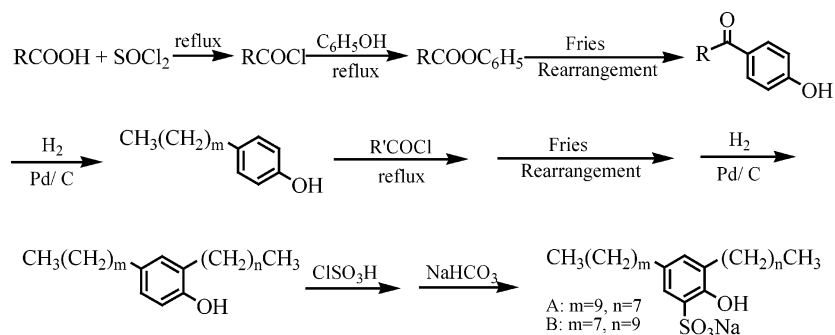
Synthesis of $C_8C_{10}OHphSO_3Na$ and $C_{10}C_8OHphSO_3Na$. $C_8C_{10}OHphSO_3Na$ and $C_{10}C_8OHphSO_3Na$ are synthesized from phenol through several processes, including Friedel–Crafts acylation, esterification, Fries rearrangement, Pd-catalyzed hydrogenation, sulfonation, neutralization, etc.⁴¹ The synthetic scheme is shown in Scheme 1. Further details on the synthesis can be found in the Supporting Information. The structures are characterized by ¹H NMR and ESI-MS methods. The contents of the surfactant in the respective product, determined by two-phase titration,⁴² are above 99%.

Surface Tension and Interfacial Dilational Rheological Measurements. Surface tension and interfacial rheological measurements are performed with use of a commercial bubble profile tensiometer (Tracker, IT Concept, France). This technique has been outlined elsewhere.^{43,44} The main elements of the method are a dosing system, a light source, CCD camera, a frame grabber, and a cuvette with a needle for bubble formation. The interface is created by injecting air or decane into an inversed stainless steel needle attached to a gas-tight syringe. The tip of the bent needle is immersed in a quartz cuvette containing the surfactant solution. A computer-controlled dosing system generates periodical oscillations of the bubble volume (5 μ L) at chosen amplitude ($\Delta A/A$, 10%) in a frequency range from 0.002 to 0.1 Hz. The image of the bubble is recorded by the CCD camera and digitized to allow the analysis of its shape by fitting the

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SCHEME 1: Synthetic Scheme Used To Prepare C₈C₁₀OHphSO₃Na and C₁₀C₈OHphSO₃Na

Laplace equation to its coordinates. 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

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

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. Dilational modulus (or viscoelastic 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 due to the transport of molecules between the bulk and the interface, which corresponds to the elasticity ϵ_d and viscosity $\epsilon_\eta = \omega\eta_d$, respectively.⁴⁵

$$\epsilon = \epsilon_d + i\omega\eta_d \quad (2)$$

The phase angle θ describing the phase difference between dynamic interfacial tension variation and interfacial area variation is calculated according to¹²

$$\tan \theta = \frac{\epsilon_\eta}{\epsilon_d} \quad (3)$$

Interfacial Tension Relaxation Measurement. Interfacial tension relaxation experiments are a reliable way to obtain surface dilational parameters.⁴⁶ This technique uses small but fast axisymmetric drop area expansion or compression to slightly disturb the monolayer equilibrium. 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 $t \leq 0$ 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 tension decay obtained from the experiment by the following relationship:^{47–49}

$$\epsilon(\omega) = \frac{FT\Delta\gamma(t)}{FT(\Delta A/A)(t)} = \frac{\int_0^\infty \Delta\gamma(t) \exp(-i\omega t) dt}{\int_0^\infty [\Delta A(t)/A] \exp(-i\omega t) dt} \quad (4)$$

where ω is the angular frequency. In an ideal system that is not diffusion controlled and in which only one relaxation mechanism occurs the decay curve of γ vs t can be represented by an exponential equation.

For a real system a number of relaxation processes may occur and the decay curve would be expressed by the summation of a number of exponential functions:^{50,51}

$$\Delta\gamma(t) = \sum_{i=1}^n A_i \exp(-\tau_i t) \quad (5)$$

where τ_i is the characteristic frequency of the i th process; A_i is the fractional contribution which that relaxation process makes to restore the equilibrium; and n is the total number of relaxation processes.

Experimental Procedure. Dilational measurements had been performed during the adsorption process at a given concentration, i.e., the modulus was measured as a function of the interfacial age.³¹ The formation of a drop or bubble in this instrument takes only a few seconds, after which the measurement of the modulus can start within 10 s. An extra regulation mode of the software allows us to superimpose the area oscillations on the transient changes in area of a bubble or drop in the course of the adsorption process. Thus, we can simultaneously measure the dynamic interfacial tension, the modulus, and the viscous phase angle from the early stages of the adsorption process until the attainment of near equilibrium, when the rate of change in tension decreases substantially. Then, we can carry out the interfacial tension relaxation measurement (the film was expanded about 10% in area by a sudden expansion in 1 s). Figure 1 shows the typical time course of the surface tension during surfactant adsorption when the area of the bubble/drop is submitted to a sinewave area deformation. All the measurements are performed at a controlled temperature of 30 ± 0.1 °C.

3. Results and Discussion

Surface Properties of C₈C₁₀OHphSO₃Na and C₁₀C₈OHphSO₃Na. The static surface tensions, γ (mN/m), of C₈C₁₀OHphSO₃Na and C₁₀C₈OHphSO₃Na in pure water vs $\log C$ (mol/L) are presented in Figure 2. As shown in Table 1, the CMC of the surfactants, which are taken as the concentration at the point of intersection of the two linear portions of the γ – $\log C$ plot, are 3.35×10^{-6} and 1.35×10^{-6} mol/L for C₈C₁₀OHphSO₃Na and C₁₀C₈OHphSO₃Na, respectively. The A_{\min} value of C₈C₁₀OHphSO₃Na is a little larger than that of C₁₀C₈OHphSO₃Na, while their γ_{CMC} values are approximately equal.

Dynamic Surface Tension and Dilational Properties of C₁₀C₈OHphSO₃Na. Dynamic surface tension measurements of C₁₀C₈OHphSO₃Na at the air–water interface are shown in Figure 3. It can be seen that the surface tension keeps a high constant value for a long period at all concentrations at first and takes 10^4 s to arrive at equilibrium at low bulk concentration (5×10^{-7} mol/L), which indicates the diffusion–adsorption

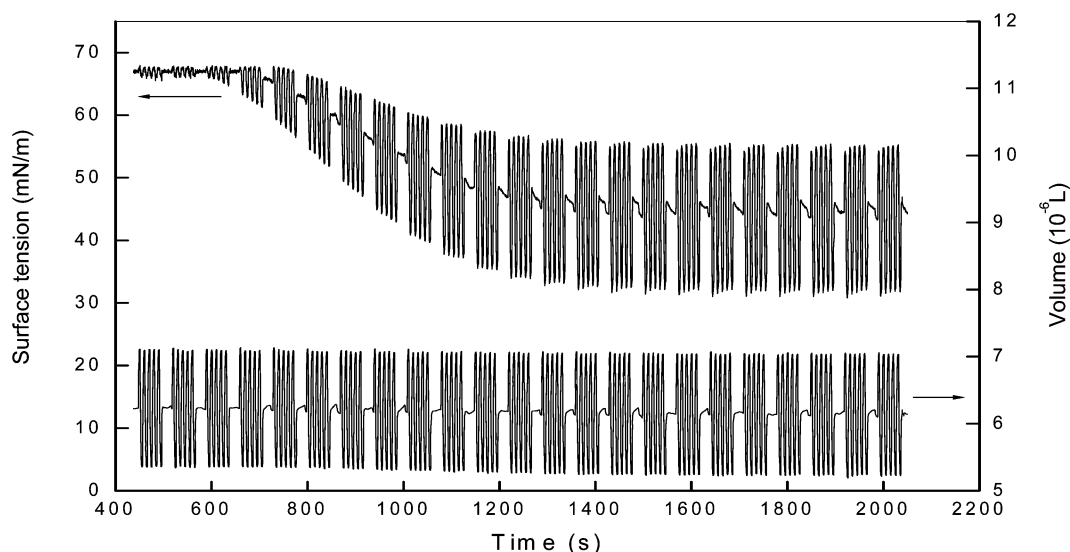


Figure 1. Time course of the surface tension during surfactant adsorption when the area of the bubble/drop is submitted to a sinewave area deformation (frequency 0.1 Hz).

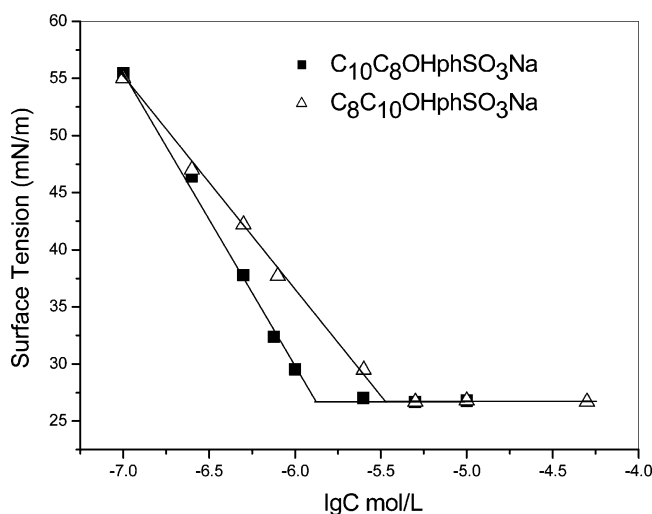


Figure 2. Plot of static surface tension versus log of the bulk-phase concentration for $C_8C_{10}OHphSO_3Na$ and $C_{10}C_8OHphSO_3Na$ at 30 °C.

TABLE 1: The CMC, A_{min} , and γ_{CMC} of $C_8C_{10}OHphSO_3Na$ and $C_{10}C_8OHphSO_3Na$ at 30 °C

parameters	$C_8C_{10}OHphSO_3Na$	$C_{10}C_8OHphSO_3Na$
CMC ($\times 10^{-6}$ mol/L)	3.35	1.35
A_{min} (nm ²)	1.06	0.73
γ_{CMC} (mN/m)	27.1	26.9

process is much slower than that of normal surfactants such as alkyl benzenesulfonates. Although surface tension measurements at very dilute surfactant concentrations can contain contributions from surface-active impurities present in the solution and should be interpreted with caution,⁴ our results show that surface tension still keeps a high constant value for several hundreds of seconds first and takes 10^3 s to arrive at equilibrium even at bulk concentrations higher than CMC, which indicates the adsorption mechanism of surfactant molecules at the air–water interface is not a diffusion-limited process. The particular dynamic surface tension behavior of $C_{10}C_8OHphSO_3Na$ may be attributed to the formation of long-range structure through hydrogen bond interaction between the surfactant molecule and the H_2O molecule, which will be discussed in detail below.

Dynamic interfacial dilational rheology measurements have been proved to be diagnostic of protein conformational stability at an interface, while adsorption amounts alone are clearly not

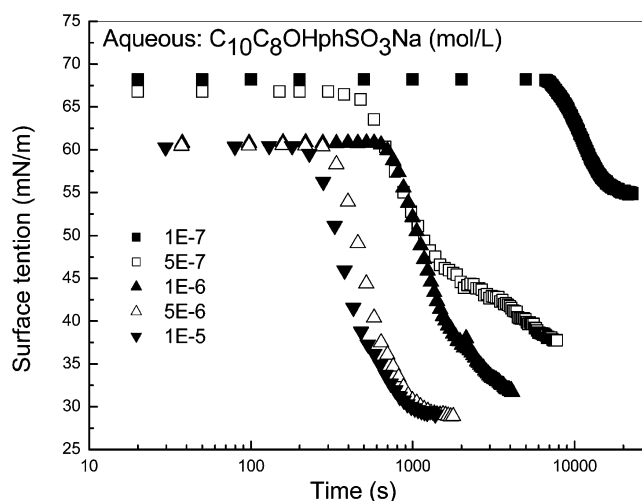


Figure 3. Dynamic surface tension of $C_{10}C_8OHphSO_3Na$ solutions at 30 °C.

sensitive to the structural state of adsorbed proteins.⁵² The dynamic surface dilational properties of $C_{10}C_8OHphSO_3Na$ solutions are shown in Figure 4. In the case of low bulk concentration (1×10^{-7} and 5×10^{-7} mol/L), the dilational modulus, dilational elasticity, and dilational viscosity remain almost zero at first, then increase when surface tensions start to reduce and finally plateau, which is accordant to the variation of surface tension with surface aging. The phase angle keeps a low constant value near zero during the experimental time scale while the dilational modulus increases up to about 100 mN/m. These results indicate that the interfacial surfactant concentration is the key factor to dominate dilational properties and the adsorption film is elastic in nature. On the other hand, it is especially interesting that the dilational modulus and dilational elasticity pass through a sharp maximum with surface aging while the dilational viscosity and phase angle increase monotonously in the case of high bulk concentration (higher than 5×10^{-7} mol/L). The dilational elasticities at short adsorption times have a value of about 20 mN/m and the corresponding surface tensions in Figure 3 are about 60 mN/m, which indicate that the surface may not be sufficiently fresh at the beginning. However, this phenomenon has little effect on the experimental results and our discussions.

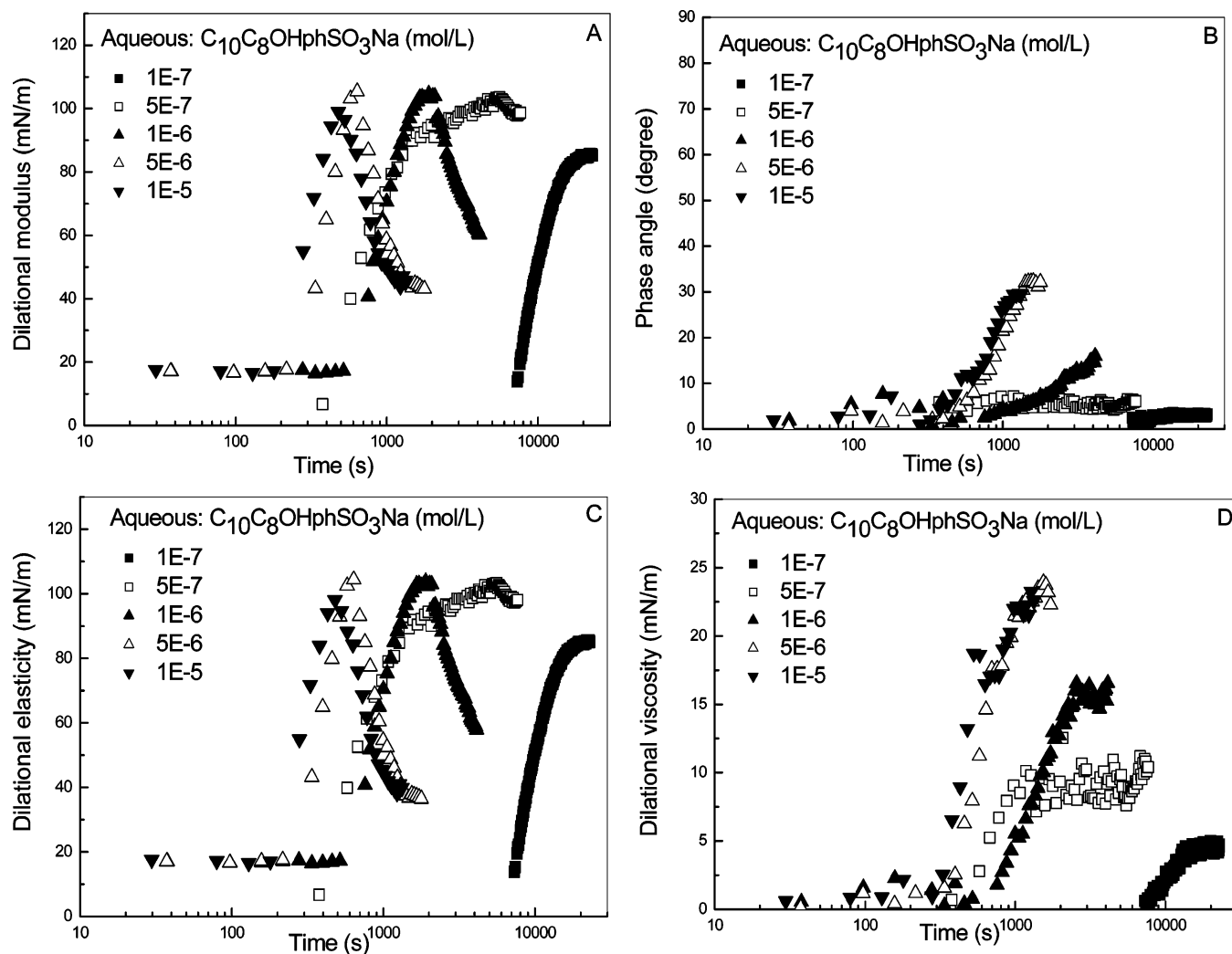


Figure 4. Surface dilational properties of $C_{10}C_8OHphSO_3Na$ solutions as a function of time at 30 °C. Shown are the dilational modulus (A), phase angle (B), dilational elasticity (C), and dilational viscosity (D).

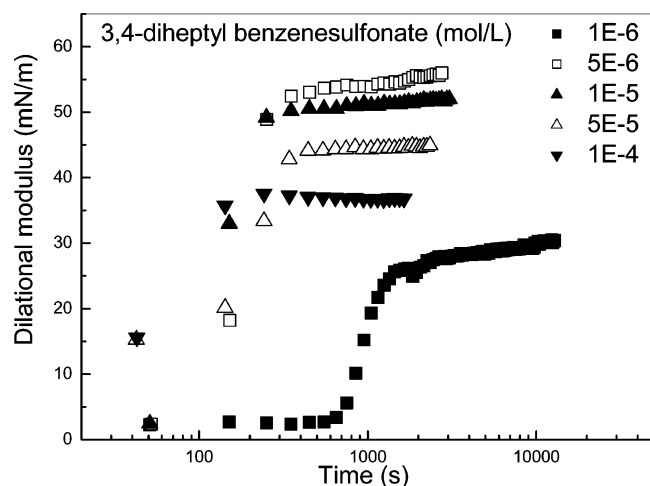


Figure 5. Dynamic surface dilational modulus of 3,4-diheptylbenzenesulfonate at 30 °C.

It has been pointed out that the rearrangement of the adsorbed protein molecule into a more unfolded and flexible conformation plays the key role for the maximum in dilational modulus vs time curve. As the adsorbed protein layer relaxes to a less compact configuration, its intrinsic intraprotein rigidity weakens, and the dilational modulus and dilational elasticity fall with time.⁵² The orientation or aggregation behavior of surfactant

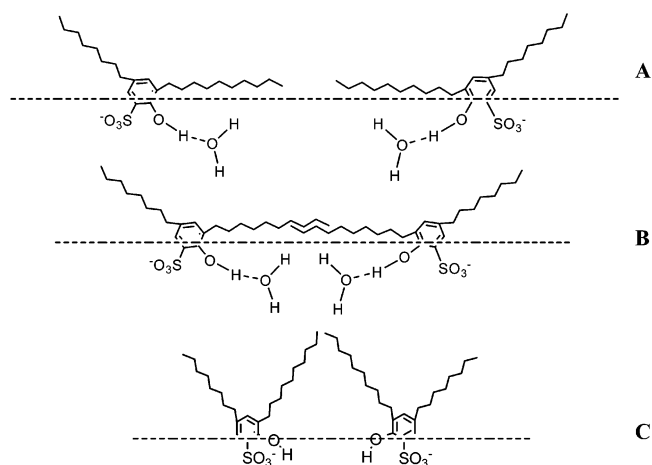


Figure 6. Schematic of adsorbed $C_{10}C_8OHphSO_3Na$ molecules at the air-water interface low surface concentration (A), medial surface concentration (B), and high surface concentration (C).

molecules at the interface have been discussed by some authors based on surface tension data and the thermodynamic adsorption model.^{53–57} However, for the surfactant with low molecular weight, the dilational modulus generally increases with time and finally arrives at a plateau due to the diffusion-limited process. We have investigated dynamic dilational properties of several kinds of alkyl benzenesulfonates with different straight

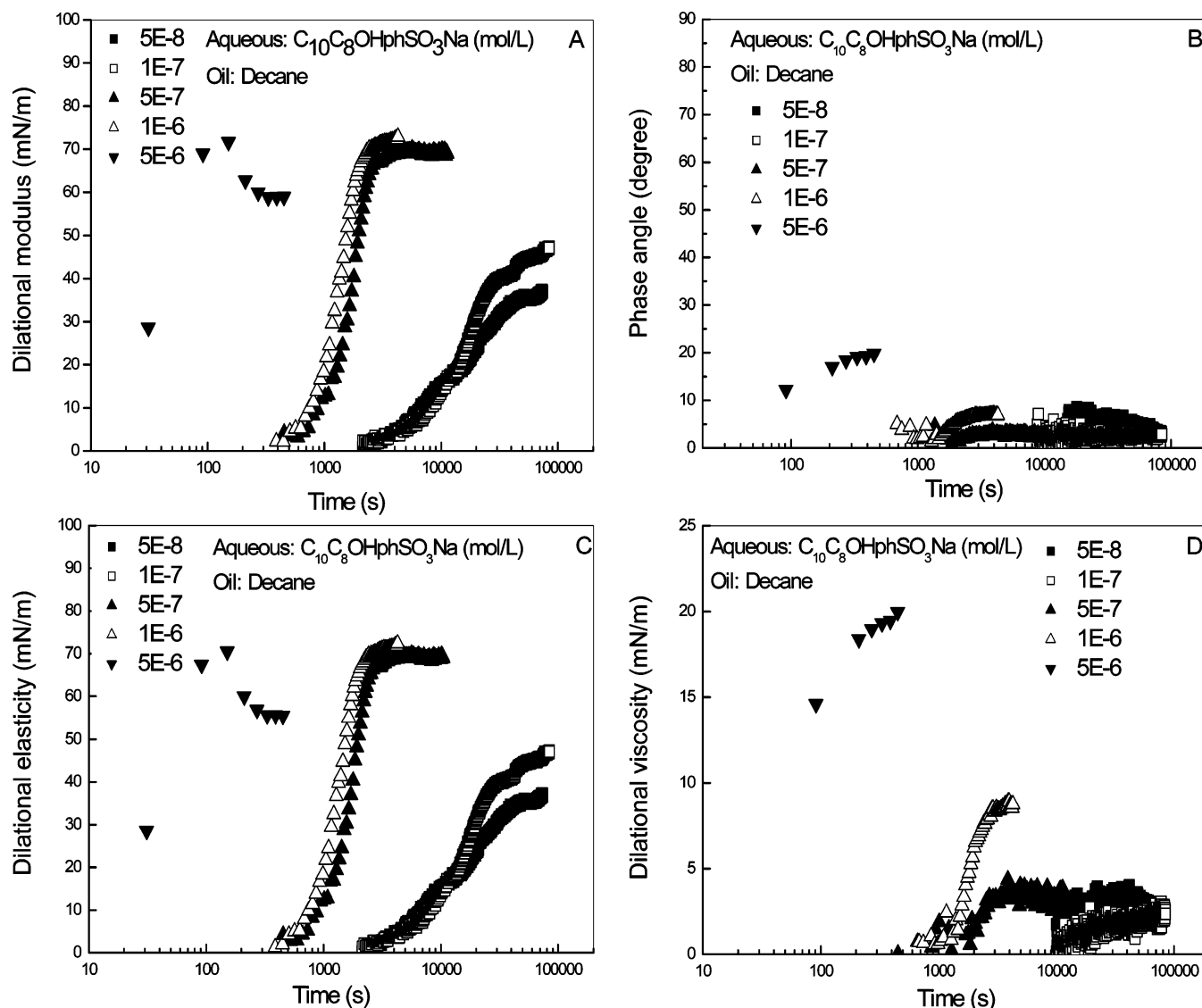


Figure 7. Dynamic interfacial dilational properties of $\text{C}_{10}\text{C}_8\text{OHphSO}_3\text{Na}$ solutions at 30 °C. Shown are the dilational modulus (A), phase angle (B), dilational elasticity (C), and dilational viscosity (D).

alkyl chains or branched alkyl chains. A typical result for 3,4-diheptylbenzenesulfonate, which is similar to $\text{C}_{10}\text{C}_8\text{OHphSO}_3\text{Na}$ in its hydrophobic part, is shown in Figure 5. Therefore, our results indicate strongly that the adsorption states of $\text{C}_{10}\text{C}_8\text{OHphSO}_3\text{Na}$ molecules have changed at the air–water interface during the experimental time.

A possible schematic of adsorbed $\text{C}_{10}\text{C}_8\text{OHphSO}_3\text{Na}$ molecules at the air–water interface is proposed in Figure 6. In the case of low surface concentration, the sulfonic group and hydroxy intervene the bulk simultaneously and 3-alkyl almost parallels the surface. With the increase of surface concentration, the hydrophobic interaction between 3-alkyl becomes strong, which enhances the dilational modulus and elasticity. Even more, $\text{C}_{10}\text{C}_8\text{OHphSO}_3\text{Na}$ molecules may form a long-range structure through the hydrogen bond formed by hydroxy and H_2O molecules. In the case of high surface concentration, the 3-alkyl will intervene the air and hydroxy partially leaves the bulk, which results in the weakening of molecular interaction and the decrease of dilational modulus and elasticity. On the other hand, the change of surfactant conformation and the arrangement of the surface layer provide new relaxation processes and enhance the dilational viscosity and phase angle.

Dynamic Interfacial Dilational Properties of $\text{C}_{10}\text{C}_8\text{OHphSO}_3\text{Na}$. We also investigate the dynamic interfacial dilational properties of $\text{C}_{10}\text{C}_8\text{OHphSO}_3\text{Na}$ at the decane–water interface, and the results are shown in Figure 7. Comparing the dynamic surface dilational properties, only at a surfactant bulk concentration of 5×10^{-6} mol/L, which is higher than CMC, do the interfacial dilational modulus and dilational elasticity pass through an inapparent maximum. This result may be explained as follows: The decane molecules will interact with the alkyl chain of the surfactant molecule and result in the orientation of 3-alkyl toward the oil phase. Consequently, the change of surfactant conformation and the arrangement of the surface layer will be weakened. Moreover, the hydrophobic interaction of 3-alkyl will also be weakened due to the intervening of the decane molecule.

Relaxation Processes of $\text{C}_{10}\text{C}_8\text{OHphSO}_3\text{Na}$. To confirm our experimental data and deductions above, the method of interfacial tension relaxation measurement has been employed to detect the microscopic relaxation processes in the interface at equilibrium. We can determine the characteristic relaxation time (τ) and contribution of different relaxation process (A), which are connected with the dynamic characteristics of surfactant

TABLE 2: Interfacial Relaxation Processes and Their Characteristic Relaxation Times at Different $C_{10}C_8OHphSO_3Na$ Concentrations

$C_{10}C_8OHphSO_3Na$ concn (mol/L)	process 1		process 2	
	A_1 (mN/m)	τ_1 (s)	A_2 (mN/m)	τ_2 (s)
air–water interface				
1×10^{-7}	1.90	238.1	4.91	7692.3
5×10^{-7}	1.21	13.9	7.67	588.2
5×10^{-6}	4.58	16.1	6.22	102.0
decane–water interface				
1×10^{-7}	0.54	52.6	4.89	4761.9
5×10^{-7}	0.53	13.9	8.79	500.0
5×10^{-6}	1.40	1.9	1.21	11.6

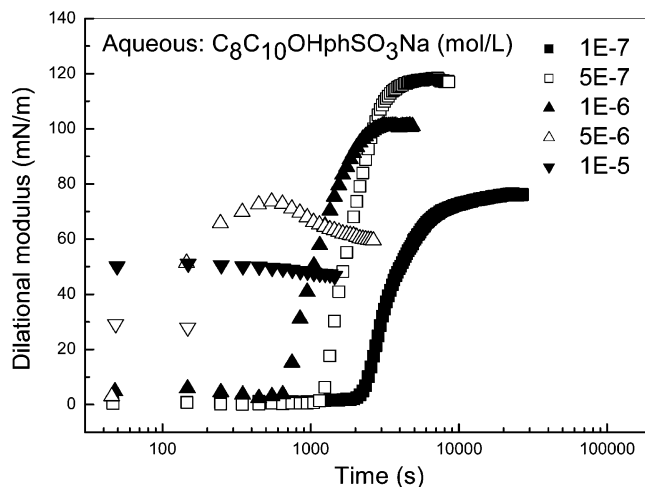
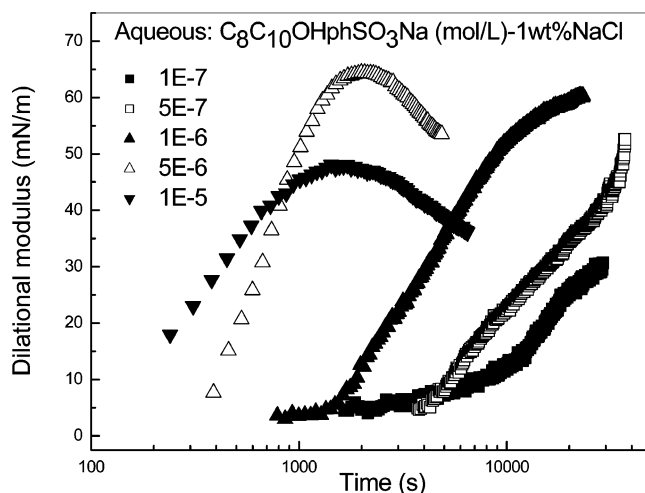
TABLE 3: Surface Relaxation Processes and Their Characteristic Relaxation Times at Different 3,4-Diheptylbenzenesulfonate Concentrations

surfactant concn (mol/L)	process 1		process 2		process 3	
	A_1 (mN/m)	τ_1 (s)	A_2 (mN/m)	τ_2 (s)	A_3 (mN/m)	τ_3 (s)
5×10^{-7}			0.92	119.1	1.98	526.3
1×10^{-6}			0.89	10.6	2.23	166.7
5×10^{-6}	1.53	2.1	2.08	19.2	2.09	66.7
1×10^{-5}	1.69	0.4	2.70	4.8	2.01	62.5
1×10^{-4}	1.58	0.4	1.15	5.0	1.18	52.6

molecules and can provide the most important information about relaxation processes, by this method (Table 2).

We can see from Table 2 that two main relaxation processes exist in the air–water interface at different concentrations: one is the fast relaxation process with a characteristic time value from several hundreds of seconds to several tens of seconds with increasing bulk concentration; the other is the slow process with a characteristic time value from several thousands of seconds to several hundreds of seconds, depending on the bulk concentration. In the case of the decane–water interface, the characteristic time values of both processes become shorter: the characteristic times for the fast process and the slow process vary from several tens of seconds to several seconds and from several thousands of seconds to several tens of seconds, respectively.

For low molecular weight surfactant systems, it is closely acquainted with the fast relaxation process involving the exchange of molecule between the bulk solution and the interface with a characteristic time from approximately 10^{-1} to 10 s in the broad concentration range.⁵⁸ The characteristic relaxation times of 3,4-diheptylbenzenesulfonate at the air–water interface are listed in Table 3. We can see from Table 3 that the characteristic relaxation times of the fast process and the slow process vary from 0.4 to 2.1 s and from 52.6 to 526.3 s, respectively, which is quite different from those of $C_{10}C_8OHphSO_3Na$ and can prove the hydroxy plays an important role in the interaction among interfacial surfactant molecules. For hydroxy-substituted alkyl benzenesulfonate $C_{10}C_8OHphSO_3Na$, the characteristic time of the fast surface relaxation process is 10 s order of magnitude and that of the slow process is 100 s order of magnitude when the bulk concentrations are above CMC, which may indicate the existence of strong intermolecular interaction and long-range structure in the surface film. The slow process may be attributed to the arrangement of the surface layer during the area change. It is reasonable that the characteristic times of the interfacial process are shorter than those of the surface process, when the weakening of the intermolecular

**Figure 8.** Dynamic surface dilational modulus of $C_8C_{10}OHphSO_3Na$ at 30 °C.**Figure 9.** Dynamic surface dilational modulus of $C_8C_{10}OHphSO_3Na$ in 1 wt % NaCl at 30 °C.

interaction resulting from the intervening of the decane molecule is taken into account. The characteristic times of the relaxation processes are in good agreement with the experimental results from the oscillating bubble/drop method.

Dynamic Interfacial Dilational Modulus of $C_8C_{10}OHphSO_3Na$. The effect of surfactant structure on dynamic dilational modulus has also been investigated. The surface dilational moduli of $C_8C_{10}OHphSO_3Na$ as a function of time are shown in Figure 8. We can find that the sharp maxima in modulus vs time curve for $C_8C_{10}OHphSO_3Na$ almost disappears, except for the indistinctive maximum at 5×10^{-6} mol/L of $C_8C_{10}OHphSO_3Na$. This result can be explained by the decrease of 3-alkyl chain carbon number (from 10 to 8) and the increase of A_{min} (from 0.73 nm² to 1.06 nm²), which can weaken the hydrophobic interaction among surfactant molecules (especially for 3-alkyl).

To ensure our understanding about the nature of the relaxation mechanism responsible for the maxima in the modulus vs time curve, we investigated the role of electrostatic forces by varying the solution ionic strength (Figure 9), as Pereira et al. deal with protein systems.⁵² With 1 wt % NaCl added electrolyte, the apparent maxima in the dynamic dilational modulus curve appear again due to the enhancement of hydrophobic interaction between 3-alkyl, which results from the strong electrostatic screening of the electrolyte.

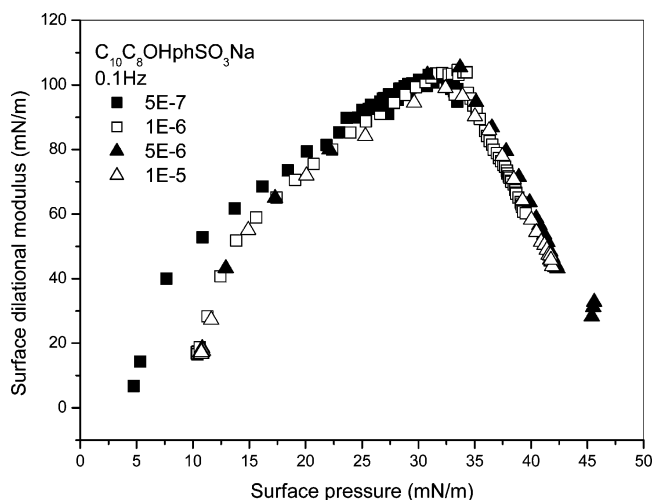


Figure 10. Dilational modulus as a function of surface pressure for $C_{10}C_8OHphSO_3Na$.

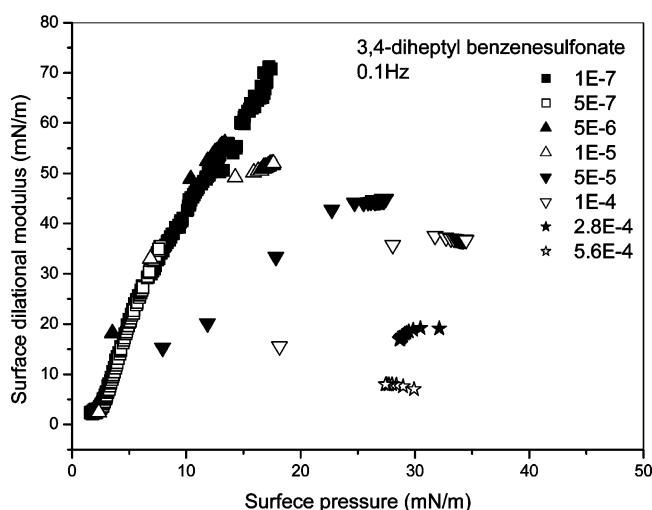


Figure 11. Dilational modulus as a function of surface pressure for 3,4-diheptylbenzenesulfonate.

Surface Dilational Modulus as a Function of Surface Pressure for $C_{10}C_8OHphSO_3Na$ and 3,4-Diheptyl Benzenesulfonate. Moreover, it is very exciting that we have found the curves of dilational modulus vs surface pressure for $C_{10}C_8OHphSO_3Na$ are quite different from those of 3,4-diheptyl benzenesulfonate (see Figures 10 and 11). It is well-known that in some cases the effect of protein concentration and adsorption time on the dilational modulus can be explained quantitatively as an effect of varying protein adsorption, which can be contributed to the irreversible adsorption of protein molecules. As a consequence, experimental data for a protein investigated at different adsorption times and at various concentrations will coincide on a single modulus vs surface pressure curve.⁵⁹ We can see clearly from Figures 10 and 11 that the moduli are quite different at the same surface pressure for 3,4-diheptyl benzenesulfonate during the higher surface pressure range, which indicates the diffusion-exchange process dominates the nature of the film. On the other hand, the dilational moduli for $C_{10}C_8OHphSO_3Na$ at different adsorption times and at various concentrations coincide on a single modulus vs surface pressure curve, which means the in-surface process dominates the film properties and the diffusion-exchange process can be neglected. These experimental results can strongly ensure our speculation of molecular reorientation and film rearrangement above.

4. Conclusion

In summary, our experimental results about dynamic interfacial dilational properties of hydroxy-substituted alkyl benzenesulfonates show the arrangement of the surfactant layer can affect the dilational properties markedly, while the surface tension remains constant. The measurement of dynamic interfacial dilational properties is a powerful tool for probing the structure of the adsorption film. To elucidate the interfacial behavior of hydroxy-substituted alkyl benzenesulfonates clearly, the measurement of static dilational properties at different frequencies has been carrying out.

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Supporting Information Available: Experimental details for the synthesis, 1H NMR data, and ESI-MS spectra for the product. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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