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Dilational surface viscoelasticity of hydroxypropyl methyl cellulose and C_nTAB at air–water surface

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Abstract

Using oscillating barriers method, the dilational surface viscoelasticity of nonionic hydroxypropyl methyl cellulose (HPMC)/C_nTAB adsorbed layers are measured at air–water surface. The evaluation of such measurements shows the information about the influence of C_nTAB surfactant on the dilational surface viscoelastic properties of HPMC. The dilational viscoelasticity of HPMC/C_nTAB adsorbed layers depends on the surfactant chain length, bulk concentration of HPMC or C_nTAB, as well as the oscillation frequency. The frequency dependent of dilational viscoelasticity for HPMC/C_nTAB surface layer is weaker than that of pure HPMC and C_nTAB systems. For HPMC/$C_{12}TAB$ surface layer, its dilational elasticity and stability are the lowest comparing with HPMC/$C_{16}TAB$ and HPMC/$C_{14}TAB$ surface layers. However, the dilational elasticity of HPMC/$C_{14}TAB$ surface layer shows a remarkably higher value than that of HPMC/$C_{16}TAB$. This phenomenon is ascribed to more HPMC molecules adsorb on the surface except some $C_{14}TAB$ molecules at this $C_{14}TAB$ concentration.

Keywords: Hydroxypropyl methyl cellulose (HPMC); Surfactant (C_nTAB); Dilational viscoelasticity; Surface tension; Surface

1. Introduction

Understanding interfacial rheology of adsorbed layers is of great importance for foam and emulsion stabilization. Indeed, destabilization of these systems is due to several mechanisms such as drainage and thin-liquid film rupture, both of which are known to be related with the interfacial rheology of the dispersion interface (Monteux, Fuller, & Bergeron, 2004; Ravera, Ferrari, Santini, & Liggieri, 2005). Interfacial rheology has been investigated for more than 40 years, mainly for the study of protein layers stabilizing dispersions in food applications (Benjamins & Lucassen-Reynder, 1998; Hambarddzumyan, Aguié-Béghin, Daoud, & Douillard, 2004; Pereira, Théodoly, Blanch, & Radke, 2003; Pezennec et al., 2000). Surprisingly, less attention has been paid to polymer/surfactant layers at the surface (Bhattacharyya, Monroy, Langevin, & Argillier, 2000; Rao, Kim, & Thomas, 2005; Ritacco, Kurlat, & Langevin, 2003). Indeed, these systems are frequently used for cosmetic, detergent formulations, pharmaceuticals and enhanced oil recovery, and their chemical characterization is often much easier than protein systems.

The equilibrium and dynamic properties of surfactant adsorption are responsible for the mechanical behavior of fluid interfaces, which determines their interfacial tension evolution and visco-elastic characteristics. When the interface is perturbed, for example with a contraction or expansion, the interface is out of the adsorption equilibrium and different processes start up contributing to the re-equilibration. There is different relaxation phenomena involved in adsorption dynamics. If soluble surfactants are concerned, diffusion is one of them. In most cases, being the slowest process, diffusion is considered as the controlling mechanism of the whole relaxation phenomenon. Other dynamic processes can occur inside the adsorbed layer depending on the nature of the surface-active species and of the liquid

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bulk phases. As a result of the time dependence of these processes, the frequency dependence of dilational viscoelasticity is particularly important for soluble surfactant layers.

Cellulose is a common material in plant cell walls and it is the most abundant form of living terrestrial biomass. Because cellulose polymers are natural, nontoxic and renewable, they have been widely applied in many fields. The hydroxyl groups of cellulose can be partially or fully reacted with various chemicals to provide derivates with useful properties. Among them, hydroxypropyl methyl cellulose (HPMC) is widely used in food industry, printing technology, and pharmaceutical industry because it is nontoxic and possesses good mechanical properties. For example, in the pharmaceutical industry, HPMC is of special interest for controlled drug-release matrixes (Ford, 1999; McCrystal, Ford, & Rajabi-Siahboomi, 1997); in food industry, HPMC is used to improve the quality of baked products (Bell, 1990; Rocell, Rojas, & Benedito de Barber, 2001). The usefulness of HPMC is essentially based upon four key attributes: efficient thickening, surface activity, film forming ability, and the capacity to form reversible thermal gels. Methyl substitutes constitute hydrophobic groups along the cellulose backbone, whereas hydroxypropyl groups are hydrophilic. The introduction of hydrophobic groups allows HPMC to adsorb at air–water surface and lower the surface tension behaving as a surfactant. Once adsorbed at the surface, HPMC chains undergo structural rearrangements. Recently, surface pressure isotherms and surface dilational viscoelasticity of HPMC adsorbed layers at the air–water surface were determined by Pérez, Sánchez, Patino, and Pilosof (2006). They present evidence that HPMC molecules are able to saturate the air–water surface at very low concentrations in the bulk phase. As bulk concentration increased, structure changes from an expanded structure to a condensed one. Although several works have focused on certain properties of HPMC, there is scarce literature referring to the dilational surface viscoelasticity of HPMC/surfactant systems. This knowledge is very important from a technological point of view for the potential applications of HPMC as a stabilizer in foams and emulsions. In the aqueous solutions of HPMC and ionic surfactants, the surfactants may form complexes with HPMC, which endows an apparent polyelectrolyte character to the originally nonionic polymer. This phenomenon usually results in an increase in the solubility of the polymer (Karlström, Carlsson, & Lindman, 1990; Kjøniksen, Nyström, & Lindman, 1998).

Recently, it is recognized that interfacial dilational rheology is highly important to many systems with surfactants and polymers (Dicharry, Arla, Sinquin, Graciaa, & Bouriat, 2006; Fainerman, Miller, & Wustneck, 1997; Ivanov, Danov, Ananthapadmanabhan, & Lips, 2005; Kovalchuk, Miller, Fainerman, & Loglio, 2005; Miller et al., 2000; Miller, Joos, & Fainerman, 1994). It is rather well established that the viscoelasticity of surface can be changed by both intra- and intermolecular interactions, as well as the adsorption/desorption dynamics of the adsorbed molecules. Recently, Babak et al extensively studied the dilational viscoelasticity of chitosan and chitosan–SDS layer at air–water surface (Babak & Desbrieres, 2006; Babak, Desbrieres, & Tikhonov, 2005). In addition, the dilational viscoelastic properties depend in a strong manner on the chemical composition of the systems (Stenvot & Langevin, 1988).

In this paper, we present studies of the dilational surface viscoelasticity of HPMC, alkyl trimethyl ammonium bromide cationic surfactant C_nTAB with different hydrophobic chain lengths ($n = 12$, 14, 16) and HPMC/C_nTAB mixtures at air–water surface using oscillating barriers method. It is found that the dilational viscoelasticity of adsorbed layers depends on the bulk concentration of HPMC or C_nTAB, frequency of oscillation and surfactant chain length.

2. Experimental

2.1. Materials and solution preparation

HPMC is provided free by Shandong Yiteng Chemical Reagent Cooperation (China, Tai'an). Its weight-average molecular weight (M_w) is $\sim 2.0 \times 10^5$, $DS_{alkyl} \approx 2$, MSalkylene oxide ≈ 0.4 and the cloud point is $\sim 55\,°C$. The critical overlap concentration of HPMC is 0.35 g/L, which was determined from viscometry. A typical HPMC structure is shown in Fig. 1. Cetyltrimethyl ammonium bromide ($C_{16}TAB$), tetradecyltrimethyl ammonium bromide ($C_{14}TAB$) and dodecyltrimethyl ammonium bromide ($C_{12}TAB$) were purchased from Ameresco, and used without further purification. Water used in the experiments was triply distilled by a quartz water purification system.

2.2. Methods

Dilational surface rheological property is obtained by measuring a change in interfacial tension caused by a specific change in interfacial area (Benjamins, Cagna, & Lucassen-Reynders, 1996; Fromyr, Hansen, Kotzev, & Laschewsky, 2001; Lucassen-Reynders, 1981). In this method, the surface is subjected to small periodic sinusoidal compressions and expansions by means of two oscillat-

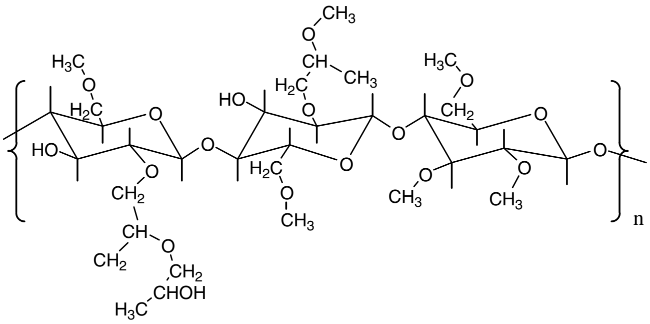

Fig. 1. Structure segment of HPMC molecule.

ing barriers at a given frequency (ω) and amplitude. The dilational modulus ε is generally defined as the ratio of a small change in surface tension (γ) to the change in surface area (A).

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

Eq. (1) is valid in the linear regime (Hilles, Maestro, Monroy, Ortega, & Rubio, 2007). Dilational modulus can also be expressed as the summation of storage modulus and loss modulus contribution.

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

where ε_d is dilational elasticity and η_d is dilational viscosity. ε_d and η_d can be calculated by

$$\varepsilon_d = |\varepsilon|\cos\theta \tag{3}$$

$$\eta_d = \frac{|\varepsilon|}{\omega}\sin\theta \tag{4}$$

where θ is phase angle.

Detailed experimental methods on dilational viscoelasticity measurements were introduced in the literature (Wu, Xu, Feng, & Li, 2007). Surface tensions of surfactant solution with and without HPMC were measured on Processor Tensiometer K-12 (Krüss Company, Germany) using ring method. The average values of surface tension were obtained by repeating three times. All the measurements are carried out at 25 ± 0.1 °C, which is higher than the Kraft temperature of C_{16}TAB.

3. Results and discussion

3.1. Dilational surface viscoelasticity of C_nTAB solution

The frequency dependence of storage modulus (dilational elasticity) and loss modulus (reveals the variance of dilational viscous component) for C_nTAB ($n = 12$, 14, 16) surfactant is depicted in Fig. 2. These dilational viscoelastic experiments were measured below surfactant critical micelle concentrations (cmc). It can be seen from Fig. 2 that dilational elasticity of C_nTAB adsorbed layers shows an increasing trend with frequency, while dilational viscous component is contrary. This could be due to the closer time-scale of surfactant diffusion with surface dilation. The values of the diffusion coefficient D are 11.6×10^{-6}, 6.02×10^{-6}, 5.73×10^{-6} cm^2/s for C_{16}TAB (Gao et al, 2004) C_{14}TAB and C_{12}TAB (Lide, 2005–2006), respectively. Surfactant molecules can move inside the monolayer, so the surface diffusion can affect the viscoelastic parameters. For C_{12}TAB adsorbed layer, its dilational elasticity shows much lower frequency dependence when its concentration is higher than 4 mM. At the same frequency, the storage modulus of C_nTAB surfactant is higher than its loss modulus, which underlies the elastic character is dominating for the surfactant layers at the air–water surface.

Fig. 2 also shows that surfactant chain length, surfactant bulk concentration and oscillation frequency are important factors that influencing its loss modulus. When oscillation frequency is higher, loss modulus appears negative values for the three surfactants. The loss modulus of surfactant layer with shorter chain length appears negative value in lower frequency. It is important to note that the negative loss modulus means a negative phase angle. Theoretical analysis and experimental results show that usually the positive loss modulus appears for the layer where the fast molecular exchange between the surface layer and the bulk phase dominates. In our experimental method, the homogeneous deformations of the liquid interface are created by a pair of barriers oscillating in sinusoidal mode in a Langmuir trough and the corresponding changes of the interfacial tension are measured using a Wilhelmy plate. The dilational modulus can be determined from the amplitude ratio of the oscillations of the interfacial tension and interface area, while the phase shift between the oscillations of the interfacial tension and interface area determines the phase angle of the interfacial dilational viscoelasticity. According to the general definition of dilational phase angle, the phase angle has a positive value when the phase of interfacial tension oscillation is ahead of that of interfacial area oscillation, while the negative one will appear when the phase of interfacial area oscillation is ahead of that of interfacial tension oscillation. When the interfacial area is compressed, one hand, surfactant concentration at surface increases, but on the other hand, surfactant molecules with much higher concentration at surface diffuse toward bulk phase. For a certain area change, the negative phase angle will appear when the oscillation frequency becomes high enough that the fast exchange of molecules cannot compensate the interfacial concentration change caused by area changing. So the higher the oscillation frequency, the larger possibility the film has to show a negative phase angle. Monroy, Kahn, and Langevin (1998) reported that the dilational viscosity of C_{16}TAB, C_{14}TAB and C_{12}TAB monolayers is negative at high frequencies using capillary wave techniques, which depends on the surfactant chain length, bulk concentration and the oscillation frequency. The dilational surface viscosity has also been obtained negative value by means of surface light scattering technique for some conventional surfactants and polymer films. (Earnshaw & McCoo, 1995; Milling, Richards, Baines, Armes, & Billingham, 2001; Monroy, Munoz, Rubio, Ortega, & Rubio, 2002).

The viscoelastic behavior of soluble monolayers can be described by the Lucassen–van den Tempel model (Lucassen & van den Tempel, 1972a, 1972b). The LVT model is the usual reference for systems in which the adsorption–desorption processes are important. It is a diffusive control model which assumes that the material transport involved in the adsorption kinetics is governed only by diffusion without energy barriers. It considers the instantaneous coupling between the surface rheology and the adsorption kinetics. The model predicts the viscoelastic moduli through the equations (van den Tempel & Lucassen-Reynders, 1983)

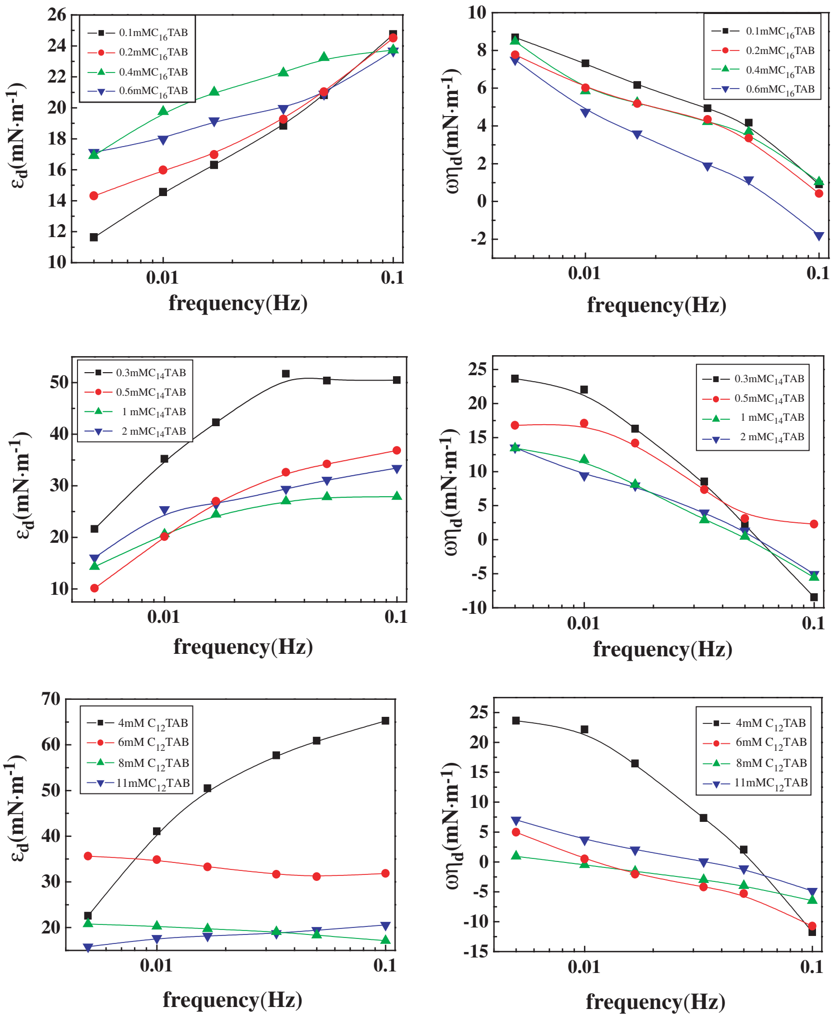

Fig. 2. Dilational surface elasticity and viscous component of C_nTAB surfactant as a function of dilational frequency.

$$\varepsilon_{\mathrm{d}}(\omega) = \varepsilon_0 \frac{1+\Omega}{1+2\Omega+2\Omega^2} \tag{5}$$

$$\omega\eta_{\mathrm{d}}(\omega) = \varepsilon_0 \frac{\Omega}{1+2\Omega+2\Omega^2} \tag{6}$$

where the reduced frequency Ω is given by $\Omega = (\omega_{\mathrm{D}}/\omega)^{1/2}$, ω_{D} being the characteristic diffusion frequency. It represents the frontier between the viscous friction regime, at low frequencies, and the elastic regime at high frequencies. It is related to the diffusion coefficient D by the following expression:

$$\omega_{\mathrm{D}} = \frac{D}{2}\left(\frac{\partial c}{\partial \Gamma}\right)^2 \tag{7}$$

where Γ and c are the surface and bulk concentrations, respectively. For a soluble monolayer in equilibrium, ε_0 is the static elasticity or Gibbs elasticity, which corresponds to the high frequency limit value, i.e., very fast compression/expansion rates compared to the solubilization kinetics. For an insoluble monolayer ε_0 corresponds to the zero frequency limit of $\varepsilon(\omega)$.

The rheology data of the monolayers has been analyzed in terms of the LVT model over the whole frequency range studied. For the sake of brevity, only C_{16}TAB surfactant will be discussed; similar behaviors are found for the other surfactants investigated in this work. Fig. 3 compares the experimental viscoelastic moduli with LVT model predic-

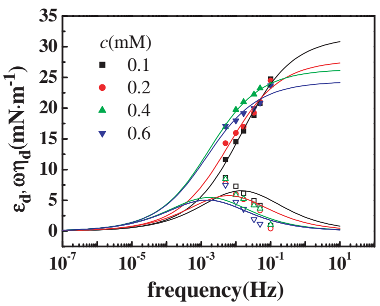

Fig. 3. Dilational surface elasticity (closed symbols) and viscous component (open symbols) versus frequency for C_{16}TAB at different concentrations. The lines show the predictions from the LVT model.

tions for Gibbs monolayers of the indicated system. As it can be noticed, the model fits properly the frequency dependence of the elasticity modulus. Even though LVT model is able to fit the frequency dependence of elasticity, it fails to predict the behavior of the loss modulus. (Díez-Pascual et al, 2007). However, the existence of negative surface viscosities indicates that the LVT rheological model used here can be no longer valid. So our loss modulus values deviate from the experimental. Fig. 3 shows that according to LVT model, at lower frequency, the dilational elasticity are all close to zero; it can be explained by the reason that the interfacial tension gradient resulting from interface deformation almost vanished during experiment time. However, at higher frequency, the dilational elasticity shows little change with increased frequency (limiting dilational elasticity), which states that the work frequency is far more than the characteristic frequency of various relaxation processes occurring at and near the interface, and the surface film embodied the character of the insoluble film. At moderate frequency, the dilational elasticity increases with an increase in the dilational frequency since at low deformation velocity of the surface the surfactant molecules have enough time to restore the surface tension gradient created by the area change of surface through diffusion from surface and bulk to new interface. Limiting dilational elasticity decreases with $C_{16}TAB$ concentration increasing. The limiting dilational elasticity actually reflects change of dynamic interfacial tension resulting from that of interfacial absorption when the interfacial area changes very quickly. Fig. 3 also reveals that the characteristic diffusion frequency ω_D, which corresponds to the inflection point of the elasticity curve, is dependent of $C_{16}TAB$ concentration within the error limits. ω_D decreases with $C_{16}TAB$ concentration increasing, which indicates that diffusion time becomes larger as concentration goes up. From Fig. 3, it can be found that the dilational viscous component passes through a maximum value with a rise in the dilational frequency. This maximum value appears at different frequency when $C_{16}TAB$ concentration is different; and the higher the concentration, the lower the dilational frequency. It is generally believed that the dilational viscous component reflects the summation of the various microscopic relaxation processes at and near the surface. Usually, it is found that the inflection point in dilational elasticity vs. frequency curve corresponds to the maximum of the viscous component vs. frequency curve. But the results presented in our work are not compatible with this general trend. This is because one hand, the frequency dependence of the dilational viscous component could not been well described by the diffusive control model of LVT; on the other hand, the appearance of negative dilational viscous component in some cases lead to the LVT model being not applicable.

Fig. 4 shows the variations of dilational elasticity and dilational viscous component versus bulk concentration for the three surfactants at the frequency of 0.05 Hz. Generally, an increase in the surfactant bulk concentration can affect the dilational surface viscoelasticity in two aspects: one is to increase the surfactant concentration at the surface; the other is to increase the ability of the surfactant molecules diffusing from the bulk to a new surface. The former can increase the interfacial tension gradients, resulting in an increase in the dilational modulus; however, the latter may create a decrease in the dilational modulus. These two factors result in the complex behavior of dilational elasticity and viscosity with surfactant concentration increasing. It can be seen from Fig. 4 that in the studied bulk concentration range, for the dilational elasticity of C_nTAB ($n = 12, 14, 16$) surfactant, $C_{16}TAB$ layer is lower; $C_{14}TAB$ layer is higher than that of $C_{16}TAB$ layer; and the dilational elasticity of $C_{12}TAB$ is remarkably concentration dependent. For soluble surfactants, the elasticity modulus at infinite frequency should coincide with the Gibbs equilibrium elasticity, while for insoluble surfactant monolayer it is the zero-frequency elasticity that corresponds to the equilibrium one. Obviously, $C_{16}TAB$ is closer to the non-soluble case than $C_{12}TAB$. From Fig. 4 it is also found that for a given frequency, the maximum of the elasticity shifts to lower concentration as the surfactant chain length increases. The dilational modulus of a surface may also be written as

$$\varepsilon = \frac{d\gamma}{d\ln A} = \left(\frac{d\gamma}{d\ln \Gamma}\right)\left(\frac{d\ln \Gamma}{d\ln A}\right) \tag{8}$$

Here Γ is the surfactant concentration at the surface. Among the different relaxation processes, several may occur in the monolayer, such as molecular reorientation processes. These processes affect the frequency depen-

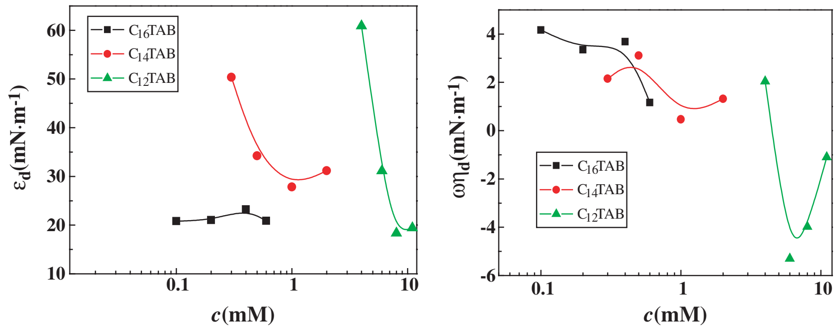

Fig. 4. Dependence of dilational elasticity and viscous component on surfactant concentration, $\omega = 0.05$ Hz.

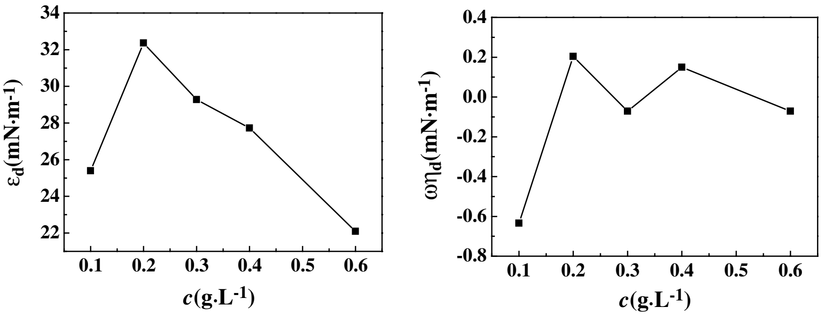

Fig. 5. Dilational elasticity and viscous component as a function of HPMC concentration, $\omega = 0.05$ Hz.

dence of ($d\gamma/d\ln\Gamma$). The second term ($d\ \ln\Gamma/d\ln A$) is mainly related to surfactant molecules exchange between bulk and surface. According to Eq. (8) the appearance of the maximum elasticity value at lower concentration for longer chain surfactant is attributed to its higher surface activity and easier exchange between bulk and surface. The dilational viscous component of three surfactants decreases in the order of $C_{16}TAB > C_{14}TAB > C_{12}TAB$. It is generally believed that the dilational viscous component reflects the summation of the various microscopic relaxation processes at and near the surfactant layer and different relaxation processes have different characteristic frequencies (Wang, Zhang, Sun, Zhao, & Yu, 2004). These results show that the dilational viscoelasticity behavior of surfactant layer is influenced by surfactant chain length.

3.2. Dilational surface viscoelasticity of HPMC solution

The dilational elasticity and viscosity of HPMC adsorbed layers are plotted as a function of bulk concentration in Fig. 5. Obviously, the dilational elasticity and viscosity appear a maximum value at $c_{\mathrm{HPMC}} = 0.2\ \mathrm{g{\cdot}L^{-1}}$. HPMC form very elastic films at the air–water surface. As bulk concentration increased, structure changes in a molecular level at the surface. Viscoelastic behavior of HPMC layers significantly differs from that of layers formed by surfactants with low molecular weight. According to the literature (Noskov, Akentiev, Bilibin, Zorin, & Miller, 2003; Noskov, Akentiev, Loglio, & Miller, 2000; Noskov, Akentiev, & Miller, 2002), the exchange of macromolecules between the surface layer and the bulk phase can be neglected, but the exchange of monomers between different regions of the surface layer has to be taken into account. There are two main parts of the surface layer: one is the proximal region (a relatively narrow concentrated region contiguous to the gas phase), the other is the distal region where tails and loops protrude into the bulk and the concentration of monomers are lower (Noskov et al., 2003). The dependence of dilational viscoelasticity of HPMC on concentration as mentioned above can be illustrated in Fig. 6. At low bulk concentration (below 0.2 g/L), the adsorbed HPMC molecules appear an expanded structure and do not form long tails and loops (Fig. 6a). With bulk concentration further increasing, the concentration of HPMC at surface increases, which hinders complete unfolding of some HPMC coils at the surface layer. Gradually some loops and tails appear and a condensed structure forms in the distal region of the surface layer (Fig. 6b). Therefore the dilational elasticity and viscosity increase remarkably. Subsequent increase of bulk concentration (above 0.2 g/L) leads to the faster exchange between the proximal and the distal regions, which results in a decrease of the dilational viscoelasticity. The faster exchange giving rise to decrease the dilational modulus dramatically is similar to that of surfactant solutions above their cmc (Wang et al., 2004). The reason why negative viscosity of HPMC solution occurs is that the slow relaxation process dominates the dilational viscoelasticity because the higher molecular weight of HPMC and intra-molecular aggregations.

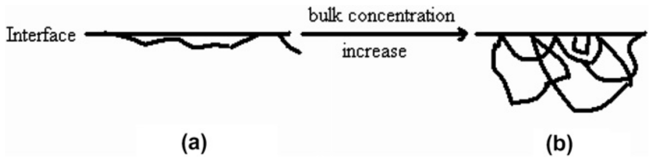

Fig. 6. Schematic illustration of HPMC structure changes with concentration increasing.

3.3. Dilational surface viscoelasticity of HPMC/C_nTAB solution

Fig. 7 presents the variations of dilational elasticity and dilational viscous component versus frequency for the HPMC/$C_{16}TAB$ system. It can be noted that dilational elasticity increases with frequency increasing; whereas dilational viscous component is contrary. The addition of HPMC results in the frequency dependence of dilational viscoelasticity of surface layer decreased comparing with that of $C_{16}TAB$ surface layer. This is because the diffusion of HPMC molecule from surface to bulk phase can be neglected, the variance of surface tension gradient caused by molecular diffusion for HPMC/$C_{16}TAB$ surface layer is lower than that of pure $C_{16}TAB$ layer.

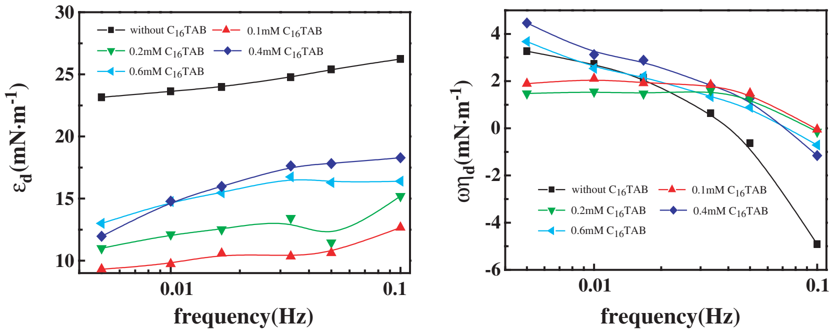

Fig. 7. Dilational surface viscoelasticity of 0.1 g/L HPMC with different $C_{16}TAB$ concentrations as a function of dilational frequency.

The dilational elasticity and viscous component of HPMC/$C_{16}TAB$ surface layers vs. concentration curve is shown in Fig. 8. The simple addition rule result in Fig. 8 is the dilational elasticity or viscous component of pure CTAB layer plus that of pure 0.1 g/L HPMC layer. Dilational surface viscoelasticity of polymer/surfactant surface layer could be influenced by the exchange of polymer monomers between different regions of the surface layer, as well as the formation of polymer/surfactant aggregates. Experimental results are much lower than simple addition rule results, indicating that there are interactions and competitive adsorption between HPMC and $C_{16}TAB$ on the surface layer. With $C_{16}TAB$ concentration increasing, more and more $C_{16}TAB$ molecules adsorb on the surface. So the dilational elasticity of surface layer increases with $C_{16}TAB$ concentration. On the contrary, the dilational viscous component decreases with $C_{16}TAB$ concentration increasing. This implies that higher elasticity of surface layer corresponds to lower dilational viscous component. The strength of surface layer against perturbation definitely increases with dilational elasticity increasing. The elasticity of HPMC/$C_{16}TAB$ surface layer is lower than that of pure 0.1 g/L HPMC layer (25.40 mN/m). This implies that the strength of surface layers formed by HPMC is higher than that of HPMC/$C_{16}TAB$ layers.

Figs. 9 and 10 present the dilational surface viscoelasticity for HPMC/$C_{14}TAB$ and HPMC/$C_{12}TAB$ solution, respectively. The variance of their dilational elasticity and viscosity with frequency is similar to HPMC/$C_{16}TAB$ surface layer. The presence of HPMC results in the frequency dependence of dilational viscoelasticity decreased. Comparing Figs. 7, 9 and 10, it can be observed that the dilational surface viscoelasticity is strongly affected by the hydrophobic chain length of surfactant.

In order to compare the dilational viscoelasticity of three surfactants in presence of HPMC, their concentration dependence curves are shown in Fig. 11. It is well known that there is a critical aggregation concentration (cac) in some cases when interactions occur between polymers and surfactants. It seems from Fig. 11 that a lower elasticity value is obtained for lower surfactant concentrations. Generally, the threshold concentration for which an increase in elasticity value is observed may be considered as the surfactant cac. This threshold concentrations for the studied three surfactants in our work are much lower than their cmc ($C_{16}TAB$: 0.85 mM, $C_{14}TAB$: 5.0 mM, $C_{12}TAB$: 12.0 mM). We are unable to measure the dilational elasticity above the surfactant cmc because the elasticity is too small to allow a longitudinal wave to propagate. The higher the dilational elasticity is, the stronger the rigidity of surface layer. It can be found in Fig. 11 that in presence of HPMC the values of dilational elasticity for the three surfactants is in the order of $C_{14}TAB > C_{16}TAB > C_{12}TAB$. This peculiar behavior correlates with the large increase in foam film stability from $C_{12}TAB$ to $C_{14}TAB$ (Bengeron, 1997). This confirms the strong influence of the surface elasticity on the stability of foam films. For pure C_nTAB solution hydrophobic interactions between surfactant molecules bring dilational surface viscoelasticity, whereas for pure HPMC adsorbed layer it is viscoelastic because of

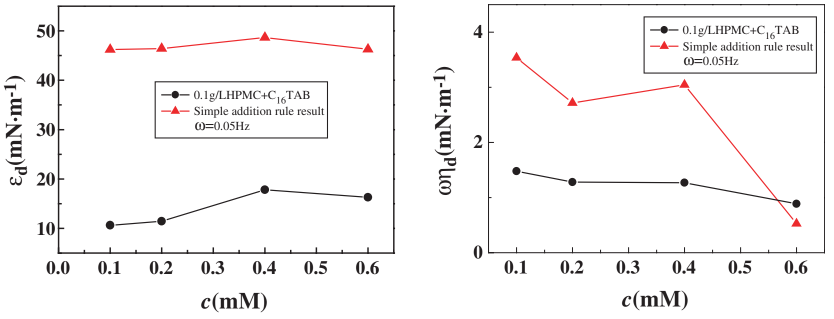

Fig. 8. The dependence of dilational elasticity and viscous component on CTAB concentration.

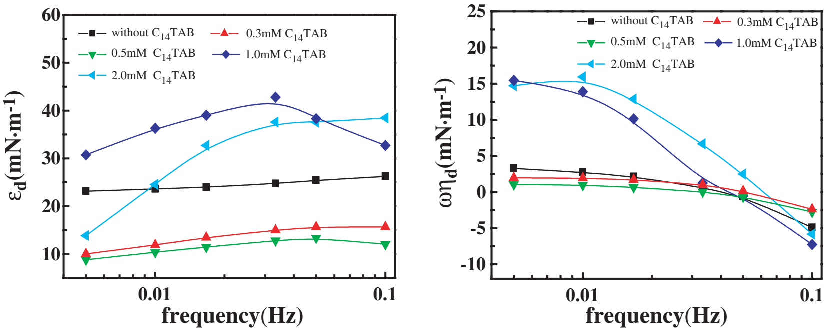

Fig. 9. Dilational surface viscoelasticity of 0.1 g/L HPMC with different $C_{14}TAB$ concentrations as a function of dilational frequency.

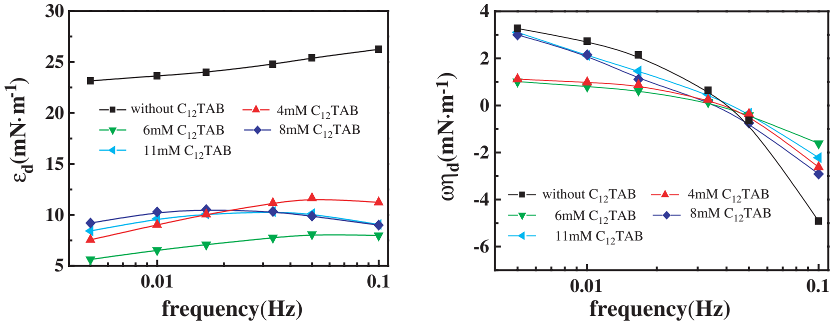

Fig. 10. Dilational surface viscoelasticity of 0.1 g/L HPMC with different $C_{12}TAB$ concentrations as a function of dilational frequency.

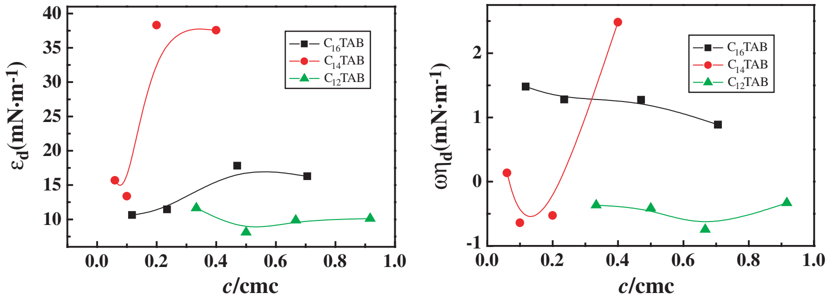

Fig. 11. The dependence of dilational viscoelasticity on the ratio between surfactant concentration and cmc ($c_{\mathrm{HPMC}} = 0.1$ g/L, $\omega = 0.05$ Hz).

its chain entanglements. The HPMC/C_nTAB systems combine chain entanglements and hydrophobic interactions to show viscoelasticity. The lower rigidity and compactness degree of surface layer for HPMC/$C_{12}TAB$ comparing with HPMC/$C_{16}TAB$ and HPMC/$C_{14}TAB$ are because of its relatively weaker hydrophobic interactions. It is clearly seen that the dilational viscous component behavior increases with the surfactant chain length increasing. It should be stressed that the bulk concentration regions where the layer reaches its maximum compacity is also shifted when the chain length is varied, and the characteristic diffusion time increases from $C_{12}TAB$ to $C_{16}TAB$.

For the three surfactants, the concentrations studied in dilational viscoelasticity properties are before their cmcs. Surface tension measurement is a simple and effective method for studying the interaction between polymer and surfactants (Langevin, 2001). In order to further investigate the surface behavior of HPMC and C_nTAB at air–water surface, their surface tension isotherms were measured. It is found that from Fig. 12 that the surface tension curves of HPMC/C_nTAB system could be divided into three stages. The first stage is that the surface tension of HPMC/C_nTAB solution is lower than that of pure C_nTAB solution, which indicates that both surfactant and HPMC molecules adsorb on the surface. In the second stage, the surface tension of HPMC/C_nTAB solution is higher than that of pure C_nTAB solution, which indicates that some HPMC molecules on the surface are displaced by C_nTAB molecules and C_nTAB surfactants form complexes with HPMC in bulk solution. In this stage, the surface is mostly occupied by surfactant molecules. In the third stage, the surface tension of HPMC/C_nTAB solution is similar to that of pure C_nTAB solution, which indicates that the surface is occupied by surfactants completely. But for $C_{14}TAB$

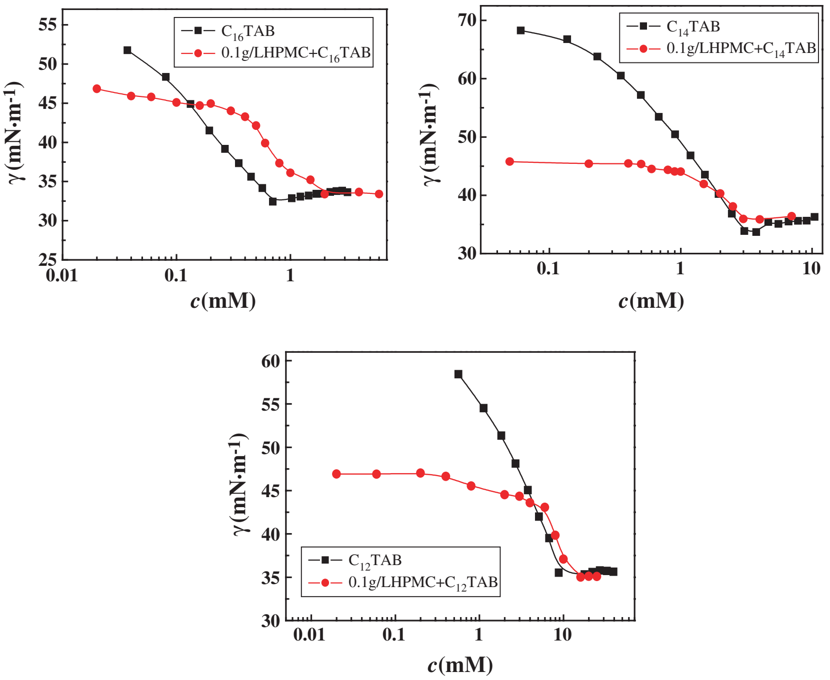

Fig. 12. Surface tension isotherms of different solutions as a function of surfactant concentration.

and $C_{12}TAB$ system, the second stage almost disappears, which is because the weaker hydrophobic interaction with HPMC comparing with $C_{16}TAB$. These surface tension curves can be used to explain the peculiar elasticity of HPMC/$C_{14}TAB$ adsorbed layers. The studied concentrations for $C_{16}TAB$ (0.1–0.6 mM) and $C_{12}TAB$ (4–11 mM) are in the second stage of their surface tension isotherms, while $C_{14}TAB$ (0.3–2 mM) is in the first stage. So the stronger elasticity of HPMC/$C_{14}TAB$ adsorbed layers can be explained with the results that in the first stage, more HPMC molecules adsorb on the surface except some $C_{14}TAB$ molecules. The elasticity of HPMC molecule is higher than that of C_nTAB surfactants.

4. Conclusions

Dilational surface viscoelasticity is an appropriate function for the characterization of surface properties of HPMC/C_nTAB system. The oscillating barriers method is used to study the dilational viscoelastic properties of adsorbed layers at lower dilational frequency (0.005–0.1 Hz). The evaluation of such measurements shows the information about the influence of HPMC on the dilational surface viscoelastic properties of C_nTAB surfactant. The dilational viscoelasticity of HPMC/C_nTAB adsorbed layers depends on the surfactant chain length, bulk concentration of HPMC or C_nTAB and the oscillation frequency. In the case of C_nTAB or HPMC/C_nTAB adsorbed layers (before cmc), dilational elasticity increases with frequency, while dilational viscous component is contrary. The addition of $C_{12}TAB$ in HPMC solution leads to the adsorbed layers showing the lowest dilational elasticity and viscosity comparing with $C_{16}TAB$ and $C_{14}TAB$. The dilational elasticity of HPMC/$C_{14}TAB$ layer at certain $C_{14}TAB$ concentration shows marked higher value than those of HPMC/$C_{16}TAB$ and HPMC/$C_{12}TAB$. This is the result of more HPMC molecules adsorb on the surface at this $C_{14}TAB$ concentration except some $C_{14}TAB$ molecules. The surface tension isotherms confirm this result.

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