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ORIGINAL CONTRIBUTION

Interfacial dilational properties of partly hydrolyzed polyacrylamide and gemini surfactant at the decane–water interface

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Abstract The dilational viscoelastic properties of partly hydrolyzed polyacrylamide (HPAM) and surfactant ($C_{12}COONa\text{-p-}C_9SO_3Na$) in the absence or presence of electrolyte were investigated at the decane–water interface by means of longitudinal method and the interfacial tension relaxation method. The polymer plays different roles in influencing the structure of HPAM–surfactant mix-adsorbed layer at different surfactant concentration. At low surfactant concentration, the addition of polymer could sharply decrease the dilational elasticity mainly due to the weakening of the "entanglement" among long alkyl chains in surfactant molecules, while the addition of the polymer may enhance the dilational elasticity due to the slow diffusivity of the polymer chains at higher surfactant concentration. And the added electrolyte, which results in screening of electrostatic interactions between the ionized groups, generally decreases the interfacial dilational elasticity and increases the dilational viscosity. The data obtained on the relaxation processes via interfacial tension relaxation measurement can explain the results from dilational viscoelasticity measurements very well.

Keywords Dilational elasticity · Dilational viscosity · Partly hydrolyzed polyacrylamide HPAM (Mo-4000) · $C_{12}COONa\text{-p-}C_9SO_3Na$ · Relaxation process · Electrolyte

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Introduction

In order to improve oil recovery, polymers have been used for a long time in enhanced oil recovery process as flooding agent. Industrial experiences show that polymer flooding can enhance oil recovery by up to 12% and plays a key role in oil exploitation [1, 2]. In this respect, the most widespread technique is based on partly hydrolyzed polyacrylamide (HPAM) [3–5], which is a low price polymer with good viscous properties and well-known physicochemical characteristics. The implementation of HPAM flooding is easy and can improve significantly the oil recovery rate under standard reservoir conditions.

It is well known that the presence of small amounts of surfactants to aqueous polymer solutions can significantly modify the properties of adsorbed polymer layer. Interactions of polymers with surfactants are one of the genuinely dominant themes of colloid and polymer chemistry; and the interactions of polymers and small molecular surfactants are of fundamental importance for many industrial applications ranging from oil recovery to latex paint technology [6]. A full understanding of these systems can help solve problems in these areas.

Rheological study is an additional source of information about the structure of adsorption layers, particularly of polymer at liquid interfaces. 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 an adsorption layer quantitatively. In recent years, progress in interfacial rheometrical instrumentation has led to an increase in the quality and availability of dilational rheological experiment [7–15].

In previous work, we have investigated the interfacial dilational properties of hydrophobically modified poly-

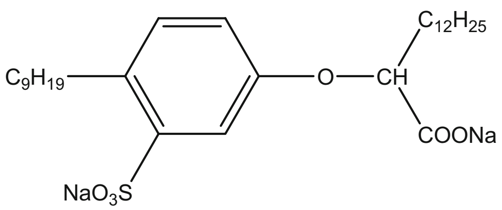

Fig. 1 The structure of the gemini surfactant $C_{12}COONa$-p-C_9SO_3Na

acrylamide–surfactant systems at oil–water interface [16–18]. In the present work, we have studied the viscoelastic properties of HPAM (Mo-4000)–surfactant ($C_{12}COONa$-p-C_9SO_3Na) in the absence or presence of electrolyte at the oil–water interface by means of longitudinal method and the interfacial tension relaxation method.

Theoretical background

The dilational elasticity is related with the ability of the system to establish a new surface tension value after an area change, and its equilibrium value (ε) is defined according to Gibbs [19, 20]:

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

In this equation, γ is the interfacial tension and A is the area of the interface. In the simplest case, the modulus is a pure elasticity with a limiting value. This limiting value is reached only if there is no exchange of surfactant with the adjoining bulk solution. Deviations from this simple limit occur when the relaxation process in or near the interface affects either γ within the time of the measurement. In such case, dilational modulus is an interfacial viscoelasticity, with an elastic part, ε_d, accounting for the recoverable energy stored in the interface and a viscous contribution, ε_η, representing the loss of energy in the relaxation process.

The dilational modulus can also be decoupled into real and imaginary, which corresponds to a real part (ε_d) and imaginary part ($\varepsilon_\eta = \omega\eta_d$), respectively:

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

Phase angle θ describing the phase difference between dynamic interfacial tension variation and interfacial area variation, which means that the elastic and viscous contributions are given by:

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

$$\varepsilon_\eta = |\varepsilon|\sin\theta \tag{4}$$

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 [21, 22]:

$$\varepsilon(\omega) = \frac{FT\Delta\gamma(t)}{FT(\Delta A/A)(t)} = \frac{\int_0^\infty \Delta\gamma(t)\exp(-i\omega t)\,dt}{\int_0^\infty [\Delta A(t)/A]\exp(-i\omega t)\,dt} \tag{5}$$

where ω is the angular frequency. In an ideal system which 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.

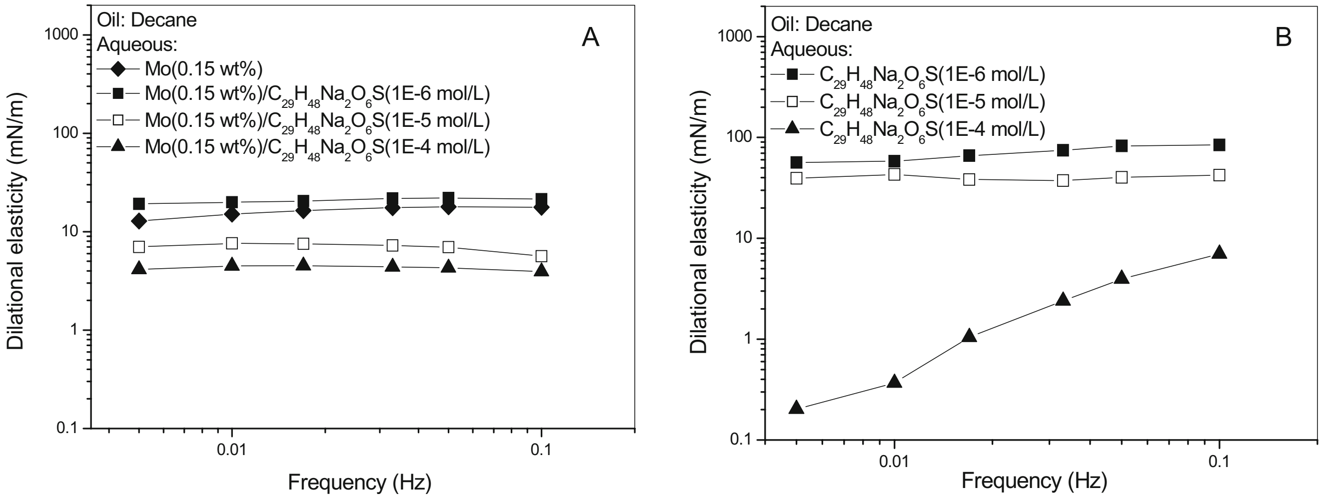

Fig. 2 Interfacial dilational elasticity as a function of frequency for 0.15 wt.% polymer at different $C_{12}COONa$-p-C_9SO_3Na concentration (**A**) and the surfactant on its own solution (**B**)

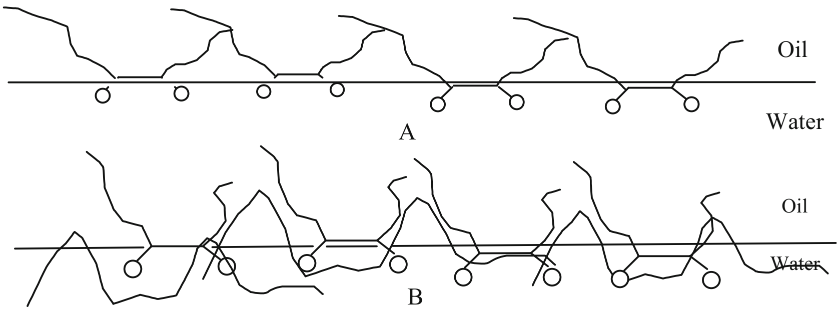

Fig. 3 Schematic diagram of mixed adsorption of surfactants and polymer molecules at low surfactant concentration. **A** Pure surfactant. **B** Surfactant–polymer mixed adsorption the structure of C_{12} COONa-p-C_9SO_3NA and polymer

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:

$$\Delta\gamma = \sum_{i=1}^{n} \Delta\gamma_i \exp(-\tau_i t) \tag{6}$$

where τ_i is the characteristic frequency of the ith process; $\Delta\gamma_i$ is the fractional contribution which that relaxation process makes to restore the equilibrium; n is the total number of the relaxation processes.

Materials and methods

The asymmetrical anionic gemini surfactant $C_{12}COONa$-p-C_9SO_3Na was synthesized in our laboratory, as shown in Fig. 1 [23]. The purity of the compounds was checked by ^1H NMR spectroscopy. Partly hydrolyzed polyacrylamide (HPAM), Mo-4000, was supplied by Mitsubishi Corporation (Japan), with 25.0% degree of hydrolysis. Its viscosity average molecular weight is about 22×10^6. Decane, A.R., was obtained from Xingjin Chemical Reagent Ltd., Tianjin, China and used as oil phase without further treatment. Sodium chloride and magnesium chloride were purchased from Beijing Fine Chemical Industry Co., Ltd., China. Water used in the experiments was distilled twice from potassium permanganate solution.

The interfacial dilational viscoelasticity meter JMP2000A (Powereach Ltd., Shanghai, China), which had been described previously, was employed [24, 25]. In order to determine the dilational rheology of the absorbed film, a Langmuir trough with coupled barrier was used. The dynamic interfacial tension was measured by the Wilhelmy plate method, using a PTFE plate suspended in the middle of the trough area from a sensitive force transducer. The Langmuir trough was filled with the water phase (90 ml) and oil phase (50 ml). The dilational viscoelasticity experiment began after 6 h of pre-equilibrium of the oil–water system. Measurements were made by oscillating the area of the trough at chosen amplitude ($\Delta A/A$, 10%) in sine oscillation mode. The frequency of the oscillations can be varied between 0.005 and 0.1 Hz. Then, the interfacial tension relaxation measurement was carried out (the film was expanded about 15% in area by a sudden expansion in 2 s). All experiments were performed at the temperature 30 °C.

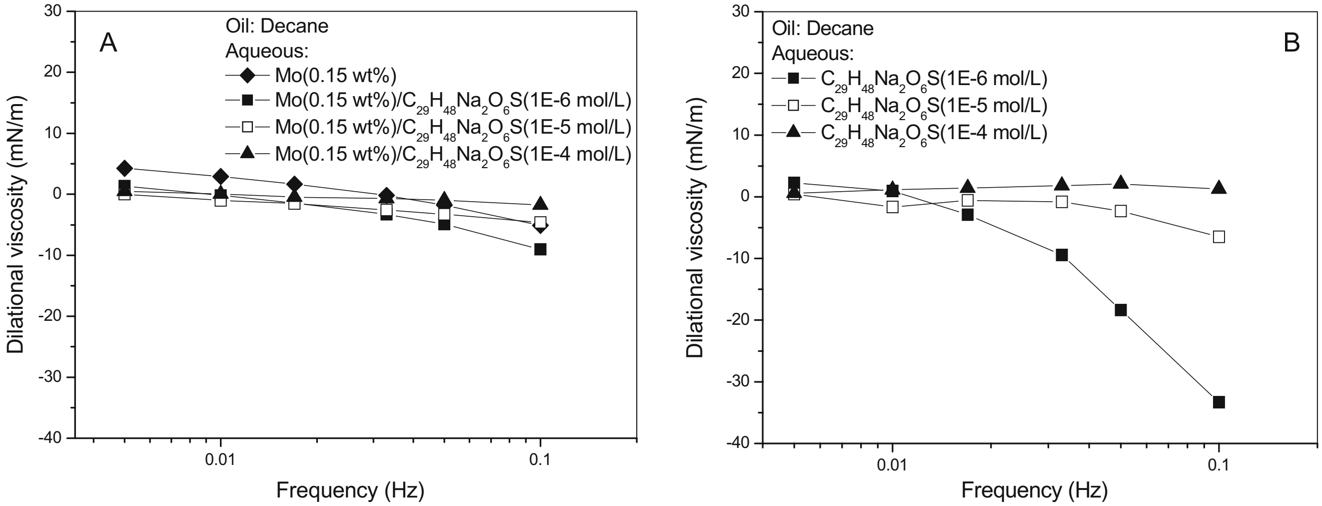

Fig. 4 Interfacial dilational viscosity as a function of frequency for 0.15 wt.% polymer at different $C_{12}COONa$-p-C_9SO_3Na concentration (**A**) and the surfactant on its own solution (**B**)

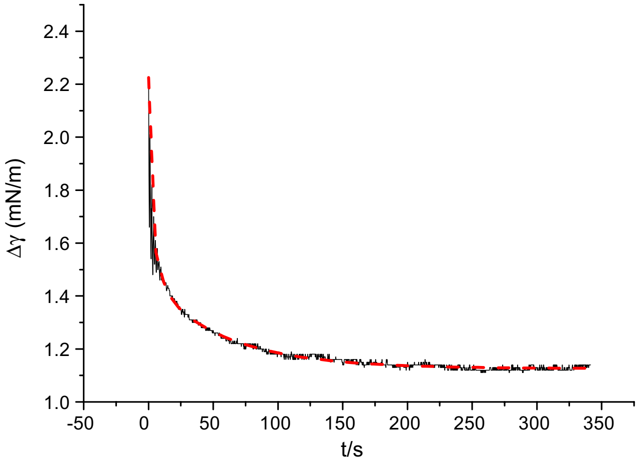

Fig. 5 Interfacial relaxation curve for Mo-C_{12}COONa-p-C_9SO_3Na (1×10^{-5} mol l^{-1}). The *black line* corresponds to the experiment curve and the *red line* corresponds to the fitted curve

Results and discussion

Influence of Mo-4000 on the interfacial dilational properties of C_{12}COONa-p-C_9SO_3Na

Interfacial dilational elasticities as a function of the dilational frequency are presented in Fig. 2 for the 0.15 wt.% polymer at different C_{12}COONa-p-C_9SO_3Na concentration and the surfactant on its own solution, respectively. The dilational elasticity shows almost no frequency dependence in Fig. 2A, which indicates that the adsorbed layer is predominantly elastic in nature. Comparing the results of Fig. 2A and B, it is fairly obvious that the polymer has remarkable influence on the C_{12}COONa-p-C_9SO_3Na films. The dilational elasticity is smaller than that of the surfactant on its own when 0.15 wt.% polymer is added at low surfactant concentration (from 1×10^{-6} mol·l^{-1} to 1×10^{-5} mol·l^{-1}). On the contrary, the dilational modulus is higher than that of the surfactant on its own when 0.15 wt.% polymer is added at high surfactant concentration (1×10^{-4} mol·l^{-1}) at low frequency; at the same time, frequency dependence also changed.

For the surfactant on its own solution, the dilational elasticity shows very low frequency dependence and has fairly high value at low bulk concentration. This elastic character arises due to the strong interactions between adsorbed surfactant molecules and the weak molecular exchange between the bulk and the interface. The gemini surfactant C_{12}COONa-p-C_9SO_3Na can form a compact adsorbed layer in the interface because it has two flexible alkyl chains that can easily "entangle". As the concentration increases, the adsorbed layer acquires a viscoelastic character due to the transport of surfactant molecules from the bulk to the interface. This transport mechanism, indicating the presence of a soluble monolayer, reduces the modulus of the adsorbed layers and, eventually, the rheological response of the interface is characterized by low values of elasticity [26]. However, the addition of polymer can significantly modify the dilational properties of adsorbed surfactant layer. The principle of interactions between polymer molecules and surfactants may be shown schematically as Fig. 3. A similar sketch of this structure has been discussed in literature [27]. For asymmetrical anionic gemini surfactant C_{12}COONa-p-C_9SO_3Na, larger vacancies between ionic heads of surfactant molecules exist at the interface due to strong electrostatic interaction, so the chain of polymer molecules may enter these vacancies and form a mixed-adsorption layer with surfactant molecules through hydrophobic interaction. At low surfactant concentration, the addition of the polymer weakens the "entanglement" of long alkyl chains of surfactants, which decreases strikingly the dilational elasticity. As surfactant concentration increases, the dilational elasticity is higher than that of pure surfactant at low frequency and still has no frequency dependence. This can be explained as follows: Compared with polymer, the surfactant molecules can adsorb at the interface more readily because of their smaller molecular size and higher diffusivity; they also desorb from the interface more easily upon compression. As a result, some surfactant molecules desorb from the interface, while the polymer chains remain at the interface upon compression. Therefore, the whole surfactant–polymer layer is more rigid than pure C_{12}COONa-p-C_9SO_3Na solution.

Interfacial dilational viscosities as a function of the dilational frequency are presented in Fig. 4 for the 0.15 wt.% polymer at different C_{12}COONa-p-C_9SO_3Na concentration and the surfactant on its own solution, respectively. It is generally believed that the dilational viscosity reflects the

Table 1 Interfacial relaxation processes and their characteristic times for 0.15 wt.% polymer at different C_{12}COONa-p-C_9SO_3Na concentration

C_{12}COONa-p-C_9SO_3Na concentration	$\Delta\gamma_1$ (mN/m)	T_1 (s)	$\Delta\gamma_2$ (mN/m)	T_2 (s)	$\Delta\gamma_3$ (mN/m)	T_3 (s)
1×10^{-6} mol l^{-1} (no polymer)	3.71	1.58	0.94	25.00	0.90	454.55
1×10^{-5} mol l^{-1} (no polymer)	5.27	1.39	0.99	18.52	0.64	208.33
1×10^{-4} mol l^{-1} (no polymer)	1.71	1.92				
1×10^{-6} mol l^{-1} + Mo-4000	1.07	7.88	1.36	71.43	1.89	434.78
1×10^{-5} mol l^{-1}+Mo-4000	0.69	9.71	0.76	51.55	0.69	270.27
1×10^{-4} mol l^{-1}+Mo-4000	0.41	4.83	0.45	44.05	0.31	370.37

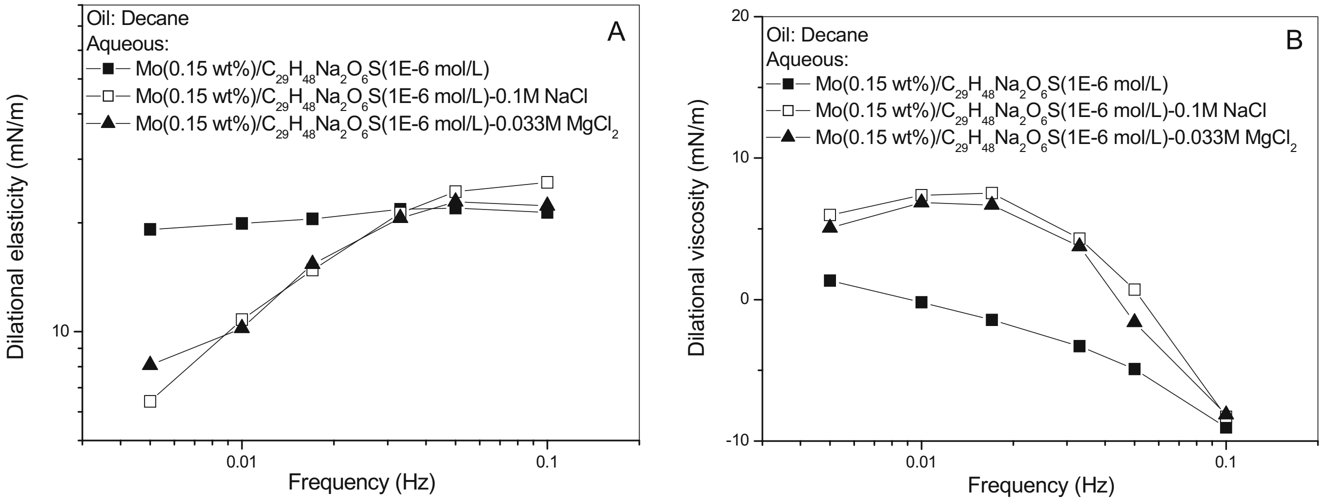

Fig. 6 Interfacial dilational elasticity (**A**) and dilational viscosity (**B**) as a function of frequency for Mo (4000)–$C_{12}COONa$-p-C_9SO_3Na solutions with and without electrolyte

summation of the various microscopic relaxation processes at and near the interface and different relaxation processes have different characteristic frequencies. The spectrum of dilational viscous component may appear more than once as maximum values at different frequencies; also, contributions of different microscopic relaxation processes may overlap when their characteristic frequencies have little difference [28].

As seen from Fig. 4A, the dilational viscosity decreases with the increase of the dilational frequency and negative values appear at high frequency. These results indicated the characteristic frequency appearing at lower frequency and the existence of the slow process at or near the interface. The negative value of the dilational viscosity stems from the negative dilational phase angle. The apparent negative value will appear when the phase of the interfacial area oscillation is ahead of that of interfacial tension oscillation, which may imply the existence of strong interfacial interaction and interfacial complex. The possible mechanism responsible for apparent negative phase angle has been discussed in our previous paper [17–18]. We can see from Fig. 4B that the phase angle shows more negative value for pure surfactant at 1×10^{-6} mol·l^{-1}, which can be explained perfectly by the weakening of "entanglement" of alkyl chains of surfactant molecules as we have proposed in Fig. 3.

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. A typical result for the experimental interfacial tension decay and the fitted curve for Mo-$C_{12}COONa$-p-C_9SO_3Na (1×10^{-5} mol l^{-1}) are shown in Fig. 5. It can be seen that the fitting is in good agreement with the experimental data. We can determine the characteristic relaxation time T_i and contribution of different relaxation process ($\Delta\gamma_i$), which are connected with the dynamic characteristics of surfactant molecules and can provide the most important information about relaxation processes, by this method.

The characteristic relaxation times and contributions of the relaxation processes with and without 0.15 wt.% polymer at different $C_{12}COONa$-p-C_9SO_3Na concentration are listed in Table 1. As can be seen from Table 1, it is an obvious tendency for pure surfactant solutions that, along with the increase of surfactant concentration, the contribution of slow relaxation processes decreased and gradually disappeared. There are three similar relaxation processes for Mo (4000)–$C_{12}COONa$-p-C_9SO_3Na mixed solutions with the increase of the surfactant concentration, which may be attributed to the molecular exchange between the interface and the bulk, the change of molecular conformation, and the arrangement of interfacial layer, respectively. Furthermore, the addition of polymer can increase the characteristic relaxation times and decrease the contribution of the first two processes, while increasing the contribution of the slowest process. Especially at the high surfactant concentration, at which the diffusion-exchange process dominates the dynamic dilational properties of pure surfactant solu-

Table 2 Interfacial relaxation processes and their characteristic times for 0.15 wt.% Mo (4000)–1×10^{-6} mol l^{-1} $C_{12}COONa$-p-C_9SO_3Na solution

Surfactant concentration	$\Delta\gamma_1$ (mN/m)	T_1 (s)	$\Delta\gamma_2$ (mN/m)	T_2 (s)	$\Delta\gamma_3$ (mN/m)	T_3 (s)
Mo–1×10^{-6} mol l^{-1} $C_{12}COONa$-p-C_9SO_3Na	1.07	7.88	1.36	71.43	1.89	434.78
Mo–C29H48Na2O6S—0.1 mol l^{-} NaCl	3.78	5.81	1.04	29.41		
Mo–C29H48Na2O6S—0.03 mol l^{-1} $MgCl_2$	1.84	10.10	1.19	35.71		

tion, the slow diffusion of the polymer as well as the entanglements between polymer chain and alkyl chains of surfactant molecules led to long relaxation time, as shown in Table 1, which is accordant with the experimental results obtained by dilational viscoelasticity measurement and the possible mechanism we have proposed above.

Influence of electrolyte on the interfacial dilational properties of Mo (4000)–C_{12}COONa-p-C_9SO_3Na systems

Figure 6 shows the influence of electrolyte on dilational viscoelastic behaviors of Mo (4000)–C_{12}COONa-p-C_9SO_3Na mixed solutions. The dilational properties of the adsorbed layer are affected strikingly by the addition of electrolyte. The interfacial dilational elasticity indicates that, in the absence of any electrolyte, the adsorbed layer is predominantly elastic in nature. However, in the presence of electrolyte, a significant difference in the viscoelastic properties of the adsorbed layer is observed, as can be seen from Fig. 6A. The dilational elasticity decreases significantly, particularly at lower frequency, and becomes almost constant at higher frequency, which resulted from the strong electrostatic screening of electrolyte. Addition of electrolyte possibly compresses the distance of molecules, which leads to a higher dilational elasticity; also, it possibly speeds up molecular exchange between bulk and interface, which results in the decrease of dilational elasticity. In our experiments, it is very obvious that the fast exchange between bulk and interface dominates the dilational properties. Furthermore, there has been a similar value of the dilational elasticity and similar trend frequency dependence in the same ionic strength of different electrolyte solution.

From Fig. 6B, it was found that the dilational viscosity decreases monotonically with frequency for Mo (4000)–C_{12}COONa-p-C_9SO_3Na solution, while a maximum value comes forth when the electrolyte is added during our experimental frequency range, which indicates that the process controlling the interfacial dilational properties moves to faster characteristic relaxation times. At the same time, the dilational viscosity increases in the presence of electrolyte. This may be due to the faster relaxation process depleting more energy when the interface is disturbed.

The characteristic relaxation times and contributions of the relaxation processes for Mo (4000)–C_{12}COONa-p-C_9SO_3Na solution in the absence or presence of electrolyte are listed in Table 2. It can be seen clearly from Table 2 that there exist three main relaxation processes for Mo (4000)–C_{12}COONa-p-C_9SO_3Na solution and the contribution of conformational change and rearrangement processes is dominating, which means the in-interface slow relaxation process controls the dynamic dilational properties. However, there exist only two faster relaxation processes when electrolyte was added to Mo (4000)–C_{12}COONa-p-C_9SO_3Na solution. At the same time, diffusion-exchange process dominates the dynamic dilational properties, which can prove that electrolyte plays an important role in affecting interfacial behavior of molecules.

As seen from Table 2, for Mo (4000)–C_{12}COONa-p-C_9SO_3Na solution, the same ionic strength of different electrolyte solution has little influence on the viscoelastic properties of the adsorbed layer. It may be seen that T_1 and T_2 values in the presence of 0.1 mol l^{-1} NaCl are lower than that in the presence of 0.03 mol l^{-1} $MgCl_2$. It clearly suggests that the interface forms a looser layer in the presence of NaCl and Na^+ is more effective than Mg^{2+} with regard to dilational property. The results from interfacial tension relaxation measurements are in good agreement with those from dilational viscoelasticity measurements.

Conclusion

The dilational viscoelastic properties of partly hydrolyzed polyacrylamide (HPAM) and surfactant (C_{12}COONa-p-C_9SO_3Na) in the absence or presence of electrolyte were investigated at the decane–water interface by means of longitudinal method and the interfacial tension relaxation method. At low surfactant concentration, the dilational modulus decreases significantly due to the weakening the “entanglement” of long alkyl chains by the insertion of the polymer chain. However, the increase of dilational modulus by the addition of polymer at higher surfactant concentration might be explained by the mixed adsorption of the polymer chains and surfactant molecules, which results in more rigid adsorbed layer than pure C_{12}COONa-p-C_9SO_3Na solution and consequently causes the increase of dilational modulus, especially at low frequency. The influence of electrolyte on dilational viscoelastic properties leads to a lower dilational elasticity and a maximum at the dilational viscous compound, probably due to the screening of electrostatic interactions between the ionized groups. There exist three similar relaxation processes for all Mo (4000)–C_{12}COONa-p-C_9SO_3Na solutions, while the slowest relaxation process disappears when the electrolytes are added to the solution. The results obtained from interfacial tension relaxation measurements are in good agreement with those from dilational viscoelasticity measurements.

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