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Surface Tension and Dilational Viscoelasticity of Water in the Presence of Surfactants Tyloxapol and Triton X-100 with Cetyl Trimethylammonium Bromide at 25 °C

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Surface tension and dilational viscoelasticity of water in the presence of surfactants Tyloxapol and Triton X-100 with cetyl trimethylammonium Bromide (CTAB) at 25 °C are investigated. The results show that there is synergistic behavior in both the mixtures at higher mole fraction of nonionic surfactant. According to the Rubingh and Rosen theory, the results predict nonideal mixing and attractive interaction between the constituent surfactants in the mixed micelle and layer. By using the Maeda theory, the results suggest the chain−chain interaction among surfactants does not seem to be high. The surface dilational viscoelasticity results show that the Tyloxapol adsorption layer has the highest dilational modulus $|\varepsilon|$ value among three single surfactants. Also, it indicates the $|\varepsilon|$ maximum values of surfactant mixtures are usually between that of the single surfactant. Moreover, it is worth noting that the $|\varepsilon|$ maximum values of Tyloxapol/CTAB mixtures are always higher than those of TX-100/CTAB ones.

Introduction

Mixtures of surfactants have received wide attention for several decades because they are often used in mixed systems to obtain some desired performance, and in particular, their properties, such as surface activity, wetting, adsorption, solubilization, emulsification, suspension, dispersion, and so forth, are often better than that of single substances.[1−3] Mixed systems of conventional surfactants have been studied extensively to develop better functions or to make clear the nature of interaction between them.[4−10]

Oligomeric surfactants are a new class of amphiphiles including dimeric (gemini), trimeric, and tetrameric, etc. Their physicochemical behavior has been widely investigated in recent years due to the fact they are characterized by much lower cmc and stronger surface tension lowering ability than that of corresponding conventional surfactants. These predominant properties have been mostly demonstrated for dimeric cationic[11−18] and anionic[19−21] surfactants. However, a few studies on dimeric nonionic surfactant are reported.[22−25] It is noticeable that trimeric and tetrameric cationic surfactants are characterized by even lower cmc values than dimeric surfactants.[26,27] Typically, from monomeric to dimeric and the trimeric and finally the tetrameric, the cmc decreases strongly and the foaming ability increases. In view of their high cost, studies on a combination of conventional/oligomeric surfactants are performed with the hope of observing synergism that would make the use of oligomeric surfactants in formulations more attractive.

Tyloxapol's physicochemical properties have been reported.[22,28−35] Recently, we have studied the interfacial tension between the complex system TX-100/CTAB/HPAM and crude oil, where the results indicate that the surfactant mixture in the presence of HPAM is capable of satisfying requirements of high viscosity and low interfacial tension under the condition of higher temperature in mineralized water. From the results of the adsorption on the quartz sands and the core flooding tests, it can be concluded that the HPAM/TX-100/CTAB complex system is suitable to be used as a displacement system in the oil field after polymer flooding.[36] The results also show that ultralow interfacial tension could be obtained by the Tyloxapol/CTAB/HPAM mixed system.[37] Moreover, it is reported that interfacial rheology plays an important role in the oil displacement process except interfacial tension and bulk viscosity.[38−40]

In the present study, surface tension and dilational viscoelasticity of water in the presence of surfactants Tyloxapol and TX-100 with CTAB at 25 °C are investigated. The surfactant/surfactant interactions in the micelles and monolayers have been analyzed using the theories of Clint, Rubingh, Rosen, and Maeda with the aim to reveal the comparative performance of these mixtures. Surface dilational viscoelasticity of surfactant mixtures with various mole fractions is investigated in detail. This work will be helpful for further potential application in enhanced oil recovery and the stability of emulsion and foam.

Experimental Section

Materials. Samples of Tyloxapol (Sigma Ultra grade), Trion X-100 (polyoxyethylene *tert*-octylphenyl ether, TX-100) and cetyl trimethylammonium bromide (CTAB) were all purchased from Sigma Chemicals and were used without further purification. Water used in the experiments was triply distilled by a quartz water purification system.

Methods. Surface Tension Measurements. Surface tension measurements of aqueous solutions of single and mixed surfactants at various concentrations were carried out on the PROCESSOR K12 processor tensiometer (Krüss Co., Germany) with a ring method. The value of surface tension was the average of readings from three separate measurements.

Surface Dilational Viscoelasticity Measurements. Detailed experimental methods of surface dilational viscoelasticity measurements were introduced in our earlier paper.[41]

All experiments were performed at (25.0 ± 0.1) °C.

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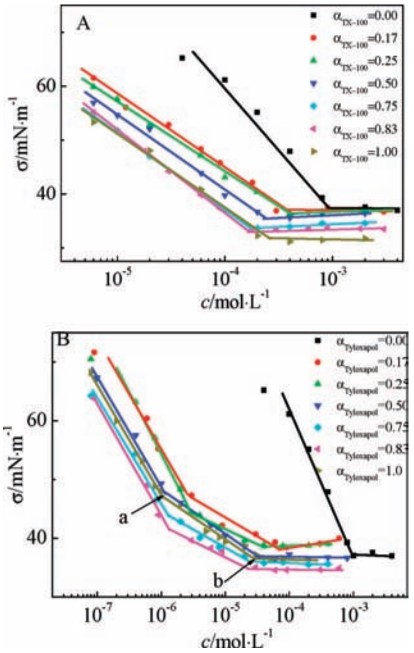

Figure 1. Surface tension vs total surfactant concentration for different mole fractions of TX-100/CTAB (A) and Tyloxapol/CTAB (B) mixtures.

Results and Discussion

Surface Activity. Surface Activity of TX-100 and Tyloxapol. The surface tension isotherms of the nonionic surfactant solutions are shown in Figure 1. Obviously, the curves differ from each other. There are two distinct break points in the surface tension isotherm of Tyloxapol, and only one is observed in that of TX-100. For Tyloxapol, the concentration at the first and the second break point is $1.0 \cdot 10^{-6}$ $\text{mol} \cdot \text{L}^{-1}$ and $3.0 \cdot 10^{-5}$ $\text{mol} \cdot \text{L}^{-1}$, respectively. According to the literature,[42] the interpretation of the two breaks arises from the broad distribution of molecular weight. It has been shown that Tyloxapol is polydisperse by chromatography in ref 35. Also it may be attributed to the change of molecular conformation at the air/water interface[43] or the formation of unimolecular micelles or oligomers[44] before cmc. In other words, the concentration corresponding to the first break point is not the "real" cmc. As a result, the second break point corresponds to the cmc value of Tyloxapol. The minimum area per molecule $A_{\min}$ at the air/water surface is calculated according to the Gibbs adsorption equation

$$\Gamma_{\max} = -\frac{1}{nRT}\left(\frac{\partial \sigma}{\partial \ln c}\right)_T \tag{1}$$

$$A_{\min} = \frac{1}{\Gamma_{\max} N_A} \tag{2}$$

where $R = 8.314$ $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; N_A is Avogadro's number; and the value of n is taken as 1. For Tyloxapol, $\Gamma_{\max}$ is obtained according to the linear parts of "ab" as in Figure 1B, and $\partial\sigma/\partial \ln c$ was the slope of the linear part of "ab".[45]

It can be seen that the cmc of Tyloxapol is about 10 times lower than that of TX-100. A similar result has been found for other ionic surfactant oligomers and the corresponding monomer systems.[25,26] However, the σ_{cmc} of Tyloxapol is higher than that of TX-100. These results indicate that the surface tension reduction efficiency of Tyloxapol is higher than that of TX-100, and the surface tension reduction effectiveness of the former is lower than that of the latter. It is strange that the calculated minimum area per molecule $A_{\min}$ at the air−water surface is 0.66 nm^2 for TX-100 and 1.24 nm^2 for Tyloxapol, respectively; i.e., the $A_{\min}$ value for Tyloxapol is twice as large as that for TX-100, although the molecule of the former is seven times as large as that of the latter. This is consistent with the result in ref 34, in which Schott has calculated that the area per Tyloxapol molecule at the air−water surface is 1.05 nm^2. Then it is proposed that the comparatively small area per molecule of the oligomer Tyloxapol indicates an unusual molecular orientation at the air/water surface, such as U- or V-shaped instead of extended horizontally. The isooctyl chains will fill the inside of the U or V and attract one another due to a hydrophobic effect, while the polyoxyethylene chains will be on the outside of the U or V in a randomly coiled conformation, surrounded by water and fully hydrated. The relatively high σ_{cmc} is attributed to the exposure of $-\text{CH}_2$ groups to the surface as the molecules adsorbed at the surface bend to assume U or V shapes.

Surface Activity of Binary Surfactant Mixtures. The surface tension of mixed surfactant solutions versus total concentration at different mole fractions in the TX-100/CTAB and Tyloxapol/CTAB systems is shown in Figure 1. The values of cmc and σ_{cmc} of binary surfactant mixtures are presented in Tables 1 and 2. It will be seen that in all surfactant mixtures the cmc value is lower than that of the single CTAB surfactant. The cmc values of binary mixtures decrease gradually with increasing mole fraction of the nonionic surfactant in solution, indicating the formation of mixed micelle due to a hydrophobic effect between ionic and nonionic surfactant hydrophobic chains. The nonionic surfactant molecules insert into the micelle of CTAB, and the electrostatic repulsion between ionic head groups of CTAB is weakened. As a result, aggregation of CTAB molecules is advantageous. It can be seen from Tables 1 and 2 that cmc values in the mixed system are even lower than that of the single nonionic surfactant when the mole fraction of TX-100 and Tyloxapol is above 0.5 and 0.75, respectively, indicating synergistic behavior in micelle formation. However, there are still two break points in the surface tension isotherms of the Tyloxapol/CTAB mixed system with different mole fractions. The values of σ_{cmc} decrease slightly with increasing nonionic surfactant mole fraction for either mixture. The decreased σ_{cmc} of the mixtures compared to that of single CTAB reflects the enhanced surface activity of the mixed system upon increasing the mole fraction of the nonionic surfactant. It is noticeable that the σ_{cmc} of the Tyloxapol/CTAB mixed system is even lower than that of Tyloxapol when the mole fraction of Tyloxapol is 0.83, indicating synergism in surface tension reduction. However, it has been found that the cmc's of TX-100 and C_{12}E_n with quaternary ammonium dimeric surfactants $\text{C}_{12}\text{-}s\text{-C}_{12} \cdot 2\text{Br}$ (s = 2, 3, 4, 6) are always between that of the single surfactants.[46,47]

Interaction Parameter in Surface Layer and Micelle. The cmc value for the mixed surfactant system (C_{12}) can be calculated theoretically using Clint's equation

$$\frac{1}{C_{12}} = \frac{\alpha_1}{C_1} + \frac{1 - \alpha_1}{C_2} \tag{3}$$

where C_{12}, C_1, and C_2 are the cmc values of the mixture, surfactant 1, and surfactant 2 respectively. α_1 is the mole fraction of surfactant 1, and α_2 (i.e., $1 - \alpha_1$) is the mole fraction of surfactant 2 in solution, respectively. The cmc values obtained experimentally (cmc_{exp}) are plotted as a function of the mole fraction of the nonionic surfactant in Figure 2. The exact values of cmc_{exp} and C_{12} are given in Table 3. It is clear that the cmc_{exp} values are lower than the C_{12} values. This indicates that there

Table 1. Various Physicochemical Parameters for the TX-100/CTAB Mixed Surfactant System

	cmc	σ_{cmc}						ΔG_{m} PS model	ΔG_{m} Maeda
$\alpha_{\text{TX-100}}$	10^4 mol·L^{-1}	mN·m^{-1}	$X^m_{\text{TX-100}}$	β^m	$X^s_{\text{TX-100}}$	β^s	B_1	kJ·mol^{-1}	kJ·mol^{-1}
0.0	10.0	37.4	0.0	—	0.0	—			
0.17	3.89	37.1	0.478	−2.16	0.655	−1.60	−0.733	−29.4	−30.1
0.25	3.72	36.7	0.545	−1.65	0.712	−1.76	−0.223	−29.5	−30.0
0.50	2.26	36.4	0.651	−2.66	0.830	−1.76	−1.23	−30.8	−30.9
0.75	2.00	34.6	0.749	−2.88	0.767	−3.38	−1.45	−31.1	−31.1
0.83	1.76	33.6	0.758	−3.68	0.820	−4.44	−2.25	−31.4	−31.4
1.0	2.40	31.4	1.0	—	1.0	—			

Table 2. Various Physicochemical Parameters for the Tyloxapol/CTAB Mixed Surfactant System

	cmc	σ_{cmc}						ΔG_{m} PS model	ΔG_{m} Maeda
$\alpha_{\text{Tyloxapol}}$	10^5 mol·L^{-1}	mN·m^{-1}	$X^m_{\text{Tyloxapol}}$	β^{m}	$X^s_{\text{Tyloxapol}}$	β^s	B_1	kJ·mol^{-1}	kJ·mol^{-1}
0.0	100	37.4	0.0	—	0.0	—			
0.17	7.00	39.3	0.665	−3.96	0.744	−5.73	−0.381	−33.6	−35.1
0.25	3.82	38.86	0.660	−5.67	0.705	−8.46	−2.09	−35.2	−36.0
0.50	3.14	37.1	0.754	−4.83	0.800	−6.04	−1.25	−35.7	−36.0
0.75	2.37	35.8	0.798	−5.53	0.759	−10.4	−1.95	−36.3	−36.3
0.83	2.28	34.6	0.819	−5.74	0.753	−11.7	−2.16	−36.4	−36.4
1.0	2.79	36.0	1.0	—	1.0	—			

Table 3. Variation of cmc$_{\text{exp}}$ and C_{12} as a Function of Mole Fraction of Nonionic Surfactant

	cmc$_{\text{exp}}$	C_{12}		cmc$_{\text{exp}}$	C_{12}
$\alpha_{\text{TX-100}}$	10^4 mol·L^{-1}	10^4 mol·L^{-1}	$\alpha_{\text{Tyloxapol}}$	10^5 mol·L^{-1}	10^5 mol·L^{-1}
0	10.0	1.00	0	100	100
0.17	3.89	6.50	0.17	7.00	14.4
0.25	3.72	5.58	0.25	3.89	10.3
0.50	2.26	3.87	0.50	3.14	5.43
0.75	2.00	2.96	0.75	2.37	3.69
0.83	1.76	2.76	0.83	2.28	3.34
1.00	2.40	2.40	1.00	2.79	2.79

are interactions between the constituent surfactants in the mixed micelle that result in nonideal behavior. Hence, to investigate the nature of interaction between the constituent surfactants in the mixed micelle and monolayer, we calculated the interaction parameters for mixed micelle formation in an aqueous solution β^m, interaction parameters for mixed monolayers at the air/water interface β^s, and the chain−chain interaction parameter B_1, using the Rubingh,[48] Rosen,[49] and Maeda theories,[50] respectively.

The β^m values are computed at σ_{cmc} of mixtures with different mole fractions. The β^s values are functions of overall surface tension, and hence they are computed at a randomly fixed σ of 45 mN·m^{-1}. The β^s and β^m values for the two mixed systems are listed in Tables 1 and 2, respectively. Both β^s and β^m values are negative, suggesting that the interaction between the two surfactants is more attractive in the mixed monolayer and mixed micelle than the self-interaction of two surfactants before mixing. Moreover, the β^s or β^m values become more negative as the nonionic surfactant content in the mixed surfactant system increases. For cationic/nonionic mixed surfactant systems, significant electrostatic self-repulsion of cations and weak steric self-repulsion (depending on the headgroup size) of the nonionics before mixing are weakened by dilution effects after mixing, and the electrostatic self-repulsion of the cationic surfactants is replaced by the attractive ion−dipole interaction between hydrophilic groups of cationic and nonionic surfactants.[7] The nonionic surfactants of the PEO class (polyoxyethylene, hydrophilic part of the nonionic surfactant) have a large number of oxygen atoms with unpaired electrons. These will have a tendency to interact Coulombically with the cationic surfactant.[51] Both β^s and β^m values are more or less the same for the TX-100/CTAB system. However, in the case of Tyloxapol/CTAB, the β^m values are less negative than the β^s in all cases, indicating the difficulty of incorporating tightly packed chains into a micelle than in a monolayer. This may be due to the greater difficulty of accommodating hydrophobic groups in the interior of a convex micelle compared to a planar interface.[48] However, Rakshit et al.[51] have observed that β^s values for the alkanediyl-α,ω type cationic gemini surfactant 16-10-16, 2Br$^-$/C$_{12}$E$_6$ system are less negative than the β^m in all cases, while in the case of 16-10-16, 2Br$^-$/TX-100 both β^s and β^m are more or less the same. Furthermore, the values of β^s and β^m are more negative for the Tyloxapol/CTAB system than that for the TX-100/CTAB system. This is probably due to the greater PEO density in Tyloxapol as it takes up a U or V shape. Moreover, these mixed micelles and monolayer are predominated by nonionic surfactants as indicated by $X_{\text{TX-100}}$ and $X_{\text{Tyloxapol}}$ in Tables 1 and 2, in conformity with the results of other studies on different cationic−nonionic mixed systems.[47,52,53]

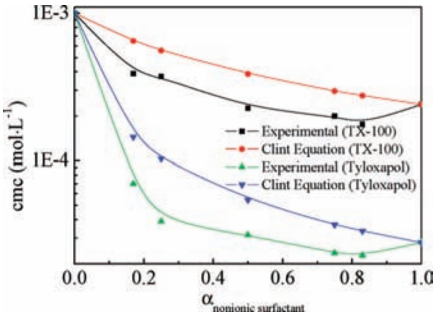

Figure 2. Variation of cmc vs mole fraction of nonionic surfactant.

However, Maeda[50] and Ruiz et al.[54] have reported that both chain/chain and headgroup/headgroup interactions may operate in the mixed system. β^m values explain the headgroup/headgroup interactions but do not encompass the chain/chain interactions between the hydrocarbon segments of the constituent surfactant molecules, particularly when the chains are of dissimilar length. The lower cmc values of the mixed system can be due to the decrease in ionic headgroup repulsions caused by the presence of nonionic surfactant molecules between the CTAB head groups. Maeda[50] suggested another parameter B_1, the chain−chain interaction parameter, which actually contributes to the stability of the mixed micelle. The free energy of micellization (ΔG_{m}) as a function of ionic component in the mixed micelle (X_1) is given by

$$\Delta G_{\mathrm{m}} = RT(B_0 + B_1X_1 + B_2X_1^2) \qquad (4)$$

where

$$B_0 = \ln c_2 \quad (c_2 \text{ is the cmc of the nonionic surfactant}) \qquad (5)$$

$$B_1 + B_2 = \ln\left(\frac{c_1}{c_2}\right) \quad (c_1 \text{ is the cmc of the ionic surfactant}) \qquad (6)$$

and

$$B_2 = -\beta^m \qquad (7)$$

where B_1 is associated with standard free energy change when an ionic surfactant replaces a nonionic surfactant (cmc of which is related with B_0). B_2 is the regular solution theory interaction parameter but with opposite sign. All quantities in the above equations are expressed on a unitary scale. The calculated values of B_0 for the TX-100/CTAB and Tyloxapol/CTAB mixed system are −12.4 and −14.5, respectively. B_1 and the free energy of micellization (ΔG_{m}) are presented in Tables 1 and 2.

It is evident that the ΔG_{m} values calculated from the phase separation model[48] ($\Delta G_{\mathrm{m}} = RT \ln X\mathrm{cmc}$, where Xcmc is cmc in mole fraction scale) and by Maeda's method[50] agree reasonably well (within ± 5 % for most of the mole fractions of the mixed system). The cationic surfactant has 16 carbons in its hydrocarbon chain, whereas the TX-100 equals to 11.5 carbons and Tyloxapol equals to seven chains of 11.5 carbons (as the phenyl group of the hydrophobic tail is equivalent to three and one-half methylene group).[51] Hence, according to Maeda theory, as the chain lengths are different, there should be chain−chain interactions helping in the stability of the micelle. The interactions may also be explained by the fact that some water molecules may be shared by different head groups as well as by the hydrophobic chains; i.e., water molecules may behave as some type of bridge between the molecules just below the water−micelle interface, and thereby attractive interaction will ensue.[9] The B_1 values do not seem to be high, and it is observed that the value is more or less the same for both of the two mixed systems, which is probably ascribed to the same elements of the hydrocarbon chain of Tyloxapol and its corresponding monomeric surfactant. However, Rakshit et al.[51] have given highly negative B_1 values for both 16-10-16, 2Br$^-$/C$_{12}$E$_6$ and 16-10-16, 2Br$^-$/TX-100 systems. In addition, the B_1 values seem to be a function of composition of the system.

Surface Dilational Viscoelasticity. Surface Dilational Viscoelasticity of Single Surfactant System. Surface dilational viscoelasticity is important in understanding the formation and stability of foam, emulsion, oil displacement as well as many other phenomena in industrial and scientific processes. Therefore, it has been studied extensively, and detailed experimental theory on dilational viscoelasticity is depicted in the literature.[55−58]

Dilational modulus is the summation of elasticity and viscosity contributions. Dilational elasticity is caused by the energy change due to departure from the equilibrium state of interfacial molecules after perturbation, which is related to molecular interaction, and dilational viscous components reflect the summation of the complex various microscopic relaxation processes at and near the interface such as the transport of molecules from the bulk to the interface and rearrangement of molecules at the interface.[59]

Figure 3 shows the variations of the dilational module |ε| and phase angle θ as a function of oscillation frequency for Tyloxapol (both TX-100 and CTAB have a similar trend, therefore it is not shown here). The data of viscoelasticity parameters are given in Table 4. It is observed that variations of both |ε| and θ depend on the change of oscillation frequency. The dilational moduli |ε| increase with increasing oscillation frequencies, which is consistent with the results in the literature,[41,60] whereas phase angles θ decrease monotonically. Two extreme cases are easy to understand: when the frequency of the compression is low, the monolayer has time to reach

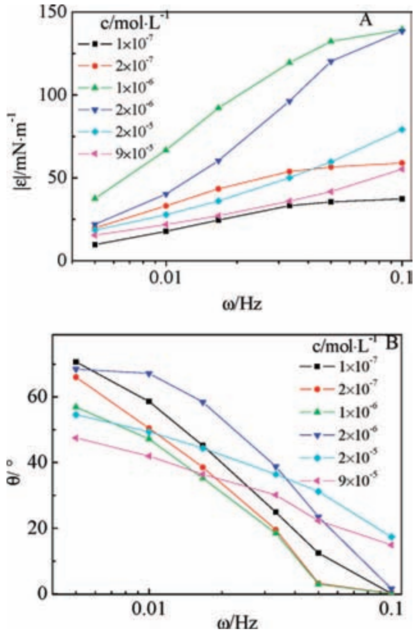

Figure 3. Surface dilational viscoelasticity of Tyloxapol s as a function of oscillation frequency: (A) dilational modulus |ε|, (B) phase angle θ.

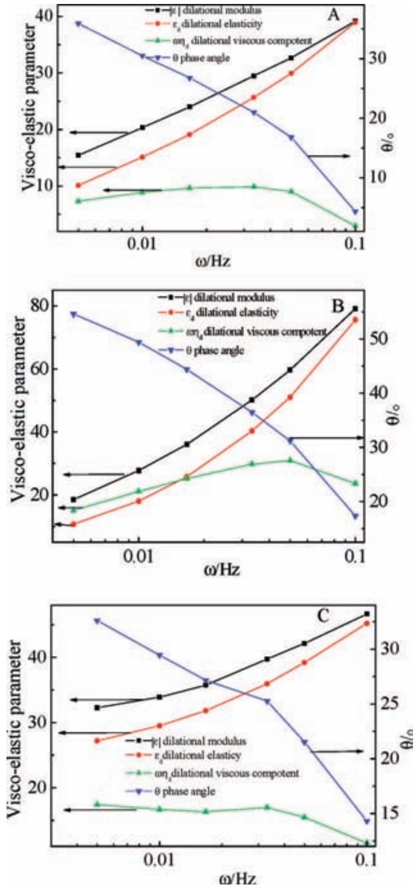

Figure 4. Viscoelastic parameter of surfactants as a function of oscillation frequency: (A) TX-100; (B) Tyloxapol; (C) CTAB.

Table 4. Variations of the Dilational Module |ε| and Phase Angle θ as a Function of Oscillation Frequency for Tyloxapol

	$C_{\mathrm{Tyloxapol}}/10^6$ mol·L^{-1}											
	0.1		0.2		1		2		20		90	
ω/Hz	|ε|/mN·m^{-1}	θ/°	|ε|/mN·m^{-1}	θ/°	|ε|/mN·m^{-1}	θ/°	|ε|/mN·m^{-1}	θ/°	|ε|/mN·m^{-1}	θ/°	|ε|/mN·m^{-1}	θ/°
0.005	9.79	70.7	19.8	66.0	37.5	56.9	22.0	68.5	18.6	54.6	15.4	47.5
0.010	17.7	58.6	33.1	50.4	66. 8	47.2	40.3	67.2	27.8	49.4	21.9	42.0
0.017	24.6	45.2	43.4	39.5	92.2	35.2	60.4	58.5	36.1	44.4	27.2	36.4
0.030	33.2	24.9	53.8	19.6	119	18.5	96.4	38.9	50.1	36.5	35.9	30.2
0.050	35.5	12.4	56.5	3.19	132	2.90	120	23.4	59.7	31.2	41.7	22.3
0.100	37.3	0.09	58.9	0.07	139	0.05	138	1.55	79.2	17.3	55.2	15.0

Table 5. Viscoelastic Parameters of Three Single Surfactants with the Same Bulk Concentration $2 \cdot 10^{-5}$ mol·L^{-1} as a Function of Oscillation Frequency

	TX-100				Tyloxapol				CTAB			
ω	|ε|	ε_d	$\omega\eta_d$	θ	|ε|	ε_d	$\omega\eta_d$	θ	|ε|	ε_d	$\omega\eta_d$	θ
Hz	mN·m^{-1}	mN·m^{-1}	mN·m^{-1}	°	mN·m^{-1}	mN·m^{-1}	mN·m^{-1}	°	mN·m^{-1}	mN·m^{-1}	mN·m^{-1}	°
0.005	15.4	10.1	7.33	35.9	18.6	10.7	15.1	54.6	32.29	27.2	17.4	32.6
0.010	20.3	15.1	8.88	30.5	27.8	18.1	21.1	49.4	33.89	29.5	16.7	29.5
0.017	24.0	19.1	9.64	26.7	36.1	25.8	25.2	44.4	35.75	31.8	16.3	27.2
0.030	29.5	25.7	9.85	21.0	50.1	40.3	29.8	36.5	39.75	35.9	17.0	25.3
0.050	32.7	30.0	9.03	16.8	59.7	51.0	30.9	31.2	42.15	39.2	15.5	21.5
0.100	39.15	39.0	2.96	4.35	79.2	75.6	23.6	17.4	46.67	45.2	11.5	14.3

equilibrium and there is no resistance to the compression (|ε| = 0 for ω→0). When the frequency is high, the monolayer has no time to respond and behaves as if it were insoluble (|ε| = $|\varepsilon_0|$ for ω→∞). Thus, |ε| increases with increasing ω until a plateau value is reached.[61] Hence, the results may be interpreted as follows: there is a long enough time for surfactant molecules to modify the interfacial concentration gradient caused by the area change through different relaxation processes at or near the interface at low oscillation frequencies. Otherwise, the time is not long enough to modify the interfacial concentration gradient through different relaxation processes at high oscillation frequencies. As a result, the dilational moduli increase with increasing oscillation frequencies, and the phase angles θ are contrary. According to the literature,[59] the rearrangement of molecules at the interface plays the main role at low surfactant concentration, while the transport of molecules from the bulk to the interface is the dominant cause at high surfactant concentration. In addition, a plateau value is not observed because of the limit in oscillation frequency.

Viscoelastic parameters of three single surfactants with the same bulk concentration $2 \cdot 10^{-5}$ mol·L^{-1} as a function of oscillation frequency are shown in Figure 4. The data of viscoelasticity parameters of different solutions is given in Table 5. The viscoelastic parameters mainly include dilational modulus, dilational elasticity, dilational viscous component, and phase angle θ. It is seen that the adsorption layer of Tyloxapol has the highest dilational modulus and elasticity values, indicating that the strength of the Tyloxapol layer against perturbation is greatest of all and the values of the CTAB adsorption layer are higher than those of the TX-100 adsorption layer. Furthermore, the dilational modulus and elasticity are most sensitive to oscillation frequency in the Tyloxapol system, and these are more sensitive in the TX-100 system than in CTAB, probably because the time scale of molecular diffusion and that of barriers expanded or compressed are closer in the Tyloxapol system. Phase angle θ values show a decreasing trend with increasing oscillation frequency. The Tyloxapol adsorption layer always has the highest phase angle θ, indicating the greatest dilational viscous contribution to the dilational modulus. The phase angle θ value is higher for the CTAB adsorption layer than that for TX-100. However, dilational viscous components of the three single surfactants are less frequency dependent.

The dilational modulus as a function of surfactant concentration at 0.03 Hz for a single surfactant is shown in Figure 5. It is observed that the dilational moduli appear at a maximum value for all surfactants. The surfactant concentration corresponding to the |ε| maximum value is far below the cmc. Furthermore, it is shown that |ε| emerges at a maximum value at different concentrations. The results show that the corresponding concentration increases in the order of Tyloxapol < TX-100 < CTAB. The appearance of the maximum is explained as in ref 40. Moreover, it is shown that in the studied concentration range the |ε| value of Tyloxapol is much higher. The |ε| maximum value of Tyloxapol is almost twice as high as that of TX-100, suggesting a slower relaxation process at or near the surface for the former. Besides, the |ε| maximum value of TX-100 is lower in comparison with that of CTAB.

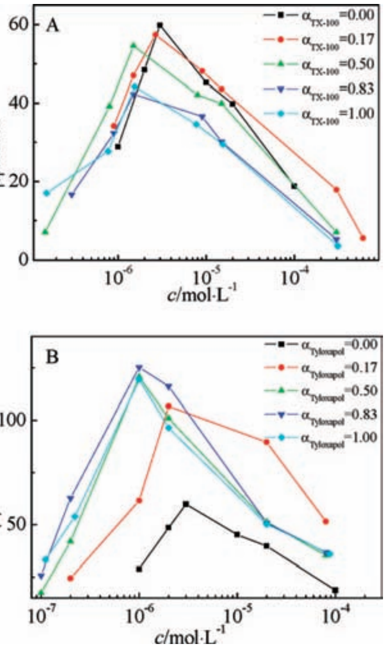

Figure 5. Surface dilational viscoelasticity of surfactant mixtures as a function of surfactant concentration: (A) TX-100/CTAB; (B) Tyloxapol/CTAB.

Table 6. Dilational Modulus Maximum Values at Different Frequency for Both the TX-100/CTAB and Tyloxapol/CTAB Surfactant Mixtures

ω		CTAB/TX-100				CTAB/Tyloxapol			
Hz	CTAB	1:5	1:1	5:1	TX-100	1:5	1:1	5:1	Tyloxapol
0.005	40.8	26.7	30.3	34.6	20.8	57.1	43.2	40.9	41.9
0.010	49.8	34.1	41.5	43.6	30.5	82.6	71.8	62.7	72.8
0.017	54.5	38.3	48.1	52.3	37.0	108	95.4	90.6	98.2
0.030	59.8	42.3	54.6	57.4	44.2	125	120	107	119
0.050	61.0	44.3	57.0	60.5	46.9	131	124	109	126
0.100	64.6	45.1	59.1	64.8	50.2	137	128	115	130

Surface Dilational Viscoelasticity of Binary Surfactant Mixtures. The dilational modulus maximum values at different frequency for both the TX-100/CTAB and Tyloxapol/CTAB surfactant mixtures are reported in Table 6. Figure 5 shows the dilational modulus as a function of surfactant concentration at 0.03 Hz for both mixtures for the sake of brevity. It is observed that the $|\varepsilon|$ appear at a maximum value for all mixed surfactants. The corresponding concentration equals that of the single nonionic surfactant when its mole fraction is 0.50 and 0.83, while the corresponding concentration is even higher when the nonionic surfactant mole fraction is 0.17.

For the TX-100/CTAB mixtures, it is found that the $|\varepsilon|$ maximum value of the adsorption layer gradually decreases with increasing TX-100 mole fraction, which is lower than that of single CTAB. Especially, the $|\varepsilon|$ maximum value is even lower than that of TX-100 for surfactant mixtures when the TX-100 mole surfactant is 0.83, whereas for Tyloxapol/CTAB mixtures the variation of the $|\varepsilon|$ value has a contrary trend as the former mixtures show. The $|\varepsilon|$ maximum value of the adsorption layer increases significantly with increasing Tyloxapol mole fraction, which is almost twice as high as that of single CTAB. It is worth noting that the $|\varepsilon|$ maximum value is a little higher than that of single Tyloxapol when the Tyloxapol mole fraction is 0.83. It is also worth noting that the $|\varepsilon|$ maximum values of Tyloxapol/CTAB mixtures are always higher than that of TX-100/CTAB mixtures. This could be explained in terms of mole fractions of nonionic surfactant in the mixed monolayer. The results suggest that the mixed monolayer is dominated by the nonionic surfactant as indicated by $X_{\text{TX-100}}$ and $X_{\text{Tyloxapol}}$ in Tables 1 and 2; namely, more nonionic surfactant adsorbs on the surface layer. That is to say, the surfactant with high surface activity has higher mole fraction in the mixed monolayer; therefore, the $|\varepsilon|$ values of the mixed surfactant get closer to that of the single nonionic surfactant. Obviously, it will be calculated that the experimental $|\varepsilon|$ maximum values for surfactant mixtures are much lower than simple addition rule results, indicating that there are interactions between the constituent surfactants.

Conclusions

Surfactants attain their maximum effectiveness and efficiency in stabilizing emulsions, suspensions, and foams at the cmc. Therefore, a surfactant with a lower cmc and σ_{cmc} can be formulated at lower use levels without compromising their effectiveness and efficiency. From this viewpoint, the fact that the cmc of the Tyloxapol/CTAB mixture only corresponds to one fifth∼one tenth that of the TX-100/CTAB is an advantage for practical use. It is noticeable that σ_{cmc} of the Tyloxapol/CTAB mixture is even lower than that of Tyloxapol when the mole fraction of Tyloxapol is 0.83, indicating synergism in surface tension reduction. Both β^s and β^m are more negative for the Tyloxapol/CTAB mixture than that for the TX-100/CTAB one; furthermore, the β^m is less negative than β^s in the former mixed system.

A potential advantage of Tyloxapol and its mixture with CTAB is that the $|\varepsilon|$ value is always higher than that of its monomer and TX-100/CTAB mixture. It is generally accepted that the dilational viscoelasticity plays an important role in stability of emulsion and foam. It is certain that the results mentioned above could offer valuable information for the correlative field.

Supporting Information Available:

List of nonionic surfactant formulas used in experiment and the equation of the Rubingh and Rosen theory. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Scamehorn, J. F. *Phenomena in Mixed Surfactant Systems*; American Chemical Society: Washington DC, 1986.

(2) Nakano, T. Y.; Sugihara, G.; Nakashima, T.; Yu, S. C. Thermodynamic Study of Mixed Hydrocarbon/Fluorocarbon Surfactant System by Conductometric and Fluorimetric Techniques. *Langmuir* **2002**, *18*, 8777–8785.

(3) Moroi, Y. *Micelles: theoretical and applied aspects*; Plenum: New York, 1992; Chapter 10.

(4) Chakraborty, T.; Ghosh, S.; Moulik, S. P. Micellization and Related Behavior of Binary and Ternary Surfactant Mixtures in Aqueous Medium: Cetyl Pyridinium Chloride (CPC), Cetyl Trimethyl Ammonium Bromide (CTAB), and Polyoxyethylene (10) Cetyl Ether (Brij-56) Derived System. *J. Phys. Chem. B* **2005**, *109*, 14813–14823.

(5) Chou, T. H.; Lin, Y. S.; Li, W. T.; Chang, C. H. Phase behavior and morphology of equimolar mixed cationic−anionic surfactant monolayers at the air/water interface: Isotherm and Brewster angle microscopy analysis. *J. Colloid Interface Sci.* **2008**, *321*, 384–392.

(6) Chen, L.; Xiao, J. X.; Ruan, K.; Ma, J. Homogeneous Solutions of Equimolar Mixed Cationic-Anionic Surfactants. *Langmuir* **2002**, *18*, 7250–7252.

(7) Dar, A. A.; Rather, G. M.; Das, A. R. Mixed Micelle Formation and Solubilization Behavior toward Polycyclic Aromatic Hydrocarbons of Binary and Ternary Cationic-Nonionic Surfactant Mixtures. *J. Phys. Chem. B* **2007**, *111*, 3122–3132.

(8) Islam, M. N.; Okano, T.; Kato, T. Surface Phase Behavior of a Mixed System of Anionic-Nonionic Surfactants Studied by Brewster Angle Microscopy and Polarization Modulation Infrared Reflection-Absorption Spectroscopy. *Langmuir* **2002**, *18*, 10068–10074.

(9) Penfold, J.; Staples, E.; Tucker, I. Neutron Small Angle Scattering Studies of Micellar Growth in Mixed Anionic-Nonionic Surfactants, Sodium Dodecyl Sulfate, SDS, and Hexaethylene Glycol Monododecyl Ether, $C_{12}E_6$, in the Presence and Absence of Solubilized Alkane, Hexadecane. *J. Phys. Chem. B* **2002**, *106*, 8891–8897.

(10) Sulthana, S. B.; Rao, P. V. C.; Bhat, S. G. T.; Nakano, T. Y.; Sugihara, G.; Rakshit, A. K. Solution Properties of Nonionic Surfactants and Their Mixtures: Polyoxyethylene (10) Alkyl Ether [C_nE_{10}] and MEGA-10. *Langmuir* **2000**, *16*, 980–987.

(11) Zheng, O.; Zhao, J. X.; Fu, X. M. Interfacial Composition and Structural Parameters of Water/C_{12}-*s*-C_{12}•2Br/*n*-Hexanol/*n*-Heptane Microemulsions Studied by the Dilution Method. *Langmuir* **2006**, *22*, 3528–3532.

(12) Zheng, O.; Zhao, J. X.; Fu, X. M. Solubilization of pyrene in aqueous micellar solutions of gemini surfactants C_{12}-s-C_{12}•2Br. *J. Colloid Interface Sci.* **2006**, *300*, 749–754.

(13) Zana, R. Dimeric (Gemini) Surfactants: Effect of the Spacer Group on the Association Behavior in Aqueous Solution. *J. Colloid Interface Sci.* **2002**, *248*, 203–220.

(14) Zhou, L. M.; Jiang, X. H.; Li, Y. T.; Chen, Z.; Hu, X. Q. Synthesis and Properties of a Novel Class of Gemini Pyridinium Surfactants. *Langmuir* **2007**, *23*, 11404–11408.

(15) Menger, F. M.; Mbadugha, B. N. A. Gemini Surfactants with a Disaccharide Spacer. *J. Am. Chem. Soc.* **2001**, *123*, 875–885.

(16) Li, F.; Rosen, M. J.; Sulthana, S. B. Surface Properties of Cationic Gemini Surfactants and Their Interaction with Alkylglucoside or–maltoside Surfactants. *Langmuir* **2001**, *17*, 1037–1042.

(17) Wu, D.; Xu, G. Y.; Sun, Y. H.; Zhang, H. X.; Mao, H. Z. Interaction between Proteins and Cationic Gemini Surfactant. *Biomacromolecules* **2007**, *8*, 708–712.

(18) Chen, Y. J.; Xu, G. Y.; Yuan, S. L.; Sun, H. Y. Dynamic study of Gemini surfactant and single-chain surfactant at air/water interface. *Chin. Chem. Lett.* **2005**, *16*, 688–690.

(19) Acharya, D. P.; Kunieda, H.; Shiba, Y.; Aratani, K. Phase and Rheological Behavior of Novel Gemini-Type Surfactant Systems. *J. Phys. Chem. B* **2004**, *108*, 1790–1797.

(20) Acharya, D. P.; Gutiérrez, J. M.; Aramaki, K.; Aratani, K.; Kunieda, H. Interfacial properties and foam stability effect of novel gemini-type surfactants in aqueous solutions. *J. Colloid Interface Sci.* **2005**, *291*, 236–243.

(21) Menger, F. M.; Littau, C. A. Gemini surfactants: a new class of self-assembling molecules. *J. Am. Chem. Soc.* **1993**, *115*, 10083–10090.

(22) Zana, R. Dimeric and oligomeric surfactants. Behavior at interfaces and in aqueous solution: a review. *Adv. Colloid Interface Sci.* **2002**, *97*, 203–251.

(23) Jones, G. P.; Regismond, S.; Kwetkat, K.; Zana, R. Micellization of Nonionic Surfactant Dimers and of the Corresponding Surfactant Monomers in Aqueous Solution. *J. Colloid Interface Sci.* **2001**, *243*, 496–502.

(24) Castro, M. J. L.; Kovensky, J.; Cirelli, A. F. New Family of Nonionic Gemini Surfactants. Determination and Analysis of Interfacial Properties. *Langmuir* **2002**, *18*, 2477–2482.

(25) Eastoe, J.; Rogueda, P. Properties of New Glucamide Surfactants. *Langmuir* **1996**, *12*, 2701–2705.

(26) Laschewsky, A.; Wattebled, L.; Arotcüaréna, M.; Habib-Jiwan, J. L.; Rakotoaly, R. H. Synthesis and Properties of Cationic Oligomeric Surfactants. *Langmuir* **2005**, *21*, 7170–7179.

(27) Wattebled, L.; Laschewsky, A.; Moussa, A.; Habib-Jiwan, J. L. Effect of Preferential Adsorption on the Synergism of a Homologous Cationic Surfactant Mixture. *Langmuir* **2006**, *22*, 2551–2557.

(28) Westesen, K. Phase diagram of tyloxapol and water-I. *Int. J. Pharm.* **1994**, *102*, 91–100.

(29) Chang, C. H.; Tseng, S. C.; Chuang, T. K. Inhibitory effects of tyloxapol on the surface activity of albumin at the air:liquid interface. *Colloids Surf. A* **2000**, *164*, 287–295.

(30) Liu, Y. L.; Chang, C. H. Inhibitory effects of fibrinogen on the dynamic tension-lowering activity of dipalmitoyl phosphatidylcholine dispersions in the presence of tyloxapol. *Colloid Polym. Sci.* **2002**, *280*, 683–687.

(31) Cheng, C. C.; Chang, C. H. Retardation Effect of Tyloxapol on Inactivation of Dipalmitoyl Phosphatidylcholine Surface Activity by Albumin. *Langmuir* **2000**, *16*, 437–441.

(32) Westesen, K.; Koch, M. H. J. Phase diagram of tyloxapol and water-II. *Int. J. Pharm. Sci.* **1994**, *103*, 225–236.

(33) Westesen, K.; Bunjes, H.; Koch, M. H. J. Phase behavior of Tyloxapol/Triton X100/water mixtures. *J. Pharm. Sci.* **1995**, *84*, 544–550.

(34) Schott, H. Comparing the Surface Chemical Properties and the Effect of Salts on the Cloud Point of a Conventional Nonionic Surfactant, Octoxynol 9 (Triton X-100), and of Its Oligomer, Tyloxapol (Triton WR-1339). *J. Colloid Interface Sci.* **1998**, *205*, 496–502.

(35) Regev, O.; Zana, R. Aggregation Behavior of Tyloxapol, a Nonionic Surfactant Oligomer, in Aqueous Solution. *J. Colloid Interface Sci.* **1999**, *210*, 8–17.

(36) Gong, H. J.; Xu, G. Y.; Zhu, Y. Y.; Wang, Y. J.; Wu, D.; Wang, L. S.; Guo, H. J.; Wang, H. B. Influencing Factors on the Properties of Complex Systems Consisting of Hydrolyzed Polyacrylamide/ Triton X-100/ Cetyl trimethylammonium Bromide: Viscosity and Dynamic Interfacial Tension Studies. *Energy Fuels*, accepted.

(37) Zhu, Y. Y.; Xu, G. Y.; Gong, H. J.; Wu, D.; Wang, Y. J. Production of Ultra-low Interfacial Tension between Crude Oil and Mixed Brine Solution of Triton X-100 and Its Oligomer Tyloxapol with Cetyltrimethylammonium Bromide Induced by Hydrolyzed Polyacrylamide. *Colloids Surf A.* **2009**, *332*, 90–97.

(38) Stoodt, T. J.; Slattery, J. C. C. Effect of the interfacial viscosities upon displacement. *AIChE J.* **1984**, *30*, 564–568.

(39) Giordano, R. M.; Slattery, J. C. Effect of interfacial viscosities upon displacement in sinusoidal capillaries[osities upon displacement. *AIChE J.* **1987**, *33*, 1592–1602.

(40) Liu, W. D.; Tong, L. X.; Li, M. Y.; Ju, Y. Interfacial Viscosity for Crude Oil/Chemical Flooding Solution Systems. *Oilfield Chem.* **2000**, *17*, 337–339.

(41) Wu, D.; Feng, Y. J.; Xu, G. Y.; Chen, Y. J.; Cao, X. R.; Li, Y. M. Dilational rheological properties of gemini surfactant 1,2-ethane bis(dimethyl dodecyl ammonium bromide) at air/water interface. *Colliods Surf. A* **2007**, *299*, 117–123.

(42) Wanka, G.; Hoffmann, H.; Ulbricht, W. Phase diagrams and aggregation behavior of poly(oxyethylene)-poly(oxypropylene)-poly(oxyethlene) triblock copolymers in aqueous solutions. *Macromolecules* **1994**, *27*, 4145–4159.

(43) Alexandridis, P.; Athanassiou, V.; Fukuda, S.; Hatton, T. A. Surface activity of poly(ethylene oxide)-block-poly(propylene oxide)-block-poly (ethylene oxide) copolymers. *Langmuir* **1994**, *10*, 2604–2612.

(44) Sedeva, R.; Steitzb, R.; Findenegg, G. H. The structure of PEO—PPO—PEO triblock copolymers at the water/air interface. *Physica B* **2002**, *315*, 267–272.

(45) Xin, X.; Xu, G. Y.; Zhang, Z. Q.; Chen, Y. J.; Wang, F. Aggregation Behavior of Star-like PEO-PPO-PEO Block Copolymer in Aqueous Solution. *Eur. Polym. J.* **2007**, *43*, 3106–3111.

(46) Zheng, Q.; Zhao, J. X.; Cheng, R. J. Micelle Formation in Mixed Aqueous Solution of C12-s-C12·2Br and Triton X-100. Chin. *J. Appl. Chem.* **2002**, *19*, 1076–1079.

(47) Zhao, J. X.; Zheng, Q.; Cheng, R. J. Mixed Micellization of C12-s-C12·2Br and C12En in Aqueous Solution. *Acta Phys. Chim. Sin.* **2002**, *18*, 463–467.

(48) Rosen, M. J. *Surfactant and Interfacial Phenomena*, 2nd ed.; Wiley-Inter-Science: New York, 2004.

(49) Rosen, M. J.; Zhou, Q. Surfactant-Surfactant Interactions in Mixed Monolayer and Mixed Micelle Formation. *Langmuir* **2001**, *17*, 3532–3537.

(50) Maeda, H. A Simple Thermodynamic Analysis of the Stability of Ionic/Nonionic Mixed Micelles. *J. Colloid Interface Sci.* **1995**, *172*, 98–105.

(51) Sharma, K. S.; Hassan, P. A.; Rakshit, A. K. Self aggregation of binary surfactant mixtures of a cationic dimeric(gemini) surfactant with nonionic surfactants in aqueous medium. *Colliods Surf. A* **2006**, *289*, 17–24.

(52) Errico, G.; Ortona, O.; Paduano, L.; Tedeschi, A.; Vitagliano, V. Mixed micellar aggregates of cationic and nonionic surfactants with short hydrophobic tails. An intradiffusion study. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5317–5324.

(53) DasBurman, A.; Dey, T.; Mukherjee, B.; Das, A. R. Solution Properties of the Binary and Ternary Combination of Sodium Dodecyl Benzene Sulfonate, Polyoxyethylene Sorbitan Monlaurate, and Polyoxyethylene Lauryl Ether. *Langmuir* **2000**, *16*, 10020–10027.

(54) Ruiz, C. C.; Aguiar, J. Mixed micelles of triton X100: interaction, composition, stability and micro-environmental properties of the aggregates. *J. Mol. Phys.* **1999**, *97*, 1095–1103.

(55) Lucassen, J.; Giles, D. Dynamic surface properties of nonionic surfactant. *J. Chem. Soc., Faraday Trans.* **1975**, *71*, 217–232.

(56) Fromyr, T.; Hansen, F. K.; Kotzev, A.; Laschewsky, A. Adsorption and surface elastic properties of corresponding fluorinated and nonfluorinated cationic polymer films measured by drop shape analysis. *Langmuir* **2001**, *17*, 5256–5264.

(57) Aksenenko, E. V.; Kovalchuk, V. I.; Fainerman, V. B.; Miller, R. Surface Dilational Rheology of Mixed Surfactants Layers at Liquid Interfaces. *J. Phys. Chem. C* **2007**, *111*, 14713–14719.

(58) Aksenenko, E. V.; Kovalchuk, V. I.; Fainerman, V. B.; Miller, R. Surface dilational rheology of mixed adsorption layers at liquid interfaces. *Adv. Colloid Interface Sci.* **2006**, *122*, 57–66.

(59) Zhang, C. R.; Li, Z. Q.; Luo, L.; Zhang, L.; Song, X. W.; Cao, X. L.; Zhao, S.; Yu, J. Y. Effect of Oxyethylene Numbers on Surface Dilational Properties of Octylphenol Polyoxyethylene Ethers. *Acta Phys. Chim. Sin.* **2007**, *23*, 247–252.

(60) Zhang, H. X.; Xu, G. Y.; Wu, D.; Wang, S. W. Aggregation of cetyltrimethylammonium bromide with hydrolyzed polyacrylamide at the paraffin oil/water interface: interfacial rheological behavior study. *Colliods Surf. A* **2008**, *317*, 289–296.

(61) Tadros, T. F. *Colloid Stability The role of surface forces-Part I*; Wiley-Vch: New York, 2007; p 295.

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