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Colloids and Surfaces A: Physicochemical and Engineering Aspects

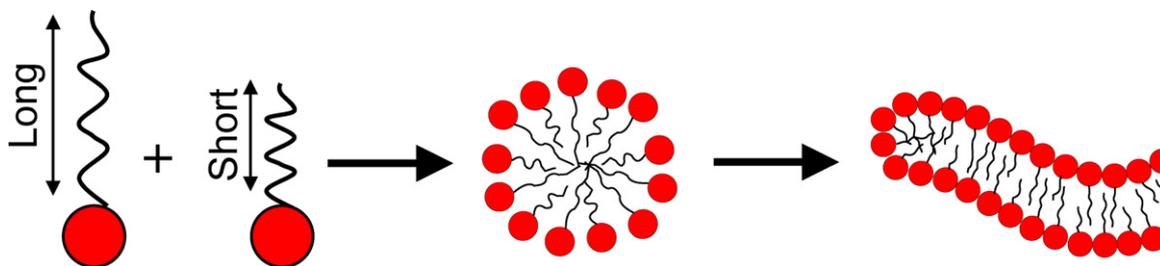# Mixed wormlike micelles of cationic surfactants: Effect of the cosurfactant chain length on the bending elasticity and rheological properties

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GRAPHICAL ABSTRACT

HIGHLIGHTS

▶ We study mixed wormlike micelles of cationic surfactants differing in chain length.
▶ Bending stiffness and rheological behavior as a function of short chain surfactant.
▶ Persistence length decreases exponentially when increasing the short chain content.
▶ Viscosity and relaxation time decrease upon increasing the short chain content.
▶ Results are explained by a progressive diminution of the micellar length.

ABSTRACT

We have investigated the behavior of mixed wormlike micelles (WLM) of cationic surfactants with hydrophobic moieties of the same nature but differing in chain length. Hexadecyltrimethylammonium bromide ($C_{16}TAB$) with $n = 16$ carbon atoms in the alkyl chain mixed with other trimethylammonium bromide (C_nTAB) surfactants with shorter hydrophobic tails ($n = 14, 12, 10$, and 8) in presence of 0.4 M KBr has been selected as model system. Mechanical high frequency rheometry experiments permit characterization of the linear viscoelasticity of the mixtures covering the frequency range up to 10^6 rad s^{-1}. From these measurements we have, for the first time, determined the variation of the persistence length l_p as a function of the addition of short chain surfactant using a recently established approach (Willenbacher et al. [46]). We found that l_p decreases exponentially when increasing the short chain content in the mixture in agreement with theoretical predictions. The zero-shear viscosity η_0 as well as the longest relaxation time T_R revealed a monotonic decrease upon increasing the concentration of cosurfactant with shorter chain length. The plateau modulus G_0 decreases for all mixtures except for the $C_{16}TAB$–$C_{14}TAB$ mixture where it increases slightly. The latter results are explained by a progressive diminution of the micellar length with increasing content of short chain cosurfactant.

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1. Introduction

Mixtures of surfactants are found in numerous applications, ranging from industrial or technological systems to household

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and personal care products, often because the materials used are not perfectly pure but more significantly because different surfactants are intentionally mixed to improve the properties of the system. Mixed amphiphilic systems, which include surfactants, polymers, and copolymers, offer a wide range of fascinating possibilities because of the complex ways they can associate into supramolecular or nanoscale structures. The properties of the systems can be tuned simply by varying the composition, which is an attractive alternative to the synthesis of new materials. Extensive studies have been carried out on various mixed surfactant systems like anionic–anionic [1], cationic–cationic [2], anionic–nonionic [3], cationic–nonionic [4], cationic–anionic [5], and nonionic–nonionic [6]. Synergistic micellization as well as formation of partially mixed systems more or less rich in one surfactant were reported. The various results reported so far show that the coexistence of incompatible hydrophobic moieties such as fluorocarbon and hydrocarbon chains is a basic requirement but often not sufficient for the formation of two distinct types of micelles in aqueous solutions. On the opposite, synergistic micellization is generally observed when ionic surfactants are mixed with non-ionic or with oppositely charged surfactants. Both surface and bulk properties of these systems have been investigated using a variety of experimental techniques [7–10]. Most of the studies were performed in the vicinity of the critical micelle concentration (cmc) [11,12]. Few studies have been performed on more concentrated systems. In particular, Kaler et al. [13–16] reported very strong synergistic gains in viscoelastic properties of mixtures of anionic and cationic surfactants compared to the parent surfactants. This synergy shows up in a huge increase of the zero-shear viscosity, up to six decades, and by a formation of a viscosity maximum. Similar behavior has been observed by Ishizuka et al. [17] studying mixtures of non-ionic and ionic surfactants and by Abe et al. [18] and Arakami et al. [19] studying mixtures of non-ionic surfactants. Concerning the micellar flexibility of surfactant mixtures, up to now literature provides only limited insight. A reduction in the bending rigidity with addition of short chain surfactant is predicted theoretically using mean-field theory assuming constant area per molecule [20–22] and assuming saturated monolayers, i.e., at zero lateral (osmotic) pressure [23,24]. Similar results are obtained from simulations using dissipative particle dynamics [25]. The only experimental data regarding l_p of mixed WLM systems have been provided by Schubert et al. [26] and Magid et al. [27]. In both studies, l_p has been measured using small angle neutron scattering (SANS). Schubert et al. [26] report a decrease of l_p from 50 nm to 20 nm with addition of a small amount of the anionic surfactant sodium dodecyl benzyl sulfonate (SDBS) to the cationic surfactant cetyl trimethylammonium tosylate (CTAT). This decrease may be due to a reduction of the surface charge density, thereby increasing the distance between charges λ_c (with $\lambda_c >$ Bjerrum length) which decreases the electrostatic contribution to the persistence length $l_{p,e}$ according to the Odijk–Skolnik–Fixman (OSF) theory. Magid et al. [27] observe a monotonic decrease in l_p for the mixed cetyltrimethylammonium 2,6-dichlorobenzoate (CTA26ClBz)/cetyltrimethylammonium chloride (CTACl) systems as the mole fraction of 26ClBz$^-$ increases. The effect of cosurfactants on bending rigidity has also been studied for microemulsions and biological membranes. Chieng et al. [28] have investigated the effect of alkyl chain length cationic n-alkyltrimethyl-ammonium bromides surfactants on the morphology and microstructure of bicontinuous microemulsions consisting of methyl methacrylate, 2-hydroxyethyl methacrylate, ethylene glycol dimethacrylate. They hypothesize that mixing of short and long chain surfactants leads to a change in interfacial film packing constraints and thus to its bending rigidity constant. But in their study no experimental results confirm this assumption. Gradzielski et al. [29] studied oil/water (O/W) microemulsions including a binary mixture of

C12E5 and C8E3 surfactant (polyethyleneglycol alkyl ethers) and found a decrease of the sum $2\kappa + \overline{\kappa}$ (with κ: mean bending modulus and $\overline{\kappa}$: Gaussian modulus) upon adding more C8E3 surfactant. In this study the bending elasticity has been obtained via the determination of the polydispersity index of the corresponding microemulsions using SANS but also from the macroscopic interfacial tension and both methods agree well. Gradzielski [30] also report, that the decrease in $2\kappa + \overline{\kappa}$ upon addition of cosurfactant depends on the difference in chain length between the short and long surfactants, for a given mole fraction the reduction of $2\kappa + \overline{\kappa}$ is more pronounced for shorter chains. A similar effect on bending rigidity has been observed for a biological membrane system consisting of di-myristoyl-phosphotidyl-choline (DMPC) when a series of embedded cosurfactant (alcohol) molecules with varying hydrocarbon chain length (between 5 and 12 carbons atoms) was studied [31].

In the present study, we were interested in the behavior of mixed wormlike micelles made of cationic surfactants with hydrophobic moieties of the same nature but differing in chain length. $C_{16}TAB$ with 16 carbon atoms in the alkyl chain mixed with other C_nTAB surfactants with shorter hydrophobic tails ($n = 8$, 10, 12, and 14) in presence of 0.4 M KBr have been selected as model system. The pure long and short chain surfactants self-assemble into structures with different curvatures, the $C_{16}TAB$ forms wormlike micelles, whereas the C_nTAB self-assembles into spherical micelles. Therefore, one expects in the mixtures, a decrease of the end-cap energy with increasing short chain content, following the change in curvature and this should result in a monotonous decrease of micellar length. We have investigated two concentration domains. In the low-concentration range ($c < 10^{-2}$ M), surface tension measurements were performed to determine the mixed critical micelle concentration (cmc) and the parameter of interaction between surfactants. Then, we have studied the rheological behavior and especially the bending stiffness of these mixtures in the entangled state as a function of the addition of short chain surfactant. The goal is to gain better understanding how length and flexibility of mixed wormlike micelles is controlled.

2. Materials and methods

2.1. Sample characteristics

Hexadecyltrimethylammonium bromide ($C_{16}TAB$), tetradecyltrimethylammonium bromide ($C_{14}TAB$), dodecyltrimethylammonium bromide ($C_{12}TAB$), decyltrimethylammonium bromide ($C_{10}TAB$), octyltrimethylammonium bromide (C_8TAB) and potassium bromide (KBr) are commercially available, they were purchased from Carl Roth GmbH (Karlsruhe, Germany). Aqueous solutions of different $C_{16}TAB/C_nTAB$ ratio at constant surfactant $C_{16}TAB$ concentration of 0.5 M in presence of 0.4 M KBr were prepared. For equilibrium measurements, they were stored for at least one day at $T = 35\,^\circ$C. All surface tension and rheological measurements were performed at this temperature as well.

2.2. Surface tension measurements

The equilibrium surface tensions of the aqueous surfactant solutions were measured with a DataPhysics (DCAT11EC) tensiometer at 35 $^\circ$C using the Wilhelmy plate method. The plate is made of platinum-iridium (length: 10 mm, width: 19.9 mm, thickness: 0.2 mm). The precision of the surface tension measurements is 0.5 mN/m.

2.3. Rotational rheometry

A rotational rheometer Thermo MARS II equipped with a cone-plate measuring cell (diameter $d = 50$ mm or 35 mm, cone angle

$\alpha = 1°$) was used to perform static as well as small amplitude oscillatory shear experiments covering the frequency range from 0.1 to 100 rad s^{-1} at a stress value of $\tau = 1$ Pa. Stress sweep experiments performed prior to the frequency sweeps confirm that this stress value is sufficiently small to provide a linear material response at all investigated frequencies. A solvent trap was used to avoid evaporation of the sample during the experiment.

2.4. Squeeze flow

Oscillatory squeeze flow experiments were performed using a piezo-driven axial vibrator (PAV) customized at the Institute for Dynamic Material Testing (Ulm, Germany). General theory of squeeze flow is covered in standard textbooks of fluid mechanics [32] The theory of the PAV as well as the mechanical and electronic setup used here are thoroughly discussed elsewhere [33–35] and therefore this is summarized here only briefly. In our squeeze flow experiments the samples are placed into a gap between two stainless steel plates. The lower plate is supported by a thin-walled quadratic copper tube carrying the piezo-elements, which exert the vibrational motion and pick-up the response signal. This lower part of the device is surrounded by a double-walled cylinder allowing for circulation of a thermostating fluid and the sample temperature is controlled with an accuracy of ± 0.1 °C. The upper boundary of the gap is a thick metal lid, which provides complete sealing of the fluid. The instrument operates at constant force amplitude and from the ratio of the dynamic displacement of the lower plate (amplitude $\sim$ 5 nm) with and without fluid the complex squeeze stiffness K^* of the fluid is obtained which is directly related to the complex shear modulus G^* [35]:

$$K^* = \frac{(3\pi R^4/2d^3)G^*}{(1 + \rho\omega^2 d^2/10G^* + \ldots)} \tag{1}$$

where ρ is the fluid density, R (here 10 mm) is the radius and d is the height of the gap. The denominator in Eq. (1) is a series expansion taking into account the inertia of the fluid in the gap. The determination of G^* strongly depends on the exact knowledge of d, which is determined by calibration using Newtonian liquids with viscosities between 1 and 2000 mPa s. Gap heights between 39 and 50 μm have been used here, corresponding to sample volumes between 100 and 200 μl. Moduli G' or G'' in the range from 0.1 Pa to 10 kPa are accessible with the set-up described here.

2.5. Torsional resonators

The theory of torsional resonators has been described elsewhere [36]. In our study, two piezoelectrically driven titanium resonators (cylindrically and dumbbell shaped) operating at four different frequencies: 8, 19, 31 and 59 kHz were used. A lock-in amplifier (model SR850, Stanford Research Systems) was used to determine their resonance characteristics. G' and G'' of the fluid surrounding the resonator were calculated from the corresponding shift of the resonance frequency and the broadening of the resonance curve as compared to the unperturbed oscillation in air. The required sample volume was typically =30 ml. This piezo-driven devices operate at strain amplitudes $\gamma_0 < 10^{-3}$. Temperature control is crucial here since resonators properties are extremely temperature sensitive. The temperature was controlled by a liquid thermostat and measured by a PT-100 temperature sensor within the resonators and processed with a digital thermometer (INFT series, Newport Electronics) Temperature stability during the individual experiments was 0.01 °C.
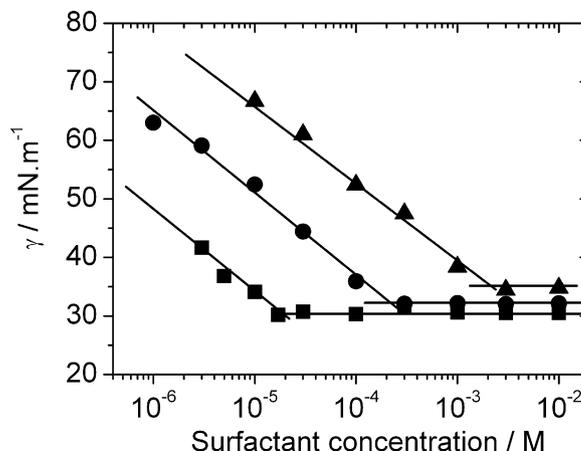

Fig. 1. Variation of the surface tension of single surfactants as a function of the logarithm of the overall surfactant concentration, $T = 35$ °C, [KBr] = 0.4 M: (■) C$_{16}$TAB, (●) C$_{14}$TAB, and (▲) C$_{12}$TAB.

3. Results and discussion

3.1. Dilute regime

3.1.1. Surface tension measurements

Variations of the surface tension as a function of the logarithm of the overall surfactant concentration are reported in Fig. 1 for pure surfactants in presence of 0.4 M KBr. For all solutions, these variations present a single change in the slope at the critical micelle concentration. The latter is found to be about 0.02, 0.2 and 2 mM for C$_{16}$TAB, C$_{14}$TAB and C$_{12}$TAB solutions, respectively. We observe that the alkyl chain length has a very strong influence on the cmc: the latter decreases as the length and/or the hydrophobicity of the surfactant chain increases. This result is well known in the literature and is consistent with the linear dependence of log(cmc) with the number of carbon atoms in the hydrophobic chain for homologous straight-chain ionic surfactants in aqueous medium, as found by Klevens [37]. For salt-free solutions of same surfactants, Basu Ray et al. [38] have found much higher cmc values about 0.93, 4.08 and 14.8 mM respectively. The addition of salt reduces the polarity of the surfactant molecules and therefore strongly reduces the cmc. For surfactant mixtures, the same single change in the slope is observed for different molar mixtures of C$_{16}$TAB–C$_{14}$TAB (Fig. 2). For 8:2, 1:1 (not shown) and 2:8 M mixtures, the cmc value of the mixture cmc$_{12}$ is 0.022, 0.026 and 0.055 mM, respectively. For the
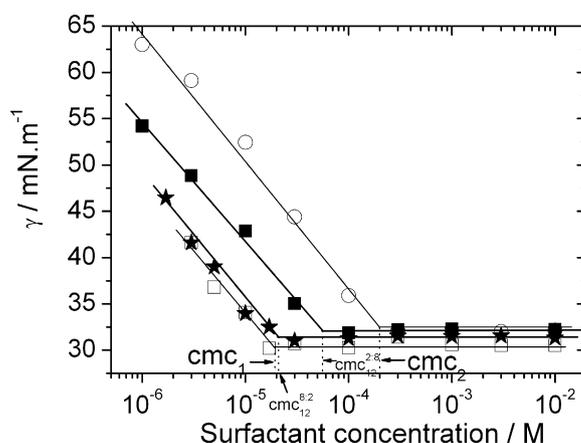

Fig. 2. Variation of the surface tension of single surfactant and mixtures as a function of the logarithm of the overall surfactant concentration, $T = 35$ °C, [KBr] = 0.4 M: (□) C$_{16}$TAB, (★) C$_{16}$TAB–C$_{14}$TAB (8:2), (■) C$_{16}$TAB–C$_{14}$TAB (2:8), and (○) C$_{14}$TAB.

Table 1
cmc for $C_{16}TAB/C_{14}TAB$ and $C_{16}TAB/C_{12}TAB$ mixtures determined by surface tension measurements, stoichiometric mole fraction of the first component $C_{16}TAB$ (α_1), its mole fraction in mixed micelles (X_1), and the interaction parameter (β) at 35 °C in presence of 0.4 M KBr.

$C_{16}TAB$–$C_{14}TAB$				$C_{16}TAB$–$C_{12}TAB$			
α_1	cmc_{12}	X_1	β	α_1	cmc_{12}	X_1	β
1	0.020	–	–	1	0.020	–	–
0.8	0.022	0.90	−2.24	0.8	0.023	0.935	−3.82
0.5	0.026	0.75	−2.28	0.5	0.024	0.78	−5.40
0.2	0.055	0.64	−1.17	0.2	0.057	0.75	−4.39
0	0.200	–	–	0	2.000	–	–

8:2 mixture, cmc_{12} is significantly lower than that of pure $C_{14}TAB$ and close to that of pure $C_{16}TAB$ but then increases slightly as the proportion of short chain surfactant increases. The same behavior is observed for the mixture $C_{16}TAB$–$C_{12}TAB$ (see Table 1). cmc_{12} has been analyzed in order to extract the parameter of interaction between surfactants, β, using the equations derived by Rubingh [39] for non-ideal mixtures of surfactants:

$$\frac{X_1^2}{(1-X_1)^2} \frac{\ln(\alpha_1 \cdot cmc_{12}/X_1 \cdot cmc_1)}{\ln[(1-\alpha_1)cmc_{12}/(1-X_1)cmc_2]} = 1 \tag{2}$$

$$\beta = \frac{\ln[\alpha_1 \cdot cmc_{12}/X_1 \cdot cmc_1]}{(1-X_1)^2} \tag{3}$$

where α_1 and X_1 are the mole fractions of $C_{16}TAB$ in the mixture and in the micelles, respectively, cmc_1 is the cmc of $C_{16}TAB$, cmc_2 is the cmc of $C_{14}TAB$, cmc_{12} that of the mixture. If $\beta \geq 2$ demixed micelles should form due to the repulsion force between surfactants. If $\beta = 0$, an ideal mixing behavior is expected whereas negative interaction parameters indicate attractive interactions in mixed micellization. By using Eqs. (2) and (3), one obtains $\beta = -2.24$, -2.28 and -1.17 for 8:2, 1:1 and 2:8 M mixtures of $C_{16}TAB$–$C_{14}TAB$, respectively. For $C_{16}TAB$–$C_{12}TAB$ mixtures, we found $\beta = -3.82$, -5.40 and -4.39. These results suggest non-ideality and synergistic interactions between short and long chain surfactant mixtures. For both mixtures, it seems that there is an apparent maximum synergy at equimolar composition and that the mixed micelles contained a greater proportion X_1 of the longer chain surfactant compared to its stoichiometric composition (see Table 1). Additionally, β values become more negative as the difference in chain length increases. Similar negative β values have been found for those mixtures in salt free systems by Moulik et al. [40].

In Fig. 3, the experimental cmc_{12} values are plotted as a function of composition of the binary mixtures and compared with values calculated from the ideal mixed micelle model ($\beta = 0$). As seen, the ideal solution theory does not predict the cmc of the mixture accurately. Negative deviation from ideality indicates and confirms that the formation of mixed micelles is enhanced. Table 1 shows all parameters deduced from surface tension measurements for single surfactant and surfactant mixtures.

3.2. Entangled regime

3.2.1. Effect of chain length on zero-shear viscosity and relaxation time

In Fig. 4, the behavior of η_0 as a function of the addition of short chain surfactant for mixtures $C_{16}TAB$–$C_{14}TAB$, $C_{16}TAB$–$C_{12}TAB$, $C_{16}TAB$–$C_{10}TAB$, and $C_{16}TAB$–C_8TAB, at a fixed $C_{16}TAB$ concentration of 0.5 M is shown. For each mixture, η_0 decreases monotonically upon addition of cosurfactant with shorter chain length. Decrease becoming stronger as the difference in chain length increases. Indeed, η_0 drops by almost one order of magnitude with addition of 5% of $C_{14}TAB$ and by several orders of magnitude with addition of 5% of $C_{12}TAB$. This result is similar to those obtained
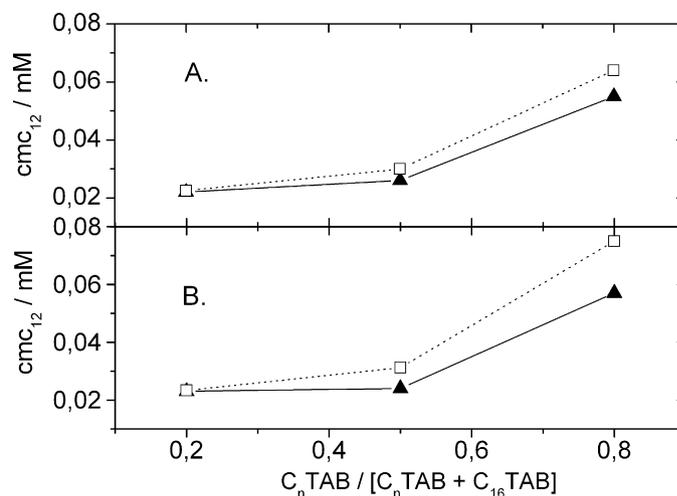

Fig. 3. cmc_{12} for the $C_{16}TAB$–$C_{14}TAB$ (A) and $C_{16}TAB$–$C_{12}TAB$ (B) mixtures as a function of the mole fraction of short chain cosurfactant: (▲) experimental data, and (□) prediction for the ideal mixing ($\beta = 0$).

by Schubert et al. [26] and Croce et al. [41] where a drastic viscosity decrease has been observed as short chain anionic surfactant is added to cationic surfactant and as non-ionic surfactant is added to cationic surfactant respectively. In our study, the decrease can be interpreted as micellar breaking by adding short chain surfactant which results in a reduction of the micellar length and therefore in lower viscosities values. Indeed, Patist et al. [42] and Hierrezuelo et al. [43] have shown that for surfactant mixtures the chain length compatibility has an influence on the stability of the system which corresponds to the average life time of the micelle. There are two factors contributing to the micellar stability. First is the Coulombic interaction between the ionic head groups and second is the difference in chain length of the surfactants. In our study only the difference in chain length plays a role as we have investigated a cationic–cationic surfactants mixture with both surfactants having similar head groups. Thus, as the difference in chain lengths of mixed surfactants increases, van der Waals interaction between the hydrophobic tails decreases (hydrophobic interaction) and this will induce the formation of less compact and stable micelles. For the terminal relaxation time T_R, variations as a function of addition of short chain surfactant as obtained from rotational rheometer and oscillatory squeeze flow are given in Fig. 5. For both methods, T_R has been directly deduced from the modulus curves, by the inverse angular frequency corresponding to the first crossover between G' and G''. A clear advantage of squeeze flow measurements is to
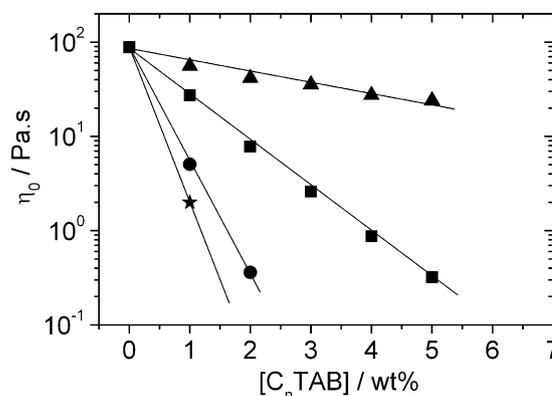
Fig. 4. Variation of the zero shear viscosity η_0 as a function of C_nTAB concentration at constant surfactant concentration of 0.5 M $C_{16}TAB$ and 0.4 M KBr obtained from rotational rheometer measurements. $n = 8$ (★), 10 (●), 12 (■), 14 (▲). $T = 35$ °C.
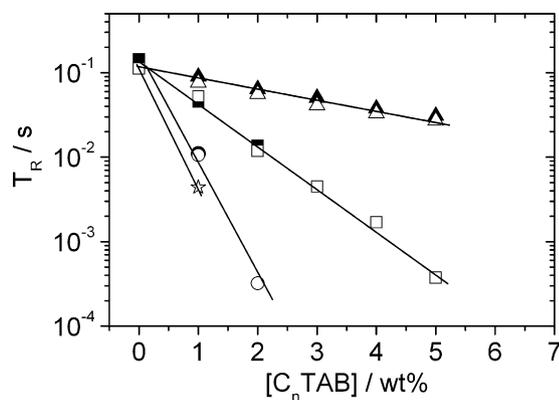
Fig. 5. Variation of the relaxation time T_R as a function of C_nTAB concentration at constant surfactant concentration of 0.5 M $C_{16}TAB$ and 0.4 M KBr obtained from rotational rheometer (closed symbols) and oscillatory squeeze flow measurements (open symbols). $n = 8$ (stars), 10 (circles), 12 (squares), and 14 (triangles). $T = 35\,°C$.

permit measurements of relaxation times less than 10^{-2} s. The variation of T_R is almost the same independent of the technique used and the absolute values are in very good agreement, the differences are within the experimental error. As for η_0, T_R decreases with addition of short chain surfactant, and it seems reasonable to attribute this variation to a decrease of the average length of the micelles.

### 3.2.2. Effect of chain length on the plateau modulus

For entangled wormlike micellar solutions, the plateau modulus G_0 is a key structural parameter. It is related to the crosslink density or mesh size ξ of the entanglement network:

$$\xi = \left(\frac{k_B T}{G_0}\right)^{1/3} \tag{4}$$

Fig. 6 shows the variation of G_0 as a function of addition short chain cosurfactant as determined from oscillatory squeeze flow measurements for the different mixtures. G_0 has been directly deduced from the modulus curve as the value of G' where it exhibits a constant plateau. It has been determined as the value of the modulus G' at the frequency at which G'' has its local minimum, G''_{min}. For the $C_{16}TAB$–$C_{14}TAB$ mixture, G_0 increases linearly with the addition of $C_{14}TAB$. This increase corresponds to an increase in the number of entanglements due to an increase of the total surfactant concentration in the system. For linear micelles, the Cates model [44,45] predicts a volume fraction dependence of G_0 in the semi-dilute regime of $G_0 \sim \phi^{\sim 2.25}$. In our study, we found a lower power law exponent value equal to 1.12, when ϕ increases due
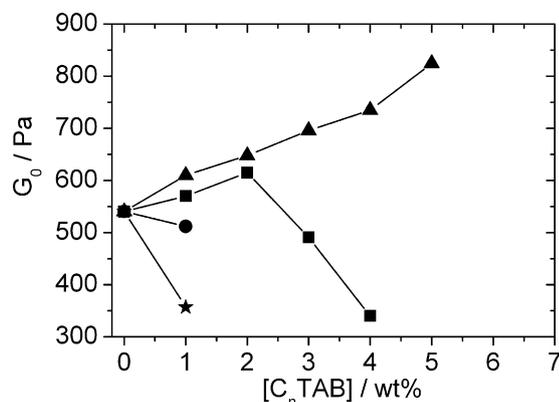
Fig. 6. Variation of the plateau modulus G_0 as a function of C_nTAB concentration at constant surfactant concentration of 0.5 M $C_{16}TAB$ and 0.4 M KBr obtained oscillatory squeeze flow measurements. $n = 8$ (stars), 10 (circles), 12 (squares), and 14 (triangles). $T = 35\,°C$.
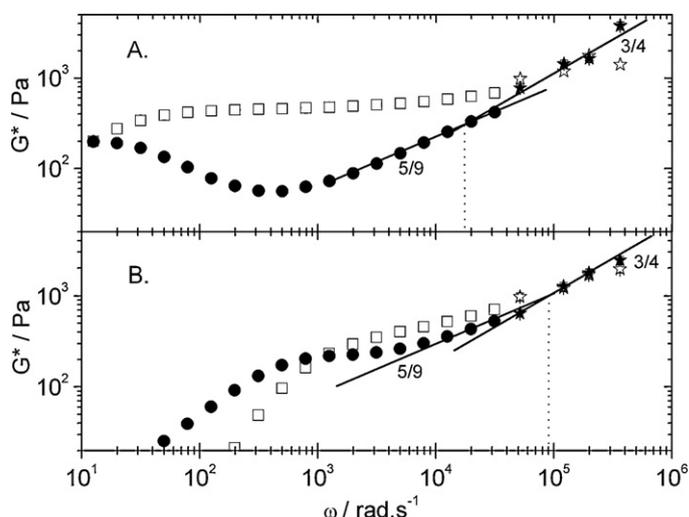
Fig. 7. Dynamic shear moduli G' and G'' obtained from oscillatory squeeze flow (G' open squares, G'' closed circles) and torsional resonator measurements (G' open stars, G'' closed stars): (A) $C_{16}TAB$ 0.5 M/KBr 0.4 M, and (B) $C_{16}TAB$ 0.5 M–$C_{12}TAB$ (4 wt%)/KBr 0.4 M. $T = 35\,°C$.

to the addition of $C_{14}TAB$. This value indicates a decrease in the number of entanglements due to the fact that the incorporation of short chain surfactant leads to a reduction of the mean micellar length and an increasing fraction of short chains not contributing to the entanglement network. This competition between increase of entanglement density due to increasing total surfactant concentration and reduction of micellar length due to the incorporation of shorter surfactant molecules results in a maximum of G_0 in the case of the $C_{16}TAB$–$C_{12}TAB$ mixture and for even shorter co-surfactants $C_{10}TAB$ and C_8TAB this latter effect is dominating, thus leading to a monotonic decrease of G_0 for these mixtures. This behavior is probably related to the instability of the system: instability increasing as the difference in chain length increases.

3.2.3. Effect of chain length on the persistence length

The persistence length l_p of wormlike micelles can be determined directly from rheological measurements, from the absolute values of G' and G'' in the high frequency regime [46]. In this regime, stress relaxation is mainly due to internal dynamics of individual micelles and the moduli G' and G'' show characteristic scaling behavior.

$$G' \sim G'' \sim \omega^\alpha \tag{5}$$

First the Rouse–Zimm modes dominate and $\alpha = 1/2$–$2/3$. At even higher frequencies internal bending modes of single Kuhn segments result in $\alpha = 3/4$ as predicted by Morse [47] and Gittes and McKintosh [48]. The transition between these scaling regimes is marked by the inverse of the shortest Rouse relaxation time $\omega_0 = \tau_0^{-1}$ which is directly related to the persistence length l_p:

$$\omega_0 = \frac{k_B T}{8\eta_s l_p} \tag{6}$$

where η_s is the solvent viscosity.

Fig. 7A and B shows the variation of the dynamic shear moduli G' and G'' as a function of frequency as determined from oscillatory squeeze flow and torsional resonance measurements for the pure $C_{16}TAB$ surfactant and the $C_{16}TAB$–$C_{12}TAB$ mixture with 4% $C_{12}TAB$ respectively. l_p is extracted from the crossover frequency of the $\omega^{5/9}$ and $\omega^{3/4}$ scaling regime. We obtain $\omega_0 = 17,000$ rad s^{-1} and $l_p = 35 \pm 3$ nm for the pure surfactant and $\omega_0 = 87,000$ rad s^{-1} and $l_p = 20.4 \pm 2$ nm for the mixture. We see clearly that the mixed
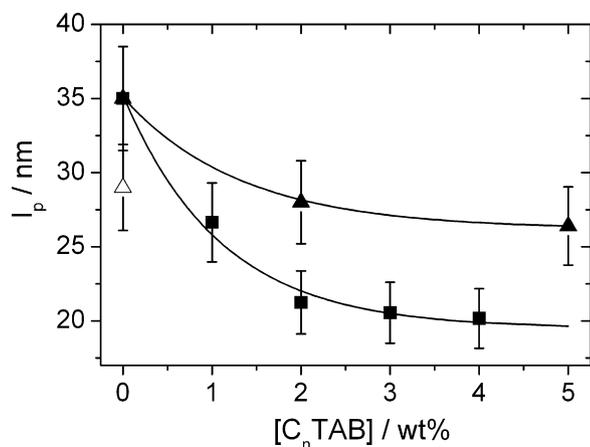
Fig. 8. Variation of the persistence length l_p as a function of C_nTAB concentration at constant surfactant concentration of 0.5 M C_{16}TAB and 0.4 M KBr obtained from high frequency mechanical measurements: $n=12$ (■) and 14 (▲). For single C_{14}TAB at surfactant concentration of 0.35 M and KBr 2 M (△). $T=35\,°C$.

Fig. 9. Dependence of the contour length $\bar{L}$ (■) as a function of C_{12}TAB concentration at constant surfactant concentration of 0.5 M C_{16}TAB and 0.4 M KBr obtained from oscillatory squeeze flow measurements. $T=35\,°C$. Variation of l_p (□) is for comparison.

micelles become more flexible when increasing the short chain cosurfactant content.

In Fig. 8, we have systematically investigated the variation of l_p with addition of short chain cosurfactant for two different mixtures: C_{16}TAB–C_{14}TAB and C_{16}TAB–C_{12}TAB. For both mixtures, the micelle becomes very flexible by adding even a small amount (1%) of cosurfactant. Also we note a nearly exponential decay of l_p with short chain content and a saturation of l_p to reach ∼26 nm and 20 nm respectively. Such behavior has been predicted for surfactant mixture by the mean-field theory at constant head group area [20,22,25]. Without the constant area constraint a linear decrease is predicted [23,25]. We have also investigated the chain length effect on the pure surfactant. C_{14}TAB forming solutions of entangled WLM at appropriate surfactant concentration and salt concentrations higher than 2 M [49,50] whereas C_{12}TAB micelles stay spherical even at higher salt content [51]. We found for the C_{14}TAB system, at a surfactant concentration of 0.3 M and KBr 2 M, a value of $l_p=29\pm3$ nm. This value is smaller than the l_p value of 35 ± 3 nm obtained for the C_{16}TAB system. Finally, using our l_p experimental values together with G_0 and G''_{min} from squeeze flow measurements, we calculated the contour length $\bar{L}$ of the micelles from the equations [52]:
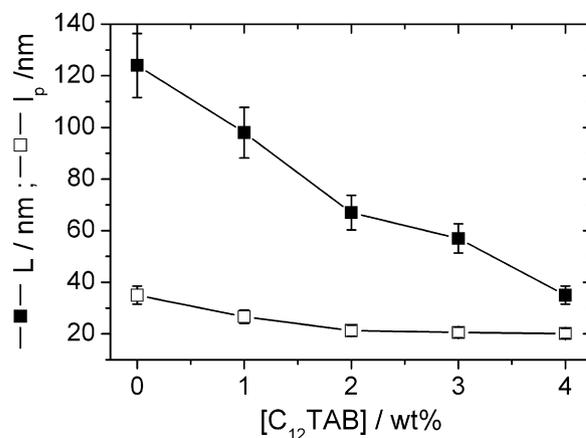
$$\frac{G''_{min}}{G_0} \approx \frac{l_e}{\bar{L}} \qquad (7)$$

with

$$l_e \approx \frac{\xi^{5/3}}{l_p^{2/3}} \qquad (8)$$

where l_e is the contour length between two successive entanglements.

Fig. 9 shows the dependence of $\bar{L}$ as a function of addition of short chain cosurfactant for the C_{16}TAB–C_{12}TAB mixtures. $\bar{L}$ decreases linearly from 124 nm for the pure C_{16}TAB down to 35 nm for the mixture with addition of 4% C_{12}TAB. For the C_{16}TAB–C_{14}TAB mixture, we have observed (result not shown) a decrease of $\bar{L}$ from 124 nm to 77 nm with addition of 5% C_{14}TAB. These results again confirm the hypothesis of a reduction of the micellar length when addition of short chain cosurfactant into the micelle. Table 2 summarizes the effect of the addition of short chain surfactant on rheological parameters for the C_{16}TAB–C_{12}TAB mixture.

Table 2
Rheological parameters for the C_{16}TAB–C_{12}TAB mixture: effect of short chain cosurfactant.

C_{12}TAB (wt%)	ξ (nm)	G''_{min} (Pa)	l_e (nm)	L (nm)	l_p (nm)
0	21	55.1	14.9	124	35
1	19.8	90.5	16.23	98	26.7
2	20.3	148	19.71	67	21.25
3	20.4	178	20.26	57	20.56
4	24.1	230	27.21	35	20.17

4. Conclusion

In this study, we have investigated binary surfactant systems of hexadecyltrimethylammoniumbromide C_{16}TAB with different alkyl-trimethylammoniumbromide C_nTAB ($n=8$, 10, 12, 14) in presence of potassium bromide (KBr). In the dilute regime, the surface tension measurements show a nonideal behavior. The negative values of the interaction parameter β for both C_{16}TAB–C_{14}TAB and C_{16}TAB–C_{12}TAB systems indicate an attractive interaction between the two surfactants that becomes stronger as the difference in chain length increases. In the entangled regime, the zero-shear viscosity η_0 as well as the relaxation time T_R decreases monotically upon increasing the concentration of cosurfactant with shorter chain length for all mixtures, at a fixed C_{16}TAB concentration of 0.5 M. For mixtures C_{16}TAB–C_{12}TAB, C_{16}TAB–C_{10}TAB, and C_{16}TAB–C_8TAB, we observe a decrease of the plateau modulus G_0 upon addition of short chain surfactant and for the C_{16}TAB–C_{14}TAB mixture G_0 increases slightly, but this increase with total surfactant concentration is less pronounced than expected for the pure C_{16}TAB system. These results are rationalized by a progressive diminution of the micellar length with addition of cosurfactant. The persistence length l_p has been determined from high frequency rheological experiments and its variation with increasing short chain surfactant content show that the mixed micelles exhibit an increased flexibility even upon addition of a small amount of short chain surfactant with a saturation effect toward the pure short chain limit.

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