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Structure and oil responsiveness of viscoelastic fluids based on mixed anionic/cationic wormlike surfactant micelles

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Abstract. In this work, a combination of small-angle neutron scattering, dynamic light scattering and rheometry was applied in order to investigate the structure and oil responsiveness of anionic/cationic wormlike surfactant micelles formed in a mixture of potassium oleate and noctyltrimethylammonium bromide (C₈TAB). A new facile method of calculating the structure factor of charged interacting wormlike micelles was proposed. It was shown that the mean distance between the micelles decreases upon the increase of the amount of cationic co-surfactant and lowering of the net micellar charge. It was demonstrated that highly viscous fluids containing mixed anionic/cationic wormlike micelles are highly responsive to oil due to its solubilization inside the micellar cores, which leads to the disruption of micelles and formation of microemulsion droplets. Experimental data suggest that solubilization of oil proceeds differently in the case of mixed anionic/cationic micelles in the absence of salt, and anionic micelles of the same surfactant in the presence of KCl.

1. Introduction

Surfactant molecules can self-assemble due to the balance between hydrophobic interaction of their alkyl tails and repulsion of polar head groups, and form wormlike (or cylindrical) micelles in aqueous solutions [1,2]. If wormlike micelles are sufficiently long, they form a network of topological entanglements, which imparts high viscosity and strong viscoelastic properties to the solutions. These properties are the key factors for numerous applications of wormlike micellar solutions, e.g. in cosmetics, drag reduction in heating and cooling systems, and oil industry [3-5].

The formation of wormlike micelles was described in numerous works [6-9] when a low-molecular weight salt was added to a solution of an ionic surfactant. Salt molecules dissociate in aqueous solution, providing sufficient screening of electrostatic repulsions between the charged surfactant head groups. This results in closer packing of head groups and formation of elongated cylindrical aggregates which can attain several micrometers in length. For instance, the network of long wormlike micelles was observed for an anionic surfactant potassium oleate [6,7] or a cationic surfactant erucyl bis(hydrohyethyl)methylammonium chloride (EHAC) [8,9] in the presence of KCl.

Long wormlike micelles can also be formed with no added salt in the mixtures of an ionic surfactant and an oppositely charged co-surfactant or hydrotrope salt [10-15]. The molecules of co-surfactant (or hydroptrope) embed into surfactant micelles, and their charged groups provide very effective screening

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of electrostatic repulsions between the surfactant polar heads. At the same time, hydrophobic part of the co-surfactant (or hydrotrope) interacts with the alkyl surfactant tails and resides closer to the micellar core. This leads to the formation of long micellar aggregates and their assembly into networks at very low surfactant concentrations. For example, wormlike micelles were observed in the mixtures of cationic surfactants cetyltrimethylammonium chloride (CTAC) [10] or EHAC [11,12] with sodium salicylate; or anionic surfactant sodium dodecyl sulfate (SDS) with *p*-toluidine hydrochloride (PTHC) [13], potassium oleate with alkyltrimethylammonium bromides [14], or sodium erucate with benzyl trimethylammonium bromide (BTAB) and tetramethylammonium bromide (TMAB) [15].

In the paper [14], the mixtures of potassium oleate and alkyltrimethylammonium bromides (C_nTAB) with different alkyl tail length n = 6, 8, 10, 12 were investigated in detail, and it was shown that an optimal asymmetry of surfactant and co-surfactant tail lengths is necessary to obtain 1-phase solution which contains a network of wormlike micelles. The best results were found in the case of *n*-octyltrimethylammonium bromide (C_8TAB): the solutions showed strong viscoelastic behavior and viscosity up to 1800 Pa s at the total concentration of surfactant of 3 wt%. Structural investigations by small-angle neutron scattering (SANS) were also performed, and they proved the formation of cylindrical surfactant aggregates at different surfactant concentrations and [C_8TAB]/[potassium oleate] molar ratios. However, the structure factor of interacting charged wormlike micelles was not analyzed.

In the present work, we propose a new facile method of calculating the structure factor of charged wormlike micelles by dividing the total intensity I(q) by the form factor of a cylinder P(q) obtained from fitting the scattering curve at high q. By using this method, we analyze the position of electrostatic structure peak at different molar ratios [C₈TAB]/[potassium oleate] and show that the mean distance between the micelles decreases when they become less charged.

Due to their self-assembled nature, wormlike micelles are highly responsive to external stimuli [16]. For example, the addition of oils (hydrocarbons) totally disrupts the micelles and drives the formation of small spherical microemulsion droplets [17-19]. This effect is explained by the solubilization of hydrophobic oil inside the micellar cores, which leads to the rearrangement of surfactant molecules packing, and is accompanied by a drastic drop of viscosity by several orders of magnitude. High responsiveness to oils is a key factor determining the use of viscoelastic micellar solutions as the main component of fracturing fluids in oil recovery [5].

However, to the best of our knowledge, the responsiveness to oils was proven only for wormlike micelles formed in the presence of low molecular weight salts. In this work, we first investigate the effect of oil (*n*-decane) on charged anionic/cationic micelles of potassium oleate and C_8TAB in the absence of salt, and we show that the addition of small amount of oil (2 wt%) leads to the complete disruption of wormlike micelles and formation of small microemulsion droplets. Surprisingly, the radius of microemulsion droplets (2 nm) is found to be much less than those for potassium oleate system in the presence of KCl [19] indicating different packing of oil and surfactant tails inside the droplet core.

2. Experimental section

2.1. Materials

Potassium oleate (TCI, purity > 98%), C_8TAB (ABCR, purity > 98%) and *n*-decane (Aldrich) were used without further purification. D₂O (99.9% isotopic purity) supplied by Deutero GmbH was used to prepare the solutions for SANS measurements. For rheological measurements, the solutions were prepared using distilled deionized water purified by the Millipore Milli-Q system.

2.2. Samples preparation

First, aqueous stock solutions of potassium oleate and C_8TAB were prepared, which were then mixed in appropriate quantities. The obtained samples were stirred for 1-3 days and then left for 1-2 weeks to remove air bubbles. To study the effect of oil, *n*-decane was added on top of the sample, which was then stirred for 1 day.

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2.3. Small-angle neutron scattering

SANS experiments were conducted using the YuMO spectrometer at the IBR-2 reactor facility (Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia). Specially made dismountable cells with parallel disk-like quartz plates and beam path of 2 mm were used. The temperature during measurements was controlled at 20.0 ± 0.3 °C by a water-circulating thermostat. The data were recorded by two detectors covering the range of scattering vectors *q* of 0.007 - 0.5 Å⁻¹.

All the samples were prepared in D₂O. The scattering length densities of the surfactant tails and D₂O are equal to ca. $-0.30 \cdot 10^{-6}$ Å⁻² and $6.36 \cdot 10^{-6}$ Å⁻², respectively. The intensity profiles were corrected for sample transmission, beam path length and electronic noise, and calibrated at the absolute scale by a vanadium standard. Incoherent scattering from blank solvent (D₂O) was subtracted from the scattering curves.

The program SasView was used to fit the scattering curves by form-factors of a cylinder or a sphere. Only a part of the scattering curve at q higher than the structure peak position q^* (q > 0.06-0.07 Å⁻¹) was used for fitting, and then the fitted form-factor was calculated in the whole q-range. One fitting parameter (radius of a cylinder or a sphere) was used.

2.4. Rheometry

Rheological measurements were made on a rotational rheometer Anton Paar Physica MCR 301. The details of the measurements are described elsewhere [20,21]. Cone-plate geometry with a diameter of 50 mm and cone angle of 1^0 was used for investigation. Temperature was controlled by a water circulating thermostat and Peltier elements at 20.00 ± 0.05 °C. A specially constructed vapor lock was used to prevent solvent evaporation from the sample.

2.5. Dynamic light scattering (DLS)

DLS experiments were performed with ALV/DLS/SLS-5022F compact goniometer system equipped with ALV-6010/EPP digital time correlator (ALV, Langen, Germany), helium-neon laser operating at a wavelength of 632.8 nm and computer controlled and stepping motor driven variable angle detection system. Prior to measurements the samples were filtered through 0.20 µm polytetrafluoroethylene Millex-LG filters (Millipore). The details of the experiments are described elsewhere [22].

In DLS experiments, the normalized time autocorrelation function $g^{(2)}(q,t)$ of the scattered intensity is measured. To obtain the decay times distribution $A(\tau)$ and extract translational diffusion coefficients, Contin analysis based on the inverse Laplace transformation was applied [23]. With Stokes-Einstein equation the diffusion coefficients were converted to hydrodynamic radii.

3. Results and discussion

In this work, we studied the structure and responsiveness to oils of surfactant solutions containing 190 mM potassium oleate and *n*-octyltrimethylammonium bromide (C_8TAB). The molar ratio [C_8TAB]/[potassium oleate] was varied in the range 0.2-0.4. According to the literature data [14], a network of long wormlike micelles is formed at these conditions. Since the amount of cationic co-surfactant is less than the amount of anionic surfactant, the micelles are negatively charged.

Scattering curves for the solutions at different molar ratios are presented in Figure 1. On all curves one can see a structure peak, which originates from electrostatic repulsion of similarly charged micelles [14]. In the intermediate and high q-range (above the structure peak position q^*) the curves can be well fitted by a form-factor of a cylinder (Figure 1).



Figure 1. Scattering curves I(q) for aqueous solutions containing 190 mM potassium oleate and different concentrations of C₈TAB: 38 mM (circles), 57 mM (squares), 76 mM (triangles) in D₂O at 20⁰C. Corresponding molar ratios [C₈TAB]/[potassium oleate] are shown in the picture. Line is a fit of the scattering curves by a form-factor of cylinder with radius $R = 18.8 \pm 0.2$ Å.

The cylinder radii (R) for different molar ratios obtained from the fit are given in Table 1. It is seen that R does not change at the variation of the molar ratio $[C_8TAB]/[potassium oleate]$ and remains close to the length of a fully extended alkyl tail of potassium oleate (1.9 nm). At the same time, R is much higher than the length of C_8TAB tail (0.8 nm). This fact indicates that the radius of mixed micelles at the excess of potassium oleate is governed only by its tail length, and not by the tail length of co-surfactant. Since the volume of C_8TAB tail is nearly 2 times smaller than those of potassium oleate, and the volume of the C_8TAB polar head is larger, one can conclude that the incorporation of more C_8TAB molecules into the micelles leads to closer packing of potassium oleate head groups, which is necessary to avoid the formation of free space inside the micellar hydrophobic cores.

Molar ratio [C ₈ TAB]/ [potassium oleate]	Oil	Form of the objects	Radius of cylinder or sphere (R), nm	Structure peak position (q*), Å ⁻¹	Average distance between the objects (d), nm
0.2	-	cylinder	1.86	0.053	11.9
0.3	-	cylinder	1.88	0.056	11.2
0.4	-	cylinder	1.88	0.059	10.6
0.4	140 mM <i>n</i> -decane	sphere	2.05	0.055	11.4

 Table 1. Structural parameters of 190 mM potassium oleate aqueous solutions in the presence of different concentrations of C₈TAB and oil obtained from SANS data

It can be seen from Figure 1 that the scattered intensity below the structure peak ($q < q^*$) decreases with decreasing q and is lower than the form-factor of a cylinder, indicating the presence of strong repulsion between the micelles. In order to obtain the structure factor S(q), the following procedure was applied. First, the scattering curves were fitted by the form-factor of a cylinder at $q > q^*$, where S(q) ~

1. Then, the structure factor was reconstructed in the whole q-range using the radii obtained from the fit. Such reconstruction is possible in our experimental range of scattering vectors ($q > 0.007 \text{ Å}^{-1}$), since for charged micelles very high values of persistence length in the order of 70-90 nm are expected [1,2], and, therefore, the crossover to a persistent cylinder lies outside or near the low-q experimental limit. Finally, S(q) was determined by division of the total intensity I(q) by P(q).

The structure factors at different molar ratios $[C_8TAB]/[potassium oleate]$ obtained using this procedure are presented in Figure 2. A well-defined structure peak can be seen at all curves. The expected position of the structure peak was calculated using the theoretical equation, which assumes locally hexagonal packing of wormlike micelles [24]

$$q^* = \frac{1}{R} \sqrt{\frac{8\pi\varphi}{\sqrt{3}}} \tag{1}$$

where φ is the volume fraction of surfactants and R is the radius of the micelles taken from Table 1. At the molar ratio 0.4 it is equal to 0.058 Å⁻¹, which coincides perfectly with q* extracted from S(q) (Table 1).



Figure 2. Calculated structure factors S(q) for aqueous solutions containing 190 mM potassium oleate and different concentrations of C₈TAB: 38 mM (circles), 57 mM (squares), 76 mM (triangles) in D₂O at 20^oC. Corresponding molar ratios [C₈TAB]/[potassium oleate] are shown in the picture. Inset: the low-q part of the same curves in log-log coordinates.

It can be seen from Figure 2 that the position of the structure peak q^* slightly shifts to lower q upon decreasing content of C₈TAB (Table 1). The q^* value is related to the mean distance between the micelles by the equation [14]

$$d = 2\pi/q^* \tag{2}$$

Therefore, the decrease of C_8TAB content in the micelles making their total charge higher results in a slight increase of average intermicellar distance. At low q (Figure 2, inset), the intensity drops with the decrease of C_8TAB content, which indicates strengthening of the repulsive electrostatic interactions between the micelles when less co-surfactant is added.

In the further study, the molar ratio $[C_8TAB]/[potassium oleate]$ was fixed at 0.4, which corresponds to less charged micelles. At these conditions, the solutions possess very high zero-shear viscosity of 3400 Pa·s (Figure 3), which is more than 6 magnitudes higher than the viscosity of water. They also

show shear-thinning behavior and strong viscoelasticity. This is indicative of a formation of a highly entangled wormlike micellar network.



Figure 3. Flow curves for aqueous solutions containing 190 mM potassium oleate and 76 mM C₈TAB (molar ratio $[C_8TAB]/[potassium oleate] = 0.4$) in the absence (triangles) and in the presence (diamonds) of 140 mM *n*-decane at 20^oC.



Figure 4. Scattering curves I(q) for aqueous solutions containing 190 mM potassium oleate and 76 mM C₈TAB (molar ratio [C₈TAB]/[potassium oleate] = 0.4) in the absence (triangles) and in the presence (diamonds) of 140 mM *n*-decane at 20^oC. The data in the presence of *n*-decane are offset by a factor of 5 for better representation. Black line is a fit of the scattering curve by a form-factor of cylinder with radius R = 18.8 ± 0.2 Å. Grey line is a fit of the scattering curve by a form-factor of sphere with radius R = 20.5 ± 0.2 Å.

We studied the effect of aliphatic oil (*n*-decane) on the rheological properties of such viscoelastic networks. It can be seen (Figure 3) that the addition of a small amount of oil (2 wt% = 140 mM) induces a dramatic drop of viscosity by 6 orders of magnitude, which is equal to $0.006 \text{ Pa} \cdot \text{s}$. This effect is accompanied by a complete loss of viscoelastic properties of the solution, which becomes liquid-like and shows Newtonian behavior. It means that mixed anionic/cationic surfactant micelles formed in the absence of salts are highly responsive to oils, as their counterparts formed in the presence of salts [18,19], and incorporation of an oppositely charged co-surfactant into the micellar surface does not alter the ability of micelles to solubilize hydrocarbon in their cores and to break.

In order to get insight into the structural changes occurring in the micellar networks upon addition of oil, SANS experiments were performed. Fig. 4 shows the scattering intensity profiles of the micellar solutions before and after the addition of oil. It is seen that in the presence of oil the scattering curve can no longer be fitted by a form-factor of a cylinder, but in the intermediate and high q-range (above the structure peak position q^*) it is well fitted by form-factor of a sphere. This means that spherical microemulsion droplets are formed as a result of solubilization of oil in the micelles.

This result is confirmed by DLS data, which show monomodal distribution of decay times τ (Figure 5a) with a narrow peak. The dependence of the decay rate $\Gamma = 1/\tau$ on q^2 is a direct proportionality (Figure 5b), which confirms that the mode is diffusive [23]. From the slope of this dependence $\Gamma = Dq^2$, the diffusion coefficient D was extracted, which was then converted to hydrodynamic radius R_h by using the Stokes-Einstein equation

$$D = \frac{kT}{6\pi\eta_s R_h} \tag{3}$$

where k is the Boltzmann constant, T is the absolute temperature, and η_s is the solvent viscosity. In this way, the value of $R_h = 2.0$ nm was obtained. It coincides perfectly with R calculated from SANS data (Table 1).

This result indicates that all cylindrical micelles are disrupted upon addition of oil, and only microemulsion droplets are present in the solution. The same effect was observed when *n*-dodecane was added to potassium oleate/KCl wormlike micelles [18,19], which were transformed into microemulsion droplets with a radius of 3.8 nm, consisting of an oil droplet in the core with radius of 1.9 nm, and a surrounding layer of surfactant molecules with thickness 1.9 nm.

Surprisingly, in the present system potassium oleate/ C_8TAB the radius of the droplets is much less and is equal to 2 nm. This value is even close to the length of potassium oleate alkyl tail (1.9 nm), meaning that if the droplet had had the same core-shell structure as in potassium oleate/KCl system, then the inner oil core would have had the radius of only ~ 0.1 nm, which is far not enough to solubilize all added oil. It should be noted that 140 mM is the maximum amount of hydrocarbon that can be solubilized in the system containing 190 mM potassium oleate, and at higher oil concentrations its excess forms a second upper phase.

We suppose that in the present system microemulsion droplets of slightly different structure are formed due to the presence of a short-chain co-surfactant. Indeed, as mentioned above, the volume of C_8TAB alkyl tail is 2 times less than that of potassium oleate. It is more probable that C_8TAB polar head resides near the micellar surface (where its charge interacts with potassium oleate charge) and does not penetrate deeply into the micellar core. It means that the surfactant layer is formed not only by long potassium oleate tails (with length 1.9 nm), but also by shorter C_8TAB tails (note that at molar ratio 0.4 there are nearly 30% C_8TAB molecules and 70% potassium oleate molecules in the mixture). One can suggest that there is some space in the surfactant tails layer where oil can be solubilized in addition to the core, and such a small radius of microemulsion droplet can be explained by the penetration of oil into this layer.

Therefore, highly viscous solutions of mixed anionic/cationic wormlike micelles with no added salt keep responsiveness to oils inherent to the micellar chains formed in the presence of salts. It opens a new way of constructing oil-responsive systems for the applications in petroleum industry.

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Figure 5. Decay time distribution at the scattering angle 90[°] (a) and the dependence of decay rate Γ on q² (b) for aqueous solutions containing 190 mM potassium oleate, 76 mM C₈TAB (molar ratio [C₈TAB]/[potassium oleate] = 0.4) and 140 mM *n*-decane at 20[°]C.

4. Conclusions

In this work, the structure of mixed potassium oleate/ C_8TAB wormlike micelles was investigated by SANS. It was shown that the radius of the micelles does not depend on the amount of cationic cosurfactant in the mixture, and is determined by the length of a fully extended anionic surfactant tail. Calculation of the structure factors revealed that the mean distance between the micelles slightly increases when they become more charged.

It was discovered that the networks formed by mixed anionic/cationic surfactant micelles are highly responsive to the addition of oil. The viscosity of the solution drops by 6 orders of magnitude when a small amount of oil is added, which is explained by the transformation of wormlike micelles into spherical microemulsion droplets. However, the radius of microemulsion droplets formed in potassium

oleate/ C_8TAB /n-decane system is nearly 2 times less than that in potassium oleate/KCl/n-dodecane microemulsions, suggesting the solubilization of alkane in the surfactant layer in the presence of a short-chain cationic co-surfactant.

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