Effect of polymer on the arrangement of mixed anionic/cationic wormlike surfactant micelles revealed by SANS

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Abstract. We report the results of small-angle neutron scattering (SANS) study of the effect of neutral water-soluble polymer poly(vinyl alcohol) on the structure of salt-free aqueous solutions of charged cylindrical micelles formed by the mixture of anionic (potassium oleate) and cationic (n-octyltrimethylammonium bromide (CsTAB)) surfactants at a fixed molar ratio [CsTAB]/[potassium oleate] = 0.46. The dependences of the scattering on surfactant concentration were examined both in the presence and in the absence of polymer. It was observed that at high q range, the scattering function is independent of surfactant concentration and added polymer indicating that the local cylindrical structure of the micelles remains unchanged. At intermediate q range, with growing surfactant concentration the scattering function becomes increasingly dominated by a structure peak that reveals enhanced interactions between neighboring micelles. The peak position q* scales with the surfactant concentration Csurf as Csurf¹.⁶ and Csurf⁰.⁵₅ in the absence and in the presence of polymer, respectively. The most important observation concerns the fact that added polymer decreases significantly the average intermicellar distance, which may be due to microsegregation of polymer and surfactant components typical for microphase separation.

1. Introduction
Mixing of two oppositely charged surfactants can lead to the formation of extremely long wormlike micelles even in the absence of low molecular weight salt [1]. In such system, the electrostatic repulsion between the ionic surfactant head groups can be strongly screened even without added salt because of alternation of oppositely charged surfactant head groups and the release of counterions, which increase the ionic strength of the solution. Reduced repulsion allows tighter packing of surfactant heads thereby favoring growth of cylindrical micelles in length permitting to decrease the number of thermodynamically unfavorable end-caps of spherical shape. The length of mixed micelles can reach micrometers [1]. Such micelles can interface thus providing viscoelastic properties to the solutions. These properties of wormlike micelles found numerous applications in oil recovery, nanotemplating, drag reduction, health care products and so on [2,3].

The viscoelastic properties of wormlike micellar solutions can be significantly enhanced upon addition of polymeric chains [4-8]. For this aim, hydrophobically modified water-soluble polymers are usually used [4-7]. Such polymers intercalate their hydrophobic groups into wormlike micelles thus
leading to the formation of a common network, in which some subchains are formed by polymer, whereas the other ones – by surfactant micelles. The structure of such polymer/surfactant networks was studied by several methods including SANS [4,6,7]. However, such polymers are poorly available commercially, which hinders their wide application.

Recently, it was shown [8] that a considerable enhancement of the viscosity of wormlike micellar solutions can be achieved by using widely available water-soluble polymer poly(vinyl alcohol). The experiments were performed with mixed micelles of anionic and cationic surfactants (potassium oleate and \( n \)-octyltrimethylammonium bromide (C12TAB), respectively) without added salt. In this case, the polymer does not interact with micelles as was evidenced by fluorescence spectroscopy with pyrene as a probe, and therefore the addition of such polymer would expect to cause the phase separation in the system. Nevertheless, the obtained polymer/surfactant solutions remain homogeneous. Most probably, the stabilization of these solutions is due to the presence of large amount of surfactant counterions, which can lose their translational entropy, if the phase separation occurs. However, the segregation of polymer and micellar components can be realized at a microscale without macrophase demixing. If the microdomain structure will propagate through the whole system, it will not impede counterions to travel in the most of the volume of the solution thus ensuring the gain in the translational entropy. At the same time, it would permit to realize the local segregation of incompatible polymer and surfactant components resulting in the gain in energy. However, a particular structure of these polymer/surfactant systems remains unclear. Also, the reasons for the observed enhancement of the viscosity of wormlike micellar solutions upon addition of polymer still need to be understood. A suitable method to clarify these points is SANS, as it allows to reveal the changes in the micellar structure and in the mutual arrangement of micelles, when they are mixed with polymer.

Thus, the aim of this paper is to consider the effect of non-interacting polymer PVA on the structure of solutions of mixed micelles of anionic (potassium oleate) and cationic (C12TAB) surfactants by using SANS technique.

2. Experimental section

2.1. Materials

Surfactants potassium oleate (TCI, purity > 98%) and C12TAB (ABCR, purity > 98%), polymer PVA Mowiol 4-86 with molecular weight of 27000 g/mol (Aldrich) as well as D2O (Deutero GmbH, 99.9% isotopic purity) were used as received.

2.2. Samples preparation

First, stock solutions of potassium oleate / C12TAB and PVA in D2O were prepared and then they were mixed in appropriate quantities. The obtained samples were stirred for 2-3 days and then left for few days to remove air bubbles.

2.3. Small-angle neutron scattering

SANS experiments were performed on the YuMO spectrometer at the IBR-2 reactor facility (Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia). The samples were put in dismountable cells with parallel disk-like quartz plates and beam path of 2 mm. The data were recorded at 20.0 ± 0.3 °C by two detectors covering the range of scattering vectors \( q \) of 0.007 - 0.5 Å\(^{-1}\).

The details of the experiments are reported elsewhere [9]. 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 scattering length densities of the surfactant tails and D2O are equal to ca. \( \sim 3.0 \cdot 10^{-6} \text{Å}^{-2} \) and \( 6.36 \cdot 10^{-6} \text{Å}^{-2} \), respectively.

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

3. Results and discussion
3.1. Surfactant solutions without polymer
In this work, we studied the structure of solutions of mixed micelles composed of anionic surfactant potassium oleate and cationic co-surfactant C₈TAB at fixed molar ratio [C₈TAB]/[potassium oleate] equal to 0.46. So, under these conditions, the micelles were strongly negatively charged.

Scattering curves of the solutions of mixed micelles in semi-logarithmic format are presented in Figure 1. When normalized with respect to surfactant concentration (Figure 2), all curves coincide perfectly at high q region indicating that the local structure of the micelles in all the samples is the same. This part of the scattering curve can be well fitted by a form-factor of a cylinder (Figure 2) suggesting that the surfactant solutions under study contain cylindrical micelles. From the fit, the radius of micelles is obtained. It equals to 18.7 Å, which is quite close to the length of fully extended olate chain (19 Å) [10]. Therefore, the radius of mixed micelles is determined by the length of potassium oleate tails, which are in the excess in the surfactant mixture. Previously, similar results were obtained at lower content of C₈TAB co-surfactant [8]. Here we show that further increase of the content of short n-octyltrimethylammonium chains up to 0.315 mol % does not affect the radius of mixed micelles.

From Figs. 1 and 2 it is seen that at the intermediate q region the scattering curves have a structure peak, which becomes more pronounced with increasing surfactant concentration. Most probably this peak arises from electrostatic repulsion between similarly charged micelles [12,13]. Fig. 3 shows that the peak position q* scales with surfactant concentration C_{surf} as q* ∝ C_{surf}^{0.6}. This scaling behavior is rather close to that expected [12] for strongly interacting cylindrical objects: q* ∝ C^{0.5}. From the peak position the average distance between cylindrical micelles d can be estimated. If we assume a hexagonal packing of the micelles, the value of d can be calculated from the following formula (as it is evident from the picture in the inset to Fig.4): d = d₀ / cos60°, where d₀ = 2π/q* [11].

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Scattering curves I(q) in semi-logarithmic format for solutions of potassium olate and C₈TAB in D₂O at a fixed molar ratio [C₈TAB]/[potassium olate] = 0.46 at 20°C. Total concentrations of the both surfactants are indicated in the figure.
Figure 2. Normalized scattering curves $I(q)$ in double logarithmic format for solutions of potassium oleate and C$_8$TAB in D$_2$O at a fixed molar ratio $[C_8$TAB]/[potassium oleate] = 0.46 at 20$^\circ$C. Total concentrations of the both surfactants are indicated in the figure. The solid line is a fit of the scattering curves by a form-factor of cylinder with radius $R = 18.7 \pm 0.2$ Å.

Figure 3. Position of the structure peak as a function of the total surfactant concentration in potassium oleate/C8TAB solutions in D$_2$O in the presence (circles) and in the absence (squares) of 4 wt% PVA at 20$^\circ$C. Molar ratio [C$_8$TAB]/[potassium oleate] = 0.46.
From Fig. 4 it is seen that the micelles come closer to each other with increasing surfactant concentration suggesting that the total number of micelles becomes higher. Simultaneously, in low $q$ region ($q < q^*$), at the increase in the surfactant concentration the scattered intensity decreases, which can be attributed to high osmotic penalty for large spatial scale fluctuations in charge density [6]. This behavior can be related to the strengthening of the intermicellar repulsion at higher content of surfactant in the solution. It should be noted that quite similar scattering curves were previously reported for cationic [6,14] and anionic [15] surfactants at low ionic strength. Here we show that the character of the curves does not change when passing to the mixture of cationic and anionic surfactant.

![Figure 4](image-url)

**Figure 4.** Average distance between cylindrical micelles $d$ as a function of the total surfactant concentration in potassium oleate/C8TAB solutions in D$_2$O in the presence (circles) and in the absence (squares) of 4 wt% PVA at 20°C. Molar ratio $[\text{C8TAB}] /[\text{potassium oleate}] = 0.46$. Inset: schematic representation of hexagonal packing of cylindrical micelles.

Thus, charged mixed surfactant micelles in salt-free aqueous solutions form cylindrical micelles, which are mutually arranged as a result of electrostatic repulsion.

### 3.2. Surfactant/polymer solutions

The effect of added neutral polymer PVA on the structure of micellar solutions was studied at different surfactant concentrations ranging from 2.7 to 9.5 wt %, whereas the polymer concentration was fixed at 4 wt %. The PVA concentration corresponds to semidilute regime, since $C^*$ value for this polymer is equal to 3.2 wt %. In the studied system, the polymer scattering is rather weak, and the overall scattering is dominated by the micelles. From Fig.5 it is seen that in the presence of polymer, all the scattering patterns show the typical characteristics similar to those of pure surfactant solutions: correlation peak at intermediate $q$ values and cylindrical form-factor at high $q$ region. At the same time, at low $q$ values the patterns for pure surfactants and polymer/surfactant systems are different. Below we discuss these features in more detail.
Figure 5. Normalized scattering curves $I(q)$ in double logarithmic format for solutions of potassium oleate and $\text{C}_8\text{TAB}$ in $\text{D}_2\text{O}$ at a fixed molar ratio $[\text{C}_8\text{TAB}]/[\text{potassium oleate}] \approx 0.46$ in the presence of 4 wt % PVA at 20°C. Total concentrations of both surfactants are indicated in the figure. Line is a fit of the scattering curves by a form-factor of cylinder with radius $R = 18.5 \pm 0.2$ Å.

Let us start with high q range. Presentation of the scattering data in the form of Porod plot (Fig.6) emphasizing the high q region evidences that the structure of micelles at this length scale is not affected by the addition of polymer. The same conclusion can be drawn from the fit of the high-q part of the scattering curves by a form-factor of cylinder (Fig.5). Moreover, the fitting results demonstrate that the radius of the cylindrical micelles (18.6 Å) is almost the same independently of the presence of polymer.

As to the intermediate q range, both in the absence and in the presence of polymer we observe a clear structure peak at a characteristic value $q^*$ (Figs.5 and 7), and its position exhibits almost the same dependence on the surfactant concentration (Fig.3) as in pure surfactant solution. However, in the presence of polymer the peak becomes narrowly and shifts to higher q values (Fig.7). This means that polymer induces better mutual ordering of cylindrical micelles and their closer packing. For instance, at 6.8 wt % surfactant the average distance between the micelles is equal to 18.5 and 12.7 nm in the absence and in the presence of 4 wt % PVA, respectively. Such behavior can be attributed to a poor miscibility between polymer chains and surfactant micelles, which leads to the local segregation between these components. The segregation pushes the micelles to come closer to each other thus inducing the increase in their local concentration.

At low q range, in the presence of polymer, the scattering intensity is much higher, which may be accounted for by the formation of microphase separated domains enriched either by polymer or by surfactant. The absence of a low q plateau suggests that these domains have the radius much larger than 900 Å ($2\pi/q_{\text{min}}$, where $q_{\text{min}}$ is the low q limit of the experiment). Thus, polymer induces better mutual ordering and closer packing of similarly charged cylindrical micelles of surfactant.
Figure 6. Holtzer plots $Iq^4(q)$ of the scattering from 4.8 wt % solutions of potassium oleate and C$_8$TAB in D$_2$O at a fixed molar ratio [C$_8$TAB]/[potassium oleate] = 0.46 in the absence (circles) and in the presence (squares) of 4 wt % PVA at 20°C.

Figure 7. Scattering curves I(q) for 8.2 wt % solutions of potassium oleate and C$_8$TAB at a fixed molar ratio [C$_8$TAB]/[potassium oleate] = 0.46 in the absence (black symbols) and in the presence of 4 wt % PVA (grey symbols) in D$_2$O at 20°C.
Closer packing suggests the increase of the local surfactant concentration, which should induce the growth of micelles in length according to a scaling law $L \sim C_{\text{sur}}^{0.5}$ derived theoretically [16,17]. Longer micelles are able to form more entanglements, and thereby enhance the rheological properties, which was indeed observed experimentally upon addition of PVA to the solution of cylindrical micelles formed in the mixture of potassium oleate and C8TAB.

Thus, the analysis of SANS data allowed not only to reveal the structure of polymer/surfactant system, but also to suggest a reason for the enhancement of rheological properties.

Conclusions
In this article, SANS was used to study the structural changes in mixed surfactant solutions induced by the addition of neutral water-soluble polymer PVA. It was shown that polymer does not affect the cylindrical form of the micelles and their radius. At the same time, it induces better mutual ordering of neighboring micelles and pushes the micelles closer to each other thus increasing their local concentration and therefore triggering the increase in their length. The later fact seems to be crucial for the enhancement of the rheological properties observed upon addition of polymer to surfactant solution.

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References
[1] Raghavan S J, Fritz G and Kaler E W 2002 Langmuir 18 3797
[2] Feng Y, Chu Z and Dreiss C A 2015 Smart Wormlike Micelles: Design, Characteristics and Applications (Berlin: Springer-Verlag)
[3] Philippova O E and Khokhlov A R 2010 Petroleum Chemistry 50 266
[4] Shashkina J A, Philippova O E, Zaroslov Y D, Khokhlov A R, Pryakhina T A and Blagodatskikh I V 2005 Langmuir 21 1524
[5] Couillet I, Hughes T, Maitland G and Candau F 2005 Macromolecules 38 5271
[6] Lodge T P, Taribagil R, Yoshida T and Hillmyer M A 2007 Macromolecules 40 4728
[7] Ramos L and Ligoure C 2007 Macromolecules 40 1248
[8] Philippova O E and Shibaev A V 2016 Abstr. World Polymer Congress Macro 2016 (Istanbul) p 97
[9] Philippova O E, Andreeva A S, Khokhlov A R, Islamov A K, Kuklin A I and Gordeliy V I 2003 Langmuir 19 7240
[10] Shibaev A V, Molchanov V S and Philippova O E 2015 J. Phys. Chem. B 119 15938
[11] Rulkens R, Wegner G and Thurn-Albrecht T 1999 Langmuir 15 4022
[12] Gamez-Corrales R, Berret J F, Walker L M and Oberdisse J 1999 Langmuir 15 6755
[13] Flood C, Dreiss C A, Croce V, Cosgrove T and Karlsson G 2005 Langmuir 21 7646
[14] Schubert B A, Kaler E W and Wagner N J 2003 Langmuir 19 4079
[15] Dreiss C A 2007 Soft Matter 3 956
[16] Cates M E 1987 Macromolecules 20 2289
[17] Magid L J 1998 J. Phys. Chem. B 102 4064