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Alexander L. Kwiatkowski*, Pavel V. Kalinin, Olga E. Philippova

Physics Department, Lomonosov Moscow State University, Moscow, Russia
*(*Corresponding author's e-mail: kvyatkovskij@physics.msu.ru)*

Effect of Salt Content on Solubilization of Hydrophobic Polymer by Wormlike Micelles of Ionic Surfactant

The effect of concentration of inorganic salt KCl on solubilization of hydrophobic polymer poly(4-vinylpyridine) (P4VP) in aqueous solutions of ionic surfactant potassium oleate was experimentally investigated. As was shown by rheology, in the range of concentrations from 1 to 5 wt.% of salt the polymer-free solutions of surfactant mainly contain linear wormlike micelles (WLMs). The formation of branched WLMs was observed in the solutions containing 5–9 wt.% of KCl. In the presence of higher salt content the phase separation occurred, indicating the formation of a highly branched saturated network of WLMs. Enhanced screening of the charged groups of potassium oleate by oppositely charged ions of KCl caused elongation and branching of micelles that reflected in zero-shear viscosity of the solutions passing through the maximum. In the phase diagram, the saturation concentration with P4VP of both linear and branched WLMs decreased with increasing salt content. In the case of linear WLMs, this could be explained by the constant number of embedded polymer chains per 1 WLM, while simultaneously decreasing number of WLMs in the system. As for the branched WLMs, it was caused by shortening of the linear parts of micelles due to the formation of branching points. For this reason, almost no P4VP was dissolved in the solution containing the highly branched saturated network.

Keywords: ionic surfactant, polymer solubilization, wormlike micelles, hybrid micelles, branched micelles, saturated network, rheology, phase diagram.

Introduction

Ionic surfactants are able to self-assemble into very long micelles with local cylindrical morphology. They are called wormlike micelles (WLMs) [1–4]. These micelles typically have a diameter of a few nanometers and a contour length of up to several micrometers producing micellar aggregates that resemble worms. These worms, when entangled in a transient network, impart significant macroscopic viscoelastic properties to solutions. Their viscoelastic properties are easy to manipulate because the non-covalently bonded network of WLMs is highly sensitive to external conditions, such as the concentration of low molecular weight salt [5–10] or hydrophobic additives [1–3, 11–13]. Ions of salt screen the electrostatic repulsion of similarly charged surfactant head groups and induce the elongation of micelles and their branching [5–10], as they make hemispherical end caps of WLMs highly unfavorable. In contrast, hydrocarbons induce shortening of micelles and finally their transformation into microemulsion droplets, because they concentrate in the micellar core [14-15].

These properties of WLMs are of extended practical significance. In particular, they allow WLMs to be used as oil-sensitive thickeners for fracturing fluids in oil recovery [16–18]. In contrast to polymer-based fracturing fluids, the surfactant-based fluids have the advantage of not requiring the addition of breakers to reduce the viscoelasticity at the back flow of oil [19], because they spontaneously transform into microemulsion droplets upon contact with hydrocarbons. At the same time, for further transportation of oil through the pipeline the polymer chains possess an advantage — they provide higher drag reducing efficiency. The advantages of both surfactant- and polymer-based fluids for hydraulic fracturing and oil transportation can be combined while using hybrid WLMs of surfactant with embedded polymer chains. Such a system has recently been proposed [20]. It consisted of WLMs of potassium oleate armored with poly(4-vinylpyridine) (P4VP) polymeric chains [20].

However, all the experiments were carried out at a single salt concentration, whereas in practical applications different salt concentrations may be encountered. The salinity of the solution significantly affects the shape of hybrid micelles and the location of the polymer within them [21]. This, in turn, impacts the maximum amount of polymer that can be solubilized inside the micelles and becomes one of the key parameters that govern hydraulic fracturing and drag reduction when using hybrid micelles.

The present paper is aimed at the experimental investigation of the effect of salt on the phase behavior of the hybrid micelles of anionic surfactant potassium oleate with embedded hydrophobic polymer P4VP and the determination of the maximum amount of polymer that can be solubilized by the micelles at different concentrations of inorganic salt KCl.

Experimental

Materials. Surfactant potassium oleate (TCI Europe, purity >98 %), salt KCl (Sigma-Aldrich, purity > 99.5 %) and polymer P4VP (Sigma-Aldrich, Mw=160000 g/mol, contour length 380 nm) were used for preparation of hybrid surfactant/polymer micelles. Polydispersity of P4VP, as evaluated by dynamic light scattering, was equal to 0.06 (see Supplementary Materials for details). P4VP was dissolved in ethanol (Merck, purity > 99 %). Other solutions were prepared with de-ionized water purified using Millipore Milli-Q system. The pH of aqueous solutions was maintained at 11 with KOH (Acros Organics, purity > 99 %).

Sample preparation. A series of polymer-free micellar solutions with constant concentration of surfactant equal to 47 mM and salt concentration ranging from 1 to 11 wt% were prepared by mixing potassium oleate and KCl with water using a magnetic stirring bar for 1 day. At high salt concentration (9, 10 and 11 wt%) the solutions became phase separated (Fig. 1).

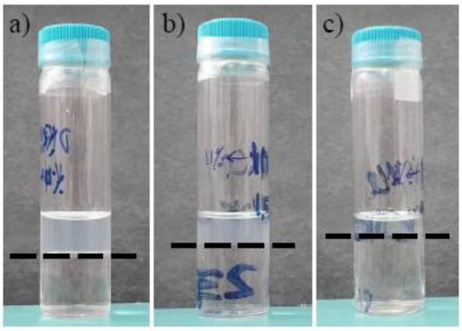

Figure 1. Phase separated polymer-free aqueous solutions of 47 mM potassium oleate containing different concentrations of KCl: 9 (a), 10 (b) and 11 wt% (c) at pH 11. The horizontal dashed lines indicate the interfaces

As P4VP is insoluble in water, the following method, previously described elsewhere [21], was used to prepare hybrid potassium oleate/P4VP micelles. First, a stock solution of hybrid potassium oleate/P4VP micelles was obtained in the absence of salt. For this purpose, an aqueous solution of potassium oleate was poured onto the thin film of polymer P4VP in the vial and stirred for 24 hours. The polymer film was preliminary formed by evaporation of ethanol from the P4VP solution during 24 hours at room temperature. The concentration of P4VP in the stock solutions was varied from 0 to 0.4 wt%. Then an appropriate amount of potassium oleate with water was added to the same vial to prepare solutions of hybrid micelles at different salt concentrations.

Rheology. The steady shear and shear oscillatory rheology was measured on a stress-controlled Anton Paar Physica MCR 301 rheometer. Aluminum cone-plate (50 mm, 1°) and Couette (i.d. 24.661 mm, o.d 26.667 mm) geometries were used as measuring cells for viscous and fluid samples, respectively. Peltier elements were used to maintain a constant temperature of 20 °C. Steady shear tests were conducted at shear rates ranging from $3 \cdot 10^{-3}$ to 300 1/s. The oscillatory shear tests were carried out in the frequency range from $2 \cdot 10^{-2}$ to 200 rad/s within the viscoelastic linear regime as previously determined by strain measurements.

Determination of the saturation concentration of hybrid micelles at high salt content. In the solutions of hybrid micelles with a high amount of embedded P4VP, at all studied concentrations of salt, the phase separation occurred leading to the precipitation of polymer. At low concentrations of KCl, the saturation concentration of hybrid micelles was visually detected by the appearance of turbidity. When a high amount of KCl was added (7, 8 and 9 wt%), for more accurate determination of the saturation concentration, the solid precipitate was carefully separated from the homogeneous liquid phase and dried in an oven until a constant mass was obtained. After weighing the dried precipitate, the dependencies of thus determined mass of the precipitate on the initial concentration of added P4VP at 7, 8 and 9 wt% of KCl were obtained. They represent straight lines (Fig. 2). The x-coordinates of their intersections with the horizontal axis correspond to the saturation concentrations of hybrid potassium oleate/P4VP micelles in the presence of different concentrations of KCl.

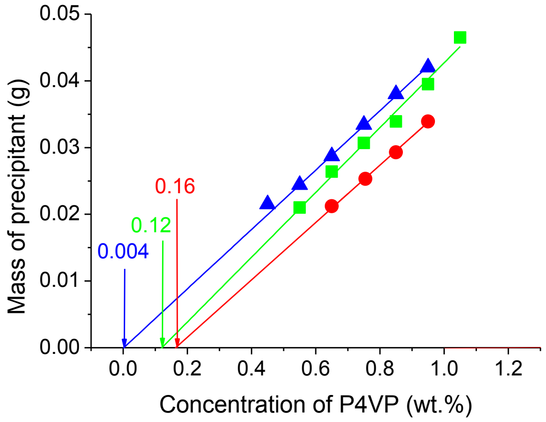

Figure 2. The dependencies of the mass of the precipitate on the initial concentration of added P4VP in 47 mM aqueous solutions of potassium oleate containing different concentrations of KCl: 7 wt% (circles), 8 wt% (squares), and 9.0 wt% (triangles) at pH 11. The arrows indicate the position of the intersection of the dependencies with the horizontal axis

Results and Discussion

Effect of salt on polymer-free micelles. The steady shear and oscillatory rheological data of the polymer-free solutions of potassium oleate at different concentrations of KCl are shown in Figures 3a and b, respectively. In Figure 3a at low shear rates the plateau of the viscosity is observed (i.e. zero-shear viscosity η_0). In the literature [1, 22–24], the plateau-value η_0 is attributed to the viscosity of the solution undamaged by shear (Figure 3a). The subsequent decrease in viscosity, called shear-thinning [9, 24–26], is the result of the alignment of the chains along the direction of the shear flow (Fig. 3a).

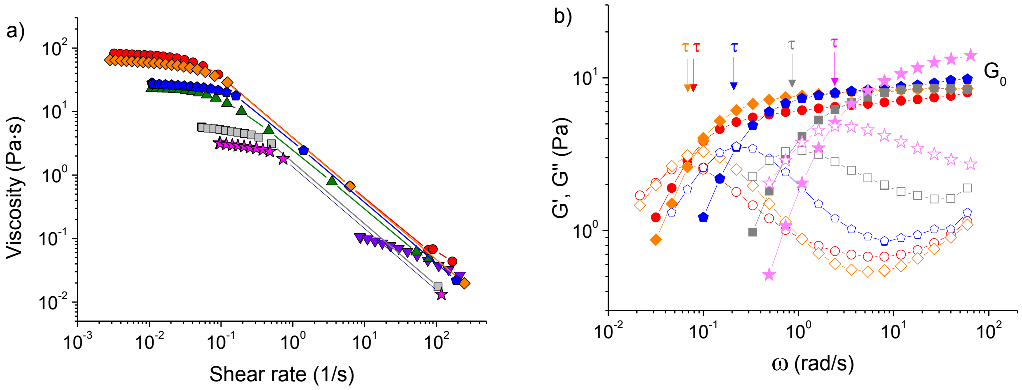

Figure 3. Apparent viscosity versus shear rate (a) and storage G' (filled symbols) and loss G'' (open symbols) moduli versus frequency of the applied stress ω (b) for 47 mM potassium oleate solutions, containing different concentrations of KCl: 4.0 wt% (circles), 6.0 wt% (diamonds), 7.0 wt% (pentagons), 8.5 wt%. (squares) and 9.0 wt% (stars) at pH 11. The arrows indicate the position of the intersection of the $G'(\omega)$ and $G''(\omega)$ dependencies

The value of η_0 passes through the maximum with increasing concentration of KCl (Fig. 4). As the K^+ ions of salt screen the repulsion of the negatively charged headgroups of potassium oleate on the surface of micelles, the increase of the amount of KCl in the solutions induces the transition of spherical micelles into the wormlike ones and their further elongation. This results in an increase of the η_0 value by 3 orders of magnitude (Fig. 4). At concentrations of KCl higher than 6 wt.%, the zero-shear viscosity decreases due to the formation of branches in the micelles [10, 26-27]. The relaxation mechanism of branched WLMs, which represents sliding of the branching points along the micelle, requires less energy, than process of reptation in semidilute solutions of linear micelles [10, 28–30]. The phase separation in the samples with high salt content (Fig. 1), is probably related to the formation of a saturated network of WLMs, which contains many branching points and almost no end-caps [26, 31-32].

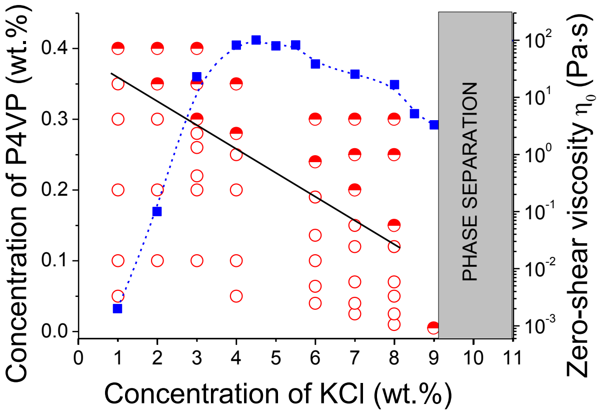

Figure 4. Zero-shear viscosity η_0 of polymer-free solutions (blue) and phase diagram of potassium oleate/P4VP hybrid micelles (red) versus concentration of KCl. Open circles indicate homogeneous and filled circles indicate phase separated samples. Solid line indicates the onset of phase separation in potassium oleate/P4VP hybrid micelles. The grey square limits the region of phase separation in 47 mM potassium oleate solutions without polymer at pH 11

The dependencies of storage G' and loss G'' moduli on the frequency ω of shear stress applied to the micellar solutions with different salt content are depicted in Figure 3b. At high frequencies, $G' > G''$, and the solutions demonstrate an elastic response to the applied stress. According to literature [2, 27, 33], the plateau value of storage modulus G_0 is proportional to the amount of elastically active entanglements between the micelles in the physical network. At low frequencies, $G' < G''$, and the samples behave as viscous liquids. The studied samples demonstrate Maxwellian behavior with single relaxation time [10, 23-24, 34]. The abscissa intercept ω_c of $G'(\omega)$ and $G''(\omega)$ defines the relaxation time of the samples τ, as $\tau = \omega_c^{-1}$ (Fig. 3b).

In Figure 3b a small increase of the plateau modulus G_0 at high salt concentration is observed. This may be due to the intermicellar linkages produced by branching of WLMs occurring upon screening of the repulsion of similarly charged headgroups of surfactant with oppositely charged ions of salt. Simultaneously, the relaxation time τ is decreasing with increasing amount of branching points, since more rapid relaxation occurs (Fig. 3b) as a result of sliding of branches along the worms. Similar results have been obtained previously for other systems containing WLMs of ionic surfactants [1, 9-10, 26, 35-36].

Solubilization of P4VP by WLMs at different salt content. In order to investigate the solubilization of P4VP by micelles of potassium oleate at different concentrations of KCl, the following phase diagram was constructed (Fig. 4). At all the concentrations, a solid precipitate was formed when a large amount of polymer was added to the system. In the solution with 6 % KCl, elemental analysis previously demonstrated that the precipitate was the pure polymer (without surfactant) [37]. The supernatant represented the solution of hybrid micelles saturated with P4VP. Therefore, in this study, the formation of a precipitate indicates that the micelles have reached their saturation with a polymer.

From Figure 4 it can be seen that the concentration of saturation of micelles with polymer decreases with increasing salt content. In the range of 1–5 wt.% of KCl mainly linear WLMs are present in the polymer-free solutions. The viscosity of the solutions increases due to elongation of micelles (Fig. 4). At constant concentration of surfactant, the elongation of micelles is accompanied by a decrease of the total number of micelles in the system. According to the literature [37], 1-2 macromolecules of P4VP are embedded into linear WLMs of potassium oleate. Solubilization of a larger number of macromolecules is energetically unfavorable, since leads to the drop of entropy. As a result, the total amount of P4VP chains in saturated hybrid micelles decreases.

Another possible reason for the decrease in the saturation concentration of linear WLMs could be the increase of the packing density of surfactant molecules in their central part. Higher screening of potassium oleate anions by counterions of KCl will provide their closer approach to each other and reduction of the volume at the boundary between the hydrophobic core and hydrophilic corona of the micelles, where P4VP is localized [37-38].

The rheological data (Fig. 3a) demonstrated the drop of viscosity of the solutions without polymer in the range 5–9 wt.% of KCl (Fig. 4) due to the enhanced amount of branched WLMs. The formation of branching points in the micelles appears simultaneously with shortening of their central cylindric parts [39-40], where P4VP chains are embedded in the hybrid micelles [37]. Consequently, the presence of branched micelles can lead to a decrease in the concentration of saturation with polymer (Fig. 4). It is unlikely that the polymer will be solubilized at the branching points due to their high mobility. This accounts for the near-absence of solubility of PVP in systems with more than 9 wt% of KCl (Fig. 4).

Thus, the increasing ionic strength of solutions similarly affects the solubilization of P4VP, both, by linear and branched WLMs of potassium oleate (Fig. 4).

Conclusions

According to rheological data, in aqueous solutions of 47 mM potassium oleate with 1–5 wt% of KCl mostly linear WLMs are present. The zero-shear viscosity η_0 of the solutions increases with increasing length of WLMs due to screening of the electrostatic repulsion of surfactant headgroups. Branched WLMs are formed at KCl concentration between 5 and 9 wt%. The faster relaxation mechanism of branched WLMs results in the decrease in η_0 and relaxation time τ as evidenced by rheology. The concentration of P4VP in the saturated hybrid micelles decreases in the whole range of KCl concentration studied. For linear WLMs, it is the result of a constant number of polymer chains being embedded per 1 WLM at the time when the total number of WLMs decreases in the system. As to the branched WLMs, the drop of saturation concentration is caused by low probability of P4VP solubilization by mobile branching points, where the boundary between the hydrophobic core and hydrophilic corona of the micelles, where P4VP is localized, is reduced, and the reduction of linear parts of the micelles. For this reason, almost no P4VP was dissolved in the solution with 9 wt.% of KCl, which contained the highly branched saturated network of WLMs.

Supplementary Materials

Supplementary Materials is available free at https://ejc.buketov.edu.kz/index.php/ejc/article/view/92/81

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*Author Information**

**The authors' names are presented in the following order: First Name, Middle Name and Last Name*

Alexander Lvovich Kwiatkowski (*corresponding author*) — Candidate of physical and mathematical sciences, Leading Researcher, Lomonosov Moscow State University, Leninskie Gory, 1, 2, Moscow, 119991, Russia; e-mail: kvyatkovskij@physics.msu.ru; https://orcid.org/0000-0002-0514-384X

Pavel Vasilyevich Kalinin — Bachelor in physics, Lomonosov Moscow State University, Leninskie Gory, 1, 2, Moscow, 119991, Russia; e-mail: kalinin@polly.phys.msu.ru

Olga Evgenievna Philippova — Doctor of physical and mathematical sciences, Professor, Lomonosov Moscow State University, Leninskie Gory, 1, 2, Moscow, 119991, Russia; e-mail: phil@polly.phys.msu.ru; https://orcid.org/0000-0002-1098-0255

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Alexander Lvovich Kwiatkowski** investigation, original draft preparation, review and editing; **Pavel Vasilyevich Kalinin** investigation; **Olga Evgenievna Philippova** original draft preparation, review and editing.

Conflicts of Interest:

The authors declare no conflict of interest.

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