Nanocomposite composed of charged wormlike micelles and magnetic particles

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Abstract. Wormlike micelles solutions of cationic surfactant were examined as surfactant concentration in the presence KCl salt. Dilute and semidilute regimes were determined. Concentration power law dependencies of the zero-shear viscosity and plateau modulus indicate on charged wormlike micelles network. SANS data prove long flexible wormlike micelles formation. Nanocomposite composed of the chains and magnetite particles was prepared. It was shown that particles addition leads to increase rheological parameters of the system which is in good agreement with suggestion that micellar chains can link to particles surface covered by surfactant to decrease number of end-caps.

1. Introduction
Surfactant molecules in aqueous solutions can aggregate into enormously long flexible cylindrical micelles so-called wormlike micelles or micellar chains [1]. Three dimensional network of these entangled polymerlike chains impact viscoelastic properties to solutions. Micellar network of entangled wormlike micelles are attract attention of many authors due to linear rheological properties, including zero-shear viscosity plateau at steady-shear measurements and elastic plateau at oscillation measurements. These properties are highly sensitive to many factors, for example, concentration of salt, presence of hydrocarbons or temperature due to shape and length changes as result of weak noncovalent binding the molecules in the micelles.

On the other hand surfactants are extensively used and investigated as stabilizers of colloidal particles that require usually low concentrations close to ccm. But the use of relatively high surfactant concentrations provided wormlike micelles can induce a loss of the stability of the dispersion. It was found [2] that negatively charged polystyrene particles suspended in zwitterionic/anionic wormlike micelles solution at significantly low colloid and micelle concentrations at the presence and at the absence salt, but the use of high surfactant concentrations can induce a loss of the stability of the dispersion. The depletion mechanism is believed to be responsible for this instability. Asakura and Oosawa [3] shown that the depletion force in the presence of polymer chains can be much greater than in solutions of spherical objects: the configurational entropy of the chains is reduced next to the particle surfaces. Therefore, the presence of wormlike micelles in solution at high surfactant concentrations should augment the depletion potential. Also the instability was observed at both negative and positive charge of the colloidal latex particles in mixture with both negative and positive surfactant at high concentrations [4].
Although described studied there are several works the colloidal particles improving rheological properties of viscoelastic wormlike micelles of surfactant at high concentrations [5-7]. In the work [5] the common system of wormlike micelles of cationic surfactant and negatively charged silica particles was investigated. The dependencies of viscosity, elastic modulus, relaxation time went through maximum that was explained in terms of electrostatic interactions similarly salt effect and adsorption of sufficient part of surfactant molecules on the particles surface at high particles content. The improvement of viscoelastic properties reduces with increasing surfactant concentration so that only fall of rheological parameters was indicated. In the other works [6] similarly charged silica particles and cationic wormlike micelles system was studied and electrostatic effect of particles was excluded. It was demonstrates that the power law exponents of the viscosity as function of surfactant concentration do not change upon addition of nanoparticles at three salt concentrations. These power law exponents are highly sensitive to the effects of electrostatic screening therefore the presence of nanoparticles does not significantly alter the electrostatic interactions between micelles. In the system homogeneity region was limited by high surfactant concentration and expanded with salt concentration.

Thus, described effects in the suspensions of colloidal particles and wormlike micelles contrary to each other and phenomena remains incompletely understood. Nevertheless, one can conclude that colloidal particles actively interact with micelles and they may play role of modifier and improve viscoelastic properties of wormlike micelles solutions. At the presence paper novel nanocomposite material composed of particles of magnetite and oppositely charged wormlike micelles of surfactant are prepared and studied. The submicron magnetite colloidal particles embedded into entangled wormlike micelles of cationic surfactant solution. The erucyl bis-(hydroxyethyl)methylammonium chloride (EHAC) was selected as cationic surfactant with long unsaturated hydrocarbon tail providing microns wormlike micelles [8] and formation of layer on negatively charged magnetite particles. Potassium chloride salt was added to induce growth of cylindrical micelles at relatively small surfactant concentrations as result of screening electrostatic repulsions on the surface of micelles.

2. Materials and methods

Aqueous solution of a cationic surfactant erucyl bis-(hydroxyethyl)methylammonium chloride (EHAC) with a long mono-unsaturated C22 tail initially containing 25 wt.% 2-propanol was provided by Akzo Nobel (Netherlands). For purification from 2-propanol crude EHAC was diluted by deionized water (1:10) and freeze-dried. The absence of 2-propanol in the EHAC thus obtained was proved by 1H NMR. Magnetite particles from Aldrich was used without further purification. Average size of the particles is 250 nm estimated from TEM.

Steady and dynamic shear rheological experiments were carried out using a stress-controlled rheometer Physica MCR 301 Anton Paar (Austria) with cone-plate geometry (diameter 50 mm, cone angle 2°) and a solvent trap.

SANS measurements were carried out with two detector system on the time-of-flight YuMO high-flux pulsed reactor IBR-2M at the Frank laboratory of neutron physics, Joint Institute for Nuclear Research, Dubna, Russia. The experiments were performed at scattering vectors Q ranging from 0.006 to 0.14 Å⁻¹. All data were treated according to standard procedures of small-angle isotopic scattering. The samples were prepared using heavy water D₂O to get higher contrast.

3. Results and Discussion

Rheological properties of EHAC solutions were studied both in steady-state and in dynamic regimes at different concentrations at the presence 1 wt.% KCl. Micellar chains formation can be assigned to the lengthening of cylindrical micelles due to the screening of electrostatic repulsion between similarly charged groups of surfactant molecules on the surface of micelles by the ions present in a solution [9]. Figure 1 shows typical results of steady-state measurements. One can see a Newtonian plateau at low shear rate called zero-shear viscosity η₀ followed by a pronounced shear thinning, which can be due to the alignment of micelles along the direction of the flow.
Figure 1. Flow curves of 0.1 wt% (circles) and of 0.6 wt.% (squares) aqueous solutions of EHAC at the presence 1 wt.% salt KCl at 25 °C.

One can see that zero-shear viscosity rises dramatically with the surfactant concentration. The concentration curve of zero-shear viscosity shown on figure 2.

Figure 2. The dependence of zero-shear viscosity of aqueous solutions of EHAC on surfactant concentration at the presence 1 wt.% salt KCl at 25 °C.

In the region of low concentrations (0.01–0.25 wt %), solution viscosity is close to that of water. This region corresponds to the dilute regime at which surfactant micelles are not yet overlapped. Beginning with concentration $C^* = 0.25$ wt %, solution viscosity sharply increases. A rise in the viscosity can be explained by the transition of solution to a semidilute regime at which cylindrical micelles begin to be overlapped.
The semidilute region is characterized by the following dependence of viscosity on the surfactant concentration: \( \sim C^{9.5 \pm 0.5} \). The exponent value is much higher than 5.25 theoretically predicted for a system of uncharged chains. According literature such strong dependence can be obtained in case of charged micellar chains [10]. Thus, the obtained dependence of solution viscosity on the surfactant concentration in the semidilute region indicates the presence of charged micelles. It can be assumed that, at these conditions the amount of salt is moderately large and they are insufficiently screen the electrostatic repulsion on surface of the micellar chains.

The dependences of storage \( G' \) and loss \( G'' \) moduli of the complex elastic modulus on the frequency of external action (shear) on the sample were obtained on figure 3.

![Figure 3](image.png)

**Figure 3.** Result of frequency sweep rheological measurement – storage (filled symbols) and (open symbols) loss modulus dependences on frequency of shear stress for 1.1 wt.% aqueous solutions of EHAC at the presence 1 wt.% salt KCl at 25 °C.

It is also seen from Fig. 3 that, in a wide range of frequencies, the storage modulus is larger than loss modulus. In this region of the surfactant concentrations, the solution represents a physical gel composed of entangled long wormlike micelles. The plateau value of storage modulus called plateau modulus or elastic modulus of the network and varies with an increase EHAC concentration by the \( G_0 \sim C^{2.3} \) law (Fig. 4), which quite satisfactorily agrees with the theoretically predicted dependence (\( G_0_{\text{theor}} \sim C^{2.25} [1] \)).
Figure 4. Concentration dependence of the plateau modulus of elasticity for aqueous EHAC solutions at the presence of 1 wt % salt KCl at 25°C.

An increase in the elastic modulus is related with the fact that, as the surfactant concentration increases, the number of micelle topological entanglements rises due to micelle lengthening.

SANS measurement was carried out for 0.6 wt.% solution that corresponds to semidilute regime. Figure 5 shows the SANS scattering curves obtained for these concentrations. They show the dependence between the intensity of scattering and scattering vector.

Figure 5. SANS profile for 0.6 wt% aqueous solutions of EHAC at the presence of 1 wt % salt KCl at 25°C. Solid line shows the Q⁻¹ law of increase of scattering intensity in low-Q region.

On scattering plots in low-Q region the shape of the aggregates can be revealed [1]. In the case of the long enough wormlike micellar chains, the intensity of I decreases as Q⁻¹ at low Q values. In case of short rodlike micelles having numbers spherical end-caps dependence I(Q) is weaker [11].
Now the magnetite particles was embedded to network of wormlike micelles at the concentration of EHAC 0.6 wt.% at the presence 1 wt.% KCl, e.i. viscoelastic solution of charged micellar chains. On figure 6 effect of particles on storage and loss moduli is represented.

![Graph showing frequency dependences of storage modulus G' (filled symbols) and loss modulus G'' (open symbols) for 0.6 wt% EHAC solutions in the presence of 1 wt% KCl without particles (squares) and with 1 wt.% magnetite particles (circles) at 25°C.](image)

**Figure 6.** Frequency dependences of storage modulus G' (filled symbols) and loss modulus G'' (open symbols) for 0.6 wt% EHAC solutions in the presence of 1 wt% KCl without particles (squares) and with 1 wt.% magnetite particles (circles) at 25°C.

In the presence of particles the system continues to display behavior typical for entangled wormlike micelles solutions. Moreover, the particles induce an increase in the the storage G' and loss G'' moduli and the frequency at the G'-G'' crossover. All these effects may be due to the appearance of additional cross-links as a result of adsorption of energetically unfavorable micellar end-caps on the surfactant monolayer formed on the surface of the particles.

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