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Viscoelasticity of Smart Fluids Based on Wormlike Surfactant Micelles and Oppositely Charged Magnetic Particles

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S *Supporting Information*

ABSTRACT: Novel viscoelastic smart suspensions based on cationic wormlike micelles (WLMs) of erucylbis(hydroxyethyl)methylammonium chloride and oppositely charged submicron magnetite particles in the presence of added low molecular weight salt were prepared and investigated. The suspensions demonstrate remarkable stability against sedimentation, which can be due to the incorporation of particles into the network of entangled WLMs by linking to energetically unfavorable micellar end-caps. Added particles enhance significantly the viscosity, the plateau modulus, and the relaxation time of the system, acting as additional multifunctional physical cross-links in the micellar network. The increase of plateau modulus stops when the concentration of particles reaches ca. 1.5 wt %, indicating that all micellar end-caps available in the system are linked to the particles. Further addition of particles may lead just to the redistribution of micellar ends between the particles without creation of new elastically active chains. The increase of rheological characteristics by added particles is more pronounced in suspensions with a smaller content of low molecular weight salt KCl when the WLMs are shorter in length and therefore contain a larger amount of end-caps responsible for the interaction with the particles. Magnetite particles not only enhance the rheological characteristics but also impart magnetoresponsive properties to the suspension. Upon application of magnetic field, the liquidlike system transforms into a solidlike one, demonstrating a constant value of storage modulus in all frequency range and the appearance of yield stress, which is due to the formation of field-aligned chainlike aggregates of particles opposing the flow. A combination of responsive properties inherent to both the matrix and the particles makes these smart fluids very competitive with other magnetic soft matter materials for various applications.
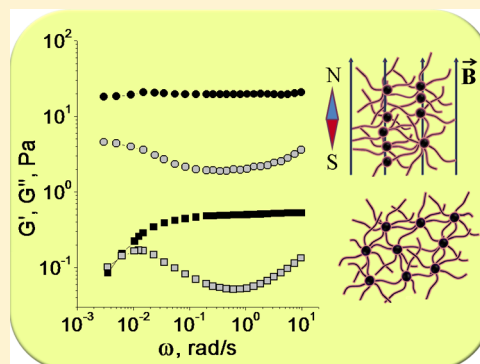
INTRODUCTION

In recent decades giant wormlike micelles (WLMs) of surfactants have received considerable and well-deserved attention in many experimental[1−8] and theoretical[1−3,8−13] works. Much interest is stimulated by their polymer-like behavior combined with highly responsive properties resulting in many industrial applications. Similar to polymers, solutions of entangled WLMs exhibit viscoelasticity[1−6] and even form physical gels.[7] At the same time, the "living" character of WLMs, which incessantly break and recombine, imparts them significant advantages over similar polymeric systems, providing to micellar gels highly responsive properties[5,14−20] as well as the ability to self-heal and to completely recover their properties after their mechanical degradation at high shear rates.[19]

The properties of WLM solutions can be significantly modified by the addition of various substances interacting with the micelles. As the WLMs are "living" objects, such interactions can cause dramatic changes in the micellar structure and therefore in viscoelastic properties of the system.

In recent years, several attempts were made to enhance the viscoelastic properties of WLM solutions by adding inorganic particles.[21−24] In most of these studies,[22−24] similarly charged WLMs and particles were used, because in this case it is much

easier to avoid phase separation. It was shown that in dilute WLM solutions nanoparticles built viscoelasticity of the system[23] whereas in semidilute solutions already exhibiting viscoelasticity nanoparticles increase the viscosity, the plateau modulus, and the relaxation time.[22,23] These effects were explained by the formation of junctions between micelles and particles leading to effective elongation and/or cross-linking of micellar chains. This suggestion was supported by DLS data, which show that the diffusion of nanoparticles in these systems proceeds through a medium with an effective viscosity higher than that of pure surfactant solution.[22] Later, the micelle−particle junctions were directly visualized by cryo-TEM.[23]

Theoretical studies based on thermodynamic considerations were performed[24,25] in order to understand the mechanism of the formation of micelle−particle junctions and the conditions of their stability. The formation of a junction is suggested to proceed via fusion of the micellar end-cap with the surfactant layer adsorbed on the surface of a particle. If the diameter of the WLM is much smaller than the surface area of a nanoparticle,
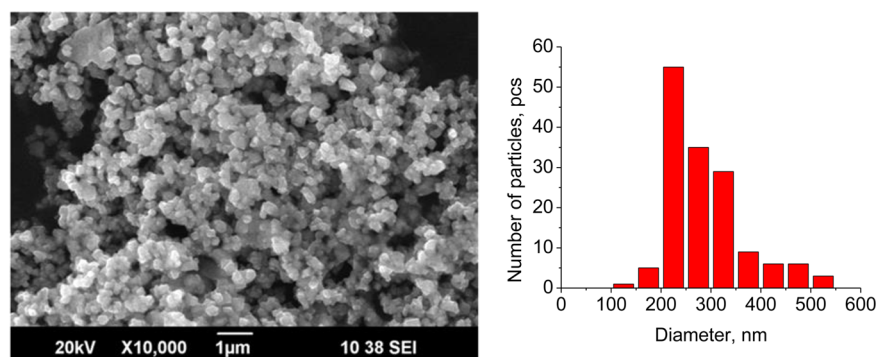
Figure 1. SEM image (left) and the size distribution (right) of magnetite particles obtained from SEM data.

two or more micellar ends can link to a single nanoparticle thus leading to elongation or cross-linking of micelles, respectively. Only the end-caps of micellar chains are involved in the interaction with particles, because they represent energetically unfavorable parts of the micelles, where the packing of surfactant molecules (semisphere) does not correspond to the optimum one (cylinder) realized at all positions along the backbone except the ends. As the end-caps of WLMs are energetically unfavorable, their fusion with a surfactant layer adsorbed on the surface of particles decreases the total free energy of the system. On the other hand, such fusion may disturb the layer, creating some defects and thus contributing to the increase of the total free energy. In general, the formation of micelle−particle junction is governed by a balance between end-cap energy and micellar adsorption energy. The junction should be thermodynamically stable when the free energy of the adsorbed micellar end-cap is smaller than that of the free end-cap. The computer simulation predicted[25] that such a situation can be realized neither for highly hydrophobic nor for highly hydrophilic particles, as they are covered by quite stable surfactant layers, which can be hardly broken to accommodate the end-cap. However, in the intermediate cases, when the surfactant layer is imperfect, the micelle−nanoparticle junctions are thermodynamically the most favorable state. Such a situation can be realized, in particular, for similarly charged surfactant and particles, when the adsorption of surfactant is governed by hydrophobic interactions.[22,23]

In contrast to like-charged systems, the suspensions containing WLMs and oppositely charged particles are much less addressed.[21] In a paper[21] on an example of WLMs of cationic surfactant cetyltrimethylammonium tosylate and negatively charged silica particles it was shown that the dependencies of viscosity, plateau modulus, and relaxation time go through a maximum with increasing content of particles. A rising branch of the curve was explained by enhanced screening of electrostatic interactions between micelles by added charged particles resulting in the growth of micelles in length. A descending branch of the curve after the maximum was assigned to the progressive decrease in the concentration of surfactant in solution as a result of its adsorption on the surface of new added particles. Therefore, in these experiments two parameters (concentration of particles and concentration of surfactant composing WLMs) were changed simultaneously, which did not allow one to reveal the net effect of particles on the rheological properties. Also, it remained unclear whether the linking of micellar end-caps to the particle can be responsible for the change of rheological characteristics induced by the addition of oppositely charged

particles to the WLMs, as it was in the case of like-charged particles. Hence, the suspensions containing WLMs and inorganic particles of opposite charge are still poorly understood. At the same time, they are quite promising, because they ensure a stronger interaction between the components. For this reason, the present paper is devoted to the investigation of such systems.

In most of the studies performed up to now, the particles play the role of a modifier aimed to improve viscoelastic properties of WLM solutions. In this paper, we propose to use particles, which will not only enhance the rheological properties but will also impart a new property to the system, namely responsiveness to the magnetic field.[26] For this aim, magnetite particles were chosen. To get a stronger magnetic response, we focused our study on rather large particles of submicron size (250 nm). So, the resulting suspension can be regarded as a new type of magnetorheological fluid (i.e. fluid containing submicrometer- to micrometer-sized magnetic particles dispersed in nonmagnetic carrier liquid).[27,28]

Thus, the goal of the present paper is to study the rheological behavior of smart fluids based on WLMs and oppositely charged magnetite particles, which combine the responsive properties of both components. The fluids are composed of aqueous solution of cationic surfactant erucylbis(hydroxyethyl)-methylammonium chloride (EHAC) containing the low molecular weight salt potassium chloride (which is necessary to obtain long WLMs) and negatively charged magnetite particles.

The rheological properties of these fluids were studied in a wide range of surfactant, salt, and particle concentrations with and without applied magnetic field. It was shown that the addition of particles leads to the increase of both viscosity and plateau modulus of the system, which seems to be due to the formation of micelle−particle junctions rather than electrostatic effects. The dependence of these rheological characteristics on the amount of added particles is nonlinear: at a certain concentration of particles, the increase of viscosity becomes much less pronounced, whereas the plateau modulus levels off. Such behavior, first observed in the present work, demonstrates the saturation of the transient network of micellar chains, when most of micellar end-caps become attached to the particles. At a given content of particles, the rheological properties can be tuned by exploiting the salt responsiveness of WLMs. For instance, a pronounced increase of viscosity and plateau modulus is observed at decreasing salt concentration, as it favors the shortening of micelles, i.e. the increase of the relative amount of micellar end-caps responsible for the interaction with the particles. On the other hand, the rheological properties

can be modified by using the responsiveness of the particles to magnetic field. Upon application of the field, the system transforms from liquidlike to solidlike state as a result of magnetic interactions leading to chaining of magnetite particles. Such multiresponsiveness of the proposed smart fluids allowing their properties to be easily tailored makes them very attractive for practical use.

■ EXPERIMENTAL SECTION

Materials. Aqueous solution of a cationic surfactant EHAC with a long monounsaturated C22 tail $C_8H_{17}CH=CHC_{12}H_{24}N-(CH_2CH_2OH)_2CH_3Cl$ containing 25 wt % 2-propanol was provided by Akzo Nobel. For purification from 2-propanol crude EHAC was diluted with deionized water (1:10) and freeze-dried. The absence of 2-propanol in the surfactant thus obtained was proved by ^1H NMR. Potassium chloride (purity >99%) from Acros Organics was used as received. Distilled water was purified by a Milli-Q system (Millipore).

Magnetite Fe_3O_4 particles were supplied by Aldrich. They have the following magnetic properties: saturation magnetization 100 emu/g, residual magnetization 19 emu/g, coercive force 95 Oe. Their average diameter was equal to ca. 250 nm as estimated from scanning electron microscopy (SEM) data (Figure 1). The pH of aqueous solutions, where the particles were immersed, was kept at 11 to provide strong negative charge of the surface of particles as a result of deprotonation of OH groups.[29] It was shown that storage of the particles for one month at this pH value does not affect their size. These data are consistent with the results of the paper,[30] demonstrating no dissolution of magnetite particles at pH 11.

Samples Preparation. A wide series of suspensions differing in the content of surfactant (0.1−2 wt %), salt (0.5−4.5 wt %), and magnetite particles (0.01−15 wt % or 0.002−3 vol %) was prepared. First, a desired amount of magnetite powder was added to aqueous solution of EHAC (pH 11) and stirred with a spatula during 1 min. Then an appropriate quantity of 15 wt % stock solution of salt KCl (pH 11) was added. The suspensions thus obtained were mixed with digital homogenizer IKA Ultra-Turrax T 25 during 25 min at a rate of 5200 rpm and left undisturbed for 7 days to allow them to release air bubbles (for details, see Supporting Information). The phase separation in the suspensions was examined at 20° C by visual observation over 6 months.

Rheology. 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. For the measurements under the action of homogeneous magnetic field a plate−plate cell with 20 mm diameter and 1 mm gap was used. The applied magnetic field was perpendicular to the direction of shear flow. All experiments were run at 20° C set to ±0.1 °C accuracy by a Peltier temperature control device. The samples were equilibrated in the measuring cell for at least 10 min prior to conducting measurements. In the static mode, the shear stresses were usually varied in the range 0.015−10 Pa. In the yield stress experiments the shear stress reached 120 Pa. Zero-shear viscosity was determined by fitting the steady shear viscosity profiles with a Carreau model. In dynamic mode, the frequency was changed in the range 0.0005−3 Hz (0.003−20 rad/s). The dynamic shear measurements were carried out in the linear viscoelastic regime as was ascertained by prior strain sweeps.

Scanning Electron Microscopy. To evaluate particle size and morphology, the magnetite particles were examined with a JEOL JSM 6490 LV (Japan) scanning electron microscope operated at 20 kV.

■ RESULTS AND DISCUSSION

Phase Behavior. When preparing the suspensions of microparticles, a proper mixing is crucial in obtaining stable systems that give reproducible and consistent results. This is especially important in the present case, as we deal with rather big and heavy submicron particles, which will be subject to increased gravitational pull, causing them to settle out.

Moreover, these particles possess some residual magnetization, which induces their attraction to each other, further favoring their precipitation. Therefore, at the first stage of our work considerable efforts were spent for the development of the technique of preparation of stable suspensions with uniform distribution of particles. It is described in detail in the Supporting Information.

The phase diagram for the systems prepared using this technique is presented in Figure 2. It is seen that stable
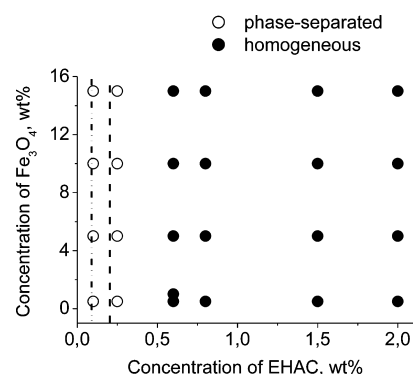
Figure 2. Phase diagram of EHAC/magnetite systems in the presence of 1−3 wt % KCl at 20 °C, pH 11. Filled circles, homogeneous systems; open circles, phase-separated systems. The C^* concentrations for EHAC solutions in the absence of magnetite particles in 1 and 3 wt % KCl are marked by dashed and dot-dashed lines, respectively.

homogeneous suspensions are obtained at surfactant concentrations above 0.6 wt % in a wide range of particle content from 0.4 to 15 wt %. The phase diagram does not depend on the amount of added salt KCl, if it is varied from 1 to 3 wt %. It should be noted that the limiting surfactant concentration, above which the homogeneous systems become stable, is larger than the overlap concentration C^* of WLMs equal to 0.2 and 0.09 wt % for 1 and 3 wt % KCl solutions,[5] respectively. Therefore, homogeneous systems were obtained exclusively with semidilute surfactant solutions containing entangled WLMs. One can suggest two reasons for this behavior. First, a highly viscous medium formed in a semidilute regime can slow the sedimentation, as it was observed for the WLM/polystyrene latex system.[31,32] Second, the particles can be involved in the formation of a common network with WLMs.[23] We believe that the second reason predominates. To the best of our knowledge, this is one of the first systems based on oppositely charged WLMs and submicron particles, which demonstrates a wide range of homogeneity for very long periods of time (at least 6 months).

Further experiments were conducted only with homogeneous samples that did not phase separate during the entire period of measurements.

Rheological Properties. Typical plots illustrating the effect of particles on the steady-shear and dynamic rheological data are presented in Figure 3. For comparison, the data for pure EHAC solutions used for the preparation of the suspensions are shown as well. Obviously, one could expect that upon immersion of charged particles in the solution of oppositely charged surfactant some of the surfactant molecules should be adsorbed on the surface of particles (Chart 1a). Knowing the surface area of one particle (2×10^5 nm²), one can estimate the average amount of surfactant needed to coat it with a double layer (the thickness of each layer being assumed to be equal to
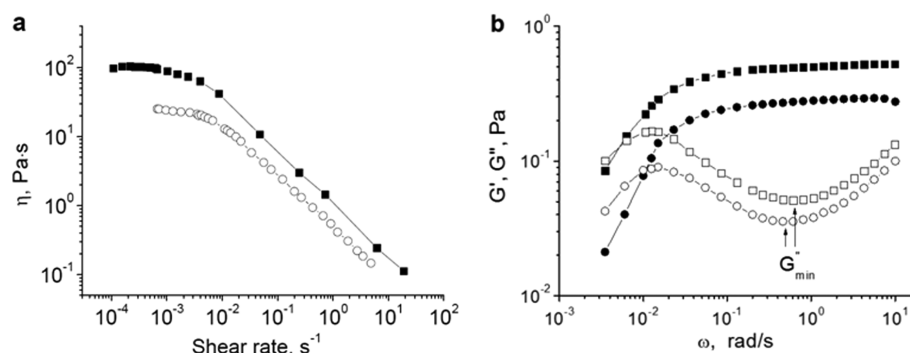
Figure 3. Viscosity as a function of shear rate (a) and frequency dependence of storage modulus G' (filled symbols) and loss modulus G'' (open symbols) (b) for 0.6 wt % EHAC solutions in the presence of 1.5 wt % magnetite particles (squares) and in the absence of the particles (circles) at 20 °C. Solvent: 1.5 wt % KCl in water, pH 11.

Chart 1. (a) Layer of Cationic Surfactant on Negatively Charged Magnetite Particle, (b) the Adsorption of Energetically Unfavorable Micellar End-Caps on the Particle through Fusion with the Surfactant Layer on Its Surface, (c) and the Redistribution of Micellar Chains between Particles in the Saturated Network without Free Micellar End-Caps
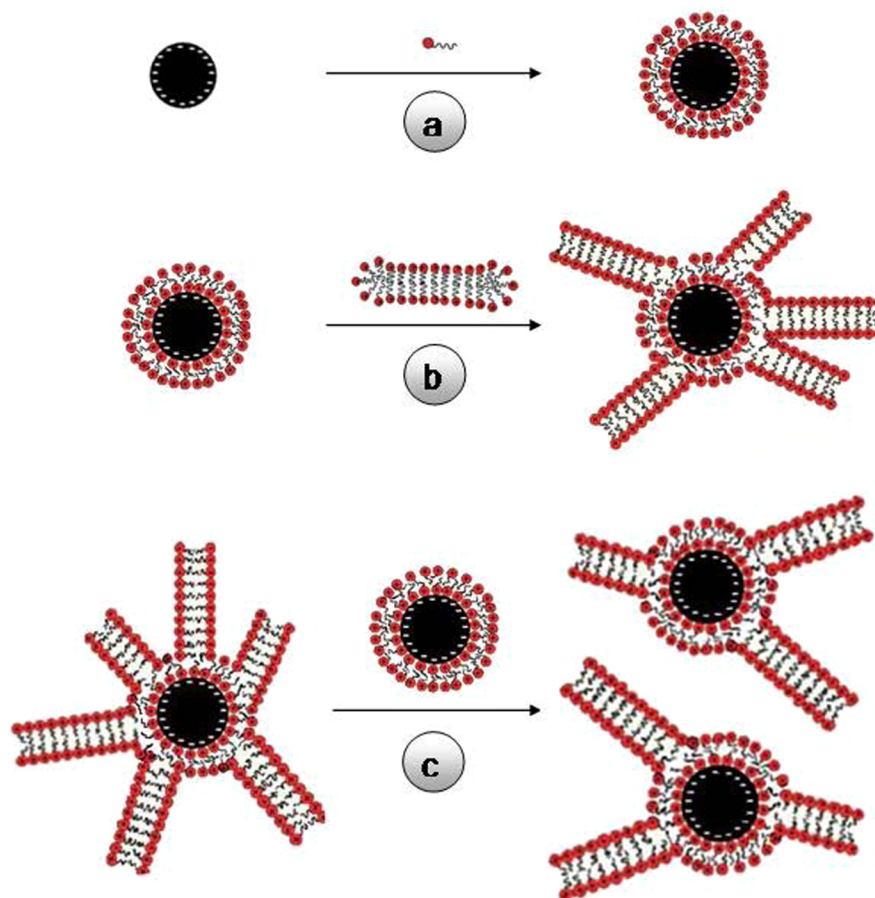
the length of fully extended chain of surfactant tail, which amounts to 2.4 nm, taking into account a bend in the unsaturated carbon chain). The estimation shows that 0.04 wt % EHAC is required to form a complete bilayer on 1.5 wt % magnetite particles. This value can be considered as an upper limit of the amount of adsorbed surfactant. Even so, it is quite small in comparison with the total concentration of surfactant in the system and therefore can be neglected.

From Figure 3 it is seen that the initial EHAC solution used for the preparation of the suspensions has rather high zero-shear viscosity η_0 (by 4 orders of magnitude larger than that of pure water) and a well-defined plateau on the frequency dependence of the storage modulus G', indicating the existence of entanglements between micellar chains. For this solution (Figure 3), the mesh size ξ of the network of entanglements estimated from the value of plateau modulus G_0 using the relation[12] $\xi \approx (kT/G_0)^{1/3}$ is equal to 240 nm, which is close to the diameter of magnetite particles.

In the presence of particles, the system continues to display behavior typical for entangled WLM solutions (Figure 3). Moreover, the particles induce an increase in the zero-shear viscosity η_0, 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 layer formed on the surface of the particles[22−25] (Chart 1b).

The influence of the concentration of particles on the zero-shear viscosity η_0 and the plateau modulus G_0 is illustrated in Figure 4. In this figure, the values of η_0 and G_0 for the
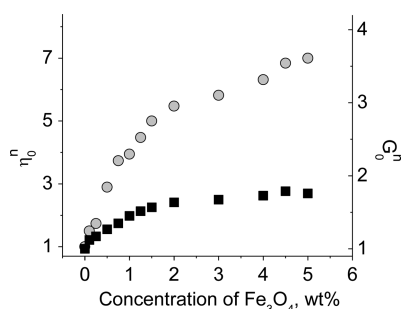

Figure 4. Dependence of the zero-shear viscosity η_0^n (circles) and plateau modulus G_0^n (squares) on the concentration of magnetite particles in 0.6 wt % EHAC solution. The values of η_0 and G_0 are normalized with respect to the corresponding values for the solution without particles. Solvent: 1.5 wt % KCl in water, pH 11.

suspensions are divided by the η_0 and G_0 values for the corresponding solutions without particles. It is seen that the most pronounced increase of both η_0 and G_0 values is observed at rather low concentrations of particles (up to 1.5 wt %). At further addition of particles, the zero-shear viscosity increases only slightly, whereas the plateau modulus remains almost unchanged.

The observed leveling off of the plateau modulus can be explained by the linking of all micellar end-caps available in the system to magnetite particles thus leading to the saturation of the network. Further addition of particles may induce only a redistribution of micellar end-caps between the particles[23] (Chart 1c), which should not affect the number of elastically active subchains.

To check this suggestion, we estimate the average concentration of micellar end-caps in the system and the effect of their linking to the particles on the value of plateau modulus G_0. To this aim, we will first evaluate the average contour length of WLM L from the rheological data using the equation[13]

$$\frac{L}{l_e} \approx \frac{G_0}{G''_{min}} \tag{1}$$

where G''_{min} is the value of the loss modulus at the high frequency minimum (Figure 3b) and l_e is the entanglement length. The latter can be found from the G_0 value by using the following expression[13]

$$G_0 \approx \frac{kT}{l_e^{9/5} l_p^{6/5}} \tag{2}$$

where l_p is the persistence length, which amounts to 30 nm for micellar chains of EHAC.[33]

For the initial surfactant solution (0.6 wt % EHAC, 1.5 wt % KCl), one can obtain from the eqs 1 and 2 the following estimates: $l_e \approx 1$ μm, $L \approx 10$ μm. Such a giant 10 μm long cylindrical micelle with the radius of 2.4 nm should consist of ca. 2.8×10^5 surfactant molecules (as estimated by dividing the

volume of the hydrophobic core of such micelles by a molecular volume of EHAC tail group equal to ca. 630 Å^3). Therefore, 0.6 wt % EHAC solution should contain 3×10^{16} 1/dm^3 WLMs or 6×10^{16} 1/dm^3 micellar end-caps. Connection of all these end-caps to particles gives rise to 6×10^{16} 1/dm^3 elastically active subchains in addition to 8×10^{16} 1/dm^3 elastically active subchains, which already existed in the initial EHAC solution due to micellar entanglements (the latter value was estimated as G_0/kT from the G_0 value for pure surfactant solution (Figure 3)). Therefore, when all end-caps become linked to the particles, the plateau modulus should increase by 75% (0.23 Pa), which perfectly corresponds to the experimental data (Figure 4). This fact counts in favor of our hypothesis that the plateau modulus reaches its limiting value, when all free end-caps are exhausted.

To the best of our knowledge, this is the first observation of the "saturation" of a micellar network by particles. The leveling off of the plateau modulus of WLM solution at the increase of particle concentration was never observed previously. In a previous paper,[22] G_0 always increased upon addition of particles (probably, in these experiments the volume fraction of particles was too low to reach the "saturation"). In another paper,[21] G_0 either passed through a maximum or continuously decreased upon addition of particles. The decrease of G_0 was assigned to progressive reduction of the concentration of surfactant upon its adsorption on the surface of new added particles. In our case, the amount of surfactant adsorbed on the particles is negligibly small, and therefore we study the effect of particles on the plateau modulus at constant concentration of surfactant in solution.

To further characterize the system, we estimate the average amount of micellar end-caps linked to one magnetite particle at the concentration of particles corresponding to the leveling off of the plateau modulus (i.e. at 1.5 wt % particles). It approximates to 160. Taking into account that the average surface area of each particle ($R = 125$ nm) is ca. 2×10^5 nm^2 and the cross-section of WLM ($R = 2.4$ nm) is 18 nm^2, one can estimate that only 1.4% of surface area of a particle is occupied by micellar grafts. In this case, the average surface area of a particle per grafted micellar chain amounts to 1250 nm^2, which corresponds to 0.0008 chains/nm^2. To get an idea about the reason for such low grafting density, we compare the lateral radius per one grafted chain on the surface of particle with the radius of the unperturbed chain. The lateral radius can be found by equating the average surface area of a particle per grafted micellar chain (1250 nm^2) to πR^2 and solving for R. The system presented in Figure 3 gives a lateral radius value of 20 nm, which corresponds to the average distance between two grafts on the surface of particles equal to 40 nm. The radius of gyration of micellar subchain $R_{g,sub}$ with contour length $L_{sub} = l_e$ in a temporary network of entangled WLMs can be estimated as[34]

$$R_{g,sub} = \frac{1}{\sqrt{6}} \sqrt{2 L_{sub} l_p} \tag{3}$$

It amounts to 100 nm. This value is five times higher than the lateral radius. In other words, the unperturbed dimensions of a single chain are much larger than the average distance between grafted chains on the surface of particle, indicating that the grafted chains are stretched and/or overlapped. Such stretching can restrict further attachment of micellar ends to the same particle.

One might think that rather big free surface area of a particle (98.6%) far exceeding the area occupied by micellar grafts (1.4%) could provide for the graft the possibility to displace along the surface of the particle thus making less pronounced the decrease of the entropy connected with the adsorption of micellar end-cap. The later process is somewhat similar to the sliding of branching point along the WLM chain.[35−37] In the branched WLMs, this process provides one of the main ways to release the stress, which leads to the drop of viscosity upon the onset of branching. Such drop of viscosity is not observed in the present system, probably, because the sliding along the surface of a particle is confined in a much more restricted space.

Now we consider the effect of the content of particles on the zero-shear viscosity η_0. From Figure 4 it is seen that the particles increase the viscosity of WLM solution. As the most pronounced increase is observed at quite low particle concentrations (smaller than 1.5 wt % or 0.3 vol %), it cannot be explained just by the presence of particles non interacting with micellar network. Such behavior is possible only if the particles represent sticking sites hindering the flow of WLMs. Figure 4 shows that upon addition of particles the zero-shear viscosity increases much more appreciably than G_0 value. A higher effect of particles on the zero-shear viscosity can arise from the increase of the relaxation time in the system. From Figure 3b it is seen that, on the one hand, a suspension containing magnetic particles has a relaxation time, ca. 65 s, identical to that of wormlike micellar solution without particles, because both samples show clear maxima in G'' curves observed at the same frequency. On the other hand, the system with magnetic particles possesses also an additional slower relaxation mode with a long relation time of ca. 250 s as it follows from the frequency at the G'-G'' crossover. This slow relaxation time can be related to the presence of new cross-linking points representing multiarm connection of WLMs to the surface of magnetic particles. This slow relaxation mode is responsible for very pronounced increase in the zero-shear viscosities upon addition of magnetic particles.

Simultaneously with the increase of the relaxation time the breaking time τ_{br} becomes shorter, since the frequency corresponding to G''_{min} value increases[22] (Figure 3). As the relaxation time in entangled WLM systems is determined by the breaking time τ_{br} and the reptation time τ_{rep}, the observed rise of the relaxation time should be due to a significant increase of the reptation time τ_{rep}, which overcompensates for a decline in τ_{br} value. The shortening of τ_{br} upon addition of particles was previously observed for cationic WLM chains mixed with like-charged silica particles.[23] One can speculate[23] that the micelle–particle junctions represent weak spots with rather short lifetime and their breakage becomes the dominant breaking mechanism in the system, which leads to the decrease of the observed τ_{br}. Whereas the shortening of τ_{br} may be due to the weakness of the micelle–particle junctions, the increase of reptation time may arise from the hindering of the reptation motion of micellar chains, when their end-caps link to the particles. Therefore, the observed increase of viscosity seems to be mainly due to hindered reptation of WLMs. Note that in the present system, the viscosity continues to slightly increase even at particle concentration larger than 1.5 wt %, when the G_0 value reaches a limiting value and a saturated network is formed. This can be accounted for by a larger amount of sticking sites (i.e. particles), which a WLM encounters during reptation.

As the end-caps play a crucial role in the interaction with particles, it would be interesting to reveal the effect of their number on the rheological properties of the system. A simplest way to increase the number of end-caps at a given surfactant concentration consists of the diminution of the amount of added salt, which promotes the enhancement of the electrostatic repulsion between similarly charged surfactant head groups thus making the hemispherical end-caps thermodynamically more favorable. Figures 4 and 5 allow one to compare the
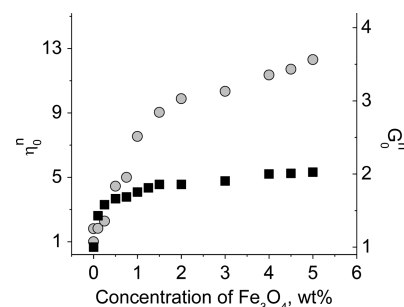

Figure 5. Dependence of the zero-shear viscosity η_0^n (circles) and plateau modulus G_0^n (squares) on the concentration of magnetite particles in 0.6 wt % EHAC solution. For better comparison the values of η_0 and G_0 are normalized with respect to the corresponding values for the solution without particles. Solvent: 1 wt % KCl in water, pH 11.

evolution of zero-shear viscosity and plateau modulus upon addition of magnetite particles at two different salt concentrations: 1 and 1.5 wt % KCl. For better comparison, the values of η_0 and G_0 are normalized with respect to the corresponding values for the solutions without particles. It is seen that in 1 wt % KCl (Figure 5) the increase of viscosity and plateau modulus is more pronounced than in 1.5 wt % KCl (Figure 4). This is obviously due to a larger amount of links between micelles and particles in the first system, because it contains many more micellar end-caps responsible for the formation of these links. These data are in contrast to the results obtained for the system containing like-charged WLMs and nanoparticles.[22,23] In that case the increase of viscosity is much more significant at higher salt concentration, which may be due to enhanced screening of electrostatic repulsion between similarly charged interacting species, when more salt is added.

It is interesting that in other aspects (i.e. increases in viscosity, shear modulus, and relaxation time upon addition of particles) our data are quite similar to those observed for cationic WLMs with like-charged silica nanoparticles.[22,23] This fact seems to be quite unexpected, because one might think that the interactions between surfactant and particles represent a crucial factor underlying the effect of particles on the rheology of WLM solutions. Indeed, the formation of WLM–particle junctions proceeds through the fusion of energetically unfavorable micellar end-caps with the surfactant layer adsorbed on the surface of the particles and therefore should depend significantly on the state of this layer. In particular, the theoretical estimations[25] show that the junctions between the end-cap of WLM and surfactant layer on the particle are thermodynamically stable only if the layer itself is only marginally stable (i.e. it is inhomogeneous or represent admicelles). In this case, the breaking or rearrangement of this layer in the process of accommodation of the micellar end-cap is not expensive in terms of free energy.[25] This situation is realized, for instance, in the system containing similarly charged

before   **1 min**   **30 min**   **120 min**   **24 h**
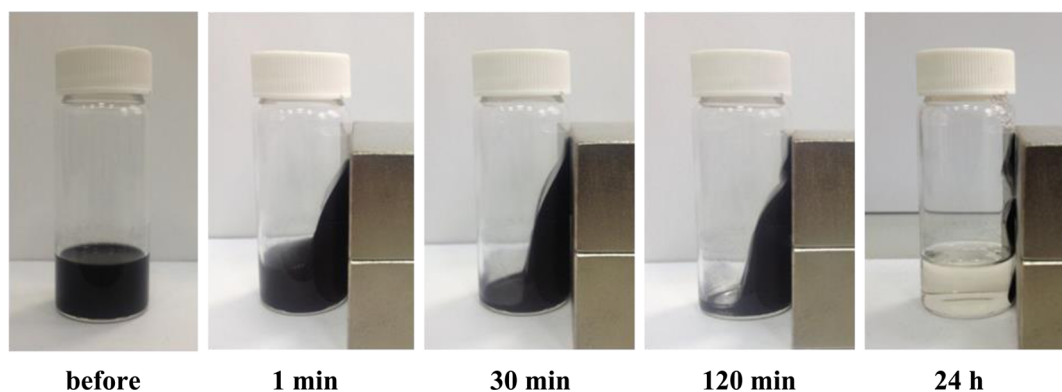
Figure 6. Photographs illustrating the behavior of 1 wt % aqueous solution of EHAC containing 1 wt % of magnetite particles before and after the application of a permanent magnet, which creates a magnetic field gradient of 0.5 Tl/cm. The time of action of magnetic field is indicated on the figure. Solvent: 1.5 wt % KCl in water, pH 11.
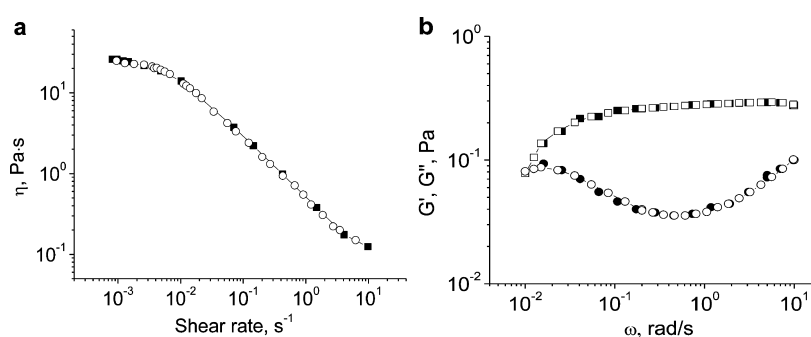

Figure 7. Dependence of viscosity (a) and elasticity moduli G' and G'' (b) for 1 wt % aqueous solution of EHAC after the removal of magnetite particles under the action of a permanent magnetic field gradient of 0.5 Tl/cm during 24 h (open symbols) and for the initial surfactant solution before the addition of particles (filled symbols). Solvent: 1.5 wt % KCl in water, pH 11.

surfactant and nanoparticles,[22,23] when hydrophobic interactions governing the adsorption of surfactant lead to the formation of hemimicelles (patches), which cover only partially the surface of the particles. In contrast, in our system the oppositely charged surfactant is expected to form a dense layer; nevertheless, its fusion with the end-caps remains energetically favorable. It may be due to some imperfections of the surfactant layer. To check this suggestion, the layer of surfactant adsorbed on the surface of particles was visualized by TEM. It was observed that the surfactant covers completely the surface of particles, but its layer is quite inhomogeneous, as its thickness varies considerably from 1.5 to 4 nm (see Supporting Information). Note that the thickness remains much smaller than that of an "ideal" bilayer of fully extended non-interdigitated EHAC tails equal to ca. 4.8 nm (as the length of single hydrophobic tail of EHAC is ca. 2.4 nm). Since some of the head groups of the surfactant should be in contact with counter charges on the surface of particles, whereas the others should be exposed to water, so low thickness may be due to the overlap of oppositely oriented hydrophobic tails or (and) to their tilting with respect to the surface normal.[39] This structure of the surfactant layer may be due to rather low charge density on the surface of particles. Indeed, despite the fact that at the experimental conditions (pH 11) all OH groups on the surface of magnetite particles should be deprotonated,[29] the charge density reaches only[38] about −0.15 C/m², indicating the presence of one charged group per ca. 5 nm² of the surface. In this case, the average distance between charged groups on the surface is ca. 2.2 nm, which far exceeds the diameter of one EHAC headgroup (ca. 0.88 nm). As a result, a complete coverage of the surface by surfactant molecules becomes possible only if the layers of oppositely oriented surfactant molecules interpenetrate each other and tilt with respect to the surface normal. As to the large variation of thickness of the surfactant layer, it can be due to the imperfections of the surface of particles, which may create some area differing in charge density and therefore in the local structure and thickness of the layer of adsorbed surfactant. Thus, the large difference in the charge density of the layer of close-packed surfactant ions and the surface of the particles may be one of the main reasons for rather marginal stability of the surfactant layer making its linking with the micellar end-caps energetically favorable.

In summary, the rheological data show that the magnetic particles induce the increase of both viscosity and plateau modulus G_0 of viscoelastic surfactant solutions. It is due to their incorporation into the network of entangled WLMs as a result of binding of energetically unfavorable end-caps of micellar chains to the surfactant layer on the surface of particles. When most of micellar end-caps become attached to the particles, the plateau modulus levels off, whereas the viscosity increases only slightly.

Behavior in the Magnetic Field. As the particles under study possess magnetic properties, a second series of experiments was devoted to the study of the behavior of suspensions under the action of magnetic field. Macroscopic observations show that the suspensions are able to move toward the magnet as demonstrated in Figure 6. The displacement of the suspension as a whole indicates rather strong binding between magnetite particles and WLMs. At a low gradient of magnetic field (0.02 Tl/cm) such a system is

stable and does not settle out during at least 10 days. If the gradient of the applied magnetic field is rather strong (0.5 Tl/cm), in several hours the system phase separates into clear transparent solution and black precipitate containing magnetite particles (Figure 6). It is interesting that the rheological properties of the supernatant solution fully coincide with the properties of initial surfactant solution before the addition of magnetite particles (Figure 7). This result indicates that the amount of surfactant adsorbed on the particles is negligible in comparison with the total amount of surfactant in the system, thus justifying its exclusion from our numerical estimations presented above. The observed phase separation induced by the magnetic field can be applied to remove the magnetic particles from the system, when necessary. Note that the extracted magnetic particles can be easily redispersed in the surfactant solution just by gentle shaking by hand (without the application of a homogenizer), which indicates that they remain protected from aggregation by the adsorbed surfactant. Therefore, varying the strength of the magnetic field and the time of its application, one can either move the suspension as a whole to the desired place or extract the magnetite particles from it.

Now we consider the effect of the magnetic field on the rheological properties of the suspensions under the conditions excluding phase separation. From Figure 8 it is seen that in the
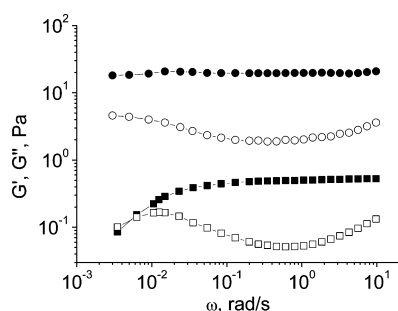

Figure 8. Frequency dependence of storage G' (filled symbols) and loss G'' (open symbols) moduli for 0.6 wt % aqueous solution of EHAC containing 1.5 wt % magnetite particles in the absence of a magnetic field (squares) and under magnetic field of 0.2 Tl (circles). Solvent: 1.5 wt % KCl in water, pH 11.

absence of field the dynamic rheological properties are typical for viscoelastic solutions demonstrating elastic response at high frequencies and viscous response at low frequencies, whereas in a field of 0.2 Tl a solidlike behavior was observed, i.e. the storage modulus G' becomes higher than the loss modulus G'' over the entire investigated frequency range. Simultaneously, the value of plateau modulus G_0 increases by more than one order of magnitude (Figure 8). Moreover, in a magnetic field a yield stress was observed (Figure 9). All these effects can be explained as follows. Upon application of an external magnetic field, the particles acquire a magnetic dipole moment and aggregate, under the influence of the magnetic dipole interaction, into columnar structures aligned along the field. As the applied field is perpendicular to the flow direction, the aggregates oppose the flow of the suspensions.

The value of yield stress estimated from the flow curve (Figure 9) as the stress that must be overcome to cause the suspension to flow is equal to 15 Pa. This yield stress is frequently associated with the stress, which should be attained in order to disrupt the columnar aggregates of magnetic particles in their weakest point.[40] The value of yield stress
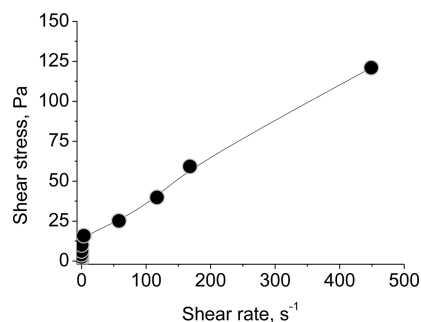

Figure 9. Flow curves for 0.6 wt % aqueous solution of EHAC containing 1.5 wt % magnetite particles under magnetic field of 0.2 Tl. Solvent: 1.5 wt % KCl in water, pH 11.

obtained in the present system is comparable to that for magnetorheological fluids containing a similar low fraction of submicron and micron magnetite particles.[41] The peculiarity of the present system consists of the fact that it contains not only smart particles responding to magnetic field but also a smart "living" network whose properties can be tuned by different triggers: temperature, addition of salt, hydrocarbons, alcohols, hydrotropic ions, etc.[14] A unique combination of two responsive components (matrix and filler) and a remarkable stability against settling out makes such a system quite prospective for various practical applications, e.g. in damper devices where the ability of the WLM network to fully recover its rheological properties after removal of the applied high shear stress or high pressure can be exploited.

■ CONCLUSIONS

In this study, stable magnetorheological smart fluids based on wormlike surfactant micelles and submicron magnetite particles were first prepared. The particles in these fluids do not settle out for at least several months, but they can be easily removed from the fluid by application of a magnetic field (with a gradient of at least 0.5 Tl/cm). The extracted particles can be redispersed in the same fluid just by gentle shaking, which indicates that they contain a protective layer of surfactant preventing their agglomeration. Such a possibility to recover the particles for reuse is attractive for various separation applications. At the same time, at a lower magnetic field gradient, the particles remain in the dispersion, and the whole dispersion responds to the magnetic field by moving to the region of highest flux as a homogeneous fluid, which may be used for precise positioning of the fluid using an external magnetic field.

The influence of magnetite particles on the rheological behavior of WLM solutions was examined. It was shown that at a low content of particles (up to 1.5 wt %) the viscosity and plateau modulus of the solution increase with an increasing amount of added particles, which is due to the formation of additional cross-links as a result of fusion of energetically unfavorable semispherical micellar end-caps with the surfactant layer adsorbed on the surface of the particle. When the total content of particles surpasses ca. 1.5 wt %, the plateau modulus levels off. Such behavior first observed in the present work was attributed to the linking of all micellar end-caps available in the system to magnetite particles thus leading to the saturation of the network, so that further addition of particles do not create new elastically active chains. The limiting value of the plateau modulus at saturation is higher in dispersions with lower

content of salt KCl, because these dispersions contain a larger amount of micellar end-caps and therefore form a larger amount of elastically active chains upon linking of all the end-caps to the particles. In the networks thus formed, several tens of WLMs are attached to the same particle, which effectively immobilizes it into the network, preventing the sedimentation.

The rheological properties can be further enhanced by exploiting the magnetoresponsive characteristics of magnetite particles. In a magnetic field, the smart fluids demonstrate the transition from liquidlike to solidlike state occurring as a result of hindering their flow by field-aligned chainlike aggregates of particles oriented perpendicularly to the flow direction.

Thus, smart fluids combining the responsive properties of the filler (magnetite particles) and the matrix (network of entangled WLMs) were elaborated. They present a rich choice of tools to tune their rheological properties in a wide range from liquidlike to solidlike state, which renders them very promising candidates for many applications of magnetosensitive materials including dampers, shock absorbers, torque transducers, dynamic sealing, etc.[30] Moreover, in contrast to common magnetorheological fluids the smart fluids based on WLMs possess controlled viscoelastic properties even without a magnetic field, which can widen the area of their use.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Dispersion of magnetite particles in WLM solutions, thickness of surfactant shell on magnetite particles, effect of salt concentration on the rheological properties of EHAC/magnetite particle suspensions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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