

Self-Assembled Networks Highly Responsive to Hydrocarbons[†]

Vyacheslav S. Molchanov, Olga E. Philippova,* and Alexei R. Khokhlov

Physics Department, Moscow State University, 119992 Moscow, Russia

Yuri A. Kovalev and Alexander I. Kuklin

Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 141980 Dubna, Russia

Received June 5, 2006. In Final Form: August 30, 2006

Rheological studies were performed with aqueous salt solutions of anionic surfactant potassium oleate and its mixtures with hydrophobically modified polyacrylamide. Semidilute solutions of the surfactant in the presence of salt (KCl) demonstrate viscoelastic properties due to the formation of a transient network of entangled wormlike micelles. These systems are highly responsive to hydrocarbons: the addition of *n*-heptane or *n*-dodecane reduces the viscosity of solutions by up to 4 to 5 orders of magnitude, thus inducing the transition of a gellike system to a fluid one. It is the transformation of cylindrical surfactant micelles into spherical ones upon absorption of hydrocarbon that disrupts the network. The addition of a small amount (0.5 wt %) of associating polymer leads to up to a 5000-fold increase in the zero-shear viscosity and enhances the susceptibility to hydrocarbons. SANS data show that independently of the presence of polymer the radius of wormlike micelles is roughly equal to the length of a surfactant molecule, whereas the radius of spheres formed upon the absorption of hydrocarbon is 2–2.5-fold higher. A possible structure of the spherical micelles is discussed.

Introduction

Highly responsive or environmentally sensitive systems are often prepared on the basis of polymeric networks.^{1–3} However, the responsive properties may be significantly enhanced if instead of polymer long micellar chains are used. These wormlike micelles can entangle with each other, forming transient networks that exhibit viscoelastic behavior. In contrast to polymer, the wormlike micellar chains of such viscoelastic surfactants (VESs) are formed as a result of weak noncovalent interactions; therefore, they can easily change their shape and size in response to the small variation of external conditions such as temperature, surfactant concentration, ionic strength, and additives.^{4–21} To get an enhanced

sensitivity to external factors, it is enough to replace only part of the polymer chains by wormlike surfactant micelles. As soon as wormlike micelles change their shape in response to an external trigger, the entire network is disrupted.

Surfactant/polymer interactions have been studied very intensively in past decades,^{20–35} but most of the investigations mainly dealt with spherical micelles. Only a few studies^{20,21,32–35} were devoted to polymers interacting with long wormlike micelles. It was shown that polymers can either destroy or strengthen transient networks formed by threadlike surfactant micelles. The addition of nonionic polymers poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) to aqueous salt solutions of anionic surfactant—potassium oleate induces the disruption of the micellar network.³³ Cryo-TEM shows³³ that it is due to the transition of cylindrical micelles of potassium oleate present in solution in the absence of polymer to spherical micelles appearing upon addition of polymer. The analogous disruption of the network as a result of the transition of wormlike micelles to spherical ones was also observed for cationic surfactant cetyltrimethylammonium salicylate interacting with nonionic polymers poly-

[†] Part of the Stimuli-Responsive Materials: Polymers, Colloids, and Multicomponent Systems special issue.

* To whom correspondence should be addressed. E-mail: phil@polly.phys.msu.ru.

(1) Tanaka T. In *Polyelectrolyte Gels: Properties, Preparation, and Application*; Harland, R. S.; Prud'homme, R. K., Eds.; ACS Symposium Series 480; American Chemical Society: Washington, DC, 1992; p 1.

(2) Shibayama, M.; Tanaka, T. *Adv. Polym. Sci.* **1993**, *109*, 1.

(3) Philippova, O. E.; Khokhlov, A. R. In *Responsive Polymer Materials: Design and Applications*; Minko, S., Ed.; Blackwell Publishing: Ames, IA, 2006; p 206.

(4) Cates, M. E. *Macromolecules* **1987**, *20*, 2289. Cates, M. E. *J. Phys.: Condens. Matter* **1996**, *8*, 9167.

(5) Cates, M. E.; Turner, M. *Europhys. Lett.* **1990**, *11*, 68.

(6) Rehage, H.; Hoffmann, H. *Mol. Phys.* **1991**, *74*, 933.

(7) Kern, F.; Zana, R.; Candau, S. J. *Langmuir* **1991**, *7*, 1344.

(8) Turner, M. S.; Marques, C.; Cates, M. E. *Langmuir* **1993**, *9*, 695.

(9) Khatory, A.; Lequeux, F.; Kern, F.; Candau, S. J. *Langmuir* **1993**, *9*, 1456.

(10) Fischer, P.; Rehage, H. *Langmuir* **1997**, *13*, 7012.

(11) Ait Ali, A.; Makhloufi, R. *J. Rheol.* **1997**, *41*, 307. Ait Ali, A.; Makhloufi,

R. *Colloid Polym. Sci.* **1999**, *277*, 270.

(12) Magid, L. J. *J. Phys. Chem. B* **1998**, *102*, 4064.

(13) Hartmann, V.; Cressely, R. *Rheol. Acta* **1998**, *37*, 115.

(14) Raghavan, S. R.; Kaler, E. W. *Langmuir* **2001**, *17*, 300.

(15) Raghavan, S. R.; Fritz, G.; Kaler, E. W. *Langmuir* **2002**, *18*, 3797.

(16) Nagarajan, R. *Langmuir* **2002**, *18*, 31.

(17) Sriwatwechakul, W.; LaFleur, T.; Prud'homme, R. K.; Sullivan, P. *Langmuir* **2004**, *20*, 8970.

(18) Croce, V.; Cosgrove, T.; Dreiss, C. A.; Maitland, G.; Hughes, T.; Karlsson, G. *Langmuir* **2004**, *20*, 7984.

(19) Kalur, G. C.; Frounfelker, B. D.; Cipriano, B. H.; Norman, A. I.; Raghavan, S. R. *Langmuir* **2005**, *21*, 10998.

(20) Shashkina, J. A.; Philippova, O. E.; Zaruslov, Y. D.; Khokhlov, A. R.; Pryakhina T. A.; Blagodatskikh I. V. *Langmuir* **2005**, *21*, 1524.

(21) Flood, C.; Dreiss, C. A.; Croce, V.; Cosgrove, T.; Karlsson, G. *Langmuir* **2005**, *21*, 7646.

(22) Goddard, E. D. *Colloids Surf.* **1986**, *19*, 255. Goddard, E. D. *J. Colloid Interface Sci.* **2002**, *256*, 228.

(23) Iliopoulos, I.; Wang, T. K.; Audebert, R. *Langmuir* **1991**, *7*, 617.

(24) Lindman, B.; Thalberg, K. In *Polymer-Surfactant Interactions*; Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; CRC Press: Boca Raton, FL, 1992.

(25) Philippova, O. E.; Starodoubtzev, S. G. *J. Polym. Sci., Part B: Polym. Phys.* **1993**, *31*, 1471.

(26) Philippova, O. E.; Hourdet, D.; Audebert, R.; Khokhlov, A. R. *Macromolecules* **1996**, *29*, 2822.

(27) Linse, P.; Piculell, L.; Hansson, P. In *Polymer-Surfactant Systems*; Kwak, J. C. T., Ed.; Marcel Dekker: New York, 1998.

(28) Hashidzume, A.; Mizusaki, M.; Yoda, K.; Morishima, Y. *Langmuir* **1999**, *15*, 4276.

(29) Zhou, S.; Chu, B. *Adv. Mater. (Weinheim, Ger.)* **2000**, *12*, 545.

(30) Noda, T.; Hashidzime, A.; Morishima, Y. *Langmuir* **2000**, *16*, 5324.

(31) Panmai, S.; Prud'homme, R. K.; Peiffer, D. G.; Jockusch, S.; Turro, N. *J. Langmuir* **2002**, *18*, 3860.

(32) Massiera, G.; Ramos, L.; Ligoure, C. *Langmuir* **2002**, *18*, 5687.

(33) Lin, Z.; Eads, C. D. *Langmuir* **1997**, *13*, 2647.

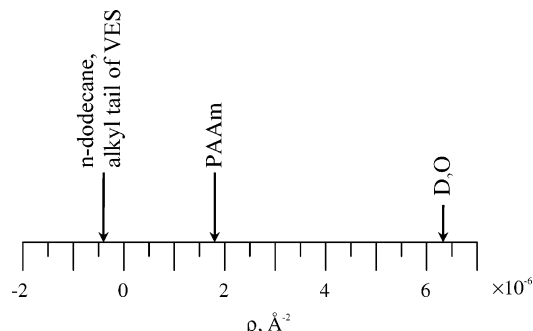
(34) Brackman, J. C.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1990**, *112*, 872.

(35) Couillet, I.; Hughes, T.; Maitland, G. *Macromolecules* **2005**, *38*, 5271.

angle. The data were recorded in the Q range of $0.009\text{--}0.5\text{ \AA}^{-1}$. The Fitter program was used to fit the experimental curves to ball models.⁴⁵

SANS arises from the spatial variations of the density of the scattering length in the sample. The values of the scattering length densities of the components of the system under study are presented in Chart 2. From these data, it is evident that when D_2O is used as

Chart 2. Scattering-Length Densities of the Components of Solutions



a solvent the alkyl tails of potassium oleate have a higher contrast and therefore cause stronger scattering in comparison with that of the polymer backbone. Therefore, it was assumed that the alkyl chains are mainly responsible for the scattering.

Results and Discussion

VES in the Absence of Hydrocarbons. In aqueous solutions, ionic surfactants can self-assemble into long wormlike micelles. These micelles are generally formed in the presence of high concentrations of salt, which screen the electrostatic repulsions between charged surfactant headgroups.⁶

Figure 1 shows the zero-shear viscosity η_0 of aqueous solutions

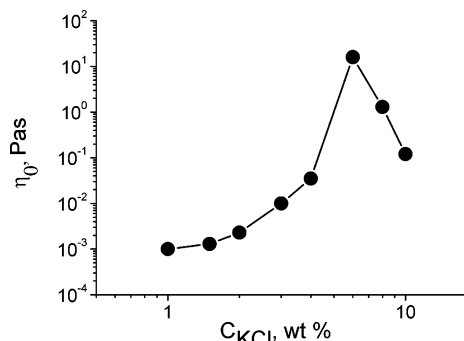


Figure 1. Zero-shear viscosity η_0 of 1 wt % aqueous solutions of potassium oleate as a function of the concentration of added salt KCl at 20 °C.

of potassium oleate as a function of the concentration of added low-molecular-weight salt KCl. It is seen that the viscosity goes through a maximum with increasing KCl content. This behavior was observed in many aqueous VES/salt systems.^{6,11,46} It is explained as follows. At low salt concentrations, the solution contains small micelles, and their contribution to the viscosity is low. With increasing salt concentration, the micelles grow in length because of the screening of electrostatic repulsion between similarly charged headgroups and begin to overlap and entangle one another, thus forming a transient network; this process induces a significant increase in viscosity. It is suggested that micelles attain their full length at the viscosity maximum.⁴⁷ Further

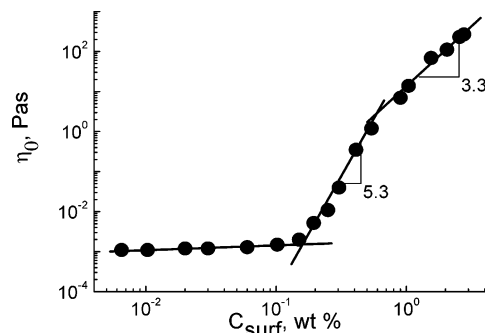


Figure 2. Zero-shear viscosity as a function of potassium oleate concentration at 20 °C. Solvent: 6 wt % KCl in water.

decreases in viscosity are attributed to the branching of micelles, when the electrostatic repulsion is sufficiently screened.⁴⁸ Branching shortens the average micellar lengths and makes the reptation faster because the branch points can freely slide along the micelles, which reduces the viscosity.

The formation of long wormlike micelles of potassium oleate upon addition of low-molecular-weight salt and the entanglement of these micelles with the formation of a transient network was visualized by cryo-TEM,^{21,33} but the rheological properties of this system have been poorly studied.

Hereafter, we fixed the concentration of KCl at 6 mol %, which corresponds to the maximum viscosity (and to the longest linear wormlike micelles), and studied the effect of surfactant concentration on the zero-shear viscosity. The results are presented in Figure 2. It is seen that the viscosity remains rather low until a potassium oleate concentration of ca. 0.105 wt % is reached but then increases dramatically. This is due to the transition from the dilute to semidilute regime, when the wormlike micelles start to entangle with each other. Therefore, concentration of 0.105 wt % can be considered to be the overlap concentration C^* for potassium oleate micelles.

Above C^* , the log–log concentration dependence of viscosity shows two different slopes: 5.3 and 3.3 (Figure 2). According to the theory,^{4,5,12} the viscosity behavior of wormlike micelles in semidilute solutions depends on the relative magnitude of micellar breaking time τ_{break} and reptation time τ_{rep} of the whole aggregate. The steeper slope (5.3) may indicate the presence of micelles, which do not break during the characteristic reptation time ($\tau_{\text{break}} \gg \tau_{\text{rep}}$). The value of the exponent (5.3) is comparable to the theoretical values (5.25) predicted for unbreakable flexible micelles.^{12,49} The second slope is inherent to micelles, which break and recombine many times while reptating ($\tau_{\text{break}} \ll \tau_{\text{rep}}$). The exponent obtained experimentally (3.3) is comparable to the theoretical value predicted for such “living” micelles (3.5).⁴

It should be noted that in most VES systems described in the literature only one slope with a power law of $\eta \approx C^{3.5}$ was observed. To the best of our knowledge, both slopes coinciding with theoretical predictions for slow and fast breaking limits, respectively, were found only for aqueous solutions of cationic VES erucyl bis(hydroxyethyl)methylammonium chloride in the presence of KCl at 20 °C.²⁰ The observation of similar slopes for anionic VES indicates that a two-slope concentration dependence of the viscosity of semidilute solutions of VES is quite general and is inherent to several VESs independent of their chemical nature.

(45) Soloviev, A. G.; Stadnik, A. V.; Islamov, A. Kh.; Kuklin, A. I. *Commun. Jt. Inst. Nucl. Res., Dubna* **2003**, E10-2003-36.

(46) Candau, S. J.; Khatory, A.; Lequeux, F.; Kern, F. *J. Phys. IV* **1993**, *3*, 197.

(47) Aswal, V. K.; Goyal, P. S.; Thiyagarajan P. *J. Phys. Chem. B* **1998**, *102*, 2469.

(48) Lequeux, F. *Europhys. Lett.* **1992**, *19*, 675.

(49) Carver, M.; Smith, T. L.; Gee, J. C.; Delichere, A.; Caponetti, E.; Magid, L. *J. Langmuir* **1996**, *12*, 691.

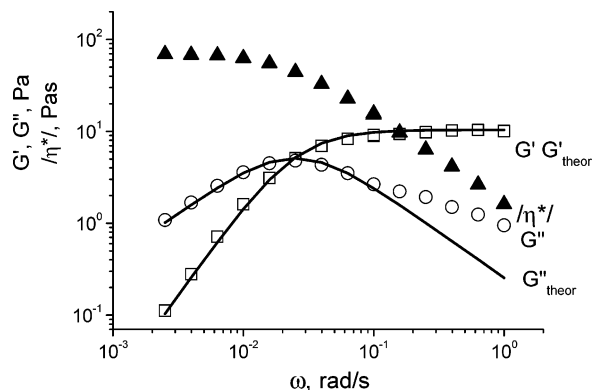


Figure 3. Viscoelastic spectra of 2 wt % potassium oleate solutions at 20 °C: storage G' and loss G'' moduli and complex viscosity $|\eta^*|$ as a function of angular frequency. Solvent: 6 wt % KCl in water. The solid lines indicate the theoretical frequency dependencies of G' and G'' calculated according to the Maxwell model.

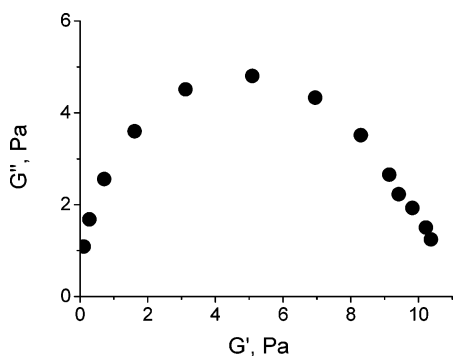


Figure 4. Cole–Cole plots for 1.5 wt % solutions of potassium oleate at 20 °C. Solvent: 6 wt % KCl in water.

The transition from the “unbreakable” to “living” regime occurs at increasing surfactant concentration, when the micelles become longer: with increasing micellar chain length, the reptation time increases and the breaking time shortens (the probability of breaking is higher for longer chains), approaching the fast breaking limit: $\tau_{\text{break}} \ll \tau_{\text{rep}}$.

The viscoelastic behavior of semidilute potassium oleate solutions is illustrated in Figure 3. It is seen that $G''(\omega)$ goes through a maximum whereas $G'(\omega)$ shows a plateau. With increasing VES concentration C , the plateau value of storage modulus G'_0 increases according to the power law $G'_0 \approx C^{2.4}$, reaching a value of 40 Pa for a 2.8 wt % solution. The rise of the G'_0 value may be ascribed to the increasing number of entanglements in the network of wormlike micelles. The obtained concentration dependence of G'_0 is consistent with the theoretical predictions of Cates ($G'_0 \approx C^{0.4}$) for an entangled system of linear wormlike micelles.⁴ From the frequency ω_R at which $G'(\omega)$ and $G''(\omega)$ cross each other, the value of the relaxation time t_R was estimated: $t_R = 1/\omega_R$. It increases with surfactant concentration, reaching a value of 45 s for a 2.8 wt % solution.

It should be noted that at potassium oleate concentrations higher than 0.8 wt % (fast-breaking regime) the solutions are characterized by a single relaxation time (Maxwellian behavior) that is evident from the semicircular shape of the Cole–Cole plot (Figure 4) and from the fitting of experimental frequency dependencies $G'(\omega)$ and $G''(\omega)$ by the relations characteristic of a Maxwell fluid¹² (Figure 3):

$$G'(\omega) = \frac{G'_0 \omega^2 t_R^2}{1 + \omega^2 t_R^2} \quad G''(\omega) = \frac{G'_0 \omega t_R}{1 + \omega^2 t_R^2}$$

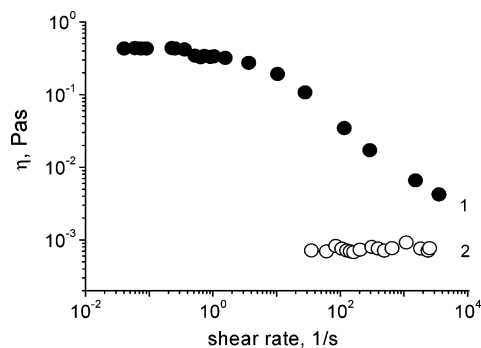


Figure 5. Steady-shear viscosity plots for 0.4 wt % solutions of potassium oleate at 20 °C before (1) and after (2) contact with n -dodecane. Solvent: 6 wt % KCl in water.

Such simple rheological behavior is always observed in VES solutions under conditions where the breakage and recombination both occur many times within the time scale of observation ($\tau_{\text{break}} \ll \tau_{\text{rep}}$).¹⁰

Therefore, in the absence of hydrocarbons, potassium oleate forms wormlike micelles that entangle with each other into a transient network, thus imparting viscoelastic properties to aqueous solutions. These solutions possess high viscosity (up to 400 Pa·s) that surpasses that of pure water by 5 orders of magnitude and a high elasticity modulus (up to 40 Pa).

VES after Contact with Hydrocarbons. The micellar structures that are formed by rather weak intermolecular interactions possess the ability to reorganize under the influence of external stimuli, in particular, upon the addition of hydrophobic substances (e.g., hydrocarbons) being solubilized in the hydrophobic cores of micelles. Absorbed hydrocarbons influence the size and the form of micelles, thereby affecting their rheological properties.

To study the effect of hydrocarbons on VES solutions, the following experiment was performed. An aqueous VES solution (3 mL) was mixed with a hydrocarbon (3 mL) and left to equilibrate for 1 day. During this period, the system separated into two transparent macroscopic phases (top – hydrocarbon phase, bottom – aqueous VES solution). Then, the VES solution saturated with hydrocarbon was removed from the hydrocarbon phase, and its rheological behavior was studied.

Even a simple visual inspection of the samples provided evidence that the hydrocarbons produce a tremendous effect on VES solutions: the highly viscous gel-like system almost instantaneously transforms into a fluid with very low viscosity.

Figure 5 illustrates the influence of n -dodecane on the steady-shear viscosity plot. It is seen that in the absence of hydrocarbons the viscosity values are high and constant at low frequencies but then decrease at higher frequencies. Such shear-thinning behavior may be due to the alignment of micelles along the flow¹⁴ as well as the breaking of wormlike micelles and their entanglements by the applied shear. By contrast, upon the contact with n -dodecane the viscosity becomes independent of the shear rate (Newtonian fluid). Thus, the hydrocarbon induces the transition from viscoelastic to Newtonian liquid.

When comparing the values of zero-shear viscosity (Figure 6), we see that after contact with the hydrocarbon they decrease by up to 4 to 5 orders of magnitude, reaching a viscosity that is close to that of pure water. The effect is the same for two different hydrocarbons: n -heptane and n -dodecane. Such a drop in viscosity induced by hydrocarbons was previously observed for VESs^{17,20,40} and was attributed to the transformation of wormlike micelles into spherical micelles, resulting in the disruption of the transient network.^{40,50} However, to the best of

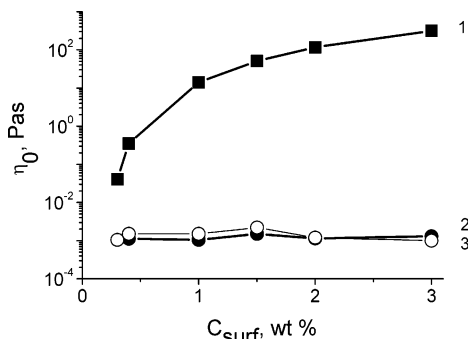


Figure 6. Zero-shear viscosity η_0 as a function of the concentration of potassium oleate before (1) and after contact with *n*-heptane (2) and *n*-dodecane (3) at 20 °C. Solvent: 6 wt % KCl in water.

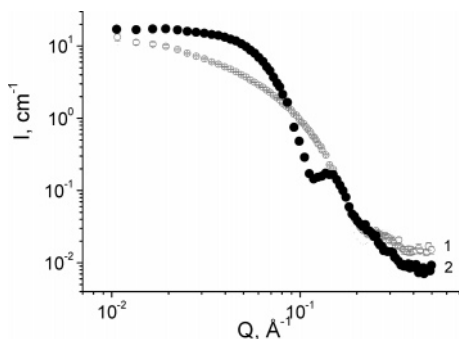


Figure 7. SANS profiles for 3 wt % potassium oleate solutions before (1) and after (2) contact with *n*-dodecane at 20 °C. Solvent: 6 wt % KCl in D₂O.

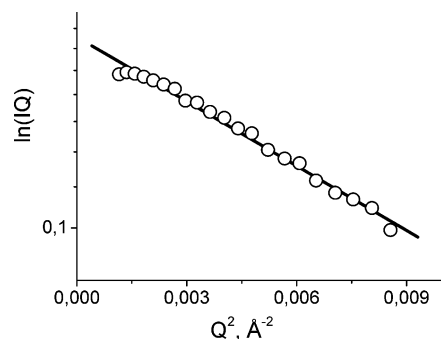


Figure 8. SANS intensity I plotted as $\ln(IQ)$ versus Q^2 for a 3 wt % potassium oleate solution before contact with *n*-dodecane at 20 °C. Solvent: 6 wt % KCl in D₂O.

our knowledge, no direct evidence of the transition has been presented up to now.

To study the hydrocarbon-induced change in the shape of potassium oleate micelles, the SANS technique was employed. Figure 7 shows the scattering curves obtained for potassium oleate solution before (a) and after (b) contact with *n*-dodecane. It is seen that the hydrocarbon essentially affects the shape of the scattering curve. The scattering spectra obtained before contact with the hydrocarbon are presented in the form of $\ln(IQ)$ versus Q^2 plots in Figure 8. It is seen that in these coordinates the scattering curves are straight lines, which is typical for cylindrical structures.⁵¹ From the slopes of these lines, the cross-sectional radii of the structures were determined. They are summarized in Table 1. It is seen that for all samples the radii are equal to ca. 19–20 Å, which seems to be reasonable because it is close to the length of the alkyl tail of the surfactant (19 Å taking into

Table 1. Characteristics of Potassium Oleate Micelles Derived from SANS Data

sample				
potassium oleate, wt %	HM PAAm, wt %	contact with <i>n</i> -dodecane	form of micelles	radius, Å
3.0		no	cylinder	19.1
4.5		no	cylinder	20.0
0.5	0.5	no	cylinder	20.5
3.0	0.5	no	cylinder	19.5
0.5		yes	sphere	47.0
0.5	0.5	yes	sphere	43.1
3.0	0.5	yes	sphere	38.2

account the bending at the cis double bond). These data are consistent with those reported recently.²¹ Therefore, we can conclude that in the absence of hydrocarbon, potassium oleate micelles are of cylindrical shape and have a cross-sectional radius close to the full length of the alkyl tail of the surfactant molecule.

Upon addition of hydrocarbon, the scattering curve can be well fit to a model of a sphere (Figure 9) (i.e., hydrocarbons

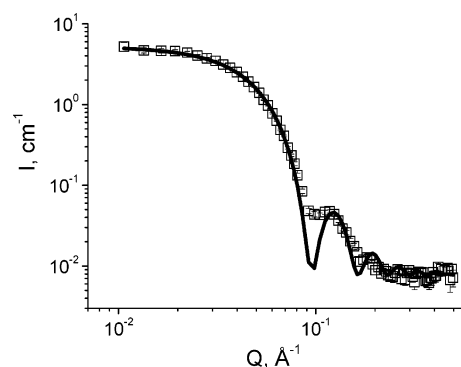


Figure 9. SANS profile for a 0.5 wt % potassium oleate solution after contact with *n*-dodecane at 20 °C. The continuous line represents the form factor of a sphere with a radius of 47 Å. Solvent: 6 wt % KCl in D₂O.

induce the change in the shape of VES micelles from cylindrical to spherical). What is the reason for this transition? Aliphatic hydrocarbons are known to be easily solubilized in the micellar interior.⁵² With solubilization, the radius of the grown micelle increases. As soon as the inner core reaches a size that allows the molecular packing parameter⁵³ R_p ($R_p = V_c/l_c A_0$, where V_c is the volume of the hydrophobic tail, l_c is its length, and A_0 is the surface area occupied by surfactant headgroup) to obtain the value characteristic of spherical micelles, the micelles change their shape.⁵⁴ The process gives a significant gain in entropy because from one wormlike micelle a giant number of spherical micelles can be formed.⁵⁵

The fitted radii of spherical micelles are listed in Table 1. It is seen that the radius of the sphere is much larger than the length of the alkyl tail of potassium oleate. This allows one to suggest that the spheres consist of a “drop” of hydrocarbon surrounded by surfactant micelles. This suggestion is consistent with the results of computer modeling,⁵⁶ demonstrating that upon solubilization of nonpolar solvent the micelles adopt a fairly well-defined three-layer structure consisting of a droplet of absorbed solvent in the center (inner core), a layer of hydrophobic tails

(50) Hoffmann, H.; Ulbrich, W. *Tenside, Surfactants, Deterg.* **1987**, *24*, 23.

(51) Zaroslov, Yu. D.; Gordeliy, V. I.; Kuklin, A. I.; Islamov, A. H.; Philippova, O. E.; Khokhlov, A. R.; Wegner, G. *Macromolecules* **2002**, *35*, 4466.

(52) Lindemuth, P. M.; Bertrand, G. L. *J. Phys. Chem.* **1993**, *97*, 7769.

(53) Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans. 2* **1976**, *9*, 1525.

(54) Kumar, S.; Bansal, D.; Kabir-du-Din. *Langmuir* **1999**, *15*, 4960.

(55) Hoffmann, H.; Ebert, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 902.

(56) Khalatur, P. G.; Khokhlov, A. R.; Mologin, D. A.; Zheligovskaya, E. A. *Macromol. Theory Simul.* **1998**, *7*, 299.

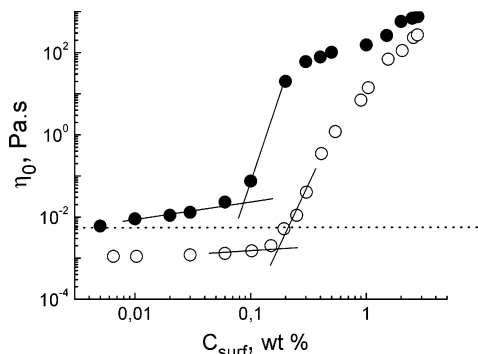


Figure 10. Effect of surfactant concentration on the zero-shear viscosity of potassium oleate (open symbols) and potassium oleate/HM PAAm system (filled symbols) at a fixed 0.5 wt % concentration of polymer at 20 °C. The dotted line shows the value of the zero-shear viscosity for a 0.5 wt % solution of polymer. Solvent: 6 wt % KCl in water.

mixed with solvent molecules (outer core), and a corona formed by headgroups exposed to water. Strong separation of solvent particles and surfactant tails takes place despite the complete compatibility of both components. The reason is that the tails should be close to the core surface to prevent the immersion of polar heads into the hydrophobic core.

In a forthcoming paper, we will describe in more detail the structural changes in the micelles upon addition of hydrocarbons derived from SANS experiments.

Thus, it was demonstrated that the addition of hydrocarbon to potassium oleate solution induces enormous rheological changes: up to a 100 000-fold drop in low-shear viscosity and the transformation of a viscoelastic system to a Newtonian fluid. This is due to the hydrocarbon-induced transition of wormlike to spherical micelles, as was evidenced by SANS measurements.

VES/Polymer System in the Absence of Hydrocarbons. To enhance further the initial viscosity before contact with oil, the HM polymer was added to potassium oleate. Figure 10 shows the zero-shear viscosity η_0 of the VES/polymer system as a function of surfactant concentration (at a fixed content of polymer). For comparison, the data for surfactant and polymer taken separately are presented as well. It is seen that the viscosity η_0 of the VES/polymer system can be up to 4 orders of magnitude higher than the viscosities of the pure-component solutions. The analogous effect was previously observed upon addition of HM PAAm to cationic VES erucyl bis(hydroxyethyl)methylammonium chloride.²⁰ It was explained by the formation of a common network²⁰ in which some subchains are composed of elongated surfactant micelles and other subchains are formed by HM PAAm polymer. At cross links, the hydrophobic C12 groups of the polymer penetrate the surfactant micelles. The SANS data (Figure 11) support this model because they show that scattering curves of potassium oleate solutions do not change upon addition of HM PAAm, indicating that polymer does not appreciably affect the structure of wormlike micelles. Also, the independence of the SANS profile with respect to the presence of polymer supports our suggestion about the low impact of HM PAAm on the scattering in comparison with VES.

The dynamic rheological data (Figure 12) demonstrate that in the VES/polymer system when comparing to pure VES both components of the complex elastic modulus increase by 1 order of magnitude. Also, the crossover point of $G'(\omega)$ and $G''(\omega)$ dependences shifts to lower frequencies, indicating a longer relaxation time in the VES/polymer system. The apparent behavior can be ascribed to the increased number of cross links upon addition of polymer. It should be noted that in contrast to pure

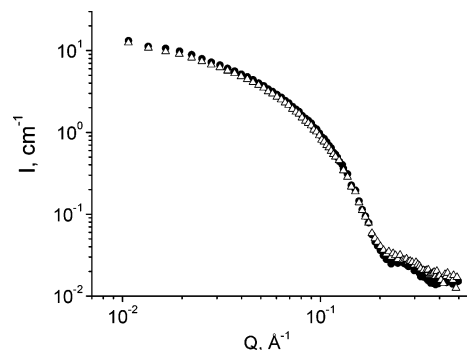


Figure 11. SANS profiles for a 3 wt % potassium oleate solution (open symbols) and for a potassium oleate/HM PAAm system (filled symbols) containing 3 wt % surfactant and 0.5 wt % polymer at 20 °C. Solvent: 6 wt % KCl in D₂O.

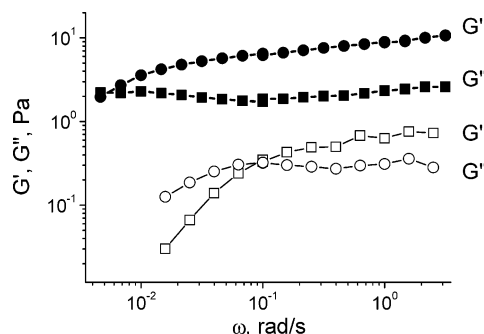


Figure 12. Frequency dependences of the storage G' and loss moduli G'' of 0.5 wt % potassium oleate (open symbols) and its mixture with 0.5 wt % HM PAAm (filled symbols) at 20 °C. Solvent: 6 wt % KCl in water.

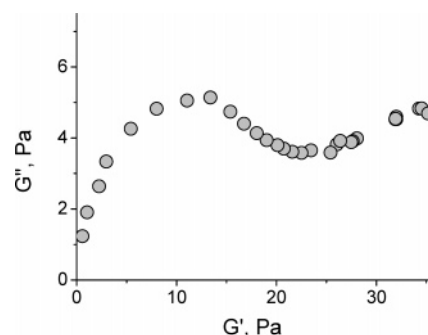


Figure 13. Cole–Cole plot for viscoelastic solutions containing 1.5 wt % potassium oleate and 0.5 wt % HM PAAm at 20 °C. Solvent: 6 wt % KCl in water.

surfactant the VES/polymer system does not exhibit simple Maxwell behavior (cf. Figures 4 and 13) (i.e., it is characterized by a set of relaxation times) similar to those of semidilute polymer solutions.

Therefore, the addition of a small amount of polymer to VES solutions leads to the formation of a physical gel with additional cross links and higher values of rheological characteristics: η_0 , G' , and G'' .

VES/Polymer System after Contact with Hydrocarbons.

As discussed above, HM PAAm does not affect the wormlike structure of the VES micelles; therefore, it is reasonable to expect that the polymer should not interfere with the susceptibility of VES to hydrocarbons. Moreover, taking into account that the initial viscosity of the system containing polymer is higher, the drop in viscosity upon addition of hydrocarbon may be even more pronounced than for pure VES.

Figure 14 shows the steady-shear viscosity plots for VES/polymer solutions before and after the addition of *n*-dodecane.

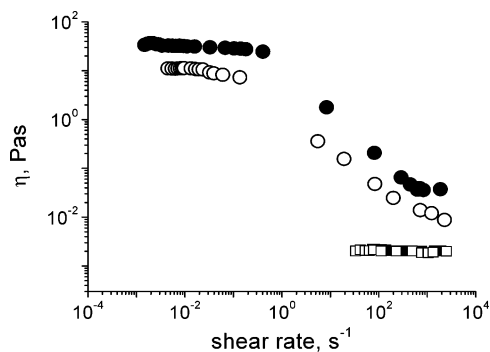


Figure 14. Steady-shear viscosity plots for 0.4 wt % (filled symbols) and 0.2 wt % (open symbols) solutions of potassium oleate in the presence of 0.5 wt % HM PAAm at 20 °C before (circles) and after (squares) contact with *n*-dodecane. Solvent: 6 wt % KCl in water.

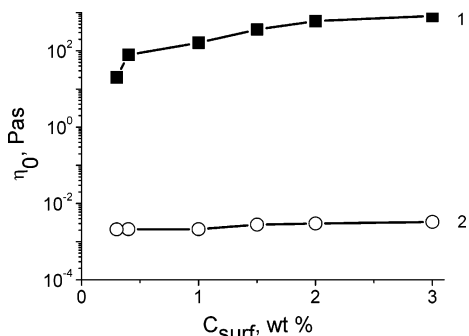


Figure 15. Zero-shear viscosity of the VES/polymer system containing 0.5 wt % polymer as a function of the concentration of surfactant before (1) and after (2) addition of *n*-dodecane at 20 °C. Solvent: 6 wt % KCl in water.

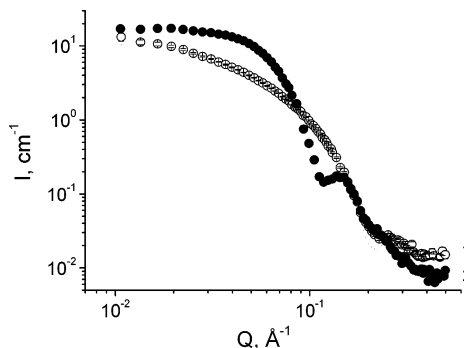


Figure 16. SANS profiles of a VES/polymer system containing 3 wt % potassium oleate and 0.5 wt % HM PAAm before (1) and after (2) contact with *n*-dodecane at 20 °C. Solvent: 6 wt % KCl in D₂O.

It is seen that in the absence of hydrocarbon the system is viscoelastic and displays a pronounced frequency dependence of viscosity that is typical of polymer networks containing cross-linked or entangled chains. After contact with the hydrocarbon, the viscosity is virtually independent of frequency, and the system displays rheological behavior typical of that of unentangled polymer solutions. These results indicate the disruption of the network when a hydrocarbon is added.

Figure 15 depicts the zero-shear viscosity of VES/polymer solutions as a function of the concentration of VES before and after the addition of *n*-dodecane. It is seen that similar to the case of pure VES the hydrocarbon triggers an enormous drop in the zero-shear viscosity (cf. Figures 6 and 15), so the susceptibility of VES to hydrocarbon remains after the addition of HM PAAm. Moreover, at low surfactant concentrations (0.2 or 0.4 wt %) the drop in viscosity is much more pronounced (by 2 to 2.5 orders of magnitude) in the polymer-containing system. This is due to

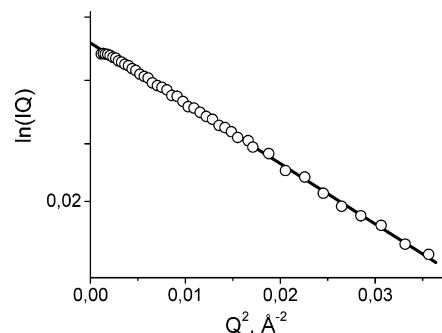


Figure 17. SANS intensity I plotted as $\ln(IQ)$ versus Q^2 for the VES/polymer system containing 3 wt % potassium oleate and 0.5 wt % HM PAAm before contact with *n*-dodecane at 20 °C. Solvent: 6 wt % KCl in D₂O.

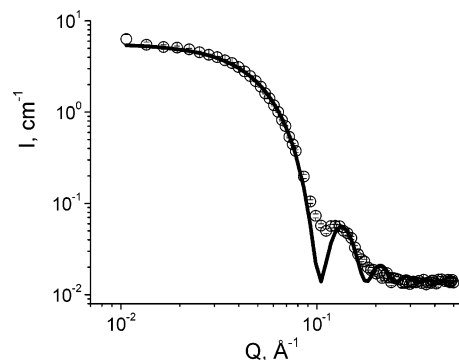


Figure 18. SANS profile for a VES/polymer system containing 0.5 wt % potassium oleate and 0.5 wt % HM PAAm after contact with *n*-dodecane at 20 °C. The continuous line represents the form factor of a sphere with a radius of 43.1 Å. Solvent: 6 wt % KCl in D₂O.

the much higher initial viscosity of the VES/polymer solution. Also, it should be pointed out that upon contact with the hydrocarbon the viscosity of the VES/polymer system is almost as low as that of pure VES (cf. Figures 6 and 15). This probably indicates the contraction of HM polymer coils upon interaction with hydrocarbon.

SANS data show (Figures 16–18) that in the VES/polymer system the hydrocarbon promotes the transformation of cylindrical micelles (Figure 17) to spherical ones (Figure 18), as was the case for pure VES. The size of the micelles is almost unaffected by polymer (Table 1).

Therefore, the data obtained reveal that the addition of a small amount of HM PAAm to VES does not modify the structure of micelles but induces quite a significant increase in viscosity. Because of this fact, the susceptibility to hydrocarbons is even enhanced.

Conclusions

The addition of hydrocarbon provides an excellent means of tuning micellar morphology and rheological properties of VES and VES/polymer solutions. In particular, hydrocarbons provoke a transition from a viscoelastic system consisting of entangled wormlike micelles to a Newtonian liquid with low viscosity. The extremely high susceptibility of these viscoelastic systems to hydrocarbons makes them very promising for applications in the oil industry (e.g., as a thickening agent for fracturing fluids).

Acknowledgment. This research was supported by the Schlumberger Company (CRDF project RP0-1301). RFBR is also acknowledged (project 05-03-32865). We thank T. A. Pryakhina for the synthesis of the polymer and I. V. Blagodatskikh for the determination of its molecular weight.