

Rheology of Viscoelastic Solutions of Cationic Surfactant. Effect of Added Associating Polymer

Julia A. Shashkina,[†] Olga E. Philippova,^{*,†} Yuri D. Zaroslov,[†]
Alexei R. Khokhlov,^{†,‡} Tatyana A. Pryakhina,[‡] and Inessa V. Blagodatskikh[‡]

Physics Department, Moscow State University, 119992 Moscow, Russia, and
Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 Vavilova Street, 119991 Moscow, Russia

Received July 9, 2004. In Final Form: November 3, 2004

Rheological studies were performed with aqueous salt solutions of viscoelastic cationic surfactant erucyl bis(hydroxyethyl)methylammonium chloride (EHAC) and its mixtures with hydrophobically modified polyacrylamide. The solutions of surfactant itself above the concentration of crossover of wormlike micelles exhibit two regions of rheological response. In the first region, they behave like polymer solutions in semidilute regime characterized by viscoelastic behavior with a spectrum of relaxation times. In the second region, unlike polymer solutions their relaxation after shear is dominated by a single relaxation time. Being composed of “living” micelles, the EHAC solutions easily lose their viscosity at the variation of the external conditions. For instance, heating from 20 to 60 °C reduces viscosity by up to 2 orders of magnitude, while added hydrocarbons induce a sudden drop of viscosity by 3–6 orders of magnitude. Polymer profoundly affects the rheological properties of EHAC solutions. The polymer/surfactant system demonstrates a 10 000-fold increase in viscosity as compared to pure-component solutions, the effect being more pronounced for polymer with less blocky distribution of hydrophobic units. A synergistic enhancement of viscosity was attributed to the formation of common network, in which some subchains are made up of elongated surfactant micelles, while others are composed of polymer. At cross-links the hydrophobic side groups of polymer anchor EHAC micelles. In contrast to surfactant itself, the polymer/surfactant system retains high viscosity at elevated temperature; at the same time it keeps a high responsiveness to hydrocarbon medium inherent to EHAC.

Introduction

Surfactants are able to form enormously long cylindrical micelles in aqueous solutions.^{1–18} These micelles can entangle with each other, forming transient networks that exhibit viscoelastic behavior. Due to viscoelastic properties the surfactants are very promising for use as thickening agents in many industrial applications, in particular, in fracturing fluids in oil recovery.^{19,20} The fracturing fluids composed of solid particles of proppant (sand or ceramics)

suspended in highly viscous medium are designed to create and to fill up the artificial fractures, thus enhancing permeability and productivity of the well. A high viscosity of the fluid is provided either by polymers or by viscoelastic surfactants (VES).

Viscoelastic behavior of VES is similar to that of polymers in semidilute or concentrated solutions.^{2,9,21–23} However, in contrast to polymer macromolecules, the surfactant micelles incessantly break and recombine which makes viscoelastic properties of VES highly responsive to the variation of external conditions, e.g. temperature, hydrophobic additives, etc.^{12–18,24,25} For instance, in contact with hydrocarbons the viscosity of VES can drop by several orders of magnitude as a result of transformation of cylindrical micelles into spherical ones.^{2,19} The responsiveness to hydrocarbons makes VES very promising for the use in fracturing fluids, especially at the stage when the porous space between proppant particles should be cleaned up from the residuals of the viscous fluid to allow oil to drain to the well bore. However, one of the weak points of VES viscosifiers in comparison to the conventional polymers is a significant deterioration of their rheological characteristics at elevated temperatures taking place in subterranean reservoirs.

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

[†] Moscow State University.

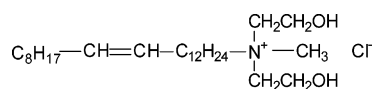
[‡] Russian Academy of Sciences.

- (1) Rehage, H.; Hoffman, H. *Mol. Phys.* **1991**, *74*, 933.
- (2) Magid, L. J. *J. Phys. Chem. B* **1998**, *102*, 4064.
- (3) Porte, G.; Appell, J.; Poggi, Y. *J. Phys. Chem.* **1980**, *84*, 3105.
- (4) Imae, T.; Ikeda, S. *J. Phys. Chem.* **1986**, *90*, 5216.
- (5) Olsson, U.; Soederman, O.; Guering, P. *J. Phys. Chem.* **1986**, *90*, 5223.
- (6) Shikata, T.; Hirata, H.; Kotaka, T. *Langmuir* **1987**, *3*, 1081.
- (7) Candau, S. J.; Hirsch, E.; Zana, R.; Delsanti, M. *Langmuir* **1989**, *5*, 1225.
- (8) Cates, M. A.; Candau, S. J. *J. Phys.: Condens. Matter* **1990**, *2*, 6869.
- (9) Kern, F.; Zana, R.; Candau, S. J. *Langmuir* **1991**, *7*, 1344.
- (10) Clausen, T. M.; Vinson, P. K.; Minter, J. R.; Davis, H. T.; Talmon, Y.; Miller, W. G. *J. Phys. Chem.* **1992**, *96*, 474.
- (11) Berret, J.-F.; Appell, J.; Porte, G. *Langmuir* **1993**, *9*, 2851.
- (12) Khatory, A.; Lequeux, F.; Kern, F.; Candau, S. J. *Langmuir* **1993**, *9*, 1456.
- (13) Candau, S. J.; Khatory, A.; Lequeux, F.; Kern, F. *J. Phys. IV* **1993**, *3*, 197.
- (14) Fischer, P.; Rehage, H. *Langmuir* **1997**, *13*, 7012.
- (15) Hassan, P. A.; Candau, S. J.; Kern, F.; Manohar, C. *Langmuir* **1998**, *14*, 6025.
- (16) Ait Ali, A.; Makhlofi, R. *J. Rheol.* **1997**, *41*, 307; *Colloid Polym. Sci.* **1999**, *277*, 270.
- (17) Hartmann, V.; Cressely, R. *Rheol. Acta* **1998**, *37*, 115.
- (18) Raghavan, S. R.; Fritz, G.; Kaler, E. W. *Langmuir* **2002**, *18*, 3797.

- (19) Chase, B.; Wells, N.; Territories, N.; Chmiliowski, W.; Marcinew, R.; Mitchell, C.; Dang, Y.; Krauss, D.; Nelson, E.; Lantz, T.; Parham, C.; Plummer, J. *Oilfield Rev.* **1997**, *9*, 20.
- (20) Miller, M.; Dismuck, K. *Russ. Chem. Zh. (Russ. Chem. J.)* **2003**, *47*, 78.

- (21) Cates, M. E. *Macromolecules* **1987**, *20*, 2289; *Europhys. Lett.* **1987**, *4*, 497; *J. Phys. (Paris)* **1988**, *49*, 1593.
- (22) Granek, R.; Cates, M. E. *J. Chem. Phys.* **1992**, *96*, 4758.
- (23) Cates, M. E.; Turner, M. *Europhys. Lett.* **1990**, *11*, 68.
- (24) Croce, V.; Cosgrove, T.; Dreiss, C. A.; Maitland, G.; Hughes, T.; Karlsson, G. *Langmuir* **2004**, *20*, 7984.
- (25) Siriwatwechakul, W.; LaFleur, T.; Prud'homme, R. K.; Sullivan, P. *Langmuir* **2004**, *20*, 8970.

Chart 1. Chemical Structure of Cationic Surfactant Erucyl Bis(hydroxyethyl)methylammonium Chloride EHAC with Cis Unsaturation at the 13-Carbon Atom Position



To combine the useful properties of polymeric and VES thickeners Couillet and Hughes proposed to use blends of hydrophobically modified polymers with VES.²⁶ It is expected that such viscosifying systems may be at once resistant to heating and responsive to hydrocarbons.

The rheological properties of polymer/surfactant systems were extensively studied to date,^{27–38} but most of the investigations concerned low surfactant concentrations (of the order of critical micelle concentration (cmc)).^{29–30,33–36} The present study deals with much higher surfactant concentrations (exceeding the cmc value by 2–3 orders of magnitude) at the conditions of existence of long wormlike micelles.

The polymer/surfactant system described in this paper consists of (i) hydrophobically modified polyacrylamide (HM PAAm), a water-soluble polymer with a small content of hydrophobic *n*-dodecyl side groups, and (ii) erucyl bis(hydroxyethyl)methylammonium chloride (EHAC), a cationic VES with a long mono-unsaturated C22 tail (Chart 1). Recently it was found that EHAC is able to form viscoelastic solutions at rather low surfactant concentrations even in the absence of hydrotropic counterions.^{39–43}

In the present work, the rheological properties of the polymer/surfactant EHAC system are compared with those of pure EHAC. It is shown that the mixed system demonstrates a 10 000-fold increase in viscosity as compared to pure-component solutions. In addition to a synergistic enhancement of viscosity, the mixed system offers a good combination of properties of single components: due to the polymer ingredient the system retains pronounced viscosity at heating, while due to the VES ingredient the system acquires a high responsiveness to hydrocarbon medium.

Experimental Section

Materials. Viscoelastic surfactant EHAC containing 25 wt % 2-propanol was provided by Schlumberger Cambridge Research

(26) Couillet, I.; Hughes, T. Pat. GB2383355, 2003; Pat. WO03056130, 2003.

(27) Goddard, E. D. *Colloids Surf.* **1986**, *19*, 255.

(28) Lindman, B.; Thalberg, K. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; CRC Press: Boca Raton, FL, 1992; p.203.

(29) Methemitis, C.; Morcellet, M.; Sabbadin, J.; François, J. *Eur. Polym. J.* **1986**, *22*, 619.

(30) Sau, A. C.; Landoll, L. M. *Adv. Chem. Ser.* **1989**, *223*, 343.

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

(32) Mast, A. P.; Prud'homme, R. K.; Glass, J. E. *Langmuir* **1993**, *9*, 708.

(33) Magny, B.; Iliopoulos, I.; Zana, R.; Audebert, R. *Langmuir* **1994**, *10*, 3180.

(34) Annable, T.; Buscall, R.; Ettelaie, R.; Shepherd, P.; Whittlestone, D. *Langmuir* **1994**, *10*, 1060.

(35) Kjøniksen, A.-L.; Nyström, B.; Lindman, B. *Macromolecules* **1998**, *31*, 1852.

(36) Kopperud, H. M.; Hansen, F. K.; Nyström, B. *Macromol. Chem. Phys.* **1998**, *199*, 2385.

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

(38) Massiera, G.; Ramos, L.; Liguore, C. *Langmuir* **2002**, *18*, 5687.

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

(40) Raghavan, S. R.; Edlund, H.; Kaler, E. W. *Langmuir* **2002**, *18*, 1056.

(41) Couillet, I.; Hughes, T.; Maitland, G.; Candau, F.; Candau, S. *J. Langmuir* **2004**, *20*, 9541.

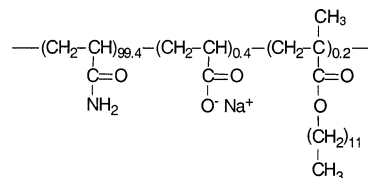
(42) Croce, V.; Cosgrove, T.; Maitland, G.; Hughes, T.; Karlsson, G. *Langmuir* **2003**, *19*, 8536.

(43) Schubert, B. A.; Wagner, N. J.; Kaler, E. W.; Raghavan, S. R. *Langmuir* **2004**, *20*, 3564.

Limited. 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.

Potassium chloride from Helicon (>99.8% purity), acrylamide, ammonium persulfate, and sodium dodecyl sulfate (SDS) from Aldrich were used as received.

Synthesis. Two polymer samples of HM PAAm were synthesized by free-radical micellar copolymerization of acrylamide (99.8 mol %) and *n*-dodecylmethacrylate (0.2 mol %) with ammonium persulfate as initiator (4.4×10^{-3} mol/L) and SDS as a surfactant solubilizing hydrophobic monomer in aqueous medium. The polymers obtained possess the following chemical structure:



The polymers are denoted in terms of type and molar content of hydrophobic and charged monomer units. For example, 0.2-C12/0.4SA indicates a polymer containing 0.2 mol % of *n*-dodecylmethacrylate (C12) units and 0.4 mol % of charged sodium acrylate units.

It is known that the micellar copolymerization leads to multiblock copolymers, if the number of hydrophobic monomers per surfactant micelle, N_h , is higher than 1, whereas the copolymers with nearly random distribution of hydrophobic groups along the backbone are obtained at $N_h \leq 1$.⁴⁴ In this work the hydrophobe/surfactant molar ratio was adequately adjusted in order get the number of hydrophobes per micelle, N_h , equal to 1.1 (sample 1) and 1.52 (sample 2).

The polymerization was allowed to proceed for 2–3 h at 50 °C. After that the polymers were twice precipitated in methanol/acetone mixture.

The molecular weight (MW) of the prepared polymers was determined by gel permeation chromatography in solvent containing 70 vol % of 0.1 M NaNO₃ aqueous solution and 30 vol % of acetonitrile according to the technique published elsewhere.⁴⁵ It was determined that both polymers under study have MW of 8×10^5 . The value of the C^* concentration for aqueous solutions of unmodified PAAm of the same MW was estimated as 0.4 wt %. The estimation was made using the formula $C^* \approx 1/[\eta]$ with $[\eta] = 9.33 \times 10^{-3} M^{0.75}$ ($[\eta]$ is in g/cm³).⁴⁶

Samples Preparation. Surfactant and polymer/surfactant samples were prepared by mixing appropriate quantities of aqueous stock solutions of surfactant, polymer, and salt with distilled–deionized water. Water was purified by the Millipore Milli-Q system. The samples were stirred and left for equilibration at room temperature for 1 day (in the case of surfactant samples) and for 7 days (in the case of polymer/surfactant samples). The concentrations of the components were varied in the following range: 0.01–2 wt % of surfactant, 0.2–0.5 wt % of polymer, and 0.5–5 wt % of KCl.

The phase behavior was determined by visual inspection. Most of the two-phase samples displayed two well-separated phases.

Rheological Measurements. Dynamic and steady rheological measurements were carried out on a controlled shear stress rheometer Haake Rheostress RS 150 L using the cone plate system (diameter, 35 mm; angle, 2°) or the system of coaxial cylinders (gap, 0.3 mm; mean radius, 20 mm). To avoid the effect of solvent evaporation, a specially constructed vapor lock filled with the solvent was used. The sample was equilibrated for at least 20 min at certain temperature prior to conducting measurements.

Dynamic measurements were carried out in the linear viscoelastic regime. The relaxation time τ_R was obtained from

(44) Volpert, E.; Selb, J.; Candau, F. *Polymer* **1998**, *39*, 1025.

(45) Blagodatskikh, I. V.; Sutkevich, M. V.; Sitnikova, N. L.; Churochkina, N. A.; Pryakhina, T. A.; Philippova, O. E.; Khokhlov, A. R. *J. Chromatogr., A* **2002**, *976*, 155.

(46) François, J.; Sarazin, D.; Schwarz, T.; Weill, G. *Polymer* **1979**, *20*, 969.

Table 1. Exponents for the Scaling Laws of the Dependence of Different Rheological Parameters on Surfactant Concentration

rheological parameters	20 °C		60 °C	theory ²¹
	0.08–0.4 wt % EHAC	0.5–1.8 wt % EHAC	0.5–2.0 wt % EHAC	for the fast-breaking regime
plateau modulus, G_0	a	2.23	2.35	2.25
terminal relaxation time, τ_R	7.00	1.30	1.60	1.25
zero-shear viscosity, η_0	5.6	3.6	3.5	3.5
G''_{min}/G_0	a	-1.60	-1.66	-1.75

^a No plateau is observed on frequency dependencies of G' .

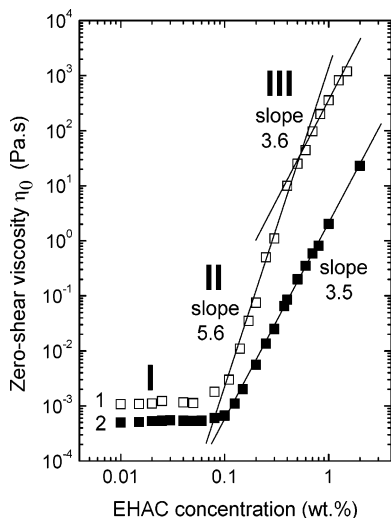


Figure 1. Zero-shear viscosity as a function of the concentration of surfactant EHAC at two different temperatures: 20 (1) and 60 °C (2). Solvent: 3 wt % KCl in water.

the intersection point of the frequency dependence of storage and loss moduli. The zero shear modulus G_0 was defined from the plateau value of the storage modulus $G'(\omega)$. For very viscous samples zero-shear viscosity η_0 was determined as a limit of the absolute value of complex viscosity $|\eta^*|$ at an angular frequency $\omega \rightarrow 0$ according to the Cox–Merz rule.⁴⁷

Results and Discussion

(1) VES without Polymer. (1.1) *Effect of Surfactant Concentration.* Figure 1 shows the zero-shear viscosity as a function of surfactant concentration at EHAC concentrations that far exceed the cmc value ($\text{cmc} = 1.7 \times 10^{-3}$ wt % or 3.7×10^{-5} mol/L⁴⁸). It is seen that the viscosity remains rather low until the surfactant concentration of ca. 0.09 wt %, but then a dramatic increase of viscosity is observed. It is due to the transition from a dilute to a semidilute regime, when the wormlike micelles start to entangle with each other. Therefore, the concentration of 0.09 wt % can be considered as a crossover concentration C^* for surfactant micelles.

Above C^* , the curve of concentration dependence of viscosity at 20 °C shows two different scaling regions (Figure 1, curve 1). The more steep slope region (II) is characterized by the power law $\eta_0 \sim C^{5.6}$. Such dependence of η_0 on the concentration of surfactant may indicate the presence of short micelles, which do not break during the characteristic reptation time (i.e. the reptation time τ_{rep} is smaller than the breaking time τ_b : $\tau_{\text{rep}} \ll \tau_b$). The value of the exponent (5.6) is comparable to the theoretical values (5.25–5.7) predicted for systems of unbreakable chains.^{2,16} In the literature this case is described as the case of “dead polymer”.

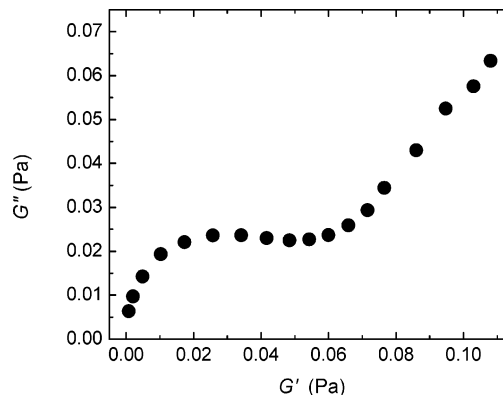


Figure 2. Cole–Cole plots for 0.3 wt % solutions of surfactant EHAC at 20 °C. Solvent: 3 wt % KCl in water.

The second slope (region III) in Figure 1 is characterized by the power law $\eta_0 \sim C^{3.6}$. Such dependence of viscosity η_0 on the concentration of surfactant is inherent to long micelles, which can many times reversibly break and recombine, while reptating from the constraining tube of entanglements (i.e. the breaking time τ_b is shorter than the reptation time τ_{rep} : $\tau_b \ll \tau_{\text{rep}}$). In the literature this case is described as the case of “living polymer”.²¹ The dynamics of such a living polymer solution was studied in details by Cates and co-workers.^{21–23} The exponent obtained experimentally (3.6) is comparable to the theoretical value predicted by Cates²¹ (Table 1). It should be noted that in most of the VES systems described in the literature only one slope with the power law $\eta_0 \sim C^{3.5}$ was observed. To the best of our knowledge, the two slopes above the C^* concentration in VES were found only for aqueous solutions of cethyltrimethylammonium chloride in the presence of potassium benzoate at 30 °C,¹⁶ but the values of exponents (4.9 and 2.4) are quite different from those observed in the present work.

So, in the present system the transition from “dead polymer” to “living polymer” regime occurs at increasing surfactant concentration. The reasons for such behavior are quite evident. When the concentration of surfactant increases, the micelles become longer; therefore, their reptation time increases, while the breaking time decreases (the probability of breaking is higher for longer chains).

Dynamic rheological measurements reveal quite different behavior of the system in the II and III concentration regions. In region II the stress relaxation function is multiexponential, which is illustrated in Figure 2 showing that the Cole–Cole plot is far from the semicircular shape that is characteristic for a single relaxation process.

By contrast, in region III the stress relaxation is monoexponential (fitting the Maxwell model), and the Cole–Cole plot has a semicircular shape. Such a simple rheological behavior can be attributed to the fact that the micelle breaking time is short compared to the reptation time. As a result, the breakage and recombination both occur often before the chain reptates out of the tube

(47) Cox, W. P.; Merz, E. H. *J. Polym. Sci.* **1958**, *28*, 619.

(48) Shashkina, Y. A.; Philippova, O. E.; Smirnov, V. A.; Blagodatikh, I. V.; Churochkina, N. A.; Khokhlov, A. R. *Vysokomol. Soedin.*, submitted for publication.

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

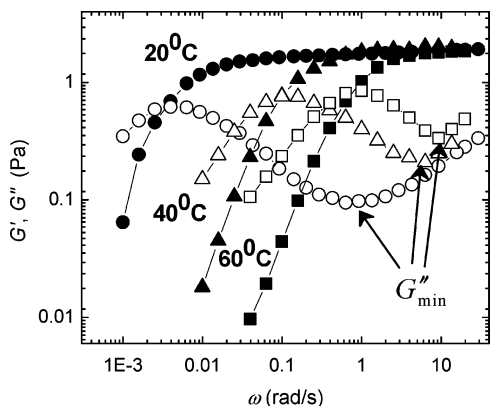


Figure 3. Effect of temperature on the dynamic frequency spectra of 1 wt % EHAC solutions. Storage moduli G' are shown by filled symbols; loss moduli G'' are shown by open symbols. Solvent: 3 wt % KCl in water.

segment. Scaling exponents obtained for concentration dependencies of different rheological characteristics in region III are also close to the theoretical values for the fast-breaking limit (Table 1).²¹ Thus, for concentrated samples ($C_{\text{EHAC}} > 0.5$ wt %) the rheology conforms to the Maxwell model.

At high surfactant concentrations ($C_{\text{EHAC}} > 0.5$ wt %) G' is higher than G'' in the whole studied frequency range, indicating the formation of physical gel. The modulus of elasticity of such a gel reaches the value of 7 Pa (at EHAC concentration of 1.8 wt %).

(1.2) *Effect of Temperature.* Figure 1 allows us to compare the dependencies of viscosity on surfactant concentration at two different temperatures. It is seen that the viscosity decreases by up to 2 orders of magnitude at heating from 20 to 60 °C. At the same time the dynamic frequency data (Figure 3) evidence that heating does not affect the value of plateau modulus G_0 , which means that the mesh size and hence the entanglement length l_e are unaffected by temperature. But simultaneously heating shifts the minimum value of the loss modulus G''_{min} to higher frequencies (Figure 3), indicating a decrease of the average contour length \bar{L} of micelles according to $G''_{\text{min}}/G_0 \approx l_e/\bar{L}$.²² Thus, the drop of viscosity at heating seems to be due to the shortening of the micelles.³⁹

Similar to the case of room-temperature measurements, at 60 °C the multiexponential stress relaxation regime switches to a monoexponential one upon increasing surfactant concentration above 0.4 wt % (Figure 4). Also, as it was observed at 20 °C, the rheological characteristics in the Maxwell region obey the scaling laws close to those predicted by Cate's theory²¹ (Table 1).

At the same time, some differences were found in the character of concentration dependencies of zero-shear viscosity at different temperatures. Figure 1 shows that above C^* the viscosity curve at 60 °C has only one slope (3.5) in contrast to the curve at 20 °C, which has two different slopes. It can be due to the acceleration of the dynamic process of breaking and recombination of micelles at elevated temperatures, as a result of which the region of the curve corresponding to the "unbreakable" chains (with slope 5.6) disappears.

(2) **VES with Polymer.** (2.1) *Phase Behavior.* In the concentration range under study (0.01–1 wt % surfactant, 0.1–1 wt % polymer) mixing of polymer and surfactant solutions can lead to a phase separation: the bottom phase is gellike, while the top phase is solution with low viscosity. Therefore, at first it was necessary to determine the

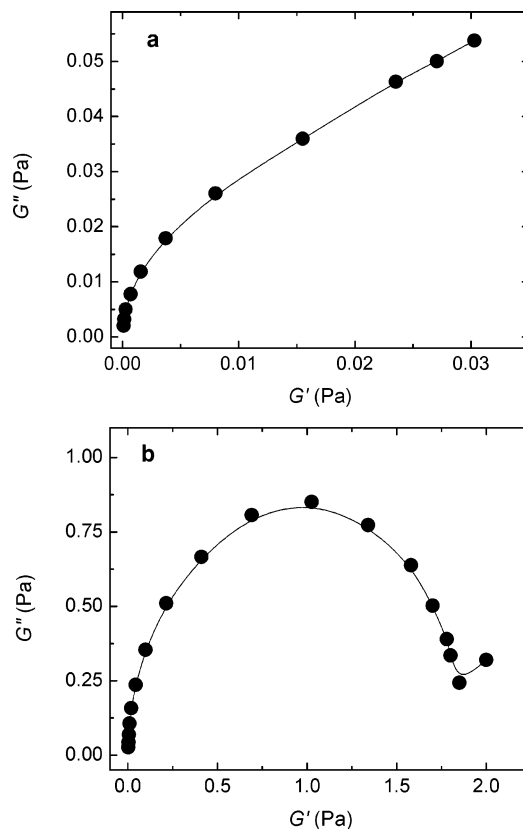


Figure 4. Cole–Cole plots for 0.3 (a) and 1 wt % (b) solutions of surfactant EHAC at 60 °C. Solvent: 3 wt % KCl in water.

conditions, at which polymer/surfactant systems are homogeneous.

It was observed that the area of miscibility of polymer/surfactant systems on the phase diagram depends significantly on the hydrophobicity of polymer. This area is quite small for unmodified PAAm, but it essentially widens with the increase of polymer hydrophobicity, i.e., with the increase of the content and of the chain length of hydrophobic n -alkyl substituents. For example, it increases in the following range of HM PAAm polymers: 0.2-C9, 0.1-C12, and 0.2-C12. This fact obviously indicates that the hydrophobic n -alkyl side chains of HM PAAm are involved in the interaction with surfactant.

For further rheological measurements we choose HM PAAm 0.2-C12, demonstrating the wider miscibility range among all polymers under study. The samples with two different degrees of blockiness in the distribution of hydrophobic groups along the backbone were prepared.

(2.2) *Effect of Added Polymer.* Figure 5 shows η_0 as a function of surfactant concentration in the polymer/surfactant system. For comparison the data for surfactant and polymer taken separately are presented as well. It is seen that the η_0 of the polymer/surfactant system can be up to 4 orders of magnitude higher than the viscosities of the pure-component solutions. It is connected with two effects induced by added polymer: (i) a significant shift of the onset of the strong rise of viscosity to lower surfactant concentrations and (ii) a strikingly sharp increase of η_0 with scaling law $\eta_0 \sim C^{12}$ (instead of $\eta_0 \sim C^{3.5}$ for pure surfactant). Such a sharp increase of viscosity may be due to the formation of a common network, in which some subchains are composed of elongated surfactant micelles, while other subchains are formed by polymer HM PAAm. At cross-links the hydrophobic C12 groups of polymer are penetrating in the surfactant micelles (Figure 6).

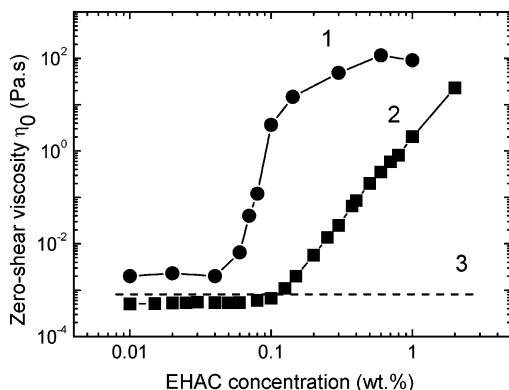


Figure 5. Zero-shear viscosity as a function of concentration of surfactant EHAC for the polymer/surfactant system (1) containing 0.5 wt % polymer 0.2-C12/0.4SA ($N_h = 1.1$) and for pure surfactant EHAC (2). The dotted line (3) shows the value of zero-shear viscosity for the 0.5 wt % solution of polymer 0.2-C12/0.4SA ($N_h = 1.1$) without surfactant. Solvent: 3 wt % KCl in water. Temperature: 60 °C.

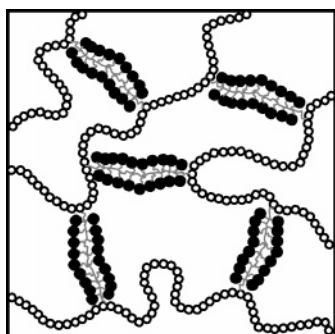


Figure 6. Schematic representation of common network formed by VES micelles and HM polymer chains. Hydrophobic side groups of polymer anchor into wormlike micelles.

The observed effect of crucial enhancement of viscosity of VES upon addition of polymer is quite different from the effect of a drop of viscosity at the addition of poly(vinyl methyl ether) (PVME) or poly(propylene oxide) (PPO) to wormlike micelles of cetyltrimethylammonium salicylate.³¹ The drop of viscosity was explained by polymer-induced transition from rodlike to spherical micellar aggregates. Probably, when polymers contain hydrophobic moieties in each repeat unit (like PVME or PPO), this favors the wrapping of polymer chains around the surface of surfactant aggregates, thereby reducing the unfavorable core–water contact at the surface of the micelles. Since the surface/volume ratio is larger for spherical micelles than for rods, polymer accumulated on the micelle surface induces the rod to sphere transition.³¹ By contrast, hydrophilic polymers that contain some hydrophobic segments, for example, poly(ethylene oxide) end-capped with *n*-octadecyl chain, do not alter the cylindrical structure of micelles.³⁸ Most probably, such polymers prefer to reside in water and contact with micelles only by hydrophobic units. Therefore, to get high viscosity in polymer/VES systems, it is necessary to use hydrophilic polymers with some fraction of hydrophobic units (like HM PAAm).

As it is suggested that the hydrophobic side chains of polymer are responsible for the interactions with surfactant, it is of particular interest to study how the distribution of hydrophobic units along the polymer chains affects the rheological behavior of the system. If the total content of hydrophobic groups is kept constant, random polymer will have a higher amount of “sticky” groups anchoring to surfactant micelles, while microblocky polymer will have

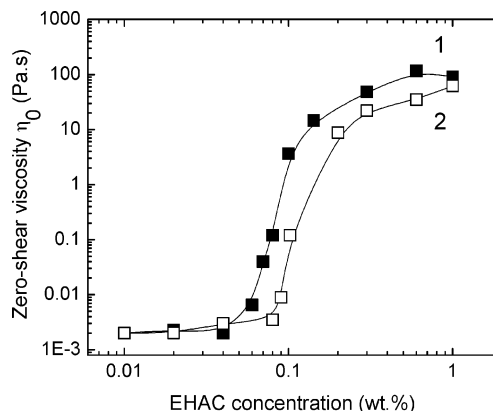


Figure 7. Zero-shear viscosity as a function of the concentration of surfactant EHAC for polymer/surfactant systems containing 0.5 wt % 0.2-C12/0.4SA polymer samples with different degrees of blockiness: $N_h = 1.1$ (1) and $N_h = 1.52$ (2) at 60 °C. Solvent: 3 wt % KCl in water.

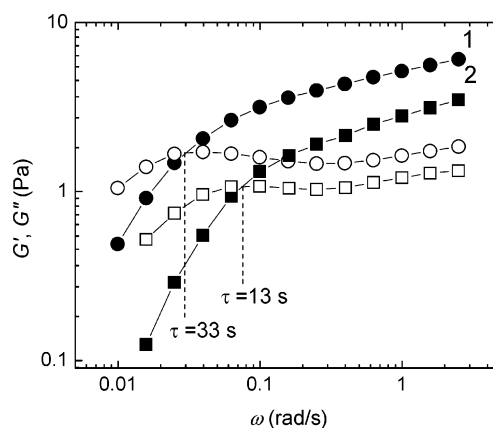


Figure 8. Dynamic frequency spectra of polymer/surfactant system containing 0.5 wt % polymer 0.2-C12/0.4SA and 0.6 wt % surfactant EHAC at 60 °C for two polymer samples differing in the degree of blockiness: $N_h = 1.1$ (1) and $N_h = 1.52$ (2). Storage moduli G' are shown by filled symbols; loss moduli G'' , by open symbols. The values of the longest relaxation times determined from the value of frequency at the intersection of G' and G'' are indicated. Solvent: 3 wt % KCl in water.

stronger sticky groups consisting of several adjacent hydrophobic side chains that can provide longer lifetime of cross-links.

Figures 7 and 8 allow us to compare two polymer/surfactant systems differing in the distribution of hydrophobic groups along the polymer chains. It is seen that the less blocky polymer ($N_h = 1.1$) imparts higher viscosity and higher elasticity modulus to the polymer/surfactant system in comparison with more blocky polymer ($N_h = 1.52$). Also, the system with less blocky polymer is characterized by longer relaxation time (Figure 8). The apparent behavior could be ascribed to a higher number of cross-links in the case of less blocky copolymer. The observed effect of blockiness of HM polymer is opposite to that found for associating polymers.⁵⁰ In these systems the dominant role is played by the lifetime of hydrophobic cross-links and the viscosity increases with increasing degree of blockiness. In the present system the lifetime of cross-links is determined by the breaking and recombination of wormlike surfactant micelles and is not affected very much by the time of residing of the polymer hydrophobic side groups inside the micelle.

(50) Regalado, E. J.; Selb, J.; Candau, F. *Macromolecules* **1999**, *32*, 8580.

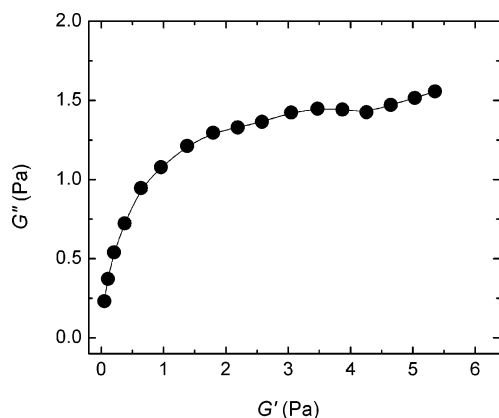


Figure 9. Cole–Cole plot for the polymer/surfactant system containing 0.5 wt % polymer 0.2-C12/0.4SA ($N_h = 1.1$) and 0.6 wt % surfactant EHAC at 60 °C. Solvent: 4 wt % KCl in water.

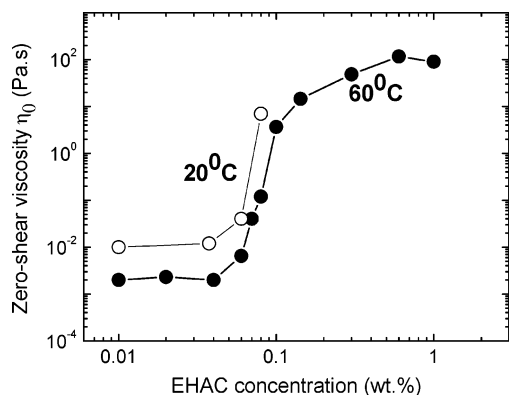


Figure 10. Zero-shear viscosity as a function of the concentration of surfactant EHAC for the polymer/surfactant system containing 0.5 wt % polymer 0.2-C12/0.4SA ($N_h = 1.1$) at two different temperatures: 20 and 60 °C. Solvent: 3 wt % KCl in water.

In contrast to pure surfactant, the polymer/surfactant system does not exhibit simple Maxwell behavior (Figure 9). So, the polymer/surfactant solutions have a spectrum of relaxation times similar to semidilute polymer solutions, while in pure surfactant solution a single relaxation time dominates (at EHAC concentration higher than 0.4 wt %).

(2.3) Effect of Temperature. Figure 10 shows the viscosity data for the polymer/surfactant system at two different temperatures (20 and 60 °C). It is seen that the viscosity decreases with temperature, but the decrease is much less pronounced than for surfactant EHAC itself without polymer (cf. Figures 1 and 10). Even at very low concentration of EHAC (0.1–0.3 wt %) the polymer/surfactant system at 60 °C has much higher viscosity than surfactant alone at 20 °C (cf. Figures 1 and 10). Therefore, the polymer/surfactant EHAC systems are much more stable with heating than surfactant itself, which is obviously due to the fact that polymer chains do not break and recombine like “living” chains of VES micelles.

(2.4) Effect of Salt. Figure 11 presents the dependence of viscosity of polymer/surfactant system on the concentration of added low molecular weight salt KCl. It is seen that the viscosity goes through a maximum with increasing KCl content. The analogous behavior is observed for pure surfactant (Figure 11, curve 2). Such behavior is not unusual and is exhibited by many aqueous surfactant/salt systems.^{1,13,16,40} The initial increase of viscosity at the addition of salt is explained by the increase of the micellar length due to the screening of electrostatic repulsion

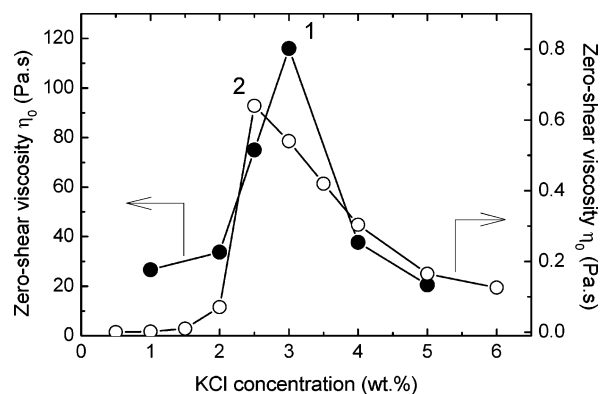


Figure 11. Zero-shear viscosity as a function of KCl concentration for the polymer/surfactant system (1) containing 0.5 wt % polymer 0.2-C12/0.4SA ($N_h = 1.1$) and 0.6 wt % surfactant EHAC and for pure surfactant EHAC (2) at the same concentration. Temperature: 60 °C.

Table 2. Viscosity of the Polymer/Surfactant System and of Pure Surfactant before and after the Contact with *n*-Heptane^a

concn, wt %		η_0 , Pa·s	
surfactant EHAC	polymer 0.2-C12/0.4SA	in absence of <i>n</i> -heptane	in presence of <i>n</i> -heptane
0.15	0.5	26 ^b	0.03
0.3	0.5	85.4 ^b	0.075
0.3	0	1.1	0.00105
1.0	0	355	0.00110
1.5	0	1200	0.00110

^a Solvent: 3 wt % KCl in water, temperature: 20 °C. ^b $|\eta^*|$ at 0.0016 Hz instead of η_0 .

between similarly charged headgroups. A further decrease of the viscosity is attributed to a transition from linear to branched micelles, when the electrostatic repulsion is sufficiently screened.⁵⁰ Branching shortens the average micellar lengths and makes the reptation faster because the branch points are free to slide along the micelles, which reduces the viscosity. From Figure 11 it is seen that the concentration of salt corresponding to maximum viscosity in the polymer/surfactant system is somewhat higher than in pure surfactant, which may indicate that the polymer at these conditions slightly hinders the branching process.

(2.5) Effect of Hydrocarbon. For possible applications in oil recovery it is important to study the behavior of polymer/VES aqueous solutions in contact with hydrocarbons. Hydrocarbons are immiscible with water, but they can diffuse into the hydrophobic interior of micelles affecting their size and form and thereby affecting the rheological parameters. To study the effect of hydrocarbons on polymer/VES solutions, the following experiment was performed. Aqueous polymer/VES solution was mixed with *n*-heptane and left to equilibrate for 3 days. During this period the system separates into two macroscopic phases (top, hydrocarbon phase; bottom, aqueous polymer/VES solution). Then polymer/VES solution was separated from hydrocarbon, and its rheological behavior was studied.

The values of the viscosity of the polymer/surfactant system before and after contact with *n*-heptane are presented in Table 2. It is seen that the addition of hydrocarbon leads to the decrease of viscosity by 3 orders of magnitude. At the same conditions a similar drop of viscosity is observed for the solution of pure surfactant (Table 2). In pure surfactant this behavior was attributed to the disruption of wormlike micelles induced by hydrocarbon penetrating into the hydrophobic interior of micelles.^{2,19} The change of the shape of EHAC micelles

from rods to spheres at contact with oil was proven by a cryotransmission electron microscopy.¹⁹

In the case of the polymer/surfactant system the drop of viscosity indicates that a significant number of the subchains of the polymer/surfactant system are formed exclusively by wormlike surfactant micelles. Breaking of the surfactant subchains as a result of transition from cylindrical to spherical micelles disrupts the network. So, the polymer/EHAC system keeps the responsiveness to hydrocarbon inherent to EHAC. A tremendous drop of viscosity of polymer/EHAC solutions in contact with hydrocarbons makes these systems promising as one of the main components of fracturing fluids in the oil industry.

Conclusions

Thus, experimental observations made in this paper indicate that addition of HM polymer enhances significantly the viscosity of EHAC especially at elevated temperature (60 °C); at the same time it does not affect the main advantage of EHAC—the drop of viscosity induced by contact with hydrocarbons. These properties make the polymer/VES system very attractive for the applications in oil recovery.

Acknowledgment. This research was supported by Schlumberger Co. via CRDF Grant No. RP0-1301. The authors thank Dr. T. Hughes for helpful discussions.

LA0482756