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Polymer-Surfactant Networks Highly Responsive to Hydrocarbons

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Summary: Hydrocarbon-sensitive hydrogels were prepared on the basis of networks, in which some subchains are composed of hydrophobically modified polyacrylamide, while others are made of long cylindrical surfactant micelles of potassium oleate. In these hydrogels, the polymer component strengthens the network, especially at elevated temperatures, whereas the surfactant component imparts a high responsiveness to the hydrocarbon medium. The rheological studies demonstrate that added hydrocarbons induce the transformation of the gel-like system to a fluid with low viscosity. SANS data evidence that the transformation is accompanied by the breaking of the cylindrical surfactant micelles, that leads to the disruption of the whole network.

Keywords: hydrogels; networks; self-assembly; surfactants; water-soluble polymers

Introduction

Among different kinds of responsive gels,[1,2] of particular interest are hydrogels responsive to hydrocarbons. They are very promising for many industrial applications, but, in particular, for the preparation of fracturing fluids[3,4] used in oil recovery to create and to fill up big subterranean fractures in oil-bearing strata. Such artificial fractures have much higher permeability with respect to oil in comparison with the rock. Also, they increase enormously the surface from which the oil is extracted. This allows one to enhance significantly the permeability and the productivity of the well. The fracturing fluids are composed of solid particles of sand or ceramics suspended in a physical gel that prevents the precipitation of particles. When oil is forced to flow through the fracture, it disrupts partially the gel, forms the channels between loosely packed particles and freely flows to the well bore. To ensure such high permeability, hydrocarbon-sensitive gels are needed.

Hydrocarbon-sensitive gels can be composed of entangled long cylindrical micelles of surfactant.[4] Micellar chains formed due to weak non-covalent interactions can be easily rearranged upon absorption of hydrocarbon, which may lead to the disruption of the surfactant network. However, such gels are also responsive to many other stimuli. In particular, they are destroyed at elevated temperatures,[5] such as those encountered in subterranean reservoirs.

We propose to construct gels responsive to hydrocarbons on the basis of networks, in which some subchains are composed of polymer, while others are made of long cylindrical surfactant micelles. In these gels, the polymer component would strengthen the network, especially at elevated temperatures, whereas the surfactant component would impart a high responsiveness to the hydrocarbon medium. Here, hydrophobically modified poly(acrylamide) (HM PAAm) is used as a polymer and potassium oleate as a surfactant.

The paper is organized as follows. In the first part, we describe the properties of the networks formed by the surfactant itself. In

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the second part, we show how these properties are modified, if some of the micellar chains are replaced by polymeric chains.

Experimental Part

Potassium oleate from Aldrich was used without further purification. Its critical micelle concentration in water is 7 – 14×10^{-4} mol L^{-1}.[6,7] HM PAAm containing 84.2 mol % of acrylamide units, 15 mol % of sodium acrylate units and 0.8 mol % of *n*-dodecylacrylamide units was synthesized by free-radical micellar copolymerization as described elsewhere.[8–11] Its molecular weight is equal to 8×10^5 g mol^{-1} as was determined by gel permeation chromatography.[11]

To study the effect of hydrocarbons the samples were prepared as follows. Potassium oleate or HM PAAm/potassium oleate aqueous solution (3 mL) was mixed with hydrocarbon (3 mL) and left to equilibrate for 1 day. During this period the system separates into two macroscopic phases (top – hydrocarbon phase, bottom – aqueous solution saturated with hydrocarbon). Subsequently, the aqueous solution was removed from the hydrocarbon, and its properties were studied.

Rheological measurements were carried out on a controlled stress Rheometer Haake 150 L. In static shear measurements, the shear stress was varied in the range 0.002 – 100 Pa. For small stress values, the experiments were carried out with double-gap coaxial cylinders (cup of 20.28 mm diameter, bob 18 mm, and height of 55 mm), while for higher stresses, a cone-plate sensor with diameter of 35 mm and a cone angle of 2° was used. Dynamic shear measurements were taken over the frequency range 0.001 – 10 Hz using a cone-plate sensor. The values of the stress amplitude were checked in order to ensure that all measurements are made within the linear viscoelastic region, where the dynamic storage modulus (G′) and loss modulus (G″) are independent of the applied stress.

SANS experiments were performed using a two-detector YuMO instrument of high-flux pulsed reactor IBR-2 at Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia. The data were recorded in the range of the scattering vectors q of 0.009 – 0.5 $Å^{-1}$. The details of the experiments are described elsewhere.[11–14] For fitting the experimental curves by different models, the program "Fitter" was used.[11]

Results and Discussion

Surfactant Networks

Let us consider the properties of networks composed exclusively of micelles of anionic surfactant potassium oleate in 6 w % KCl aqueous solutions.

Figure 1a shows the zero-shear viscosity as a function of surfactant concentration at 20 °C. The viscosity remains close to that of pure water until the surfactant concentration reaches 0.105 w %, but then it increases dramatically. This is due to the transition from the dilute to the semi-dilute regime, when the wormlike micelles start to overlap.[11,15] The presence of entangled wormlike surfactant micelles under these conditions was confirmed by cryo-TEM.[16]

In the semidilute regime, two distinct slopes on the log-log concentration dependence of viscosity were found: 5.3 and 3.3 (Figure 1a). Up to now, in most of the

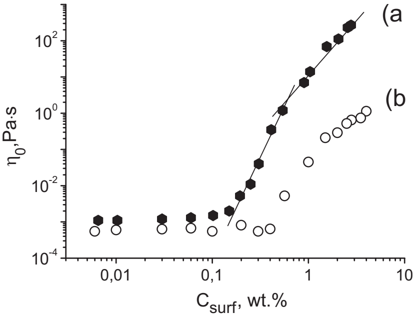

Figure 1.
Zero-shear viscosity η_o as a function of the concentration of potassium oleate at 20 °C (a) and at 60 °C (b). Solvent: 6 w % KCl in water.

papers, only one slope was observed, 3.5. This slope corresponds to the so-called regime of breaking chains.[17] It is well-known that micellar chains are ‘‘living’’ objects: they incessantly break and recombine. The regime of breaking chains means that the breaking time of the micelles is much shorter than the reptation time: $\tau_{break} << \tau_{rep}$.

In our work, in addition to this well-known slope, we also observed another slope equal to 5.3. This slope perfectly corresponds to the theoretical predictions for the co-called regime of unbreakable chains,[18,19] for which the breaking time is much longer than the reptation time: $\tau_{break} >> \tau_{rep}$. This is one of the first experimental observations of the transition from unbreaking to breaking micellar chains. The transition takes place at increasing surfactant concentration. Indeed, when the concentration of surfactant increases, the micelles become longer; therefore, their reptation time increases, while the breaking time decreases, thus approaching the fast breaking regime: $\tau_{break} << \tau_{rep}$.

The same two exponents were recently observed also for the cationic surfactant erucyl bis(hydroxyethyl)methylammonium chloride,[5] indicating that a two-slope concentration dependence of viscosity of semidilute solutions of surfactant is inherent to several surfactants independently of their chemical nature.

Figure 1a shows that the viscosity of surfactant solutions can be higher than that of pure water by 5 orders of magnitude. Such systems represent physical gels formed by entangled surfactant micelles. Figure 2a illustrates the network nature of the material, which does not flow upon the inversion of its container.

For such gel-like systems, the storage modulus is higher than the loss modulus in most of the studied frequency range, and a plateau is observed on the frequency dependence of the storage modulus (Figure 3).

The fact that surfactant micelles incessantly break and recombine makes the viscoelastic properties of the surfactant highly responsive to the variation of the external conditions, for instance, temperature and presence of additives. For example, heating from 20 to 60 °C leads to the drop of viscosity by two orders of magnitude (Figure 1). It was shown[11] that this is due to the shortening of surfactant micelles at increasing temperature.

Much more pronounced is the effect of hydrocarbons. Table 1 shows that the addition of hydrocarbon leads to the drop of viscosity by up to 5 orders of magnitude, independently of the type of hydrocarbon (*n*-heptane or *n*-dodecane). This effect is quite spectacular. Before the addition of hydrocarbon, we have a gel-like system. As soon as a few drops of hydrocarbons are added, the gel instantaneously transforms to a fluid with low viscosity (Figure 2).

To understand the reason for such behavior, the SANS technique was employed.[11] For enhanced contrast, heavy

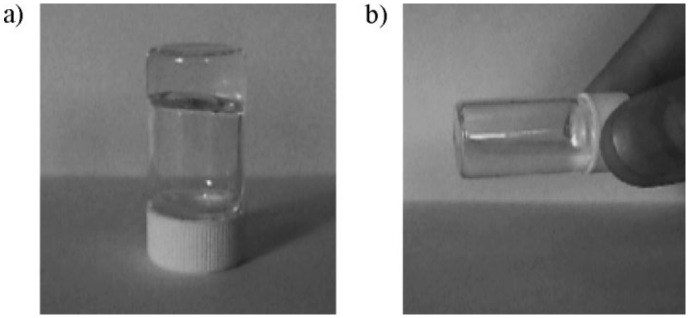

Figure 2.
3 w % solution of potassium oleate before (a) and after (b) the addition of *n*-dodecane.

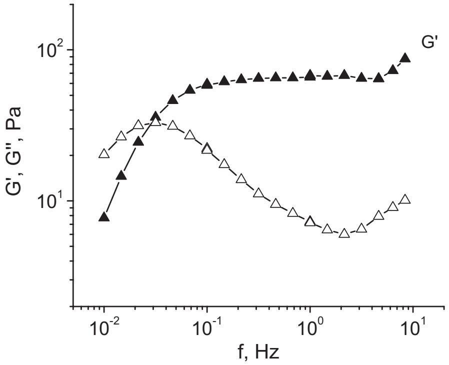

Figure 3.
Frequency dependences of the storage and loss moduli of 3 w % potassium oleate solution at 20 °C. Solvent: 6 w % KCl in water.

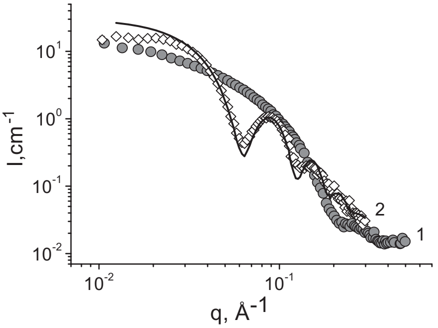

Figure 4.
SANS profiles for 3 w % potassium oleate solutions before (1) and after (2) the addition of deuterated cyclohexane at 20 °C. The line shows the fit of the curve by a spherical shell with a thickness of 18.5 Å and an inner radius of 43 Å. Solvent: 6 w % KCl in D_2O.

water was used as the solvent. The changes of the SANS curve of potassium oleate solutions upon the addition of deuterated hydrocarbon are illustrated in Figure 4. The treatment of these data evidences that in the initial solution the scattering objects are cylinders with radii close to the length of the alkyl tail of the surfactant (19 Å). Upon addition of hydrocarbon, the scattering curve can be well-fitted to a model of a spherical shell with a thickness of 18.5 Å and an inner radius of 43 Å. This indicates that the cylindrical micelles are transformed into hydrocarbon emulsion droplets surrounded by a layer of surfactant molecules.

Thus, the enormous drop of viscosity upon addition of hydrocarbons is due to the breaking of the cylindrical micelles, which leads to the disruption of the network structure. This property is very important for fracturing fluids, especially at the stage when the porous space between sand particles should be cleaned up to allow oil to drain to the well bore.

Polymer-Surfactant Networks

We just considered the properties of the surfactant itself. Now let us see, what will happen if some of the micellar chains are replaced by the polymeric chains of HM PAAm. At first, the phase behavior of the polymer/surfactant system was studied. It was shown that, to avoid phase separation, the HM PAAm instead of pure PAAm should be used. This indicates that the hydrophobic side chains of the polymer interact with the surfactant.

Figure 5 shows the effect of added polymer on the dependence of the zero-shear viscosity on the surfactant concentration. In the system, we fix the concentration

Table 1.
Zero-shear viscosity η_0 of potassium oleate solutions before and after the addition of *n*-heptane and *n*-dodecane at 20 °C. Solvent: 6 w % KCl in water.

Potassium oleate concentration	η_0 before the addition of hydrocarbon	η_0 after the addition of *n*-heptane	η_0 after the addition of *n*-dodecane
w %	Pa·s	Pa·s	Pa·s
0.3	0.04	0.0011	0.0011
0.4	0.35	0.0012	0.0011
1.0	14	0.0012	0.0012
1.5	51	0.0014	0.0015
2.0	117	0.0012	0.0012
3.0	315	0.0012	0.0013

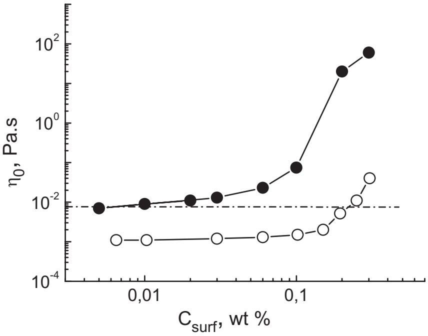

Figure 5.
Effect of surfactant concentration on the zero-shear viscosity of potassium oleate (open symbols) and the HM PAAm / potassium oleate system (filled symbols) containing 0.5 w % of polymer at 20 °C. The dotted line shows the value of zero-shear viscosity for a 0.5 w % solution of polymer. Solvent: 6 w % KCl in water.

of polymer at 0.5 w % (this is of the order of the C* value), we fix the concentration of low molecular weight salt KCl at 6 w % and we vary only the concentration of surfactant. It is seen that the viscosity of the mixed system (filled symbols) becomes by 3-4 orders of magnitude higher than the viscosities of polymer or surfactant taken separately (open symbols and dotted line). This result is not quite expected, because up to now the addition of polymer usually led to the drop of the viscosity instead of its increase.[20,21]

Thus, the large increase in the viscosity of the system upon addition of polymer may be due to the formation of a common network, in which some subchains are composed of surfactant micelles, while others are formed by polymer. At the cross-links, the hydrophobic *n*-dodecyl groups of the polymer are penetrating in the surfactant micelles. The fact that the cylindrical structure of micelles is preserved in the mixed system was confirmed by SANS.[11]

The dynamic rheological data demonstrate[11] that in the polymer/surfactant system, when comparing to pure surfactant, both the components of the complex elastic modulus increase by one order of magnitude. Also, the crossover point of the $G'(\omega)$ and $G''(\omega)$ curves shifts to lower frequencies indicating longer relaxation times in the surfactant/polymer system. This behavior was ascribed[11] to an increased number of cross-links upon addition of polymer.

Figure 6 shows dynamic rheological data for pure surfactant and polymer/surfactant systems at elevated temperature (60 °C). It is seen that, in the absence of polymer, the loss modulus G“ dominates in most of the studied frequency range. In contrast, the mixed system still demonstrates a gel-like behavior: G’ displays a plateau and G’ is higher than G” in most of the studied frequency range. This is due to the fact that polymer chains formed by strong covalent bonds do not break and recombine like micellar chains.

At the same time, the mixed system keeps the responsiveness to hydrocarbons inherent to pure surfactant. The contact of the mixed system with hydrocarbon results in the drop of viscosity by 4 orders of magnitude (Figure 7). This indicates that a significant number of subchains of the mixed system are formed exclusively by surfactant micelles. Breaking of these cylindrical micelles disrupts the whole network. Thus, the susceptibility of the surfactant to hydrocarbon remains after the addition of HM PAAm.

The hydrocarbon induced disruption of wormlike micelles in the polymer/surfactant

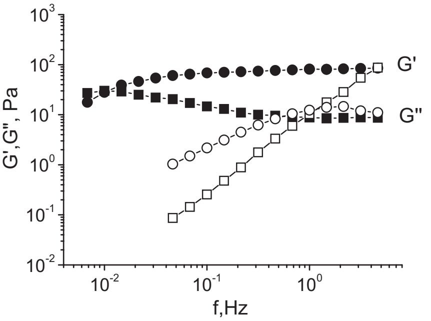

Figure 6.
Frequency dependences of the storage G’ and the loss moduli G” of 2.8 w % potassium oleate (open symbols) and HM PAAm / potassium oleate system (filled symbols) containing 0.5 w % of polymer and 2.8 w % of surfactant at 60 °C. Solvent: 6 w % KCl in water.

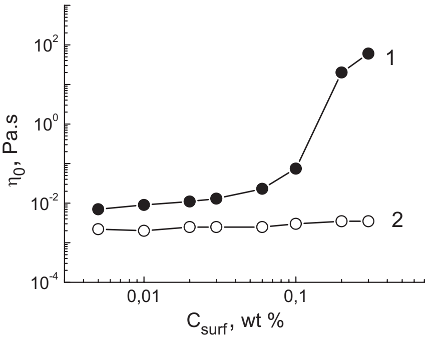

Figure 7.
Zero-shear viscosity of the HM PAAm / potassium oleate system as a function of the concentration of the surfactant before (1) and after (2) the addition of *n*-dodecane at 20 °C. Solvent: 6 w % KCl in water.

system was proved by SANS (Figure 8). It was shown that upon addition of deuterated hydrocarbon, the cylindrical micelles are transformed into emulsion droplets with an inner radius of 44 Å, surrounded by a layer of surfactant molecules with thickness close to the length of the alkyl tail of the surfactant (17.5 Å). Thus, the transformation of micelles upon addition of hydrocarbon in the polymer/surfactant system is similar to that in pure surfactant. Moreover, the size of the micelles and of the emulsion droplets is almost unaffected by the polymer.

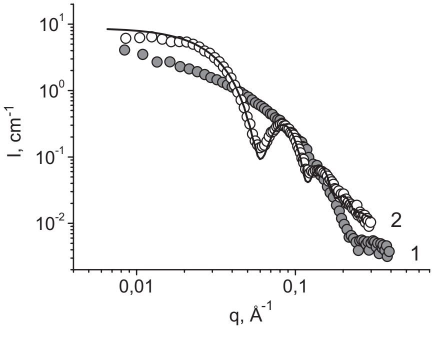

Figure 8.
SANS profiles for the polymer/surfactant system containing 0.7 w % potassium oleate and 0.5 w % HM PAAm before (1) and after (2) the contact with deuterated cyclohexane at 20 °C. The line shows the fit of the curve by a model of a spherical shell with a thickness of 17.5 Å and an inner radius of 44 Å. Solvent: 6 w % KCl in D_2O.

Conclusion

It was shown that the replacement of some of the surfactant cylindrical micelles in potassium oleate networks by polymer chains of HM PAAm enhances significantly the viscosity of the network, especially at elevated temperature (60 °C), without affecting the main advantage of the surfactant network: the drop of viscosity induced by hydrocarbons. These properties make the polymer/surfactant hydrogels very attractive for application in oil recovery.

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