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Fluorocarbon polymerizable surfactants: viscometric behavior, micellar polymerization and interactions with associating polymers

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Abstract The micellar aggregation of two fluorocarbon surfactants bearing a polymerizable acrylamido group and differing only in the degree of amido substitution (CONH or $CONC_2H_5$) has been investigated by viscometry. The two surfactants exhibit distinct solution properties with a micellar growth occurring at a much lower concentration for the *N*-monosubstituted sample which shows in addition a shear thickening and rheopectic behavior. The ability of the latter surfactant to form hydrogen bonding is responsible for this difference in behavior. Micellar copolymerization of acrylamide with these surfactants or with a hydrocarbon analogue gives copolymers with a polysoap-like behavior. The copolymers in aqueous solution show a pronounced intramolecular hydrophobic aggregation expressed by relatively low-viscosity values when compared with those of other hydrophobically modified water-soluble polymers reported in the literature. Surfactant–polymer mixed systems do not show a strong incompatibility between fluorocarbon and hydrocarbon moieties.

Key words Fluorocarbon polymerizable surfactants – worm-like micelles – viscometric behavior of flurocarbon surfactants – micellar polymerization – acrylamide copolymers – polymer–surfactant interactions

Introduction

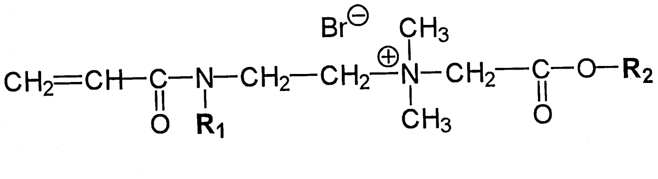
Fluorocarbon surfactants exhibit distinct micellization properties from those of analogous hydrocarbon surfactants. Besides a pronounced hydrophobicity of the fluorocarbon chains that leads to a large increase in surface activity, their bulkiness increases the molecular packing parameter and enables the organization into worm-like micelles or vesicles at relatively low surfactant concentrations in salt-free aqueous solutions. For example, cylindrical micelles are formed in aqueous ammonium perfluoro-octanoate solutions with hexagonal packed head groups and helical ordered chains, whereas the hydrocarbon analogues form spherical micelles [1]. Single-chain perfluorinated phosphocholines without additional stiffening elements (usually biphenyl or azobenzene groups) form lamellar double layers that are visible as viscoelastic gels at surfactant concentrations of 3 wt% [2, 3].

During the last decade, numerous physico-chemical studies have focused on the rheological behavior of worm-like micelles [4–14]. In the semi-dilute regime, the entangled flexible micelles provide viscoelastic properties [4–9]. In dilute aqueous solutions of certain types of ionic surfactants, different micellar microstructures, preformed in solution or induced by flow, may exhibit different flow behaviors [10–12, 14]. Most often, material orientation in flow direction is accompanied by a decrease in viscosity (shear thinning effect). In some rare cases, an increase of the apparent viscosity (shear thickening effect), of the rheopexy and of the flow birefringence are observed at concentrations around the overlap concentration [10–12, 14]. This is due to a simultaneous micellar growth and a shear-induced phase separation into surfactant-rich gels and surfactant-poor phases [14].

In a previous paper, we reported the solubilization of pyrene and of a fluorocarbon dye (4-trifluoromethyl) (4-(*N*-1H, 1H, 2H, 2H perfluorooctyl)carbamatophenyl)diazene) in equally concentrated micellar solutions of cationic polymerizable fluorocarbon (FS3) and hydrocarbon surfactants (HS2) of similar chemical structure [15] (see Scheme 1). The uptake of pyrene in HS2 micelles was found to increase linearly as a function of surfactant concentration above the cmc. This behavior is common for solutions of conventional amphiphiles that form spherical micelles and do not change significantly in size with increasing surfactant concentrations [16]. On the other hand, in FS3 fluorocarbon surfactant solutions, a relatively small maximum in the fluorocarbon dye uptake was observed at a concentration slightly above the cmc and another sharp increase occurred above 0.4 wt% of FS3 in water. This dramatic change in solubilization capacity was accounted for by a strong micellar growth caused by a transition from spherical to cylindrical micelles [15, 16]. The micellization of those surfactants being susceptible to form rod-like aggregates should be particularly influenced by weak attractive forces such as hydrogen bonds, favoring intermolecular associations especially if these forces are cooperative.

The aim of the first part of this study was to investigate the differences in aqueous solution properties of two fluorocarbon surfactants of similar chemical structure, FS3 and FS5, differing only in the degree of acrylamido function substitution (Scheme 1). The monosubstituted FS3 surfactant is able to form hydrogen bonds due to its CONH group in contrast to the disubstituted FS5 surfactant that contains the CONR function. The second part of this study deals with the radical micellar copolymerization of these hydrocarbon or fluorocarbon surfactant monomers (surfmers) with an excess of a water-soluble monomer such as acrylamide. This process allows one to prepare a variety of hydrophobically modified water-soluble polymers. A viscometric study has been performed on these copolymers, both in the absence and in the presence of fluorocarbon and hydrocarbon surfactants. The results provide some information on the influence of the hydrophobicity of fluorocarbon and hydrocarbon moieties on the aggregation properties in aqueous solution. Moreover, the interactions between the copolymers and the various monomeric surfactants are expected to depend on the nature of the hydrophobic surfactant tail due to the mutual incompatibility between fluorocarbon and hydrocarbon chains.

Scheme 1 Structure and nomenclature of the polymerizable surfactants



$$CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{R_1}{|}}{N}{-}CH_2{-}CH_2{-}\overset{Br^{\ominus}\;\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{\oplus}{N}}}{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}O{-}R_2$$

FS3: $R_1 = H$, $R_2 = C_2H_4C_8F_{17}$

FS5: $R_1 = C_2H_5$, $R_2 = C_2H_4C_8F_{17}$

HS2: $R_1 = H$, $R_2 = C_{14}H_{29}$

Materials and methods

The fluorocarbon (FS3, FS5) and hydrocarbon (HS2) surfactants of *N*-alkoxycarboxymethyl, *N*-[2′-(*N*-alkylacrylamido) ethyl], *N*,*N*-dimethyl ammonium bromide type (Scheme 1) have been synthesized as described previously [15]. Acrylamide, received from Aldrich, was recrystallized three times from chloroform before polymerization. 4-4′-azobis(4-cyano valeric acid) (ACVA, Aldrich) was recrystallized from ethanol. Deionized water of a conductivity $<1\ \mu S$ and a surface tension of 72.8 mN/m (25 °C) was obtained from a Millipore system. The polyacrylamide ($M_w = 10^6$) which was hydrophobically modified with 1 mol% of dihexylacrylamide and 0.07 mol% of *N*-[4-(1-pyrenyl)butyl]-*N*-*n*-hexyl-acrylamide was a gift from Ian Harrison.

Polymerization reactions were carried out at 50 °C in a 200 ml thermostated glass reactor equipped with a nitrogen inlet, a stirrer and a condenser. Acrylamide (3 g, 0.0422 mol) and 1 or 2 mol% of the polymerizable surfactant based on acrylamide (either HS2, FS3 or FS5) were dissolved in water to give a 2 g/dl solution and purged with nitrogen for 1 h at room temperature. The reaction was initiated by the addition of ACVA (96 mg, 3.3×10^{-4} mol) and the polymerization was complete after 4 h. The polymers were precipitated in a methanol/acetone mixture, of equal volumes, and washed three times with the same solvent mixture in order to remove unreacted monomers and initiator. The polymer was dried under vacuum for 48 h at 30 °C. The amount of surfmer incorporated in the copolymers was determined by bromine elemental analysis. The nomenclature used for the copolymers refers to the nature and content of the surfmers in the monomer feed. For example, FS3P2 stands for a copolymer containing 2 mol% of FS3.

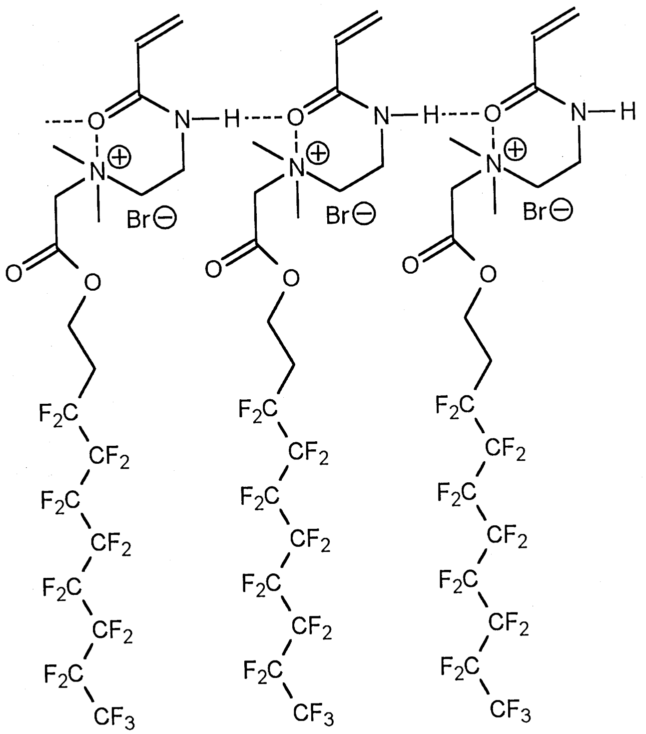
Molecular weights of the polymers were determined by static light scattering in formamide as described elsewhere [17]. The viscosity measurements were performed at 25 °C in a Couette cell using a Contraves LS 30 low-shear rheometer. The samples were prepared by gently stirring the surfactants or the polymers in deionized water for 3 days. The surface tension of the surfactant solutions were measured with a Lauda Tensiometer at 20 °C using the du Nouy ring method.

Results and discussion

Scheme 1 shows the chemical structure of the cationic fluorocarbon surfactants and a similar hydrocarbon amphiphile (HS2) containing a C14 alkyl chain. The two fluorocarbon surfactants differ only in the degree of acrylamido function substitution. A short hydrophobic ethyl group was introduced into the polar head group of the FS5 surfactant instead of the H for FS3. Therefore, only the FS3 surfactant is able to form hydrogen bonds via the amido function. Single hydrogen bonds between fully dissolved molecules in aqueous solution are not favoured in comparison to the multitude of possible interactions with water [18]. However, hydrogen bonding between head groups of amphiphilic substances may play an important role for molecular self-organization as previously shown for example with lipid and cholesterol derivatives [19, 20]. For the fluorocarbon surfactants discussed here, a special type of H-bonding can be assumed. Due to the acrylamido function which acts both as a proton donor and acceptor, and also due to the strong self-aggregation tendency of the fluorinated amphiphiles, cooperative hydrogen bonding can occur (Scheme 2). These interactions are known to be generally much stronger than isolated H bonds involving the same type of donor and acceptor atoms.

Critical micelle concentration and surface activity

In a previous study, the cmc values and the free energies of micellization at 25 °C were determined by conductivity measurements and found to be 0.77 mM and 55.4 kJ/mol for FS3, and 0.56 mM and 57.0 kJ/mol for FS5, respectively [15]. The slightly larger hydrophobicity of FS5 is caused by the presence of the ethyl group in the polar head of this surfactant. Furthermore, it can be assumed that in extremely dilute surfactant solutions ($C \ll \mathrm{cmc}$) H-bonding between FS3 and water increases the solubility of this compound. The adsorption isotherms of FS3 and FS5 solutions (Fig. 1) reveal a much more pronounced efficiency in reducing the surface tension γ of the water/air interface as compared to the hydrocarbon amphiphile homologues. For instance, the surface tension value at the cmc is $\gamma_{\mathrm{cmc}} = 17$ mN/m for FS3 and $\gamma_{\mathrm{cmc}} = 32$ mN/m for the corresponding hydrocarbon surfactant (HS2) [15]. This behavior is well known for fluorinated surfactants [21] and results from the higher hydrophobicity of the fluorocarbon chains. Furthermore, the FS3 surfactant exhibits a higher surface activity than FS5 (γ_{cmc} is 3.5 mN/m lower, Fig. 1). This additional lowering of the surface tension is caused by cooperative hydrogen bonds between the FS3 molecules at the water/air interface, even though both fluorocarbon molecules are almost identical. Such a clustering trend should reduce the contact between water and the hydrophobic surfactant tail, and thus, increase the stability of the surface layer. Less energy will be needed for a surface/bulk exchange of single surfactant molecules than for the motion of mutually interacting molecules. The apparent contradiction between surface behavior and bulk properties in dilute solutions of FS3 and FS5 shows that H-bonding becomes only relevant as a secondary effect for molecular organization. The most important feature in this case is the self-aggregation due to strong hydrophobic interactions, either in surface films or in micelles.



Scheme 2 Schematic representation of H-bond interactions between surfactant head-groups

The surface area occupied by one surfactant molecule at the water/air interface is given by the slope $\mathrm{d}\gamma/\mathrm{d}\ln C$ of the descending section of the isotherm. For the CONH-containing FS3 surfactant, the calculated area is 0.70 nm^2.

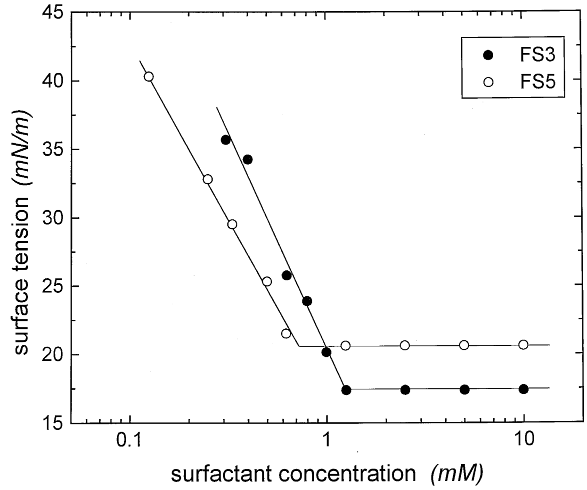


Fig. 1 Variation of the surface tension as a function of surfactant concentration for FS3 and FS5 fluorocarbon surfactants in aqueous solution ($T = 30\,^\circ\mathrm{C}$)

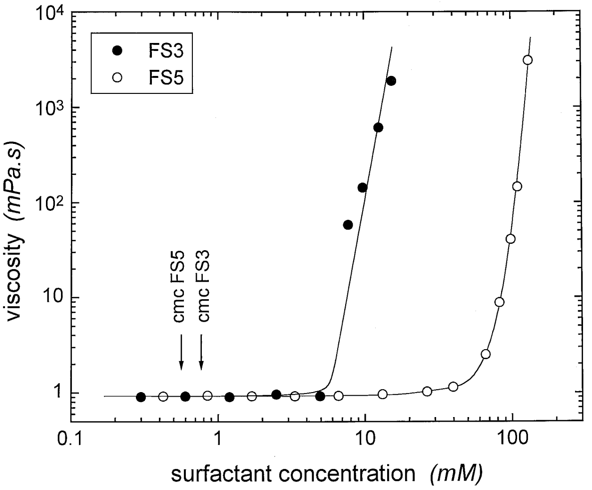


Fig. 2 Variation of the viscosity as a function of surfactant concentration for FS3 and FS5 fluorocarbon surfactants in aqueous solution ($\dot{\gamma} = 0.1\,\mathrm{s}^{-1}$, $T = 25\,^\circ\mathrm{C}$)

For the disubstituted FS5 surfactant, the head group area increases to 0.79 nm^2. This difference may be attributed to two distinct phenomena: an additional surface area contribution of the ethyl group (FS5) and/or a tighter packing of the molecules in the adsorption layer due to mutual H-bonding (FS3). In fact, the maximal surface area increase in terms of the geometry of the ethyl-group compared to H can only be 0.06 nm^2 for the FS5 surfactant. However, this maximal area increase is likely to be reduced if the ethyl groups of several neighbouring head groups overlap or interact with the vinyl functions. The six-ring structure, previously proposed for this type of cationic acrylamido surfactants (interaction between the quaternary ammonium ion and the amido group), would enhance this possibility [15]. Therefore, the contribution of the ethyl group to the surface area of the FS5 surfactant alone cannot explain the difference observed between the two surfactants. It is likely that cooperative H-bonding causes a decrease of the surface area occupied per molecule. This increases the molecular packing parameter and should affect the bulk behavior of FS3 micellar solutions, since it can be assumed that the molecules occupy a similar area in micelles and in films [22].

Rheological properties of the fluorocarbon surfactants in aqueous solutions

The behaviors of FS3 and FS5 micellar solutions in a salt-free aqueous medium are quite different. Aqueous solutions of FS3 surfactant need to equilibrate several days whereas FS5 is dissolved after a few minutes. FS3 solutions under shearing show optical birefringence for concentrations larger than 0.5 wt% (6.9 mM). After shearing, the birefringence relaxes over a period of some minutes to several hours. Conversely, the FS5 solutions do not show any shear-induced birefringence.

Figure 2 shows the viscosity of FS3 and FS5 aqueous solutions ($\dot{\gamma} = 0.1\,\mathrm{s}^{-1}$), plotted as a function of surfactant concentration. In the dilute regime, the viscosity of both solutions is close to the value of pure water, indicating that micelles in both cases are well separated and of spherical or ellipsoidal shape. The break points in the curves are generally related to the C^* concentration at which small ellipsoidal micelles tend to grow rapidly into large cylindrical aggregates [4, 5, 9, 23]. The large increase in viscosity with increasing surfactant concentration beyond C^* is attributed to entanglement of worm-like micelles.

From the data of Fig. 2, the C^* concentration is ≈40 mM (3 wt%) for the FS5 surfactant. Note that the onset of micellar growth occurs at much lower concentrations in these solutions of fluorocarbon ionic surfactants than in those of classical hydrocarbon surfactants as long as the latter do not hold strongly binding organic counterions [4, 24]. This is due to the smaller volume of the hydrocarbon chains compared to the fluorinated ones. Consequently, the spherical curvature is favored for the hydrocarbon surfactants owing to a smaller molecular packing parameter $V/(A \times L)$ (V being the volume of the hydrophobic surfactant chain, A the head group area and L the optimal length close to the fully extended chain length). For the fluorocarbon molecules, the spherical geometry is energetically unfavored, and the parallel ordering in cylindrical micelles is preferred.

In Fig. 2 it can also be observed that, for FS3 solutions, the C^* concentration is very low (≈ 6 mM $\equiv 0.45$ wt%), almost one order of magnitude lower than that found of FS5. This result confirms previous solubilization studies: the capacity of FS3 micellar solutions to solubilize a fluorocarbon dye increases strongly beyond C^* [15]. In accordance with the literature, such a sharp increase of micellar solubilization efficiency can be attributed to the existence of cylindrical micelles with high aggregation numbers [16]. The increased tendency of FS3 to form elongated micelles is a consequence of the reduced head group area due to H-bonding between surfactant molecules in the micelles.

Further significant differences between FS3 and FS5 micellar solutions appear in flow experiments. In FS5 solutions, the viscosity remains constant in the range of shear rates investigated, up to high surfactant concentrations (10 wt%) (Fig. 3A). For FS3 solutions, the Newtonian flow is only observed at concentrations below the cmc (Fig. 3B), whereas a shear thickening effect is observed at concentrations ranging between $\approx 2 \times$ cmc and $\approx C^*$. Above a critical shear rate, which is shifted to lower values with increasing FS3 concentrations, the viscosity rises to maximum and falls again. For concentrations higher than C^*, the shear thickening effect disappears and the micellar solutions exhibit above $0.01\,s^{-1}$ a shear thinning behavior, as classically observed for entangled worm-like micelles or polymer solutions.

The shear-thickening effect observed for the FS3 sample below C^* is accompanied by a rheopectic behavior. Figure 4 shows an illustration of the time dependence of the viscosity measured at a given shear rate of $10\,s^{-1}$ for FS3 and FS5 solutions at various concentrations. The viscosity is time independent for FS5 solutions whereas a large increase in viscosity is observed for FS3 solutions with relaxation times in the order of some minutes.

All these features have already been observed in more classical hydrocarbon surfactant systems [4, 5, 10, 11, 14, 23–28]. The explanation of this effect is not clear at the moment. It was first suggested that the observed shear-induced transition was due to the alignment of small rod-like micelles which undergo collisions in the shear flow and adhere for some time [4, 5, 26, 28]. More recent experiments of Oda et al. by optical observations and electron microscopy on gemini surfactants suggest that this shear effect is linked to a phase separation between small surfactant-rich gel domains and a surfactant-poor continuous phase [14]. Under shear, the gel phase occupies more and more space and when the network extends to the gap of the cell, shear thickening occurs. The shear thinning which takes place at higher shear rates is attributed to the disruption of the gel phase [14].

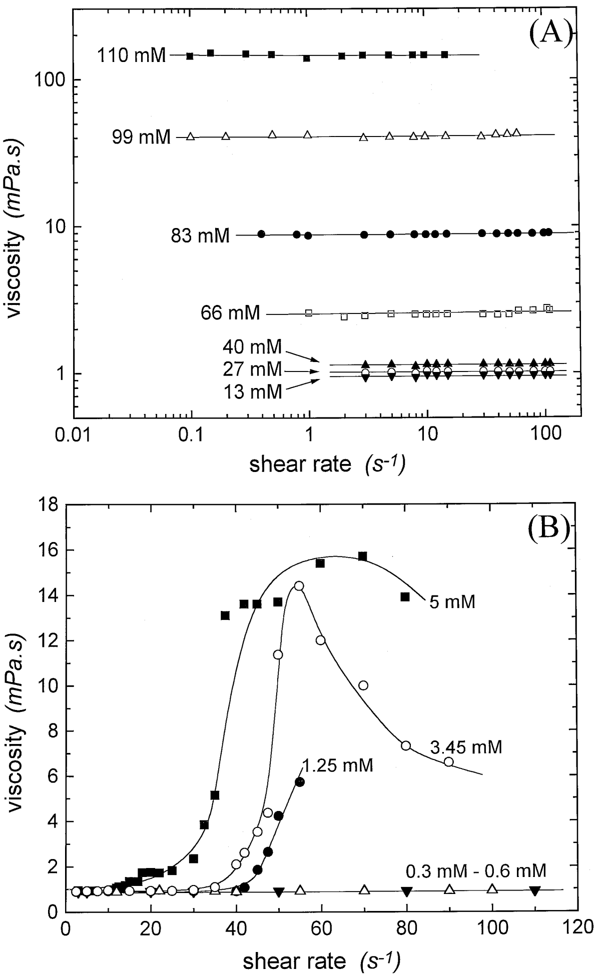


Fig. 3 Effect of shear rate on the viscosity for aqueous solution of FS5 (A) and FS3 (B) surfactants at various concentrations (mM) ($T = 25\,°C$)

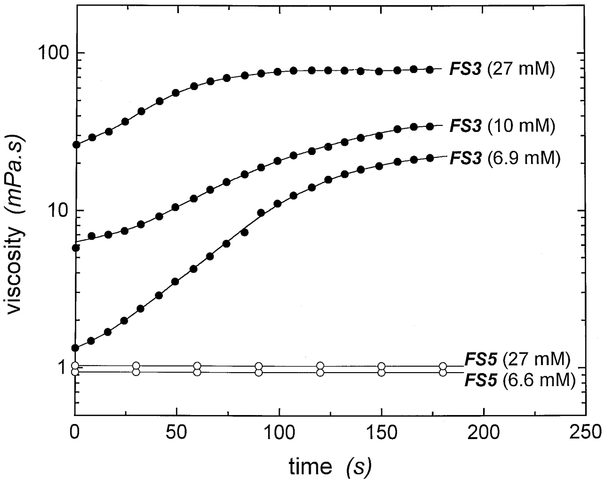


Fig. 4 Variation of the viscosity as a function of time at a constant shear rate ($\dot{\gamma} = 10\,s^{-1}$) for various concentrations (mM) of FS3 (●) and FS5 (○) surfactants in aqueous solution ($T = 25\,°C$)

Table 1 Characteristics of the polymers

Polymers	Surfmer content in the monomer feed [mol%]	Surfmer content in the copolymer [mol%]	Yield [%]	$M_w \times 10^{-6}$
FS3P1	1	0.95	84	1.1
FS3P2	2	2.12	80	1.4
FS5P2	2	1.58	80	–
HS2P1	1	0.93	73	1.5
HS2P2	2	2.02	96	1.4
PAM	–	–	93	1.5

From the data reported in the literature, it appears that such a shear-induced phase transition occurs only for salt-free micellar systems with low C^* values ($C^* \lesssim$ 1 wt%). Up to now, this was observed for ionic surfactants with strongly binding counter-ions [4, 27, 28] or gemini surfactants in which the polar heads are chemically connected [14]. In the present study, the very strong hydrophobicity and the large volume of the fluorocarbon tails favors the formation of cylindrical micelles. Furthermore, one observes for FS3 systems a remarkable effect of hydrogen bonding between the polar heads, which promotes a lowering of the C^* and a pronounced shear-thickening behavior.

Copolymerization and polymer solution properties

Copolymers were prepared by free-radical copolymerization of acrylamide with either FS3, FS5 or HS2 surfactants in the micellar state, and their characteristics are given in Table 1. The surfmers are quantitatively incorporated into the copolymers taking into account the experimental accuracy of elemental analysis. All the copolymers are soluble in water. The values of the molecular weights of the copolymers are very close to those measured for the homopolyacrylamide. As previously reported for similar polymerization experiments of acrylamide in the presence of other hydrophobic comonomers or amphiphiles [17], the kinetics of the copolymerization process can be well described by the theoretical conversion-time behavior of acrylamide homopolymerization. This is due to the relatively low amount of the surfmer in the moment feed.

Figure 5 shows the variation of the molar percentage of the surfactant monomers in the copolymers as a function of monomer conversion. The data obtained for the various surfactants lie on the same curve, whatever, their nature, mono- or di-substituted, hydrogenated or fluorinated. It can be seen that in all cases, the acrylamido surfactants are consumed more rapidly than acrylamide, despite the fact that the polymerizable functions are the same which should imply similar reactivity ratios particularly in homogeneous media. The average hydrophobic content decreases toward the feed composition at higher degrees of conversion and therefore the copolymers obtained at full conversion are quite heterogeneous in composition. A compositional heterogeneity was also observed when acrylamide is copolymerized with N-monosubstituted alkylacrylamides in aqueous micellar media, the latter being solubilized in SDS micelles [17, 29–31]. This behavior was attributed to the capability of monosubstituted acrylamides to form intermolecular hydrogen bonding in media of low polarity. This causes an increased reactivity of the hydrophobic monomers within the micelles. The use of N-N-disubstituted acrylamide derivatives, for which H-bonding is not possible, allowed us to suppress the drift in copolymer composition [29]. Note that the concentration of the hydrophobic monomers in this case does not usually exceed 5–7 molecules per SDS micelle. The data of Fig. 5 show that a disubstitution of the amido function does not improve the compositional homogeneity of the copolymers, since the same compositional drift is observed for FS3 and FS5 fluorocarbon surfmers. This result suggests that the increased reactivity of the polymerizable surfactants is due to micellar effects, their local concentration

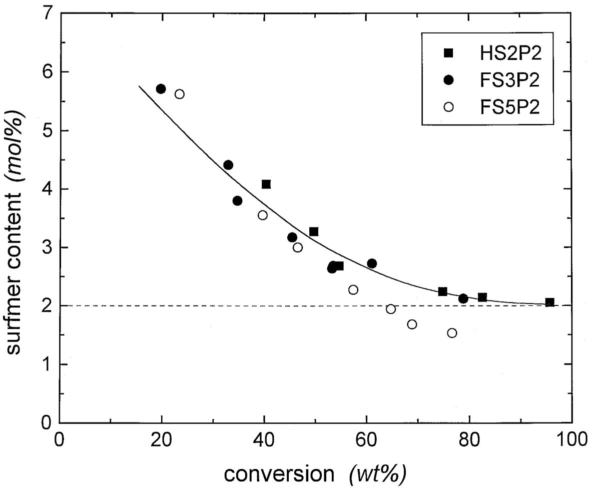


Fig. 5 Composition of acrylamide/surfmer copolymers (see Table 1) as a function of conversion (surfmer content in the monomer feed: 2 mol%)

(close to that of the bulk with $N_{agg} \approx 50$–100) being much higher than that of the alkylacrylamides solubilized in conventional surfactant micelles. It is well known that the rate of polymerization of amphiphilic monomers is much higher above the cmc than in the molecularly dispersed state [32].

Turning back to the comparison between hydrocarbon and fluorocarbon surfactants, the similar behavior observed for HS2 and FS3 surfactants indicates that there is no strong effect of the hydrophobicity on the polymerization reaction (Fig. 5). This result could be expected since under the experimental conditions ($T = 50\,°\mathrm{C}$ and $C_{surfmer} = 2.8$–5.6 mM), the micelles are quasi-spherical as shown from rheological experiments.

The compositional copolymer heterogeneity is also shown by the variation of the viscosity of aqueous solutions as a function of conversion (Fig. 6). In contrast to homopolyacrylamide where the viscosity is almost independent on monomer conversion degree, the viscosity of the hydrophobically modified polymers decreases sharply with increasing conversion. This behavior is a direct consequence of the sample heterogeneity. The low conversion samples consist of rather homogeneous copolymer chains with a hydrophobe content significantly higher than the average value of the full conversion samples. The improved thickening ability is then due to the formation of intermolecular hydrophobic interactions. Note that the polymer concentration (0.5 wt%) is somewhat smaller than C^* but intermolecular associations have often been found to occur below C^* for other types of associating polymers [33–37]. On the other hand, the copolymer heterogeneity of the full conversion samples which consist of a mixture of modified and not modified polyacrylamide chains is certainly at the origin of their poor thickening ability. The copolymer chains have difficulty to associate via hydrophobic interactions throughout the whole sample volume and form rather isolated clusters in a matrix of homopolyacrylamide chains, as previously reported for polyacrylic acid modified with small amounts of styrene [38]. The high conversion samples still exhibit a weak thickening ability, reflecting the existence of a few intermolecular interactions. Finally, from the comparison of the data between HS2P2 and FS3P2 samples, it is difficult to infer a net effect of the hydrophobicity on the viscous properties of the samples with monomer conversion.

In Fig. 7 is plotted the viscosity ($\dot{\gamma} = 3\,\mathrm{s}^{-1}$) against copolymer concentration for FS3P and HS2P samples obtained at full conversion containing either 1 mol% (P1) or 2 mol% (P2) of surfmer. The viscosity of the copolymers is significantly larger than that of unmodified homopolyacrylamide solutions. This is again an indication that intermolecular aggregation between hydrophobic groups occurs even in the dilute regime. Furthermore, flow experiments show a shear thinning behavior at shear rates higher than $5\,\mathrm{s}^{-1}$, indicating the disruption of these links by shear forces, as classically observed for associative thickeners [39, 40]. The results of Fig. 7 also show that for a given polymer sample, the viscosity increases with the hydrophobic content, as could be expected for this type of systems. More surprisingly, the fluorocarbon FS3P samples exhibit a weaker thickening power than the hydrocarbon polymer analogues (HS2P), despite a stronger hydrophobic character of the former. This may be a hint that the fluorocarbon side chains enhance the formation of intramolecular aggregation as compared to the copolymers containing less hydrophobic hydrocarbon moieties. In this respect, it must be reminded that the surfactant

Fig. 6 Viscosity as a function of conversion for various polymer samples in aqueous solution ($C = 0.5$ wt%, $\dot{\gamma} = 0.3\,\mathrm{s}^{-1}$, $T = 25\,°\mathrm{C}$)

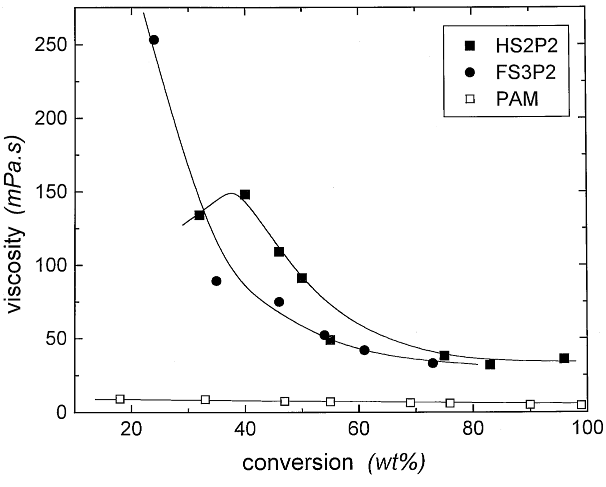
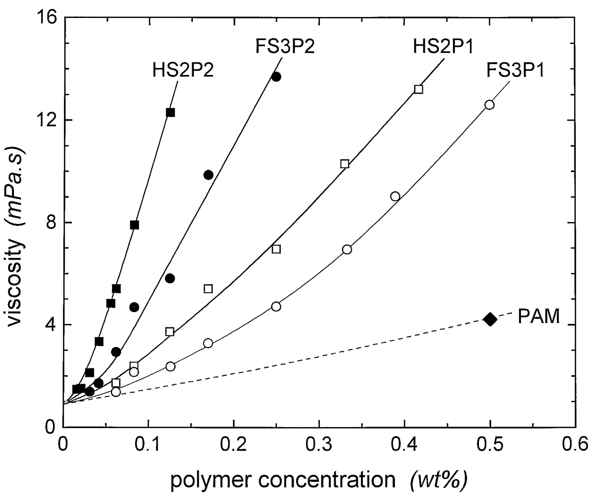


Fig. 7 Variation of the viscosity as a function of polymer concentration for various acrylamide/surfmer copolymers ($\dot{\gamma} = 3\,\mathrm{s}^{-1}$, $T = 25\,°\mathrm{C}$)



comonomers self-organize into micelles with high aggregation numbers resulting in the formation of relatively large block-like hydrophobic domains along the polymer backbone rather than a random distribution. These large hydrophobic aggregates confer to the polymer molecules a polysoap structure with strong intramolecular interactions, the more hydrophobic the sample, the stronger the interactions.

As a matter of fact, for hydrophobically modified water-soluble polymers, the balance between inter- and intramolecular associations, i.e. the balance between an associate thickener behavior and a polysoap behavior, is controlled by the number, distribution and hydrophobicity of water-insoluble side chains, disregarding the influence of polymer concentration and molecular weight. These effects tend to render the rheological behavior of this type of systems more complex, as already discussed by other groups [30, 41–43]. Our results clearly show that the polysoap properties are favored by the incorporation of large blocks exhibiting a strong hydrophobicity.

Polymer–surfactant interactions

Another way to investigate the specific hydrophobic character of associative polymers is to look at their interactions with added surfactant. To illustrate this effect, we have studied the viscometric behavior of a hydrocarbon-modified copolymer (HS2P1) as a function of the concentration of fluorocarbon or hydrocarbon surfactants (FS5, HS2) in order to characterize distinct polymer surfactant interactions caused by the mutual phobicity between fluorocarbon and hydrocarbon moieties.

The effect of HS2 and FS5 addition on the viscosity of 0.5 or 1 wt% HS2P1 solutions is shown in Fig. 8. If the HS2 hydrocarbon surfactant is added to an aqueous solution of the polymer containing 1 mol% of the same compound (HS2P1), a net viscosity maximum is observed for the 1 wt% polymer concentration. This maximum occurs at a surfactant concentration close to the cmc. Further addition of HS2 causes a progressive decrease in viscosity. For this type of systems, the observed effects can be explained as follows [44–46]: at low concentration, the surfactant adsorbs preferentially onto the hydrophobic blocks of the polymer whose viscosity does not change significantly because the chain conformation remains similar to that of pure polymer solutions with only a low adsorbed surfactant content. The increase in viscosity is related to the adsorption of the free surfactant forming intermolecular hydrophobic links between the polymer chains. Several macromolecules can share the surfactant molecules and form a network. At higher surfactant concentrations, the polymer–surfactant network is broken due to the saturation of all hydrophobic polymer sites with surfactant, resulting in a lowered viscosity. The maximum observed in Fig. 8 is very small compared to those reported for associative polyacrylamides of similar hydrophobic content, molecular weight and polymer concentration [33, 45]. In those cases, the viscosity can increase by several orders of magnitude. This shows the relative inefficiency of the surfactant to form intermolecular bridging which can be attributed to the polysoap structure of these systems with favored intramolecular associations.

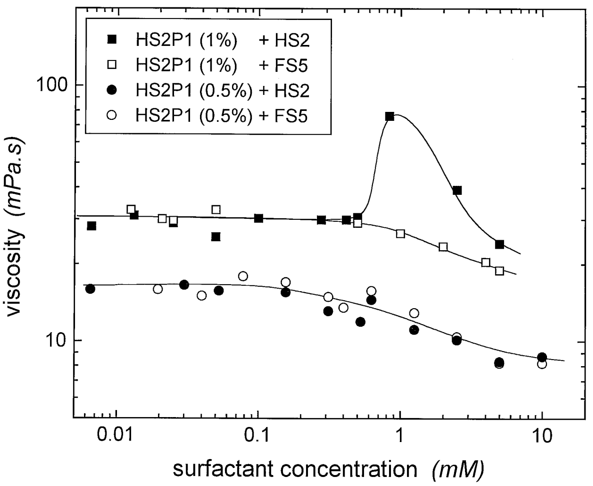


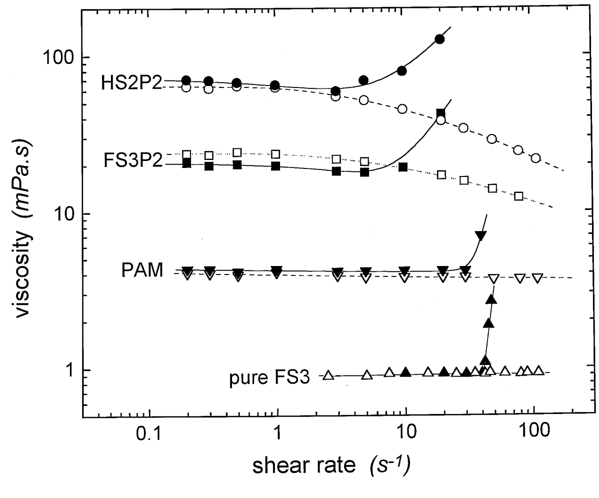
Fig. 8 Effect of the addition of HS2 hydrocarbon surfactant (closed symbols) or of FS5 fluorocarbon surfactant (open symbols) on the viscosity of HS2P1 copolymer solutions at two concentrations (1 and 0.5 wt%, $\dot{\gamma} = 0.3\,s^{-1}$, $T = 25\,°C$)

When the FS5 fluorocarbon surfactant is added to the hydrocarbon-modified HS2P1 polymer, the viscosity first shows a plateau value as long as the concentration is smaller than the cmc of the surfactant, followed by a viscosity decrease. The absence of a maximum in this case is due to the mutual phobicity between fluorocarbon and hydrocarbon moieties. The decrease in viscosity observed at concentrations above the cmc can be accounted for by a partial solubilization of the hydrocarbon blocks of HS2P1 sample by FS5 surfactant leading to a destruction of the preexisting intermolecular links. Similar viscosity changes with surfactant concentration were reported by Petit et al. [43] for aqueous solutions of sodium pentadeca-fluoro-octanoate and a poly(sodium acrylate) weakly modified with fluorocarbon or hydrocarbon side chains. For the compatible surfactant/polymer solutions, a viscosity maximum was observed but not for the F-surfactant/hydrocarbon copolymer system. Therefore, the authors assume that no interaction between surfactants and polymer takes place due to the mutual phobicity of alkyl and perfluoroalkyl chains. However, this conclusion does not take into account the decrease of the viscosity at high surfactant concentrations observed in both studies. Such an effect obviously indicates that some kind of interactions takes place even for systems involving partially incompatible moieties. At lower polymer concentrations (0.5 wt%, Fig. 8), only the latter effect remains for both surfactants with no maximum characteristic of the formation of a network as observed for the HS2P1/HS2 pair at 1 wt% copolymer concentration.

Another illustration of the polymer–surfactant interactions is provided by flow experiments. In Fig. 9 are reported the flow shear rate curves for PAM, FS3P2 and HS2P2 samples in the presence of 0.62 mM (just below the cmc) or 1.25 mM (just above the cmc) of FS3 surfactant. In the same plot are also reported the data obtained for the pure FS3 aqueous surfactant solution showing the characteristic shear thickening behavior discussed before (see Fig. 3B). When the surfactant concentration is below the cmc, one observes no effect for the PAM solutions whereas the two associating polymers show the classical shear thinning behavior. Conversely, the addition of FS3 surfactant at the concentration beyond the cmc induces a shear thickening behavior similar to that observed for the pure surfactant solutions. It is however less pronounced and occurs at much lower shear rates. Such a shift reflects the presence of polymer-induced attractive forces between surfactant micelles. This causes the formation of elongated micellar aggregates that play the role of nuclei in the shear-induced transition.

A further experimental evidence of interactions between these fluorocarbon surfactant hydrocarbon water-soluble polymers is provided by fluorescence experiments. In pure water, an associative polyacrylamide labelled with pyrene (see experimental) exhibits pyrene excimer emission resulting from interactions between labelled hydrophobic sequences. On the other hand, excimer fluorescence disappears by adding FS3 surfactant which shows that the fluorocarbon surfactant is able to disrupt polymer/polymer hydrophobic associations.

Fig. 9 Effect of shear rate on the viscosity for pure FS3 surfactant and various polymer/FS3 systems, at two surfactant concentrations: 0.62 mM (open symbols, dashed lines) and 1.25 mM (closed symbols, solid lines)



Conclusions

A comparative study of the viscometric behavior of two polymerizable fluorocarbon surfactants has been performed. The two surfactants differ only in the degree of amido substitution, the CON–H of the monosubstituted FS3 surfactant being replaced by CON–C_2H_5 for the disubstituted FS5 surfactant. The FS3 sample has thus the ability of forming hydrogen bonds between the surfactant polar head groups and these weak but cooperative forces change the molecular geometry by slightly decreasing the head group area. Consequently, the formation of cylindrical micelles becomes energetically preferred and the micellar growth occurs at much lower concentrations for FS3 than for FS5. In the vicinity of the concentration characteristic of the onset of micellar growth, solutions of FS3 exhibit a shear thickening and a rheopectic behavior in contrast to the Newtonian flow behavior of the FS5 analogue, containing the CON–C_2H_5 function.

Radical copolymerization of FS3, FS5 or of a hydrocarbon analogue HS2, with acrylamide in excess yields copolymers with a polysoap-like structure which undergo preferentially intramolecular hydrophobic interactions, particularly in the case of fluorocarbon-modified polyacrylamides. The pronounced self-aggregation of single polymer molecules can be attributed to the coexistence of (i) a neutral and hydrophilic polymer backbone which does not hinder chain collapse and (ii) the blocky structure of the strongly hydrophobic moieties.

Viscosity studies on aqueous mixtures of hydrophobically-modified polyacrylamides and the respective monomeric surfactants show only slight differences of interactions between fluorocarbon and hydrocarbon species. However, no network formation between the fluorocarbon surfactant (FS5) and hydrocarbon polymer domains was observed, which is an indication of some partial incompatibility between F- and H-carbon chains. When in excess, the FS5 and HS2 surfactants are adsorbed on interchain alkyl links leading to a progressive destruction of the hydrophobic aggregates.

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