

EXPERIMENTAL CHARACTERIZATION OF FLUOROCARBON-MODIFIED POLYACRYLAMIDE/SURFACTANT AQUEOUS SOLUTIONS*

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Abstract The interaction between surfactants and fluorocarbon-modified polyacrylamide (FC-PAM) in aqueous solutions was evaluated by rheological means and fluorescence spectroscopy and was found to be strong regardless of the surfactant's nature. Two representative surfactants, anionic sodium dodecyl sulfate (SDS) and nonionic Triton X-100, were used. The origin of the interaction and its dependence on the surfactant concentration were discussed.

Key words Polyacrylamide, Fluorocarbon-modified Polyacrylamide, Surfactant, Rheology, Fluorescence Spectroscopy

INTRODUCTION

The interaction between water-soluble polymers and surfactants in aqueous solutions has become a very interesting topic in extensive applications as well as in fundamental studies. There were many studies concerning the interaction between surfactants and polymers such as poly(ethylene oxide)^[1, 2], poly(propylene oxide)^[3], and ethyl(hydroxyethyl)cellulose^[4–6]. The interaction between polymers and ionic surfactant is strong and becomes more pronounced with the enhancement of the hydrophobicity of polymers, yet it is weak between nonionic surfactants and polymers^[7–10]. No interaction was detected between unmodified polyacrylamide (PAM) and surfactants, but the interaction between hydrophobically modified PAM and surfactants was remarkable^[11–20].

It is known that the hydrophobicity enhancement efficiency of fluorocarbons is higher than that of their corresponding hydrocarbons, thus fluorocarbon-modified PAM (FC-PAM) is more hydrophobic resulting in much higher aqueous solution viscosity due to hydrophobic association than the hydrocarbon-modified ones. A strong association of the hydrophobic pendant group in aqueous solutions will result in an increase of the hydrodynamic volume. In this study, we mainly characterized the interaction between FC-PAM and two typical surfactants (anionic and nonionic ones) by using rheometer and fluorescence spectrometer. The results will help us to understand the rheological properties and their dependence on micro-environmental changes of the solutions.

EXPERIMENTAL

Materials

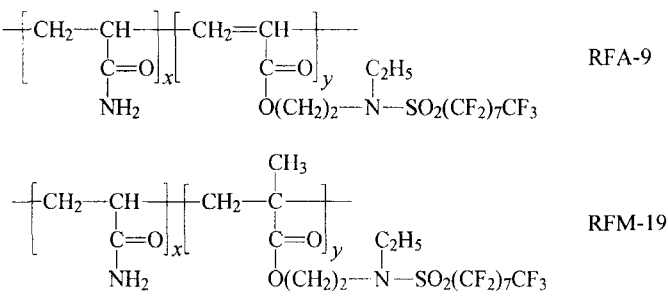
FC-PAM was synthesized according to Zhang's procedure^[21–23]. The structures of the copolymers are depicted in

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Scheme 1. Some characteristic data of the polymers are specified in Table 1. The critical overlap concentration $c^* = 1/[\eta]$ ($[\eta]$: intrinsic viscosity) was determined using an Ubbelohde viscometer at $30 \pm 0.1^\circ\text{C}$. Since the content of the fluorocarbon-containing comonomer is very low, the molecular weight of the samples was calculated by Mark-Houwink’s equation^[24] using the same parameter as that of polyacrylamide.



Scheme 1 Chemical formulae of the copolymers

Table 1. Characteristic data of the samples

Sample	Comonomer	Comonomer content (mol%)	M_η ($\times 10^6$)	$[\eta]$ (mL/g)	c^* (g/mL)
PAM			1.908	620.9	0.00161
RFA-9	RFA	0.28	2.018	645.4	0.00155
RFM-19	RFM	0.28	2.085	652.6	0.00153

Two surfactants, anionic surfactant sodium dodecyl sulfate ($\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$, SDS) of 99% analytical purity and nonionic surfactant Triton X-100 of commercial grade, were both purchased from Acros Co., and used without further purification. The fluorescence probe pyrene (Aldrich) was recrystallized from ethanol and dissolved in acetone to obtain a stock solution of 6×10^{-4} mol/L.

Rheological Characterization

PAM and FC-PAM samples were provided in the form of aqueous solutions with 10 wt% solid content. 0.1 mol/L stock solutions of SDS and Triton X-100 were prepared by dissolving a known amount of SDS and Triton X-100 in de-ionized water, respectively. By mixing a designated amount of PAM or FC-PAM stock solutions with the surfactant stock solutions, a series of PAM-surfactant and FC-PAM-surfactant complex solutions were prepared. The polymer concentration was maintained at 1 wt%. After the complex solutions were gently stirred for 2 h followed by standing for 48 h to eliminate air bubbles, the homogeneous solutions were obtained and stored at 20°C .

The rheological properties were measured by a strain-controlled ARES rheometer (Advanced Rheometric Extension System). The Couette fixture was used, whose cup and bob diameter is 34 mm and 32 mm, respectively. All the measurements were conducted at 30°C . Before performing a dynamic frequency sweep test, a dynamic strain sweep test was conducted to determine the linear viscoelastic range. The dynamic frequency sweep experiments were conducted within the linear viscoelastic range. The viscosity measurement was conducted in a shear rate range of $0.02\text{--}200\text{ s}^{-1}$ covering both linear and nonlinear viscoelastic regions.

Fluorescence Spectroscopic Measurement

A Hitachi F-4500 fluorescence spectrophotometer was used to measure the micro-environmental changes in the solutions. The slit width is 5 mm, and the exciting laser wavelength λ_{ex} is 338 nm. The measurement was conducted at 30°C . A small amount of pyrene/acetone stock solution in acetone was added into each sample to ensure a pyrene concentration of about 6×10^{-7} mol/L. All samples were stored at room temperature for 24 h before measurement so as to achieve equilibrium.

RESULTS AND DISCUSSION

Rheological Behavior of FC-PAM/SDS Complex Solutions

Dynamic moduli versus frequency plots of RFA-9/SDS complex solutions at three SDS concentration levels are shown in Fig. 1. Storage modulus G' is smaller than loss modulus G'' within the whole frequency region. This means that viscous behavior dominates for all the solutions in the detected frequency region. The RFM-19/SDS systems show the same tendency (not shown here).

The steady shear viscosity of RFA-9/SDS complex solutions is shown in Fig. 2. All the samples display a pseudoplastic behavior, which is most likely due to the destruction of the intermolecular hydrophobic association. The critical shear rate at which viscosity begins to drop is dependent on SDS concentration. The pseudoplastic behavior becomes more profound at 15 mmol/L SDS, and the corresponding critical shear rate is the lowest. The RFM-19/SDS solutions also show the same behavior. All the samples show a Newtonian plateau at low shear rate, which is equal to zero-shear viscosity η_0 . The effects of comonomer and surfactant concentration on η_0 are depicted in Fig. 3.

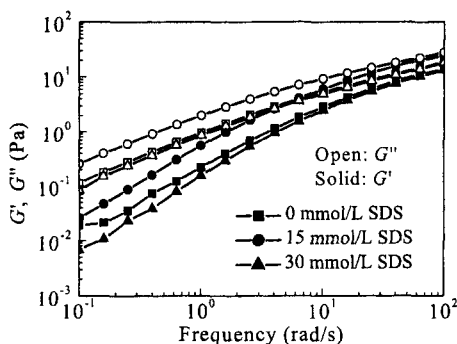


Fig. 1 Frequency dependence of the storage modulus G' and the loss modulus G'' for 1 wt% RFA-9/SDS complex aqueous solution

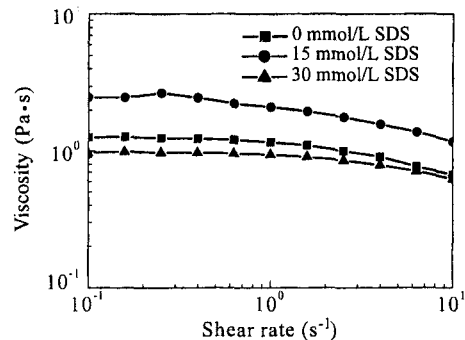


Fig. 2 Steady shear viscosity for 1 wt% RFA-9/SDS complex aqueous solutions

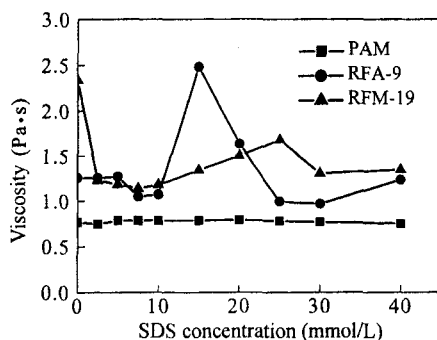


Fig. 3 Effects of comonomer and SDS concentration on zero-shear viscosity of the complex solutions

The viscosity of unmodified PAM solutions is independent of the surfactant concentration. But, it is complicated for the FC-PAM (RFA-9 and RFM-19)/SDS complex solutions. The viscosity initially decreases with SDS concentration through a minimum and then increases to a maximum. The viscosity decreases again and levels off to a plateau. The zero-shear viscosity of the two complex solutions reaches the corresponding minimum values at the same SDS concentration range of 8–10 mmol/L. SDS concentration corresponding to the maximum viscosity shifts from 15 mmol/L for RFA-9/SDS solutions to 25 mmol/L for RFM-19/SDS systems. These

findings reveal that there exists no interaction between PAM and SDS, while the interaction between FC-PAM and SDS varies with SDS concentration, the comonomer structure and content. The viscosity of FC-PAM solutions is higher than that of PAM solution, which is related to the intermolecular hydrophobic association for FC-PAM. Wu *et al.*^[25] reported that the critical aggregate concentration is 1.34×10^{-4} g/mL of FC-PAM (containing 0.227 mol% RFA) solutions. When the polymer concentration increases, intermolecular association dominates over the intramolecular one. This results in expansion of the hydrodynamic dimension of polymer coils and accordingly in an increase in solution viscosity. The additional methyl group on the RFM-19 copolymer chain facilitates the hydrophobic aggregation compared to the corresponding RFA-9, and therefore it possesses higher viscosity. The dynamic viscosity shows the same dependence on the variables as the zero-shear viscosity (not shown here).

Rheological Behavior of the FC-PAM/Triton X-100 Complex Solutions

The steady shear viscosity of RFA-9/Triton X-100 complex solutions is shown in Fig. 4. The pseudoplastic behavior is also found, which becomes more remarkable at 20 mmol/L Triton X-100. The case is the same for RFM-19/Triton X-100 complex solutions. Zero-shear viscosity η_0 of unmodified PAM solution is less influenced by the addition of Triton X-100 (Fig. 5), while η_0 of FC-PAM solutions experiences a minimum followed by an increase to a maximum. η_0 of RFM-19/Triton X-100 complex solutions is higher than the corresponding value of RFA-9/Triton X-100 ones. This is consistent with the fact that the former polymer is more hydrophobic owing to the methyl groups.

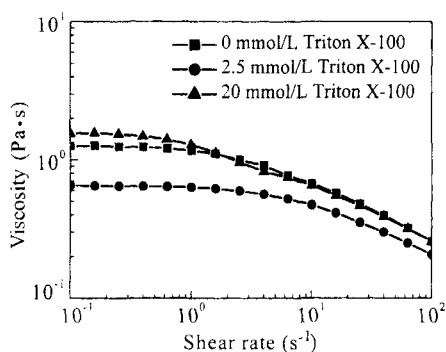


Fig. 4 Steady shear viscosity for 1 wt% RFA-9/Triton X-100 complex aqueous solutions

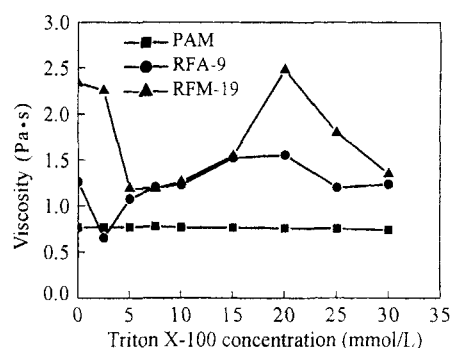


Fig. 5 Effects of comonomer and Triton X-100 concentration on zero-shear viscosity of the complex solutions

Fluorescence Spectroscopic Results

Fluorescence spectroscopy is useful to detect the interaction between surfactants and hydrophobically modified polymers. The intensity ratio of the first band to the third one (I_1/I_3) of the pyrene molecule emission spectrum is sensitive to the local medium polarity; thus it was widely used to indicate the polarity of the surrounding environment of pyrene^[26, 27]. In a polar solvent, *e.g.* water, the ratio of I_1/I_3 is higher than the corresponding value in a non-polar solvent. The values of I_1/I_3 for SDS, Triton X-100, and the complex solutions are shown in Fig. 6 and Fig. 7, respectively. I_1/I_3 values in FC-PAM solutions without surfactants are all lower than that in water due to the existence of hydrophobic polymer chains. Because of the additional introduction of a methyl group into RFM-19 as compared with RFA-9, the I_1/I_3 value of the former solution is lower than that of the latter one. When surfactant is added to water, the I_1/I_3 value decreases with the surfactant concentration to a plateau at the critical micelle concentration (CMC) because the pyrene molecules reside in the hydrophobic micelle core. In the presence of polymers, the I_1/I_3 value is lower than that in water and decreases relatively slowly, indicating the association of pyrene molecules onto the hydrophobic chains.

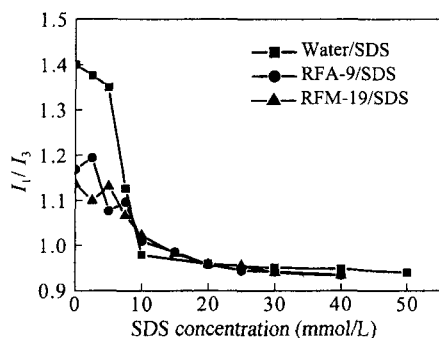


Fig. 6 I_1/I_3 values and their dependence on SDS concentration in water and 1 wt% FC-PAM solutions

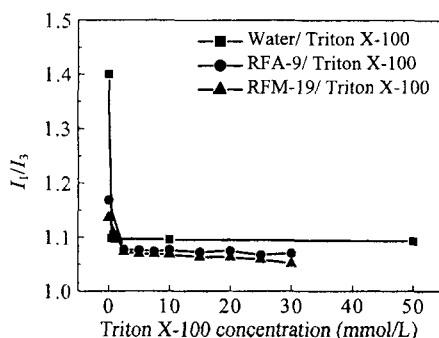


Fig. 7 I_1/I_3 values and their dependence on Triton X-100 concentration in water and 1 wt% FC-PAM solutions

Discussions

When the polymer concentration of the complex solutions is fixed, two critical surfactant concentrations c_1 and c_2 exist. c_1 and c_2 correspond to the onset of polymer/surfactant interaction and the saturation of the interaction, respectively^[28]. Since c_1 is generally less than the CMC of the surfactant, the initial aggregation between polymer and surfactant requires lower energy than that for micelle formation. After c_2 , the excess surfactant molecules form micelles.

In the detected systems without surfactants, the pendant hydrophobic groups on the polymer chains are intermolecularly associated, thus the viscosity and modulus of FC-PAM solutions are higher than those of the unmodified ones. With the addition of surfactants below c_1 corresponding to the minimum viscosity in Fig. 3 and Fig. 5, the surfactants associate onto the hydrophobic chains of FC-PAM. The hydrophobic aggregation among FC-PAM macromolecules is hindered, thus the viscosity decreases accordingly. When the surfactant concentration is in the range of $c_1 < c < c_2$ (c_2 corresponding to the maximum viscosity), mixed micelles are formed between the surfactants and the hydrophobic pendant groups of the polymers. The viscosity of FC-PAM solution increases due to the enhanced strength of the association junctions. When the surfactant concentration increases above c_2 , the mixed micelle junctions are saturated by surfactant molecules, and the network structure is destroyed by the formation of isolated mixed micelles containing only a single hydrophobic pendant group^[14]. As a result, the polymer association network is progressively broken, and the viscosity decreases accordingly. The detector pyrene molecules reside in the mixed micelle cores of less polarity when the surfactant concentration is in the c_1 to c_2 range, thus the I_1/I_3 value is lower than that below c_1 . When excess surfactant is introduced, the micelles will transform from mixed micelles associated with several hydrophobic pendant groups to those containing one pendant group. Therefore, the environment of pyrene is less changed, which is consistent with the plateau I_1/I_3 in Fig. 6 and Fig. 7.

CONCLUSION

The rheological properties of FC-PAM (RFA-9, RFM-19)/surfactants (SDS, Triton X-100) complex aqueous solutions were characterized. Both their viscosities and dynamic moduli decrease with increasing surfactant concentration to the minimum values followed by an increase to the maximum values. When the surfactant concentration is very high, the parameters level off to their plateau values. This finding reveals that there is strong interaction between FC-PAM and the surfactant in aqueous solutions. The interaction becomes more pronounced when the additional methyl group is introduced into the polymers to replace hydrogen atom. In combination with the fluorescence spectroscopic results, the interaction between surfactants and FC-PAM in solutions is discussed.

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