



Effect of Surfactant on Solution Properties of Amphoteric Hydrophobically Associating Polymer

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Received: 23 September 2013;

Accepted: 25 February 2014;

Published online: 16 September 2014;

AJC-15931

The interactions of sodium dodecylbenzenesulfonate with amphoteric hydrophobically associating polymer in aqueous solution were studied by laser light scattering and rheometer. The viscosity of the polymer has exhibited an increase at first and then decrease with the increase of surfactant concentration when salt concentration is low. Sodium dodecylbenzenesulfonate has a great influence on the elastic modulus of the polymer solution, while has a little influence on the viscous modulus. Moreover, the surfactant also has a great effect on the root mean square radius of gyration ($\langle R_g \rangle$), hydrodynamic radius ($\langle R_h \rangle$), the ratio of $\langle R_g \rangle$ to $\langle R_h \rangle$ and the apparent weight average molecular weight (M_w) of polymer.

Keywords: Amphoteric hydrophobically associating polymer, Laser light scattering, Rheology, Aggregation behaviour.

INTRODUCTION

Over the past two decades, hydrophobically associating polymers have attracted considerable attention because of their outstanding solution properties and numerous practical applications¹⁻⁵. These polymers exhibit a strong tendency to self-associate *via* inter- or intrapolymeric interactions of the hydrophobic side chains and have possible applications in food thickeners, coatings, paints, enhanced oil recovery and water treatment, *etc.*⁶⁻¹⁵.

Amphoteric polymer is an important class of compound which contains cationic and anionic groups on the same molecule of polymer¹⁶. Due to electrostatic attraction, the amphoteric polymer generate the key bonding in the intramolecular and intermolecular, resulting in the shrinkage of its molecular chain. However, when the electrolyte is added to amphoteric polymer aqueous solution, the physical attraction between the anions and cations are weakened and the amphoteric polymer will stretch to a random coil conformation, so the viscosity of the polymer solution increases with the addition of salt¹⁷. This is known as the antipolyelectrolyte effect¹⁸. Therefore, in recent years, amphoteric polymer research has aroused widespread attention.

The mixed system of polymer and surfactant is a very important "soft matter" system. The interactions of the polymer and surfactant, not only affect the properties of surfactant solution, but also change the chains conformation, morphology and the solution properties of polymer¹⁵⁻¹⁷. So the mixed system

of surfactant and macromolecular, not only has an important significance in theoretical studies, but also has a wide range applications in many fields and has always been a very interesting research topic. In this paper, the effect of sodium dodecylbenzene-sulfonate (SDBS) on the self-assembly behaviour of amphoteric hydrophobically associating polymer was studied by dynamic and static light scattering and rheometer. Amphoteric hydrophobically associating polymer was composed of acrylamide, dimethyl-dodecyl-allyl ammonium chloride (MDAC) as hydrophobic monomer and 2-(4-acrylamido-propyl-dimethyl ammonic)-sodium acetate (AMPA) as functional monomer. The chemical structure of polymer is shown in Fig. 1.

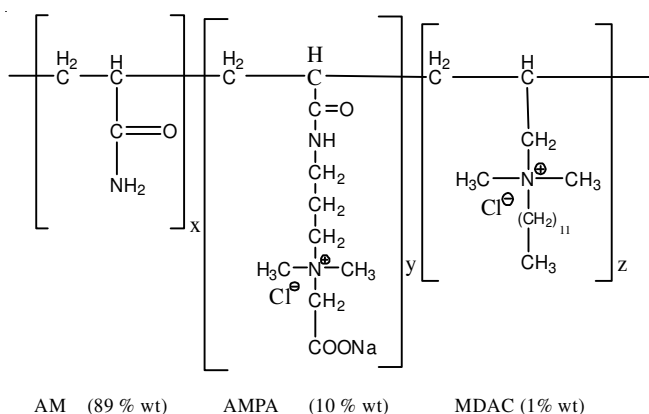


Fig. 1. Chemical structure of amphoteric hydrophobically associating polymer

EXPERIMENTAL

Sodium dodecylbenzenesulfonate (SDBS) was provided by the Chengdu Kelong Reagent Company, AR.

The polymer used in this paper is a terpolymer obtained through copolymerization of an acrylamide betaine functional monomer, a hydrophobic monomer and acrylamide. The synthesis of amphoteric hydrophobically associating polymer is reported elsewhere¹⁸.

Methods

Laser light scattering: Laser light scattering measurements were performed with a Brookhaven instrument BI-200SM at a wavelength of 532 nm with the experimental temperature being 25 °C. For light scattering experiments, solvent, surfactant solutions and polymer solutions were respectively filtered through 0.2, 0.2 and 0.8 μm Millipore filter into the cylindrical scattering cells before the experiment. By static light scattering, apparent weight average molecular weight (M_w) and root mean square radius of gyration ($\langle R_g \rangle$) of amphoteric hydrophobically associating polymer were obtained. By dynamic light scattering, the hydrodynamic radius ($\langle R_h \rangle$) and the distribution $f(R_h)$ of the hydrodynamic radius were obtained¹⁹⁻²³.

Rheology: The apparent viscosity and viscoelastic behavior of solution were studied by MARS III HAAKE rheometer under 25 °C. The plate system and P60 TiL rotor of rheometer were used in the experiment.

RESULTS AND DISCUSSION

Effect of SDBS on the apparent viscosity of amphoteric hydrophobically associated polymer: The apparent viscosities of polymer solutions were measured with the increasing concentration of SDBS at 25 °C and a constant shear rate 7.34 s^{-1} , while the polymer concentration is 5000 mg L^{-1} . In order to investigate the effect of salt on the solutions properties of mixed system, the amphoteric hydrophobically associating polymer and SDBS were dissolved in salt water (NaCl solution) at different concentration. The results are shown in Fig. 2.

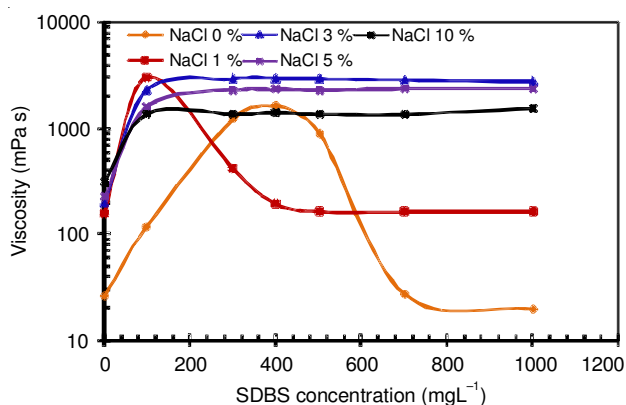


Fig. 2. Effect of SDBS surfactant concentrations on the apparent viscosity of polymer with different NaCl concentrations

Fig. 2 showed that the viscosities of the polymer solutions first increase and then decrease with the increasing of concentration of SDBS when the salt concentration of the solvent is

less than 1 %. When the viscosity of polymer reaches maximum value in free salt solvent, the concentration of surfactant is about 400 mg L^{-1} which is close to the CMC of the surfactant. In the 1 % salt solution, the surfactant concentration is about 100 mg L^{-1} when the viscosity of polymer reaches maximum value. The reason of this phenomenon may be that the addition of salt reduces the CMC of the surfactant. When the salt concentration of the solvent is higher than 1 %, the viscosities of the polymer solutions show the trend of increase at first and then change little with the increasing of concentration of SDBS. The reason of the phenomenon may be that the solubility of SDBS in salt water is so low when the salt concentration is too high that only the thickening effect of surfactant on polymer solutions can be observed. Because high brine water can make the surfactant precipitate in solution, the distilled water is used as the solvent in the following experiments.

Effect of SDBS on the viscoelastic of amphoteric hydrophobically associated polymer: The mixed system of amphoteric hydrophobically associating polymer and SDBS was prepared with pure water as solvent. In each mixed system the concentration of polymer is fixed 5000 mg L^{-1} . With the plate system and P60 TiL rotor of MARS III Haake rheometer, the elastic modulus (G') and viscous modulus (G'') of polymer/surfactant system was measured with the different scanning frequency under the condition of 25 °C and a constant shear stress (0.1 Pa). The results are shown in Figs. 3 and 4.

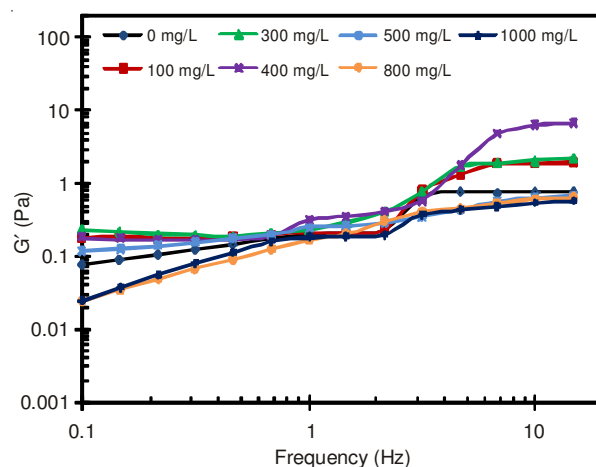


Fig. 3. Effect of scanning frequency on the elastic modulus (G') of polymer/surfactant system

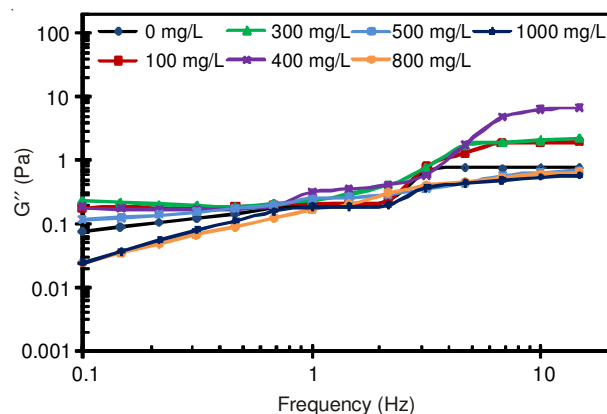


Fig. 4. Effect of scanning frequency on the viscous modulus (G'') of polymer/surfactant system

Figs. 3 and 4 showed that the elastic modulus (G') and viscous modulus (G'') of polymer/surfactant system of different SDBS concentration increase with the increasing of frequency.

When the frequency is 1 Hz, the viscoelasticity of polymer/surfactant system as a function of surfactant concentration is shown in Fig. 5.

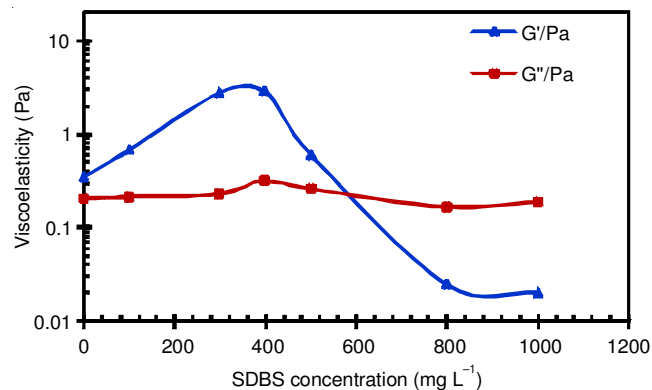


Fig. 5. Effect of SDBS surfactant concentration on the elastic modulus (G') and viscous modulus (G'') of polymer ($f = 1\text{ Hz}$)

Fig. 5 shows that the elastic modulus (G') has a little change with the increasing concentration of SDBS, while the viscous modulus (G'') undergoes a maximum. It indicates that the surfactant has a greater influence on the elastic modulus (G') than on the viscous modulus (G''). When the surfactant concentration is less than 600 mg L^{-1} , the elastic modulus is greater than the viscous modulus, indicating that the elastic behavior of the amphoteric polymer/surfactant is more significant than the viscous behavior. However, when the surfactant concentration is more than 600 mg L^{-1} , the viscous modulus is greater than the elastic modulus, so the viscous behavior is more significant.

Laser light scattering: According to the theory of light scattering, we can obtain the apparent weight average molecular weight (M_w), root mean square radius of gyration ($\langle R_g^2 \rangle$), second virial coefficients and other parameters by static light scattering. For long chain polymers of larger molecular weight, we use the Berry Algorithm²⁴⁻²⁶:

$$\left(\frac{KC}{R_{vv}(q)} \right)^{1/2} \approx \left(\frac{1}{M_w} \right)^{1/2} \left(1 + \frac{1}{6} \langle R_g^2 \rangle q^2 \right) (1 + A_2 M_w C)$$

In the above formula: $K = 4\pi^2 n_0^2 (dn/dc)^2 (N\lambda_0^4)$ and K is a constant related to the solvent nature and the incident light frequency; n_0 is the solution refractive index, because of the low concentration of solutions in the experiment, it is usually replaced by the solvent refractive index; c is concentration, mg L^{-1} ; $R_{vv}(q)$ is the scattered light intensity of different angles after removal of the solvent effect; λ_0 is wavelength of incident light, λ is wavelength of incident light in the solution; dn/dc is the refractive index increment, *i.e.*, the ratio of solution' refractive index to concentration; N is Avogadro; $\langle R_g^2 \rangle$ is the root mean square radius of gyration of polymer. When the scattering angle (θ) and concentration (c) all approach 0, the $\langle R_g^2 \rangle$ and M_w can be obtained by extrapolation^{27,28}.

In the light scattering experiment of this paper, the concentration of polymer is 2 mg L^{-1} . Therefore, the term of $A_2 M_w C$

in the above formula can be omitted for the low concentration of polymer, and then the above formula can be simplified as follows:

$$\left(\frac{KC}{R_{vv}(q)} \right)^{1/2} \approx \left(\frac{1}{M_w} \right)^{1/2} + \frac{1}{6} \left(\frac{1}{M_w} \right)^{1/2} \langle R_g^2 \rangle q^2$$

when $(KC/R_{vv}(q))^{1/2}$ as vertical axis and q^2 as abscissa axis, a straight line will be obtained. The result is shown in Fig. 6.

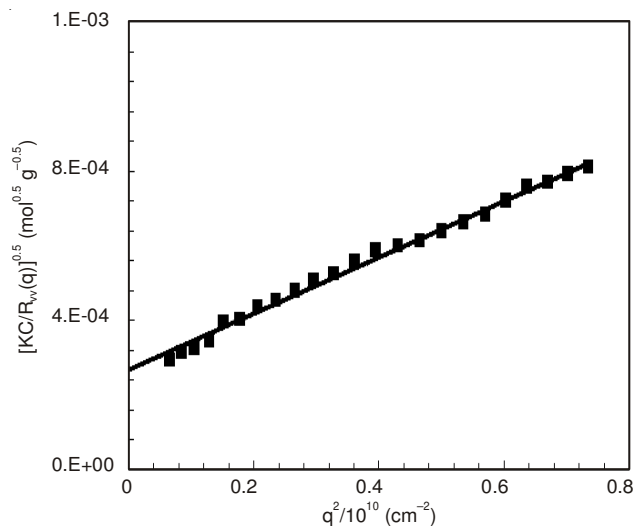


Fig. 6. Plot of $[KC/R_{vv}(q)]^{1/2} - q^2$ ($C_{\text{poly}} = 2\text{ mg L}^{-1}$, $C_{\text{surf}} = 0$)

Because the polymer in this paper is an amphoteric hydrophobically associating polymer, the association can lead to the formation of supramolecular aggregates in aqueous solution. Therefore, the weight average molecular weight (M_w) measured by static light scattering is not the real weight average molecular weight of amphoteric hydrophobically associating polymer, only being the molecular weight of supramolecular aggregates formed in solution, which is the apparent weight average molecular weight of amphoteric associative polymers. At $25\text{ }^\circ\text{C}$, the values of the apparent weight average molecular weight (M_w) of amphoteric associative polymers with the different surfactant concentration are shown in Fig. 7.

Form Fig. 7, it can be seen that the M_w of polymer undergoes a maximum with the increasing of surfactant concen-

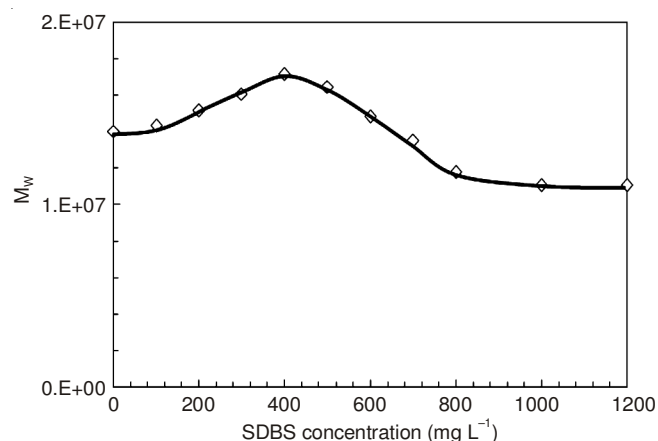


Fig. 7. Effect of SDBS surfactant concentrations on the apparent molecular weight (M_w) of polymer

tration and the concentration of surfactant corresponding to the maximum M_w is about 400 mg L^{-1} .

The effect of surfactant concentration on root mean square radius of gyration ($\langle R_g \rangle$) of polymer is shown in Fig. 8.

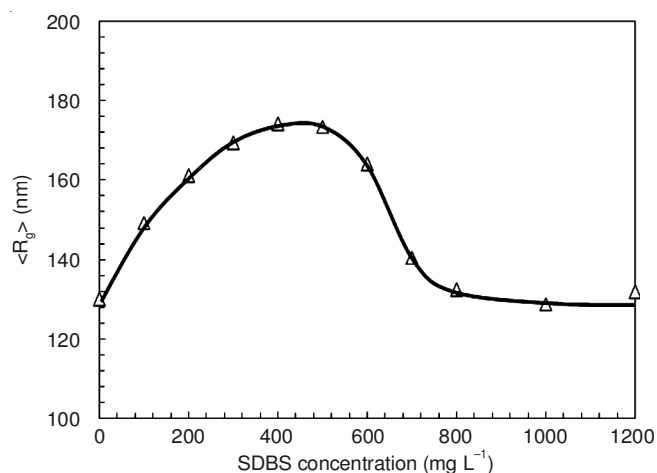


Fig. 8. Effect of SDBS surfactant concentration on root mean square radius of gyration ($\langle R_g \rangle$) of polymer ($C_{\text{poly}} = 2 \text{ mg L}^{-1}$)

Fig. 8 showed that the root mean square radius of gyration ($\langle R_g \rangle$) of polymer also undergoes a maximum with the increase of surfactant concentration and the surfactant concentration corresponding to the maximum $\langle R_g \rangle$ is about 400 mg L^{-1} .

The amphoteric polymer is inclined to form a coil curl because of its inner salt bond in water, and hydrophobic groups can enhance this effect. With the addition of surfactant, mixed micelle-like aggregates can be formed by interaction of the hydrophobic groups of polymer and surfactant. Firstly, the addition of surfactant is favor to enhance the intermolecular interaction of polymer, which results in the increase of the viscosity, the elastic modulus, the apparent weight average molecular weight (M_w) and the root mean square radius of gyration ($\langle R_g \rangle$) of polymer. When the surfactant concentration or the amount of surfactant micelles exceeds a certain value, the hydrophobic groups in polymer molecular chains will be separated by the surfactant micelles, which results in the weakness of the associating interaction between polymer chains, the disassemble of supramolecular aggregates, and the breakdown of polymer network. Therefore, the viscosity, the elastic modulus, the apparent weight average molecular weight (M_w) and the root mean square radius of gyration ($\langle R_g \rangle$) of polymer decrease.

In the dynamic light scattering experiments, the polymer concentration is 2 mg L^{-1} while the surfactant concentration is variable. The hydrodynamic radius ($\langle R_h \rangle$) is measured under the condition of 25°C and scattering angle²⁹ is 90° . The results are shown in Fig. 9.

The hydrodynamic radius ($\langle R_h \rangle$) of polymer is related to the polymer conformation and stretch behavior in solution. From Fig.9, we can see that the $\langle R_h \rangle$ undergoes a maximum with the increase of surfactant concentration, the same as that of $\langle R_g \rangle$ and M_w .

The root mean square radius of gyration ($\langle R_g \rangle$) of polymer is related to the space which the polymer chains actually extend. However, the hydrodynamic radius ($\langle R_h \rangle$) is the radius of the

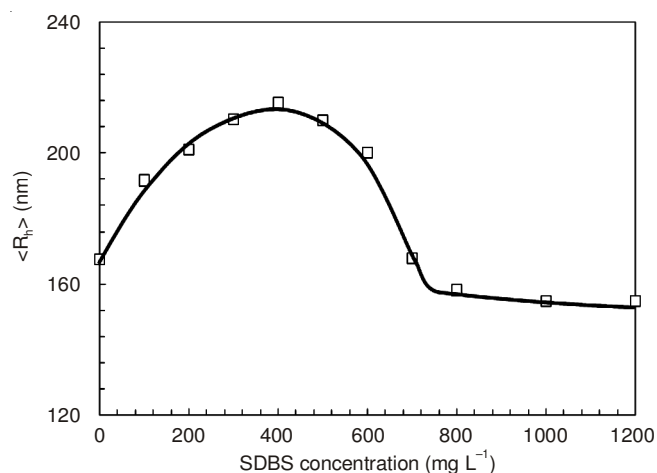


Fig. 9. Effect of SDBS concentration on the hydrodynamic radius ($\langle R_h \rangle$) of polymer ($C_{\text{poly}} = 2 \text{ mg L}^{-1}$)

equivalent sphere which have the same translational diffusion coefficient with the polymer³⁰. We can calculate the parameters $\langle R_g \rangle / \langle R_h \rangle$ through the root mean square radius of gyration ($\langle R_g \rangle$) and hydrodynamic radius ($\langle R_h \rangle$) measured by light scattering, which reflecting the segments density and polydispersity of the polymer. The results are shown in Fig. 10.

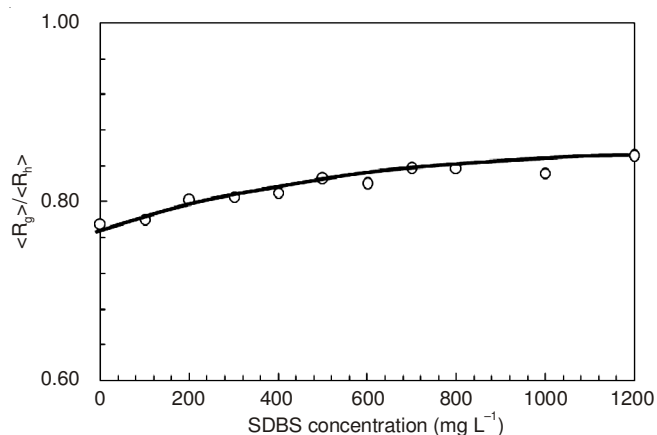


Fig. 10. Effect of SDBS surfactant concentration on the $\langle R_g \rangle / \langle R_h \rangle$ value of polymer ($C_{\text{poly}} = 2 \text{ mg L}^{-1}$)

From Fig.10, we observed that the ratio of $\langle R_g \rangle$ to $\langle R_h \rangle$ is less than 1 and it gradually increase with the increasing of surfactant concentration. There are some reasons to explain the phenomena. Firstly, the coils of polymer exhibit curl and shrink because there are inner salt bond and hydrophobic association in the amphoteric associating polymer chains, which result the increase of the central density of polymer and the radius of the actually space occupied by the polymer chains is less than the radius of the equivalent sphere. When the surfactant is added, mixed micelles form for the interaction of polymer chains and the molecules of surfactant, which weaken the association of hydrophobic groups of the polymer and result in the stretch of the polymer chain, so the value of $\langle R_g \rangle / \langle R_h \rangle$ gradually increase with the increasing of surfactant concentration. When the surfactant concentration reaches a certain value, the hydrophobic groups of the polymer chains are separated by the surfactant micelles and the association between polymer chains are weakened, so the value of $\langle R_g \rangle /$

$\langle R_h \rangle$ has little change with the increase of the surfactant concentration.

ACKNOWLEDGEMENTS

The financial supports of Major National S&T Program (2011ZX05024004) and Comprehensive Research Project of CNOOC (CCL2012RCPS0187ESN) are gratefully acknowledged.

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