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SHORT COMMUNICATION

Amphoteric hydrophobic associative polymer: I synthesis, solution properties and effect on solution properties of surfactant

Zhiyu Huang · Hongsheng Lu · Yan He

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Abstract Using acrylamide, acrylic acid and octadecyl dimethyl allyl ammonium chloride as monomers, a kind of amphoteric hydrophobic associative polymer was prepared by solution polymerization. The polymer's molecular weight is from 0.71 to 1.46×10^6 g/mol. And the hydrolysis degree of the polymer is about 14.5%. The polymer solution exhibits good association interaction, and the higher the hydrophobic group content is, the stronger the association interaction is. The adding of the polymer makes the surface tension curves of the mixture solution deviate from the parent solution curve. Both the hydrophobic group content and polymer solution's concentration exaggerate the deviation with their self-quantity increase. There exist an interaction between the polymer and surfactant, which almost has no direct relationship with the surfactant charge. The major interaction could be a hydrophobic association interaction.

Keywords Amphoteric · Hydrophobic associative polymer · Surfactant · Interaction

Z. Huang (✉) · H. Lu · Y. He
College of Chemistry and Chemical Engineering,
Southwest Petroleum University,
Chengdu, Sichuan 610500, People's Republic of China
e-mail: hzy3019@163.com

H. Lu
Chengdu Institute of Organic Chemistry,
Chinese Academy of Sciences,
No.9, Section 4, Renmin South Avenue,
Chengdu, Sichuan 610041, People's Republic of China

Introduction

Hydrophobically modified water-soluble polymers and polyelectrolytes have attracted an increase in interest over the past decades due to their ability in controlling viscosity at various shear rates [1–7]. Among these polymers, hydrophobically modified polyacrylamides, which is derived from polyacrylamide by incorporating a relatively small amount (generally less than 2 mol%) of hydrophobic groups onto an acrylamide backbone [8–22], are especially attractive, in particular, for many oilfield exploitations including drilling, polymer-augmented water flooding, chemical flooding and profile modification. The role of the polymer in most improved oil recovery field applications is to increase the viscosity of the aqueous phase. This increase in viscosity can improve sweep efficiency during enhanced oil recovery processes. In drilling fluids, the solution rheology is very important. Shear thinning fluids that can suspend drilling cuttings at low shear rates but offer little resistance to flow at high shear rates are desired [12–16].

In aqueous environments, the non-polar alkyl groups have a strong tendency to associate together through inner-molecular and inter-molecular interactions, because the contact of a hydrophobic group and water is unfavourable. At high concentration, inter-molecular hydrophobic association is predominant, which yields a transient network structure to offer excellent viscosity building capacity [4–8]. Because the applied environments are mostly aqueous environments, which are less harmful to mankind, these kinds of polymers became the hot research point.

Nowadays, most of the hydrophobic associative polymers consist of an ionic framework with a non-ionic hydrophobic unite, a non-ionic framework with an ionic hydrophobic unite or a non-ionic framework with a non-

ionic hydrophobic unite [6–20]; the research of an ionic framework with an ionic hydrophobic unite are relatively scarce [19, 30, 31]. However, the last kind of polymer may exhibit an additional electrostatic attraction if appropriate disposal is implemented (we may call them amphoteric hydrophobic associative polymer). In this paper, an amphoteric hydrophobic associative polymer is synthesized and characterized. Its effect on the properties of a surfactant is discussed, too.

Experimental

Materials

Some inorganic materials were purchased from Beibei Reagent (Chongqing, China); these materials include sodium sulphite (Na_2SO_3) and potassium persulphate (KPS). Other organic materials were purchased from Chengdu Kelong Reagent (Chengdu, China); these reagents included acrylamide (AM), acrylic acid (AA) and ethanol. The polymerizable surfactant octadecyl dimethyl allyl ammonium chloride (C_{18}DMAAC) was supplied by Southwest Petroleum University.

Synthesis

A 150-ml jar was charged into a certain amount of AM, AA, C_{18}DMAAC and water. The mixture's concentration was 25%. The mixture was stirred, and the jar was put into a 40 °C water bath. After 30 min, some Na_2SO_3 were dropwised into the jar. About 10 min later, 0.05% KPS was charged into the mixture solution. Then the temperature was kept for 12 h. After the reaction, the polymer solution was cooled and then precipitated by a 1,000-ml cool ethanol under stirring. The white precipitate was sliced with scissors and washed by ethanol three times; the white polymer slice was dried under a vacuum at 50 °C for 24 h. At last, the white slice was shattered, and the white powder was obtained.

Intrinsic viscosity and nomenclature

There is no special equation to calculate the molecular weight of a hydrophobic associative water-soluble polymer, so we use for reference GB12005.1-89 (GB, Guojia Biaozhun) and GB12005.10-92 to calculate the average molecular weight of the hydrophobic associative water-soluble polymer synthesized in this paper [28, 29]. An Ubbelohde capillary viscometer was employed to measure the intrinsic viscosity of the hydrophobic associative water-soluble polymer. Measurements were performed at 25± 0.1 °C. The capillary is 0.56 mm.

As listed in Table 1, the sample codes refer to the hydrophobic length, hydrolysis degree and hydrophobic unite content. For example, in the sample code for 18–15–0.25, '18' stands for the hydrophobic length, the number '15' means the hydrolysis degree (mol%), and '0.25' indicates the hydrophobic unite content.

Hydrolysis degree

Potentiometric titration is a classical way to determine the charge content in a partially hydrolyzed polyacrylamide. In this paper, for there is a little of the hydrophobic group that could not affect the measured result, we determined the hydrolysis degree according to GB12005.6-89 [30].

Rheology

Concentrated stock polymer solutions were prepared by dissolving appropriate amounts of the polymer with distilled water in a 500-ml flask. Gentle magnetic agitation was applied after 1 day of prehydration. The final solutions of the desired concentration were made up in 50-ml conical flasks by diluting the stock solutions with distilled water and mixed in a thermostatic water bath shaker (25 °C) for about 12 h. Before measurements, polymer solutions were left without agitation for at least 1 day to reach equilibrium. The viscosity was measured at 25±0.1 °C using the Brookfield DV-III programmable rheometer (Hebei Chengde Lab Instrument [China]) [4, 19, 31].

Table 1 The basic characteristic parameters

Sample	Feed ratio (mol%)			Hydrolysis degree (%)	Specific viscosity (ml/g)	Molecular weight × 10^{-6} (g/mol)
	AM	AA	C_{18}DMAAC			
18–15–0.25	84.75	15	0.25	14.6	412.90	1.49
18–15–0.5	84.50	15	0.5	14.9	303.51	1.01
18–15–0.75	84.25	15	0.75	14.3	230.30	0.93
18–15–1.00	84.00	15	1.00	14.2	284.68	0.71

Surface tension

The surface tension was measured at 25±0.1 °C using the tensiometer JZHY-180 (Hebei Chengde Lab Instrument), equipped with a Pt-Ir-20 ring. Equilibrium was confirmed by multiple measurements of a constant surface tension, and at least three measurements were taken for each point. Every point in the surface tension plot is an average value of three runs of measurement. In the course of experiments, the solutions were diluted step-by-step, and the temperatures were maintained at 25.0±0.1 °C by heating the sample cell with a reservoir of fluid circulating from a water bath. Before each measurement, the surface tension values were corrected by the subtraction of the pure water value. When the adsorption balance was reached, the surface tension was measured [10, 14, 31].

Results and discussion

Intrinsic viscosity and hydrolysis degree

As noted in Table 1, the hydrolysis degree is close to the feed ratio. The difference maybe ascribed to a reactivity difference. The molecular weight gradually decreased with the increase in hydrophobic unite content, which can be explained by the difficult reaction of hydrophobic unite. The specific viscosity decreased from 412.90 to 230.30 ml/g, then it increases. This is not similar to ordinary copolyacrylamide-acrylic. It also shows that there exists a strong inter-molecular interaction, because the molecular weight of 18–15–0.75 is larger than that of 18–15–1.00, but the specific viscosity of 18–15–0.75 is smaller than that of 18–15–1.00.

Properties of polymer solution

The relationship between polymer solution concentration and viscosity

As shown in Fig. 1, the viscosities of copolymers increase linearly with the increasing copolymers' concentration from 0 to 3,500 mg/l. Above this polymer's concentration, about 3,500 mg/l, four kinds of copolymers' viscosity increase dramatically with the polymer concentration variance. For the pure copolymer of AM and AA (18–15–0.00), none of this kind of phenomenon exist. This apparent upturn is called the critical association concentration (C*) [19, 30, 31]. It is worth noting that these kinds of copolymers' C* is near 3,500 mg/l. This kind of phenomenon could be easily understood: When an amphoteric associative polymer is dissolved in water, the static repulsion makes the polymer chain spread, which enlarges the hydrodynamical volume

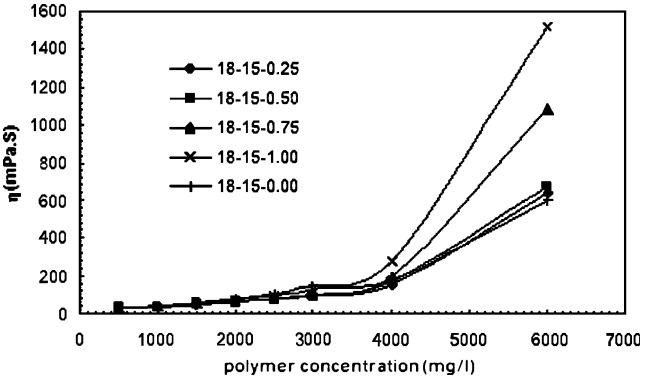

Fig. 1 Effect of polymer solution concentration on viscosity

of polymer; at the same time, the hydrophobic interaction (van der Waals' force) orients the hydrophobic unite to form a hydrophobic microdomain, like physical cross-link point, which makes linear molecules entangle with each other and augment the viscosity of the polymer solution [4, 19]. In other words, because of that kind of physical cross-linking point, the size of the particle in the solution becomes larger, which results in the non-linear increase in the polymer solution, especially above the copolymers' C*. It also indicated that this phenomenon becomes much obvious with the increase in hydrophobic unite content. This accounts for a greater opportunity to form hydrophobic microdomain in the same polymer solutions.

The relationship between shear rate and shear stress

Figure 2 shows the 18–15–*X* series' rheology curves of a 3,000 mg/l polymer solution. As noted in Fig. 2, the shear stress of amphoteric associative polymer solution increases with the shear rate; these four curves almost present linearity. By using the mathematical method to dispose the curves, it was found that the four curves could be stimulated with the Bingham model [8–19], and the coefficient of the correlation is more than 0.99. It further showed that this kind of amphoteric associative polymer solution exhibits a yield stress that opens out the existence

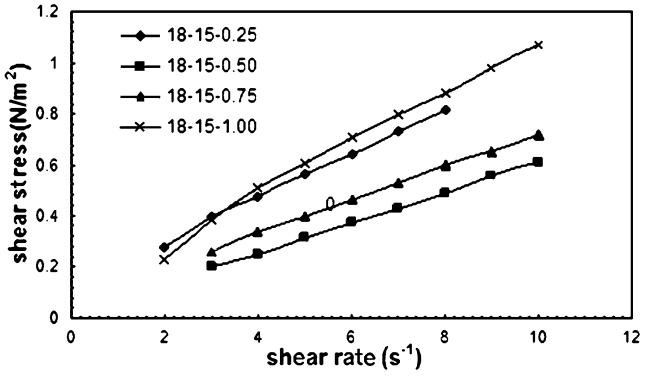

Fig. 2 Effect of shear rate on shear stress

of a three-dimensional net structure of amphoteric associative polymer solution. If this kind of physical cross-linking point formed by hydrophobic microdomain was broken, the exterior energy is necessary. Accordingly, the amphoteric associative polymer solution presents a yield stress.

The relationship between shear rate and polymer solution's viscosity

As shown in Fig. 3, except for 18–15–1.00, the polymer solutions of 18–15–*X* are shear dilute. Because the hydrophobic association is a kind of a weak interaction, the combination strength is low. This association could be easily broken when it reaches the shear stress, and the net structure in the solution could be collapsed, which means that the structure–viscosity of the system would be lost, and the apparent viscosity would decrease sharply. If the shear stress had been removed, the viscosity of the system would have recovered rapidly. This illustrates that the association is reversible.

As for the 18–15–1.00, the polymer solution presents shear thickening and then shear dilution. It could be explained that the high content of hydrophobic unite leads to the major inner-molecular association, the molecular coil shrinks excessively and the low shear stress makes the molecular coil spread, which is favourable in inter-molecular association. As a result, the polymer solution's viscosity increases. If the shear rate runs more than that certain value, the inter-molecular association could be broken too. The viscosity continues to decrease; therefore, the polymer solution shows shear dilution [25–30].

Effect of hydrophobic associative water-soluble polymer (HAWP) on the surface tension of non-ionic surfactant

As noted in Figs. 4 and 5, the polymers of 18–15–*X* of about 500 and 3,000 mg/l affect the surface activity of octyl phenyl ther (OP-10). At low concentration of OP-10, this kind of affection is more obvious than that of a phenomenon at high concentration of OP-10. At low concentration of OP-10, the degree of effect becomes more and more serious with the increase in the concentration of OP-10. However, the effect of the polymer almost keeps invariable. This could account for the adsorption of OP-10 to an amphoteric associative polymer chain. According to the "three-stage model," the adsorption of OP-10 to the amphoteric associative polymer chain is not a concurrent process but a non-concurrent process when compared with the adsorption of a surfactant to a common water soluble polymer. It also indicates that the adsorption makes the free surfactant molecules' concentration decline in the solution, and this effect is independent from the range of the surfactant's concentration. There, 18–15–*X* could accord with this model [22–32].

The two figures also indicate that the increase in the content of the hydrophobic group results in the increase in adsorption quantity, because the total volume of the hydrophobic microdomain will become larger if the number of the hydrophobic unite increases. And the hydrophobic section of OP-10 can much easily approach that kind of

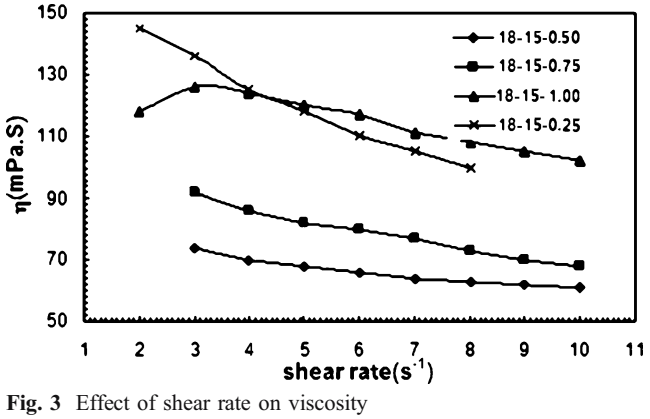

Fig. 3 Effect of shear rate on viscosity

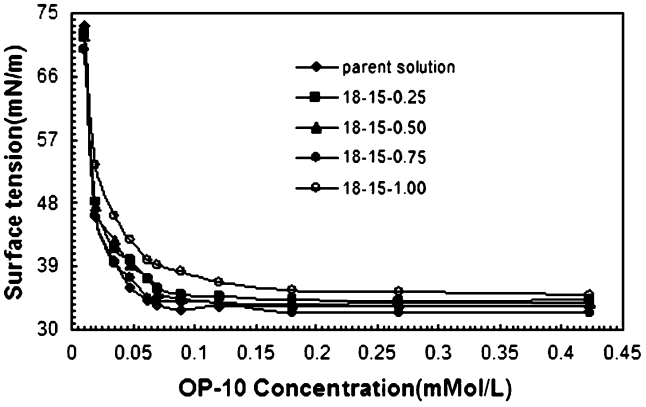

Fig. 4 OP-10 concentration versus surface tension in 500 a mg/l polymer solution

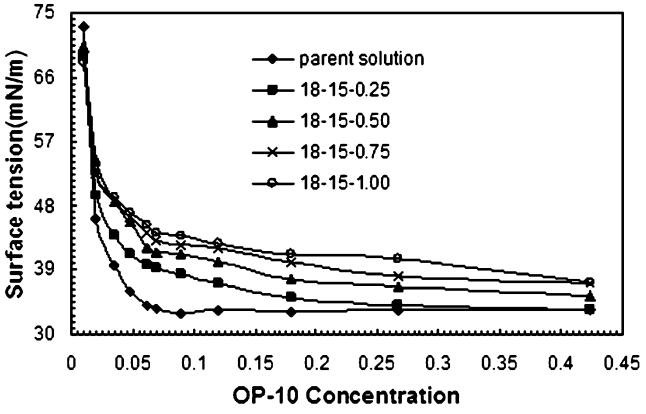

Fig. 5 OP-10 concentration versus surface tension in a 3,000 mg/l polymer solution

hydrophobic microdomain on the basis of the comparability theory. As a result, the number of free surfactant molecules in the solution will decrease, and the solution's surface tension arises [31].

As compared with Fig. 4, Fig. 5 shows that the higher the concentration of the amphoteric associative polymer is, the deeper the degree of the effect on the solution's surface is, and the higher the surfactant's concentration is when the curves become flat, and so did the content of the hydrophobic unite. Owing to the higher surfactant's concentration, the microdomain that existed in the polymer solution becomes more and more, which provides much position as to where the surfactant molecules adsorb to. Therefore, the number of free surfactant molecules in the solution will decrease, and the solution's surface tension arises [30, 31].

As far as the increase in the polymer's concentration is concerned, there is a deep means: The ratio of the surfactant molecule adsorbed arises with the increase in the hydrophobic group's concentration. In Fig. 4, the surfactant's concentration is 0.12 mM/l when the curves become flat, but in Fig. 5, it is 0.36 mM/l. All these show that amphoteric associative polymer concentration gives drastic impact on the OP-10 surface tension, especially for the high hydrophobic unite content polymer, like 18–15–1.00.

Effect of HAWP on the surface tension of ionic surfactant

As compared with Figs. 4 and 5, Figs. 6 and 7 indicate that the resulting effect is similar; the difference is the effect's degree. It is obvious that the effect on sodium dodecylbenzene sulphonate (SDBS) is much stronger, especially in the high polymer concentration. It is easy to draw a conclusion that the hydrophobic associative interaction is the major interaction between the polymer and the surfactant, because the curves do not exhibit a virtual difference in both

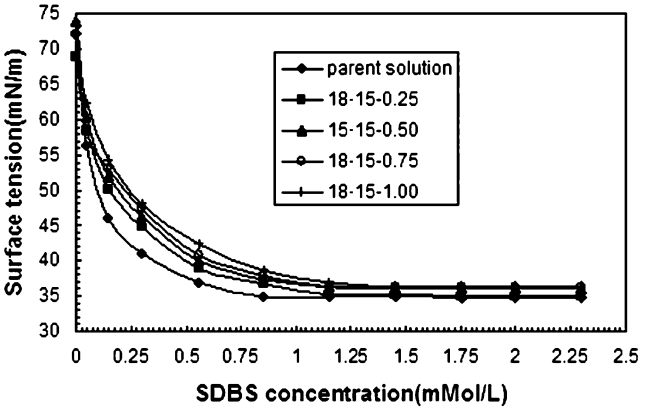

Fig. 6 SDBS concentration versus surface tension in 500 mg/l polymer solution

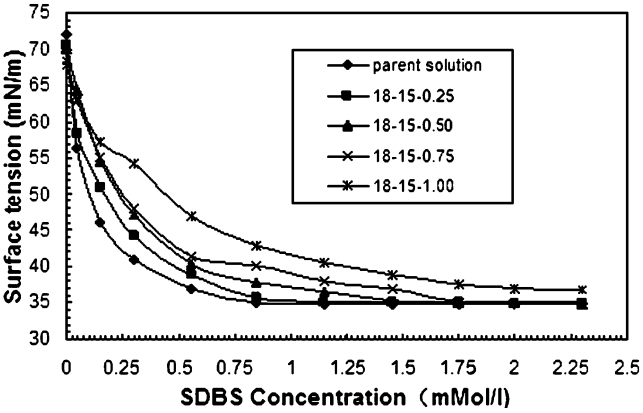

Fig. 7 SDBS concentration versus surface tension in 3,000 mg/l polymer solution

SDBS's and OP-10's curve mixture solutions. The degree of difference could be ascribed to the difference of SDBS's and OP-10's curve mixture concentration.

Conclusion

In this paper, the amphoteric hydrophobic associative water-soluble polymer was synthesized by solution polymerization using three monomers: AM, AA and C_{18}DMAAC. The polymer's molecular weight is from 0.71 to 1.46× 10^6 g/mol. And the hydrolysis degree range is from 14.9 to 14.2%. This kind of polymer exhibits a good association interaction, including inner-molecular association and intermolecular associations, and the stronger the association phenomenon is, the higher the hydrophobic unite content is. The C* is about 3,500 mg/l. By using the mathematical method to dispose the curves, it is found that the curves could be stimulated with the Bingham model. As for the low content of the hydrophobic unite of the polymer, it exhibits shear dilution, but for the high content of the hydrophobic unite of the polymer, it can show both shear thickening and shear dilution. Through investigation of the surface tension, it was found that the polymer made the surface tension of the surfactant solution increase, and the surface curves deviate from the parent-solution curve. Both the hydrophobic unite content and the polymer solutions' concentration exaggerate the deviation with their self-quantity increase. The interaction between the polymer and the surfactant almost has no business with the surfactant's property of charge. The major interaction could be a hydrophobic association interaction.

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