Effect of Temperature and pH Values on Aggregation Behavior of Polymeric Surfactants in Aqueous Solution

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ABSTRACT: A novel kind of polymeric surfactant based on carboxymethyl cellulose and poly(ethylene oxide) dodecyl ether acrylate (CMC-AR$_{12}$EO$_9$) was synthesized through ultrasonic irradiation. Aggregation behavior in aqueous solution at different temperatures and pH values was investigated by dynamic laser scattering and fluorescence probe. The results show that, with the increase of temperature, polymeric surfactants are favorable to form multimolecular micelles with narrower polydispersity of size distribution. At a higher temperature, the multimolecular micelles tend to aggregate bigger sized particles that are unstable and would be disaggregated at higher shear rate. At the elevated pH values, the size of micelles reduces drastically because of strong damage of alkali to aggregates, whereas nonpolar and insoluble domains formed by the hydrophobic blocks of polymeric surfactants are insensitive to pH changes. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 945–949, 2005

Key words: block copolymers; surfactants; micelles

INTRODUCTION

Polymeric surfactants, sometimes called amphiphilic copolymers, dissolved in a selective solvent may aggregate to form micelles, which presumably consist of a core of the insoluble block surrounded by a corona of the soluble block. These micelles can solubilize materials such as drugs or aggregate to give large changes in properties. Thus, the aggregation behavior of polymeric surfactants in solutions plays an important role in surfactancy, stabilization of colloidal particles, and rheological behavior.[1–4]

To some extent, polymeric surfactants serve all the same functions as low-molecular-weight surfactants. Because of their high molecular weight and complex structure, however, they have some unique characteristics, for example, the formation of monomolecular micelles in the dilute solution, various shapes of micelles at different concentrations, etc.[5,6] With the change of solution conditions such as solvent, electrolyte, temperature, and pH values, they would also make complex conformational changes, which may have great influence on their application performance of interfacial activity, viscosity, and emulsification.[7–10] However, few studies have so far been conducted on the effect of temperature and pH value changes on the aggregation behavior of polymeric surfactants because of their complicated influences, especially for hydrophilic polymeric surfactants.

Our preliminary work on the synthesis of a novel series of amphipathic copolymers by ultrasonic irradiation was reported.[6,11] Because of the unique ultrasonic copolymerization mechanism, the polymeric surfactants based on carboxymethyl cellulose (CMC) and alkyl poly(etheroxy) acrylate have a special block structure. The products show excellent surface and interfacial activity, comparable to those of low-molecular-weight surfactants. Their micellar conformation in aqueous solution was studied and the results show that conformation of copolymer molecules is totally different from that of CMC because of the introduction of the surface-active macromonomers. They may form monomolecular micelles or aggregates to form multimolecular micelles having various shapes.

In this study, the research centered on the investigation of aggregation conformation of the polymeric surfactants at different temperatures or pH values in aqueous solution, which was studied by dynamic laser scattering (DLS) and fluorescence probing.

EXPERIMENTAL

Materials

Modified sodium CMC, supplied by Guangzhou Nanxiu Chemical and Engineering Co. (Guangzhou, China), was purified by acetone precipitation. The degree of substitute (DS) of —CH$_2$COONa is 1.02, and $\bar{M}_v = 2.18 \times 10^5$ g mol^{-1}.
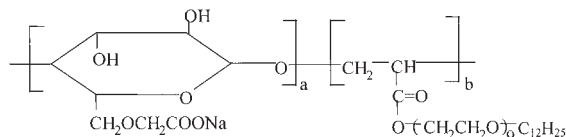
Figure 1　CMC-based polymeric surfactant.

Surface-active macromonomers, poly(ethylene oxide) dodecyl ether acrylate ($AR_{12}EO_9$, the number of oxyethylene units is 9), were synthesized by reaction of acryloyl chloride with poly(ethylene oxide) dodecyl ether.[12]

Apparatus

Ultrasound with a frequency of 20 kHz was produced with a Sonics and Materials 1500 Ultrasonic Generator (USA), the power output being adjustable.

Synthesis of polymeric surfactants

The polymeric surfactants were prepared by subjecting the aqueous solution of 0.6% CMC in the presence of 0.5% surface-active macromonomers $AR_{12}EO_9$ to ultrasonic irradiation for 20 min at 25 ± 1°C. The methods of preparation and purification were reported earlier.[11] The reaction mixture was dried and extracted by a Soxhlet apparatus with acetone for 36 h to get rid of unreacted macromonomers. The solid was dissolved in a mixture of CH_3OH/H_2O (70/30, v/v). By adding CH_3CH_2OH to the solution, pure CMC was precipitated out, whereas the copolymer was left in the solution. The solvent was evaporated and solid copolymer products were obtained. Finally, the products were purified by washing with acetone several times and drying under vacuum at 40°C. After purification, unreacted macromonomers and pure CMC were washed out.

The molecular structure of CMC-based amphipathic copolymers is represented in Figure 1. The average composition of CMC-$AR_{12}EO_9$ was determined by titration of the COONa groups of CMC under acidic conditions (according to the degree of COONa substitution of CMC, 1.02), and the composition of segments $AR_{12}EO_9$ is 9.0%. The average molecular weight ($\bar{M}_w$) of the copolymers is 16.9×10^4 g mol^{-1}, which was determined by static laser scattering.

Measurements

Apparent viscosity of aqueous solution was determined with a Brookfield TC500 (model DV-III) viscometer at 0–200 s^{-1} by using appropriate spindles.

Weight-average molecular weight ($\bar{M}_w$) of samples was measured by static laser scattering (DLS-700, Japan) at 25°C.

The size and distribution of micelles in aqueous solutions were measured by DLS (BI-9000AT, BI-200SM, Brookhaven Instruments Corp., USA) at 25°C. The laser wavelength is 514.5 nm; scattering angle is 90°. The fluctuation of the scattered light intensity can be expressed in terms of the normalized second-order autocorrelation function $g^{(2)}(\tau)$

$$g^{(2)}(\tau) = A \, (1+b[g^{(1)}(\tau)]^2) \qquad (1)$$

where $g^{(1)}(\tau)$ is the normalized first-order autocorrelation function, b is an empirical constant, and A is baseline.

As the usual micelles of the copolymers are a polydisperse system, $g^{(1)}(\tau)$ is then

$$g^{(1)}(\tau) = \int_0^\infty G(\Gamma)\exp(-\Gamma\tau)d\Gamma \qquad (2)$$

with

$$\int_0^\infty G(\Gamma)d\Gamma = 1 \qquad (3)$$

where $G(\Gamma)$ is the distribution function of decay rates Γ. Since the CONTIN program tends to deal statistically with the representation of particle size distribution with more than a single peak (polydisperse system), the hydrodynamic radius R and intensity-averaged particle size distribution function $F(R)$ were determined by the CONTIN program.[13]

Microscopic polarity and microscopic viscosity of copolymer solution were tested by Hitachi F-4010 fluorescence spectroscopy (Japan), using a probe of pyrene and rhodamine B (RhB), respectively.[14] For the microscopic polarity test, the concentration of pyrene is $10^{-5}M$, slot Ex = 5.0 nm, Em = 5.0 nm, scanning speed = 100 nm/min, λEx = 241 nm. The microscopic polarity was determined by intensity ratio (I_{III}/I_I) of the third peak (band O-2) to the first peak (band O-O) of adsorption fluorescence spectrum of pyrene. The polarization degree of RhB (P_f) directly correlates with the microscopic viscosity. P_f is defined by

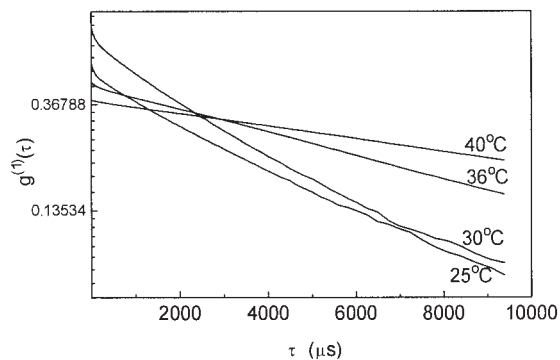$$P_f = (P_{f\parallel} - P_{f\perp})/(P_{f\parallel} + P_{f\perp}) \qquad (4)$$

Figure 2 The normalized first-order autocorrelation function of 0.5% CMC-AR$_{12}$EO$_9$ solution at different temperatures.

The microscopic viscosity was determined by polarization degree $P_{580\,nm}$ of RhB at 25°C (concentration of RhB is $1 \times 10^{-6}M$).

RESULTS AND DISCUSSION

Temperature

The normalized first-order autocorrelation functions of 0.5% CMC-AR$_{12}$EO$_9$ micelle solutions at different temperatures were measured. The decay curves are displayed in Figure 2. At the lower temperature, the autocorrelation functions of CMC-AR$_{12}$EO$_9$ are represented by multiexponential decay functions, which indicate the polydisperse distributions of micelle size. With the increase of solution temperature, the autocorrelation function tends to be represented by a single-exponential decay function, which may mean the narrow distributions of aggregate size.

Figure 3 shows a series of distribution function curves $F(R)$ of CMC-AR$_{12}$EO$_9$ solutions versus the hydrodynamic radius R over a range of temperatures from 25 to 40°C, as determined by the CONTIN program. Our preliminary work has reported that mono-
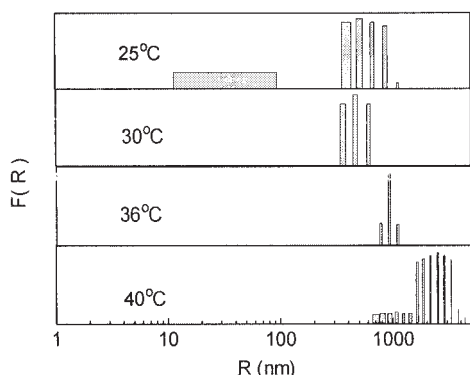

Figure 3 The intensity-averaged distribution curve $F(R)$ of 0.5% CMC-AR$_{12}$EO$_9$ micelle solution as a function of temperatures.
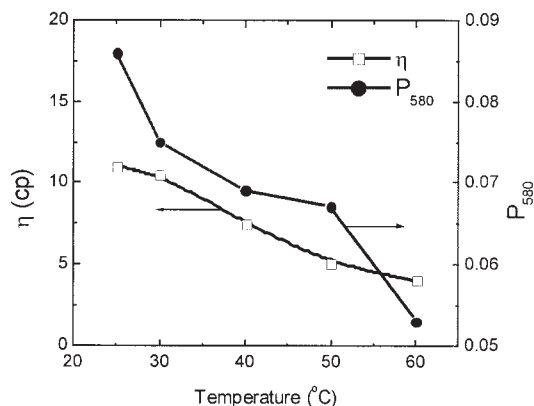

Figure 4 Influence of temperature on apparent viscosity at 132 s^{-1} and polarization degree (P) of 0.5% CMC-AR$_{12}$EO$_9$ aqueous solution.

molecular micelles exist at all concentrations tested at 25°C, which correspond to the distribution region of smaller R (30–150 nm).[6] As shown in Figure 3, at the elevated temperature, the monomolecular micelle region disappears, and the size of multimolecular micelles is becoming first smaller and then larger above 30°C. It is indicated that the polymeric surfactants tend to form multimolecular micelles with narrow size distribution in aqueous solution at the elevated temperatures. Because of the quickened thermal movements of molecules, hydrogen bonds formed by ethylene oxide chains and water are destroyed easily, which result in the decrease of hydrophilicity of copolymers and the formation of larger aggregates. Thus, CMC-based polymeric surfactants still represent the characteristics of nonionic surfactants.

The apparent viscosity at a shear rate of 132 s^{-1} and microscopic viscosity of CMC-AR$_{12}$EO$_9$ aqueous solutions were shown in Figure 4. Obviously, the macroscopic viscosity and microscopic viscosity of CMC-AR$_{12}$EO$_9$ aqueous solutions reduce simultaneously with the increase of temperature. However, the above results of DLS show that, at the elevated temperature, the polymeric surfactants are favorable to form larger aggregates, and the solution viscosity would increase accordingly. It seems that these results are contradictory.

The samples in DLS are in static state. Thus, the apparent viscosity of 0.5% CMC-AR$_{12}$EO$_9$ aqueous solution at a very low shear rate (13.2 s^{-1}) versus temperature was studied (as shown in Fig. 5). At 13.2 s^{-1}, there is a minimum viscosity at 30°C. Above 30°C, the solution viscosity improves greatly, which completely agrees with the results of DLS.

Obviously, as the temperature elevates, the size of micelles decreases, leading to the declining microscopic viscosity of copolymer solutions. At the same time, unstable larger aggregates would be formed by several micelle particles because of the quickened
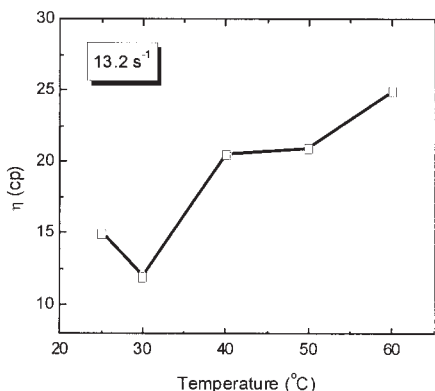
Figure 5 The apparent viscosity at 13.2 s^{-1} of 0.5% CMC-AR$_{12}$EO$_9$ aqueous solution as a function of temperature.

Figure 7 The normalized first-order autocorrelation function of 0.5% CMC-AR$_{12}$EO$_9$ aqueous solution at pH = 12.0.

thermal movements of micelles and aggregation trend among neighboring micelles, which represent big hydrodynamic radius in DLS and higher viscosity of solutions in static state. While the viscosity of solutions is measured at high shear rate, it decreases sharply because of disaggregation of unstable large particles.

pH values

The aggregation morphology and size distribution of 0.5% CMC-AR$_{12}$EO$_9$ aqueous solution at different pH values were studied by DLS. From Figures 6 and 7, the curves of normalized first-order autocorrelation functions of CMC-AR$_{12}$EO$_9$ in aqueous solution (pH = 6.8), acid solution (pH = 3.0), and alkali solution (pH = 12.0) exhibit totally different features. Compared with $g^{(1)}(\tau)$ of CMC-AR$_{12}$EO$_9$ aqueous solution (pH = 6.8), $g^{(1)}(\tau)$ of acid or alkali solutions is a departure from a single-exponential decay function, so the aggregates may have different morphology. Especially in alkali solution, the irregularity of $g^{(1)}(\tau)$ indicates the polydispersity of particle morphology and size distribution.
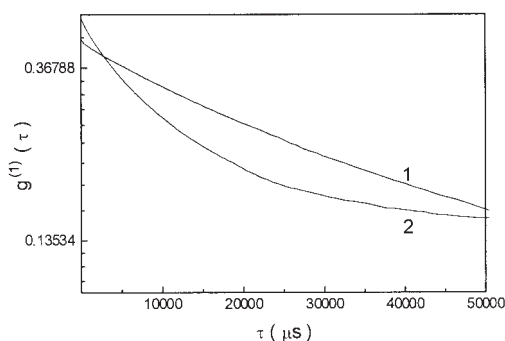
As a further attempt to prove the different shape of micelles formed by the copolymers, the influence of pH value changes on the distribution $F(R)$ of hydrodynamic radius R was examined (as shown in Fig. 8). In HCl aqueous solution, very big particles are observed and the averaged hydrodynamic radius R is $\sim$ 1200 nm. Because of the great amount of H$^+$ in the solution, ion groups COO$^-$ of polymeric surfactants based on CMC are screened. Therefore, the repulsion force among micelles is weakening and some big aggregates are formed.

While in alkali solution, the most obvious change is a drastic reduction of the size of micelles. As the pH values are elevated, there is a sharp reduction of the micellar hydrodynamic radius. In aqueous solution, the average R of micelles is $\sim$ 600 nm. When pH = 12.0, R of particles is $\sim$ 75 nm. That means that most

Figure 6 The normalized first-order autocorrelation function of 0.5% CMC-AR$_{12}$EO$_9$ aqueous solutions: 1, pH = 6.8; 2, pH = 3.0.
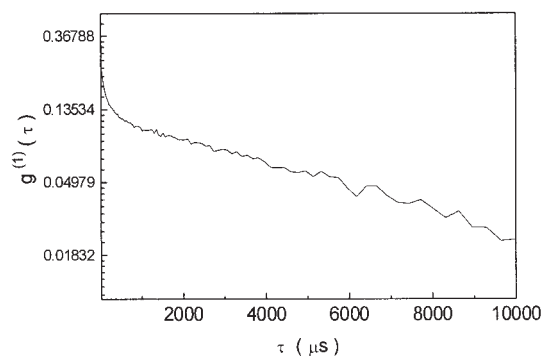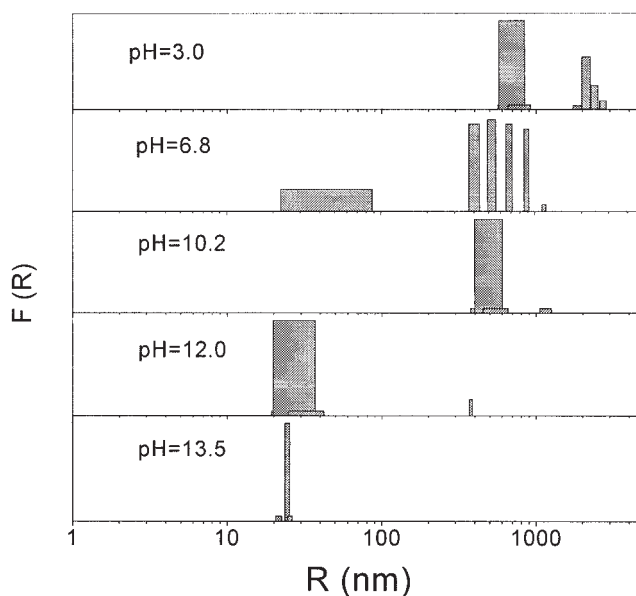

Figure 8 The intensity-averaged distribution curve $F(R)$ of 0.5% CMC-AR$_{12}$EO$_9$ in aqueous solution at varied pH values (determined by CONTIN).
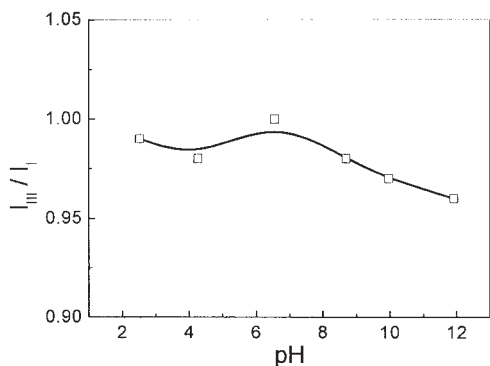
Figure 9 Relative intensity ratio (I_{III}/I_I) of pyrene fluorescence in 0.1% CMC-AR$_{12}$EO$_9$ aqueous solution as a function of pH.

micelles are destroyed. In a previous study, we reported that this kind of polymeric surfactant would form monomolecular micelles and multimolecular micelles simultaneously in aqueous solution. The size region of the monomolecular micelles is $\sim$ 30–150 nm. As can be seen from Figure 8, in the solutions having highest pH value, only the monomolecular micelle region is in existence. That means that chains of copolymers are curled and freely dispersed in alkali solutions. The results prove that alkali can destroy the molecular and micellar aggregation of polymeric surfactants.

The relative intensity of pyrene in the fluorescence spectra in 0.1% CMC-AR$_{12}$EO$_9$ aqueous solution at different pH values are shown in Figure 9. The microscopic polarity is determined by intensity ratio I_{III}/I_I of the third peak (band O-2) to the first peak (band O-O) of adsorption fluorescence spectrum of pyrene. In water, the ratio I_{III}/I_I is $\sim$ 0.64; in alkane, the ratio is $\sim$ 1.65. Little pyrene could solve in water, but it can solubilize in nonpolar cores of micelles. In Figure 9, as the pH values of the solutions change from 2 to 13, little change of I_{III}/I_I occurs, indicating a little change of the polarity of microstructure where pyrene positions. Therefore, in different pH value solutions (i.e., acid aqueous solutions or alkali solutions), although the morphology and size of aggregations of CMC-AR$_{12}$EO$_9$ change significantly, their hydrophobic chains still tend to aggregate to form nonpolar domains. In addition, when the pH value is larger than 7, the ratio I_{III}/I_I slows down a little, corroborating the damage of alkali to aggregates of copolymers.

CONCLUSIONS

The aggregation behavior of polymeric surfactants CMC-AR$_{12}$EO$_9$ is influenced heavily by the temperature and the pH value of solutions. With the increase of temperature, the monomolecular micelle region disappears, and the size of multimolecular micelles becomes first smaller and then larger above 30°C, indicating that polymeric surfactants CMC-AR$_{12}$EO$_9$ tend to form multimolecular micelles with narrow size distribution in aqueous solution at elevated temperatures. Thus, CMC-based polymeric surfactants still represent the characteristics of nonionic surfactants. While at the high temperature, the very large particle size and relatively lower microscopic viscosity indicate the size of single micelle may reduce but the neighboring micelles have a trend to aggregate forming larger particles. These particles are not stable and would be disaggregated at the higher shear rate.

The effect of pH changes on aggregation behavior of polymeric surfactants in aqueous solutions is complex. Because ion groups COO$^-$ of CMC-AR$_{12}$EO$_9$ are screened, very big particles are observed in acid aqueous solution. With the increase of pH values of solutions, the most obvious change is a drastic reduction of the size of micelles. That means alkaline conditions can destroy the aggregations of polymeric surfactants in solution. Although the morphology and size of aggregates of CMC-AR$_{12}$EO$_9$ change significantly in aqueous solutions at different pH values, nonpolar domains formed by their hydrophobic chains always exist.

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