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Preparation and Unimolecular-Micellization Behavior of Homopolymer of Surface-Active Monomer AMC₁₄AB

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(Dated: Received on April 11, 2008; Accepted on August 23, 2008)

(2-acrylamido) ethyl tetradecyl dimethylammonium bromide (AMC₁₄AB) was polymerized in aqueous solution to form the homopolymer P(AMC₁₄AB). The physicochemical properties of P(AMC₁₄AB) in aqueous solution were mainly studied with fluorescent probe method, surface tension measurement and conductometry. The experimental results show that the aggregation morphology of P(AMC₁₄AB) in aqueous solution is unimolecular micelle as expected. Being different from conventional multimolecular micelle systems, the unimolecular micelle system of P(AMC₁₄AB) not only shows critical micellar concentration (CMC=0), (i.e. once added to pure water, the surface tension decreases immediately in spite how small the density is), but also the surface tension stays almost the same with the concentration increasing. That is to say, there is no mutational point on the relationship curve between surface tension and concentration. Furthermore, the unimolecular micelle system of P(AMC₁₄AB) has no Krafft temperature, i.e. at any temperature, so long as it is dissolved in water, the unimolecular micelles will form. Besides this, for the solubilization of hydrophobic organic substances, the unimolecular micelle system of P(AMC₁₄AB) is obviously different from the common multimolecular micelle system, having no turning point on the relationship curve between solubilization amount and P(AMC₁₄AB) concentration, and the solubilizing ability of the unimolecular-micelle system of P(AMC₁₄AB) for hydrophobic organic substances is much higher than that of the conventional multimolecular micelle solutions of common surfactants, such as cetyl trimethyl ammonium bromide.

Key words: Surface active monomer, Unimolecular micelle, Zero critical micellar concentration, Krafft temperature

I. INTRODUCTION

Surface active monomers (surfmers) are one kind of functional surfactants, whose molecules not only possess of amphiphilic structure composed of hydrophobic tail and hydrophilic head group, which imparts them surface activity, but also contain polymerizable vinyl double bonds [1,2], which can be initiated and polymerized, so they are called as polymerizable surfactants. Surfmers have potential application in many scientific and technical fields: for example, they can be used to prepare vesicles for performing biological simulation, prepare functional polymer microspheres, construct soft templates for synthesizing functional inorganic nano-materials and inorganic/organic composite nano-materials, be applied in emulsion polymerization as polymerizable emulsifiers, and adjust the thickness of fluidic materials [2-7]. Recently, although surfmers have attracted wide attention of academia and industrialists, the studies on surfmers have still been concentrated on improving emulsion polymerizations [4,8-11]. Their unique physical chemistry properties should be thoroughly researched, and the applications of these polymer in other scientific and technical fields should be

developed. In our previous work, anionic surface active monomers and their copolymers were studied [11,12]. Afterwards, a cationic surfmer (2-acrylamido) ethyl tetradecyl dimethylammonium bromide (AMC₁₄AB) was synthesized and characterized [13], homopolymer P(AMC₁₄AB) was prepared and its physicochemical properties in aqueous solution were studied. Regarding the aggregation morphology of P(AMC₁₄AB) in water, the author theorized that P(AMC₁₄AB) would exist as unimolecular micelles, and the experimental results confirm this viewpoint. Actually, as early as in 1983, Paleos *et al.* proposed this concept in terms of polymerized micelle [14], and afterwards Sherrington followed and expressed this concept in terms of unimolecular micelle [7,15]. The so-called unimolecular micelle means that for the homopolymer of surfmers, single macromolecules form a micelle because of strong intramolecular hydrophobic association. Unimolecular micelles have many peculiar physicochemical properties, to which scientists have not paid much attention. In this work, the preliminary indicates that the physicochemical property of unimolecular micelles is greatly different from that of multimolecular micelles formed by common small surfactants. Unimolecular micelles exhibit zero critical micellar concentration (CMC=0), i.e. at all concentrations above zero, micelles can form, and furthermore, they have much stronger solubilization ability for hydrophobic organic substances than micelles of conventional surfactants, and this is probably

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related to the greater cavity inside of the unimolecular micelle. It can be predicted that the physicochemical characteristics of unimolecular micelles have potential in micellar catalysis, template media of limited space, and so on. So far, profound studies on unimolecular micelles are scarce.

II. EXPERIMENTS

A. Materials and instruments

AMC₁₄AB was prepared and recrystallized from ethyl acetate three times. Pyrene (Aldrich) was recrystallized twice by ethonal before use. Both of cetyl trimethyl ammonium bromide (CTAB, Beijing Zhonglian Chemical Reagent Factory) and Ammonium persulphate (Beijing Chemical Reagent Institute) were analytical grade. The used water in this research were all redistilled.

Experimental instruments were as follows: Shimadzu-8400S FTIR spectrometer (Japanese Shimadzu Company), Unic-2602 UV spectrometer (American Unic Company), HITACHUI F2500 fluorescence spectrometer, DDS-11Ar digit conductivity meter (Leici Instrument Limited Company of Shanghai), and JYW200B automatic tensiometer (Chengteh testing machine Co. Ltd., China). Proton nuclear magnetic resonance (NMR) spectroscopy was performed at 20 °C using Varian VXR-Unity 300 MHz and Vanrian Unity Fnova 600H Mz NMR spectrometers.

B. Homopolymerization of AMC₁₄AB

0.724 g AMC₁₄AB was dissolved in 200 mL distilled water (AMC₁₄AB concentration was about 0.05 mol/L), then added into a four-necked flask equipped with mechanical agitator, thermometer, N₂ inlet and condenser. Nitrogen was bubbled through the solution under stirring for 30 min to eliminate oxygen, after that the reactor was placed in a thermostatic water bath. The reaction temperature increased slowly to 45 °C at which point the initiator (NH₄)₂S₂O₈ was added. Then the polymerization reaction was performed under condition of continuous stirring, constant temperature 45 °C and nitrogen atmosphere. The solution became turbid after the reaction was carried out for a certain period, and 4 h later the reaction was ended and a white solid of P(AMC₁₄AB) was obtained after being freeze-dried. The solid P(AMC₁₄AB) was washed three time with 80/20 (V/V) ethyl acetate and acetone mixture to remove the residual monomer, then the polymer was dried under vacuum at 40 °C for 24 h. FTIR of P(AMC₁₄AB) was measured with KBr pellet method.

In order to study kinetic characteristics of AMC₁₄AB homopolymerization, the conversions in different periods of time were determined with potassium bromide-

potassium bromate method, and the polymerization kinetic curves of AMC₁₄AB as well as AM (acrylamide) were plotted.

C. Physicochemical property of P(AMC₁₄AB) in aqueous solution

1. Fluorescence spectra of pyrene in P(AMC₁₄AB) aqueous solution

Different concentration P(AMC₁₄AB) solutions were prepared with aqueous solutions containing saturated pyrene, the fluorescence spectra of these solutions were measured by fluorescence spectrometer under excitation at 335 nm, slit width of 2.5 nm and in the scanning range of 350-450 nm. The strength ratios (I_1/I_3) of the first peak at $\lambda=372$ nm to the third peak at $\lambda=385$ nm were calculated. The value I_1/I_3 varying with concentrations of P(AMC₁₄AB) was plotted. For analysis and comparison, pyrene fluorescence spectra in other three solutions were also measured: CTAB aqueous solution, polyacrylamide (PAM) aqueous solution, and hydrophobic association polyacrylamide (NaAMC₁₄S/AM) aqueous solution that was copolymer prepared by AM and surfmer named sodium 2-acrylamido-tetradecane sulfonate (NaAMC₁₄S) [12].

2. Critical micellar concentration

Different concentration P(AMC₁₄AB) solutions were prepared, then placed in a thermostatic bath at temperature of 25.0±0.1 °C. The surface tensions of these solutions were measured by tensiometer, and the relationship between surface tension (γ) and concentrations (C) was plotted. Comparatively, the curve of γ vs. C for CTAB solution was also measured.

The conductivity of the above solutions were determined by conductivity meter. the conductivities (κ) as the function of the concentrations (C) were plotted for P(AMC₁₄AB) and CTAB solutions.

3. Solubility in water

The saturated aqueous solutions of P(AMC₁₄AB) and CTAB at different temperatures were prepared, and immediately their solubility was determined via measuring the UV absorptions and the solubility curves of P(AMC₁₄AB) and CTAB were plotted.

4. Solubilization amount of toluene in micellar solutions

Firstly, the standard curve of toluene was measured by UV absorption method with a characteristic absorption at 266 nm. A certain amount of P(AMC₁₄AB) aqueous solutions with different concentrations were

placed in several separating funnels. Excess toluene was added into these solutions, then the mixtures were inverted and shaken repeatedly to make toluene fully solubilized in the micellar solutions. The solutions were then placed statically for 24 h until clearly demixed, after which the mixtures were filtrated, and the solubilization amounts of toluene were determined by UV absorption method. Afterward the value as a function of P(AMC₁₄AB) concentration was plotted. In order to analyze and compare, the solubilization amount of toluene in the micellar solution of CTAB was also determined.

III. RESULTS AND DISCUSSION

A. Homopolymerization process

Figure 1(a) displays the FTIR spectra of monomer AMC₁₄AB and homopolymer P(AMC₁₄AB). In AMC₁₄AB spectrum, the bands at 3083, 1630, 905, and 996 cm⁻¹ are C=C bond characteristic absorptions, among which the band at 1630 cm⁻¹ is the stretch vibration absorption of C=C bond, whereas the bands at 3083, 905, and 996 cm⁻¹ are the vibration absorptions of =C-H. The characteristic absorptions

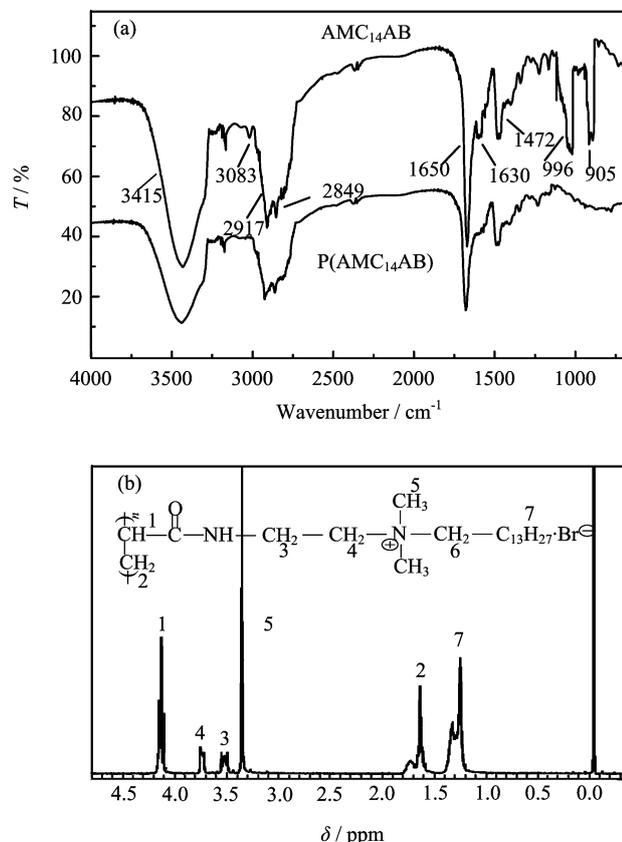
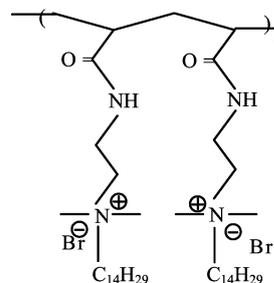


FIG. 1 FTIR spectrum (a) and ¹H NMR (b) spectrum of homopolymer P(AMC₁₄AB).

of methylene on long chain alkyls, acylamino and quaternary ammonium cation are at 2849 and 2917, 1650, 1472, and 3415 cm⁻¹, respectively. In P(AMC₁₄AB) spectrum, all the characteristic absorptions of C=C bond disappeared, whereas other absorptions of the monomeric unit of AMC₁₄AB remains. ¹H NMR spectra of homopolymer P(AMC₁₄AB) is shown in Fig.1(b), which indicates that the homopolymerization of P(AMC₁₄AB) has been obtained from AMC₁₄AB monomer; ¹H NMR: (δ/ppm; 4.16 (H1, 1, t), 3.74 (H4, 2, t), 3.53 (H3, 2, t), 3.31 (H5, 6, s), 1.50-1.83 (H2, 2, d; H6, 2, t), 1.1-1.4 (H7, 27, m)).

The structure of homopolymer P(AMC₁₄AB) can be expressed as shown in Scheme 1 according to that of AMC₁₄AB [13]. It can be clearly seen that homopolymer P(AMC₁₄AB) chemical structure takes on the following features: (i) the macromolecules have comb-like structure, a hydrophobic tetradecyl side chain hangs on every monomeric unit backbone of polyacrylamide; (ii) there are two hydrophilic groups, acrylamide group and quaternary ammonium cation, which directly covalently bound onto the backbone. Obviously, the macromolecular chains of P(AMC₁₄AB) have amphipathic structure, but their hydrophobicity is stronger because of a hydrophobic tetradecyl side chain hanging on each monomeric unit, so that its solubility in water is limited. Also, during polymerization turbid phenomena appeared when the polymer content in aqueous solution reached a certain extent. In this research, the micellar behaviour of P(AMC₁₄AB) was studied in its solubility range.

Figure 2 shows the polymerization kinetic curves of AMC₁₄AB and AM, it appears that the polymerization rate of AMC₁₄AB is much greater than that of AM, furthermore the conversion reaches to 90% nothing more than 40 min, whereas AM needs several hours for AM to reach same conversion. The reason is that in the process of poly merization, AMC₁₄AB concentration (about 0.05 mol/L) was above its CMC, which was measured to be 6.51 × 10⁻⁴ mol/L [13]. AMC₁₄AB exist as micellar form in the solution, so that the aggregation of the monomers caused rapid polymerization rate [16].



SCHEME 1 Schematic representation of chemical structure of P(AMC₁₄AB).

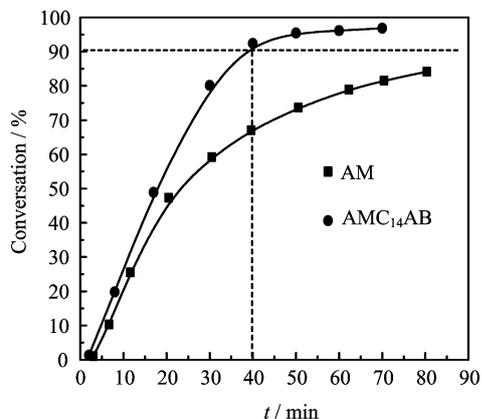


FIG. 2 Polymerization kinetics curve for monomer AMC_{14}AB .

B. Fluorescence spectrum of pyrene in $\text{P}(\text{AMC}_{14}\text{AB})$ aqueous solution

The fluorescence spectra of pyrene in the aqueous solutions of $\text{P}(\text{AMC}_{14}\text{AB})$ and CTAB were determined, and the I_1/I_3 values as a molar concentration are shown in Fig.3(a). Note for $\text{P}(\text{AMC}_{14}\text{AB})$ the molar concentration of the monomeric unit.

Pyrene is an oil-soluble fluorescence substance, the I_1/I_3 value is a characterization of the polarity of the surrounding around pyrene molecules, and the smaller the I_1/I_3 value is, the weaker the polarity of the surrounding is, so the I_1/I_3 value is called the “polarity staff”. The fluorescence probe can reflect the hydrophobically associating behaviour of the hydrophobic association species at molecular level. From Fig.3(a) it is clearly seen that for the solution of common surfactant CTAB, as its concentration is very low, the I_1/I_3 value is greater (about 1.75 that is equal to the I_1/I_3 value in water actually), and does not change until its concentration reach CMC, across the value an abrupt transition of I_1/I_3 value happens and the I_1/I_3 value decreases continuously to 1.31. At CMC, a mass of micelles that consists of multiple molecules form in the solution, pyrene molecules transfer from water medium into the hydrophobic cores of these micelles, the polarity of the surrounding around pyrene molecule is greatly weakened, so that the I_1/I_3 value decrease rapidly.

From Fig.3(a) it is found that for the solution of $\text{P}(\text{AMC}_{14}\text{AB})$, once $\text{P}(\text{AMC}_{14}\text{AB})$ is added into water, the I_1/I_3 value decrease immediately to about 1.45 in spite of how small concentration is, and it nearly does not change with the concentration, i.e. there is no mutational point. The reason why the phenomenon occurs is needed to be searched from the aggregation morphology of $\text{P}(\text{AMC}_{14}\text{AB})$ in water. It can be speculated from the structural representation of $\text{P}(\text{AMC}_{14}\text{AB})$ in Scheme 1 that because each monomeric unit of $\text{P}(\text{AMC}_{14}\text{AB})$ is amphiphilic and there are dense hydrophobic side chains on the macromolecules, strong intramolecular

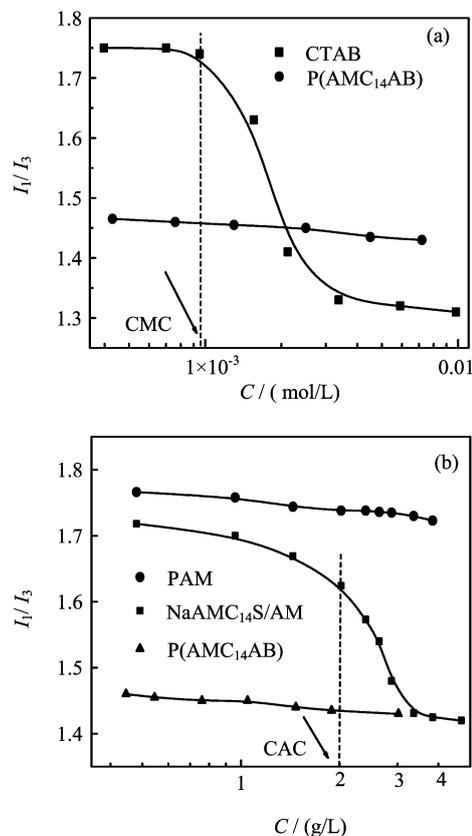


FIG. 3 Variation of I_1/I_3 with concentration for different solutions. (a) The first contrast group. (b) The second contrast group.

hydrophobic association leads to forming unimolecular micelle regardless of how low concentration is. Pyrene molecules enter into these hydrophobic microdomains, so the I_1/I_3 value is reduced to 1.45 at once with the addition of $\text{P}(\text{AMC}_{14}\text{AB})$. By this token, the critical micellar concentration does not exhibit for the unimolecular micelle solution of $\text{P}(\text{AMC}_{14}\text{AB})$, or in other words, the unimolecular micelle solution has zero critical micellar concentration, and this is the basic feature of unimolecular micelle [14].

Figure 3(b) gives the relationship curve I_1/I_3 values and concentrations for another contrast groups, $\text{P}(\text{AMC}_{14}\text{AB})$, hydrophobic association polyacrylamide $\text{NaAMC}_{14}\text{S}/\text{AM}$ and PAM three kind solutions. Homopolymer PAM is non-associated hydrophobically, there are no hydrophobic microdomains in PAM solution, so the I_1/I_3 value is similar to that in pure water and nearly does not change with PAM concentrations. For the solution of $\text{NaAMC}_{14}\text{S}/\text{AM}$, the I_1/I_3 value is higher similar to that in pure water until critical association concentration, which is measured to be about 2 g/L [12], once the concentration attains to CAC, the inflexion of I_1/I_3 value is promptly produced. At CAC, the intermolecular hydrophobic association results in forming hydrophobic physical crosslink-

ing networks, pyrene molecules transfer into these hydrophobic microdomains, so the I_1/I_3 value decreases [12]. For the solution of P(AMC₁₄AB), as above described, as long as added P(AMC₁₄AB) in water, the I_1/I_3 value immediately decrease to about 1.45 because of forming unimolecular micelles. Through comparing the three solutions, it is again proved that homopolymer P(AMC₁₄AB) form unimolecular micelles in water and have zero critical micellar concentration.

C. Surface tension and conductivity

The surface tensions as a function of concentrations for the solutions of P(AMC₁₄AB) and CTAB were determined by ring method, and the result is shown in Fig.4.

From Fig.4, it is seen that for the common surfactant CTAB, the concentration corresponding to the turning point on the curve of γ vs. C is namely its CMC. As the concentration is below CMC, CTAB are dispersed in solution as single molecule state, at the same, molecules are adsorbed on the surface, and the surface tension is reduced; then the surface adsorption amount increases with the enhancement of the concentrations, and the surface tension gradually decreases; finally, the concentration reaches to CMC, multimolecular micelles form in the solution, whereas the surface adsorption gets up to saturation, the surface tension no longer decreases, so there appears a inflection point on the curve of γ vs. C .

For the solution of homopolymer P(AMC₁₄AB), the surface tension is reduced but non-gradual, the surface tension nearly does not change with the concentration and no inflection point appears. These display the characteristics of zero critical micellar concentration for the unimolecular micelle system of P(AMC₁₄AB) once again.

It can be found from Fig.4 that the surface ten-

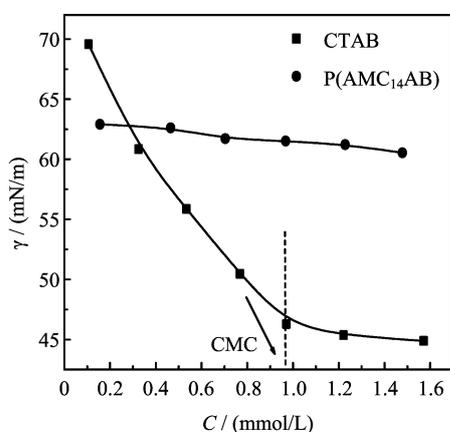


FIG. 4 Variation of surface tension with concentration of P(AMC₁₄AB) and CTAB at 25.0±0.1 °C.

sion of P(AMC₁₄AB) solution only decreases to about 62 mN/m, so obviously the ability to decrease surface tension for P(AMC₁₄AB) is poor. The reason for this is correlated with the adsorbed form of P(AMC₁₄AB) macromolecules on the solution surface. For surface-active substances, the ability to decrease surface tension greatly depends on the extent of replacing water molecules by the hydrophobic section at water-air interface [17]. As P(AMC₁₄AB) macromolecules are adsorbed on the solution surface, the macromolecular backbone with comb-like structure lies flat on the solution surface, the two hydrophilic groups enter the water, and the hydrophobic side chains extend out of water, pointing to air. It is not possible that the hydrophobic side chains are close to each other due to the repulsion between ionic groups and the tension of chemical bonds, so the extent of substituting water by the hydrophobic side chains on the surface is limited, resulting in poor ability to decrease surface tension.

From the curve of conductivities vs. concentrations in Fig.5, similarly, it can be seen that the behaviours of P(AMC₁₄AB) and CTAB are widely different. For P(AMC₁₄AB), no inflection point appears on the curve, indicating the characteristics of zero critical micellar concentration. Moreover, Figure 5 also displays that the conductivity of P(AMC₁₄AB) aqueous solution is lower at all definite concentrations than that of CTAB solution, and the conductivity changes slowly, which also reflects the forming of unimolecular micelles from another point of view. Once P(AMC₁₄AB) are added into water, each macromolecule will forms a unimolecular micelle, small ions Br⁻ as counter ions encircle around unimolecular micelle by electrostatic attraction, so the electromigration moving of ions Br⁻ is hindered and the conductivity of P(AMC₁₄AB) aqueous solution keeps at a lower level.

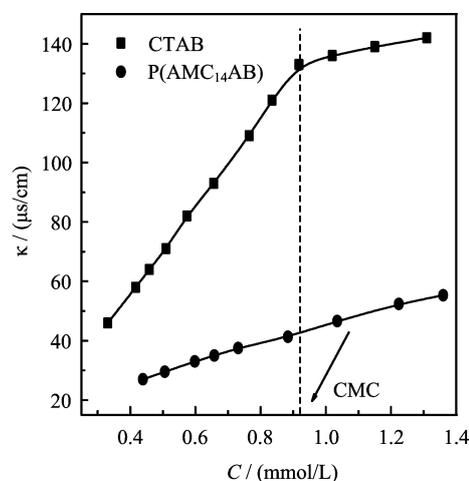


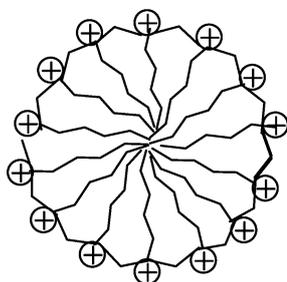
FIG. 5 Variation of conductivity with concentration at 25.0±0.1 °C.

D. Model of unimolecular micelle

The model of the unimolecular micelle is schematically expressed in Scheme 2. Two hydrophilic groups closely linked to backbone combine with water molecules, and this results in the hydrophilicity of the backbone (in Scheme 2 quaternary ammonium cation represents the hydrophilic group, actually there is another hydrophilic group, acylamino); whereas the hydrophobic side chains associate with each other, and constitute hydrophobic cores, so that unimolecular micelles form. The homopolymers unimolecular micelle model will vary with the structure of their surfmers [3], the mainly affecting structure factors are relative locations of hydrophilic groups and hydrophobic side chains with aspect to backbone. For surfmer AMC_{14}AB , the model of homopolymer $\text{P}(\text{AMC}_{14}\text{AB})$ shown in Scheme 2 is considered to be reasonable [3].

E. Solubility

Figure 6 shows the solubility of $\text{P}(\text{AMC}_{14}\text{AB})$ and CTAB as function of temperature. It can be found a



SCHEME 2 Schematic representation of model of unimolecular micelle for $\text{P}(\text{AMC}_{14}\text{AB})$.

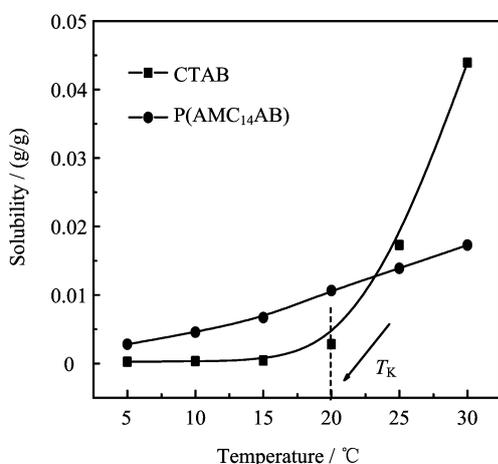


FIG. 6 Saturated solubility of CTAB and $\text{P}(\text{AMC}_{14}\text{AB})$ in pure water as functions of temperature.

turning point on the curve of CTAB, and the corresponding temperature is Krafft temperature that is a property of ionic surfactants, micelle cannot form when temperature below the value. However, no turning point appears on the solubility curve of $\text{P}(\text{AMC}_{14}\text{AB})$, and its solubility increases slowly with temperatures. This fact implies that for the unimolecular micelle system, no Krafft temperature emerges, in other words, at all aqueous solution temperatures, unimolecular micelle can form. No Krafft temperature is another basic characteristic of unimolecular micelle, in addition to zero critical micellar concentration.

F. Solubilization property for toluene

As is well known, micellar solution can solubilize oil-water organic substances. So then, what is the solubilization property of the unimolecular micelle solution for oil-water organic substances? The solubilization amounts of toluene in the aqueous solutions of CTAB and $\text{P}(\text{AMC}_{14}\text{AB})$ were determined, and the results are shown in Fig.7.

From Fig.7, we can find (i) For CTAB solution, as its concentration is smaller and micelles are not formed, the dissolution amount of toluene in CTAB solution is nearly similar to the saturation solubility of toluene in pure water that almost does not change with CTAB concentration; only as CTAB concentration reaches CMC, a turning point appears on the solubility curve because of forming multimolecular micelles and solubilizing of toluene in the micelles; afterward with the increase of CTAB concentration, the solubilizing amount of toluene enhances owing to the increase of micelle amount. (ii) For $\text{P}(\text{AMC}_{14}\text{AB})$ solution, with increasing of $\text{P}(\text{AMC}_{14}\text{AB})$ concentration, the solubilizing amount of toluene continuously enhances; and there is no turning point on the solubility curve, which is also a reflection of zero critical micellar concentration.

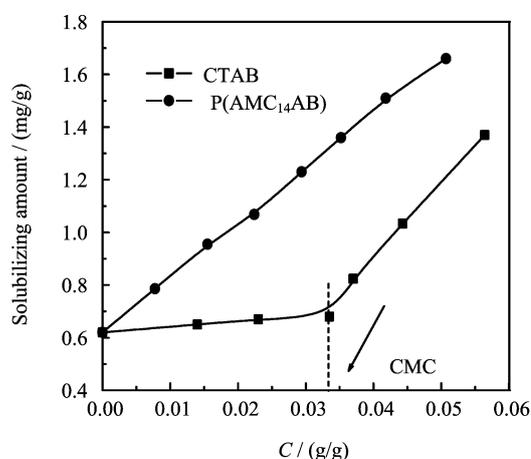


FIG. 7 Variation of toluene solubilization amount with different concentration of CTAB and $\text{P}(\text{AMC}_{14}\text{AB})$.

Once P(AMC₁₄AB) is added into water, unimolecular micelles will form in spite, however small concentration is, and toluene will be solubilized in these unimolecular micelles. With the increase of P(AMC₁₄AB) concentration, the amount of the unimolecular micelles continually increases, resulting in continuously enhancing of toluene solubilizing amount. (iii) At the same concentration, the solubilization amount of toluene in P(AMC₁₄AB) solution is much greater than that in CTAB solution. In other words, the P(AMC₁₄AB) unimolecular micelle solution has stronger ability to solubilize oil-soluble organic substances than CTAB multimolecular micelle solution, which is probably attributed to the greater core space of the unimolecular micelle compared with the conventional multimolecular micelle of common surfactants.

IV. CONCLUSION

In this work, the homopolymer of a cationic surfmer AMC₁₄AB was synthesized, and its physicochemical properties in aqueous solution were studied. Because the structure of each monomeric unit is amphiphilic and contains a hydrophobic side chain for P(AMC₁₄AB), in aqueous solution, unimolecular micelle will form due to strong intramolecular hydrophobic interaction. Compared to the conventional multimolecular micelle formed by common surfactants, the unimolecular micelle possesses some special physicochemical properties: zero CMC value, no Krafft temperature, stronger solubilizing ability for oil-soluble organic substances, and so on. The unimolecular micelle's physicochemical properties and aggregation morphology are affected by surfmer structures and the molecular weights of homopolymers. The relationship between structure and property as well as the interaction between molecular weight and property for the unimolecular micelles needs to be further studied. The unimolecular micelle not only has the unique physicochemical properties as described above,

but also has no dissociation and exchange equilibrium, whereas for the conventional multimolecular micelle of common surfactants, this equilibrium always exists, so the unimolecular micelle is more stable than the multimolecular micelle [3]. It can be anticipated that the multimolecular micelles will have promising and potential use in many scientific and technical fields.

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