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VARIOUS TECHNOLOGICAL PROCESSES

Salt Stimulus Response of a Carboxyl Betaine Amphoteric Hydrophobic Associative Polyacrylamide[1]

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Abstract—A carboxyl betaine amphoteric hydrophobic associative polyacrylamide (CBAHAPAM) was synthesized in water solution through radical polymerization, which was made of polyacrylamide, *N,N′*-dimethyl octadecyl allyl ammonium chloride (DOAC), 1-carboxy-*N,N′*-dimethyl-*N*-(3-methylacryl-amidopropyl) ethanaminium inner salt (CBMAA-1) and 2-acrylamide-2-methyl propanesulfonic acid (AMPS). Self-assembly associative properties in CBAHAPAM solution and the effects of salt and temperature on the associative behavior were investigated by the means of viscosimetry, rheological test, fluorescence spectroscopy, and environmental scanning electron microscope (ESEM). Results showed that the critical association concentration (CAC) of the CBAHAPAM was about 0.30–0.32 wt %. The addition of the calcium chloride made the apparent viscosity of CBAHAPAM solution improve drastically than NaCl. Meanwhile, CBAHAPAM solution with NaCl and $CaCl_2$ showed up better heat and shearing resistance than CBAHAPAM solution itself. The network structures of CBAHAPAM aqueous or salt solution was observed by ESEM. NaCl and $CaCl_2$ reinforced the network structures, which further indicated that CBAHAPAM solution had a excellent capacity of salt thickening.

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INTRODUCTION

Hydrophobically associating polymer is a special kind of polymer containing main chain macromolecules and a small amount of hydrophobic side chains, which has attracted both scientific and industrial interest on account of its excellent solution properties and a lot of applications, such as stabilizers, paint thickeners, enhanced oil recovery agents and so on [1–5]. The hydrophobic side chains form hydrophobic microdomains in solutions because the nonpolar alkyl groups have a strong tendency to associate together through intra- and intermolecular interactions. In dilute solution, macromolecule mainly exists in the form of intra-association, which leads to curling up molecular chains. While copolymer concentration is over the critical association concentration (CAC), intermolecular hydrophobic association is predominant, which yields a dynamic physical cross-linked reticulation to gain the hydrodynamic volume and increase apparent viscosity obviously [6–9].

However, the property of salt tolerance for most hydrophobically associating polymers is poor, which much restricts its application. Amphoteric polymer has both cationic and anionic groups on the same molecule of polymer [10–17]. When the electrolyte is added to amphoteric polymer solutions, the physical attraction between the equivalent anions and cations is impaired and the amphoteric polymer will stretch to a outstretched configuration, so the viscosities of the polymer solutions can rise with increasing salt concentration originating from the anti-polyelectrolyte effect [18–25]. This special property helps the amphoteric hydrophobically associating polyacrylamides applied

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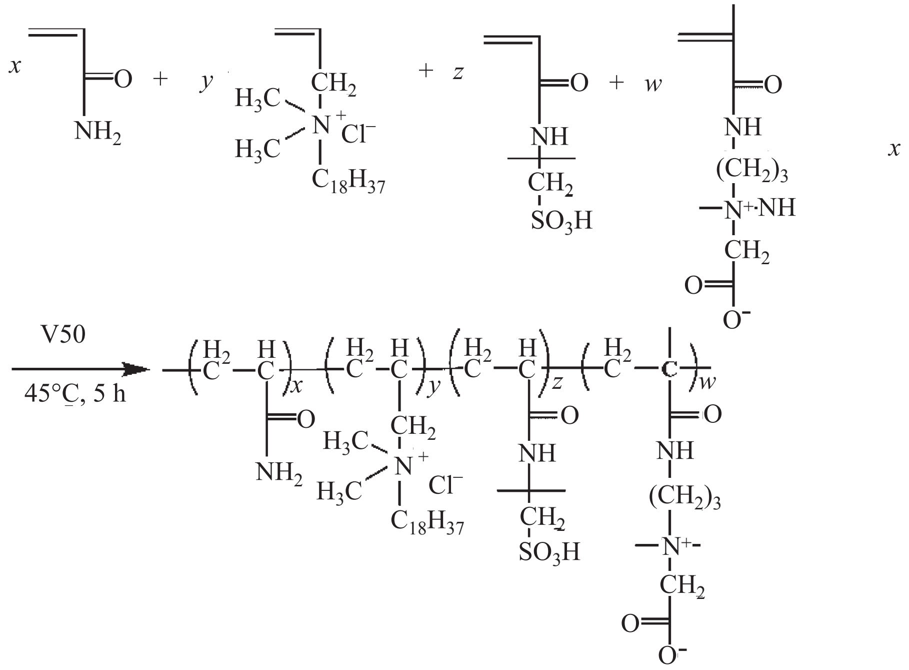
[1] The text was submitted by the authors in English.

Scheme 1. Synthesis route of CBAHAPAM.



in bioseparations [26], DNA assay [27], and many other fields [28–30].

In this article, we have introduced 1-carboxy-*N,N'*-dimethyl-*N*-(3-methylacrylamidopropyl) ethanaminium (CBMAA -1) into the amphoteric hydrophobically associating polymer. A new kind of carboxyl betaine amphoteric hydrophobic associative polyacrylamide (CBAHAPAM), containing hydrophilic polyacrylamide backbones, *N,N'*-dimethyl octadecyl allyl ammonium chloride (DOAC) as cationic hydrophobic monomer, 1-carboxy-*N,N'*-dimethyl-*N*-(3-methylacrylamidopropyl)ethanaminium (CBMAA -1) as functional monomer and 2-acrylamide-2-methyl propanesulfonic acid (AMPS) as anionic monomer was synthesized. The structure of the prepared CBAHAPAM was verified by the IR spectrum and the ^{1}H NMR spectra. Self-assembling behaviors of CBAHAPAM were researched by fluorescence analysis, rheological test and environmental scanning electron microscope (ESEM). The mechanism of the self-assembling behavior in salt solutions was analyzed too.

MATERIALS AND METHODS

Material

Acrylamide (AM), sodium chloride (NaCl), calcium chloride ($CaCl_2$) and absolute ethyl alcohol were supplied by Chengdu Kelong Chemical Factory, 2,2'-azobis(2-methylpropionamidine)dihydrochloride (V50, 97%) and 2-acrylamide-2-methylpropanesulfonic acid (AMPS, 98%) were purchased from Aladdin chemicals, *N,N'*-dimethyl octadecyl allyl ammonium chloride (DOAC, 99%) was supplied by Sigma–Aldrich chemicals. 1-Carboxy-*N,N'*-dimethyl-*N*-(3-methylacrylamidopropyl)ethanaminium (CBMAA-1) was prepared in laboratory.

Synthesis of CBAHAPAM

The synthesis route of CBAHAPAM copolymer is illustrated in Scheme 1. At first, AM (13.31 g) and CBMAA-1 (0.77 g) were dissolved in a 150 mL three-necked flask equipped with magnetic stirrer, and then DOAC (0.72 g) and AMPS (0.1 g) were added. The monomer concentrations was 20%. The flask was put into a water bath, and then the mixture was purged with N_2 for 30 min at 25°C. The reaction was initiated by V50. Temperature polymerization was 45°C and time of polymerization was 5 h. After that, the reaction was finished and the crude product was precipitated by ethanol to remove all traces of water, initiator and residual monomers. The CBAHAPAM was obtained by purification with ethanol and dried in a vacuum drying oven at 50°C for one day.

Characterization and Measurements

Structure characterization. Nicolet Nexus 170SX Fourier transform infrared spectrophotometer was employed. The sample was prepared by KBr pressed-disk method. The ^{1}H NMR spectra of CBAHAPAM in deuteroxide (D_2O) were recorded on a Bruker ASCEND –400 NMR.

The intrinsic viscosity of the copolymer. The intrinsic viscosity of the polymer was determined with a Ubbelohde viscometer according to the dilution extrapolation method in a NaCl aqueous solution with a concentration of 0.2 M at 30.0 ± 0.1°C, and formamide was added to CBAHAPAM solution with a 60% volume concentration so as to restrain intramolecular hydrophobic interaction. The molecular weights of the polymer were calculated by the intrinsic viscosity.

Fluorescence measurement. The fluorescence spectra were obtained with a PerkinElmer Fluorescence Spectrometer LS 55 in a scanning range of 360–460 nm using pyrene as fluorescent probe in this study. CBAHAPAM solutions were prepared by first pipetting 0.04 mL pyrene solution (1×10^{-3} M in ethanol) into 50 mL volumetric flask. After the ethanol was dried, different concentrations CBAHAPAM solutions with different concentrations were prepared in the flasks.

Rheological measurement. Apparent viscosity of polymer aqueous or salt solution with different concentrations was measured by NDJ-8S at 25°C. The viscoelasticity was measured at 25°C on the Malvern CVOR-200 Rheometer equipped with cone-plate geometry.

A strain value (1 Pa) was determined to make sure that the sample under this strain value was in linear viscoelastic region. The apparent viscosity of aqueous or salt polymer solution at 100°C was tested by HAAK MARSIII Rheometer.

ESEM measurement. The microstructure of the copolymer aqueous or salt solution can be observed by Phenom Pro scanning electron microscopy.

RESULTS AND DISCUSSION

Characterization of CBAHAPAM. The FTIR spectrum of CBAHAPAM is shown in Fig. As it can be seen, the absorption bands at 3512 and 1682 cm^{-1} can belong to the N–H and C=O stretching vibration peaks of amide group of AM, which can indicate that the copolymer contains PAM units. The peaks at 2925 and 2853 cm^{-1} are due to the C–H stretching vibrations of $-CH_2-$ and $-CH_3$ in CBAHAPAM molecule backbones and hydrophobic carbon chains. The methyl group of $-N^+(CH_3)_2R$ deformation vibration bond at 3152 cm^{-1} confirms the existence of the quaternary ammonium-based group. The characteristic peaks of $-SO_3-$ at 1184, 1125, and 1040 cm^{-1} confirm the existence of AMPS. The peak at 1397 cm^{-1} belongs to the stretching vibrations of –COO– of betaine monomer. And it can be concluded that there were no the rest of monomers due to the absence of characteristic absorption peak of C=C in 3132 and 890 cm^{-1}. The above analysis results indicated that a carboxyl betaine amphoteric hydrophobically associating polyacrylamide (CBAHAPAM) was synthesized successfully.

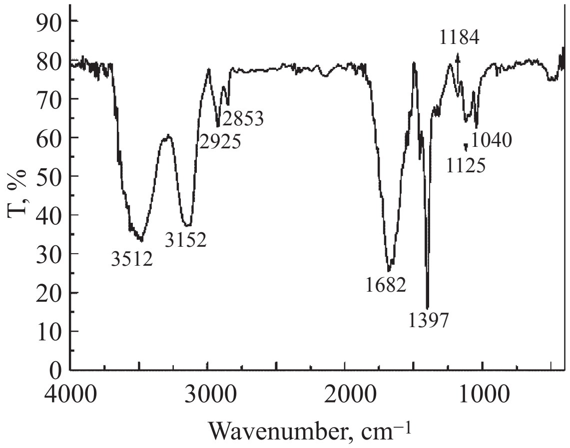


Fig. 1. The FTIR spectrum of CBAHAPAM.

Further to indicate the molecular structure of synthesized CBAHAPAM, the ^{1}H NMR spectrum of CBAHAPAM was obtained and shown in Fig. 2, the chemical shifts appeared at 1.58, 2.14, and 6.18 ppm could be ascribed to the protons of hydrophilic polyacrylamide backbones marked as 1, 2, and 3, respectively. The chemical shift peaks of the protons corresponding to $-CH_2-$ and $-CH_3$ bonded with N atom of quaternary ammonium of DOAC are at 3.02 and 3.58 ppm (marked as 6 and 7). The two peaks at 1.12 and 0.95 ppm (marked as 9 and 10) are due to the protons of the hydrophobic chains. The chemical shifts appearing at 1.24 and 3.02 ppm could be attributed to the $-CH_3$ and $-CH_2-$ protons of AMPS, marked as 14 and 15, respectively. The chemical shift peaks of the protons

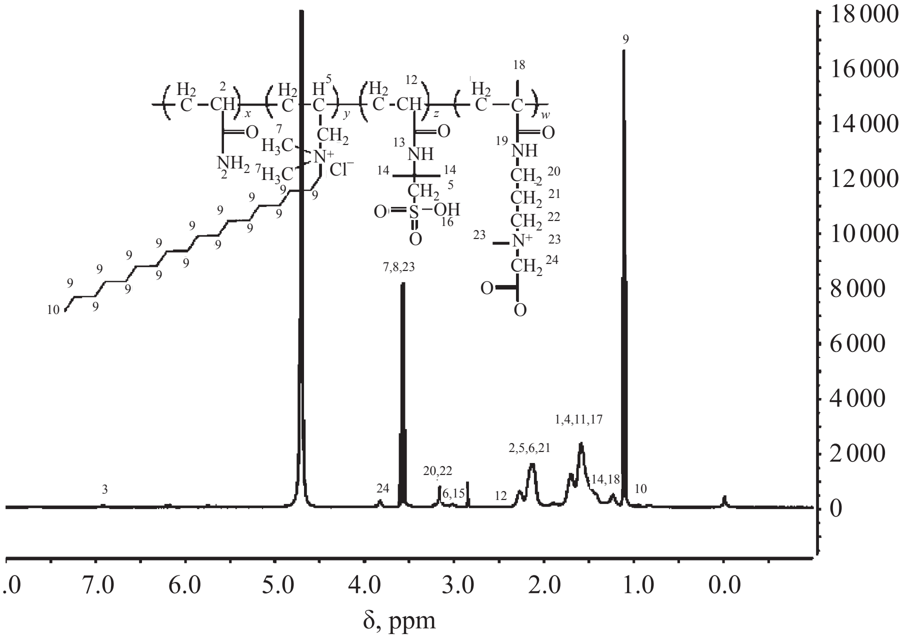


Fig. 2. The ^{1}H NMR (400 MHz, D–O) spectrum of CBAHAPAM.

belonging to $–CH_2–$ and $–CH_3$ bonded with N atom of quaternary ammonium of CBMAA-1 are at 3.16 and 3.58 ppm (marked as 22 and 23). The molecular structure of polymerized CBAHAPAM uncovered by ^{1}H NMR is well consistent with the consequences of FTIR spectrum. And the polymer compositon (mol %) calculated from the integral area of ^{1}H NMR is 97.23 AM : 0.43 AMPS : 1.54 CBMAA-1 : 0.80 DOAC, and it is close to feed compositon (mol %) which is 97.00 AM : 0.25 AMPS : 1.75 CBMAA-1 : 1.00 DOAC. The intrinsic viscosity $[\eta]$ of CBAHAPAM is shown to be 423.6 mL g^{-1} according to the dilution extrapolation method (Fig. 3). Meanwhile, the molecular weights M_η of the polymer are 642319.6, calculated by the Mark–Houwink equation $[\eta] = KM_\eta^\alpha$ at $K = 1.25 \times 10^{-2}$ and $\alpha = 0.78$, and value of K and α refers to calculation of molecular weights for polyacrylamide.

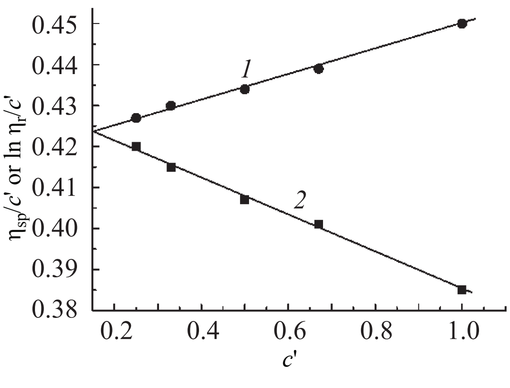


Fig. 3. Measuring the intrinsic viscosity $[\eta]$ of CBAHAPAM by the dilution extrapolation method. (*1*) η_{sp}/c', (*2*) $\ln \eta_r/c'$.

Self-Aggregate Behavior of CBAHAPAM Aqueous Solution Varying with Concentration

The long carbon chains (C-18) of CBAHAPAM tend to self-assemble by an intense hydrophobic associating action, which results in a dynamic physical cross-linking network and an increase in the hydrodynamics volume. To be specific, in relatively dilute solution, CBAHAPAM embodies intra-molecular association more than inter-molecular one, which makes hydrophobic chains to curl up and reduces the apparent viscosity. Nevertheless, when CBAHAPAM concentration surpasses CAC, inter-molecular aggregates turn into the main role and the apparent viscosity increases sharp.

It is seen from Fig. 4 the apparent viscosity of the CBAHAPAM aqueous solution varying with concentration. The slopes of two straight line by linear fitting are 40 and 2010. The apparent viscosity of the CBAHAPAM solution gradually increased with increasing polymer concentration, the apparent viscosity of solution increased slowly at low concentrations, and increased suddenly. The inflexion concentration is the CAC which indicates a transformation from intramolecular hydrophobic interactions to intermolecular

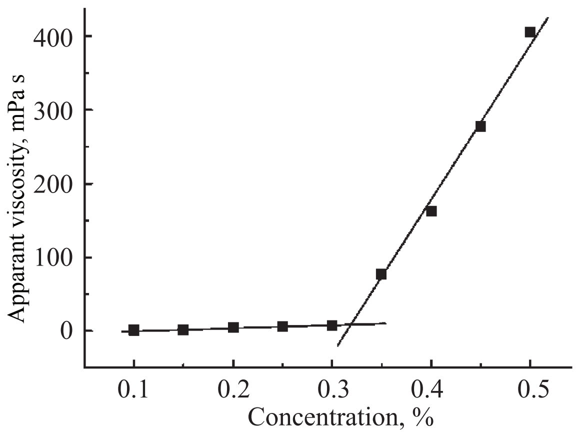


Fig. 4. The relationship between concentration and apparent viscosity of CBAHAPAM.

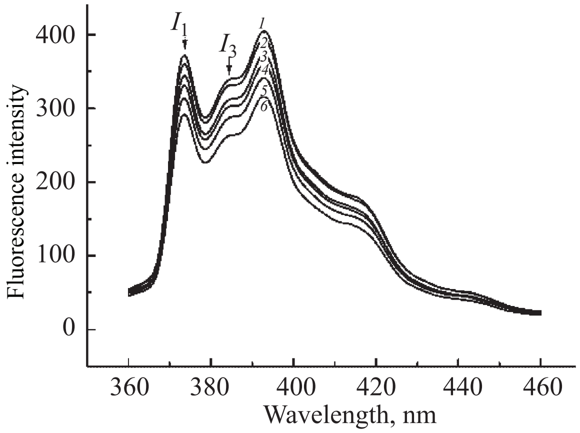


Fig. 5. The fluorescence spectra of CBAHAPAM at different concentrations (%): (*1*) 0.38, (*2*) 0.50, (*3*) 0.25, (*4*) 0.40, (*5*) 0.34, (*6*) 0.30.

hydrophobic interactions. At concentration above the 0.32 wt % self-aggregate behaviors of the CBAHAPAM molecules are dominated by inter-molecular hydrophobic associations, resulting in network configuration of macromolecular chains.

Pyrene is a strongly hydrophobic polyaromatic hydrocarbon with very low solubility in water. The hydrophobically associating polymers spontaneously form micelles and the small hydrophobic domains, which can dissolve pyrene that might be used as a fluorescence probe to reflect the intensity of hydrophobically associating effect. The fluorescence emission spectrum of a pyrene solution has five fluorescence peak, approximately at 373, 379, 384, 394, 480 nm respectively. The value of I_1/I_3 in fluorescence spectra is equal to the ratio of pyrene intensities of the first emission peak (I_1 = 373 nm) to the third emission peak (I_3 = 384 nm). The stronger the polarity of the microenvironment around the pyrene probe, the higher the value of I_1/I_3. Therefore, once polymer molecules form an apparent dynamic physical cross-linked network, the value of I_1/I_3 will reduce obviously.

The fluorescence spectroscopy of pyrene at CBAHAPAM solutions with different concentrations was shown in Fig. 5 (I_1 and I_3 were marked). Figure 6 exhibits the change of I_1/I_3 at different CBAHAPAM concentrations. The value of I_1/I_3 decreased abruptly when the concentration was 0.30 wt %. This fact indicated that polymer molecules form a large number of hydrophobic domain and the polarity of the microenvironment around the pyrene probe was weakened, when the concentration of CBAHAPAM solution was over 0.30 wt %.

As a result, the CAC was determined via apparent viscosity and fluorescence spectroscopy, so the CAC of CBAHAPAM can be determined as 0.30–0.32 wt %.

The rheology of CBAHAPAM solution. Dynamic moduli tests are necessary to explore the viscoelastic property of CBAHAPAM solution. The interdependence of *G*′ and *G*″ (the storage and the loss moduli) on the frequency can reflect the relative motion of CBAHAPAM molecules.

As shown in Fig. 7, both *G*′ and *G*″ moduli increase with increasing CBAHAPAM concentration, demonstrating that the loss moduli *G*″ was always higher than the storage moduli *G*′ during the measurement scope of frequency and illustrating that CBAHAPAM aqueous solution was emplastic fluid. The reasonable reason for the viscoelastic behavior is that the carboxyl betaine amphoteric

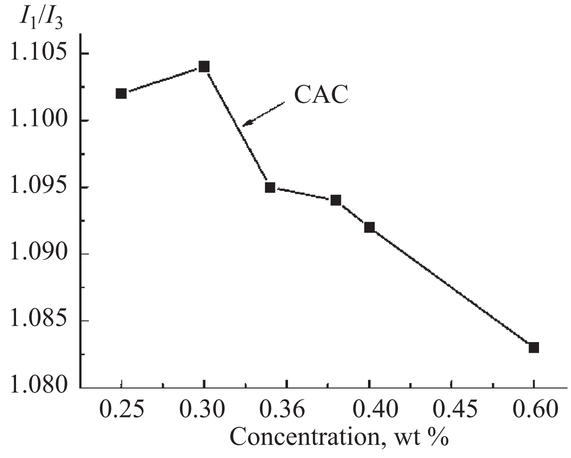


Fig. 6. The ratio of I_1/I_3 at different CBAHAPAM concentrations.

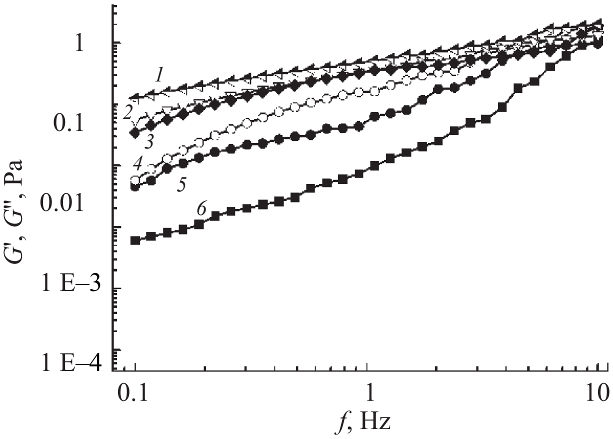


Fig. 7. The dynamic moduli of CBAHAPAM with different concentrations. (*1*) G'' 0.60 wt %, (*2*) G'' 0.50 wt %, (*3*) G' 0.60 wt %, (*4*) G' 0.50 wt %, (*5*) G'' 0.28 wt %, (*6*) G' 0.28 wt %.

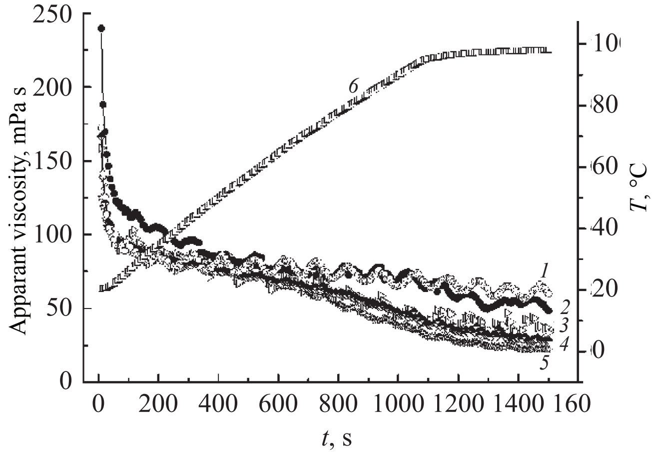


Fig. 8. Effect of temperature on 0.5 wt % CBAHAPAM solution with different concentrations of salt at 170 s^{-1}. (*1*) 5 wt % $CaCl_2$, (*2*) 10 wt % NaCl, (*3*) 10 wt % $CaCl_2$, (*4*) 5 wt % NaCl, (*5*) none salt, (*6*) T.

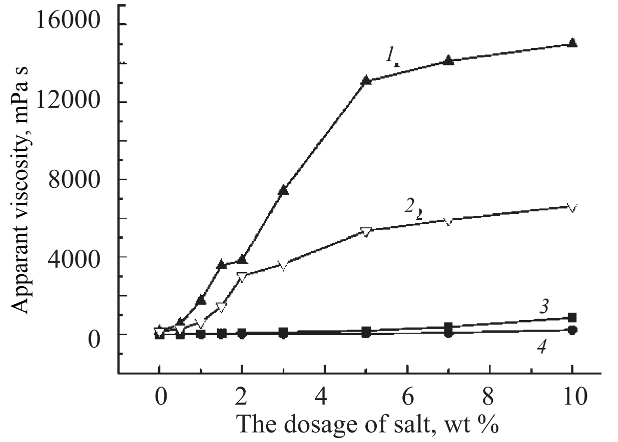


Fig. 9. The effect of sodium chloride and calcium chloride on apparent viscosity of different concentrations of CBAHAPAM solution, wt %: (*1*) 0.40 $CaCl_2$, (*2*) 0.40 NaCl, (*3*) 0.28 $CaCl_2$, (*4*) 0.28 NaCl.

hydrophobic associative polyacrylamides contain three ionic monomers and they interact with each other, which leads to hydrophobically associating intensity weakened and confines its elasticity, so CBAHAPAM aqueous solution displays viscosity.

The temperature and shear rate can have marked influence on apparent viscosity of polymers. Intermolecular aggregation would weaken and be broken at high shear rate or high temperature. Therefore, it is important to study the effect of the temperature and shear rate on rheological property of CBAHAPAM solution. Figure 8 showed the effect of temperature from 20°C to 100°C on 0.5 wt % CBAHAPAM solution viscosity with none salt, 5 wt % and 10 wt % NaCl and 5 wt % and 10 wt % $CaCl_2$, respectively at 170 s^{-1} shear rate therewith the length of each testing period was 25 min.

As shown in Fig. 8, the variation tendency of apparent viscosity with increasing temperature was similar. Firstly the viscosity was reduced rapidly because the high shear rate (170 s^{-1}) broke three-dimensional network structure of CBAHAPAM aqueous solution, then the apparent viscosity declined relaxedly with temperature increasing. This was attributed to two aspects, on the one hand, thermal motion between polymer molecules resulted in a decrease in the apparent viscosity by breaking hydrophobically associating effect of CBAHAPAM solution, but on the other hand, increasing temperature in a certain range can enhance hydrophobically associating intensity, which tends to increase apparent viscosity. So the two factors make the apparent viscosity remain unchanged or declined relaxedly in a range of temperature. From Fig. 8, 0.5 wt % CBAHAPAM solution containing NaCl or $CaCl_2$ has the better temperature resistance than one with no salt, because of anti-polyelectrolyte effect, resulting to strengthen hydrophobic association. Furthermore, CBAHAPAM solution with 5 wt % $CaCl_2$ or 10 wt % NaCl has the better temperature resistance and it can remain 55 mPa s or so at 100°C and 170 s^{-1} shear rate.

Sodium chloride or calcium chloride as a electrolyte added into the solution can observably increase the polarity of the solution, which can affect self-aggregate property of the polymer solution. Figure 9 shows the influence of sodium chloride and calcium chloride on apparent viscosity at different CBAHAPAM concentrations. Sodium chloride or calcium chloride had more notable effect on the apparent viscosity of the solution of high CBAHAPAM concentration (>CAC) than on that of the solution of low CBAHAPAM concentration (<CAC). In Fig. 9 the apparent viscosity of 0.28% CBAHAPAM solution increased slowly with the variation of NaCl or $CaCl_2$ concentrations from 0 to 10 wt %, meanwhile, increasing range was small and apparent viscosity of both solutions did not appear to be much different. However, the apparent viscosity of 0.4% CBAHAPAM solution increased sharply, and increasing range was large. Therewith the increasing range of 0.4% CBAHAPAM solution with $CaCl_2$ was much larger than that with NaCl. The change trend was attributed to anti-polyelectrolyte effect, and salt thickening capacity of >CAC CBAHAPAM solution was stronger clearly than that of <CAC CBAHAPAM solution. The result indicated that the CBAHAPAM solution had excellent capacity of salt thickening.

The Reasonable Mechanism of the Self-Aggregate Behavior in Salt Solution

It is well known that the self-aggregate behavior of hydrophobic associated polymer is dominated by the hydrophobic association interaction. For the 0.40 wt % CBAHAPAM aqueous solution without salt, inter-molecular hydrophobic association was weak among the hydrophobic side chains (DOAC), so its initial apparent viscosity was relatively low, only about 163 mPa s. when the NaCl was added to the CBAHAPAM aqueous solution, the solution polarity increased and NaCl made the CBAHAPAM aqueous solution generate anti-polyelectrolyte phenomenon, which led to a reinforce of hydrophobic association intensity and the increase in the solution apparent viscosity. When the $CaCl_2$ was added to the CBAHAPAM aqueous solution, Ca^{2+} not only could result in generating anti-polyelectrolyte phenomenon as well as enhance remarkably a hydrodynamic volume of CBAHAPAM molecules by forming ion interaction with surrounding carboxyl betaine groups, in other words, the hydrodynamic volume of 3D-network become stronger because of the formation of connections between Ca^{2+} and carboxyl betaine groups of polymer (Fig. 10). Thus, the thickening ability of CBAHAPAM aqueous solution with $CaCl_2$ is superior to that of the solution with NaCl.

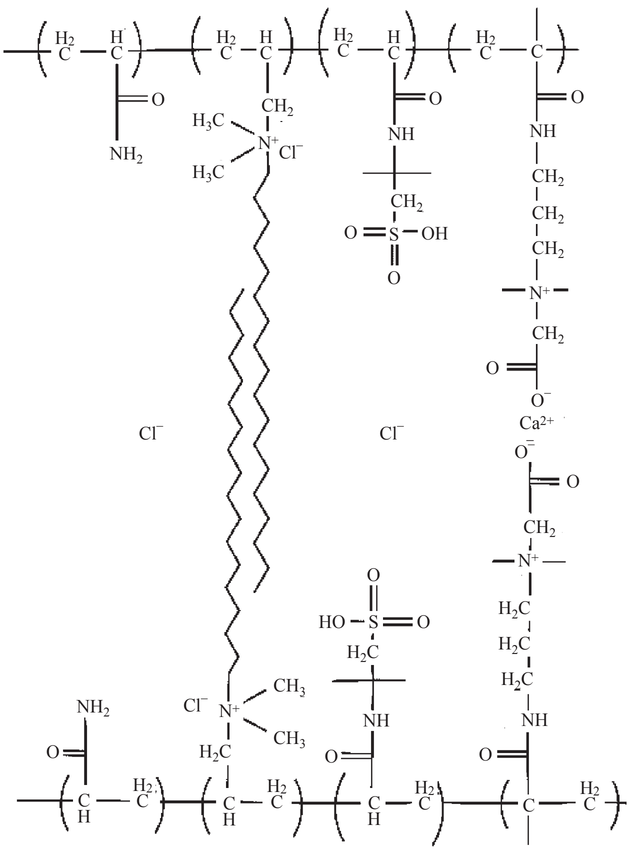


Fig. 10. Schematic mechanism of the self- aggregate behavior in $CaCl_2$ solution.

Figures 11a–11d show the environmental scanning electron microscope (ESEM) images of the 0.28 and 0.5 wt % CBAHAPAM solutions. As shown in Fig. 11a in the <CAC solution the inter-molecular aggregates were weak and there are primarily intra-molecular aggregates therefore the net structure was littery and scattered. From Fig. 11b it can be observed visually that cross- linking network is more intensive, which was produced by the inter-molecular hydrophobic association. Figure 11c shows that inter-molecular aggregates of 0.5% CBAHAPAM solution are further strengthened by adding the 1 wt % NaCl，which can be explained by an increase in the polarity of the solution and by the antipolyelectrolyte effect. From Fig. 11d we can deduce that anti-polyelectrolyte effect and the formation of links between Ca^{2+} and carboxyl betaine groups made the hydrophobic association of CBAHAPAM solution become stronger than that with NaCl. Thus, the apparent viscosity of CBAHAPAM aqueous solution with $CaCl_2$ was so high that we can not see the polymer structure.

CONCLUSIONS

A new kind of carboxyl betaine hydrophobic associative amphoteric polyacrylamide was prepared via aqueous solution polymerization, which was composed

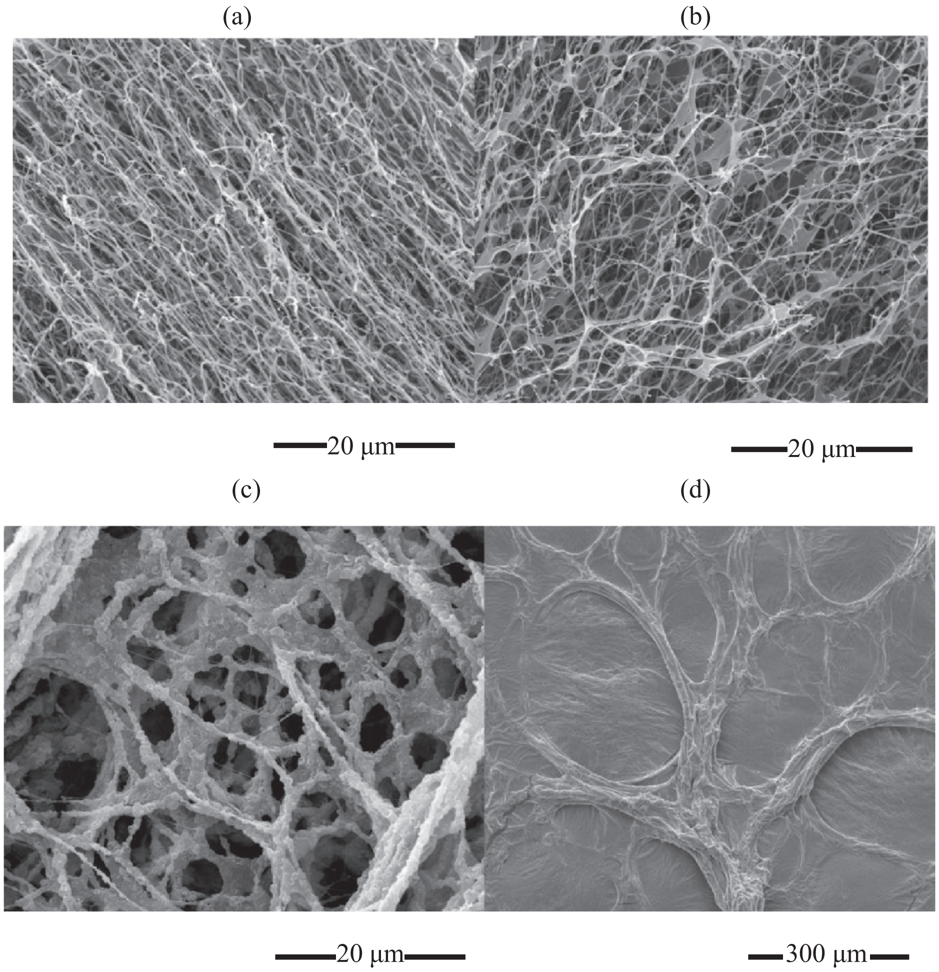


Fig. 11. ESEM image of CBAHAPAM aqueous solution (magnification 5000×): (a) 0.28 wt % concentration, (b) 0.5 wt % concentration, (c) 0.5 wt % concentration with NaCl (1 wt %), (d) 0.5 wt % concentration with $CaCl_2$ (1 wt %) (magnification 300×).

of AM, DOAC, AMPS, and CBMAA-1. The rheological test demonstrated the G' of CBAHAPAM aqueous solution was always lower than the G'', which implied that CBAHAPAM aqueous solution was viscous fluid. CBAHAPAM aqueous solution showed noticeable salt thickening behavior, specially in $CaCl_2$ solution, e.g., the apparent viscosity of CBAHAPAM solution (0.4 wt %) changed from 163 mPa s to 15000 mPa s while the $CaCl_2$ solution concentration ranged from 0–10.0 wt %. Salt thickening property of CBAHAPAM in $CaCl_2$ solution was stronger than in NaCl, because not only there was the anti-polyelectrolyte effect in $CaCl_2$ CBAHAPAM solution, but also the Ca^{2+} enhanced remarkably volume expansion of CBAHAPAM molecules by forming ion interaction with surrounding carboxyl betaine groups of polymer. This polymer has a great prospect in enhancing oil recovery from oil layers, especially in very high salinity brine environment.

ACKNOWLEDGMENTS

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