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ORIGINAL CONTRIBUTION

Role of added amphiphilic cationic polymer in the stabilization of inverse emulsions

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Abstract The amphiphilic cationic polymer, poly(acryloyloxyethyl dimethylbenzyl ammonium chloride) (PAODBAC), has been studied as an additive for the stabilization of water-in-oil inverse emulsions prepared from mixed surfactants. The interaction behavior of PAODBAC with the surfactants, the effect of the PAODBAC concentration on the stability of the inverse emulsion obtained after polymerization, the characteristics of the polymer particle after polymerization, and the rheological properties with different concentrations of PAODBAC have been systematically investigated. A mechanism is proposed to account for the stabilizing effect of PAODBAC on the inverse emulsion system. The PAODBAC chains can interact with the surfactant molecules. When the concentration of PAODBAC was 0.067% (w/w), the interactions between the polymer chains and surfactant molecules were optimized, resulting in the best stability of the inverse emulsion. The presence of PAODBAC in the inverse emulsion system aided the establishment of a small mean polymer particle size distribution.

Keywords Inverse emulsion · Surfactants · Amphiphilic cationic polymer · Phase behavior · Stability

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Introduction

Polyacrylamide and its co-polymers are important synthetic water-soluble polymers [1, 2]. Generally, these polymers can be classified as anionic, nonionic, or cationic polyacrylamides according to their covalently bound ionic groups [3]. Acrylamide-based polymers are used as coagulants and flocculants in waste and potable water treatment applications, as pushing fluids in enhanced oil recovery, drag reduction agents and drilling fluids, and as water clarifying agents in mining and paper making [4–9].

Emulsions are thermodynamically unstable liquid/liquid dispersions generally formed by water, oil, and surfactant mixtures [10]. The mechanistic origin of the stability of inverse (water-in-oil) emulsions differs from that of conventional (oil-in-water) emulsions, which can be stabilized by both steric and electrostatic repulsions. An inverse emulsion is stabilized only by steric forces. An inverse emulsion generally shows low stability because of the low electrical conductivity of the continuous phase and the large density difference between the oil and the water phases [11, 12], such that a high mobility of polymer particles in an inverse emulsion can easily cause sedimentation, flocculation, or coalescence [13]. In the case of inverse emulsion polymerization, the majority of attention has hitherto been focused on the mechanism and kinetics of polymerization [14–16], and there has been little research on the stability of inverse emulsions.

Among the characteristics of inverse emulsions, stability is of great importance. Better understanding of the interactions between water, oil, and emulsifier at the interface and the factors that affect the emulsion stability would allow the preparation of stable inverse emulsions. In recent years, the stability of emulsions has been improved by introducing inorganic electrolytes [17–19], modifying the polymeric surfactant [20–23], or introducing an amphiphilic polymer to strengthen

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the adsorption of surfactants at the interface [24–26]. When an emulsion is stabilized solely by a modified polymer, the presence of polymeric chains at the interface of emulsion droplets makes a significant contribution to the stability of the colloidal droplets, especially at high ionic strength, because the polymeric chains act as steric barriers against aggregation. When an emulsion is stabilized by both a surfactant and a polymer, surfactant–polymer interactions occur, leading to their adsorption at the interface of the emulsion droplets. Interactions between amphiphilic polymers and surfactants also have some positive effects on solutions, such as solubilization enhancement, viscosity enhancement, surface conditioning, and so on [27, 28].

The stability of an emulsion prepared from a surfactant and an amphiphilic polymer largely depends on the chemical structure of the amphiphilic polymer, such as the ratio of hydrophilic and lipophilic groups, the activities of these groups, and the steric hindrance between them. In this study, the amphiphilic cationic polymer poly(acryloyloxyethyl dimethylbenzyl ammonium chloride) (PAODBAC) has been used as an additive to enhance the stability of water-in-oil emulsions prepared from mixed surfactants. The amphiphilic cationic polymer introduced in the system has the same applications as the cationic water-soluble polymer and does not reduce the utility of the inverse emulsion or its products. In the work described herein, the interactions between the polymer and the surfactant have been explored, and a mechanism whereby PAODBAC stabilizes the inverse emulsion system is proposed. The influence of the amphiphilic cationic polymer concentration on the stability of the inverse emulsion has also been studied, as well as the polymer particle size distributions and rheological properties of the inverse emulsions with various concentrations of the amphiphilic cationic polymer.

Experimental

Materials

Acrylamide (AM, 99.9%, Acros Organics) was dried in vacuo at 45 °C. Methacryloxyethyltrimethyl ammonium chloride [DMC, 78% (w/w) aqueous solution] and acryloyloxyethyl dimethylbenzyl ammonium chloride [AODBAC, 80% (w/w) aqueous solution] were purchased from Spark Group Chemical Co., Ltd. Sorbitan monooleate (Span 80), polyethylene glycol sorbitan monooleate (Tween 80), and liquid paraffin [viscosity (40 °C) 38 mPa·s, 99%] were purchased from Sinopharm Chemical Reagent Co., Ltd. 2,2′-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044, 98%) was purchased from Runxing Optoelectronic Materials Co., Ltd. Other reagents were of analytical grade and were used without further purification. Deionized water was used throughout this work.

Synthesis of PAODBAC

The amphiphilic cationic polymer PAODBAC was synthesized in the reactor by polymerizing AODBAC as a 20 wt% aqueous solution under argon atmosphere, using 0.1 wt% (based on the weight of AODBAC) VA-044 as an initiator, at 50 °C for 10 h. The weight-average molecular weight of the PAODBAC was calculated on the basis of gel permeation chromatography (Waters 1525/2414; USA) with 0.1 mol/L $NaNO_3$ as solvent and narrowly distributed polyoxyethylene (PEO) as standard results as around 10^4 g/mol (PDI = 2.1).

Inverse emulsion preparation and polymerization

Solutions of PAODBAC in deionized water were prepared at a series of concentrations, specifically 0.033, 0.067, 0.167, 0.333, 0.5, and 0.667% (w/w). The requisite amounts of emulsifier and liquid paraffin were placed in a 100-mL jacketed reactor and stirred with a mechanical stirrer at high speed for 30 min. The PAODBAC solution, containing AM and DMC, was added dropwise to the liquid paraffin solution at a constant stirring speed over a period of 30 min. The weight ratio of liquid paraffin to water was 1:1, as was the molar mass ratio of AM to DMC. The mixture was stirred for 15 min to give an inverse pre-emulsion. Polymerization was carried out using VA-044 as an initiator at 50 °C for 8 h at a low stirring speed. The conversion of inverse emulsion polymerization approximately reached 98%.

Preparation of an oil–water interface with surfactants and PAODBAC

Tween 80 was added to deionized water to form the water phase, Span 80 was added to liquid paraffin to form the oil phase, and then PAODBAC was added to the water phase. After the PAODBAC had completely dissolved, certain amounts of the oil and water phases were mixed, and the mixture was placed in an oscillating water bath (Julabo SW22; Germany) and shaken for 30 min at 25 °C. Finally, the sample was transferred to a constant temperature water bath at 25 °C for a set period.

^{1}H-NMR analysis of PAODBAC

The structure of cationic polymer PAODBAC was characterized by ^{1}H-NMR (400 MHz Bruker AVANCE II NMR spectrometer, Bruker BioSpin Co., Switzerland) with deuterated water (D_2O) as solvent. The peak of the solvent (δ = 4.79 ppm) was used as the reference.

Evaluation method for the stability of inverse emulsions

The stability of each inverse emulsion was measured by centrifugal force. An appropriate amount of emulsion was placed in a centrifugal test tube, which was placed in the centrifuge (TG20; China) and spun at 3000 r/min for 10 min. The stability of the emulsion was evaluated from the ratio (V_t) of the remaining emulsion volume to the initial emulsion volume.

Analysis of polymer particle size and size distribution

The polymer particle size was determined using a laser particle size analyzer (Coulter LS-230; USA). The inverse emulsion after polymerization was diluted to 0.2% solid content with a 10 wt% solution of Span 80 in liquid paraffin. In order to disperse the polymer particles and avoid the presence of bubbles, ultrasound was applied for 10 min after the dilution.

The polydispersion of the size distribution was evaluated through the following span value:

$$\text{span} = \frac{(d_{90} - d_{10})}{d_{50}}$$

where d_{90}, d_{50}, and d_{10} are the polymer particle diameters below which 90, 50, and 10% of the polymer particle size distribution lies, respectively.

Measurement of the transmittances of the water and oil phases

The transmittances of the oil and water phases at a wavelength of 510 nm were measured using a UV/Vis spectrophotometer (Shimadzu UV-1800; Japan) equipped with a temperature controller. For these measurements, liquid paraffin and water were used as the respective baseline standards, and the temperature was set at 25 °C.

Optical microscope analysis of polymer particles

The inverse emulsion obtained after polymerization was diluted to 0.2% solid content with a 10 wt% solution of Span 80 in liquid paraffin, and ultrasound was applied for 10 min after the dilution to avoid the presence of bubbles. A drop of the diluted emulsion was deposited on a glass slide and analyzed using an optical microscope (Leica DM100; Germany).

Rheological measurements on inverse emulsions

The rheology of the inverse emulsion obtained after polymerization was measured with an AR-G2 rheometer (TA; USA) using a 100 mm cone–plate geometry with a cone angle of 1° and a gap of 25 μm. A linear viscoelastic region test was conducted at strains from 0.01 to 1000%, and frequency sweep tests were conducted at a strain of 0.3% and frequencies ranging from 0.1 to 100 Hz.

Determination of the amounts of surfactants in the water phase

Since the chains of Tween 80 and Span 80 contain carbon–carbon double bonds, the surfactant remaining in the aqueous phase was determined by bromine titration. About 1 mL sample was diluted with 10 mL of deionized water in an iodine flask, 2 mL of 0.1 mol/L KBrO$_3$/KBr solution (KBrO$_3$ (3 g) and KBr (25 g) dissolved in deionized water (1 L)) and 1 mL of dilute HCl solution were sequentially added, and the flask was kept protected from light for 1 h. Thereafter, 10 mL of ethanol and 1 mL of 20 wt% aqueous KI solution were added, and the mixture was titrated with standard aqueous Na$_2$S$_2$O$_3$ solution.

Results and discussion

Structure analysis of PAODBAC

The structure of cationic polymer PAODBAC determined by ^{1}H-NMR spectrum in deuterated water was shown in Fig. 1. The proton resonance shift of hydrogen in vinyl groups was about 6.0 ppm; the disappearance of peak at 6.0 ppm in ^{1}H-NMR proved that the synthesis of PAODBAC was completed successfully. The peak with chemical shift of 7.4 ppm represents the proton resonance of hydrophobic benzyl group, and the structure of quaternary ammonium salt makes the polymer be hydrophilic. The presence of hydrophilic groups and lipophilic groups allow the cationic polymer PAODBAC to be amphiphilic.
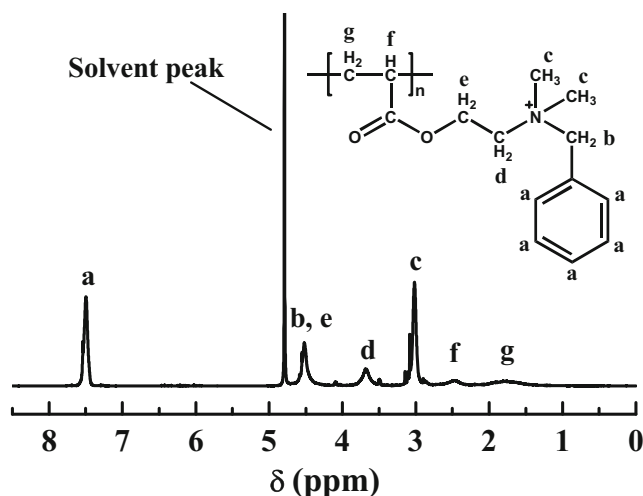

Fig. 1 ^{1}H-NMR spectrum of PAODBAC

Interaction behavior of PAODBAC and surfactants in the oil and water phases

It is generally accepted that an amphiphilic polymer bearing hydrophilic and lipophilic groups may interact with surfactant molecules or form polymer–surfactant aggregate complexes [29]. PAODBAC, as an amphiphilic cationic polymer, may associate with the surfactant, and this may be responsible for its effect on the inverse emulsion systems. Thus, the interactions of PAODBAC with surfactants in the oil and water phases were investigated. In this work, in order to highlight the action of PAODBAC in the system, Tween 80 was kept at its critical micelle concentration (CMC), that is, 0.014 g/L in pure water at 25 °C [30]. The amount of Span 80 used was that required to maintain a hydrophilic/lipophilic balance (HLB) of six. For comparison, PAODBAC was omitted from the system in a further set of experiments. The results are shown in Fig. 2.

In Fig. 2, it can be seen that the oil and water phases were separated by an interface. The lower water phase containing PAODBAC was more turbid than the water phase without PAODBAC, while the upper oil phase was relatively clear, as quantified by the transmittances of the respective phases shown in Table 1. Without PAODBAC, the system separated into water and oil phases within about 1 min, but when PAODBAC was added, phase separation required about 10 min. The water phase containing PAODBAC showed lower transmittance than that without PAODBAC, while the oil phase showed slightly higher transmittance. Since PAODBAC in the water phase could interact with the surfactants (including the Span 80 dissolved in the oil phase) or form polymer–surfactant aggregate complexes, the insolubility of Span 80 in the water phase and oil-in-water emulsion was formed in the water phase could render that with PAODBAC more turbid. As the amount of Span 80 bearing hydrophilic groups in the oil phase decreased, fewer water droplets could be supported therein, and hence, the oil phase was relatively clear.

Figure 3 shows the transmittances of the water and oil phases with and without PAODBAC at various

Table 1 Transmittance of water phase and oil phase without and with PAODBAC addition

| PAODBAC (% w/w)	Transmittance of the lower water phase	Transmittance of the upper oil phase
0	85.85%	30.70%
0.167	44.30%	36.69%

$W_{\text{liquid paraffin}}/W_{\text{water}} = 1$, $C_{\text{Tween 80}} = 0.014$ g/L, HLB = 6, $C_{\text{PAODBAC}} = 0.167\%$, $T = 25$ °C

concentrations of the surfactants. When PAODBAC was omitted from the system, the transmittance of the water phase decreased as the concentration of the surfactants was increased within a certain range. This was because the surfactant molecules were relatively loosely arranged at the oil–water interface and did not completely cover it. Hence, more Span 80 molecules could enter the water phase, lowering its transmittance. When the weight of surfactants was increased to 0.0264 g, the surfactant molecules largely covered the oil–water interface, the interactions between surfactant molecules were enhanced. Consequently, the amount of Span 80 molecules in the oil phase entering the water phase was reduced, and so, the transmittance of the latter was increased. When the weight of surfactants was increased to 0.033 g, the oil–water interface was completely covered, the interactions between surfactant molecules were enhanced to the greatest extent, and so, the water phase showed the highest transmittance. When the concentration of surfactants was further increased, surplus molecules were not arranged at the oil–water interface, causing a decrease in the transmittance of the water phase.

When PAODBAC was added to the systems, the transmittance of the water phase increased with increasing surfactant concentration within a certain range. Because the molecular chains of PAODBAC could interact with surfactant molecules at the oil–water interface, a more effective barrier was produced, the interactions between surfactant molecules and PAODBAC were strengthened, so that fewer Span 80 molecules could enter the water phase. Hence, the transmittance of the water phase increased. When the weight of surfactants was increased to 0.0066 g, the molecular chains of the polymer could interact with the surfactants optimally, and the amount of Span 80 molecules entering the water phase was minimized. Accordingly, the transmittance of the water phase was maximized. When the concentration of surfactants was further increased, the transmittance of the water phase decreased, as described previously for systems without PAODBAC.

In Fig. 3, it is evident that, compared to the systems without PAODBAC, the highest transmittance of the systems with PAODBAC appeared at a lower surfactant concentration, implying that in the latter case, the oil–water interface was

Fig. 2 Performance of water phase and oil phase without (left) and with (right) PAODBAC addition: $W_{\text{liquid paraffin}}/W_{\text{water}} = 1$, $C_{\text{Tween 80}} = 0.014$ g/L, HLB = 6, $C_{\text{PAODBAC}} = 0.167\%$, $T = 25$ °C

Fig. 3 Transmittance of water phase and oil phase without (left) and with (right) PAODBAC addition at varied concentration of surfactants. $W_{\text{liquid paraffin}}/W_{\text{water}} = 1$, HLB = 6, $C_{\text{PAODBAC}} = 0.067\%$, $T = 25\ °C$
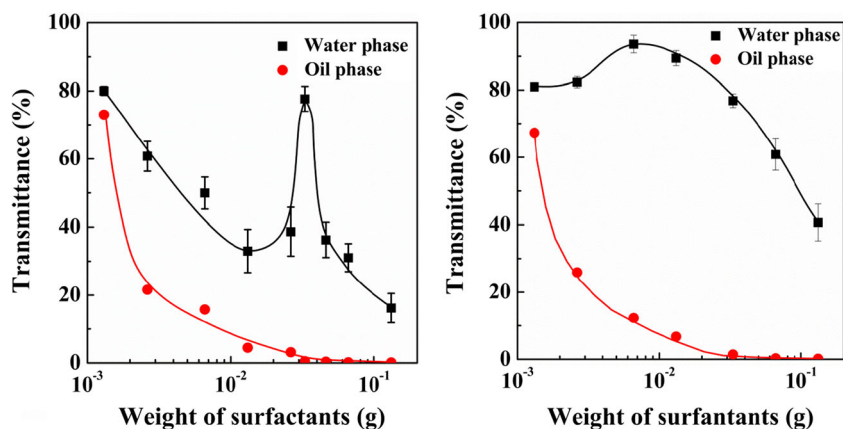
completely covered at a lower surfactant concentration. Thus, the addition of a certain concentration of PAODBAC could enhance the effectiveness of the surfactants through interaction, potentially stabilizing the inverse emulsion.

The critical aggregation concentration (CAC) of PAODBAC was measured as 0.44 g/L in water at 25 °C by fluorescence probe method. Thus, different concentrations of PAODBAC might affect the interaction mode with surfactants. The masses of surfactant remaining in the water phase at various concentrations of PAODBAC were measured by bromine titration. As shown in Table 2, the weight of surfactant remaining in the water increased with increasing PAODBAC concentration up to 0.067%. Because the interaction between the polymer and the surfactant was enhanced, more Span 80 from the oil phase moved into the water phase to bind with the polymer chains. When the concentration of PAODBAC was more than 0.067%, greatly exceeding its CAC, the weight of surfactant in the water phase decreased. This may have been due to aggregation of the polymer chain reducing the number of sites available for interaction with the surfactants and thus weakening its efficacy.

Table 2 Weight of the surfactant (Span 80 and Tween 80) remaining in the water phase at varied concentration of PAODBAC in an aqueous solution

PAODBAC (% w/w)	Concentration of surfactant (10^{-6} mol/L water)
0	3.75
0.017	4.75
0.033	5.50
0.067	6.88
0.167	5.25
0.333	4.25
0.667	3.50

Weight of water and liquid paraffin was 15 g respectively, weight of surfactant was 0.5 g (0.0795 g Tween 80 and 0.4205 g Span 80), and the experiment was carried out at 25 °C and stored for 7 days

Effect of the amphiphilic cationic polymer on the stability of inverse emulsions

Different amounts of PAODBAC could affect its interaction with the surfactant, and hence, different contents could affect its mode of action in the inverse emulsion system. The influence of the amount of PAODBAC on the stability of the inverse emulsion was investigated, and the results are shown in Fig. 4.

When an inverse emulsion without PAODBAC was centrifuged at 3000 r/min for 10 min, the emulsion stability was evaluated as $V_t = 0.9267$ (27.8 mL/30 mL). As the concentration of PAODBAC was increased, the stability of the inverse emulsion increased within a certain concentration range. The inverse emulsion stability was maximized, $V_t = 0.9667$ (29.0 mL/30 mL), at a PAODBAC concentration of 0.067%, and then decreased at higher concentrations.
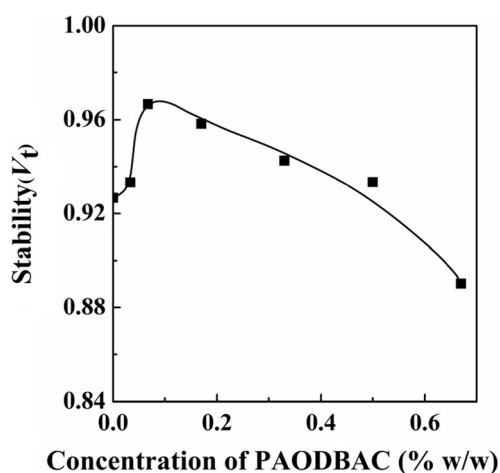

Fig. 4 Effect of the concentration of PAODBAC added to the water phase on the stability of inverse emulsion. $W_{\text{liquid paraffin}}/W_{\text{water}} = 1$, $n_{\text{AM}}/n_{\text{DMC}} = 1$, $W_{\text{(AM + DMC)}}/W_{\text{water}} = 1:3$, HLB = 6, consumption of mixed surfactants = 7.5% (weight percentage between mixed surfactants and water/liquid paraffin mixture), $W_{\text{VA-044}}/W_{\text{(AM + DMC)}} = 0.15\%$

After measured at 25 °C, the interfacial tension of the system added PAODBAC was 43.87 mN/m, and that without PAODBAC was 43.98 mN/m. It indicated that the ability of PAODBAC to decrease interfacial tension could be ignored. The amphiphilic cationic polymer forms a layer on the surface of the polymer particles following adsorption, such that the inverse emulsion is mainly stabilized by steric repulsion and secondly by electrostatic repulsion [26]. The stability of the inverse emulsion increased with increasing PAODBAC concentration up to 0.067%. Since the amphiphilic cationic polymer interacted or associated with the surfactant molecules, the hydrophobic groups of the polymer extended into the oil phase and the hydrophilic groups extended into the water phase. This reinforced the interfacial layer strength of the polymer particles and provided strong steric repulsion. Meanwhile, electrostatic repulsion produced by the positive charge on the polymer chain was favorable for the stability of the inverse emulsion. However, the stability of the inverse emulsion decreased when the PAODBAC concentration was increased beyond 0.067%, since this concentration greatly exceeded its CAC and the polymer chains spontaneously aggregated. Consequently, the amount of amphiphilic cationic polymer adsorbed on the surface of the polymer particles was reduced. Aggregation of the polymer chains induced the formation of clusters of droplets, which was not conducive to stability of the inverse emulsion.

Optical microscopy imaging and polymer particle size distribution

Microscope images of inverse emulsions prepared with various concentrations of PAODBAC are shown in Fig. 5. It can be seen that the inverse emulsions prepared with Span 80 and Tween 80 were composed of small spherical polymer particles. The micrographs showed that increasing the concentration of PAODBAC resulted in a significant decrease in the proportion of small polymer particles, thus favoring a smaller mean polymer particle size distribution and hence greater stability of the inverse emulsion [31]. The polymer particle size distributions of inverse emulsions prepared with various concentrations of PAODBAC are shown in Fig. 6. The volume-weighted mean diameters and the span values are presented in Table 3.

From the obtained data, it can clearly be seen that an inverse emulsion produced without PAODBAC consisted of small polymer particles, showing a bimodal polymer particle size distribution in accordance with the optical microscopy images. As described previously, the stability of the inverse emulsion improved with increasing the PAODBAC concentration up to 0.067%. This was at variance with the observation that the average polymer particle size tended to increase with increasing polymer concentration (shown in Fig. 6), as demonstrated by Howe et al. [32]. When the concentration of PAODBAC was low, the inverse emulsion showed high

Fig. 5 Optical microscopy images of inverse emulsion with varied concentration of PAODBAC. $W_{\text{liquid paraffin}}/W_{\text{water}} = 1$, $n_{\text{AM}}/n_{\text{DMC}} = 1$, $W_{(\text{AM} + \text{DMC})}/W_{\text{water}} = 1/3$, HLB = 6, consumption of mixed surfactants = 7.5% (weight percentage between mixed surfactants and water/liquid paraffin mixture), $W_{\text{VA-044}}/W_{(\text{AM} + \text{DMC})} = 0.15\%$, the scale bar is 2 μm
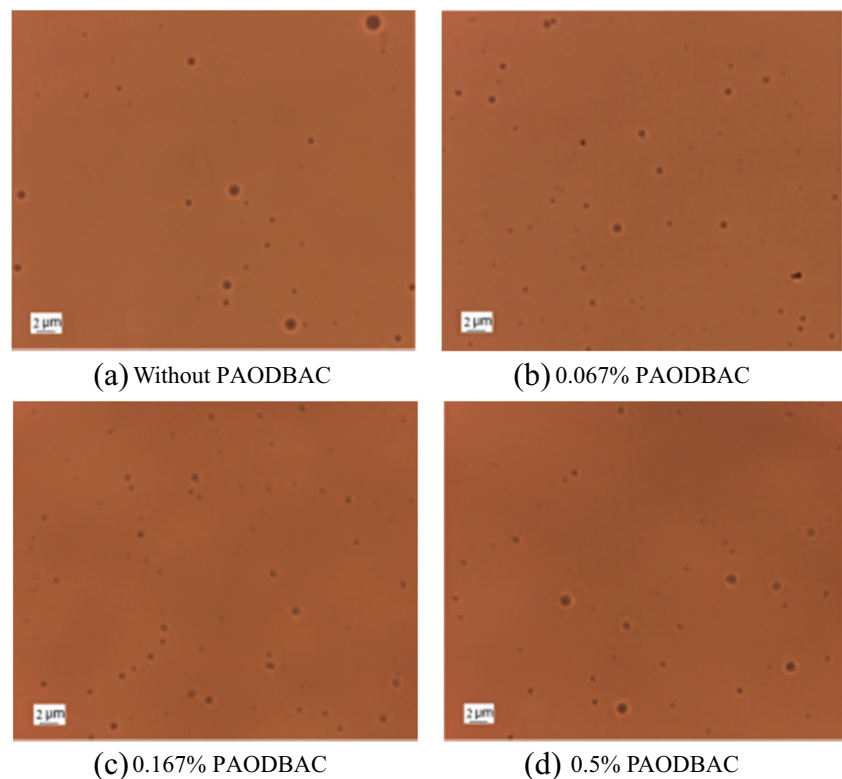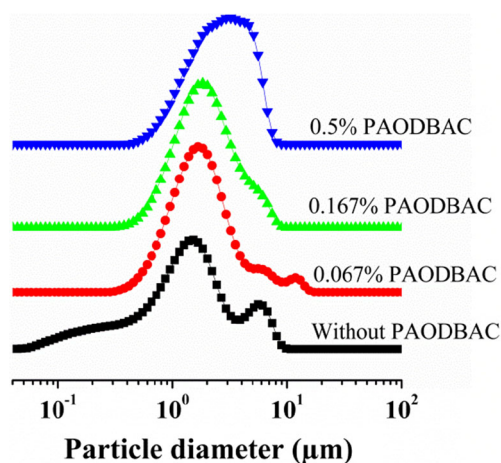

(a) Without PAODBAC

(b) 0.067% PAODBAC

(c) 0.167% PAODBAC

(d) 0.5% PAODBAC

Fig. 6 Polymer particle size distribution of inverse emulsion with varied concentration of PAODBAC. $W_{liquid\ paraffin}/W_{water} = 1$, $n_{AM}/n_{DMC} = 1$, $W_{(AM\ +\ DMC)}/W_{water} = 1/3$, HLB = 6, consumption of mixed surfactants = 7.5% (weight percentage between mixed surfactants and water/liquid paraffin mixture), $W_{VA-044}/W_{(AM\ +\ DMC)} = 0.15\%$

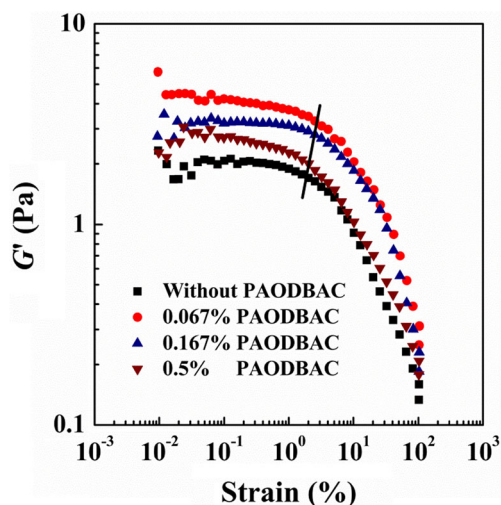**Fig. 7** Strain sweep tests of inverse emulsion prepared with varied concentration of PAODBAC. $W_{liquid\ paraffin}/W_{water} = 1$, $n_{AM}/n_{DMC} = 1$, $W_{(AM\ +\ DMC)}/W_{water} = 1/3$, HLB = 6, consumption of mixed surfactants = 7.5% (weight percentage between mixed surfactants and water/liquid paraffin mixture), $W_{VA-044}/W_{(AM\ +\ DMC)} = 0.15\%$

stability. This was because the amphiphilic cationic polymer chains associated with the surfactant molecules co-adsorbed at the oil–water interface and thereby significantly modified the strength of the interfacial layer. This was corroborated by the rheological properties described as follows. With increasing PAODBAC concentration, the average polymer particle size increased, yet, the stability of the inverse emulsion improved, indicating that the role of the interface effect was stronger. The small mean polymer particle size distribution shown by the span value also implied high stability. When the concentration of the polymer exceeded 0.067%, the stability of the inverse emulsion decreased, due in part to the larger polymer particle size. With the increase of polymer aggregation, the polymer particle size increased. This was probably because a significant proportion of the polymer associated with the surfactants could not be adsorbed at the oil–water interface.

Rheological properties of inverse emulsions

In viscoelastic measurements of inverse emulsions with various concentrations of PAODBAC, determination of the linear

Table 3 Volume-weighted mean diameter and span value of the polymer particle size distribution of inverse emulsion with different concentrations of PAODBAC

PAODBAC (% w/w)	Volume-weighted mean polymer particle diameter (μm)	Span value
0	1.949	3.368
0.067	2.424	2.042
0.167	2.368	1.800
0.500	3.085	1.547

viscoelastic region was important, because this can reveal the zone in which the strain amplitude cannot perturb the structure of the inverse emulsion. Beyond a threshold value, some breakage of the structure of the inverse emulsion can occur [33].

As shown in Fig. 7, when the strain was increased in a certain range, the elastic modulus G' remained almost unchanged, which could determine the linear viscoelastic region of the emulsion. When the strain exceeded a certain value, G' appeared to decline, indicating that the structure of the emulsion polymer particles was destroyed. The linear viscoelastic
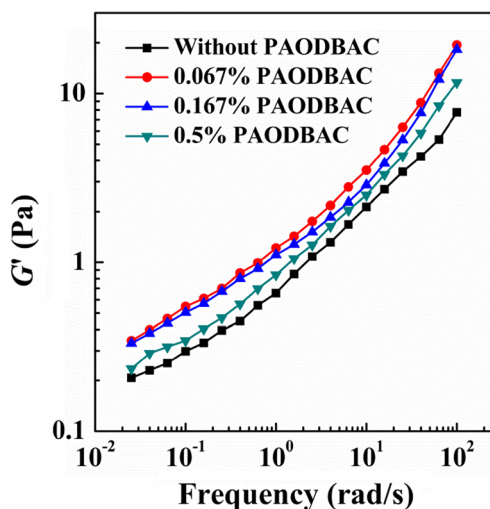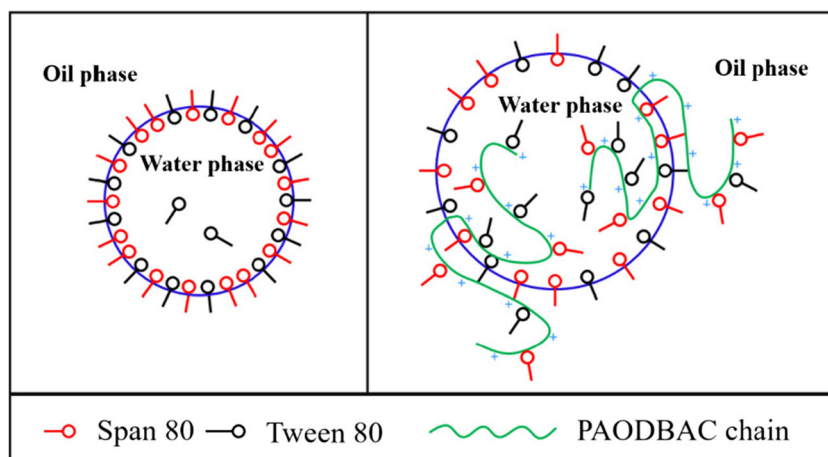

Fig. 8 Frequency sweep tests of inverse emulsion prepared with varied concentration of PAODBAC. $W_{liquid\ paraffin}/W_{water} = 1$, $n_{AM}/n_{DMC} = 1$, $W_{(AM\ +\ DMC)}/W_{water} = 1/3$, HLB = 6, consumption of mixed surfactants = 7.5% (weight percentage between mixed surfactants and water/liquid paraffin mixture), $W_{VA-044}/W_{(AM\ +\ DMC)} = 0.15\%$

Fig. 9 Stabilization mechanism of inverse emulsion system without (left) and with (right) PAODBAC addition

region of the inverse emulsion corresponded to strains between 0.01 and 0.5%. Therefore, frequency sweep tests were conducted with a strain of 0.3% and frequencies ranging from 0.1 to 100 Hz.

According to Filho et al. [34], inverse emulsion stability and elastic modulus G' are connected, that is, an increase in G' corresponds to emulsion stability enhancement. As shown in Fig. 8, the elastic behavior of the inverse emulsions with different concentrations of polymer was characterized by frequency sweep tests, whereby the G' of the inverse emulsions increased with increasing frequency. The G' of the inverse emulsion with a PAODBAC concentration of 0.067% was higher than those at the other concentrations. When the concentration of polymer was less than 0.5%, the G' values of inverse emulsions prepared with PAODBAC were higher than those of inverse emulsions without PAODBAC, consistent with the inverse emulsion stabilities reported above. This indicated that the amphiphilic cationic polymer chains could associate with the surfactant molecules at the interparticle oil–water interface, so that a spatial network structure was formed between the polymer particles. Thus, inverse emulsion systems with the amphiphilic cationic polymer displayed highly elastic behavior.

Mechanism by which the amphiphilic cationic polymer stabilizes inverse emulsion systems

Figure 9 shows the proposed mechanism of stabilization of the inverse emulsion systems with and without PAODBAC. Without PAODBAC, Span 80 molecules and Tween 80 molecules were arranged at the oil–water interface to stabilize the polymer particles of the inverse emulsion. When PAODBAC was added to the inverse emulsion system, its chains could interact with surfactant molecules at the oil–water interface, forming a tighter arrangement, which reinforced the interfacial layer strength of polymer particles and provided permanent steric repulsion. Meanwhile, electrostatic repulsion produced

by the positive charge on the polymer chain was also favorable for the stability of the inverse emulsion.

Conclusions

The stability of inverse emulsions prepared with mixed surfactants could be enhanced by adding appropriate concentrations of the amphiphilic cationic polymer PAODBAC. The PAODBAC chains could interact with the surfactant molecules. With the addition of PAODBAC, the oil–water interface could be completely covered by the surfactants at a lower concentration thereof. When the concentration of PAODBAC was 0.067% (*w/w*), the interactions between its chains and the surfactant molecules were optimized and, accordingly, the stability of the inverse emulsion was maximized. At PAODBAC contents of 0–0.067% (*w/w*), the stability of the inverse emulsions increased with increasing polymer content due to increased interfacial layer strength between the polymer particles. However, when the concentration of PAODBAC exceeded 0.067% (*w/w*), the stability of the inverse emulsions decreased because of aggregation of the polymer chains. The presence of PAODBAC in the inverse emulsion system aided the establishment of a small mean polymer particle size distribution. The linear viscoelastic region of the inverse emulsion corresponded to strains between 0.01 and 0.5%. At polymer concentrations below 0.5%, the G' values of inverse emulsions prepared with PAODBAC were higher than those of inverse emulsions without it. The most stable inverse emulsion exhibited the best elastic behavior.

Compliance with ethical standards

Conflict of interest   The authors declare that they have no conflict of interest.

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