

A new cation-modified Al-polyacrylamide flocculant for solid-liquid separation in waste drilling fluid

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ABSTRACT: A new cation-modified Al-polyacrylamide (CAPAM) flocculant was prepared by the *in situ* polymerization of acrylamide (AM) and (2-methacryloyloxyethyl) trimethyl ammonium chloride (DMC) with Al(OH)₃ sol. The optimum preparation conditions were obtained by a one-factor experimental design: as the amount of AlCl₃ was fixed at 0.025 mol, the polymerization time, polymerization temperature, $n(\text{AM}) : n(\text{AlCl}_3)$, $n(\text{DMC}) : n(\text{AlCl}_3)$, and $n(\text{K}_2\text{S}_2\text{O}_8) : n(\text{AM})$ were 4 h, 70°C, 8, 0.9, and 1.82×10^{-3} , respectively. The CAPAM was characterized by thermogravimetric analysis, Fourier transform infrared spectroscopy, scanning electron microscopy, and transmission electron microscopy. The solid-liquid separation performance of the CAPAM was evaluated in terms of water content. The CAPAM showed better flocculation performance than cationic polyacrylamide and polyaluminum sulfate at a fixed concentration of 0.3% in waste drilling fluid and tended to perform well in alkaline solution. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 41641.

KEYWORDS: acrylamide; cation; flocculant; solid-liquid separation; waste drilling fluid

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INTRODUCTION

High molecular weight polymer flocculants have been widely used for solid-liquid and solid-solid separation in waste water treatment and dewatering treatment for more than 50 years.^{1,2} Most polymer flocculants in the market are acrylamide-based nonionic, anionic, or cationic copolymers. Compared with inorganic flocculants, polymer flocculants offer the following advantages when used in waste water treatment: lower coagulant dose requirements, a smaller volume of sludge, a smaller increase in the ionic load of the treated water, and cost savings of up to 30%.^{3,4}

The flocculation efficiency of polyacrylamides (PAMs) is determined by several factors including the molecular weight and charge density of the polyelectrolytes, the pH and ionic strength of the suspending medium, the size and surface charge of the dispersed particles, and the adsorption density and conformation of the adsorbed flocculants.⁵⁻¹⁰ These properties can be modified by the nature and proportions of the monomers; therefore, several kinds of PAMs can be prepared. These polymers are made by the combination of acrylamide monomer with other kinds of monomers, such as acrylates,^{11,12} carboxymethyl tamarind,¹³ and dicyandiamide.¹⁴ Compared with these polymer flocculants, the inorganic-organic composite flocculant,

such as Al(OH)₃-polyacrylamide, was found to be more effective in solid-liquid separation,¹⁵ this is mainly because of the star-like structure of the flocculant to improve the flocculation performance and to form the pellet like floccules. Zeng *et al.*¹⁶ prepared a composite chitosan flocculant by chitosan, polyaluminum chloride (PAC), and silicate, and compared with PAC, the percentage of removing COD (organic contaminant), SS (solid suspending substances), and Al³⁺ in the treated water using this composite chitosan flocculant was enhanced by 1.8–23.7%, 50%, and 61.2–85.5%. Another inorganic-organic composite flocculant-based chitosan, PAM, and TiO₂ prepared by Zhu *et al.*¹⁷ were used in solid-liquid separation for high-density waste drilling fluid also more effect than the conventional PAMs. Except for water treatment, the inorganic-organic flocculant also can use as the performance enhancer for aerated submerged membrane bioreactor.¹⁸ Though the inorganic-organic composite flocculants are paid more attentions recently, there did not have few flocculation mechanisms of the composite flocculants in these studies.

Nowadays, the disposal of large quantities of waste drilling fluids has proven to be one of the most difficult environmental problems in the world because waste drilling fluids have complex components, such as minerals, clay, and organic materials,

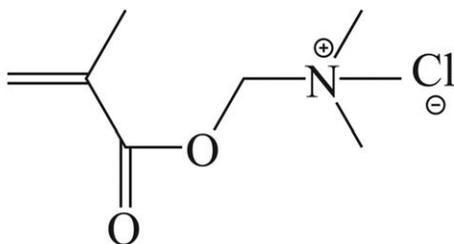


Figure 1. Structural formula of DMC.

and these fluids have a deep chroma.¹⁹ There has not been any effective method to treat these fluids. Many inorganic and organic polymer flocculants have been used to flocculate the suspended solids in the waste drilling fluids, but the effect is not good. The objective of this work was to prepare a cation-modified Al(OH)₃-polyacrylamide copolymer (CAPAM) and to examine its flocculation performance in waste drilling fluids. This flocculant was prepared by *in situ* polymerization in our laboratory. Different factors affecting the preparation were investigated: the doses of acrylamide (AM), (2-methacryloyloxyethyl) trimethyl ammonium chloride (DMC), and K₂S₂O₈ (KPS), and the polymerization time and temperature. Moreover, some factors affecting the flocculation properties were studied, such as the concentration of CAPAM, flocculation temperature, and pH of the waste drilling fluid.

MATERIALS AND METHODS

Materials

Sodium hydroxide, hydrochloric acid, acrylamide, potassium persulfate, acetone, ethanol, sodium carbonate, disodium salt of EDTA, and aluminum chloride were of analytic grade and supplied by Beijing Chemical Reagent Co., Ltd. (2-Methacryloyloxyethyl) trimethyl ammonium chloride (DMC) as the cationic reagent and cationic polyacrylamide (CPAM) with a molecular weight of 8×10^6 g mol⁻¹ were bought from Le Tai Chemical Supermarket, Beijing, China. The structural formula of DMC is shown in Figure 1.

The waste drilling fluid was supplied by Shandong Shengli Oil Field, China, and the basic characteristics of the waste drilling fluid are summarized in Tables (I–III).

Preparation of CAPAM

The amount of AlCl₃ was fixed at 5 mmol. First, AlCl₃ was added under stirring to a 250 mL three-necked flask containing 20 mL deionized water and 20 mL ethanol at room temperature. Second, a solution of Na₂CO₃ and NaOH in the molar ratio of 1 : 1 was added dropwise to adjust the pH of the content to 7, and stirring was continued until a smooth colloid was formed. A solution of 10 mL of disodium salt of EDTA at the concentration of 5 wt % was added to combine with some metal ions that could prevent copolymerization. Afterwards, AM and DMC of different masses were added into the flask at the same time, and the mixture was heated to the reaction temperature ranged in 40–80°C under continuous stirring. KPS aqueous solution (10 mL) at a concentration of 0.2 wt % was slowly added into the flask through a guttate funnel. The reaction was allowed to continue for several hours (1–6 h). N₂ was

bubbled through the reaction system throughout the polymerization time. After the reaction, the flask was cooled to room temperature, and the reaction mixture was precipitated with ethanol and filtered. The precipitate was extracted for 48 h using an acetic acid : acetone mixture (40 : 60, v/v) to remove the homopolymers and unreacted monomers. The flocculant CAPAM was finally obtained by drying the precipitate in a vacuum oven at 60°C for 24 h.

Determination of Intrinsic Viscosity of CAPAM

The intrinsic viscosity of CAPAM was measured with an Ubbelohde capillary viscometer at 30°C according to the method proposed by Shirzad-Semser *et al.*²⁰ In this method, CAPAM solutions were prepared at the concentrations of 0.5, 0.75, 1.00, 1.25, and 1.50 g dL⁻¹ with deionized water as solvent.

The specific viscosity (η_{sp}) was calculated according to the following equation:

$$\eta_{sp} = \frac{t - t_0}{t_0}, \quad (1)$$

where t and t_0 are the times (s) taken by the solution and solvent, respectively, to pass through the two calibrated lines of the viscometer. The intrinsic viscosity was determined from a plot of ratio of specific viscosity to concentration (η_{sp}/C) versus concentration (C). The intercept at the η_{sp}/C -axis ($C = 0$) of the fitted straight line gives the intrinsic viscosity:

$$\eta_i = \lim_{C \rightarrow 0} \frac{\eta_{sp}}{C}, \quad (2)$$

where C is the concentration of the solution (g dL⁻¹), η_{sp} is the specific viscosity.

Fourier Transform Infrared, Scanning Electron Microscopy, Transmission Electron Microscopy, and Thermogravimetric Analyses

The Fourier transform infrared (FTIR) spectrum of CAPAM was obtained using a Bruker IFS 66/S spectrometer (Bruker, Germany). The flocculant sample was uniformly mixed with previously dried KBr by moderate grinding to minimize particle break up. Scanning electron microscopy (SEM) observations of CAPAM were made using a scanning electron microscope (Hitachi S-4700, Japan). The sample was dried and then coated with a thin layer of gold in vacuum before investigation. Transmission electron microscopy (TEM) observations of CAPAM were made using a transmission electron microscope (Hitachi H-800, Japan). A drop of CAPAM dispersion (10 wt % in ethanol) was dripped on the surface of a copper grid to form a film. The

Table I. Basic Characteristics of Waste Drilling Fluid

Item	Numerical value
Density (g mL ⁻¹)	1.62
Apparent viscosity (mPa s)	41.50
Plastic viscosity (mPa s)	26.70
Dynamic cutting force (Pa)	9.80
Solid content (%)	54.40
Oil content (%)	5.00
pH	11.64

Table II. Pollutants of Waste Drilling Fluid

Number	Pollutant	Concentration (mg L ⁻¹)	Number	Pollutant	Concentration (mg L ⁻¹)
1	Overall Cr	1.55	5	Pb	1.2
2	Hg	0.0004	6	Zn	0.12
3	Cd	0.22	7	Cu	<0.1
4	As	0.024	8	Fluoride	5.27

thermal degradation of CAPAM was studied using a thermogravimetric analyzer (TGA 209F1, Netzsch, Germany). The instrument was calibrated with calcium oxalate before test. An aluminum pan containing 10 mg of CAPAM was put into the oven and heated at 20°C min⁻¹ from 25 to 500°C with nitrogen flowing at a rate of 40 mL min⁻¹ as a purge gas.

Flocculation Experiments

Flocculation was investigated in a batch test using a series of beakers each containing 100 g of waste drilling fluid. A dispersion of the above prepared CAPAM was added in different doses to the beakers, respectively. Immediately after the addition of the flocculant, the fluid was stirred for 3 min at a speed of 60 rpm. The flocs were then allowed to settle down for 10 min. The flocs and liquid in each beaker were transferred to a centrifuge cup and centrifuged at a speed of 3500 rpm for 10 min. After centrifugation, the liquid in the upper part of the centrifuge cup was poured out, and the precipitate at the bottom of the cup was weighed before and after drying. The water content of the precipitate was used to express the solid-liquid separation performance of the flocculant. The water content of the precipitate was defined as follows¹⁶:

$$\text{Water content(\%)} = \left(1 - \frac{m_2}{m_1}\right) \times 100, \quad (3)$$

where m_1 and m_2 are the weights of the flocculated precipitate before and after drying, respectively.

RESULTS AND DISCUSSION

Effect of Preparation Conditions for CAPAM on Intrinsic Viscosity

The effect of preparation conditions for CAPAM on the intrinsic viscosity of CAPAM was investigated by a one-factor experimental design. The intrinsic viscosity was calculated according to eq. (2).

Effect of Molar Ratio of AM to AlCl₃ on Intrinsic Viscosity

The effect of molar ratio of AM to AlCl₃ ($n(\text{AM}) : n(\text{AlCl}_3)$) on intrinsic viscosity was studied and the results are shown in Figure 2. The dose of AM was varied at fixed doses of AlCl₃ (5 mmol) and DMC (5 mmol). The initiator concentration ($n(\text{KPS}) : n(\text{AM})$) was kept constant at 1.5×10^{-3} . The polymerization time and temperature were 60°C and 3 h, respectively. As $n(\text{AM}) : n(\text{AlCl}_3)$ increases, the intrinsic viscosity first

increases, reaches a maximum at a molar ratio of AM to AlCl₃ of 8, and then decreases. The maximum in intrinsic viscosity indicates that there is an optimum molar ratio of AM to AlCl₃. The increase in intrinsic viscosity is the result of increases in the degree of crosslinking and molecular weight of CAPAM with increasing dose of AM. However, as the molar ratio of AM to AlCl₃ exceeds 8, the concentration of free radicals AM increases, and the AM monomers take part in homopolymerization to form PAM and P(AM-DMC). As a result, the intrinsic viscosity of CAPAM decreases.

Effect of Molar Ratio of DMC to AlCl₃ on Intrinsic Viscosity

The effect of molar ratio of DMC to AlCl₃ ($n(\text{DMC}) : n(\text{AlCl}_3)$) on the intrinsic viscosity of CAPAM was studied and the results are shown in Figure 3. The polymerization temperature and time, molar ratio of AM to AlCl₃, and molar ratio of KPS to AM were 60°C, 3 h, 8, and 1.5×10^{-3} , respectively. As $n(\text{DMC}) : n(\text{AlCl}_3)$ increases from 0.3 to 1.3, the intrinsic viscosity increases first, reaches a maximum, and then decreases. The maximum in intrinsic viscosity indicates that there is an optimum ratio of DMC to AlCl₃. However, excessive amounts of DMC, which is water soluble and has higher steric hindrance than AM, can largely prevent the polymerization reaction.

Effect of Molar Ratio of KPS to AM on Intrinsic Viscosity

KPS was used as the initiator to initiate the polymerization. KPS hydrolyzed and became free radicals. Because the free radicals readily formed H₂O, the polymerization was mainly initiated. Al(OH)₃, AM, and DMC were initiated to produce the free radicals (a), (b), and (c) (see Figure 4), respectively. Then (a), (b), and (c) polymerized to form CAPAM. Figure 5 shows the effect of molar ratio of KPS to AM on the intrinsic viscosity of CAPAM. The polymerization temperature, polymerization time, molar ratio of AM to AlCl₃, and molar ratio of DMC to AlCl₃ were 60°C, 3 h, 8, and 0.9, respectively. As the molar ratio of KPS to AM increases from 0.26×10^{-3} to 1.82×10^{-3} , the intrinsic viscosity increases from 3.14 to 7.53 dL g⁻¹ because the increase in the concentration of free radicals increases the ratio of grafting and hence the molecular weight of the flocculant. However, further increases in the molar ratio of KPS to AM lead to a decrease in the intrinsic viscosity because the excessive KPS favors monomer homopolymerization, which reduces the molecular weight of CAPAM.

Table III. Primary Composition of and Contents of Solid Particles in Waste Drilling Fluid

Mineral substance	Quartz	Plagioclase	Calcite	Dolomite	Barite	Clay minerals
Content (%)	10.5	1.6	9.3	7.3	68.8	2.5

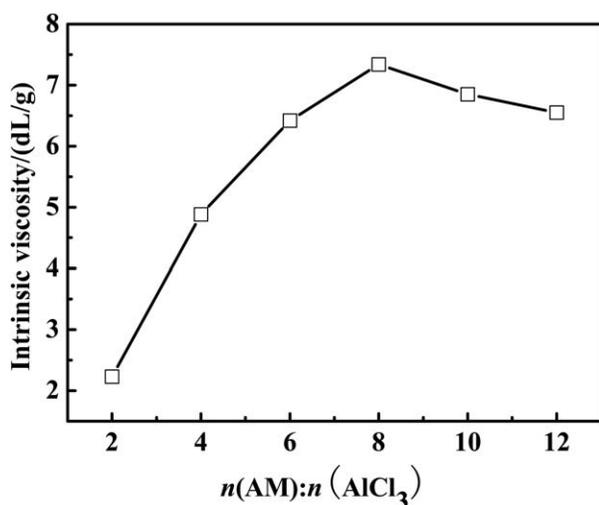


Figure 2. Effect of molar ratio of AM to AlCl_3 on intrinsic viscosity.

Effect of Polymerization Time on Intrinsic Viscosity

The intrinsic viscosity at various polymerization times for the preparation of CAPAM is shown in Figure 6. The polymerization temperature, $n(\text{AM}) : n(\text{AlCl}_3)$, $n(\text{DMC}) : n(\text{AlCl}_3)$, and $n(\text{KPS}) : n(\text{AM})$ were 60°C , 8, 0.9, and 1.82×10^{-3} , respectively. Figure 6 shows that the intrinsic viscosity increases with the polymerization time from 1 to 4 h. The polymerization efficiency reached a maximum in 4 h. With further increases in polymerization time, the grafting between the reactants increased and the molecular weight of the product increased until the polymerization reached its limits with significant reduction in the amount of reactants.

Effect of Polymerization Temperature on Intrinsic Viscosity

Experiments were conducted at five different temperatures from 40 to 80°C to evaluate the effect of polymerization temperature on intrinsic viscosity. Other factors were kept constant: polymerization time, $n(\text{AM}) : n(\text{AlCl}_3)$, $n(\text{DMC}) : n(\text{AlCl}_3)$, and $n(\text{KPS}) : n(\text{AM})$ were 4 h, 8, 0.9, and 1.82×10^{-3} , respectively. The intrinsic viscosity increases as polymerization temperature increases from 40 to 70°C and decreases thereafter, as shown in Figure 7. As the polymerization temperature increased, the reaction efficiency and the molecule weight of CAPAM increased. The intrinsic viscosity decreases with further increases in temperature because the molecular chains derived from AM and DMC may break at high temperatures.

FTIR, SEM, TEM, and TGA Analysis

The CAPAM samples used for FTIR, SEM, TEM, and TGA studies were prepared under the following conditions: the polymerization time, polymerization temperature, $n(\text{AM}) : n(\text{AlCl}_3)$,

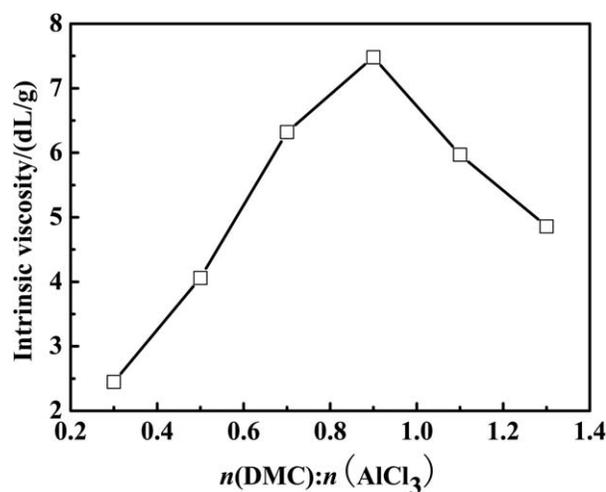


Figure 3. Effect of molar ratio of DMC to AlCl_3 on intrinsic viscosity.

$n(\text{DMC}) : n(\text{AlCl}_3)$, and $n(\text{KPS}) : n(\text{AM})$ were 4 h, 70°C , 8, 0.9, and 1.82×10^{-3} , respectively.

FTIR Analysis

Figure 8 shows the FTIR spectrum of CAPAM. The bands at 627 cm^{-1} and 480 cm^{-1} are assigned to $\text{Al}-\text{O}$ stretching vibration. The broad band at 3400 cm^{-1} is assigned to $\text{N}-\text{H}$ stretching vibration. The bands around 1122 cm^{-1} and 2927 cm^{-1} are due to $-\text{CO}$ and $-\text{C}-\text{H}$ stretching vibration, respectively. The bands at 3187 cm^{-1} and 1450 cm^{-1} are for $-\text{NH}$ stretching vibration and $-\text{CH}$ bending vibration, respectively. The bands at 1315 cm^{-1} and 1411 cm^{-1} are for $-\text{CN}$ stretching vibration. The band at 1662 cm^{-1} is for the amide carbonyl group. These results confirm that AM and DMC have been grafted onto the alumina backbone.

SEM Analysis

Scanning electron microscopy (SEM) was used to investigate the surface morphology of CAPAM. The SEM images of CAPAM at different magnifications are shown in Figure 9. The surface of CAPAM is ragged and porous. The molecular chains of the AM and DMC are connected to form a network structure, thus promoting the adsorption and bridging performance of CAPAM as a flocculant for the solid-liquid separation of waste drilling fluid.

TEM Analysis

Figure 10 shows the TEM images of CAPAM at the reaction times of 4 h and 5 h. It can be seen that the $\text{Al}-\text{O}$ core lies at the center of CAPAM. The diameter of the grafted Al core is from 225 to 450 nm, and the thickness of the AM-DMC shell is from 290 to 470 nm. Particle diameters are not uniform (they

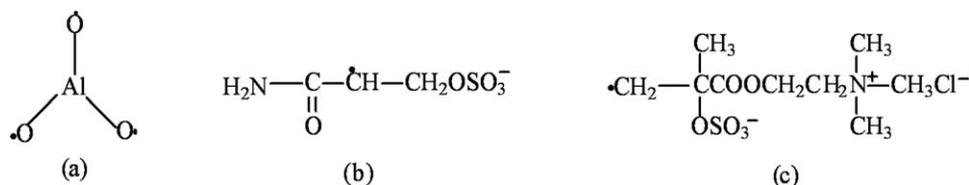


Figure 4. (a) Free radicals of AlCl_3 , (b) AM, and (c) DMC initiated by KPS.

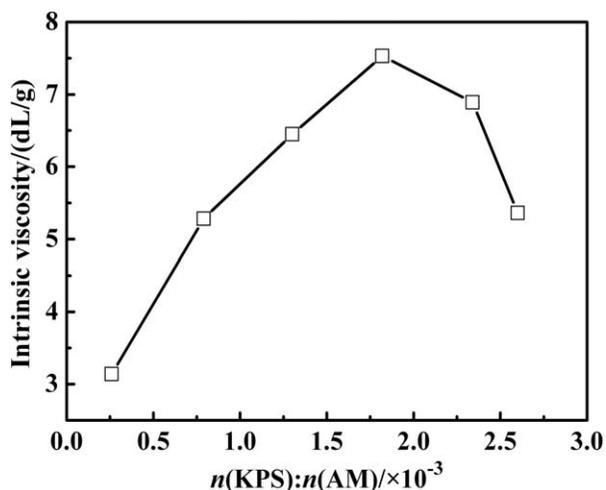


Figure 5. Effect of molar ratio of KPS to AM on intrinsic viscosity.

vary from 640 nm to 1.16 μm), and the size of the particles increases as the reaction time increases. Figure 9(b) shows that most particles form chain-like aggregations as the reaction time increases because of particle surface tension.

TGA Analysis

The thermogram for CAPAM is shown in Figure 11, which shows a decrease in mass as the temperature increases. The mass difference of about 10% between the baseline at 100% mass and the first inflection point of the curve at 131°C can be attributed to the loss of the moisture that the sample had adsorbed. The initial decomposition temperature of CAPAM is 208°C, which is higher than that of PAM (about 200°C),²¹ and the half-life temperature is 400°C. The higher decomposition temperature of CAPAM indicates that the $\text{Al}(\text{OH})_3$ colloid particles and AM formed ionic bonds in the *in situ* polymerization, thus weakening the thermal motion of the macromolecular chains of P(AM-DMC).

Flocculation Tests in Waste Drilling Fluid

The waste drilling fluid used was a brownish black turbid liquid, the basic characteristics of which are shown in Tables (I–III). In this section, the influences of the concentration of

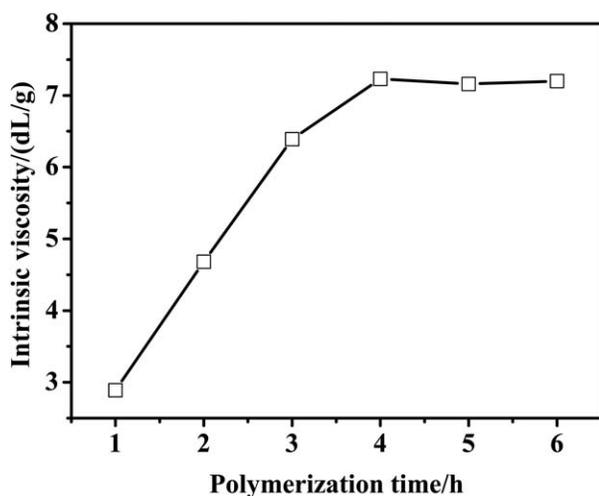


Figure 6. Effect of polymerization time on intrinsic viscosity.

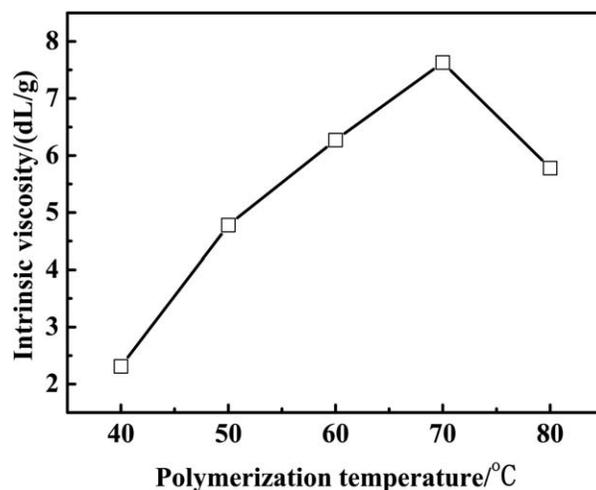


Figure 7. Effect of polymerization temperature on intrinsic viscosity.

CAPAM, flocculation temperature, and pH on flocculation efficiency are discussed, and the flocculation properties of CPAM and polyaluminum sulfate (PAS) are compared with those of CAPAM under the same conditions.

Comparison of Solid–Liquid Separation Performance of CAPAM, CPAM, and PAS in Waste Drilling Fluid

CAPAM, CPAM, and PAS were compared in terms of their solid–liquid separation performance in waste drilling fluid. Each of the three flocculants was added into 100 g of waste drilling fluid at different concentrations at room temperature (25°C), and the water content results are shown in Figure 12. The water content of the precipitate decreases as the dose of CAPAM increases from 0.1% to 0.3% and increases thereafter. The minimum water contents for CAPAM, CPAM, and PAS are 22.34% at a dose of 0.3%, 35.78% at a dose of 0.4%, and 34.67% at a dose of 0.5%, respectively. These results indicate that CAPAM has better solid–liquid separation performance at a smaller dose than CPAM and PAS because of the effects of the $\text{Al}(\text{OH})_3$ core and the P(AM-DCM) chains, suggesting that CAPAM has the properties of both organic and inorganic flocculants.

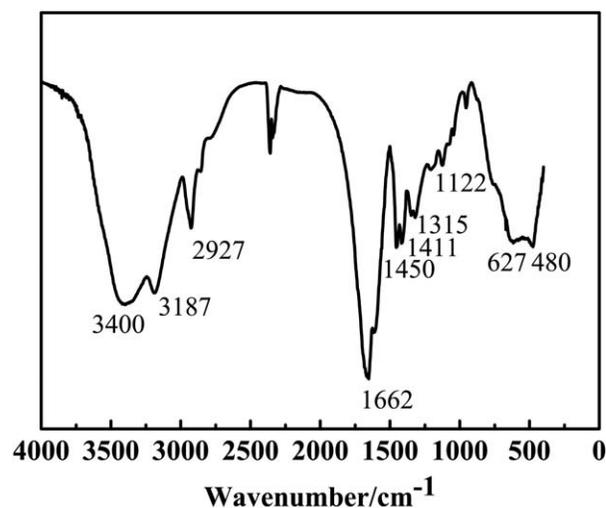


Figure 8. FTIR spectrum of CAPAM.

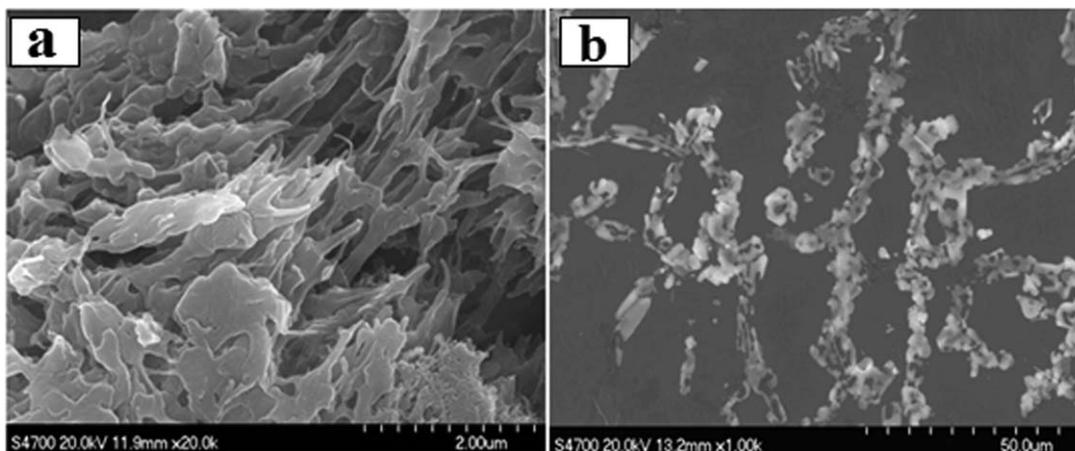


Figure 9. SEM images of CAPAM at different magnifications: (a) $\times 20,000$ and (b) $\times 1000$.

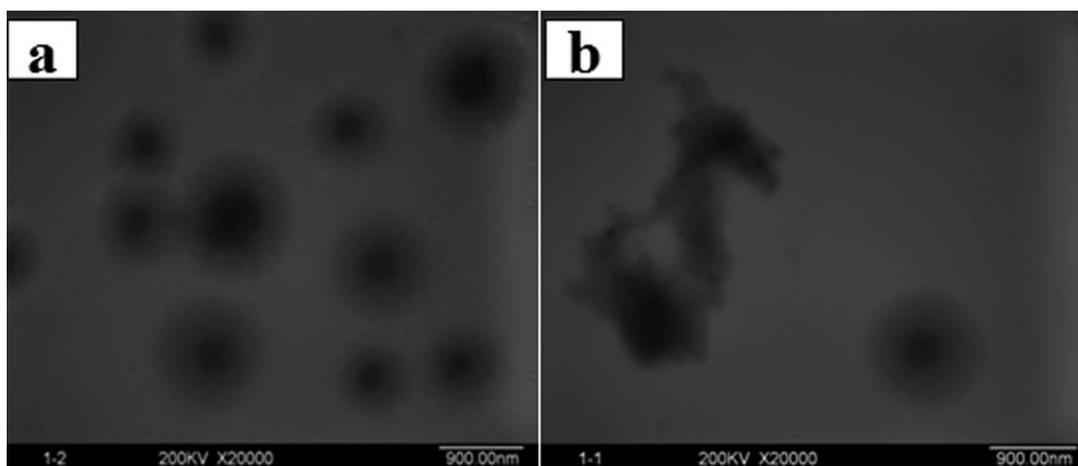


Figure 10. TEM images of CAPAM at reaction times of (a) 4 h and (b) 5 h.

Temperature on Flocculation Efficiency of CAPAM in Waste Drilling Fluid

Flocculation reactions were performed to study the temperature effect on the solid–liquid separation efficiency of CAPAM at the

concentration of 0.3%. Figure 13 showed that the temperature has a significant effect on the flocculation efficiency of CAPAM. The solid–liquid separation efficiency of CAPAM increases by 25% as the temperature increases from 5 to 35°C. The

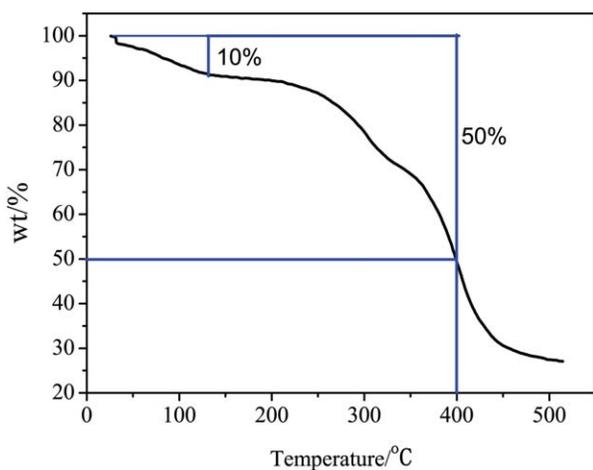


Figure 11. Thermogram for CAPAM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

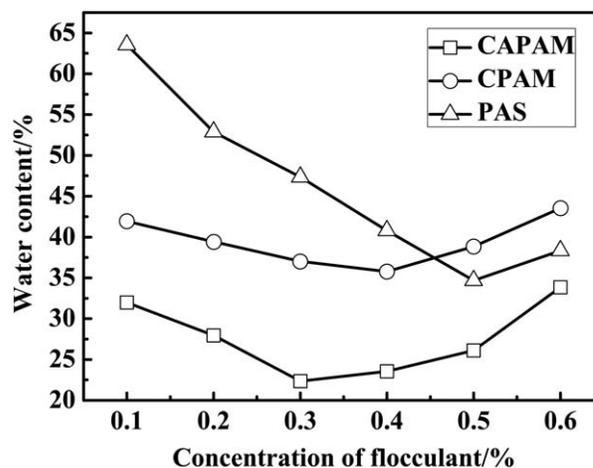


Figure 12. Water content as a function of concentration of flocculant.

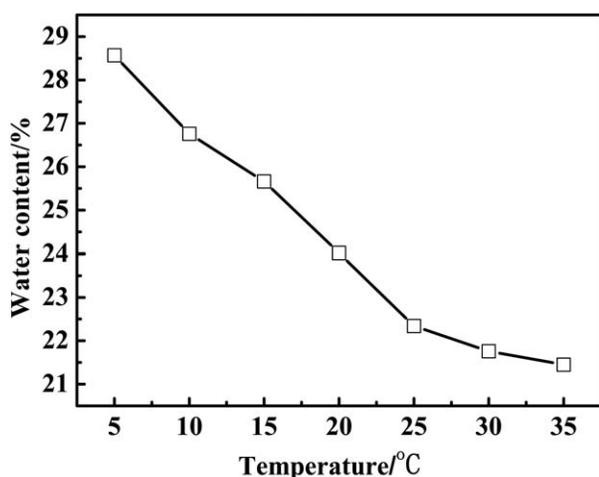


Figure 13. Flocculation efficiency of CAPAM at various temperatures.

adsorption of CAPAM on the suspended particles in waste drilling fluid was slow because the rate of aggregation and frequency of collisions of particles were slow at low temperatures. As the temperature increased, the flocculation reaction of CAPAM, an endothermic process, was accelerated.

Effect of pH on Flocculation Efficiency of CAPAM in Waste Drilling Fluid

The effect of pH on the flocculation efficiency of CAPAM was investigated while other factors were kept constant (CAPAM dosage was 0.3% and temperature was 25°C). The water content results are shown in Figure 14. CAPAM performs better as a flocculant in alkaline environment than in acidic environment. The water content reaches the minimum value of 21.12% at a pH 9, probably because of the effects of pH on the surface charge and surface properties of the colloidal particles in the waste drilling fluid and the positively charged characteristic of CAPAM. So the suspended particles are assembled rapidly onto the surface of CAPAM by charge neutralization, adsorption, bridging, and Vander Waals force after CAPAM added into the waste drilling fluid.

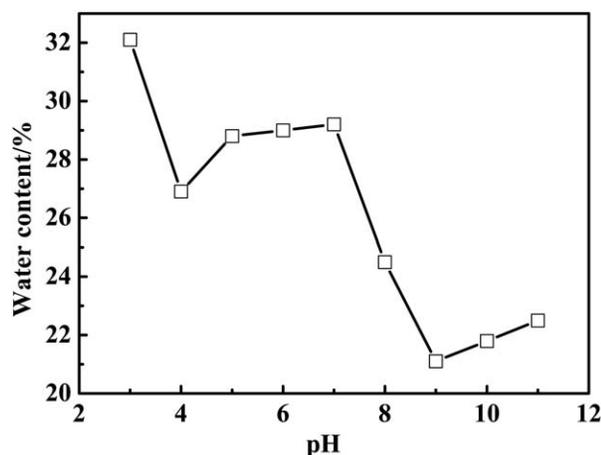


Figure 14. Flocculation efficiency of CAPAM at various pH.

Acidic and alkaline environment may lead to surface charge screening and thus reduce the electrostatic repulsion between particles.

CONCLUSIONS

CAPAM, an effective flocculant for solid–liquid separation in waste drilling fluid was prepared by the *in situ* polymerization of acrylamide and (2-methacryloyloxyethyl) trimethyl ammonium chloride with $\text{Al}(\text{OH})_3$ colloid. The optimal preparation conditions were obtained as follows: when the amount of AlCl_3 was fixed at 5 mmol, the polymerization time, polymerization temperature, $n(\text{AM}) : n(\text{AlCl}_3)$, $n(\text{DMC}) : n(\text{AlCl}_3)$, and $n(\text{KPS}) : n(\text{AM})$ were 4 h, 70°C, 8, 0.9, and 1.82×10^{-3} , respectively. When CAPAM, CPAM, and PAS were used for solid–liquid separation in waste drilling fluid, the results indicated that CAPAM had better flocculation properties than CPAM and PAS. CAPAM also had good solid–liquid separation efficiency at high temperatures and in alkaline environment for the waste drilling fluid.

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