

1 **Novel Rosin-based Hydrophobically Modified Cationic Polyacrylamide for Kaolin**
2 **Suspension Flocculation**

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13 **ABSTRACT:** A novel hydrophobically modified cationic polyacrylamide (HMPAM) was synthesized
14 via copolymerization of acrylamide (AM), diallyl dimethyl ammonium chloride (DMAAC), and
15 diallylmethyl dehydroabiatic acid propyl ester ammonium bromide (DMDHAE). **Optimum**
16 **conditions for preparing HMPAM were such that the amount of initiator was 0.075 wt % of the total**
17 **monomer mass, the monomer concentration was 20 wt %, and the amount of DMAAC was 18**
18 **mol % of the total monomer molar mass.** HMPAM was characterized using a UV-Vis spectrometer,
19 ¹H NMR, Ubbelohde viscometer, rotational viscometer, and rotational rheometer. HMPAM
20 solutions exhibited strong hydrophobic associations, and the critical association concentration
21 (CAC) of the HMPAM aqueous solution was about 0.7 wt %; HMPAM solutions also showed salt
22 thickening and shear resistance. Surface morphology of freeze-dried HMPAM samples (1 wt %) was also observed via scanning electron microscopy (SEM). Compared with unmodified cationic polyacrylamide (CPAM), HMPAM-0.5 exhibited a stronger flocculation capacity, and the optimal transmittance of the supernatants was above 95 %. HMPAM-0.5 had a significant flocculation performance for 3 - 4 wt % and 3 - 5 wt % kaolin suspensions at 40 mg/L and 50 mg/L, respectively. Moreover, flocculation performance was enhanced with the addition of NaCl and CaCl₂.

1 INTRODUCTION

2 With industrial and economic developments, water pollution has become an important
3 factor that threatens human survival. One of the serious problems in wastewater treatment is
4 purification of high solid content wastewater, which is caused by soil erosion, agriculture,
5 mining, papermaking, and industrial activities.¹⁻³ To solve this issue, many technologies
6 have been developed, such as coagulation, precipitation, flocculation, membrane filtration,
7 and adsorption.^{4, 5} In particular, flocculation is regarded as one of the most common and
8 important purification techniques used in wastewater treatment because of its low cost and
9 high efficiency.^{6, 7}

10 The most critical issue of flocculation is choosing a suitable flocculant for promoting the
11 agglomeration of suspended particles in larger flocs for separation from wastewater.^{6, 8}
12 Flocculants used in wastewater treatment are mainly inorganic coagulants, such as
13 polyaluminum chloride and ferric chloride.^{9, 10} However, it has been shown that there are
14 numerous disadvantages to using inorganic coagulants in wastewater treatment. Inorganic
15 coagulants are sensitive to pH and a large amount is needed for high efficiency in the
16 flocculation process.¹⁰ Moreover, using inorganic coagulants produces large volumes of
17 metal hydroxide sludge and increases metal ions (Al^{3+}) in water, which may lead to
18 Alzheimer's disease.^{12, 13}

19 To reduce the use of inorganic flocculants, polymers have been used as flocculants to
20 enhance flocculation performance. In general, polymeric flocculants are water-soluble
21 polymers, such as polyacrylic acid, cationic polyacrylamide (CPAM), and anionic
22 polyacrylamide (APAM).¹⁴ CPAM is a polymer extensively used as a flocculant because of
23 its high efficiency, even when used in small quantities, and can be prepared with different
24 molecular weights, positive charge densities, and structures. The flocculation mechanism
25 with CPAM as a flocculant can be explained with a bridging mechanism, a charge
26 neutralization mechanism, and a patching mechanism; of these, the charge neutralization
27 mechanism plays the most important role.^{15, 16} CPAM with high positive charge density is
28 absorbed on the surface of kaolin particles via charge neutralization, and this results in a

1 decrease in electrostatic repulsion between Kaolin particles, which results in formation of
2 larger flocs. Therefore, CPAM exhibits high flocculation efficiency.

3 Hydrophobically modified cationic polyacrylamide (HMPAM), in which a small amount
4 of hydrophobic monomers (less than 2 mol%) is copolymerized in the polyacrylamide
5 backbone, can improve the rheological properties of its aqueous solution.¹⁷ At high
6 concentration, hydrophobic groups form intermolecular interactions in the aqueous solution
7 via hydrophobic associations of hydrophobic groups, and these produce a transient network
8 to provide a viscosity building capacity.^{18, 19} In the flocculation process, a strong
9 hydrophobic association forms between the flocs via HMPAM intermolecular interactions,
10 charge neutralization, and bridging absorption to improve flocculation performance.²⁰⁻²²

11 Rosin (90% rosin acids and 10% neutral compounds) is an abundantly renewable resource
12 extracted from various species of pine, and production of rosin is more than 1 million tons
13 per year.^{23, 24} Rosin acids with hydrophenanthrene structures provide cycloaliphatic and
14 aromatic structures, which given rosin and its derivatives excellent hydrophobicity.²³⁻²⁵ In
15 general, rosin-based derivatives, such as epoxy resin, cured oil-based resin, and polyamide,
16 are advantageous for improving the glass transition temperature and mechanical properties
17 of polymers.^{25, 26} However, rosin-based derivatives used in water-soluble CPAM to improve
18 their flocculation properties have rarely been reported. If rosin structures that have renowned
19 hydrophobicity are incorporated into the CPAM molecular chain, strong hydrophobic
20 associations can form between the polymer molecules. HMPAM on the surface of the flocs
21 can form larger flocs via hydrophobic associations, and thus the flocculation efficiency of
22 the polymer can be improved.

23 In this work, HMPAM flocculant was prepared via free radical copolymerization of AM,
24 DMDAAC, and DMDHAE. Effects of initiator dosage, monomer molar ratios, and monomer
25 concentrations on intrinsic viscosity were investigated. Rheological properties of HMPAM
26 were evaluated using a rotational viscometer and rotational rheometer. HMPAM solutions
27 exhibited shear resistance, salt thickening, and hydrophobic associations when the
28 concentration of HMPAM was greater than that of CAC. In the flocculation processes,
29 effects of flocculant dosage, pH, salt concentration, and initial concentration of kaolin
30 suspension on flocculation performance were investigated. HMPAM exhibited a more

1 effective flocculation performance than CPAM for various concentrations of kaolin
2 suspensions, and flocculation performance was enhanced in the salt solutions. The
3 flocculation mechanism was analyzed simply. **HMPAM had strong hydrophobic**
4 **associations because of the incorporated rosin structure, which improved salt resistance,**
5 **viscosity, and shear resistance of HMPAM. HMPAM shows great potential for application in**
6 **thickeners, rheology modifiers, and water-based coatings.**

7 **EXPERIMENTAL**

8 **Materials**

9 Dehydroabiatic acid (DHA, ~90 wt %) was purchased from Wuzhou Chemical Company
10 (Wuzhou, China); oxalyl chloride (98 wt%), 3-bromopropan-1-ol (97 wt%),
11 methyldiallylamine (98 wt%), and acrylamide (AM 99 wt%) were purchased from Energy
12 Chemical Co., Ltd. (Shanghai, China); diallyl dimethyl ammonium chloride solution
13 (DMDAAC, 60 wt% aqueous solution), triethylamine (TEA, 99 wt%), and 2,2'-azobis(2-
14 methylpropionamide) dihydrochloride (V-50, 97 wt%) were produced by Aladdin Reagent
15 Co., Ltd. (Shanghai, China); sodium chloride (NaCl, 99.9 wt%), calcium chloride (CaCl₂,
16 99 wt %), and kaolin were sourced from Sinopharm Chemical Reagent Co., Ltd. (Shanghai,
17 China). All of the reagents were used without any further purification.

18 **Synthesis of DMDHAE**

19 See supporting information. Synthesis procedures for DMDHAE, ¹H NMR, ¹³C NMR, and
20 MS are described in supporting information.

21 **Synthesis of Hydrophobically Modified Cationic Polyacrylamide (HMPAM)**

22 Certain masses of AM, DMDAAC, and DMDHAE were dissolved in deionized water under
23 an inert nitrogen atmosphere, and then copolymerization was initiated using V-50 at 50 °C
24 for 10 h. After reaction, the copolymers were soaked in ethanol for 24 h to remove unreacted

1 monomer. Finally, the copolymers were dried in a vacuum at 60 °C for 24 h. HMPAM-x
2 denotes hydrophobically modified cationic polyacrylamide where x is the molar ratio of
3 DMDHAE.

4 **Measurements of Intrinsic Viscosity**

5 HMPAM was dissolved in an aqueous NaCl solution with a concentration of 1 mol/L, and
6 the intrinsic viscosities of polymers were measured using an Ubbelohde viscometer at 30 ±
7 0.1 °C.

8 **Measurements of Apparent Viscosity and Rheological Properties**

9 Apparent viscosities of copolymers were measured using a rotational viscometer (NDJ-5S,
10 China) at 25 °C with a shear rate of 6 s⁻¹. Rheological properties of copolymers were
11 measured at 25°C using a rotational rheometer (Haake Mars II, Germany) with a measured
12 geometry (radius of 20mm and gap of 0.10 mm). Shear property measurements were
13 performed with shear rates ranging from 2 to 800 s⁻¹. For dynamic viscoelastic
14 measurements, a constant strain of 1% was applied to conduct a dynamic frequency sweep
15 within the linear region of the solution over an angular frequency range of 0.01 to 10 Hz.
16 Storage modulus (G') and loss modulus (G'') were recorded as functions of frequency to
17 obtain the dynamic mechanical spectra.

18 **Characterization**

19 UV-Vis spectra of DMDHAE and copolymers (at a concentration of 0.5 wt % and with
20 deionized water as solvent) were measured using a UV2450 UV-Vis spectrometer
21 (Shimadzu, Japan). Surface morphology was observed using a 3400NI scanning electron
22 microscope (SEM, Hitachi, Japan). The nuclear magnetic resonance (NMR) spectrum of
23 HMPAM was recorded with a 300 MHz spectrometer (Bruker Company, Germany) at room
24 temperature with deuterioxide.

1 **Flocculation Evaluation**

2 Flocculation tests were carried out according to the method reported in the literature²⁶.
3 Samples (0.1 g) were dissolved in deionized water (100 mL), and the solution was then
4 diluted to different concentrations for tests. Kaolin suspension (3 wt %) was stirred for 15
5 min at 500 rpm using a magnetic stirrer. In the flocculation process, flocculants (10 mL) and
6 kaolin suspension (90 mL) were added in a mixing cylinder that was stoppered. The mixture
7 solution was shaken up and down 10 times. The supernatant (30 mL), which was below the
8 water surface, was then collected after free-settling for 30 min. Transmittance of the
9 supernatant was measured using a UV-Vis spectrophotometer at 600 nm. The time (t) of the
10 kaolin suspension settling at a height of 40 mL was recorded. Therefore, the settlement rate
11 was defined as $40/t$ (mL/s).

12 **Toxicity test**

13 The HeLa cells were cultured in high glucose DMEM (10% fetal bovine serum, 100 U/mL
14 penicillin, 100 μ g/mL streptomycin) at 37 °C in humidified, 5% CO₂ incubator. HeLa cells
15 were seed in T-75 cell culture flask at a density of 1×10^5 cell/mL. After 24 h, the cell culture
16 medium was replaced with fresh medium either without or with HMPAM. The cells were
17 then further cultured for 72 h. The optical density of sample (ODs) and control test (ODc)
18 were measured by microplate reader at 570 nm. Cell survival rate (CSR) defined as follow:

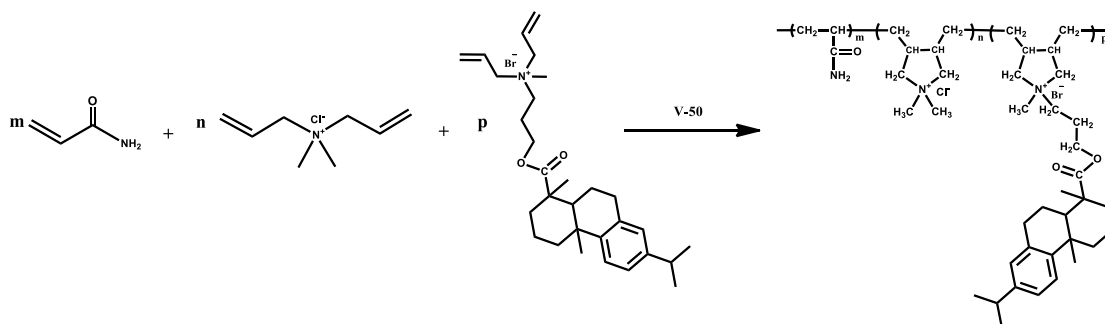
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$$CSR = \frac{ODs}{ODc} \times 100\%$$

20 **RESULTS and DISCUSSION**

21 **Synthesis of HMPAM and Measurements of Solution Properties**

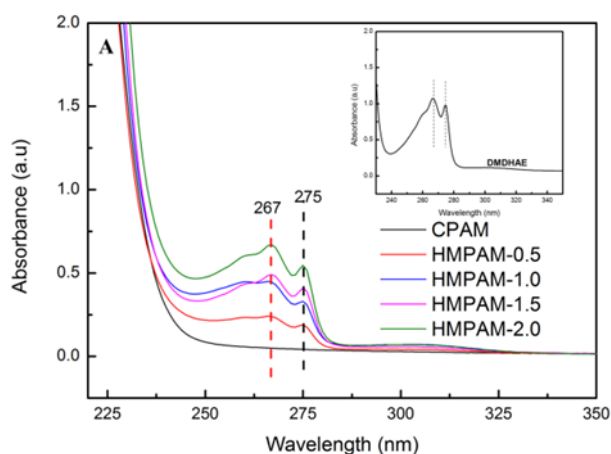
22 **HMPAM Preparation.** HMPAM was prepared via copolymerization of AM, DMDAAC,
23 and DMDHAE in deionized water via free radical polymerization, and the synthesis route of

1 HMPAM is described in Fig.1. Because of the low hydrophobic content, UV spectroscopy,
 2 which has higher sensitivity, was suitable for determining the composition of HMPAM. UV-
 3 vis spectra for HMPAM and DMDHAE are shown in Fig.2A. Absorption peaks at 267 nm
 4 and 275 nm in the spectrum for DMDHAE are attributed to the aromatic ring structure of
 5 DMDHAE. Compared with the spectrum for CPAM, these characteristic peaks for the
 6 aromatic ring (at 267 nm and 275 nm) appear in the spectrum for HMPAM (Fig.2B).
 7 Moreover, the intensity of the absorption peak increased with an increase in the amount of
 8 DMDHAE. The chemical shift at 1.3 – 1.8 ppm in the ^1H NMR spectrum of HMPAM
 9 (Fig.2B) was assigned to the protons of $-\text{CH}_2$ in the polymer chain. The peaks at 1.9 – 2.5
 10 ppm were attributed to the protons of $-\text{CH}$. The protons of N^+-CH_3 and N^+-CH_2 in
 11 DMDAAC and DMDHAE appeared at 3.3 – 3.7 ppm. The proton signals of the aromatic
 12 ring were observed at 6.8 – 7.9 ppm. These results clearly suggest that DMDHAE was
 13 successfully copolymerized in the HMPAM copolymer structure.



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Fig.1. The synthesis route of HMPAM



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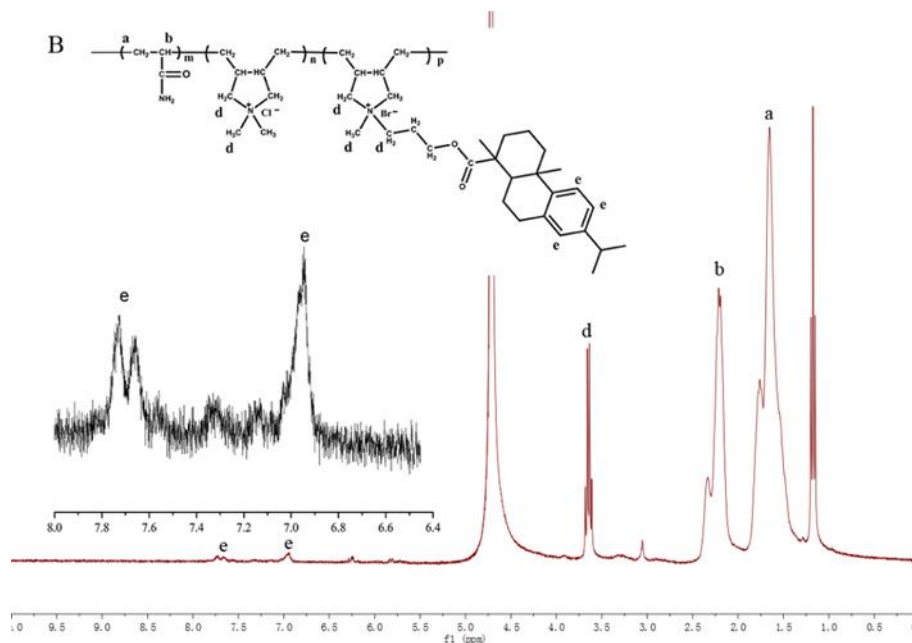


Fig.2. UV-vis spectra (A) and ^1H NMR spectrum (B) of HMPAM

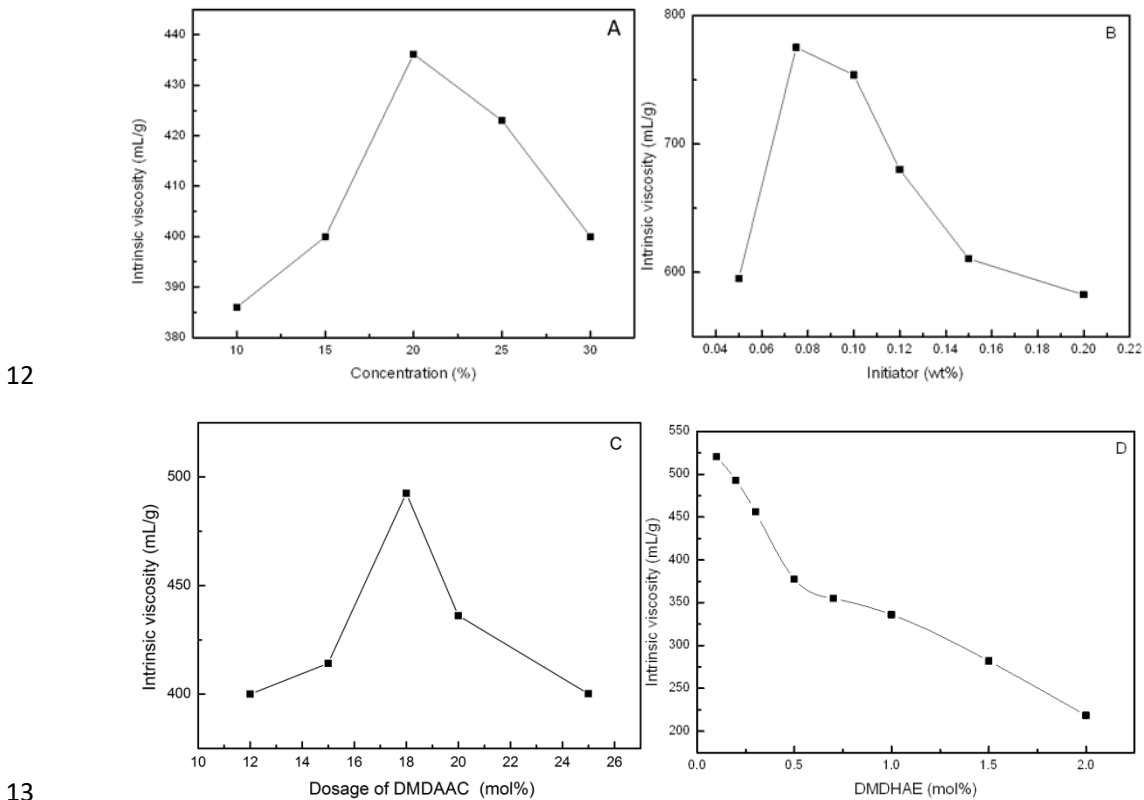
Optimization of the Synthesis Conditions.

The molecular weight of polyacrylamide is commonly determined via the intrinsic viscosity method. At extremely low concentration, there were no interactions between the polyacrylamide molecules, and hence, intrinsic viscosity of solution represents the molecular weight of polyacrylamide.

Effects of monomer concentrations on intrinsic viscosity are described in Fig.3A. At first, the intrinsic viscosity increased and then decreased with an increase in monomer concentration. Collision frequency of monomer molecules was low and resulted in low molecular weight of polymers. At high monomer concentration, polymerization was fast and released a lot of heat, which led to a decrease in the degree of polymerization. When monomer concentration was 20 wt%, a maximum value of intrinsic viscosity was obtained. Effects of initiator on intrinsic viscosity are shown in Fig.3B. Effects of initiator on intrinsic viscosity show a similar trend as the trend in effects of monomer concentration on intrinsic viscosity. This phenomenon was because the efficiency of the initiator was low due to the “cage effect” at relatively low concentration, and this resulted in low intrinsic viscosity of HMPAM; with an increase in the concentration of the initiator, termination and the chain

1 transfer rate increased, and this resulted in low intrinsic viscosity.²⁷ The optimum amount of
2 initiator was 0.075 wt % of the total monomer mass.

3 As seen in Fig.3C, intrinsic viscosity reached a maximum value when the amount of
4 DMDAAC was 18 mol % of the total monomer molar mass. Effects of DMDHAE on
5 intrinsic viscosity are described in Fig.3D. Intrinsic viscosity of HMPAM decreased with
6 an increase in the molar ratio of DMDHAE. This phenomenon can be explained as follows:
7 on one hand, the induction period and time to reach the maximum temperature increased
8 with an increase in the DMDHAE content, and this led to an increase in the chain transfer
9 rate of acrylamide; on the other hand, DMDHAE, which had a characteristic
10 hydrophenanthrene structure, had large steric hindrance, and this hampered polymerization
11 of active centers and monomers.^{28, 29}

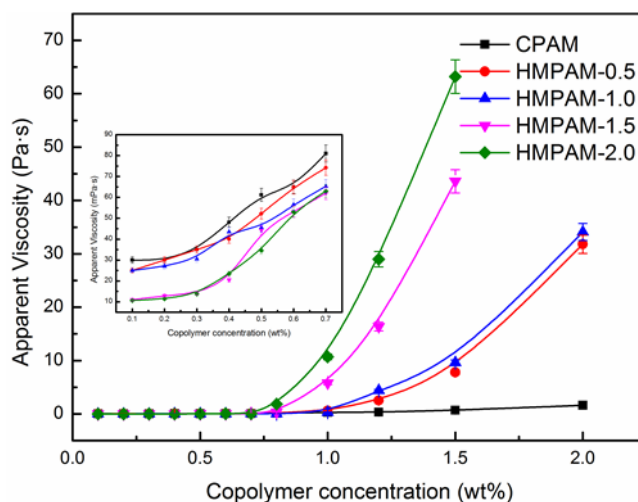


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14 Fig.3. Effects of synthetic factors on intrinsic viscosity: (A) monomer concentration
15 (n(DMDAAC):n(AM) = 20:80 and 0.5 wt% initiator); (B) initiator (n(AM):n(DMDAAC) = 85:15);
16 (C) DMDAAC; (D) DMDHAE (n(AM):(n(DMDAAC) + n(DMDHAE)) = 82:18).

17

1 **Hydrophobic Association Properties of HMPAM.** Fig.4 shows the relationships between
2 apparent viscosity and concentration of polymers. Apparent viscosity increased with an
3 increase in copolymer concentration, but the apparent viscosities of HMPAM were much
4 greater than those of CPAM at high concentrations of polymer. It is clearly observed that the
5 apparent viscosities of HMPAM increased sharply when the concentration of HMPAM
6 exceeded about 0.7 wt %. This indicates that 0.7 wt % (or about 0.7 wt %) was the critical
7 association concentration (CAC) for HMPAM solutions, at which point dominant
8 associations began to change from intramolecular associations to intermolecular
9 associations.³⁰ Transient networks were formed via hydrophobic intermolecular
10 associations, which resulted in high solution viscosity.³¹ Below 0.7 wt%, the apparent
11 viscosity of CPAM was the highest; for HMPAM, apparent viscosities decreased with an
12 increase in DMDHAE dosage. This indicates that molecular weight at low concentration
13 determined the apparent viscosities; for HMPAM, because of intramolecular associations,
14 HMPAM molecules, which had a small hydrodynamic volume, decreased the apparent
15 viscosities of the solutions. Above 0.7 wt%, apparent viscosities increased with an increase
16 in hydrophobic monomer dosage, and this was because of the increase in the degree of
17 hydrophobic associations with an increase in hydrophobic monomer content. Moreover,
18 HMPAM exhibited stronger hydrophobic association properties than HMPAM modified
19 with other hydrophobic side chains (such as fatty alcohol,³² phenyl,^{17, 28} dialkyl,³³ or stearic
20 acid groups³⁴), and this proves that the hydrophenanthrene structure of DMDAAC makes
21 HMPAM more hydrophobic.

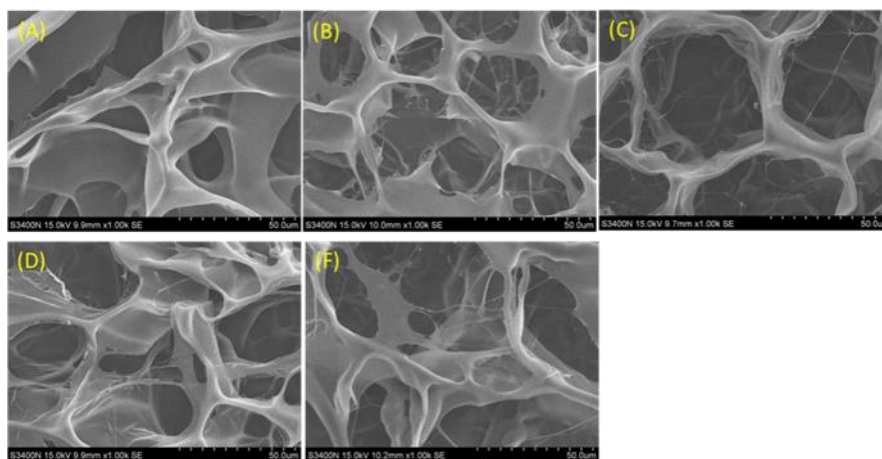
22 SEM images of CPAM and HMPAM are shown in Fig.5. Copolymers (1 wt %
23 concentration) were dissolved in water (above CAC), and then the samples were obtained
24 via freezing and drying. As shown in Fig.5, the micropores of CPAM were irregular and
25 appeared to be “smooth”, but HMPAM appeared to be more regular and some of the
26 filaments were like “spider silk” stuck to the micropores. This phenomenon indicates that
27 aggregates of the HMPAM macromolecule formed via hydrophobic association with
28 evaporated water, and this led to formation of a network structure forming in the micropores.



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Fig.4. Apparent viscosity of aqueous solution as a function of copolymer concentration.



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Fig.5. SEM images of CPAM and HMPAM (1 wt %): (A) CPAM, (B) HMPAM-0.5, (C) HMPAM-

5

1.0, (D) HMPAM-1.5, and (F) HMPAM-2.0.

6

Effects of Salt on Apparent Viscosity of HMPAM. Apparent viscosities of HMPAM

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exhibited remarkable salt thickening properties, as shown in Fig.6. Apparent viscosities of

8

CPAM sharply decreased in salt solution, and this is because CPAM macromolecular chains

9

expand in brine solution, which leads to lower hydrodynamic volumes and apparent

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viscosities.^{32, 34} However, apparent viscosities of HMPAM dramatically increased with an

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increase in the concentration of NaCl or CaCl₂. There are two reasons for this phenomenon:

12

(1) polarity of the solution increased in salt solution, which reinforced intermolecular

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hydrophobic associations, and (2) hydrophobic moieties of HMPAM had low solubility in

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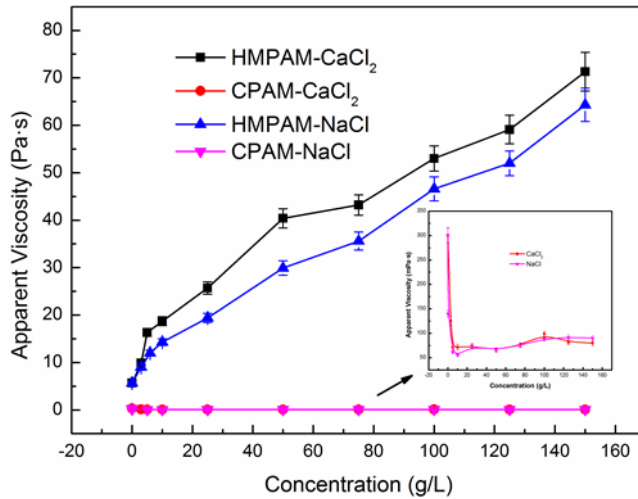
salt solution, which resulted in an increase in the degree of hydrophobic associations.^{35, 36}

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Because the polarity of CaCl₂ solution is stronger than that of NaCl solution, the apparent

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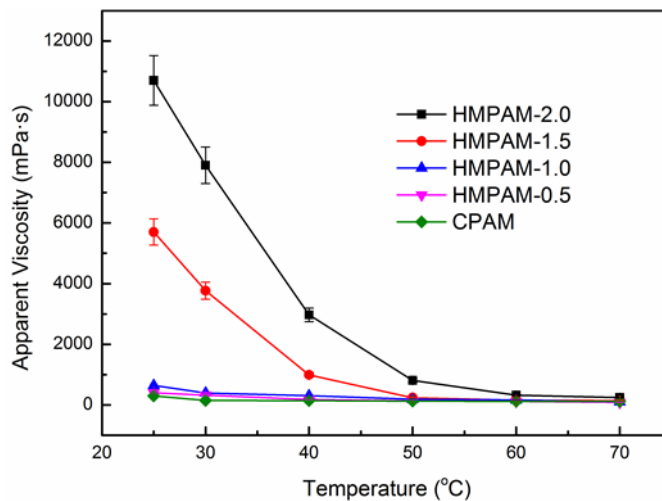
viscosities of HMPAM in CaCl₂ solutions are higher than those in NaCl solutions.



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Fig.6. Apparent viscosities of HAPAM solution with different NaCl or CaCl₂ concentrations (1 wt % HMPAM-1.5 aqueous solution).

4 **Effects of Temperature on Apparent Viscosity of the HMPAM Solution.** Effects of
5 temperature on the apparent viscosity of HMPAM solution are shown in Fig. 7. With an
6 increase in temperature, the apparent viscosity of HMPAM dramatically decreased, and the
7 lower reduced rates increased with an increase in DMDHAE contents. These results are
8 attributed to the destruction of intermolecular hydrophobic associations, and this reduced the
9 degree of the physical crosslinked network with an increase in temperature, which resulted
10 in low apparent viscosities.



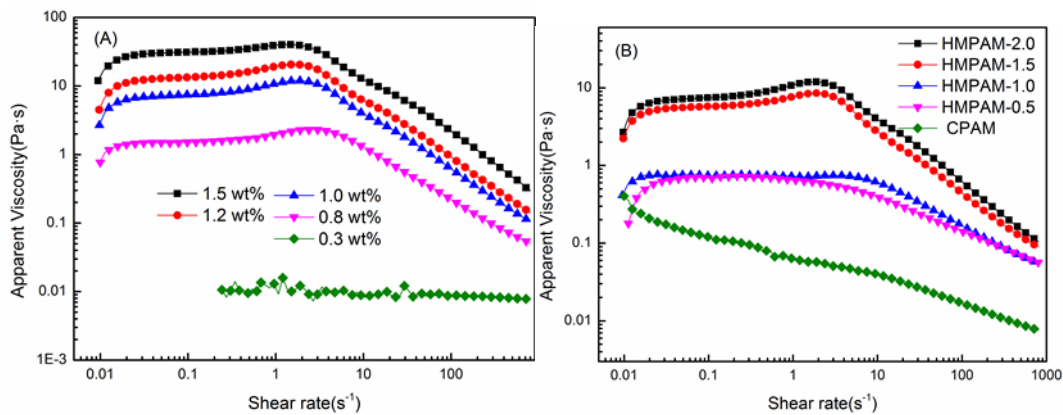
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Fig.7. Effects of temperature on apparent viscosity of HMPAM solution (1 wt %).

13 **Shear Resistance of HMPAM Solutions.** Effects of HMPAM solution concentrations on
14 shear properties of HMPAM-2.0 are shown in Fig.8A. For 0.8 wt%, 1.0 wt%, 1.2 wt%, and

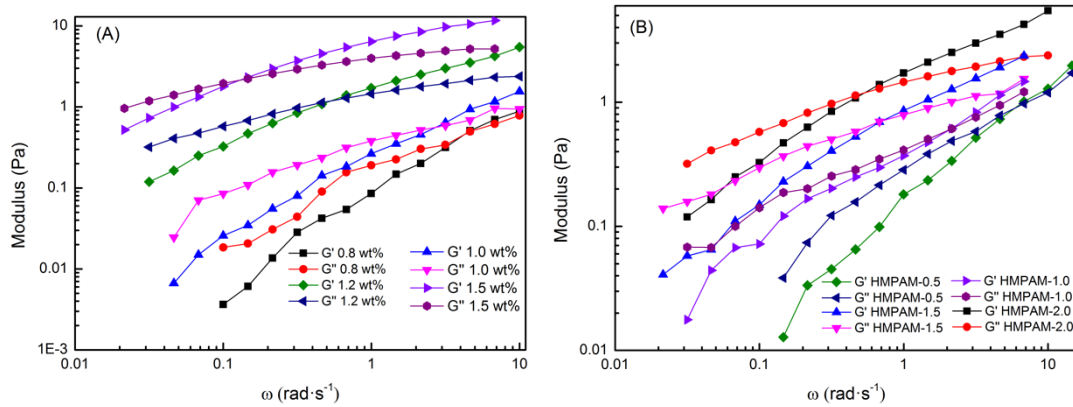
1 1.5 wt% HMPAM solutions (above CAC), apparent viscosity increased with an increase in
 2 shear rate at low shear rates. However, a sharp decrease in apparent viscosity accompanied
 3 an increase in the shear rate, and HMPAM solutions exhibited significant pseudoplasticity.
 4 The phenomena can be explained as follows: at low shear rates, intramolecular associations
 5 were destroyed, and HMPAM molecules expanded, which enhanced intermolecular
 6 associations; then, with an increase in shear rates, the network that was formed via
 7 intermolecular associations was broken, which resulted in a decrease in apparent viscosity.
 8 For 0.3 wt% HMPAM solution, HMPAM molecules mainly formed intramolecular
 9 associations in aqueous solution, which caused the apparent viscosity to remain almost
 10 constant with an increase in shear rates. Also, apparent viscosity increased with an increase
 11 in the concentration of HMPAM solutions.

12 Effects of DMDHAE dosage on shear properties are shown in Fig.8B. HMPAM solutions
 13 have higher apparent viscosity with an increase in DMDHAE content of HMPAM. With an
 14 increase in the shear rate, the trends in apparent viscosity of the HMPAM solutions were
 15 same as that in Fig.8A. However, apparent viscosity of CPAM solution showed shear
 16 thinning with an increase in the shear rate. This demonstrates that when DMDHAE content
 17 is higher, the physical network in the HMPAM solution is stronger, and this led to an increase
 18 in the shear resistance of HMPAM solutions.



19
 20 Fig.8. (A) Effects of shear rate on apparent viscosity of HMPAM-2.0 solution at different
 21 concentrations. (B) Effects of shear rate on apparent viscosity of HMPAM containing different
 22 amounts of DMDHAE (1.2wt %).

1 **Viscoelastic Property.** Viscoelastic properties of HMPAM solutions were investigated
 2 using oscillatory-shear (frequency sweep) measurements, and the results are shown in Fig.9.
 3 At low frequency, the loss modulus (G'') was higher than the storage modulus (G'), and
 4 hence the solutions exhibited viscous behavior; the elastic behavior was dominant when the
 5 value of G' was greater than the value of G'' with an increase in frequency. Effects of
 6 concentrations on viscoelasticity are shown in Fig.9A. With an increase in HMPAM solution
 7 concentration, the values of G' and G'' increased, and the crossing point (G'/G'') moved to
 8 the left. As shown in Fig.9B, effects of DMDHAE content on the crossing point (G'/G'') and
 9 the values of G' and G'' were that same as the trends for effects of HMPAM solution
 10 concentrations on the crossing point (G'/G'') and the values of G' and G'' . These indicate that
 11 hydrophobic association were improved with an increase in the concentration of solutions
 12 and an increase in the content of hydrophobic monomers. When the hydrophobic
 13 associations in HMPAM solutions were stronger, the frequency at which the solutions
 14 changed from viscous behavior to elastic behavior was lower.



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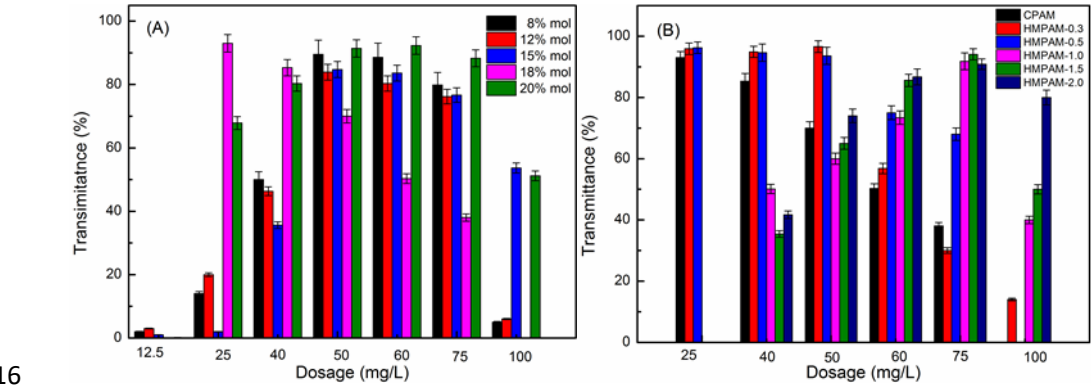
16 Fig.9. (A) Effects of HMPAM-2.0 concentrations on viscoelasticity. (B) Effects of DMDHAE
 17 contents on viscoelasticity (1.2 wt %).

18 Flocculation Performance

19 **Effects of Monomer Mole ratio on Flocculation.** As illustrated in Fig.10 (A), transmittance
 20 of the supernatant initially increased and then decreased with an increase in DMDAAC
 21 content, and the value of transmittance reached a maximum when DMDAAC content was

1 18 mol%. This phenomenon occurred because of the following reasons. At low dosages, low
 2 densities of positive charges were insufficient for neutralizing the negative charges of kaolin
 3 particles¹. With excess flocculants, the surfaces of kaolin particles interacted with the
 4 positive charges of the flocculants, and this resulted in electrostatic repulsion between kaolin
 5 particles, thus decreasing the transmittance of the supernatant³⁷. The values of maximum
 6 transmittance were 89.5 %, 83.9 %, 85.3 %, 93.77 %, and 91.4 %, when the DMDAAC
 7 contents in CPAM were 8 mol %, 12 mol %, 15 mol %, 18 mol %, and 20 mol %,
 8 respectively.

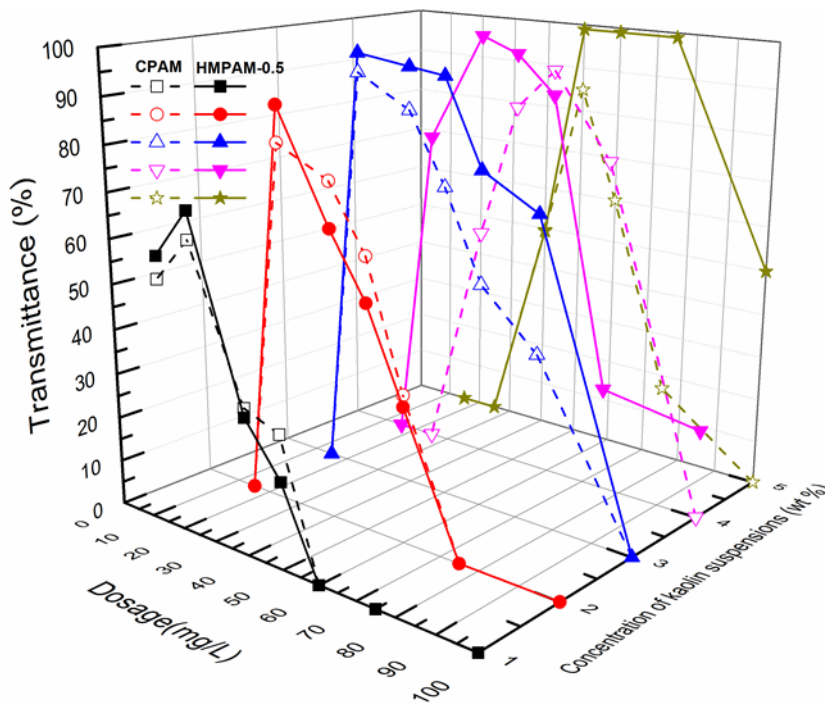
9 Effects of hydrophobic monomer contents on flocculation are shown in Fig.10 (B). With an
 10 increase in HMPAM dosage, transmittance of the supernatant shows a similar trend with an
 11 increase in the CPAM dosage. Compared with CPAM, HMPAM-0.3 and HMPAM-0.5
 12 exhibit effective flocculation properties over a wide concentration range of 25 – 50 mg/L.
 13 The optimal dosages of HMPAM-1.0, HMPAM-1.5 and HMPAM-2.0 increased because of
 14 the lower intrinsic viscosities of HMPAM with high hydrophobic monomer contents. The
 15 optimal dosages of HMPAM-1.0, HMPAM-1.5, and HMPAM-2.0 are each 75 mg/L.



16
 17 Fig.10. Effects of DMDAAC contents (A) and DMDHAE contents (B) on flocculation.

18 **Effects of Initial Concentration of Kaolin Suspension on Flocculation.** Effects of
 19 initial concentration of kaolin suspension (1 – 5 wt %) on flocculation are illustrated in
 20 Fig.11. Compared with the flocculation property of CPAM, HMPAM-0.5 had a higher
 21 flocculation capacity. The optimal dosage of CPAM was only effective for a specific
 22 concentration of kaolin suspension. The optimal dosages of CPAM were 25 mg/L, 25 mg/L,
 23 25 mg/L, 40 mg/L, and 50 mg/L for 1 wt %, 2 wt %, 3 wt %, 4 wt % and 5 wt %

1 concentrations of kaolin suspension, respectively. A wide concentration range of HMPAM-
 2 0.5 was sufficient for 3 – 5 wt % kaolin suspension, and the optimal transmittances of the
 3 supernatants were above 95 %. The optimal HMPAM concentration ranges for 3 wt %, 4 wt
 4 %, and 5 wt % kaolin suspension were 25 – 50 mg/L, 40 – 50 mg/L, and 50 – 75 mg/L,
 5 respectively. Transmittance of the supernatants can reach 99 % when the initial
 6 concentration of kaolin suspension was 5 wt %. Moreover, it was clear that 40 mg/L and 50
 7 mg/L HMPAM-0.5 showed significant flocculation for 3 – 4 wt% and 3 – 5 wt% kaolin
 8 suspension, respectively. The possible reason for this may be the formation and destruction
 9 of hydrophobic associations between HMPAM molecules in the kaolin suspensions with
 10 various concentrations.

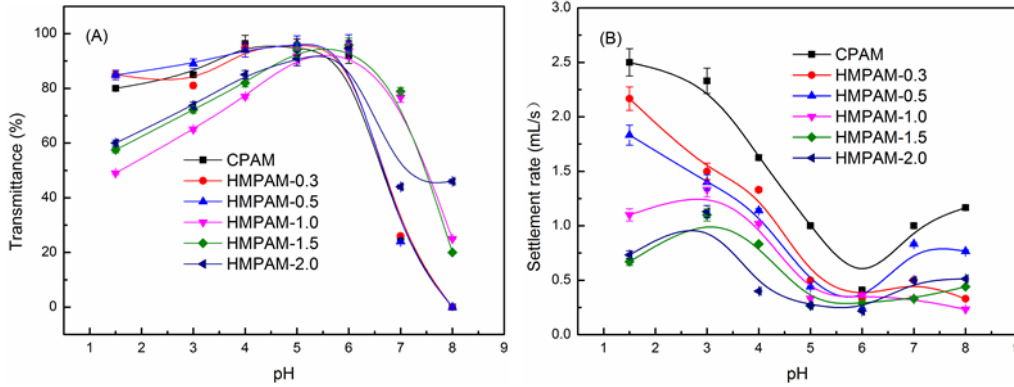


11

12 Fig.11 Effects of initial concentration of kaolin suspension (1 – 5 wt %) on flocculation

13 **Effects of pH on Flocculation and Settlement Rate.** Effects of pH on flocculation and
 14 settlement rates were investigated, and the results are shown in Fig.12. As seen in Fig.12
 15 (A), transmittance of the supernatant initially increased, and then decreased with an increase
 16 in pH; this is because the positive charges of the flocculants are neutralized by OH⁻ in
 17 alkaline conditions³⁸. Optimal pH values were 4 – 6 for CPAM, HMPAM-0.3, and
 18 HMPAM-0.5 and 5 – 6 for HMPAM-1.0, HMPAM-1.5, and HMPAM-2.0. As seen in
 19 Fig.12 (B), settlement rates initially decreased and then increased with an increase in pH,

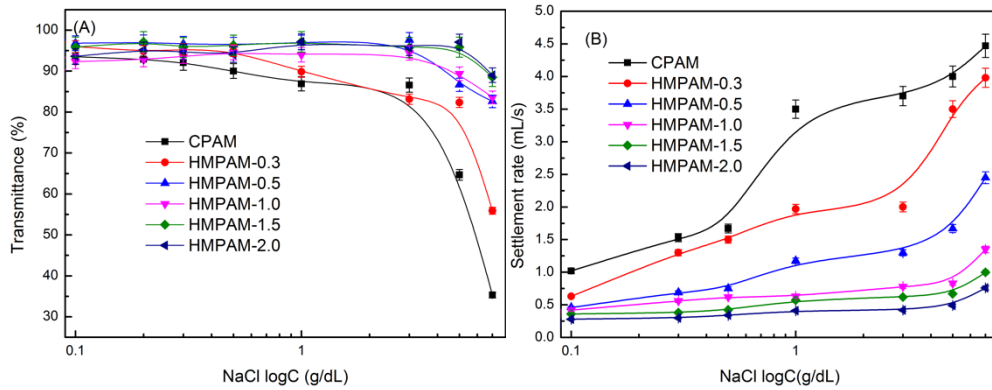
1 reaching a minimum value at pH = 6. With an increase in DMDHAE contents, the
2 settlement rates of flocculants also decreased, and this is because copolymer with high
3 intrinsic viscosity tends to form larger flocs that settle.³⁷



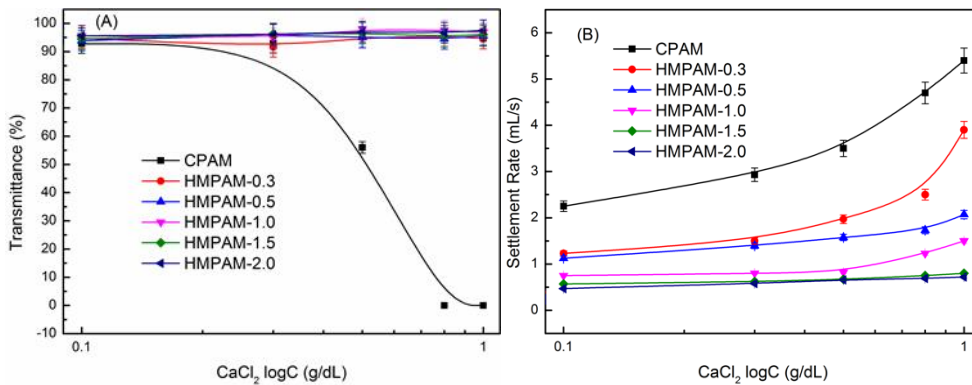
4
5 Fig.12. Effects of pH on flocculation (A) and settlement rate (B). Concentrations of CPAM,
6 HMPAM-0.3, and HMPAM-0.5 were each 25 mg/L, and concentrations of HMPAM-1.0,
7 HMPAM-1.5 and HMPAM-2.0 were each 75 mg/L.

8 **Effects of Salts on Flocculation and Settlement Rate.** Effects of NaCl on flocculation and
9 settlement rates are shown in Fig.13. As illustrated in Fig.13 (A), transmittance of the
10 supernatant sharply decreased with an increase in the concentration of NaCl solution when
11 CPAM was used as the flocculant, and this was because electrostatic repulsion increased in
12 NaCl solution, which led to low flocculation. When the DMDHAE contents were above 0.5
13 mol%, HMPAM exhibited excellent flocculation in NaCl solution, and transmittance of the
14 supernatants was higher than 95 %. Polarity of the kaolin suspension increased with an
15 increase in the concentration of NaCl solution, and this enhanced hydrophobic associations
16 of HMPAM molecules, which formed larger flocs.²¹ Thereby, flocculation efficiency was
17 improved. When the concentration of NaCl was too high, electrostatic repulsion increased,
18 which resulted in decreased flocculation. As shown in Fig.13 (B), settlement rates of all of
19 the copolymers increased with the addition of NaCl. The combination of kaolin particles and
20 HMPAM molecules was promoted to form larger flocs because of an increase in charge
21 density. Effects of CaCl₂ (< 1 wt%) on flocculation and settlement rates are shown in Fig.
22 14. Because of the higher polarity, the flocculation of CPAM sharply decreased, and

1 HMPAM showed better flocculation. These results indicate that HMPAM was suitable for
 2 flocculation in salt solutions.



3
 4 Fig.13. Effects of NaCl on flocculation (A) and settlement rate (B). Concentrations of CPAM,
 5 HMPAM-0.3, and HMPAM-0.5 were each 25 mg/L; concentrations of HMPAM-1.0, HMPAM-
 6 1.5 and HMPAM-2.0 were each 75 mg/L.



7
 8 Fig.14. Effects of CaCl₂ on flocculation (A) and settlement rate (B). Concentrations of CPAM,
 9 HMPAM-0.3, and HMPAM-0.5 were each 25 mg/L; concentrations of HMPAM-1.0, HMPAM-
 10 1.5, and HMPAM-2.0 were each 75 mg/L.

11 **Toxicity Test.** The results of toxicity test were carried out as shown in table 1 and Fig.s5. The cells
 12 incubated with HMPAM retained the same phenotypical morphology as the control cells. More-
 13 over, cells cultured with HMPAM at concentrations as high as 500 mg/L in 48 h, and the CSR is
 14 about 100%. It demonstrated that toxicity of HMPAM was considered to be negligible.

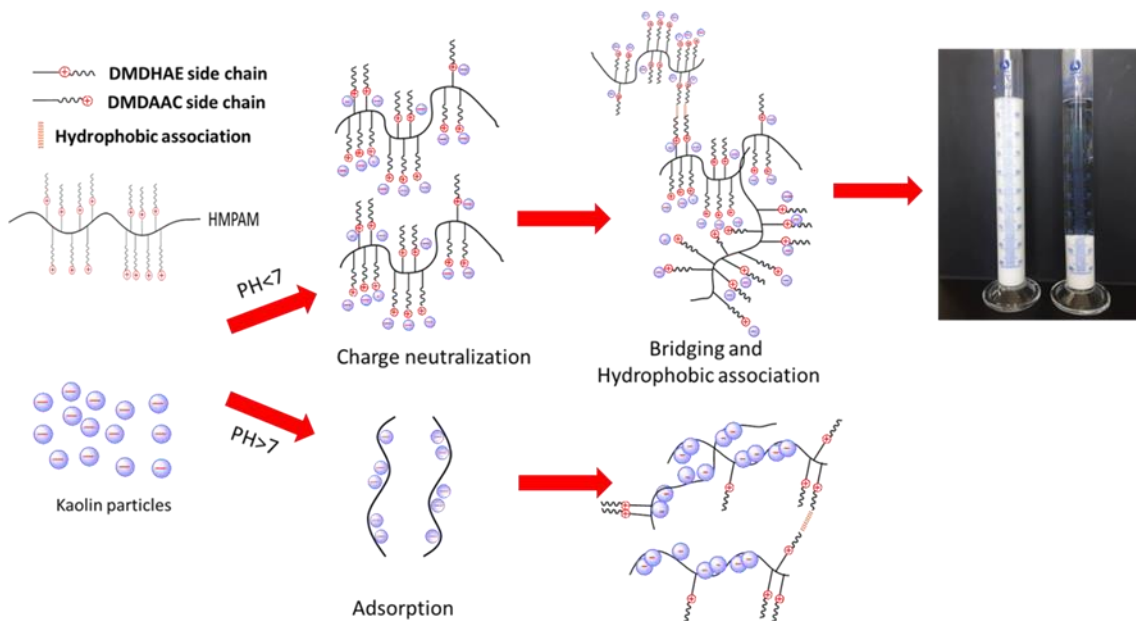
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Table 1 the CSR of HMPM

	CSR/%		
	500 mg/L	50 mg/L	5 mg/L
CPAM	100.4	99.85	100.3
HMPAM-0.5	101.25	100.8	101.9
HMPAM-1.0	99.8	102.45	100
HMPAM-1.5	99.1	102.2	100.8
HMPAM-2.0	96.05	100.1	102.2
control test	99.45	99.8	102.8

2 **Flocculation Mechanism.** A possible flocculation mechanism of kaolin suspension with
3 HMPAM is described in Fig.15. In acidic solution, HMPAM, which had positive charges,
4 reduced the surface charges of kaolin particles though charge neutralization and generation
5 of numerous microflocs in water. Furthermore, these particles aggregated via regional static
6 electricity and formed long molecular chains of HMPAM via bridging effects and hydrophobic
7 associations to form larger flocs.³⁹ However, in an alkaline environment, OH⁻ neutralized
8 the positive charges of flocculants and charge neutralization exhibited an auxiliary role.
9 Kaolin particles are mainly adsorbed on the surfaces of flocculants via van der Waals forces,
10 which resulted in looser and lighter flocs that formed via bridging effects and hydrophobic
11 associations during the agglomeration period.



12

13

Fig.15 Possible flocculation mechanism of kaolin suspension with HMPAM

1 **CONCLUSIONS**

2 In this study, a novel rosin-based hydrophobically modified cationic polyacrylamide
3 (HMPAM) was evaluated and compared with CPAM. HMPAM had strong hydrophobic
4 associations because of the rosin structure introduced in HMPAM, and the CAC was about
5 0.7 wt%. HMPAM exhibited excellent properties in terms of positive salinity thickening,
6 shear resistance, and thickening. In the flocculation progress, HMPAM exhibited a
7 flocculation capacity that was superior to that of CPAM and had a wider concentration range
8 of flocculant than that of CPAM. HMPAM had excellent flocculation performance in salt
9 solution; HMPAM-0.5 also showed a significant flocculation performance for 3 – 5 wt%
10 concentration of kaolin suspensions.

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16 **.REFERENCES**

- 17 1. Ma, J.; Shi, J.; Ding, H.; Zhu, G.; Fu, K.; Fu, X., *Chemical Engineering Journal* 2017, 312, 20.
18 2. Lahtela, V.; Mustonen, K.; Kärki, T. *Industrial Crops and Products* 2017, 104, 129.
19 3. Lal K, Garg A. *Separation Science and Technology*, 2017, 52, 1583.
20 4. Verma, A. K.; Dash, R. R.; Bhunia, P. *Journal of environmental management* 2012, 93, 154.
21 5. Radoiu, M. *Journal of Hazardous Materials* 2004, 106, 27.
22 6. Zheng, H.; Sun, Y.; Guo, J.; Li, F.; Fan, W.; Liao, Y.; Guan, Q. *Industrial & Engineering*
23 *Chemistry Research* 2014, 53, 2572.
24 7. Li, X.; Zheng, H.; Wang, Y.; Sun, Y.; Xu, B.; Zhao, C. *Chemical Engineering Journal* 2017, 319,
25 119.
26 8. Jia, S.; Yang, Z.; Yang, W.; Zhang, T.; Zhang, S.; Yang, X.; Dong, Y.; Wu, J.; Wang, Y. *Chemical*
27 *Engineering Journal* 2016, 283, 495.
28 9. Jiang, J. Q. *Current Opinion in Chemical Engineering* 2015, 8, 36.
29 10. Lee, C. S.; Robinson, J.; Chong, M. F. *Process Safety and Environmental Protection* 2014, 92,
30 489.
31 11. Ma, J.; Fu, K.; Shi, J.; Sun, Y.; Zhang, X.; Ding, L. *Carbohydr Polym.* 2016, 151, 565-575.

- 1 12. Banks, W. A.; Niehoff, M. L.; Drago, D.; Zatta, P. *Brain research* 2006, 1116, 215.
- 2 13. Liu, Z.; Wei, H.; Li, A.; Yang, H. *Water Res.* 2017, 118, 160.
- 3 14. Guan, Q.; Zheng, H.; Zhai, J.; Zhao, C.; Zheng, X.; Tang, X.; Chen, W.; Sun, Y. *Industrial &*
4 *Engineering Chemistry Research* 2014, 53, 5624.
- 5 15. Yu, J.; Wang, D.; Ge, X.; Yan, M.; Yang, M. *Colloids and Surfaces A: Physicochemical and*
6 *Engineering Aspects* 2006, 290, 288.
- 7 16. Zheng, H.; Feng, L.; Gao, B.; Zhou, Y.; Zhang, S.; Xu, B. *Materials* 2017, 10, 487.
- 8 17. Wu, G.; Jiang, X.; Yu, L.; Yan, X. *Polymer Engineering & Science* 2016, 56, 1203.
- 9 18. Jiang, G.; Liu, F. *Journal of Macromolecular Science, Part A* 2013, 50, 1209.
- 10 19. Feng, Y.; Billon, L.; Grassl, B.; Bastiat, G.; Borisov, O.; François, J. *Polymer* 2005, 46, 9283.
- 11 20. Ren, H.; Chen, W.; Zheng, Y.; Luan, Z. *Reactive and Functional Polymers* 2007, 67, 601.
- 12 21. Ren, H.; Li, Y.; Zhang, S.; Wang, J.; Luan, Z. *Colloids and Surfaces A: Physicochemical and*
13 *Engineering Aspects* 2008, 317, 388.
- 14 22. Zhou, Y.; Zheng, H.; Gao, B.; Gu, Y.; Li, X.; Liu, B. *RSC Adv.* 2017, 7, 28733.
- 15 23. Wilbon, P. A.; Chu, F.; Tang, C. *Macromolecular rapid communications* 2013, 34, 8.
- 16 24. Yadav, B. K.; Gidwani, B.; Vyas, A. *Journal of Bioactive and Compatible Polymers* 2015, 31,
17 111.
- 18 25. Ma, Q.; Liu, X.; Zhang, R.; Zhu, J.; Jiang, Y. *Green Chemistry* 2013, 15, 1300.
- 19 26. Liu, X.; Xin, W.; Zhang, J. *Green Chemistry* 2009, 11, 1018.
- 20 27. Shogren, R. L. *Carbohydrate Polymers* 2009, 76, 639.
- 21 28. Xue, W.; Hamley, I. W.; Castelletto, V.; Olmsted, P. D. *Industrial & Engineering Chemistry*
22 *Research* 2014, 53, 11193.
- 23 29. Liao, Y.; Zheng, H.; Qian, L.; Sun, Y.; Dai, L.; Xue, W. *Desalination* 2011, 270, 206.
- 24 30. Lee, K. E.; Morad, N.; Poh, B. T.; Teng, T. T. *Macromolecules* 2008, 41, 2890.
- 25 31. Gao, B.; Guo, H.; Wang, J.; Zhang, Y. *Polymer* 2001, 42, 336.
- 26 32. Ye, Z.; Jiang, J.; Zhang, X.; Chen, H.; Han, L.; Song, J.; Xian, J.; Chen, W. *Journal of Applied*
27 *Polymer Science* 2016, 133, 43195.
- 28 33. Xue, W.; Hamley, I. W.; Castelletto, V.; Olmsted, P. D. *European Polymer Journal* 2004, 40, 47.
- 29 34. Wan, T.; Li, R.; Wu, D.; Hu, Z.; Xu, M.; Cheng, W.; Zou, C. *Polymer Bulletin* 2014, 71, 2819.
- 30 35. Sarsenbekuly, B.; Kang, W.; Fan, H.; Yang, H.; Dai, C.; Zhao, B.; Aidarova, S. B. *Colloids and*

- 1 *Surfaces A: Physicochemical and Engineering Aspects* 2017, 514, 91.
- 2 36. And, X. X.; Hogenesch, T. E. *Macromolecules* 1996, 29, 1734.
- 3 37. Zheng, H.; Sun, Y.; Zhu, C.; Guo, J.; Zhao, C.; Liao, Y.; Guan, Q. *Chemical Engineering Journal*
- 4 2013, 234, 318.
- 5 38. Z. Yang, Z.; Yan, H.; Yang, H.; Li, H.; Li, A.; Cheng, R. *Water Res.* 2013, 47, 3037.
- 6 39. Ma, J.; Fu, K.; Fu, X.; Guan, Q.; Ding, L.; Shi, J.; Zhu, G.; Zhang, X.; Zhang, S.; Jiang, L.
- 7 *Separation and Purification Technology* 2017, 182, 134.