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A NEW POLYMER FLOODING AGENT PREPARED THROUGH INTERMACROMOLECULAR COMPLEXATION

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Key Words: Enhanced oil recovery; Polymer flooding agent; Polymer solution viscosity; Intermacromolecular complexation

ABSTRACT

This paper reports a new polymer flooding agent used for enhanced oil recovery (EOR), poly(acrylamide–acrylic acid) [P(AM–AA)]/poly(acrylamide–dimethyldiallylammonium chloride) [P(AM–DMDAAC)] polyelectrolyte complex. The solution viscosity of prepared P(AM–AA)/P(AM–DMDAAC) complex is enhanced due to the strong interaction between the two oppositely charged copolymers, i.e., P(AM–AA) and P(AM–DMDAAC), which were prepared through radical copolymerization. The ionic content could be controlled by changing the reaction conditions. The structures of the two copolymers were characterized through FT-IR, ^{1}H NMR, and acidic and precipitation titration. The formation as well as the factors affecting the P(AM–AA)/P(AM–DMDAAC) polyelectrolyte complex were investigated by means of viscosity measuring and light transmittance testing. The experimental results show that the composition of the copolymers, the pH value, and the concentration of the polymer solutions have remarkable effects on the formation of P(AM–AA)/P(AM–DMDAAC) polyelectrolyte complex and the solution viscosity. When DMDAAC content in P(AM-DMDAAC) is 3.2 mol%, AA content in P(AM-AA) is 48-58 mol%, the weight ratio of P(AM-AA) to P(AM-DMDAAC) is 70/30-30/70, the pH value of the solution is 6-10, and the concentration of solution is 1000-3500 ppm, then a homogeneous solution of P(AM-AA)/P(AM-DMDAAC) polyelectrolyte complex could be obtained which exhibits a much higher solution viscosity compared with its components.

INTRODUCTION

As an important energy resource and industrial material, petroleum plays a key role in worldwide economic development. With increasing consumption and the huge demand for oil, new techniques for enhanced oil recovery are badly needed.

Oil is usually recovered by injecting water or gas into an oil well, by which the oil recovery rate can be increased to 25-50%. The big problems with water flooding are "fingering" [1] of the ejected water through the mobile fluid front and the higher and higher water-to-oil ratio. These result in difficulties for the efficient recovery of oil. In order to reduce "fingering," water-soluble polymers of high molecular weight are added to the water to increase its viscosity; this is called polymer flooding. In this way, the oil recovery rate can be enhanced by 5-14%. There is no doubt that polymer flooding agents will play a more and more important role in enhanced oil recovery, and they have become an attractive subject to polymer researchers worldwide.

The crucial property of a polymer flooding agent is its ability to hold high viscosity at low polymer concentration under the operating conditions of oil exploration, e.g., high minerality, high temperature, and high shear rate. Great efforts have been devoted for many years to develop effective and cheap polymer flooding agents, e.g. [1-3].

- Developing synthetic polymer flooding agents, such as polyacrylamide (PAM), partially hydrolyzed polyacrylamide (HPAM), and the sodium salt of polyacrylic acid (PAANa). These polymer flooding agents could enhance solution viscosity but are unstable under high shear and minerality.
- Developing biopolymer flooding agents such as Xanhan. They are good for enhancing viscosity and resisting shear and salt, but they are prone to biological degradation and their cost is high.
- Developing new copolymers, such as *N*-substitutes of PAM. By introducing hydrophobic groups onto the polymer chains, the viscosity of the solution and its tolerance to temperature, salt, shear, etc. can be enhanced. The problem with this technology is the difficulty of synthesis and the high price.

As this paper reports, intermacromolecular complexation through Coulomb forces between oppositely charged polymers was employed as a new strategy to prepare a new polymer flooding agent having high viscosity at low concentration. Two copolymers containing either an adjustable anion or cation content, namely poly(acrylamide-acrylic acid) [P(AM-AA)] and poly(acrylamide-dimethyldiallylammonium chloride) [P(AM-DMDAAC)], were prepared through radical copolymerization. The formation of the P(AM–AA)/P(AM–DMDAAC) intermacromolecular complex through Coulomb forces and its solution viscosity were studied.

It is well known that the viscosity of a polymer solution greatly depends on the macromolecular weight, the structure and conformation of a macromolecule in solution, the intermacromolecular interaction, the hydrodynamic volume of a macromolecule, and the concentration. A larger macromolecular weight and hydrodynamic volume, a stronger interaction between macromolecules, and an expanded macromolecular conformation all favor the enhancement of the viscosity of a polymer solution.

Intermacromolecular complexation [4–7] occurring among macromolecules with complementary structures through such secondary forces as Coulomb forces, hydrogen bonding, van der Waals forces, etc. will confine the mobility of polymer chains, resulting in a supermolecular structure different from that of its constituents. Therefore, it may be regarded as an innovative way to tailor the structure and properties of polymer materials. Based on the main interaction forces, intermacromolecular complexes can be divided into four classes: polyelectrolyte complexes, hydrogen-bonding complexes, stereocomplexes, and charge-transfer complexes. The early studies on polyelectrolyte complexes dealt mostly with natural polymers of comparatively low charge density. The first report of complex coacervation with synthetic polyelectrolyte appears to have been that of Fuoss and Sadek [8], who studied mixtures of poly (4-vinyl-*N*-butylpyridinium bromide) with sodium polyacrylate or sodium poly(styrenesulfonate). The system poly(vinylbenzyltrimethylammonium chloride)/sodium poly(styrenesulfonate) was later studied in detail by Michaels and coworkers [9, 10]. Because of the importance of polyelectrolyte complexes in theories and applications, great efforts have been devoted worldwide to this field, and many excellent reviews and books have addressed this issue [4–6, 10–13]. Studies on polyelectrolyte complexes mainly focus on phase separation upon mixing of the oppositely charged polymer solutions, the structure and properties, and applications of the precipitated complexes. The factors affecting polyelectrolyte complexation, such as pH value, concentration, molecular weight, mixing ratio, and ionic strength, are also studied by means of many characterization methods, among which viscosimetry is often used. The general conclusion obtained from viscosimetry is that polyelectrolyte complexation usually results in reduction of solution viscosity due to phase separation [11, 12]. From the viewpoint of applications, a homogeneous solution of polyelectrolyte complexes is needed to make homogeneous membranes, fibers, or coatings from the complexes, so the solubility of polyelectrolyte complexes is also studied. It is a well-established fact that stable soluble polyelectrolyte complexes can be formed under certain conditions, depending on the ionic strength, solvent system, and the composition of the complex [11, 12]. A ternary solvent, an excess of polyanions or polycations, and a high ionic strength favor the formation of soluble polyelectrolyte complexes. It was recently reported [13, 14] that hydrophobically associating water-soluble polymers, another kind of intermacromolecular complexation due to van der Waals forces and hydrophobic interaction, enhances viscosification efficiency because of the larger hydrodynamic size formed by complexation.

Inspired by these interesting discoveries, we report for the first time in this paper that intermacromolecular complexation through Coulomb forces, i.e., polyelectrolyte complexation, may be employed as a new strategy to prepare effective polymer flooding agent because polyelectrolyte complexes have a larger hydrodynamic size than their constituents due to intermacromolecular complexation, and the forces between oppositely charged polymers, i.e., Coulomb forces, are much stronger than the forces between hydrophobically associating water-soluble polymers, i.e., van der Waals forces and hydrophobic interactions, and the good solubility of the polyelectrolyte complexes in water can be reached by controlling the complexation conditions. If a homogeneous solution of intermacromolecular complexed polymers which have oppositely charged groups can be prepared, the viscosity of the solution would be expected to be enhanced [15-17] due to the following reasons:

- Intermacromolecular complexation of two oppositely charged polymers through Coulomb forces will confine the mobility of the polymer chains, resulting in a more expansive conformation of the polymer chains in solution.
- Complexation of the paired polymer chains will enlarge the hydrodynamic volume of the polymer chains.
- Complexation of polymer chains having complementary structures will balance, to a greater or lesser extent, the screening effect of small electrolytes on the polymer electrolyte. That is, intermacromolecular complexation will increase the tolerance of the polymer solution to salts.
- The dynamic network structure formed in an intermacromolecular complex through physical crosslinking among the complementary polymer chains will improve the shear resistance of the polymer solution.

It is evident that the challenging problem involved in the technology of enhancing the solution viscosity by means of intermacromolecular complexation is how to prepare the complexed solution without phase separation. In principle, this can be realized by controlling the ionic content and distribution along the polymer chains as well as the ratio of the two complementary polymers. To this purpose, a series of P(AM-AA) and P(AM-DMDAAC) with different AA or DMDAAC contents were prepared by means of radical copolymerization, while the structure of the two copolymers were characterized through FT-IR, ^{1}H NMR, and acidic and precipitation titration. The formation of a P(AM-AA)/P(AM-DMDAAC) intermacromolecular complex through Coulomb force and its efficiency for enhancing the solution viscosity were identified by means of viscosity measurements and light transmittance testing.

EXPERIMENTAL

Materials

Acrylamide (AM) was purchased and recrystallized with chloroform. Acrylic acid (AA), a product of Beijing Xinguang Chemical Factory (China), was purified by rectification. Dimethyldiallylammonium chloride (DMDAAC), from Beijing Oilfield Chemistry Corporation (China), was used without further purification.

Synthesis of P(AM-AA)

P(AM-AA) copolymers were prepared by radical copolymerization of AM with AA in aqueous solution using potassium persulfate-sodium sulfite as the initiator under a nitrogen atmosphere. The AA content in P(AM-AA) was adjusted by varying the monomer ratio of AM to AA. The copolymers obtained were purified by reprecipitation with ethyl alcohol.

Synthesis of P(AM-DMDAAC)

P(AM-DMDAAC) copolymers were synthesized through the radical copolymerization of AM with DMDAAC in aqueous solution using potassium persulfate-sodium sulfite as the initiator under a nitrogen atmosphere. The DMDAAC content in P(AM-DMDAAC) was controlled by changing the monomer ratio of AM to DMDAAC. The copolymers obtained were purified by reprecipitation with ethyl alcohol.

Preparation of P(AM-AA)/P(AM-DMDAAC) Complex Solution

Polyelectrolyte complex solutions of P(AM-AA) with P(AM-DMDAAC) were prepared by mixing the two copolymer solutions with the same concentration (i.e., 500-4000 ppm) at room temperature.

Characterization

The structure and composition of the P(AM-AA) copolymers were studied by means of FT-IR (Nicolet 20SXB FTIR Spectrometer) and acidic titration (PHS-3D digital pH meter), while that of the P(AM-DMDAAC) copolymers were confirmed through ^{1}H NMR (Varian FT-80A NMR Spectrometer) and precipitation titration.

The viscosity and rheological properties of the solutions were investigated through viscosity measurements on a NDJ-I rotation viscometer (at 6 rpm) and a Haake RV20/CV20N, M10 rotation viscometer at 25°C, respectively. The transmittance of the complex solution was measured at room temperature using a 721-A type spectrophotometer at 580 nm.

RESULTS AND DISCUSSION

Structure and Composition of P(AM-AA)

Figure 1 is the IR spectrum of P(AM-AA). The analytical results of the IR spectrum are listed in Table 1. It can be seen that the typical infrared absorption bands of the $-CONH_2$ group appear at 3490-3400 and 1671 cm^{-1}, and those of the $-COO^-$ group appear at 1561 and 1407 cm^{-1}, indicating that P(AM-AA) copolymer can be easily obtained by the copolymerization of AM with AA under the conditions described in the Experimental Section.

The reactive ratios of AM (1) with AA (2), i.e., r_1 and r_2, are 1.42 and 1.18, respectively [20]. Figure 2 shows that the AA content in P(AM-AA) increases with an increase of the AA monomer concentration. Therefore, one way to adjust the composition of P(AM-AA) is to change the monomer ratio.

Structure and Composition of P(AM-DMDAAC)

Figure 3 is the ^{1}H-NMR spectrum of P(AM-DMDAAC). The analytical results are listed in Table 2. The results confirm that P(AM-DMDAAC) copolymer can be prepared under the conditions described in the Experimental Section.

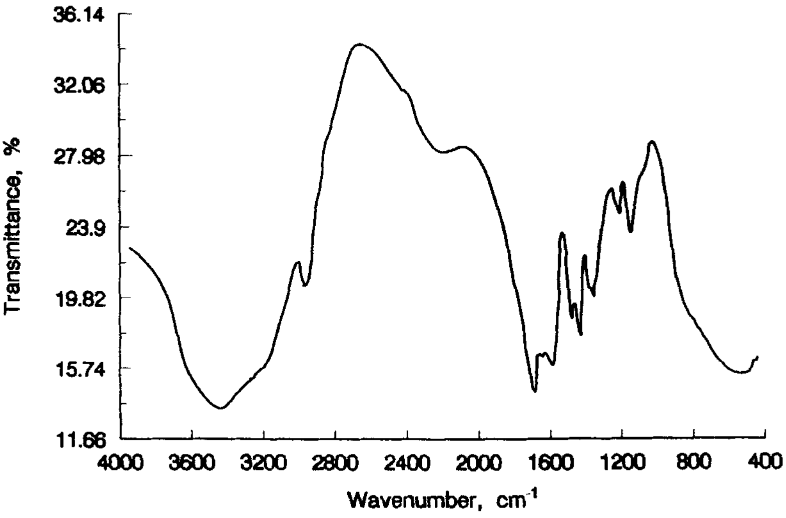


FIG. 1. IR spectrum of P(AM-AA).

Figure 4 shows the effect of monomer ratio on the composition of P(AM-DMDAAC).

Since the reactive ratios of AM (1) with DMDAAC (2), i.e., r_1 and r_2, are 6.7 and 0.58, respectively [21], P(AM-DMDAAC) with a higher DMDAAC content can be prepared by using a higher DMDAAC monomer content.

Complexation of P(AM-AA) with P(AM-DMDAAC) through Coulomb Forces

The formation of the P(AM-AA)/P(AM-DMDAAC) complex was investigated by means of viscosity measurement.

Under the condition of pH 4-10, P(AM-AA) and P(AM-DMDAAC) dissociate into $-COO^-$-containing polyanions and $-\overset{|}{\underset{|}{N^+}}-$-containing polycations in aqueous solution, respectively, resulting in a more expanded conformation of macromolecules because of the increase of intramolecular electrostatic repulsion. Moreover, when those oppositely charged macromolecular ions meet in solution, they

TABLE 1. IR Spectrum of P(AM-AA) [18-20]

Wavenumber, cm^{-1}	Functional group
3490-3400	$-CONH_2$
1671	$-CONH_2$
1561	$-COO^-$
1407	$-COO^-$

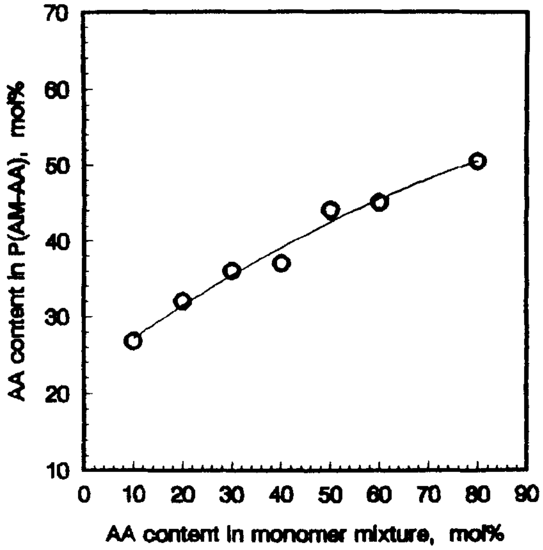


FIG. 2. Effect of monomer mol ratio on the composition of P(AM-AA).

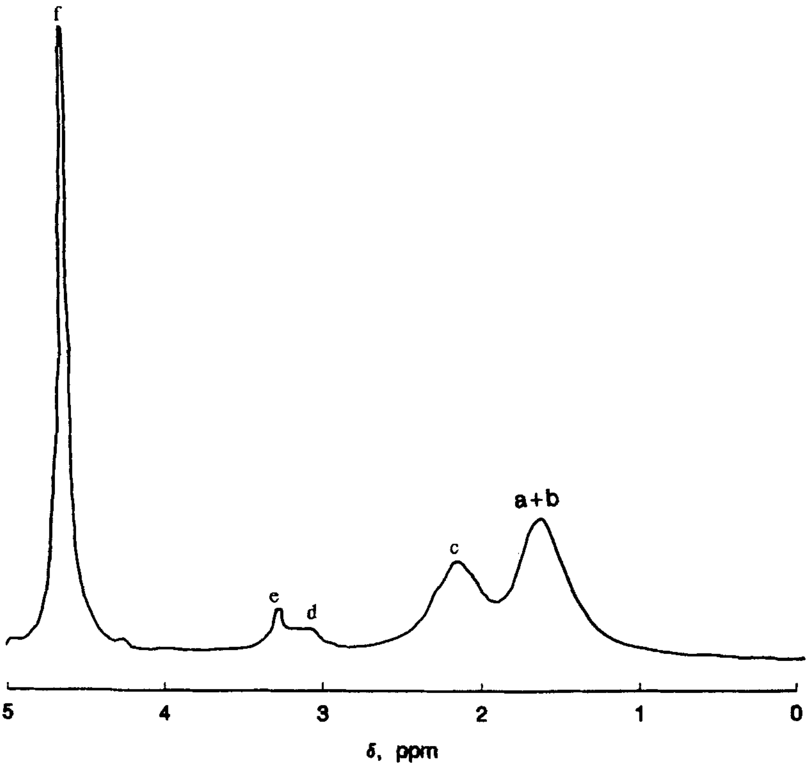
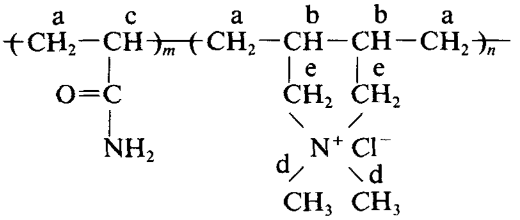


FIG. 3. ^{1}H-NMR spectrum of P(AM-DMDAAC).

TABLE 2. ^{1}H-NMR Spectrum of P(AM-DMDAAC)

Repeat unit	No. of H	δ, ppm
	a + b	1.72
	c	2.22
	d	3.15
	e	3.33
	f, H in DHO	4.7

may combine to form polyelectrolyte complexes through Coulomb forces, producing a larger hydrodynamic volume and an even more expanded conformation compared to the constituents. If, at the same time, there is no phase separation, i.e., there still exists proper hydration, the viscosity of the solution will increase. Thus, a complexed and homogeneous solution of two oppositely charged polymers may result in an increase in the solution viscosity.

Equation (1) [2] demonstrates the blend rule of a two-component solution, where η_1 and η_2 are the viscosity of component solution 1 and component solution 2, respectively; x is the weight ratio of the component solution 1 to the total blend solution of the two components solution; and η_{12} is the viscosity of the blend solution:

$$\lg \eta_{12} = x \lg \eta_1 + (1 - x) \lg \eta_2 \tag{1}$$

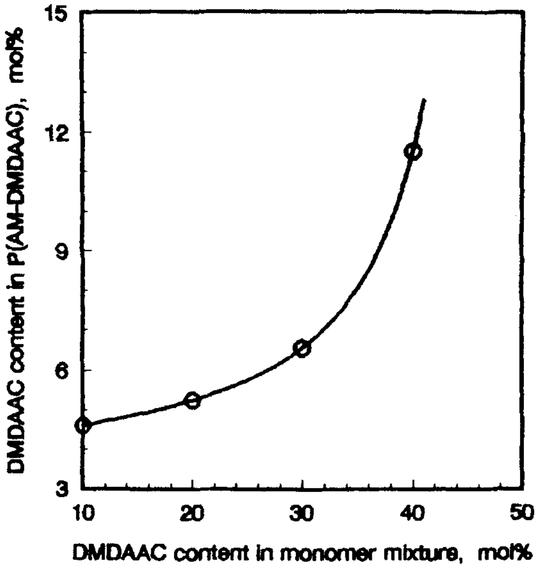


FIG. 4. Effect of monomer mol ratio on the composition of P(AM-DMDAAC).

If the observed viscosity η for the solution of the two components is significantly higher than the calculated viscosity η_{12} according to Eq. (1), the only possible reason is that an intermacromolecular complex has formed and the strong interaction between P(AM-AA) and P(AM-DMDAAC) is responsible for the increase of the solution viscosity.

Figure 5 shows the change of solution viscosity after mixing the P(AM-AA) with P(AM-DMDAAC) solutions at 2000 ppm as well as the viscosity-shear rate relationship of the complex solution and the constituents. It can be seen that the observed viscosity of the P(AM-AA)/P(AM-DMDAAC) complex solution is higher than the calculated viscosity based on Eq. (1) and the viscosity of the constituents, even at a higher shear rate (e.g., 100 s^{-1}), confirming that the interaction between the $-COO^-$ group in the P(AM-AA) chain and the $-\overset{|}{\underset{|}{N^+}}-$ group in the P(AM-DMDAAC) chain through strong Coulomb forces results in association of the P(AM-AA) with P(AM-DMDAAC) chains, as shown in Fig. 6, and enlarges the hydrodynamic volume of the macromolecules, thereby enhancing the viscosity of the solution.

Effect of pH Value on Complexation

Figure 7 shows effect of the solution pH value on the complexation of P(AM-AA) with P(AM-DMDAAC). At a concentration of 2000 ppm, when the pH value of the solution is 5–10, the increase in solution viscosity is remarkable when compared to either a lower pH value (i.e., pH < 5) or a higher pH value (i.e., pH > 12), probably due to the fact that nonequimolar complexation of P(AM-AA) with P(AM-DMDAAC) takes place in the pH 5–10 range, leading to a more expansive

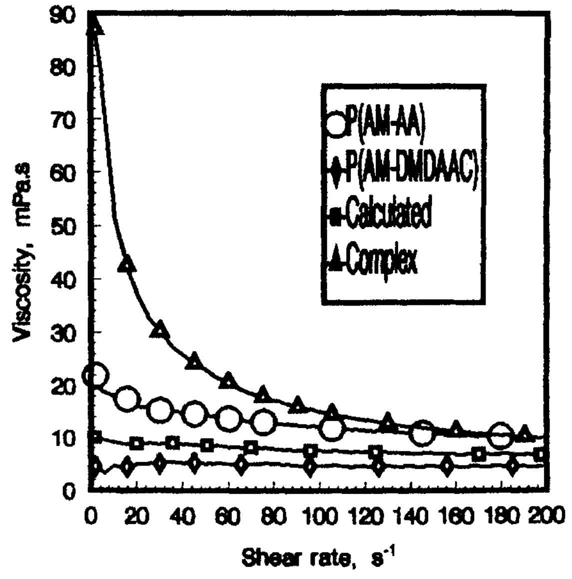


FIG. 5. Dependence of solution viscosity on shear rate.

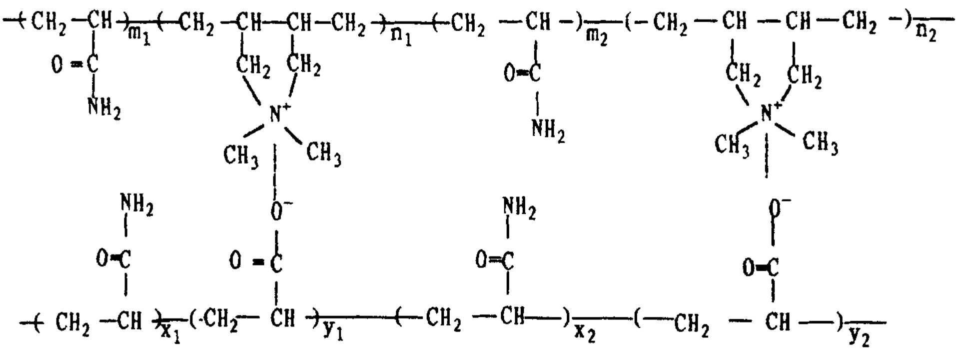


FIG. 6. Association of P(AM-AA) with P(AM-DMDAAC).

conformation. The surplus $-COO^-$ anions in the P(AM-AA) macromolecular chain can interact with the water molecules around them (as shown in Fig. 8), prohibiting phase separation and favoring the increase in solution viscosity.

When the pH value is higher than 12, the viscosity of the complex solution decreases because of the screening effect of excessive Na^+ cations on the dissociation of P(AM-AA) polyelectrolyte, which results in a transition of the polymer chain from expansive conformation to compact comformation. When the pH value is less than 5, on the other hand, dissociation of the P(AM-AA) polyelectrolyte is limited and the electrostatic repulsion of intramolecules is weakened. The lack of the $-COO^-$ group in the P(AM-AA) chain at a low pH value and the possible formation of an equimolar P(AM-AA)/P(AM-DMDAAC) complex may result in precipitation of the complex from the solution, and decrease the solution viscosity.

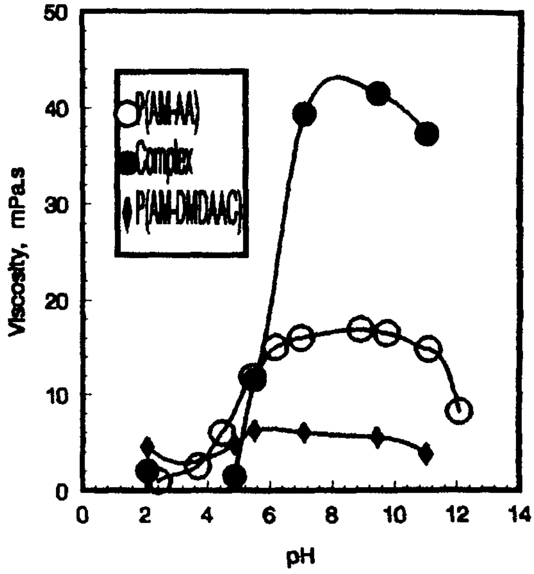


FIG. 7. Effect of pH value on complexation.

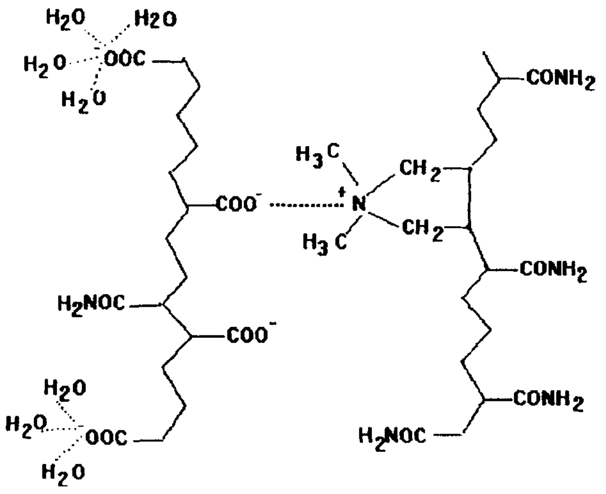


FIG. 8. Hydration of P(AM-AA)/P(AM-DMDAAC) complex.

In conclusion, pH values of the two component polymer solutions have a significant effect on the complexation of P(AM-AA) with P(AM-DMDAAC) through Coulomb forces since the dissociation of the two component polymers into polyions occurs only in a certain pH range, and the dissociation state of the weak polyelectrolyte P(AM-AA) directly affects the complexation ability and the composition of the complex obtained, and hence the solution viscosity.

Effect of Polymer Concentration on Complexation

Figure 9 shows the effect of polymer concentration on the viscosity of the P(AM-AA)/P(AM-DMDAAC) polyelectrolyte complex solution at pH 7. It can be seen that in the polymer concentration range from 1200 to 4000 ppm, the viscosity of the complex solution is much higher than that of the two component polymer solutions and that of the blend solution as calculated from Eq. (1), i.e., increases in complex solution viscosity because of the intermacromolecular complexation of P(AM-AA) with P(AM-DMDAAC) through Coulomb forces are remarkable. At 3000 ppm concentration, for example, the viscosity of the complex solution is about 3 times as high as that of the P(AM-AA) solution and 6 times as high as that of the blend solution. This is an encouraging result for employing the strategy of intermacromolecular complexation to enhance solution viscosity. At lower polymer concentrations the distances between macromolecules are too long (i.e., beyond critical distance ξ) for strong interactions to form among the molecules, and the enhancement in solution viscosity is not obvious [22]. At higher polymer concentrations, on the other hand, the increase of concentration leads to either the suppression of the dissociation of the polyelectrolyte components or the interpenetration of polymer chains, thereby changing the composition and structure of the complex or enhancing the strength of the complexation of the two polymer chains. This may result in phase separation and, therefore, the solution viscosity cannot be increased. Only in the middle concentration range is the strength of interactions between

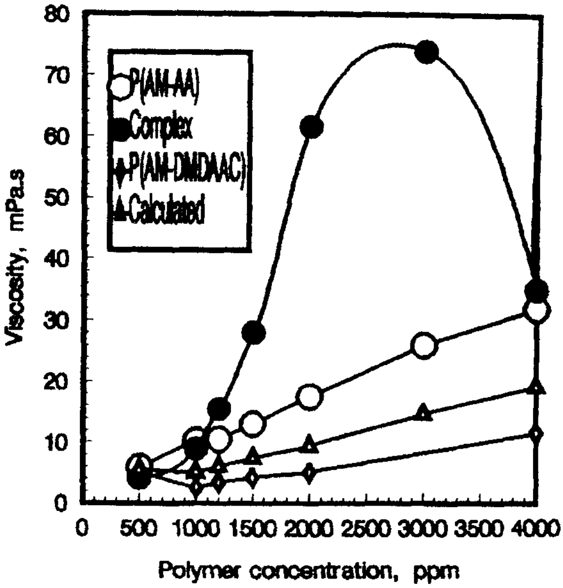


FIG. 9. Effect of polymer concentration on complexation.

macromolecules proper, and there is a remarkable enhancement in solution viscosity.

Effect of AA Content in P(AM-AA) and the Ratio of P(AM-AA) to P(AM-DMDAAC) on Complexation

Table 3 shows that when the AA content in P(AM-AA) is less than 35 mol%, phase separation may occur due to a decrease in hydration, leading to a decrease in solution viscosity. When the AA content in P(AM-AA) is between 48 and 59 mol%, a complexed and homogeneous solution can form, i.e., for the complex solution, not only is the light transmittance 100% but also the observed viscosity is higher

TABLE 3. Effect of AA Content in P(AM-AA) on Complexation

AA content, mol%	Transmittance, %	Observed viscosity η, mPa·s	Theory viscosity η_{12}, mPa·s	η/η_{12}
28.7	Precipitation	–	–	–
35.0	Precipitation	–	–	–
39.9	100	8.0	11.9	0.67
48.4	100	63.5	10.1	6.29
50.7	100	29.0	7.7	3.77
58.7	99.9	10.8	4.6	2.35

than the calculated viscosity. For example, when the AA content is 48.4 mol%, the observed viscosity is 6 times as high as the calculated value.

Table 4 indicates that the P(AM-AA)/P(AM-DMDAAC) solution ratio has an influence on complexation. With a decrease of the P(AM-AA) to P(AM-DMDAAC) ratio, the solution viscosity increases while the transmittance of the solution is unchanged. The maximum of the solution viscosity appears at a 1/1 weight ratio of P(AM-AA) to P(AM-DMDAAC). A further decrease of P(AM-AA) results in precipitation and decreases the transmittance as well as the viscosity of the solution. As mentioned before, the complexation strength of P(AM-AA) with P(AM-DMDAAC) can be adjusted by changing their mixing ratio. When P(AM-AA) polyanions are present in excess, a complexed and homogeneous complex solution is produced because the excessive $-COO^-$ group can interact with water molecules. When an equimolar complex is formed, the possible precipitation of the complex from the solution will reduce the solution viscosity. However, if the presence of polyanions and polycations is nearly equal but with a slight excessive of the former, complexation is much stronger and hydration is retained. Therefore, the complex solution is homogeneous with a transmittance of 100%, and the viscosity is high.

To sum up, in order to obtain a complexed and homogeneous polyelectrolyte complex solution of P(AM-AA)/P(AM-DMDAAC) with a remarkable enhanced solution viscosity, it is necessary to control the macromolecular ionic content of both $-COO^-$-containing polyanions and $-\overset{|}{\underset{|}{N^+}}-$-containing polycations. The phase diagram of the complexation (see Fig. 10) is based on the results listed in both Tables 3 and 4. A complex precipitate forms in Area A due to the too strong complexation, the content of polymers dissolved in the aqueous solution decreases, and hence the solution viscosity decreases. The content of polyanions is much higher than that of polycations in Area C, i.e., there is only weak complexation between these polyions, and increases in the solution viscosity are not obvious. In Area B, not only is the complexation of polyanions with polycations strong, but there are also plenty of polyanions $-COO^-$ to interact with water molecules, enhancing the hydration and, therefore, the solution viscosity.

TABLE 4. Effect of P(AM-AA)/P(AM-DMDAAC) Ratio on Complexation

P(AM-AA)/P(AM-DMDAAC), g/g	Transmittance, %	Observed viscosity η, mPa·s	Theory viscosity η_{12}, mPa·s	η/η_{12}
50/0	100	17.0	17.0	1.0
45/5	100	19.0	15.3	1.2
35/15	100	46.4	12.4	3.7
25/25	100	63.5	10.1	6.3
15/35	91.0	1.5	8.2	0.2
5/45	Precipitation	—	—	—
0/50	99.8	6.0	6.0	1.0

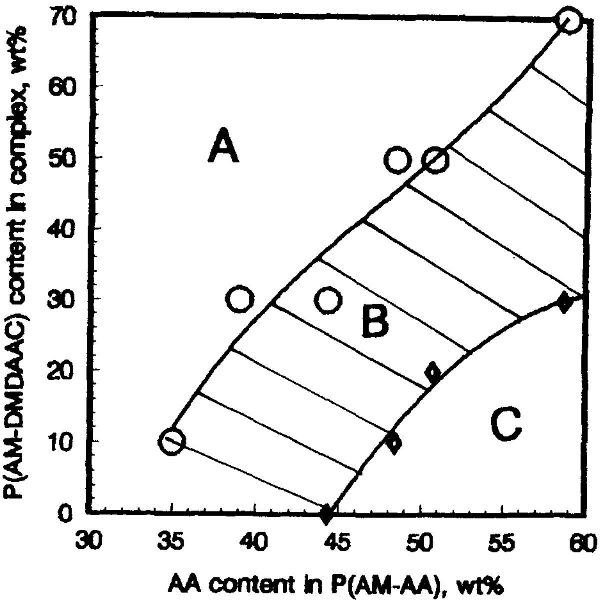


FIG. 10. Area of the complexation.

CONCLUSIONS

Intermacromolecular complexation through Coulomb forces is a novel and effective way to enhance solution viscosity and hence to prepare a new polymer flooding agent. The key to the technique is to prepare a homogeneous complex solution with enhanced viscosity. This can be done by adjusting such factors as the content of ionic groups and their distribution along the macromolecular chain, which can be realized by normal radical copolymerization of AM with AA and AM with DMDAAC, as well as the ratio of polyanions to polycations, the concentration and pH value of the solutions, etc. For the P(AM-AA)/P(AM-DMDAAC) complex solution, when the AA content in the P(AM-AA) chain is 48-58 mol%, the weight ratio of P(AM-AA) to P(AM-DMDAAC) is 70/30-30/70, the pH value is 6-10, and the polymer concentration is 1000-3500 ppm, a complexed and homogeneous complex solution of P(AM-AA)/P(AM-DMDAAC) with a remarkably enhanced viscosity can be obtained. That is, the viscosity exhibited by the complex solution is substantially increased compared to that of the individual polymer solutions at the same polymer concentration. By further tailoring the supermolecular structure of the complex formed through intermacromolecular forces, the challenging problems encountered in enhanced oil recovery may be solved.

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