Solution Properties of a Hyamine Based on *N,N*-Dimethyl Diallyl Ammonium Chloride–Acrylamide Copolymer

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ABSTRACT: A hyamine based on *N,N*-dimethyl diallyl ammonium chloride–acrylamide copolymer was successfully synthesized in this study. Solution properties of this hyamine including electrical conductivity and viscosity behavior were studied in detail, and effects of temperature and counter ion concentration on electrical conductivity of the solution were also discussed. It was found that a solution of hyamine in water showed a typical viscosity behavior of polyelectrolytes, which followed the Fuoss equation. With the increase of ion radius (cationic ion or anionic ion), or with the increase of salt concentration, the shrinkage degree of the polymer chain increased, with a concomitant decrease in reduced viscosity and intrinsic viscosity and an increase of Huggins constant. © 203 Wiley Periodicals, Inc. J Appl Polym Sci 90: 765–771, 203

Key words: polyelectrolytes; solution properties; viscosity; copolymerization; Fuoss equation

INTRODUCTION

Characterized by many good properties such as water solubility, flocculation, and dispersing property, cationic polymers—a kind of polyelectrolytes—have attracted much attention because of their important applications in the fields of biomedicine, pharmacy, and the chemical industry.[1–5] Although there have been numerous studies concerned with the solution property of polyelectrolytes,[6] most of the attention has focused on anionic polymers. Because cationic polymers were usually dissolved in water when used as flocculating agents, the present investigators believed it necessary to understand the solution property and behavior of cationic polymers. In this study, a kind of cationic polymer of polymeric hyamine was prepared with the primary focus on the solution property and behavior of this polymeric hyamine. The effects of some factors such as temperature and counter ion concentration on solution behavior were also studied.

EXPERIMENTAL

Chemicals and characterization

N,N-Dimethyl diallyl ammonium chloride (DMDAAC) was prepared according to procedures described in the literature.[7] Acrylamide (AAm), $K_2S_2O_8$, and $NaHSO_3$, A.R. grade, were obtained from Shanghai Chemicals Factory (China). Potassium polyvinyl sulfate (PVSK),

A.R. grade, was from Sigma Chemical Co. (St. Louis, MO). We also used distilled water, with a specific conductivity $< 1 \times 10^{-6}$ S cm^{-1}.

Infrared spectra analysis was carried out on a Bruker Vector 22 FTIR analyzer (Bruker Instruments, Billerica, MA). Molecular weights of the polymers were tested on a UIC model 070 vapor pressure osmometer (Joliet, IL) with calibration curves of NaCl/ H_2O. The cation content of copolymer was determined by colloid titration.[8,9] Here, the cation content was defined as the molar percentage of cationic group (or cationic monomer) in copolymer. Specific conductivity (k) and equivalent conductance (λ) of water solution of copolymer were tested on a DDS-11A conductivity analyzer (Shanghai No. 2 Analyzer Factory, China). Viscosity was tested by Umstatter viscometer at 25°C; each test was performed five times (SD < 0.02), and the average value was used to plot the curves.

Synthesis of *N,N*-dimethyl diallyl ammonium chloride–acrylamide copolymer

Copolymerization was carried out according to Scheme 1.

DMDAAC and AAm were dissolved in water (molar ratio of DMDAAC to AAm was 3 : 7). Under N_2 atmosphere, a water solution of $K_2S_2O_8$ and $NaHSO_3$ was gradually added to initiate the reaction. The reaction temperature was maintained at 50°C for 9 h, after which time the reacting system was cooled to end the reaction. The reaction mixture was immersed in acetone. The copolymer product was obtained after vacuum drying. The copolymer had a number-average molecular weight (M_n) of 22,300 and a cation

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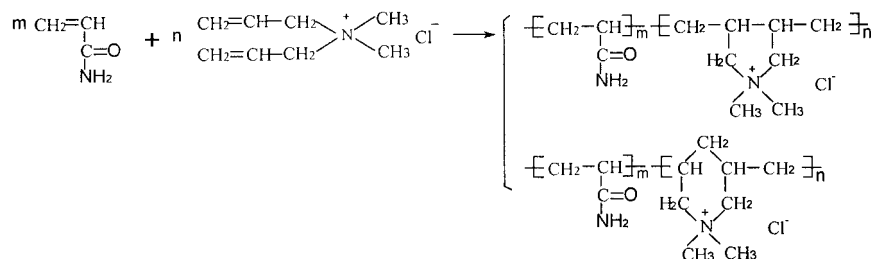
Scheme 1 Copolymerization of *N,N*-dimethyl diallyl ammonium chloride and acrylamide.

content of 29.28%, which meant that the value of "n" (in **Scheme 1**) of the copolymer was about 3.

The IR spectrum of this copolymer is shown in Figure 1. A peak of 1637.3 cm^{-1} attributed to ν (C=O) of AAm unit and a peak of 1477.7 cm^{-1} attributed to δ (CH$_3$—N$^+$—CH$_3$) of DMDAAC could be found in this spectrum, which meant the successful preparation of the copolymer.
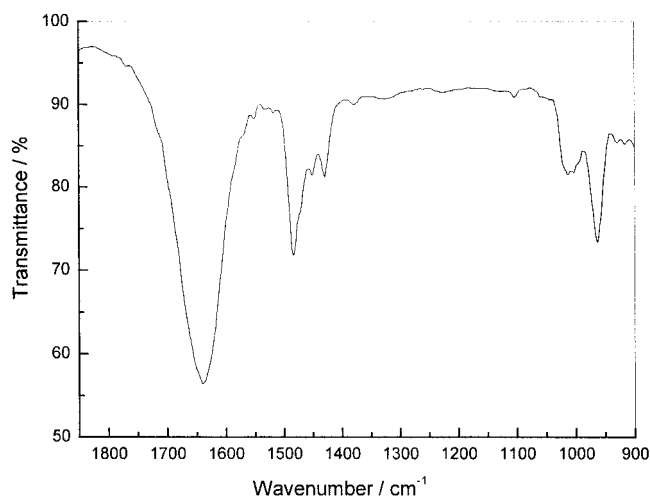
The copolymerization process was repeated with different molar ratios of DMDAAC to AM (1 : 9, 2 : 8, 4 : 6, and 5 : 5). M_n and cation content data of the copolymers are listed in Table I.

The copolymer discussed in the present study had a cation content of 29.28%, unless specified otherwise.

RESULTS AND DISCUSSION

Conductive property

In general, when hyamine-based polyelectrolyte is dissolved in water, polymeric ions and counter ions are generated by ionization. The conductance of a polymeric hyamine solution is attributed to transmission of counter ions, and chain movement of polymeric ions contributed to transportation of the electric charge.[10] The conductance of hyamine solution was proportional to the concentration of counter ions in the solution.

Figures 2 and 3 show that, for polymeric hyamine prepared in this study, temperature and hyamine concentration had great effects on specific conductivity and equivalent conductance of its solution in water. With increase of temperature, both specific conductivity and equivalent conductance increased with increase of hyamine concentration, specific conductivity increased, whereas equivalent conductance decreased.

In fact, ionization of polyelectrolyte was usually endothermal. When temperature increased, the ionization degree and then concentration of counter ions increased, and at the same time movement of counter ions also increased; all these phenomena resulted in the increase of specific conductivity and equivalent conductance.

When solution concentration increased, the concentration of counter ions also increased and resulted in an increase of specific conductivity. By definition, equivalent conductance was determined by the ratio of specific conductivity to solution concentration, and solution concentration usually increased to a greater degree than specific conductivity did when solution concentration increased, which resulted in a decrease of equivalent conductance.

The relationship between specific conductivity (and equivalent conductance) and cation content (Fig. 4) showed that, when solution concentration was kept constant, with an increase of cation content, the concentration of counter ions increased, resulting in in-

Figure 1 IR spectra of *N,N*-dimethyl diallyl ammonium chloride–acrylamide copolymer.

TABLE I
Data of Number-Average Molecular Weight and Cation Content of the Copolymers

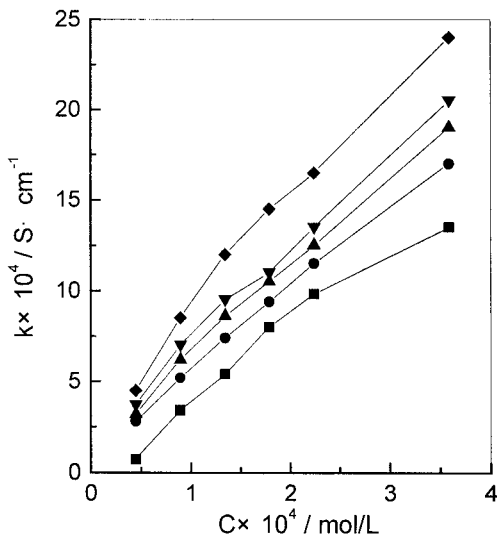| Molar ratio of DMDAAC to AM	M_n (g/mol)	Cation content (%)	n^a	m^a
1:9	27,010	9.91	0.991	9.009
2:8	20,150	20.24	2.024	7.976
3:7	22,300	29.28	2.928	7.072
4:6	25,120	39.89	3.989	6.011
5:5	19,850	48.98	4.898	5.102

^{a} Used in **Scheme 1.**

Figure 2 Relationship between *k* and *c* (♦, 55°C; ▼, 45°C; ▲, 35°C; ●, 25°C; ■, 17°C).

creases of specific conductivity and equivalent conductance.

Viscosity behavior

Polymeric hyamine prepared in this study was a kind of polyelectrolyte and its water solution showed a viscosity behavior different from that of normal nonionic polymer. For normal nonionic polymer, its reduced viscosity decreased linearly with a decrease of solution concentration, whereas reduced viscosity of polyelectrolyte solution increased nonlinearly with a decrease of solution concentration.

The effect of solution concentration on reduced viscosity, when polymeric hyamine was dissolved in wa-
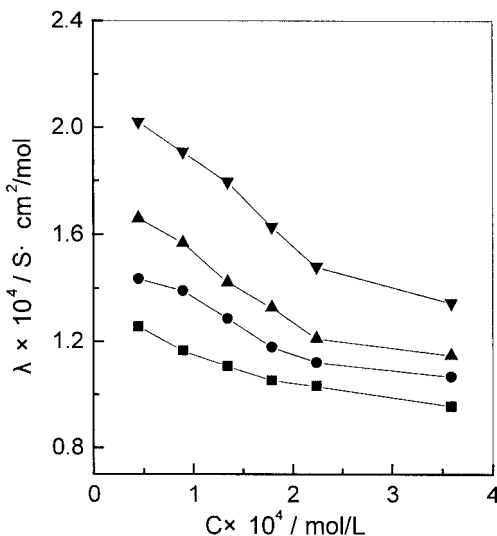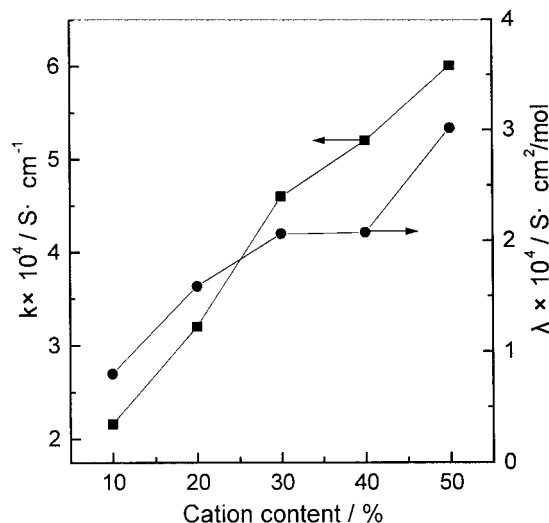

Figure 4 Relationship between specific conductivity (and equivalent conductance) and cation content (solution concentration of 0.45×10^{-4} mol/L, 55°C; copolymers with different cation content were used here).

ter, is shown in Figure 5. This solution showed the typical viscosity behavior of a polyelectrolyte, and its reduced viscosity increased rapidly with a decrease of solution concentration.

When polyelectrolyte was dissolved in water, polymeric ions and counter ions were generated by ionization. With dilution of solution, the distance between polymeric ions and counter ions increased, such that restriction on counter ions by polymeric ions decreased. At the same time, the ionization degree of polyelectrolyte increased, charge density of polymeric ions increased, and electrostatic repulsion between quaternary ammonium ions in polymer chain increased, which resulted in the extension of polymer chain and increase of reduced viscosity. All of these
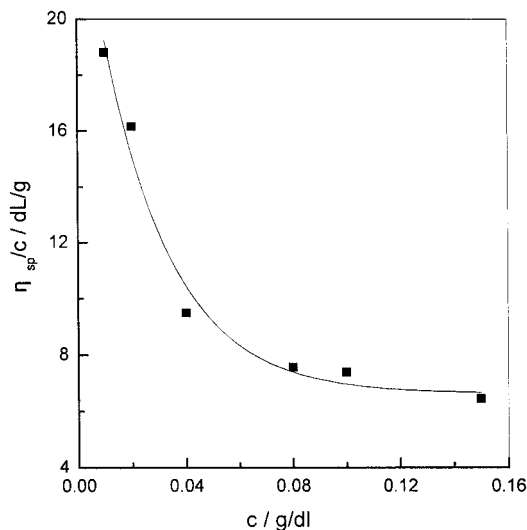

Figure 3 Relationship between λ and *c* (▼, 55°C; ▲, 45°C; ●, 35°C; ■, 25°C).

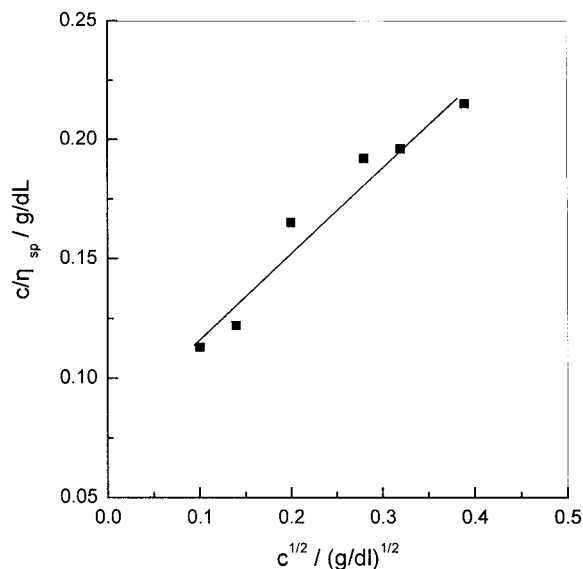**Figure 5** Effect of solution concentration on η_{sp}/c.

Figure 6 Relationship between c/η_{sp} and $c^{1/2}$.

phenomena account for the difference of viscosity behavior between polyelectrolyte and normal nonionic polymer.

Interactions between polymeric ions and counter ions had a significant effect on the solution property of polyelectrolyte—called either the "polyelectrolyte effect" or the "Fuoss effect." For polyelectrolyte solution, the change of reduced viscosity also reflected the size change of polymeric ions. With a decrease of solution concentration, reduced viscosity increased, which meant an increase in the size of polymeric ions.

The relationship between reduced viscosity and solution concentration of polyelectrolyte dissolved in water may be expressed by the Fuoss equation[11]:

$$\frac{\eta_{sp}}{c} = \frac{A}{(1 + B\sqrt{c})} + D \quad \frac{1}{\eta_{sp}/c - D} = \frac{1}{A} + \frac{B}{A}\sqrt{c}$$

where A is the limited value of reduced viscosity when solution concentration approached zero, equivalent to intrinsic viscosity $[\eta]$ of the polyelectrolyte; B is a constant reflecting the interaction between polymeric ions and counter ions, with regard to the nature of the solvent, and the value of B increased with a decrease of solvent's dielectric constant; C is the limited value of reduced viscosity (when the solution concentration approached infinity, almost all the charge of polymeric ions was shielded by counter ions in this condition); and D is the shielding intrinsic viscosity $[\eta]_\infty$. When $D \ll \eta_{sp}/c$, the above equation was transformed into

$$\frac{c}{\eta_{sp}} = \frac{1}{A} + \frac{B}{A}\sqrt{c}$$

A linear relationship between c/η_{sp} and $\sqrt{c}$ is found from the above equation. Figure 6 shows good linearity between c/η_{sp} and $\sqrt{c}$. This means that, for the water solution of polymeric hyamine prepared in this study, the relationship between reduced viscosity and solution concentration satisfactorily followed the Fuoss equation, thus showing the typical viscosity behavior of a polyelectrolyte.

According to Figure 6, from the slope and intercept of the line, the values of intrinsic viscosity $[\eta]$, A, and B may be obtained; these Fuoss data are presented in Table II [related coefficient (R) of the linear regression was 0.977, and standard deviation (SD) of the linear regression was 0.009].

Effect of bivalent cation on viscosity of polymeric hyamine solution

For polymeric hyamine dissolved in either $MgCl_2$, $CaCl_2$, or $BaCl_2$ solutions of $0.5M$ and $0.25M$, the relationship between reduced viscosity and solution concentration are shown in Figure 7. The "polyelectrolyte effect" was restrained well with other salts in solution, and there was linearity to some degree between η_{sp}/c and c, whereas the effects of different divalent cations on reduced viscosity and intrinsic viscosity of polymeric hyamine solution were different.

When a low molecular weight electrolyte (salt) was added to a polymeric hyamine solution, the ionization of counter ions of polymeric hyamine was restrained, although the ionization degree of polymeric hyamine decreased and the association degree of polymeric ions and counter ions increased. All these phenomena resulted in a decrease of charge density of polymeric ions and a decrease of electrostatic repulsion between quaternary ammonium ionic groups in the polymer chain, and in turn resulted in shrinkage of the polymer chain, then a decrease of reduced viscosity.

Reduced viscosity and intrinsic viscosity of polymer reflected the extension or shrinkage of polymer chain in solution, and reflected the size of polymer random coil. With extension of the polymer chain, the size of the random coil increased and reduced viscosity increased.

With additional salt, in the range of linearity, viscosity followed the Mark–Huggins equation

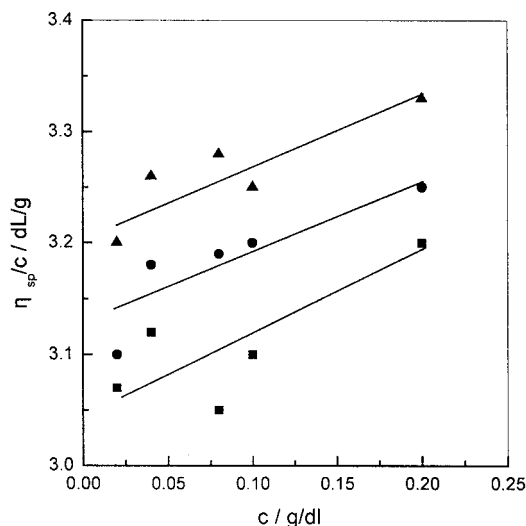$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c$$

TABLE II
Fuoss Data of Polymeric Hyamine Dissolved in Water

Sample	A	B	$[\eta]$ (dL/g)
Polymeric hyamine	12.56	4.61	12.56
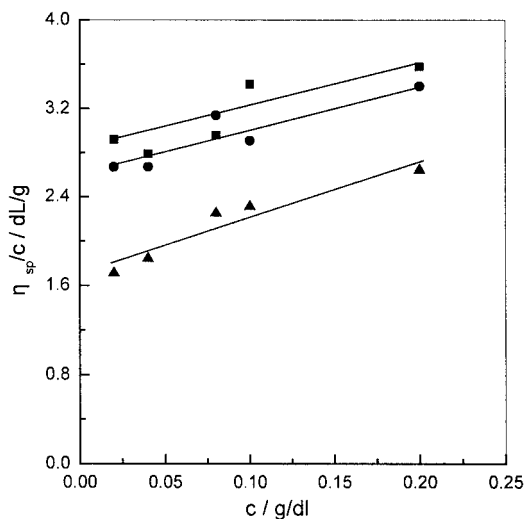
(■ 0.5MMgCl$_2$, ● 0.5MCaCl$_2$, ▲ 0.5MBaCl$_2$)

(a)

(▲ 0.25MMMgCl$_2$, ● 0.25MCaCl$_2$, ■ 0.25MBaCl$_2$)

(b)

Figure 7 Relationship between η_{sp}/c and c (in salt solution with different cations). (a) ■, 0.5M MgCl$_2$; ●, 0.5M CaCl$_2$; ▲, 0.5M BaCl$_2$. (b) ▲, 0.25M MgCl$_2$; ●, 0.25M CaCl$_2$; ■, 0.25M BaCl$_2$.

where $[\eta]$ is the intrinsic viscosity of polymer when there was additional salt; k' is the Huggins constant, pertaining to the interaction between polymer and solvent.

From Figure 7, when the solution concentration was extrapolated to zero, $[\eta]$ was obtained, and k' could be obtained according to the slope of the line. All these data are listed in Table III [R of the linear regression

was greater than 0.8, and SD of the linear regression was less than 0.12].

With the different divalent cations, the values of reduced viscosity and intrinsic viscosity of polymeric hyamine solution followed the order $Mg^{2+} > Ca^{2+} > Ba^{2+}$, and this result may be explained by Pearson theory.[12]

The Pearson theory of acid and alkali indicates that hard acid ions (anion) prefer to bond with hard alkali ions (cation) and soft acid ions prefer to bond with soft alkali ions. Hard ions are those ions with small size and are polarized with difficulty, whereas soft ions are those ions with large size and are easily polarized.

Here, counter ions of Cl^- were hard anions and preferred to bond with hard cations of Mg^{2+}. As a result, Mg^{2+} could reduce the restriction degree of Cl^- on polymeric ions to a greater degree than either Ca^{2+} or Ba^{2+}. In the order of Mg^{2+}, Ca^{2+}, and Ba^{2+}, the ionization degree of polymeric hyamine decreased, the charge density of polymeric ions decreased, the shrinkage degree of polymer chain increased, then reduced viscosity and intrinsic viscosity of polymeric hyamine solution decreased.

Therefore, when anions were kept constant, the effects of different divalent cations on viscosity of polymeric hyamine were as follows: with decrease of cation size, the bonding degree of cations with hard anions in solution increased, the ionization degree of polymeric hyamine increased and charge density of polymeric ions increased, then electrostatic repulsion between quaternary ammonium ions in the polymer chain increased, which resulted in extension of the polymer chain, increase of reduced viscosity and intrinsic viscosity, and decrease of Huggins constant.

Effect of anion on viscosity of polymeric hyamine solution

The size of counter ions (anion) affected the restriction of polymeric ions on counter ions, and then affected the viscosity behavior of the polymer solution.

For polymeric hyamine dissolved in KCl, KBr, and KI solution of 0.5 and 0.25M, the relationship between reduced viscosity and solution concentration was treated according to the Mark–Huggins equation. Val-

TABLE III
Viscosity Data of Hyamine Solution with Different Divalent Cations (25°C)

Salt solution (0.5M)	Slope	$[\eta]$ (dL/g)	k'
MgCl$_2$ (0.5M)	4.362	2.750	0.577
CaCl$_2$ (0.5M)	4.110	2.596	0.610
BaCl$_2$ (0.5M)	5.122	1.699	1.774
MgCl$_2$ (0.25M)	0.592	3.212	0.057
CaCl$_2$ (0.25M)	0.683	3.124	0.070
BaCl$_2$ (0.25M)	0.644	3.051	0.069

TABLE IV
Viscosity Data of Hyamine Solution with Different Anions (25°C)

Salt solution (0.25M)	Slope	[η] (dL/g)	k'
KCl (0.25M)	0.868	3.012	0.096
KBr (0.25M)	1.900	2.643	0.272
KI (0.25M)	4.482	1.576	1.805
KCl (0.5M)	3.900	2.583	0.585
KBr (0.5M)	5.031	2.237	1.005
KI (0.5M)	5.083	2.067	1.190

TABLE V
Viscosity Data of Hyamine Solution with Different Salt Concentrations (25°C)

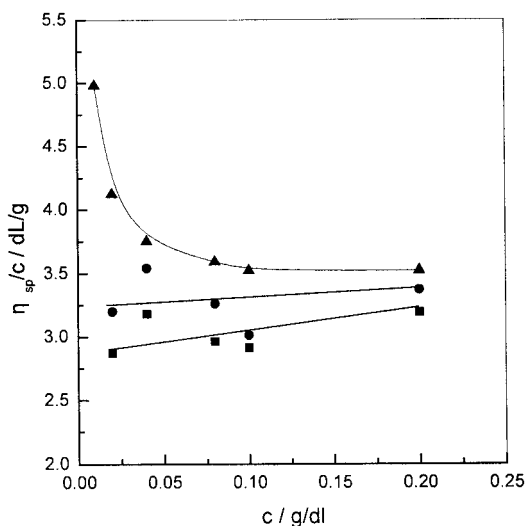| Concentration of NaCl	Slope	[η] (dL/g)	k'
0.15M	−0.002	3.276	−0.0002
0.25M	1.053	2.929	0.123

ues of [η] and k' obtained are listed in Table IV [R of the linear regression was greater than 0.9, and SD of the linear regression was less than 0.05].

With different anions, the values of reduced viscosity and intrinsic viscosity of polymeric hyamine solution followed the order $Cl^- > Br^- > I^-$, and this result followed the Pearson theory.

Of Cl^-, Br^-, and I^-, I^- had the largest size, was easily polarized, and easily restricted by polymeric ions; then the ionization degree of polymeric hyamine decreased, charge density of polymeric ions decreased, and electrostatic repulsion between quaternary ammonium ions in polymer chain decreased, which resulted in shrinkage of the polymer chain, a decrease of reduced viscosity and intrinsic viscosity, and an increase of Huggins constant.

Effect of salt concentration on viscosity of polymeric hyamine solution

Concentration of additional salt into polymeric hyamine solution significantly affected the ionization degree of hyamine, which in turn significantly affected

the size of the polymer chain. These phenomena are reflected in the value of viscosity.

Figure 8 shows that, when the concentration of additional salt was high, the relationship between reduced viscosity and solution concentration was linear and the "polyelectrolyte effect" was completely restrained, whereas when the concentration of additional salt was low, the relationship was not linear and the "polyelectrolyte effect" was effective in some degree.

Data of Figure 8 were treated further according to the Mark–Huggins equation. Values of slope, intrinsic viscosity [η], and Huggins constant k' are listed in Table V [R of the linear regression was greater than 0.85, and SD of the linear regression was less than 0.10].

When the concentration of NaCl increased, the ionic strength of solution increased, the restriction degree of Cl^- on polymeric ions increased, the shielding degree of polymeric ions by counter ions increased, and the bonding degree of polymeric ions with counter ions increased; then the ionization degree of polymeric hyamine decreased and the charge density of polymeric ions was reduced, after which electrostatic repulsion between polymer chains decreased, which led to an increase of shrinkage degree of polymer chains,

Figure 8 Relationship between η_{sp}/c and c (with different salt concentrations): ▲, 0.05M NaCl; ●, 0.15M NaCl; ■, 0.25M NaCl.
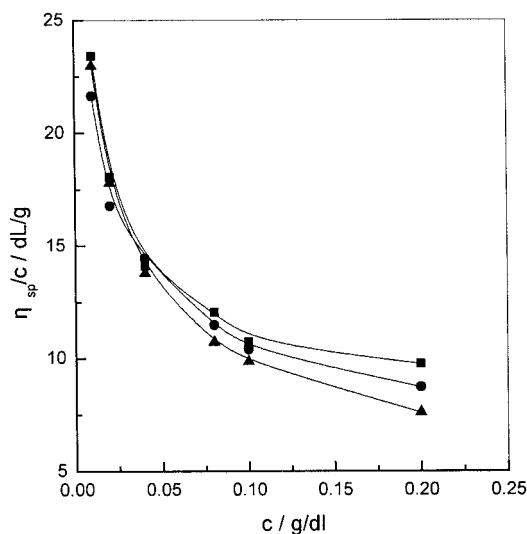
Figure 9 Relationship between η_{sp}/c and c (with different ratios of methanol to water): methanol/water (volume): ■, 20/80; ●, 40/60; ▲, 50/50.

a decrease in reduced viscosity and intrinsic viscosity, and an increase of Huggins constant.

Effect of methanol on viscosity of polymeric hyamine solution

Figure 9 makes clear that, with methanol added, the solution of polymeric hyamine still showed the typical viscosity behavior of a polyelectrolyte. With an increase of methanol content, reduced viscosity decreased. With the increase of methanol, the ionization degree of polymeric hyamine decreased, which ultimately led to a decrease of reduced viscosity.

CONCLUSIONS

For polymeric hyamine prepared in this study, the factors of temperature and solution concentration had a significant effect on conductive properties. A study of the viscosity of solution showed that a solution of polymeric hyamine in water had the typical viscosity behavior of a polyelectrolyte, which followed Fuoss equation. It was found that for solutions of polymeric hyamine, with an increase of ion radius (cationic ion or anionic ion), or with an increase of salt concentration, the shrinkage degree of the polymer chain increased, with a concomitant decrease in reduced viscosity and intrinsic viscosity and an increase of Huggins constant. Results also showed that additional salt and methanol into solution also had a further significant effect on the solution's viscosity behavior.

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