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Poly(sulfobetaine)s and corresponding cationic polymers: 5. Synthesis and dilute aqueous solution properties of poly(sulfobetaine)s derived from acrylamide–maleic anhydride copolymer

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The copolymer prepared by copolymerizing acrylamide with maleic anhydride was imidized with *N,N*-dimethylaminopropylamine. The obtained acrylamide–*N,N*-dimethylaminopropylmaleimide (ADAPM) copolymer was then reacted with propane sultone to yield a novel acrylamide–*N,N*-dimethylmaleimidopropylammonium propanesulfonate (ADMMAPS) copolymer. The properties of this ampholytic ADMMAPS copolymer in aqueous salt solution were studied by measurement of reduced viscosity and intrinsic viscosity. The intrinsic viscosities of this polyampholyte were related to the type and concentration of the added salts. 'Soft' salt cations and anions were more easily bound to the quaternary ammonium (R_4N^+) and sulfonate group (SO_3^-) of ADMMAPS than were 'hard' salt cations and anions. The tendency of the intrinsic viscosity for ADMMAPS in various aqueous salt solutions is similar to that of other zwitterionic poly(sulfobetaine)s. The Huggins constant for ADMMAPS in an aqueous salt solution shows a marked distinction from the sulfobetaine copolymer, styrene–*N,N*-dimethylmaleimidopropylammonium propane sulfonate (SDMMAPS). This phenomenon is attributed mainly to the presence of the acrylamide/styrene segment, a hydrophilic/hydrophobic group, on the ADMMAPS/SDMMAPS copolymer, respectively. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polyampholyte; sulfobetaine; intrinsic viscosity)

INTRODUCTION

Synthetic polyampholytes can be prepared from zwitterionic monomers that exhibit the requisite net charge of zero at the appropriate pH. The positive charge is provided by a quaternary ammonium group and the negative charge is provided by a carboxylate or sulfonate group (carboxybetaine or sulfobetaine). A number of investigations have focused on the unusual properties of zwitterionic polyampholytes.

Zwitterionic monomers of sulfobetaines derived from dimethylaminoalkyl acrylates and dimethylaminoacrylamides have been widely used in industries concerned with textiles, medical products, charged dispersing agents, protective colloids and other related materials[1-9]. These ampholytic monomers are of two types, sulfobetaines and carboxybetaines[10-25]. The synthesis and aqueous solution properties of these betaine monomers were reported by several authors, including Ladenheim *et al.*[10], Hart *et al.*[11], Salamone *et al.*[12-14], Galin *et al.*[15,16], Schulz *et al.*[17], Asonova *et al.*[18,19], Topchiev *et al.*[20], Laschewsky *et al.*[21] and Liaw *et al.*[22].

Ladenheim and Morawetz reported the reaction of poly(4-vinylpyridine) with ethyl bromoacetate followed by hydrolysis of the ester to give high-charge-density polyampholytes[10]. Hart and Timmerman prepared sulfobetaine polyampholytes by reacting poly(2-pyridine) with sultones or by polymerizing the sultone derivative of 4-vinylpyridine[11]. Salamone *et al.* synthesized a series of sulfobetaines based on vinylimidazole[12-14].

Galin and coworkers conducted an elegant study of poly(sulfobetaine)s with various structures[15,16]. They described the synthesis of a series of polyampholytes by the quaternization of vinylaines with 1,3-propane sultone. Utilizing the Mark–Houwink–Sakurada relationship, the existence of specific dipolar intermolecular interactions between lateral zwitterions was established. They concluded that, in the presence of electrolytes, a polyampholyte behaved like a random coil of moderate flexibility in a thermodynamically very poor solvent.

Schulz *et al.* have examined the phase behaviour and solution properties of the homopolymer of the commercially available monomer *n*-(3-sulfopropyl)-*N*-methacryloyloxyethyl-*N,N*-dimethylammonium betaine (SPE). Negative second virial constant (A_2) values were found for the polyampholyte in solutions of low ionic strength; positive values were found as the ionic strength

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increased. Highly alternating copolymers of *N*-vinylpyrrolidone (NVP) with SPE which showed polyampholyte behaviour in solution were also studied[17].

During studies[26–31] of the binding interaction of salt ions and polymers according to the Huggins constant k', the counter ion size was found to affect the degree of binding for salt-ion-attracting polymers[12–16,19,22–24,32], i.e. 'soft' salt anions and cations are more effective solubilizers than hard' anions and cations[33,34].

A series of poly(sulfobetaine)s and corresponding cationic polymers prepared from zwitterionic sulfobetaine and corresponding cationic monomers with different electron-withdrawing groups and by varying the methylene units between the charge groups were studied previously in our laboratory. The solution properties of a cationic poly(trimethylacrylamidopropylammonium iodide) (poly(TMAAI)), poly(*N,N'*-dimethyl acrylamidopropylammonium propanesulfonate) (poly(DMAAPS)) and poly(*N, N'*-dimethylmethacryloyloxyethylammonium propanesulfonate) (poly(DMAPS)) were reported in previous papers[22,25,34,35]. The poly(DMAAPS) article concluded that soft salt anions and cations were bound easily by the quaternary ammonium and sulfonate group of poly(DMAAPS); the poly(TMAAI) article showed that soft salt anions were more easily bound than hard salt anions by the quaternary ammonium of poly(TMAAI). Recently, studies of polyampholytes prepared from copolymers having high purities and similar structural characteristics have been the focus of our work. For example, a styrene–*N,N*-dimethylmaleimidopropylammonium propanesulfonate (SDMMAPS) copolymer was prepared from styrene–maleic anhydride copolymer (SMA). The properties of this ampholytic SDMMAPS copolymer in aqueous salt solution were studied by measurement of cloud point and intrinsic viscosity[36]. Even though the tendency to a minimum of salt concentration and intrinsic viscosity for SDMMAPS in various aqueous salt solutions is similar to that of other zwitterionic poly(sulfobetaine)s, the Huggins constant for SDMMAPS in aqueous salt solution shows a marked distinction from sulfobetaine homopolymers, especially poly(*N, N'*-dimethylacrylamidopropylammonium propanesulfonate) (poly(DMAAPS))[25]. This phenomenon is attributed mainly to the presence of the styrene segment, a hydrophobic group, in the pendent group of the SDMMAPS copolymer.

The synthesis and aqueous solution properties of poly(sulfobetaine) derived from acrylamide–maleic anhydride (AA–MA) copolymer, especially the intrinsic viscosity in the presence of various salts, will be investigated in this paper.

EXPERIMENTAL

Materials

Acrylamide (AA, m.p. 83–84°C) and maleic anhydride (MA, m.p. 56°C) were recrystallized from reagent-grade benzene and dried in a vacuum at room temperature. Azobisisobutyronitrile (AIBN) was recrystallized from reagent-grade methanol prior to use. Deionized water used in this study has a resistivity of 18 MΩ.

Synthesis of acrylamide–maleic anhydride (AA-MA) copolymer

Acrylamide (7.108 g, 0.1 mol), maleic anhydride (9.806 g, 0.1 mol) and benzene (or methyl ethyl ketone (MEK), dioxane; 250 ml) were introduced into a 300 ml three-necked flask equipped with a stirrer, a condenser and a thermometer. The contents were stirred at 80°C for complete dissolution. To the solution was then added AIBN (0.20 g, added in four steps) as an initiator, and it was stirred at the same temperature or 3 h under a nitrogen atmosphere. The polymer precipitated from the solution as polymerization continued. After the polymerization was completed, the precipitated product was washed with acetone several times and a hygroscopic white solid was obtained. The yield of copolymers was more than 60 wt%. The products were placed into a large volume of a mixture of methanol/water (1/1), which is a solvent for these two monomers and the AA homopolymer, and the insoluble copolymer was recovered by filtration and dried under vacuum to constant weight at room temperature. A large volume of methanol (more than 1/10) was added to the filtrate to check that the AA homopolymer was absent[37].

Imidization of AA-MA copolymer

The AA-MA copolymer (8 g) was slurried with 60 ml of dimethylsulfoxide (DMSO) at 80°C until the polymer particles were completely dissolved in DMSO. 3-Dimethylaminopropylamine (9.67 g) was added dropwise over 1 h. Heat was applied gradually until the addition was completed, and the solution was stirred under a gentle reflux for 1 h and then subjected to distillation until the reaction system reached 180°C and sparged with nitrogen for 30 min in order to conduct the dehydration reaction. To check that the dehydration reaction was completed, a 10 ml sample was drawn from the reaction mixture and poured into a large volume of methanol; the precipitated product was collected by filtration. The sample was then dissolved in deionized water and precipitated with methanol three times, washed with acetone several times to remove DMSO, and then dried at 80°C for 24 h under vacuum to obtain the acrylamide–dimethylaminopropylmaleimide (ADMAPM) copolymer. The imidization degree of the ADMAPM copolymer was determined by elemental analysis.

*Synthesis of acrylamide–*N,N*-dimethylmaleimidopropylammonium propanesulfonate (ADMAPS) copolymer*

The imidized copolymer mixture obtained from the above procedure was subsequently cooled to room temperature using a waterbath. A solution of propane sultone (12.2 g) in DMSO (10 ml) was then introduced dropwise into the copolymer mixture with stirring under a nitrogen atmosphere over 1 h. The temperature of the reaction was maintained at 20°C. After completion of the addition, the mixture was stirred at the same temperature for several hours and then allowed to stand overnight. The resulting reaction mixture was precipitated by pouring the solution slowly into a large volume of reagent-grade methanol under stirring. The brown precipitate that formed was recovered by filtration; the product was an acrylamide–*N,N*-dimethylmaleimidopropylammonium propanesulfonate (ADMMAPS) copolymer. The crude yield of the ADMMAPS copolymer was greater than 70%. For purification, the crude ADMMAPS copolymer was dissolved in deionized

Table 1 The average viscosimetric molecular weight ($\bar{M}_v$) obtained with various reaction solvents

No.	Monomer ratio (AA:MA)	Solvent	$[\eta]^a$ (dl g^{-1})	$K \times 10^6$	α	$\bar{M}_v$
1	1:1	Benzene	0.096	10.5	0.66	3.06×10^4
2	1:1	MEK	0.048	59.5	0.66	2.55×10^4
3	1:1	Dioxane	0.060	10.5	0.66	1.50×10^4

[a] The intrinsic viscosity $[\eta]$ in 0.6 N $NaNO_3$ solution at 25°C was determined using an Ubbelohde viscometer

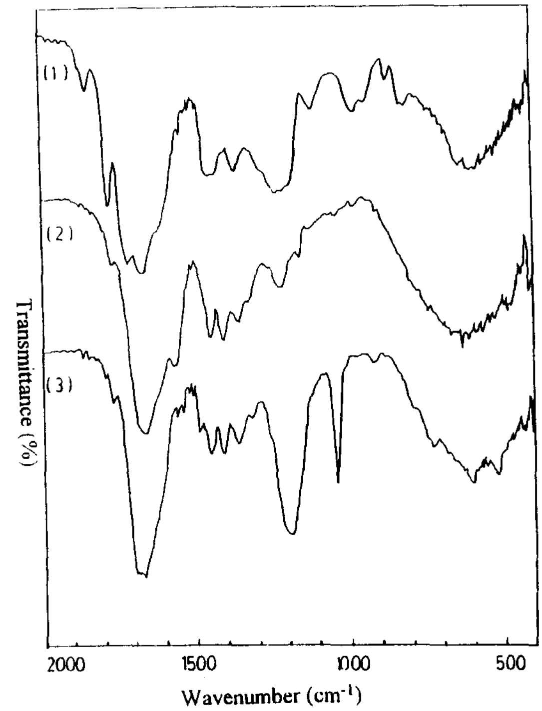


Figure 1 I.r. spectra of AA-MA (1), ADMAPM (2) and ADMMAPS (3) copolymers

water and precipitated with methanol three times and washed with acetone several times until all the DMSO was removed. The hygroscopic brown–white product was dried under vacuum at 80°C for 24 h.

Characterization techniques

I.r. spectra were recorded with a Jasco FT/IR 7000 spectrophotometer using KBr discs in the range 400–2000 cm^{-1}.

Elemental analysis for carbon, hydrogen and nitrogen in the ADMAPM and ADMMAPS copolymers was conducted with a Perkin-Elmer 2400. Elemental analysis for sulfur in the ADMMAPS was conducted using a Tacussel Coulomax 78 (S).

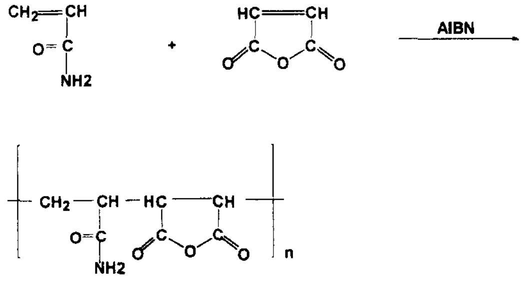
Viscometric measurements

Viscometric measurements were carried out with an Ubbelohde viscometer (flow time 129.25 s for pure water) at 30 ± 0.01°C. The polymer samples were dissolved in a salt solution of varying concentration to yield stock solutions of approximately 1.0 g polymer per 100 ml solvent.

Viscosity data were calculated according to the Mark–Huggins equations:

$$\eta_{sp}/C = [\eta + k'[\eta]^2 C \qquad (1)$$

where η_{sp} is the specific viscosity; C is the concentration of polymer; $[\eta]$ is the intrinsic viscosity; and k' is the Huggins constant. The value of η_{sp}/C is plotted *versus* C; $[\eta]$ and k' are, respectively, determined from the intercept and slope of the straight line.



(I)

Scheme 1

RESULTS AND DISCUSSION

Synthesis of AA-MA copolymers

The synthesis of the copolymer of AA and MA was carried out, using AIBN as initiator at 80°C, in different solvents, i.e. benzene, MEK and dioxane. The monomer ratio, viscosity-average molecular weight ($\bar{M}_v$), and the constants α and K (from the Mark–Houwink equation, $[\eta] = K\bar{M}_v^{\alpha}$) for AA-MA copolymers are given in *Table 1*[38].

The results shown in *Table 1* indicate that the molecular weight of AA-MA was dependent on the solvent used in the synthesis. The structure of the AA-MA copolymer is alternating according to the literature data[39] (the copolymerization reactivity ratios were given as 0.75 for AA and 0.00 for MA) and the i.r. spectrum (*Figure 1* (1)). The characteristic absorption peaks of the i.r. spectra for MA and AA units are 1775, 1720 and 1216 cm^{-1}, and 1671 and 1363 cm^{-1}, respectively. The polymerization reaction is shown in *Scheme 1*.

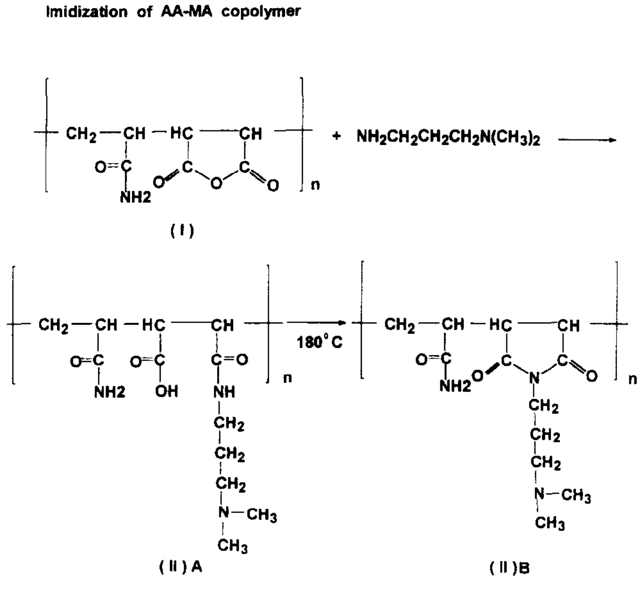
*Synthesis of acrylamide–*N,N*-dimethylmaleimidopropylammonium propanesulfonate (ADMMAPS) copolymer*

After addition of 3-dimethylaminopropylamine to an AA-MA copolymer solution in DMSO (see *Table 1*, No.1) and refluxing (1 h) to form acrylaide–maleimidic acid (ring-opened reaction) (*Scheme 2* IIA), the system was heated to 180°C to carry out a dehydration reaction (ring-closing reaction) to obtain the acrylamide–dimethylaminopropylmaleimide (ADMAPM) (*Scheme 2* IIB). The identification of the copolymer was confirmed by i.r. spectroscopy; the characteristic absorption peak of the MA group (ν(C–O) at 1216 cm^{-1}) disappeared after the acrylamide–maleimidic acid copolymer was dehydrated at 180°C (see *Figure 1* (2)). The degree of imidization was evaluated by elemental analysis for nitrogen. The product of ADMAPM was subject to elemental analysis. Anal. calcd for ($C_{12}H_{19}O_3N_3$): C, 56.90%; H, 7.56%; N, 16.58%. Found: C, 56.85%; H, 7.46%; N, 16.47%. The imidization degree was 98.10 mol%.

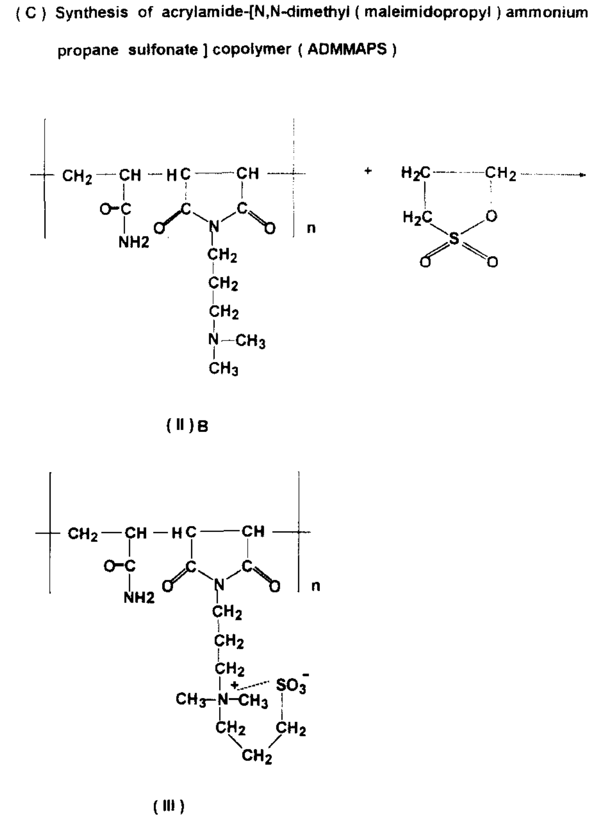
ADMMAPS was synthesized by the ring-opening reaction of 1,3-propane sultone (PS) with ADMAPM (*Scheme 3*). The structure of ADMMAPS was characterized by i.r. spectroscopy (see *Figure 1* (3)). The i.r. spectrum of the ADMMAPS copolymer exhibits the characteristic absorption of the sulfonate group (ν(S=O) at $1044\,cm^{-1}$). The degree of the formation of the sulfobetaine was calculated by elemental analysis for sulfur. Anal. calcd for ($C_{15}H_{25}O_6N_3S$): S, 8.62%. Found S, 8.45%. The degree of the formation of the sulfobetaine was 98.05 mol%.

Viscometric measurements

Intrinsic viscosity is a good measure of hydrodynamic volume for polymers. Polyampholytes are a class of polymers that contain both positive and negative charges on the same macromolecular chain. These polymers exhibit what has been termed an 'antipolyelectrolyte' behaviour in solution, i.e. higher intrinsic viscosities are observed with increasing solution ionic strength, which is related to the type and concentration of the added salt. ADMMAPS copolymer is an ampholytic copolymer in which binding of the sulfonate group (SO_3^-) with the quaternary ammonium group (R_4N^+) forms an ionically crosslinked network (tight ion pair) in solutions in water or low concentration of salt. Schulz *et al.*[17] reported that these intramolecular aggregates are of both the intragroup and intrachain type. Such intramolecular aggregates are broken up by external electrolytes (e.g. NaCl), with a consequent modest expansion of the polymer coil (*Scheme 4*). This occurrence resulted in an increase of intrinsic viscosity. Determination of the intrinsic viscosity of ADMAPS in the presence of different electrolytes can reflect the influence of those salts on the hydrodynamic volume of the polymeric chain.



Scheme 2



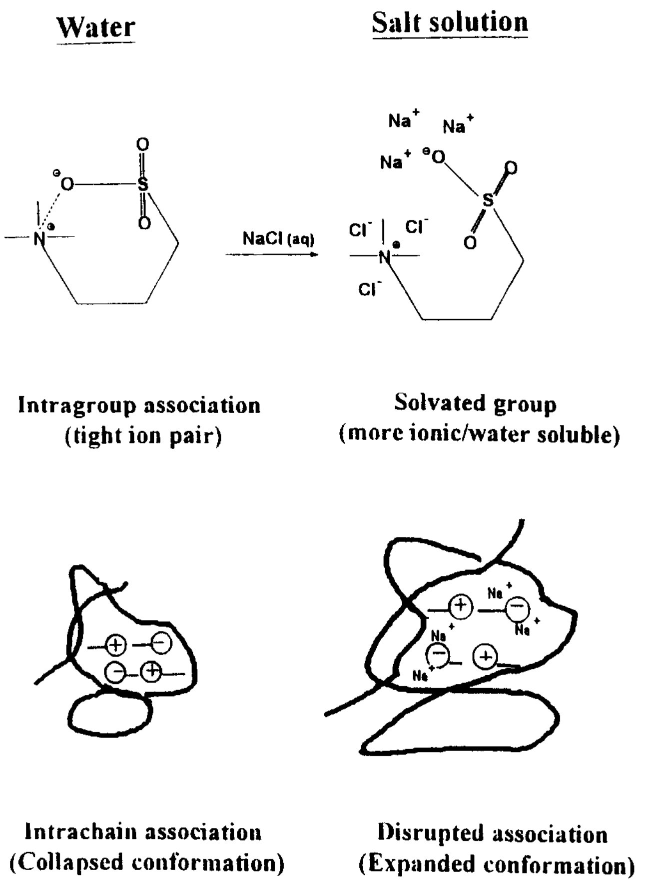
Scheme 3

Influence of cations with a common anion on the intrinsic viscosity of ADMMAPS copolymer

The influence of various electrolytes having a common anion (Cl^-) on the intrinsic viscosity of ADMMAPS copolymer is shown in *Tables 2* and *3*. The data show increased intrinsic viscosity of this copolymer in aqueous salt solution (0.5 M) in the order $Li^+ < Na^+ \approx K^+$ for LiCl, NaCl and KCl; and in the order $Mg^{+2} < Ca^{+2} \approx Sr^{+2} \approx Ba^{+2}$ for $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$, respectively. The result indicates that ions with a small charge density easily infiltrate the sulfonate of the ionically crosslinked network of the DMMAPS unit in ADMMAPS copolymer to rupture this network. This result is similar to poly(DMAPS)[22] and poly(DMAAPS)[34] and other poly(sulfobetaine)s[12–16,21,33]. The Huggins constant k' for ADMMAPS in an aqueous salt solution shows a marked distinction from sulfobetaine copolymer (styrene-*N,N*-dimethylmaleimidopropylammonium propane sulfonate, SDMMAPS)[36]. This phenomenon is attributed mainly to the presence of the acrylamide/styrene segment, a hydrophilic/hydrophobic group, of the ADMMAPS/SDMMAPS. The solubility of poly(ADMMAPS) in water is different from that of poly(DMAPS), poly(DMAAPS) and SDMMAPS. This abnormal property may be attributed to the fact that the acrylamide structure on the ADMMAPS copolymer, the hydrophilic group, makes the polymer–solvent interaction between ADMMAPS copolymer and water increase (the hydrogen-bonding effect). This phenomenon was also observed by Schulz *et al.*[17].

Influence of anions with a common cation on the intrinsic viscosity of ADMMAPS copolymer

The data of intrinsic viscosity under the effect of



Scheme 4

Table 2 Effect of various monovalent cations on the viscosity behaviour of poly(ADMMAPS) at 30°C

Salt solution (0.5 M)	Slope × 100	[η] (dl g^{-1})	k'
LiCl	0.80	0.094 ± 0.86%	0.90
NaCl	0.80	0.101 ± 0.87%	0.78
KCl	0.50	0.098 ± 0.33%	0.52

Table 3 Effect of various divalent cations on the viscosity behaviour of poly(ADMMAPS) at 30°C

Salt solution (0.5 M)	Slope × 100	[η] (dl g^{-1})	k'
$MgCl_2$	0.06	0.106 ± 0.83%	0.05
$CaCl_2$	−0.08	0.116 ± 0.33%	−0.06
$SrCl_2$	0.10	0.113 ± 0.54%	0.08
$BaCl_2$	−0.10	0.114 ± 0.54%	−0.08

Table 4 Effect of various anions on the viscosity behaviour of poly(ADMMAPS) at 30°C

Salt solution (0.5 M)	Slope × 100	[η] (dl g^{-1})	k'
KF	0.90	0.083 ± 0.42%	1.31
KCl	1.00	0.094 ± 0.93%	1.13
KBr	0.10	0.110 ± 0.86%	0.08
KI	−0.30	0.122 ± 0.87%	−0.20

Table 5 Effect of various acidic groups on the viscosity behaviour of poly(ADMMAPS) at 30°C

Salt solution (0.5 M)	Slope × 100	[η] (dl g^{-1})	k'
CH_3COONa	−0.09	0.097 ± 1.29%	−0.10
$NaNO_2$	0.20	0.108 ± 0.37%	0.17
$NaNO_3$	0.00	0.111 ± 0.52%	0.00
$NaClO_3$	−0.10	0.114 ± 0.57%	−0.08
$NaClO_4$	−0.30	0.121 ± 1.18%	−0.20

Table 6 Effect of various divalent acidic groups on the viscosity behaviour of poly(ADMMAPS) at 30°C

Salt solution (0.5 M)	Slope × 100	[η] (dl g^{-1})	k'
Na_2CO_3	0.00	0.122 ± 0.74%	0.00
Na_2SO_3	0.00	0.099 ± 0.68%	0.00
Na_2SO_4	−0.10	0.099 ± 0.70%	−0.10
$Na_2S_2O_3$	−0.08	0.098 ± 0.52%	−0.08

various anions with a common cation (K^+) are shown in *Table 4*. The intrinsic viscosity in aqueous solution (0.5 M) shown in *Table 4* increases in the order $F^- < Cl^- < Br^- < I^-$ or KF, KCl, KBr and KI, respectively. The reason is that an ion with a small charge density is easily polarized as it approaches and becomes bound to the quaternary ammonium group (R_4N^+) on the ADMMAPS unit. The intrinsic viscosity hence increases with increasing degree of salt binding on the DMMAPS unit[34]. A similar tendency was also observed for various acidic groups (see *Table 5*) in the order $ClO_4^- > ClO_3^- > NO_3^- > NO_2^- > CH_3COO^-$ for $NaClO_4$, $NaClO_3$, $NaNO_3$, NaNo$_2$ and CH_3COONa, respectively. Because the acetate ion (CH_3COO^-) is a weakly acidic group that easily associates in forming acetic acid in aqueous solution, the ionic intensity is small and the intrinsic viscosity of the ADMMAPS was lower than that of any other anions in aqueous salt solution (0.5 M). These tendencies conform to the previous work[22,34,36].

For the various divalent acidic groups, the data (see *Table 6*) show a decrease of the intrinsic viscosity for ADMMAPS in 0.5 M aqueous salt solution in the order $CO_3^{2-} > SO_3^{2-} \approx SO_4^{2-} \approx S_2O_3^{2-}$ for Na_2CO_3, Na_2SO_3, Na_2SO_4 and $Na_2S_2O_3$, respectively. The reason is that the divalent acidic groups (SO_3^{2-}, or SO_4^{2-}, or $S_2O_3^{2-}$), with a large charge density and a high degree of ionization, were easily attracted to the neighbouring quaternary ammonium groups on the side chain of the ADMMAPS in aqueous solution. This attraction resulted in aggregation of the polymeric main chain and this diminished the expansion of the polymeric chain resulting from destruction of the ionically crosslinked network. In other words, it was concluded that strong intramolecular Coulombic attractions were the dominant factor in the solubility behaviour of poly(sulfobetaine)s in these divalent anions. This interesting phenomenon was also observed in previous studies on poly(DMAAPS)[34].

According to the Pearson theory, the quaternary ammonium group (R_4N^+) and sulfonate group (SO_3^-) on the DMMAPS unit of the ADMMAPS copolymer can be considered as a soft acid and a soft base, respectively. Thus soft bases (anions) from a salt (larger anionic radius) bind more easily to sites on the quaternary ammonium group (R_4N^+) on the DMMAPS unit of the copolymer than hard bases, and soft acids (cations) from a salt (larger cationic radius) bind more easily on the sulfonate group (SO_3^-) on the DMMAPS unit of the copolymer than hard acids. This result conforms to the Pearson principle that hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases (the hard species, both acids and bases, tend to be small, slightly polarizable species, whereas soft acids and bases tend to be large and greatly polarizable)[33,40]. These results also hold for poly(sulfobetaine)s derived from acrylates, acrylamides or vinylimidazoline, etc.[12-16,22,34].

Effect of salt concentration in aqueous solution on the intrinsic viscosity of ADMMAPS copolymer

If the above concept of chain expansion of the ADMMAPS copolymer when salt ions bind to the copolymer is correct, then the phenomenon of increased reduced viscosity with increased salt concentration might be rationalized. The effect of various concentrations of NaCl on the reduced viscosity of the ADMMAPS copolymer is illustrated in *Figure 2* and *Table 7*, respectively. The hydrodynamic volume of a polymer depends on the polymer–solvent interaction when the concentration of a polymer approaches zero. At this condition, the interaction between the polymers can be neglected. According to *Table 7*, there is a significantly increased reduced viscosity and intrinsic viscosity with increasing concentration of NaCl. The degree of salt attraction of the DMMAPS unit increased with increasing concentration of salt; that is, the amount of sodium ions (Na^+) binding to the sulfonate groups (SO_3^-) and chloride ions (Cl^-) binding to the quaternary ammonium groups (R_4N^+) increased at small concentration of salt (0–0.1 M). This occurrence diminishes the degree of ionic crosslinking of the network of the ADMMAPS copolymer and removes the entanglement of polymeric chains, thus expanding the copolymer. When the concentration of salt was increased to 0.1 M, more and more of the potential binding sites were increasingly occupied, resulting in a decreased tendency of site binding[22,26-31]. According to *Figure 2* and *Table 7*, the intrinsic viscosity increased and Huggins constant k' decreased when the salt concentration was increased from 0 M to 0.05 M (interchain association was disrupted). The reason is that the polymer and solvent interacted until the concentration of NaCl approached 0.05 M. At this concentration, the binding sites were increasingly occupied and formed a region of large local charge density. This concentration is called 'the concentration of saturated binding'. This phenomenon was also observed in poly(DMAAPS) and SDMMAPS aqueous salt solution reported in previous work[34,36]. Above this concentration, the Huggins constant k' increased because the interaction between polymeric side chains was increased. The stronger salt–polymer interaction caused disruption of intragroup association and made the polymeric main chain wind around the polymeric side chain at a large concentration of NaCl (3–5.0 M). When the concentration of NaCl exceeded 4.5 M, the ions became closer to the neighbouring side chain on the polymer chain, making the polymeric side chain twist. This behaviour makes the polymeric main chain bend and diminishes the intrinsic viscosity. This phenomenon was similar to the results for a cationic and anionic polyelectrolyte in aqueous solution of salts[28-31].

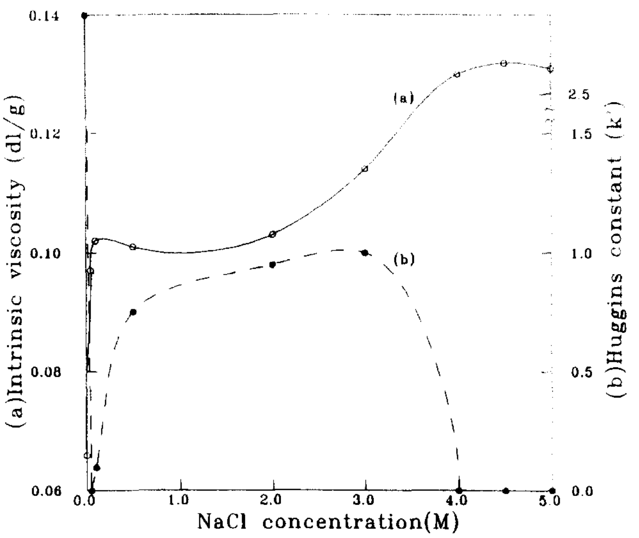


Figure 2 Intrinsic viscosity (a) and Huggins constant (b) of ADMMAPS copolymer as a function of concentration of NaCl

Table 7 Effect of NaCl concentrations on the intrinsic viscosity and percentage Huggins constant of poly(ADMMAPS) at 30°C

NaCl concentration (M)	Slope × 100	$[\eta]$ ($dl\,g^{-1}$)	k'
0.00	1.23	0.066 ± 1.77%	2.82
0.05	0.00	0.097 ± 0.93%	0.00
0.1	0.10	0.102 ± 1.03%	0.10
0.5	0.80	0.101 ± 0.86%	0.78
2.0	0.10	0.103 ± 1.03%	0.94
3.0	1.30	0.114 ± 0.57%	1.00
4.0	0.00	0.130 ± 0.77%	0.00
4.5	0.00	0.132 ± 0.52%	0.00
5.0	0.00	0.131 ± 0.40%	0.00

Thus, macroscopic viscosity measurements are consistent with a model for the ADMAPS copolymer that is intramolecularly associated in water or low-salt aqueous solutions. These intramolecular aggregates are of both the intragroup and intrachain type. Such intramolecular aggregates are broken up by external electrolytes (e.g. NaCl), with a consequent modest expansion of the polymer coil. Thus, the solution properties for sulfobetaine zwitterionic copolymer with acrylamide also confirm earlier trends reported for sulfobetaine zwitterionic homopolymers[11,14,15,33], and sulfobetaine zwitterionic copolymers with *N*-vinylpyrrolidone[17].

CONCLUSION

The novel sulfobetaine copolymer (ADMMAPS) derived from AA-MA copolymer has been synthesized. The aqueous solution behaviour for ADMMAPS is distinguished from other poly(sulfobetaine)s due to the presence of the acrylamide segment, a hydrophilic unit, on the ADMMAPS structure. The Huggins constant for the ADMMAPS in aqueous salt solution shows a marked distinction from the sulfobetaine copolymer (styrene–*N*,*N*-dimethylmaleimidopropylammoniumpropane sulfonate, SDMMAPS). This phenomenon is attributed mainly to the presence of the acrylamide/styrene segment, a hydrophilic/hydrophobic group, on the ADMMAPS/SDMMAPS copolymer, respectively. Additionally, the aqueous solution properties and behaviour for ADMMAPS are similar to those of other poly(sulfobetaine)s. The behaviour of an aqueous solution of ADMMAPS alters as salt is added to it.

When the radius of the salt ion is large, the degree of attraction of DMMAPS unit on the ADMMAPS for the salt and the intrinsic viscosity are increased. The intrinsic viscosity increased as the salt concentration is increased until the concentration of saturated binding of the salt is reached.

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