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Synthesis and solubility of the poly(sulfobetaine)s and the corresponding cationic polymers: 2. Aqueous solution properties of poly[*N,N'*-dimethyl-(acrylamido propyl) ammonium propane sulfonate]

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The properties of ampholytic poly[*N,N'* – dimethyl(acrylamido propyl) ammonium propane sulfonate] (poly(DMAAPS)) in aqueous solution were studied by measurements of cloud point determination and intrinsic viscosity. The minimum salt concentration and intrinsic viscosity of this polyampholyte were related to the type and concentration of added salt. 'Soft' salt cations and anions bound more easily to the quaternary ammonium (R_4N^+) and sulfonate groups (SO_3^-) of poly(DMAAPS) than 'hard' salt cations and anions. For the measurements of cloud point and intrinsic viscosity in aqueous salt solution of various divalent acidic groups, the divalent acidic groups ruptured the ionically crosslinked network of sulfobetaine at a small concentration of salt and the divalent acidic groups attracted the neighbouring polymeric side chains to make the polymeric main chains twist and agglomerate. A similar degree of expansion of the polymeric main chain at the saturated binding concentration of various monovalent salts (LiCl, NaCl, KCl) was observed from measurement of intrinsic viscosity.

(Keywords: sulfobetaine; intrinsic viscosity; ampholyte)

INTRODUCTION

The ampholytic monomers of sulfobetaines derived from dimethylaminoalkyl acrylates and dimethylaminoalkyl acrylamides have been widely used in industry concerned with textiles, medical products, charged dispersing agents, protective colloids, and other related materials[1–9]. These ampholytic monomers of two types are sulfobetaines and carboxybetaines[10–25]. Asonova *et al.* reported the synthesis of carboxybetaine and its polymeric aqueous properties[11,12]. The syntheses of sulfobetaine and cationic electrolytes derived from acrylate, acrylamide, pyridinium acrylate, pyridinium acrylamide and vinyl pyridinium were reported by Laschewsky and Zerbe[17] and by Galin, Monroy Soto and coworkers[18,19], respectively. They also studied the bulk and surface activity and properties in aqueous solution of such polymers. The synthesis and solution properties of poly(sulfobetaine)s were examined by Salamone and coworkers, especially in the vinylimidazole series[20–22]. The solution properties of copolymers of cationic and anionic electrolytes were also investigated[26–35]. Salamone *et al.* investigated ampholytic ion-pair comonomers of cationic and anionic electrolytes, the mechanism of polymerization of comonomers and the properties of these copolymers in aqueous solution[33–35].

During studies[36–41] of binding interaction of salt ions and polymers according to the Huggins equation and Huggins constant k', the counterion size was found to affect the degree of binding for salt-ion-attracting polymers[12,18–25,42]; i.e. 'soft' salt anions and cations are more effective solubilizers than 'hard' anions and cations[43,44]. The divalent acidic groups rendered the polymeric aqueous solution turbid in the present article; this phenomenon was similar to the behaviour of the corresponding cationic polymer, poly(trimethyl acrylamido propyl ammonium iodide) (poly(TMAAI)), in aqueous solution[45]. The difference of aqueous solution properties between poly(sulfobetaine) (poly(DMAAPS)) and cationic polyelectrolyte (poly(TMAAI)) is also interesting. In this paper the aqueous solution properties of poly(DMAAPS), especially the intrinsic viscosity in the presence of various salts, is discussed.

EXPERIMENTAL

Preparation of N,N'*-dimethyl(acrylamido propyl) ammonium propane sulfonate (DMAAPS)*

The monomer DMAAPS was prepared as described previously[16]. The monomer, characterized by elemental analysis and ^1H and ^{13}C n.m.r. spectra, was hygroscopic (m.p.: 105°C, yield: 92%).

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Preparation of poly [N,N′-dimethyl(acrylamido propyl) ammonium propane sulfonate] (poly(DMAAPS))

The polymer poly(DMAAPS) was prepared as described previously[16]. The dried, brittle, white polymer was obtained in 93% yield (T_g: 141.5°C).

Cloud point determinations

Poly(DMAAPS) (0.1 g) was dissolved in an appropriate aqueous salt solution (10 ml). Cloud point titrations to determine the point at which the polymer solution becomes insoluble in the aqueous salt solution (25 ± 5 ml) were performed by dissolving the material in an aqueous salt solution with sufficient salt content and titrating the stirred solution with deionized water to the first indication of turbidity. For divalent acidic groups in aqueous salt solution, the aqueous solution of polymer that was turbid at a high concentration of salt was titrated with deionized water until the solution became clear to obtain the salt concentration.

Viscometric measurements

Viscometric measurements were carried out with an Ubbelohde viscometer (flow time 76.23 s for pure water) at 30.00 ± 0.01°C. The polymer samples were dissolved in salt solutions of varying concentration to yield stock solutions of approximately 0.8 g polymer per 100 ml solvent.

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

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

where η_{sp} is the specific viscosity, C is the concentration of polymer, $[\eta]$ is the intrinsic viscosity, and k' is the Huggins constant.

RESULTS AND DISCUSSION

Determination of cloud point

The monomer DMAAPS was hygroscopic and soluble only in water, not in organic solvents. Poly(DMAAPS) was insoluble in water and became a transparent gel in aqueous solution. The group of positive charge on the poly(DMAAPS) attracted the group of negative charge to form an ionically crosslinked network that made the polymer gel in aqueous solution. For this reason, salts were added to this polymeric aqueous solution to make it dissolve.

In aqueous salt solution of poly(DMAAPS), the cation (or anion) of the salt was attracted to a binding site on the sulfonate group (SO_3^-) (or quaternary ammonium group (R_4N^+)) of poly(DMAAPS) thereby collapsing the ionically crosslinked network and expanding the polymeric chain; the poly(DMAAPS) then dissolved in the aqueous salt solution[17–25]. The greater the capability of poly(DMAAPS) for attracting salt, the greater the expansion of the polymeric chain, and the smaller the quantity of a salt needed to make poly(DMAAPS) dissolve in aqueous solution.

For salt solutions containing a common anion (Cl^-) but varied cations, the data presented in *Table 1* show that the solubility of poly(DMAAPS) in aqueous salt solution increased in the order $Li^+ < NH_4^+ < Na^+ < K^+$ and $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$ for LiCl, NH_4Cl, NaCl, KCl and $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, respectively. These trends indicate that a small ionic radius is accompanied by a small attraction to poly(DMAAPS). A similar tendency was observed for the binding of these cations to polyelectrolytes containing pendent sulfonate groups, with the potassium ion (barium ion) being bound most strongly and the lithium ion (magnesium ion) being bound most weakly[17,24,25,39–43].

The cloud points of the polymer solutions containing salts with a common cation (K^+) but varied anions appear in *Table 2*. For these salts, the data indicate increased solubility of the polymer in the order $Cl^- < Br^- < I^- < ClO_4^-$ for KCl, KBr, KI and $KClO_4$, respectively. Anions with smaller ratio of charge to radius were more easily bound on the quaternary ammonium (R_4N^+) of poly(DMAAPS), because such larger anions are more easily polarized. Larger anions, therefore, easily infiltrated into the ionically crosslinked network of poly(DMAAPS) and expanded the polymeric chain.

For the acidic groups, the data shown in *Table 2* exhibit increased solubility of poly(DMAAPS) in aqueous salt solution in the order $ClO_4^- > NO_3^- > NO_2^- > SO_4^{2-} > CH_3COO^-$ for $NaClO_4$ ($KClO_4$), KNO_3, $NaNO_2$, Na_2SO_4 and CH_3COONa, respectively. This tendency resembled that of the monovalent common cations (varied anions). The neighbouring quaternary ammonium groups on the side chain of poly(DMAAPs) were easily attracted by the sulfate ion (SO_4^{2-}) in aqueous solution. This attraction resulted in coagulation of the polymeric main chain, and this occurrence diminished the polymeric chain expansion resulting from destruction of the ionically crosslinked network[22,24]. Because the acetate ion (CH_3COO^-) is a weakly acidic group easily associated to form acetic acid in aqueous solution, the ionic intensity is small and the minimum salt concentration is large (see *Table 2*).

Table 1 Minimum concentration of salt for poly(DMAAPS) in salt solutions with a common anion (25°C)

Salt	Minimum concentration of salt ($\times 10^{-2}$ M)
NH_4Cl	4.09
LiCl	4.26
NaCl	3.60
KCl	3.57
$MgCl_2$	2.81
$CaCl_2$	2.44
$SrCl_2$	2.27
$BaCl_2$	2.08

Table 2 Minimum concentration of salt for poly(DMAAPS) in salt solutions with a common cation (25°C)

Salt	Minimum concentration of salt ($\times 10^{-2}$ M)
KCl	3.60
KBr	2.08
KI	0.94
$NaClO_4$	0.77
$KClO_4$	0.86
KNO_3	2.86
$NaNO_2$	3.80
Na_2SO_4	4.48
CH_3COONa	22.11

According to the above results and discussion, those cations (anions) with a large radius bind easily to the sulfonate (quaternary ammonium) group of poly(DMAAPS). 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)[43,44].

A range of concentration of transparent polymer solutions was found for salts with a common cation but varied divalent acidic groups (*Table 3*). For sodium salts, the data indicate increased solubility of the polymer in the order $SO_3^{2-} < SO_4^{2-}$ for Na_2SO_3 and Na_2SO_4, respectively, similar to the monovalent common cations (*Table 2*).

When the concentration of salt was increased in the small ranges of concentration, potential binding sites were increasingly occupied and the polymeric chain increasingly expanded. However, the polymeric chain exhibited turbidity until a large concentration of divalent acidic groups was reached. This turbidity was similar to that of cationic and anionic polyelectrolytes at large concentrations of salt in aqueous solution (a result proved from the measurement of viscosity).

Although the aqueous solution was turbid during the measurement of the cloud point for Na_2CO_3 and $Na_2S_2O_3$, polymer aqueous salt solutions at nearly the same range of concentration of salt were clear. This interesting phenomenon is explained by the greater concentration of salt enhancing binding of the salt on poly(DMAAPs) to expand the polymeric chain.

Table 3 Range of transparency of poly(DMAAPS) in salt solutions with various acidic groups (25°C)

Salt	Maximum concentration of salt (M)	Minimum concentration of salt (M)
Na_2SO_4	0.71	4.48×10^{-2}
Na_2SO_3	0.35	12.76×10^{-2}
$Na_2S_2O_3$	Turbidity (0.04)	Turbidity (0.02)
Na_2CO_3	Turbidity (0.04)	Turbidity (0.01)
$BaCl_2$	Turbidity (0.03)	Turbidity (0.02)

Viscosity measurement

The intrinsic viscosity is a good measure of hydrodynamic volume of polymer containing the same molar mass. Poly(DMAAPS) is an ampholytic polymer in which binding of the sulfonate group (SO_3^-) with the quaternary ammonium group (R_4N^+) forms an ionically crosslinked network that gels the polymer. Salts are added to these polymeric aqueous solutions in order to make this polymer dissolve in water. When there is a greater attraction of the salt for poly(DMAAPS), the polymeric chain becomes expanded and intrinsic viscosity increases. Therefore determination of the intrinsic viscosity of poly(DMAAPS) in the presence of different electrolytes reflects the influence of these salts on the hydrodynamic volume of the polymer chain. It is the characteristic of polyelectrolytes that the reduced viscosity increases with decreasing concentration of polymer at low polymer concentrations, because there is enough space to expand the polymeric chains owing to the mutual repulsion of charges on the side chains. At lower concentrations of polymer, the mutual attraction between positive and negative charges causes bending of the polymeric main chains to decrease the reduced viscosity (*Figure 1A*).

Influence of cations with a common anion on intrinsic viscosity of poly(DMAAPS). The influence of various electrolytes having a common anion (Cl^-) on the intrinsic viscosity of poly(DMAAPS) is shown in *Figures 1* and *2* and *Table 4*. The data show increased intrinsic viscosity of poly(DMAAPS) in aqueous salt solution (0.5 M) in the orders $NH_4^+ < Li^+ < Na^+ < K^+$ for NH_4Cl, LiCl, NaCl and KCl, and $Mg^{2+} < Ca^{2+} \simeq Sr^{2+}$ for $MgCl_2$, $CaCl_2$ and $SrCl_2$. This phenomenon is similar to the result of cloud point determination (*Table 1*). The result indicates that ions with a small density of charge easily infiltrate the sulfonate of the ionically crosslinked network of

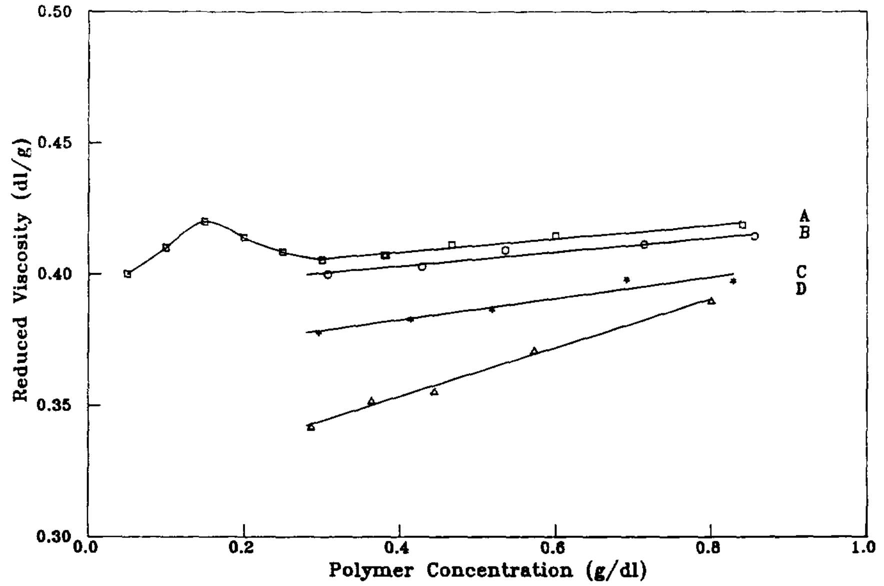

Figure 1 Reduced viscosity of poly(DMAAPS) as a function of concentration for salts containing a common anion: (A) 0.5 M KCl; (B) 0.5 M NaCl; (C) 0.5 M LiCl; (D) 0.5 M NH_4Cl

poly(DMAAPS) to rupture this network. The slope, intrinsic viscosity and Huggins constant *k'* (*Table 4*) are calculated by means of *Figures 1* and *2* and equation (1). The value of the Huggins constant decreases with increased intrinsic viscosity. The decreased Huggins constant is associated with an increased interaction between polymer and solvent, which was reaffirmed by the cloud point determinations (*Table 1*)[22,24,37,38].

Table 4 Effect of various cations on the viscosity of poly(DMAAPS) at 30°C

Salt solution (0.5 M)	Slope	$[\eta]$ (dl g^{-1})	*k'*
NH_4Cl	0.09	0.32	0.90
LiCl	0.04	0.37	0.29
NaCl	0.02	0.39	0.16
KCl	0.02	0.40	0.15
$MgCl_2$	0.11	0.50	0.45
$CaCl_2$	0.14	0.55	0.48
$SrCl_2$	0.16	0.54	0.53

Influence of anions with a common cation on intrinsic viscosity of poly(DMAAPS). The data of intrinsic viscosity under the influence of various anions with a common cation (K^+) are shown in *Figure 3* and *Table 5*. In aqueous salt solution (0.5 M) the intrinsic viscosity increases in the order $Cl^- < Br^- < I^-$ for KCl, KBr and KI, respectively. The reason is that the ion with a small density of charge is easily polarized as it approaches and becomes bound to the quaternary ammonium (R_4N^+) of poly(DMAAPS). Hence, the intrinsic viscosity increased and the Huggins constant (*k'*) decreased with increasing degree of salt binding on poly(DMAAPS). A similar tendency was observed from the varied acidic groups (*Figure 4*, *Table 6*) in the order $CH_3COO^- < SO_4^{2-}$

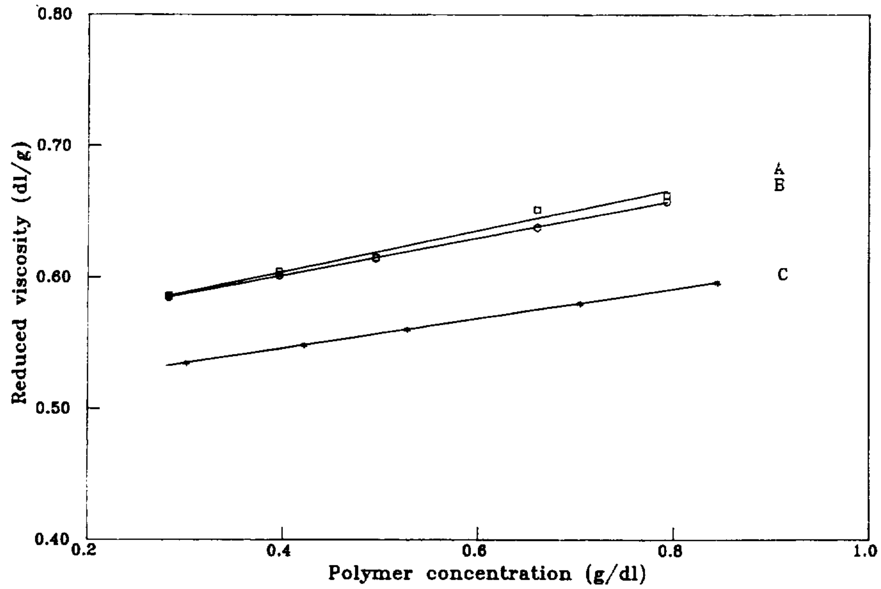

Figure 2 Reduced viscosity of poly(DMAAPS) as a function of concentration for salts containing a common anion: (A) 0.5 M $SrCl_2$; (B) 0.5 M $CaCl_2$; (C) 0.5 M $MgCl_2$

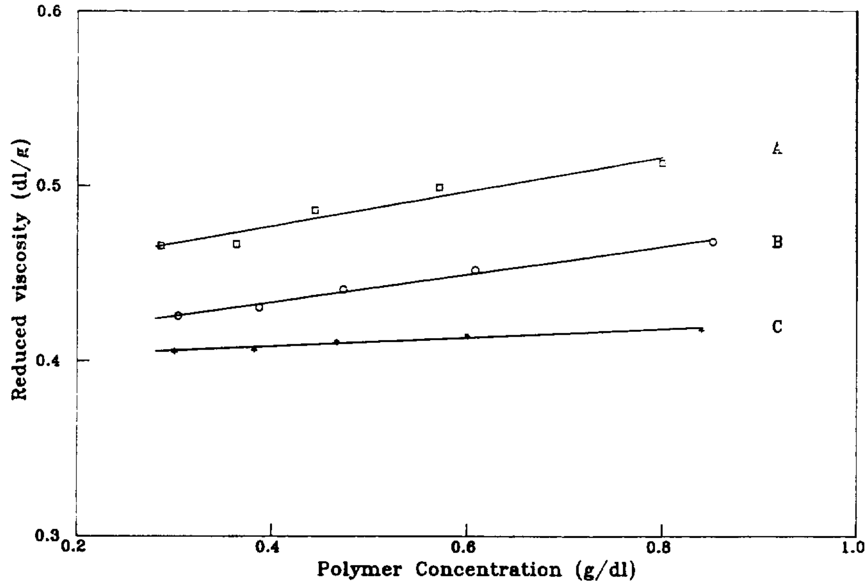

Figure 3 Reduced viscosity of poly(DMAAPS) as a function of concentration for salts containing a common cation: (A) 0.5 M KI; (B) 0.5 M KBr; (C) 0.5 M KCl

Table 5 Effect of various anions on the viscosity of poly(DMAAPS) at 30°C

Salt solution (0.5 M)	Slope	$[\eta]$ (dl g^{-1})	k'
KCl	0.02	0.40	0.15
KBr	0.08	0.40	0.48
KI	0.10	0.44	0.51

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

Salt solution (0.5 M)	Slope	$[\eta]$ (dl g^{-1})	k'
$NaNO_3$	0.04	0.57	0.12
$NaClO_4$	0.18	0.64	0.43
Na_2SO_4	0.07	0.29	0.85
$NaNO_2$	0.08	0.51	0.29
CH_3COONa	0.05	0.29	0.58

$< NO_2^- < NO_3^- < ClO_4^-$ for CH_3COONa, Na_2SO_4, $NaNO_2$, $NaNO_3$, and $NaClO_4$, respectively. The sulfate group (SO_4^{2-}), with a large charge density, was easily attracted to the neighbouring quaternary ammonium groups on the side chain of poly(DMAAPS) in aqueous solution. This attraction resulted in coagulation of the polymer and this occurrence diminished expansion of the polymer resulting from destruction of the ionically crosslinked network. Because the acetate ion (CH_3COO^-) is a weakly acidic group that easily associates to form acetic acid in aqueous solution, the ionic intensity is small and the intrinsic viscosity of poly(DMAAPS) was greater than that of any other anions in aqueous salt solution (0.5 M). These tendencies resemble those of cloud point determination (*Table 2*).

The results and discussion from cloud point and intrinsic viscosity correspond to Pearson's principle in *Tables 1–5* and *Figures 1–4*. The quaternary ammonium group (R_4N^+) and sulfonate group (SO_3^-) on the

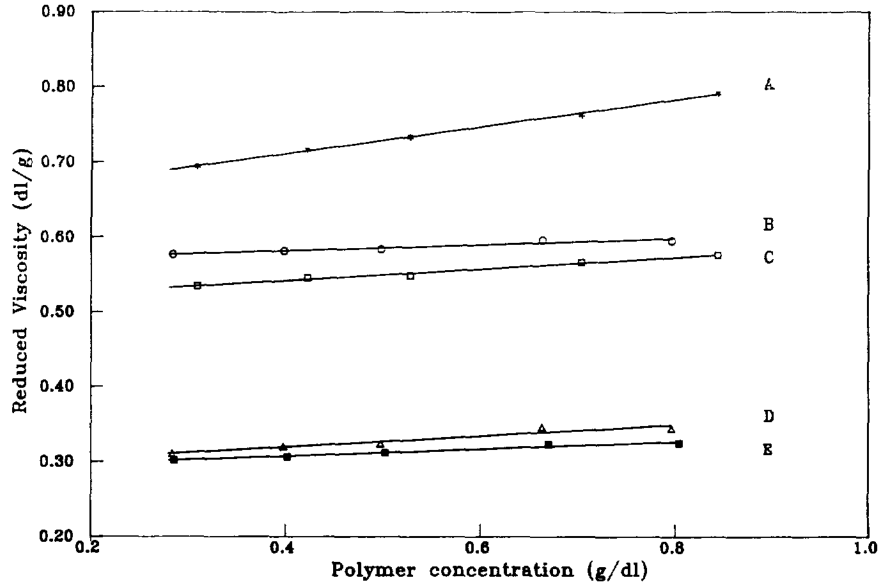

Figure 4 Reduced viscosity of poly(DMAAPS) as a function of concentration for acids: (A) 0.5 M $NaClO_4$; (B) 0.5 M $NaNO_3$; (C) 0.5 M $NaNO_2$; (D) 0.5 M Na_2SO_4; (E) 0.5 M CH_3COONa

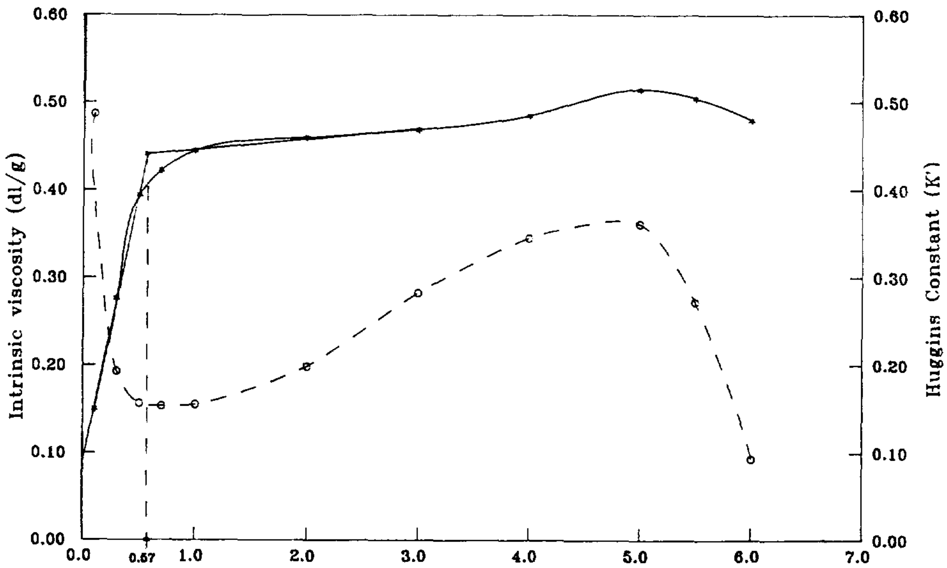

Figure 5 Intrinsic viscosity (★) and Huggins constant k' (○) of poly(DMAAPS) as a function of concentration of NaCl

poly(DMAAPS) behave 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 of poly(DMAAPS) than hard bases, and soft acids (cations) from a salt (larger cationic radius) bind more easily on the sulfonate group of poly(DMAAPS) than hard acids.

Effect of salt concentration in aqueous solution on intrinsic viscosity of poly(DMAAPS). If the above concept of chain expansion of the poly(sulfobetaine) when salt ions bind to the polymer is correct, then the phenomenon of increased reduced viscosity with increased salt concentration might be rationalized. The effect of various concentrations of NaCl on intrinsic viscosity of poly(DMAAPS) is illustrated in *Figure 5*. There is a significantly increased reduced viscosity and intrinsic viscosity with increasing concentration of NaCl.

When the salt concentration is increased, some of the positive and negative ions of the salt bind to sites on the sulfonate and quaternary ammonium groups of the poly(DMAAPS). The polymeric charges are neutralized by the remaining counterions in aqueous solution. This occurrence diminishes the degree of ionically crosslinked network of poly(DMAAPS) and removes the entanglement of the polymeric chain, thus expanding it. The hydrodynamic volume of a polymer depends on the polymer–solvent interaction when the polymer concentration approaches zero. At this condition, the polymer–polymer interaction can be neglected. According to *Figure 5* and *Table 7*, the degree of salt attraction of poly(DMAAPS) increased with increasing concentration of salt; that is, the amount of sodium ions binding to the sulfonate groups and chloride ions binding to the quaternary ammonium groups increased at small concentrations of salt (0.1–0.5 M). When the concentration of salt was increased to 0.57 M, more and more of the potential binding sites were increasingly occupied, resulting in a decreased tendency of site binding[24,36–41]. When the concentration of NaCl exceeded 5.5 M, the ions became closer to the neighbouring side chain on the polymer, making the polymeric side chain twist. This behaviour makes the polymeric main chain bend and diminishes the intrinsic viscosity. This phenomenon was similar to that reported for cationic and anionic polyelectrolyte in aqueous solutions of salts[38–41].

According to *Figure 5* and *Table 7*, the intrinsic viscosity increased and the Huggins constant *k′* decreased when the salt concentration was increased from 0.1 to 0.57 M. The reason is that the polymer and solvent interacted until the concentration of NaCl approached 0.57 M. At this concentration, the binding sites were increasingly occupied and formed a region of large local density of charge. This concentration of salt is called 'the concentration of saturated binding'. Above this concentration, the Huggins constant *k′* increased because the interaction between polymeric side chains increased. The stronger salt–polymer interaction made the polymeric main chain wind around the polymeric chain at a large concentration of NaCl (5.5 M), so decreasing the Huggins constant *k′* (refs 36 and 37).

A comparison between the concentration of saturated binding of LiCl, NaCl and KCl appears in *Table 8*. The

Table 7 Effect of concentration of NaCl on the viscosity of poly(DMAAPS) at 30°C

Concentration (M)	Slope	[η] (dl g^{-1})	*k′*
6.00	0.02	0.50	0.09
5.50	0.07	0.53	0.27
5.00	0.10	0.54	0.36
4.00	0.08	0.49	0.35
3.00	0.06	0.47	0.28
2.00	0.04	0.46	0.20
1.00	0.03	0.44	0.16
0.75	0.03	0.42	0.15
0.50	0.02	0.39	0.16
0.25	0.01	0.28	0.19
0.10	0.01	0.15	0.49

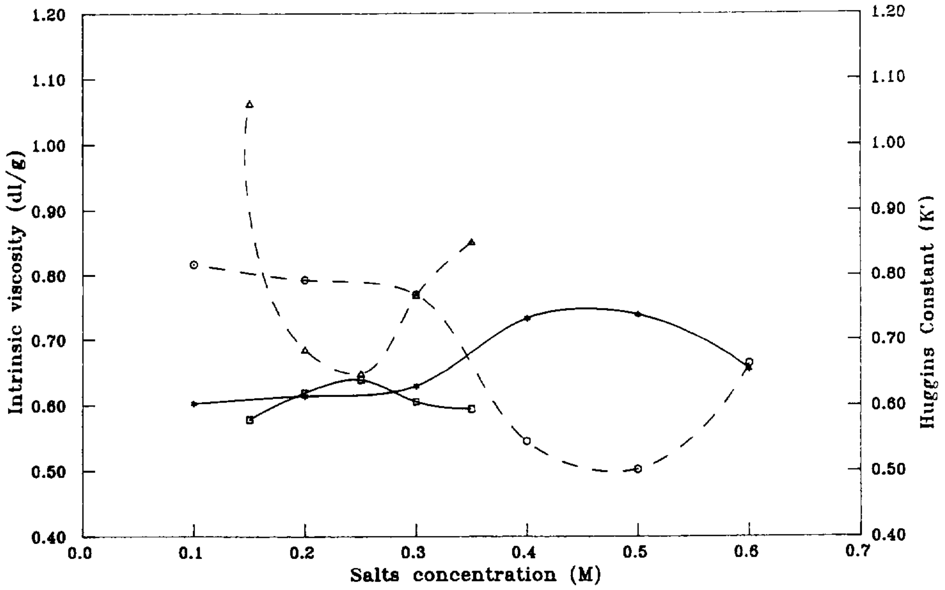

Figure 6 Intrinsic viscosity (★, □) and Huggins constant *k′* (○, △) of poly(DMAAPS) as a function of concentration of Na_2SO_4 (★, ○) and Na_2SO_3 (□, △)

stronger the salt–polymer interaction, the smaller the concentration of salt that bound; the concentration of saturated binding was in the order LiCl > NaCl > KCl. The hydrodynamic volumes of polymer were similar at the concentration of saturated binding in aqueous solutions of LiCl, NaCl and KCl; hence the intrinsic viscosities at these concentrations of saturated binding of the various salts were similar.

Recoil of polymeric chain in some salt aqueous solutions. For the measurement of cloud point, the polymeric solution was turbid in some ranges of concentration of salts such as Na_2SO_3, Na_2SO_4, $Na_2S_2O_3$ and Na_2CO_3. This interesting phenomenon appeared also in the viscometric measurement at large concentrations of NaCl. The intrinsic viscometric measurement was a good measure of the hydrodynamic volume of the polymer containing the same molecule in the clear range of polymeric aqueous Na_2SO_3 and Na_2SO_4 solutions (intrinsic viscosity could not be measured because the aqueous solution of poly(DMAAPS) was turbid in aqueous $Na_2S_2O_3$ and Na_2CO_3 solution). According to *Figure 6* and *Table 9*, there was a significantly increased reduced viscosity and intrinsic viscosity as the concentration of Na_2SO_4 and Na_2SO_3 increased. This result indicates that the salt–polymer interaction increased as the ionic intensity increased. When the Na_2SO_4 (Na_2SO_3) concentration increased to 0.45 M (0.25 M), the salt ions pulled closer to the neighbouring side chain on poly(DMAAPS); the polymeric side chain became entangled and the polymeric chain underwent coagulation until the concentration of Na_2SO_4 (Na_2SO_3) was 0.71 M (0.35 M), the point of turbidity of the polymeric aqueous solution. This explanation is consistent with the fact that k' decreased (increased) as the salt was increased (decreased). The Huggins constant k' is generally considered to be related to the polymer–solvent interaction.

Table 8 Effect of salt on the concentration of saturated binding and intrinsic viscosity of poly(DMAAPS) at 30°C

Salt solution	Concentration of saturated binding (M)	Intrinsic viscosity at saturated binding ($dl g^{-1}$)
LiCl	0.62	0.44
NaCl	0.59	0.45
KCl	0.41	0.43

Table 9 Effect of concentration of Na_2SO_4 and NA_2SO_3 on the viscosity of poly(DMAAPS) at 30°C

Salt	Concentration (M)	Slope	$[\eta]$ ($dl g^{-1}$)	k'
Na_2SO_4	0.60	0.29	0.66	0.66
	0.05	0.27	0.74	0.50
	0.40	0.29	0.73	0.55
	0.30	0.31	0.63	0.77
	0.20	0.30	0.62	0.79
	0.10	0.30	0.60	0.81
Na_2SO_3	0.35	0.30	0.59	0.85
	0.30	0.28	0.61	0.77
	0.25	0.27	0.64	0.65
	0.20	0.26	0.62	0.69
	0.15	0.36	0.58	1.06

CONCLUSIONS

The behaviour of an aqueous solution of the polyampholyte poly(DMAAPS) alters as salt is added to it. When the radius of the salt ion is large, the degree of attraction of poly(DMAAPS) for the salt and the intrinsic viscosity are increased. The Huggins constant k' is affected by polymer–solvent and polymer–polymer interactions. The intrinsic viscosity increases as the salt concentration is increased until the concentration of saturated binding of the salt is reached. The polymeric chain agglomerates at large concentration of divalent ion and the intrinsic viscosity decreases.

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