

# Synthesis and viscometric properties of low charge density ampholytic ionomers

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The addition of ionic groups onto the molecular structure of a macromolecule produces marked changes in its physical properties. A large volume of literature exists pertaining to the solution and solid phase properties of these charged species spanning a broad range of charge densities. Until recently, however, little work has been published on ionomers containing opposite charges (i.e., polyampholytes) except with regard to highly charged species. In this study, we focus on the synthesis and solution properties in fresh and high ionic strength solutions of low charge density acrylamide-based polyampholytes not necessarily possessing an equimolar ratio of anionic and cationic units. The results show that the separation of these oppositely-charged monomer units via neutral acrylamide moieties establishes a control over physical properties not readily attainable in the highly-charged polyampholytes (generally insoluble in fresh water) or conventional polyelectrolytes.

At low charge densities, typically < 10 mole per cent, the solution properties of these polyampholytes are controlled primarily through intermolecular interactions. That is, gel-like properties are observed above the chain overlap concentration in fresh water due to the anionic-cationic interactions. As a result the viscosity decreases as the ionic strength of the solution is increased. Interestingly, at moderate charge densities, generally 10 mole per cent or higher, intramolecular interactions dominate behaviour in fresh water. As a result, the dilute solution viscosity in fresh water is relatively low, but is markedly enhanced as the ionic strength of the solution is increased. That is, gel-like properties are approached as the chains expand and begin to overlap. Moreover, these results are influenced by the nature of the chain backbone, molecular weight, the chemistry of the dissolved salt, and the level of mobile charge situated on the chain backbone.

(Keywords: polyampholyte; anionic-cationic charge; acrylamide; viscosity; ionic strength; polyelectrolyte)

## INTRODUCTION

The placement of ionic groups into a polymer chain profoundly influences its physical properties in both the solid phase and in solution. In most instances, these changes can be correlated with the structure and concentration of the ionic groups attached to the polymer chain. In aqueous solutions, these groups will ionize, resulting in expansion of the chain due to electrostatic, repulsive forces. This is a common feature of most polyelectrolyte solutions<sup>1</sup>. A corresponding increase in solution viscosity is reflected in this increase in chain dimensions. Interestingly, dissolution of a simple electrolyte shields the repulsive forces producing a diminution in the hydrodynamic extension of the chain even at low charge density<sup>2</sup>. Numerous studies have detailed the viscosity behaviour of these materials<sup>1</sup>. In general, these polymers possess a homogeneous ionic charge.

It has been recognized, however, that polymers containing acid and base groups (i.e., polyampholytes) exhibit complex solution behaviour in acidic and basic media<sup>3-7</sup>. Typically, the above copolymers are readily soluble below and above their isoelectric point, but totally insoluble at the isoelectric point<sup>3,4</sup>. The location of this point is determined by the acid/base ratio in the copolymer<sup>8</sup>. It was further noted that the viscosity increased on both sides of the isoelectric point, which is attributed to the

uncoiling of the polymer chain caused by the electrostatic repulsions of the net charge carried by the copolymer. The viscosity behaviour in acid solution is similar to a cationic polymer, while in alkaline solutions the behaviour is similar to an anionic copolymer<sup>4</sup>. However, relatively little work focused on the viscometric behaviour in neutral salt solutions. Hart *et al.*<sup>9</sup> examined the viscosity and solubility of the butylsulphobetaine of poly(4-vinylpyridine). This ampholyte, though insoluble in water at any pH, became soluble with the addition of a neutral salt at all pH values. Furthermore, a critical salt concentration was required to dissolve the polymer, independent of the polymer level. The specific salt concentration depended directly on the nature of the salt with the results following the Hofmeister series. Detailed investigation of the aqueous solution properties of a poly(vinyl imidazolium sulphobetaine) confirms these findings<sup>10</sup>. The above results on these and other polyampholytes<sup>11-18</sup> appear to describe the general behaviour of these materials.

More recently, Salamone *et al.*<sup>19-24</sup> reported on a new class of polyampholytes which have positive and negative charges on two pendent groups situated along the chain backbone. These materials were synthesized via a zwitterionic monomeric salt in which both the anionic and cationic components were polymerizable. The new salts were termed ion-pair comonomers<sup>20</sup>. It was pointed out that each vinyl moiety is the counterion to its oppositely

charged counterpart whereby each individual unit is polymerizable. These salts do not have nonpolymerizable counterions present. A variety of novel polyampholytes<sup>21,22</sup>, copolymers, ampholytic polystyrene<sup>21,23</sup>, and acrylamide ionomers<sup>24</sup> were formed utilizing a free radical polymerization approach in aqueous solution. In all instances, the composition of these polymers contain equimolar concentrations of anions and cations, although these charged species may not be necessarily located on the same chain backbone. The possibility does exist that a predominance of one charge over another can occur giving an individual polymer chain an overall charge. However, the overall charge of the system is neutral in averaging over many macromolecules. That is, a single chain is effectively 'self-neutralized', since for every positive charge there exists a negatively-charged counterpart. When these groups dissociate, they are incapable of escaping from the vicinity of the chain into the bulk solution. Although relatively few extensive studies can be found, a review of the literature indicates that these materials may possess interesting solution and possibly solid state properties. As detailed earlier, an interesting consequence of this molecular structure is the ability to readily dissolve and viscosity aqueous solutions containing relatively high levels of acid, base or salt.

This paper describes the viscometric properties of several families of polyampholytes possessing dissimilar charge ratios. Depending on the initial monomer concentration, the overall charge can be either cationic or anionic in a salt-free environment. In the first case, polyampholytes composed of methacrylamidopropyltrimethylammonium chloride (MAPTAC) and sodium styrene sulphonate (SSS) or sodium vinyl sulphonate (SVS) were synthesized. These high charge density materials can serve as a base for understanding the viscometric behaviour of anionic and cationic units 'separated' by neutral monomers, i.e., acrylamide (AM) along the chain. As we shall see, similarities do exist between these ampholytic materials; however, marked differences in the solution behaviour are observed between these materials and typical homogeneously-charged polyelectrolytes. These differences become quite pronounced as the charge concentration and distribution, molecular weight, and the nature of the added inorganic solutes are varied.

## EXPERIMENTAL

Two series of polyampholytes were synthesized for this study. The first material is essentially a high charge density copolymer composed of the cationic monomer, methacrylamidopropyltrimethylammonium chloride (MAPTAC) (Texaco Chemical Company) and the anionic monomers, sodium styrene sulphonate (SSS) (Air Products Corporation) or sodium vinyl sulphonate (SVS) (Polysciences, Inc.). The copolymer was prepared by direct polymerization of the two monomers using a free radical initiator. An aqueous solution of MAPTAC and SSS (or SVS) with their corresponding nonpolymerizable counterions was stirred for approximately one hour under a nitrogen blanket at room temperature. Typical initial monomer concentrations, dissolved in 300 ml of distilled water, are shown in *Table 1* (polymers 1 and 2). The monomers constituted ~10 wt% of the solution. The catalyst, potassium persulphate, was then added (typically 0.05 g), and the solution temperature adjusted to 50°C.

The temperature was continually monitored throughout the course of the polymerization (24 h). In all instances, the polymerization temperature did not exceed 60°C. In addition, the solution was continually stirred and kept under a nitrogen blanket during the entire course of the reaction. Subsequently, the polymer was precipitated from solution with a large excess of ethanol. The sample was then dissolved into deionized water, reprecipitated with ethanol, and dried in a vacuum oven at 60°C for 24 h. In some instances, this washing procedure was continued through several more cycles with insignificant change in properties.

The MAPTAC monomer contains an inhibitor which was removed by vigorously agitating 3% (by weight) activated charcoal into the aqueous solution for 24 h and subsequently filtering the mixture through standard Whatman filter paper. It was found that only a small amount of the MAPTAC monomer is adsorbed from solution.

The composition of these ampholytic polymers (polymers 1 and 2 in *Table 2*) was determined by nitrogen, sodium, chlorine and sulphur elemental analysis. The results show that the MAPTAC-co-SSS contained 6 mol% sodium neutralized sulphonated styrene, while MAPTAC-co-SVS contained 20 mol% sodium neutralized vinyl sulphonate. That is, these materials were not completely self-neutralized.

The acrylamide (AM) based low charge density polyampholytes (see *Figure 1*) were synthesized by an aqueous solution polymerization using a free radical initiator. The specific reaction conditions are equivalent to those described previously. Typical initial monomer concentrations are presented in *Table 1*. Again the MAPTAC, SSS and AM monomers are dissolved in 300 ml distilled water.

Elemental analysis shows that these materials are not completely self-neutralized (see *Table 2*). The general structure is shown in *Figure 1*. Typically, B and C (as defined in *Figure 1*) are present in their stoichiometric amounts, while 'residual' sodium (X) or chloride (Y) ions of the respective monomers are still present within the polymer structure. The exact amount of these latter ions are a direct function of both the initial monomer concentrations and their corresponding reactivity ratios. The specific details are clearly shown in a comparison of the data in *Tables 1* and *2*.

Under these polymerization conditions<sup>25</sup>, the acrylamide-based polyampholytes are probably linear with no indication of bimodality in the molecular weight distribution and, more importantly, the hydrolysis of the amide bonds is insignificant.

**Table 1** Initial monomer concentrations\* (mole per cent)

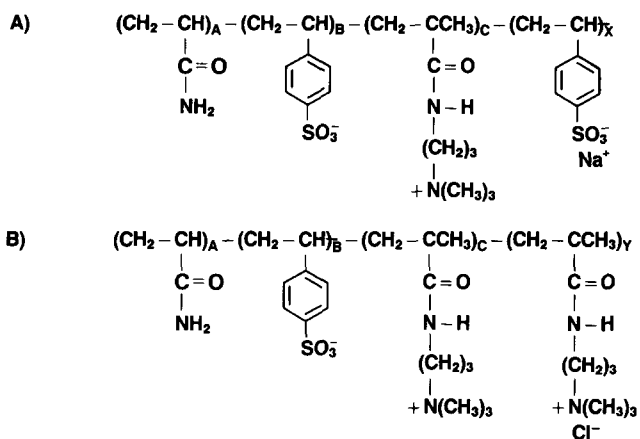
Sample	AM(A)	SSS(X)	MAPTAC(Y)	SVS
1	---	50.0	50.0	---
2	---	---	50.0	50.0
3	95.0	2.5	2.5	---
4	90.0	5.0	5.0	---
5	80.0	10.0	10.0	---
6	70.0	15.0	15.0	---
7	60.0	40.0	---	---
8	90.0	---	10.0	---

\* See *Figure 1* for the appropriate definition of the symbols used in this Table

**Table 2** Acrylamide polyampholyte compositions\* (mole per cent)

Designation	A	B+C	X	Y
1	--	94.0	6.0	--
2	--	80.0 (SVS MAPTAC)	20.0 (SVS)	--
3	95.1	3.7	1.2	--
4	90.2	7.7	2.1	--
5	83.4	12.3	4.34	--
6	70.1	22.6	7.30	--
7	67.1	--	32.9	--
8	96.3	--	--	3.7

\* See Figure 1 for the appropriate definition of the symbols used in this Table



**Figure 1** Basic molecular structure of acrylamide-based polyampholytes

Reduced viscosities at concentrations less than  $0.5 \text{ g dl}^{-1}$  were measured with a standard Ubbelohde viscometer placed into a temperature controlled water bath ( $25^\circ\text{C}$ ). The solutions were temperature equilibrated for  $\sim 15$  min prior to viscosity measurement. The measurement was repeated several times until reproducible values were obtained.

All viscosity measurements pertaining to solutions containing concentrations greater than  $0.5 \text{ g dl}^{-1}$  were performed on a Brookfield viscometer (Model LVT) utilizing a UL adapter for low viscosity solutions and various size spindles for the higher viscosity measurements. Unless otherwise specified, the viscosity values reported correspond to 12 RPM at  $25^\circ\text{C}$ .

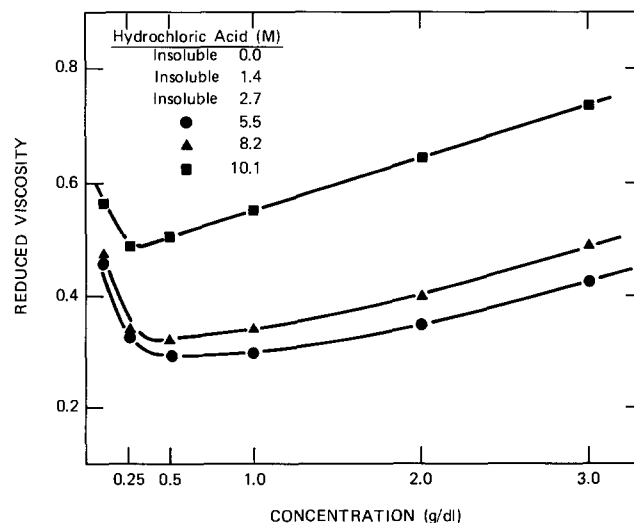
## RESULTS AND DISCUSSION

### Behaviour of high charge-density polyampholytes

Synthesis of a polyampholyte from two oppositely charged monomers produces a high charge-density polymer with a nonstoichiometric anionic-cationic charge ratio. As noted previously, the stoichiometry of the resultant polyampholyte is determined by several factors, including monomer concentrations and their corresponding reactivity ratios. No attempt was made in this study to form an equimolar copolymer. Therefore, each polymer system has a specific quantity of charge to which a low molecular weight, nonpolymerizable counterion is attached. Typical dilute solution viscosity data containing this polymer type (in hydrochloric acid, HCl, solutions) are shown in Figure 2, where reduced viscosity is plotted

against polymer concentration. The polymer (designated as polymer 1) is composed of essentially an equimolar ratio of MAPTAC and SSS units each a counterion to itself, but, in addition, contains approximately 6 mol% sodium neutralized sulphonate styrene (see Table 2). Accordingly, the polymer is a terpolymer from a composition viewpoint. Moreover, since the backbone structure, degree of polymerization, and level of ionic character are completely invariant in these solutions, it can be argued that any change in the viscosity behaviour is due solely to the nature and concentration of the inorganic solute. A cursory examination of Figure 2 shows that the ionic strength of the solution is important since it controls both the solubility of the polyampholyte and the magnitude of the reduced viscosity at a fixed polymer level.

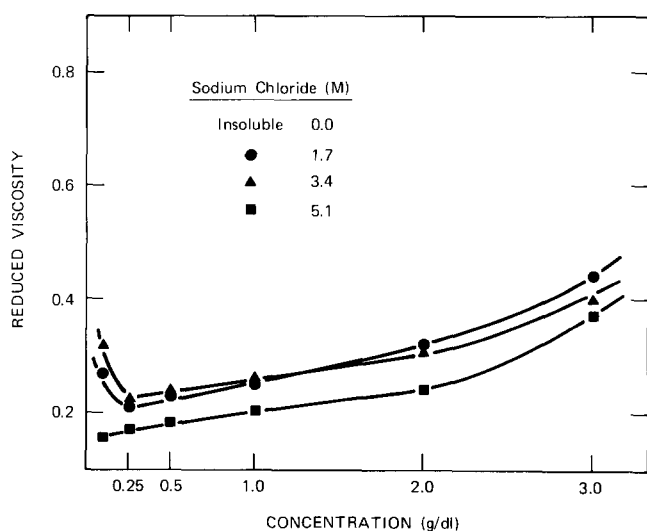
Solubility, in this particular instance, is defined as the point where a sufficient concentration of solute has been added to produce an optically clear solution. Below approximately the 3 M hydrochloric acid level, these solutions are quite milky indicating that the polymer is dispersible, but still rather insoluble in this particular aqueous environment. Since phase separation does not occur on prolonged storage, the dispersibility and stability characteristics of this polymer are aided by the presence of the residual mobile charge. Moreover, this charge does not inhibit the expansion of the tightly collapsed coil in a high ionic strength medium, even as the acid concentration increases. The data in Figure 2 shows that in the dilute solution regime, an upturn in reduced viscosity is observed which in a typical polyelectrolyte<sup>1</sup> or ionomer<sup>26</sup> solution (salt-free) would be attributed to the ionization and subsequent repulsion of the ionic groups attached to the chain backbone. It is highly probable that this mechanism can also account for our observations; since, the repulsive forces likely originate from the larger overall association of the chloride anions as compared to the hydronium ions with the MAPTAC-SSS chain. The repulsion between these 'complexed' ionic charges facilitates the expansion of the hydrodynamic volume of the terpolymer as is reflected in the observed reduced viscosity behaviour. In addition, the data confirm that as this complexation process continues, a further elevation in viscosity occurs.



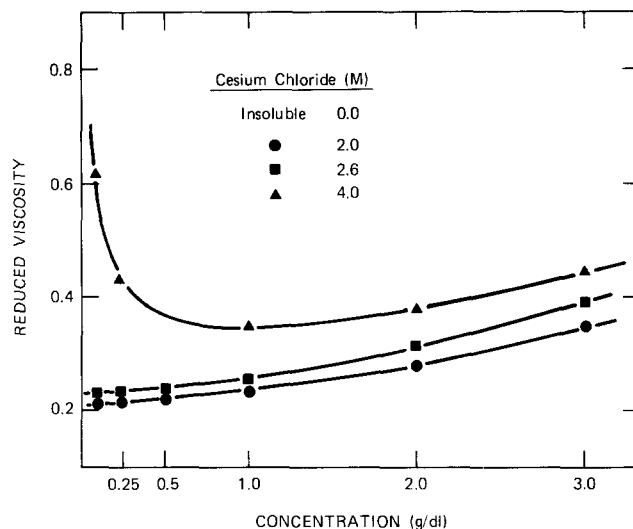
**Figure 2** Reduced viscosity-concentration behaviour of a very high charge density MAPTAC-SSS copolymer (1) in aqueous hydrochloric acid solutions

Investigation of the solution properties of this polyampholyte in a variety of alkali chloride solutions reveals the influence of the solute structure. For example, *Figures 3* and *4* show the reduced viscosity in a number of sodium chloride (NaCl) and cesium chloride (CsCl) solutions, respectively. As before, solubility occurs only with the addition of modest concentrations of salt. However, we observe in NaCl solutions a progressive decrease in the reduced viscosity with increasing salt levels and the complete disappearance of the polyelectrolyte effect at the highest salt level investigated. In general, this behaviour occurs at all polymer levels. Contrary to the results noted in HCl solutions, this data leads to the conclusion that the sodium and chloride ions interact with the high charge density polyampholyte in a roughly equivalent manner producing charge parity along the chain. As a result, this quasi-neutral polyampholyte would possess dilute solution properties that remain relatively invariant to large changes in ionic strength. Undoubtedly, this interpretation of the data becomes increasingly less straightforward as the NaCl concentration is increased further, since the structure of water will be modified and intramolecular hydrophobic forces could become operative. Both of these factors will result in a reduced hydrodynamic volume in NaCl solutions resulting in a reduction in the reduced viscosity. Interestingly, CsCl behaves in a similar fashion as the HCl solutions as indicated by the enhanced overall reduced viscosity and the development of a pronounced polyelectrolyte effect.

These results can be rationalized in terms of the specific complexing ability of the anions and cations (from the alkali chlorides) with the charges attached to the polymer chain. If, for example, the anion interacts to a greater extent than its corresponding cation, then the overall charge on the polymer will become progressively negative with increasing ionic strength (as in HCl environments). In turn, this will cause an expansion of its hydrodynamic volume with a concomitant rise in reduced viscosity. An interesting consequence of these interactions is the development of a polyelectrolyte effect in high ionic strength media. A strongly complexing cation (as in CsCl solutions) will produce qualitatively similar results even



**Figure 3** Reduced viscosity-concentration behaviour of a very high charge density MAPTAC-SSS copolymer (1) in aqueous sodium chloride solutions



**Figure 4** Reduced viscosity-concentration behaviour of a very high charge density MAPTAC-SSS copolymer (1) in aqueous cesium chloride solutions

though the polyampholyte acquires an overall positive charge. However, if both the anion and cation interact to an approximately equivalent extent (as in NaCl solutions), then such marked expansion of the hydrodynamic volume will not result, and as a consequence, the polyampholyte behaves as a conventional nonionic polymer.

Two additional structural features within the polyampholyte could affect the properties of these materials. The first concerns hydrophobic interactions which are related, in qualitative terms, to the amount of hydrocarbon character of the polymer. This force originates from the water structure-enhancing properties of hydrocarbon-based molecules in an aqueous solution<sup>27</sup>. Basically the hydrocarbon portions of the chain are squeezed together due to a tighter water structure. In a polymer molecule, this will undoubtedly force the hydrodynamic volume of the chain to shrink. An examination of the MAPTAC-SSS polymer structure reveals that the styrenic moieties may possess sufficient hydrocarbon character capable of reducing the chain expansion in salt solutions. The second feature concerns the quantity of charge associated with unattached mobile counterions. In the extreme instance, a significant amount of these charges within a polyampholyte could produce a material possessing analogous properties to a homogeneously-charged polyelectrolyte. That is, chain contraction will occur in a high ionic strength medium.

A typical example of a polyampholyte material possessing less hydrocarbon structure and a significantly larger amount of 'free' charge is a MAPTAC-SVS polymer containing approximately 20 mol% sodium neutralized vinyl sulphonate (*Table 2*—Polymer 2). The reduced viscosity of this material in a number of HCl solutions is presented in *Figure 5*. As expected, the response of this material is similar to the styrene sulphonate polyampholyte. Again, insolubility occurs in a salt-free solution, with enhanced solubility as the ionic strength of the solvent is increased. However, contrary to expectations, solubility occurs at a much lower acid level. These data confirm that with the reduced amount of hydrocarbon in the chain structure a more facile expansion of the chain takes place. In addition, this large amount of mobile charge does not inhibit the polyampholytic re-

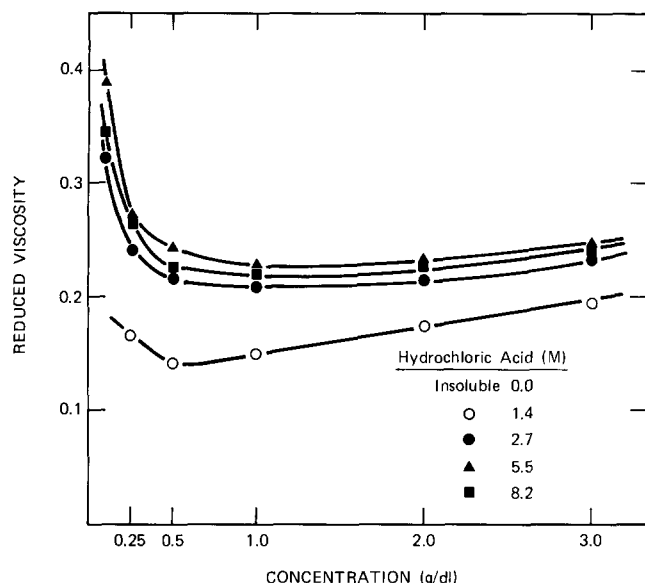


Figure 5 Reduced viscosity-concentration behaviour of a very high charge density MAPTAC-SVS copolymer (2) in aqueous hydrochloric acid solutions

response from continuing to dominate the potentially large polyelectrolyte behaviour of this material. However, the data does show that at the highest acid level, the reduced viscosity does decline to a modest extent. Further decreases are anticipated at higher acid strengths with a concomitant loss of the polyelectrolyte effect.

A direct quantitative comparison of these data with the styrene sulphonate polyampholyte is not meaningful due to the differences in molecular weight and structure. Moreover, it is not easy to determine the molecular weight characteristics and their specific influence on physical properties, since extensive intra- and intermolecular ionic interactions would undoubtedly influence the molecular properties of the chain in an unpredictable manner. However, as we shall see, separation of these ionic groups with neutral units establishes a degree of control over physical properties unattainable in the highly charged polyampholytes.

#### Acrylamide-based polyampholytes

**Low charge density.** The separation of charges along or between macromolecules is facilitated by polymerizing the anionic and cationic monomers in the presence of a neutral monomer such as acrylamide. Under the polymerization scheme previously described, the amount of mobile charge can be varied with relatively modest modifications in the initial monomer concentration. Again the reader is referred to Tables 1 and 2 for the specific details concerning the initial monomer concentration and resultant macromolecule stoichiometry.

From the viewpoint of the polymerization conditions and monomer reactivity ratios, it is quite likely that the charged vinylic monomers are incorporated in a random fashion within the chain structure. The extent to which a specific charged moiety will interact with its opposite counterpart in an aqueous solution (i.e., good solvent) will be a strong function of the molecular weight of the chain and the density of charge along its backbone. If, for example, the anion-cation density along the chain is low, then it becomes highly probable that the charges on neighbouring chains will interact forming a gel-like

network structure at polymer levels above the chain overlap concentration. This situation becomes even more favourable if the solvent permits a marked expansion of the chain, since any intramolecular charge interactions will decrease sharply the chain expansion. Alternatively, the probability of intramolecular charge interactions eventually dominating dilute solution behaviour becomes more likely as anion-cation charge density increases. The properties of these polymers should be easily differentiated from the low charge density gel forming polyampholytes, especially with regard to their interaction with simple electrolytes. It is unreasonable to assume at the present time however that at a specific anion-cation concentration all ionic groups will contribute in an equivalent manner with regard to the physical properties of the overall system. It is interesting to note that from these purely probabilistic arguments, some properties observed in low charge density polyampholytes can be qualitatively understood.

The viscometric behaviour of a low charge density acrylamide-based polyampholyte in several HCl solutions is presented in Figure 6 as a function of polymer concentration. In a fresh water environment, the polyampholyte is soluble with an overall viscosity that is exceptionally high in the semidilute regime. A distinguishing characteristic of this curve is the exponential rise at the higher polymer levels. However, the viscosity values drop precipitously upon the addition of a small amount of HCl. Progressively less deterioration is observed with further changes in ionic strength. Similar behaviour is noted in NaCl solutions (Figure 7), except for the modest rise at the higher salt level.

Since the distance between interacting groups is large in these highly solvated chains, the ability to form intramolecular linkages is sharply curtailed. These results can be rationalized by assuming that the solution behaviour

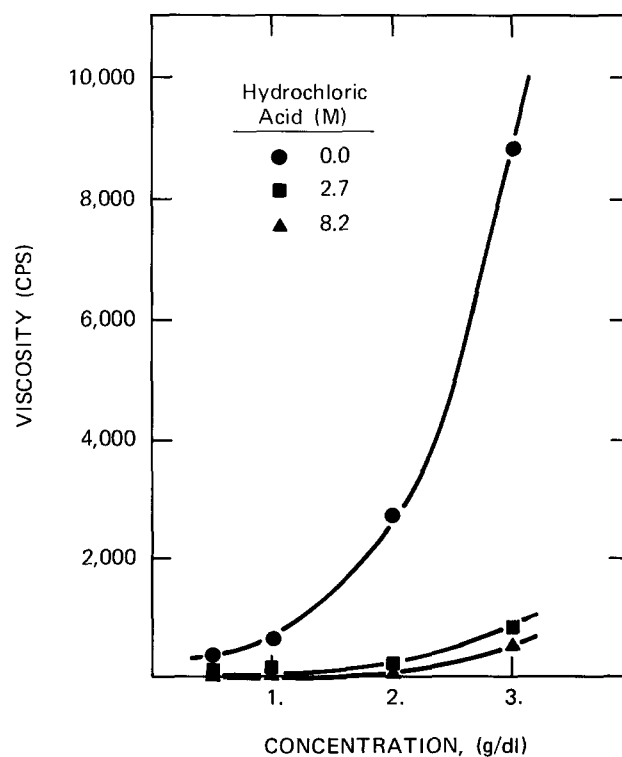


Figure 6 Viscosity-concentration profiles of a low charge density acrylamide-based polyampholyte (3) in fresh and acidified water

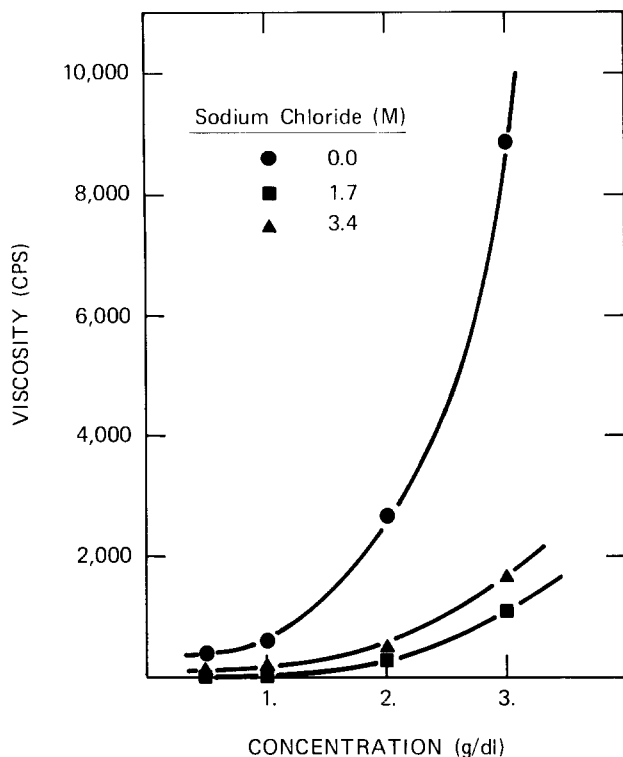


Figure 7 Viscosity-concentration profiles of a low charge density acrylamide-based polyampholyte (3) in fresh and salt water

at these very low charge levels is dominated by intermolecular charge interactions. As the data show, in the pure aqueous solution, the charges interact strongly increasing the apparent molecular weight of the system. The high viscosity at all polymer levels is a direct consequence of these interactions. Also, these increased intermolecular chain interactions and the strong ionic interactions can account for the very sharp rise in viscosity at the higher polymer levels. As described earlier, the solvated inorganic anions and/or cations can interact with these intermolecular linkages. The resulting complexation phenomena shields these interactions with a subsequent loss in apparent molecular weight. A direct result of this process is the precipitous drop in viscosity with the addition of minute amounts of acid or salt.

Interestingly, these materials behave as nonionic polymers in higher ionic strength media. This behaviour is expected of a low charge density chain, since it is well known that the nature of dissolved salts can have a profound influence on the solution characteristics of nonionic, lightly charged polymers<sup>2,28-31</sup>. In general, a water structure-breaking anion (or cation) increases the viscosity of a nonionic polymer, while structure-enhancing ions force the hydrodynamic volume to shrink in size. Interestingly, Figure 7 shows a decrease followed by a modest increase in viscosity in NaCl solutions, while a continual decrease is observed in HCl over a wide range of ionic strength. Although the macromolecular structure is complicated by the presence of the anionic-cationic groups, these results followed the anticipated trends based on the perturbation by dissolved salts of the structure of water in the vicinity of the chain.

In the dilute solution regime, behaviour is assumed to be controlled by the individual molecular species. It is of interest to investigate the dilute solution behaviour of these materials in salt and salt-free solutions. The reduced viscosity of polymer 3 in fresh water is shown in Figure 8.

Again, we observe a sharp rise in viscosity at high polymer levels due to intermolecular anion-cation associations. In the dilute region, a modest upturn of reduced viscosity or polyelectrolyte behaviour is observed. This is due to repulsion between like charges which tends to enlarge the hydrodynamic volume of the chain.

This polyelectrolyte effect is attributable to the small excess of polymerized sodium sulphonate salts, where the mobile sodium atoms no longer shield the repulsive anionic charges. Furthermore, the addition of inorganic solutes produce a marked suppression over the entire reduced viscosity curve as compared to fresh water solutions (Figure 9). Superimposed on these results are the effects of ionic strength and nature of the dissolved salt on the magnitude of the reduced viscosity. A close examination of these curves confirms that these results closely parallel, in a qualitative manner, the high concentration polymer solution data. Not unexpectedly, a polyelectrolyte effect is not observed at least within the polymer concentration range investigated here.

Further increases in the charge density along the polymer backbone (as in polymer 4) produces a polyampholytic material with substantially different dilute and semidilute solution properties. As compared to polymer 3, the ampholytic 'character' has been increased by approximately 4 mol%. Typical viscosity data in HCl at high polymer concentrations are detailed in Figure 10. An inspection of the data shows that the viscosity is increased at low acid levels and decreases at higher concentrations. This behaviour differentiates these materials from the low charge density polymers, but the results appear to parallel in a qualitative manner the properties of the previously detailed high charge density polyampholytes. It is noted that the expansion of the hydrodynamic volume is considerably enlarged in these materials, i.e., polymer 4. In addition, these polyampholytes are soluble in fresh water. This solubility is

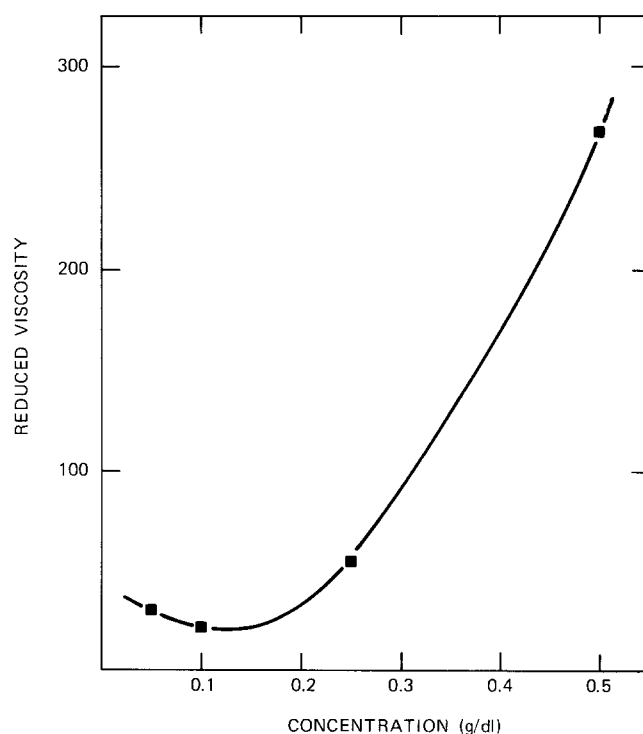


Figure 8 Reduced viscosity-concentration behaviour of a low charge density polyampholyte (3) in fresh water

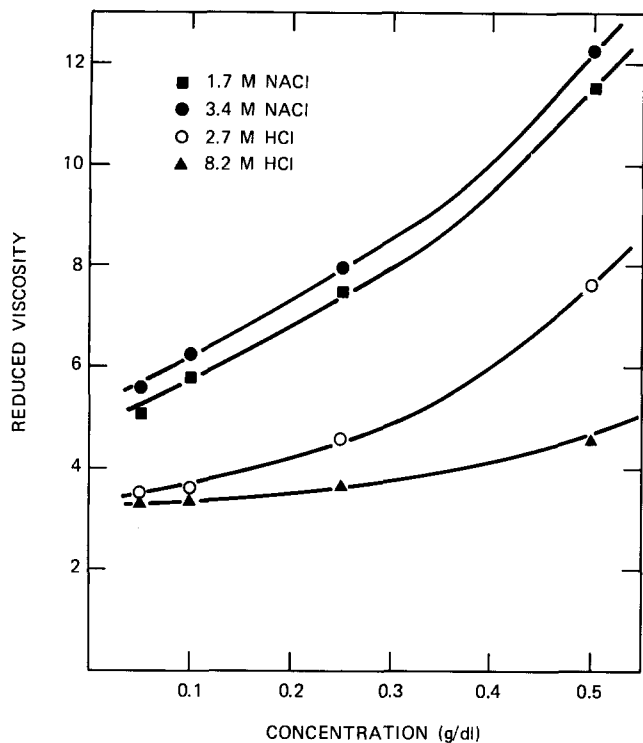


Figure 9 Reduced viscosity-concentration behaviour of a low charge density polyampholyte (3) in salt and acidified solutions

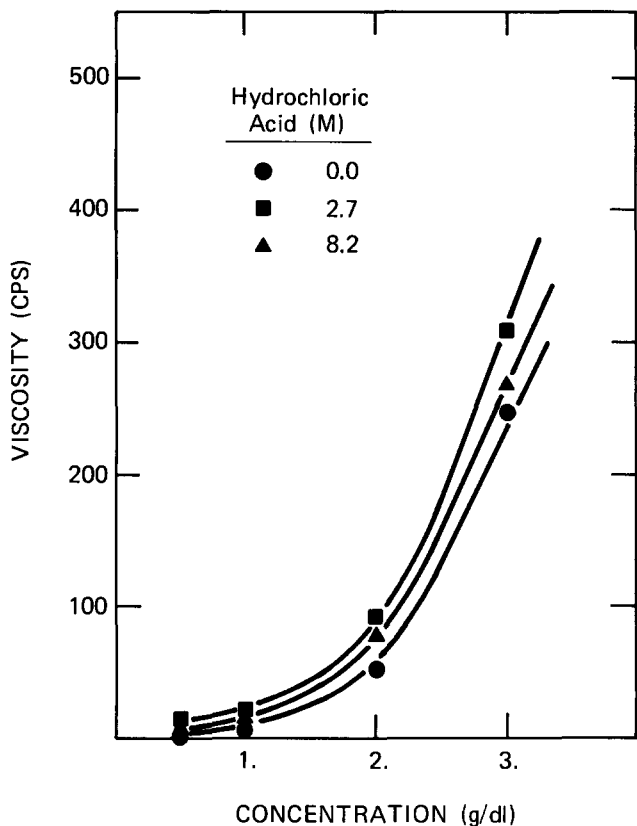


Figure 10 Viscosity-concentration behaviour of a low charge density acrylamide-based polyampholyte (4) in fresh and hydrochloric acid solutions

due, in part, to the presence of the unassociated charge situated along the chain backbone. Interestingly, the fresh water solutions are translucent in dilute solutions and quite milky in appearance in the semidilute regime, but they become rapidly transparent with the addition of

small amounts of solute. Therefore, in dilute solution it is apparent that intramolecular anion-cation interactions exhibit dominant behaviour, but Debye-Huckel screening effects do begin to occur as the ionic strength is further increased causing the hydrodynamic volume of polymer to collapse. An interesting conclusion derived from these results is the marked change in solution behaviour over a relatively modest charge density change. Even further differences become clearly manifested with changes in the nature of the dissolved salt.

Figure 11 shows the influence of NaCl concentration on polymer 4 behaviour as the polymer concentration is varied. We observe a continual rise in viscosity within a moderate salt concentration range; however, the viscosity does begin to drop slightly at higher ionic strength (not shown in Figure 11). On the basis of these results on polyampholyte 4, it is clear that a minor increase in charge density dramatically influences the salt 'tolerance' of these polymers.

A further indication of these effects is shown in Figure 12, where the reduced viscosity of polymer 4 is plotted as a function of polymer concentration in a variety of aqueous solutions. As before, the magnitude of the reduced viscosity is affected by the addition of inorganic solutes. Due essentially to the mobile charge, a polyelectrolyte effect appears in fresh water. Interestingly, these charges do not inhibit the chain expansion of this polyampholyte in HCl and CsCl solutions.

*Moderate charge density.* At the present time, it is rather an arbitrary matter where the boundary is between low and moderate charge density polyampholytes. Many factors contribute to their properties including ampholytic 'character', density of 'free' charge, structure of the

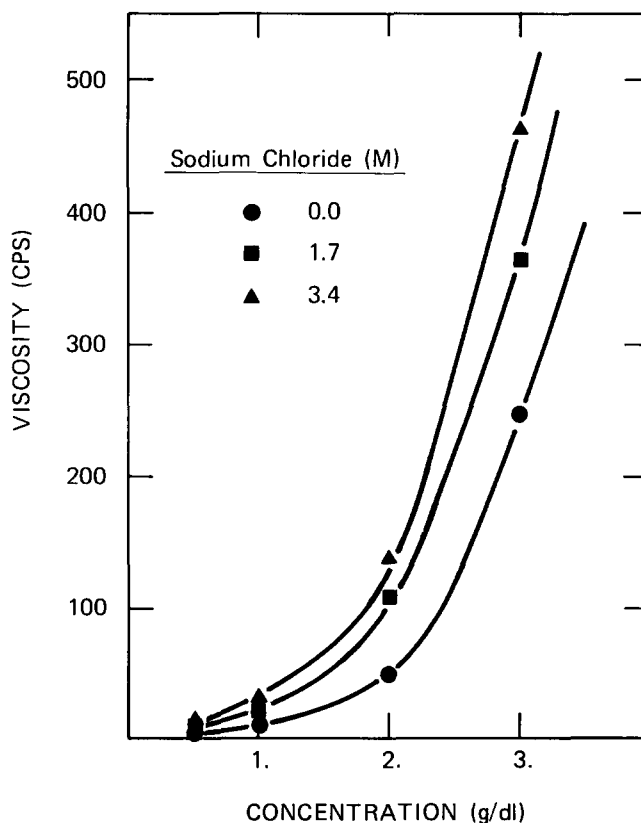


Figure 11 Viscosity-concentration behaviour of a low charge density acrylamide-based polyampholyte (4) in fresh and salt water

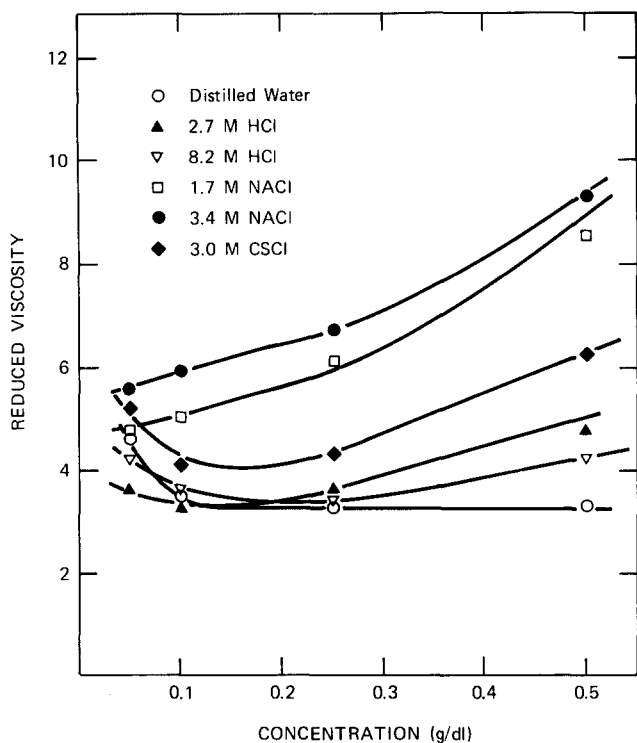


Figure 12 Reduced viscosity-concentration profiles of a low charge density acrylamide-based polyampholyte (4) in fresh, salt and acidified water

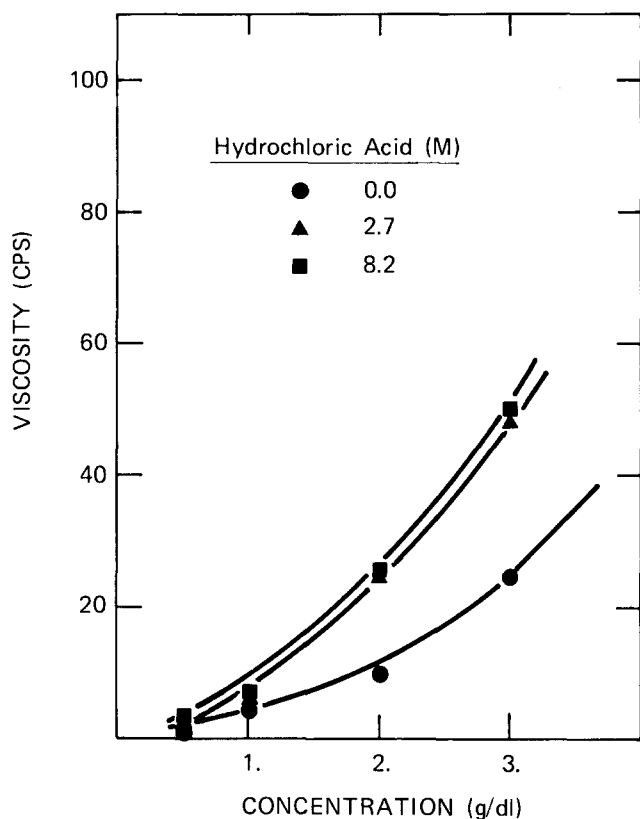


Figure 13 Viscosity-concentration behaviour of a moderate charge density acrylamide-based polyampholyte (5) in fresh and hydrochloric acid solutions

ionic charges, nature, and concentration of dissolved inorganic species. The latter two variables, as we have seen, determine to a large extent whether a polyampholyte is soluble in a high ionic strength media. We have arbitrarily defined 'moderate' charge density as the level

of charge whereby we observe continual expansion of the chain in the acid and salt solutions previously described. Charge densities greater than  $\sim 8$  mol% are required for this to occur in these ampholytic ionomers.

The material designated polymer 5 contains  $\sim 12.3$  mol% (Table 2) ampholytic 'character', and its viscosity behaviour at high polymer levels in both acid and salt solutions are detailed in Figures 13 and 14, respectively. The data show the polymer chain expands at all ionic strengths. At high salt concentrations, sites are still present on the chain which are capable of binding with the inorganic ions. This is readily possible, since the polymer has a larger number of sites available, and at these ionic activities, site 'saturation' has not occurred. However, it is expected that site saturation will occur at much higher acid or salt levels.

We further note the overall viscosities of this material are lower than for the previously reported polyampholytes. This may be due simply to lower molecular weight, but it is more probable that the coil is highly contracted due to the larger number of intramolecular crosslinks resulting in the appearance of a lower molecular weight. As of the present time, we have not explored this point. However, we do note that the hydrodynamic volume will continually expand in even higher ionic strength media. This type of study could be useful as a molecular weight probe, but the results are complicated by Debye-Hückel screening effects.

Similar viscosity behaviour (polymer 6) is found in higher charge density polyampholytes (Figure 15). This material possesses approximately 22.6 mol% ampholytic 'character', and as before, these charges strongly influenced the hydrodynamic volume at all salt levels.

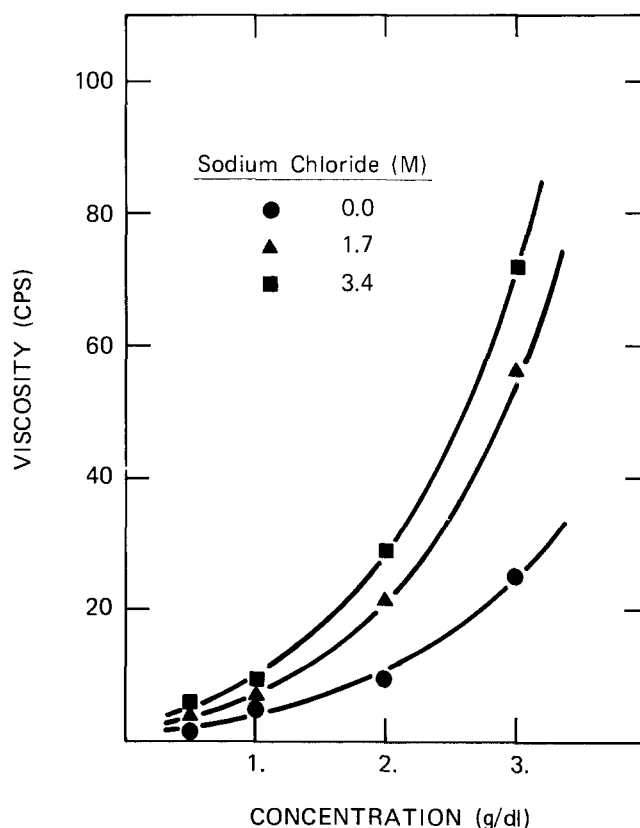


Figure 14 Viscosity-concentration behaviour of a moderate charge density acrylamide-based polyampholyte (5) in fresh and salt water



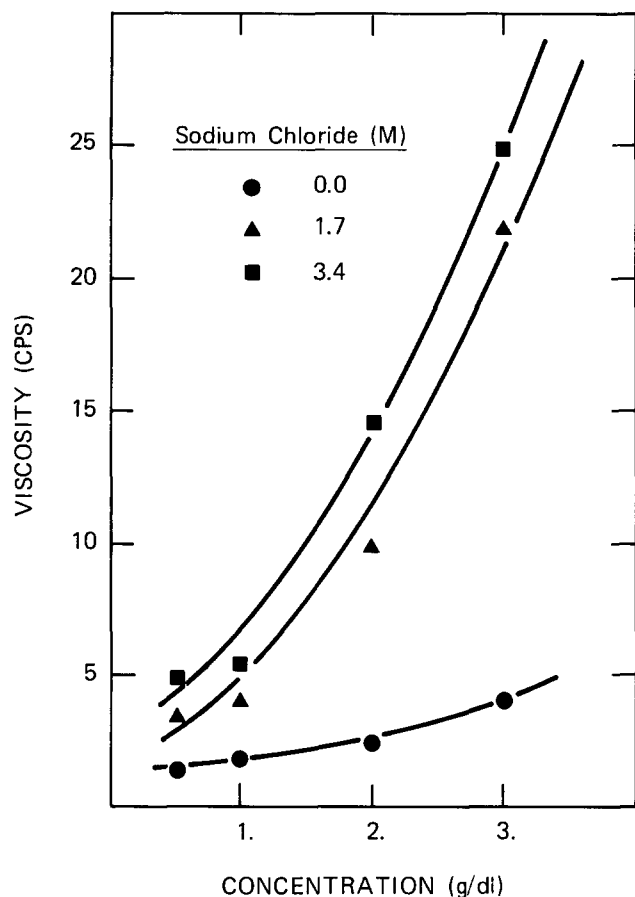


Figure 15 Viscosity-concentration behaviour of a moderate charge density acrylamide-based polyampholyte (6) in fresh and salt water

*Behaviour of copolymers in high ionic strength solutions*

In the previous section, we detailed the behaviour of a low charge density polyampholyte in a high ionic strength solution. The results show that their behaviour is directly dependent on the charge level and to a lesser extent on the nonionic characteristics of the backbone. Saito<sup>31</sup> has shown that the salt effect on a nonionic polymer is strongly dependent upon the water structure-forming or breaking characteristics of the counter-anions. A structure-breaking anion will generally produce a salting-in of the polymer. Although HCl was not examined, NaCl is considered a strong salting-out salt. Therefore, this property of the chloride ion does not appear to impair to any significant extent the expansion of the polyampholytic ionomers.

One pertinent factor related to the interpretation of the previous results on low charge density polyampholytes pertains to the interaction of acid or salt with the homogeneous, singly-charged species (i.e., copolymers). This comparison is helpful in differentiating polyelectrolyte from polyampholyte behaviour. Two copolymers were synthesized under virtually the identical conditions as for polymer 3. The first is an AM-SSS copolymer (polymer 7) containing 32.9 mol% anionic charge with the viscosity characteristics presented in Figure 16. As anticipated, a strong polyelectrolyte effect is observed in fresh water (not shown), while the addition of HCl causes a dramatic loss in viscosity. This behaviour is a common feature of conventional polyelectrolytes. Similarly, Mock *et al.*<sup>32</sup> have shown that a vinyltoluene-styrene copolymer sulphonic acid has very similar solution characteristics over a broad HCl concentration

range. The second copolymer (sample 8, MAPTAC-co-AM) contains a low level of cationic charge (3.7 mol% MAPTAC). This material is of interest, since a direct comparison can be made concerning the addition of a homogeneous low charge density onto the chain backbone with the corresponding polyampholyte (such as polymer 3). Figure 17 shows the effect on adding acid to polymer 8 solutions. As expected, screening of the homogeneous charges causes some collapse of the chain with a concomitant viscosity loss. However, the loss is not as large as observed in the low density polyampholyte material (Figure 6) which is probably not too surprising, since the viscosity in the latter material is a strong function of intermolecular ionic linkages in fresh water solutions.

*Polyelectrolyte vs. polyampholyte behaviour*

In the previous discussions, we observe that relatively minor modification in the charge density of a polyampholyte produces marked changes in its rheological characteristics. For example, chain expansion is observed at moderate charge densities in all high ionic strength solutions investigated. Moreover, this behaviour can be contrasted with conventional homogeneously-charged polyelectrolytes where dramatic reductions in viscosity

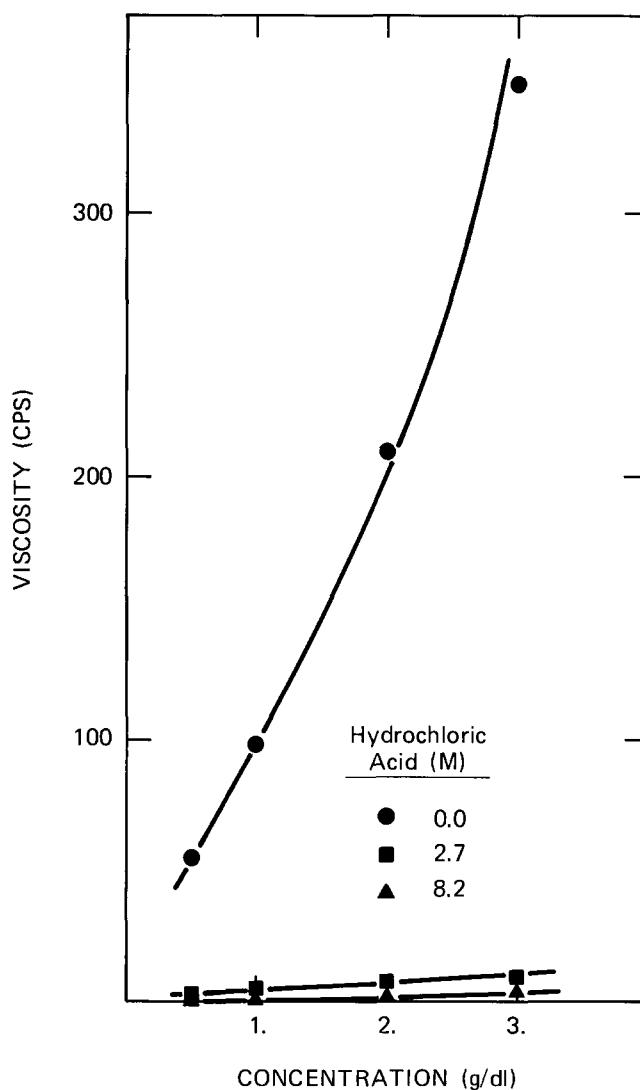


Figure 16 Viscosity-concentration behaviour of an acrylamide-SSS copolymer (7) in fresh and hydrochloric acid solutions

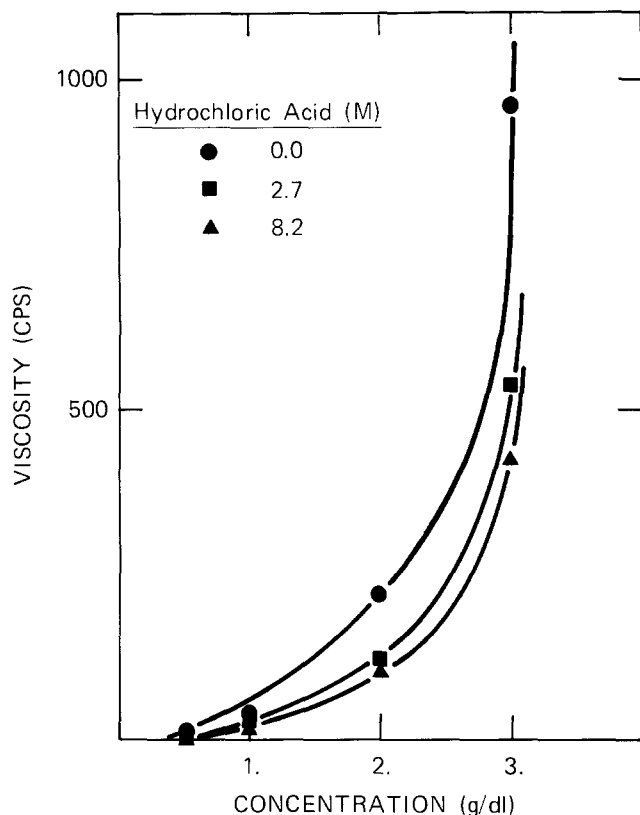


Figure 17 Viscosity-concentration behaviour of an acrylamide-MAPTAC copolymer (8) in fresh and acidified water

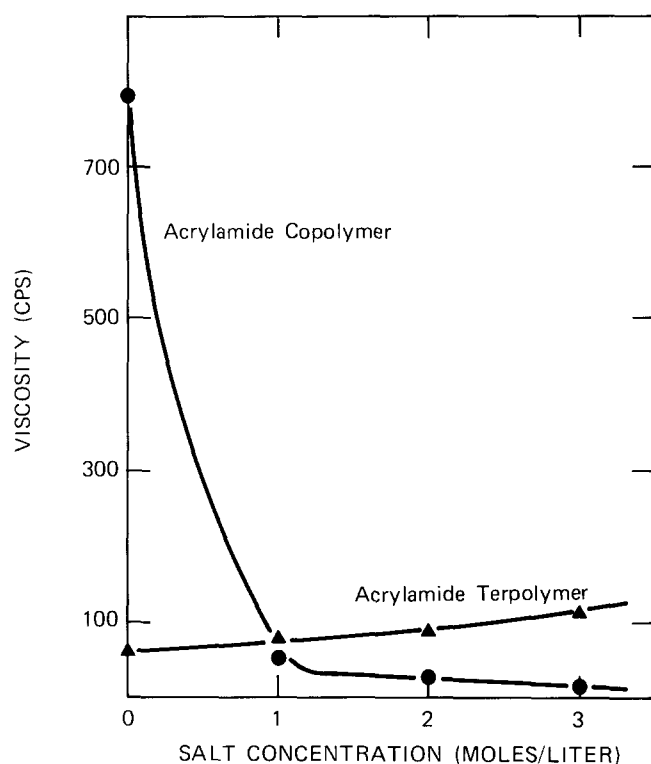


Figure 18 Comparison of the viscometric properties in salt solution of a typical polyelectrolyte copolymer and a polyampholyte terpolymer with equivalent charge densities

are noted. At the present time, it is of interest to combine the properties of a polyelectrolyte and a polyampholyte in a single chain whereby the resultant material may possess rheological characteristics invariant to changes in ionic strength of the solution. This can be achieved if the

polymer has the appropriate level of both mobile charge and anionic-cationic charge. Such a comparison is made in Figure 18 where we observe the viscometric properties in a brine environment of an acrylamide-MAPTAC (9.8 mol%) copolymer and its acrylamide-based polyampholyte terpolymer counterpart containing both ampholytic and polyelectrolytic character. As anticipated, the modified copolymer has a low degree of salt tolerance, however, the polyampholyte shows only a modest change in viscosity as the salt level is increased. Thus, we observe that the normal expansion of the polyampholyte can be curtailed to the point where the hydrodynamic volume of the chain will remain essentially invariant due to the screening of the mobile charge by the dissolved simple electrolyte.

## CONCLUSION

The rheological properties of dilute and semidilute solutions of low, moderate and highly charged density polyampholytes synthesized for the study were investigated. The viscometric properties were measured since this parameter is directly related to changes in the hydrodynamic volume of the polymer molecule. The viscometrics are dominated by intermolecular ionic linkages at low anion-cation charge levels. Since the strength of this interaction can be modulated through the dissolution of a low molecular weight salt, the initial gel-like solution properties are dramatically reduced with an increase in ionic strength of the solution. Interestingly, intramolecular interactions begin to dominate behaviour at higher charge levels. Thus, contrary to expectations, relatively low viscosity is observed in fresh water, while the viscosity is correspondingly enhanced with increasing ionic strength. That is, the initially collapsed coil is allowed to expand upon release of the strong intraionic restrictions. Our results show that the extent to which this polyampholyte influences solution rheology is a strong function of charge density level, solvent ionic strength, molecular weight of the polymer, level of the mobile dissociable charges and chemistry of the dissolved salt.

This approach to controlling rheology of high ionic strength aqueous solutions through precise control of the concentration of the dissociable charge and anion-cation charge density on an ion-containing macromolecule eliminates some of the limitations of the well-known homogeneously-charged polyelectrolytes. Moreover, these low charge density polyampholytes permit an exploration of novel physical properties of macromolecules not readily observed in other macromolecular systems.

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