Synthesis and Solution Properties of Ampholytic Acrylamide Ionomers

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SYNTHESIS AND SOLUTION PROPERTIES OF AMPHOLYTIC ACRYLAMIDE IONOMERS

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ABSTRACT

The synthesis and semiconcentrated and dilute solution properties of two series of ampholytic acrylamide ionomers, poly(acrylamide MPTMA/AMPS) and poly(acrylamide METMA/MES), are reported as a function of the ionic content and added salt concentration. The viscosity dependence on shear rate was measured with a cone/plate Brookfield viscometer for semiconcentrated solution and with a Cannon-Ubbelohde four-bulb shear dilution capillary viscometer for dilute solution at $25 \pm 0.1°C$. The two series of ampholytic acrylamide ionomers showed a characteristic pseudoplastic shear-thinning behavior under both conditions. The semiconcentrated solution viscosity parameters m and n in the power-law model, $\eta = m\dot\gamma^{n-1}$, were determined and found to be functions of the ionic content. The viscosity at selected shear rates was found to be a complex function of the salt concentration. The intrinsic viscosity $[\eta]$ was determined and compared with molecular parameters determined by light scattering under identical conditions. The dilute-solution properties of the ampholytic ionomers were found to resemble the properties of neutral polyacrylamide previously reported in the literature.

INTRODUCTION

In recent years we have begun a detailed investigation into the synthesis as well as the solution and solid-state properties of ampholytic polymers. Three categories of polymers have been studied: a) polysulfobetaines, in which each pendent group contained both positive and negative charges [1-3]; b) homocopolymers, in which ion-pair comonomers derived from vinylic cation/vinylic anion monomer pairs were homopolymerized [3-9]; and c) ampholytic ionomers, in which neutral comonomers were copolymerized with smaller concentrations of ion-pair comonomers [10-13]. The principal ion-pair comonomers studied have included 3-methacrylamidopropyltrimethyl-ammonium 2-acrylamido-2-methylpropanesulfonate, **MPTMA/AMPS (I)**, and 2-methacryloyloxyethyltrimethylammonium 2-methacryloyloxyethanesulfo-nate, **METMA/MES (II)**.

$$
\begin{array}{llll}
\text{CH}_3 & & \text{CH}_3 & \text{CH}_3 \\
| & & | & | \\
\text{CH}_2\text{=C} & \text{CH}_2\text{=CH} & \text{CH}_2\text{=C} & \text{CH}_2\text{=C} \\
| & | & | & | \\
\text{C=O} & \text{C=O} & \text{C=O} & \text{C=O} \\
| & | & | & | \\
\text{NH} & \text{NH} & \text{O} & \text{O} \\
| & | & | & | \\
(\text{CH}_2)_3 & \text{CH}_3\text{–C–CH}_3 & (\text{CH}_2)_2 & (\text{CH}_2)_2 \\
| & | & | & | \\
\text{CH}_3\text{–N}^+\text{–CH}_3 & \text{CH}_2 & \text{CH}_3\text{–N}^+\text{–CH}_3 & \text{SO}_3^- \\
| & | & | & \\
\text{CH}_3 & \text{SO}_3^- & \text{CH}_3 & \\
\end{array}
$$

$$\qquad\qquad \mathbf{I} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{II}$$
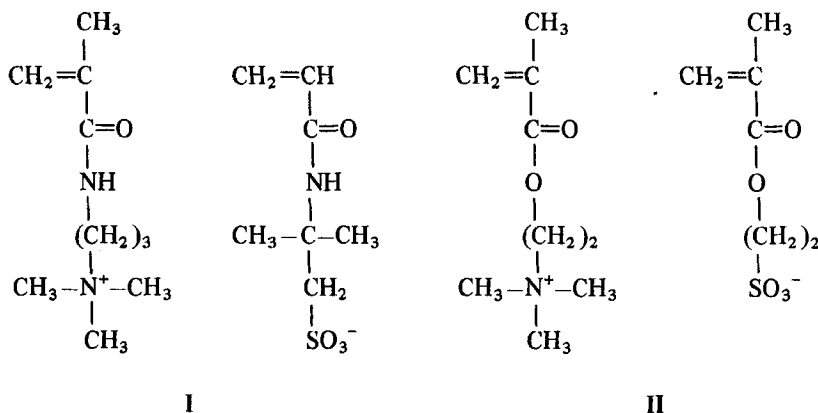
For the polyampholytes studied, it has been shown that, in aqueous salt solutions, such polymers can display an increase in viscosity with an increase in salt concentration [3, 6, 8, 9]. Because of the commercial and academic importance of acrylamide-containing polymers, the present study was undertaken to ascertain the solution properties of ampholytic acrylamide ionomers with **MPTMA/AMPS** and with **METMA/MES**. In this report the semiconcentrated-solution viscosity (Brookfield), the dilute-solution viscosity, and light-scattering studies for these new classes of ampholytic ionomers are discussed.

EXPERIMENTAL

Materials

A 50% aqueous solution of 3-methacrylamidopropyltrimethylammonium chloride (Jefferson Chemical Co.) was decolorized twice with activated carbon and diluted with an equal volume of distilled water prior to use. A refined grade of 2-acrylamido-2-methylpropanesulfonic acid was obtained from Lubrizol Corporation and was recrystallized twice from anhydrous methanol.

2-Methacryloyloxethyltrimethylammonium chloride obtained from Alcolac Inc. as a 75% active material in water was diluted with distilled water, followed by treatment with activated carbon twice prior to use. 2-Sulfoethyl methacrylate, 95% purity (Polysciences Inc.), was diluted with water and treated three times with charcoal to remove impurities and polymeric residues.

The ion-pair comonomers of MPTMA/AMPS [6] and METMA/MES [8] were prepared by previously reported procedures.

Acrylamide, AAm, monomer (Eastman Kodak) and 4,4′-azobis-4-cyanovaleric acid, ACVA (Aldrich), were recrystallized, respectively, from freshly distilled chloroform and deionized water before use. Sodium chloride (Fisher Scientific) was used as received.

Polymerization

A homogeneous solution of a mixture of the ion-pair comonomers, MPTMA/AMPS or METMA/MES, and acrylamide in deionized water was prepared in a glass ampule. A known amount of initiator, ACVA, was added to the above solution, and the final volume was adjusted with deionized water. The ampule was degassed by the freeze-thaw technique, evacuated, and sealed. The solution was allowed to melt at room temperature and then placed in a water bath at 50 ± 0.5°C. The polymerization proceeded for a time period determined by the visual observation of viscosity of the reaction mixture. The polymer solution was then transferred to a dialysis bag of molecular weight cut-off of 12 000-14 000 and dialyzed against distilled water for 5 d. The purified polymer was obtained by freeze-drying and finally dried *in vacuo* at 80°C for 6 h.

Elemental Analysis

Carbon, hydrogen, nitrogen, and sulfur were analyzed by Atlantic Microlab Inc. of Atlanta, Georgia. The polymer compositions expressed in mol%

of either MPTMA/AMPS or METMA/MES and acrylamide were calculated
by using the sulfur percentages.

NMR Measurements

^{13}C-NMR measurements were made on a Bruker 270 MHz spectrometer
at 90°C, using deuterium oxide as solvent and p-dioxane as an internal
reference.

Viscosity Measurements

Viscometric properties were determined under semiconcentrated (1%) and
dilute (<0.1%) conditions. For semiconcentrated polymer solutions, a Wells-
Brookfield cone/plate digital viscometer was used. The spindle dimensions
were 2.4 cm cone radius and 1.565° cone angle. The sample cup was jacketed
for constant temperature measurements. A Brookfield viscosity standard
(12 000 cP) was used to assure the viscometer calibration prior to the polymer
solution measurements. The viscosity (cP) and shear rate ($\dot{\gamma}$, s^{-1}) were obtained
by converting digital readout and rotational speed (rpm), respectively, using
the range tables supplied by the manufacturer.

A Cannon-Ubbelohde four-bulb shear dilution capillary viscometer was used
to determine the dilute solution viscosity. The apparent relative viscosity, η_r,
at each bulb was obtained from flow-time measurements of the polymer solu-
tions relative to those of solvent. The shear rate (s^{-1}) at the wall of the capil-
lary was calculated by dividing the shear rate constant of each bulb by the re-
spective flow time in seconds.

Polymer samples were dissolved in an appropriate solvent at room tempera-
ture. A period of 24-48 h was required for the polymers to dissolve complete-
ly. All polymer solutions were homogeneous, and precautions were taken to
keep all solutions dust-free. Viscosities were determined at 25 ± 0.1°C.

Light-Scattering Measurements

The light-scattering measurements were carried out on a laser light-scattering
photometer, DAWN Model F (Wyatt Technology Corp., Santa Barbara, Califor-
nia), which employs a He-Ne 5 mW vertically polarized lazer (λ = 632.8 nm) as
a light source and an array of photodiodes at 15 different angles (35-123°) as
detectors. The normalization factors for all detectors and the calibration of
the instrument were obtained by a previously reported procedure [9].

Mother liquor solutions (0.1%) for all polymer samples were prepared in an

appropriate salt solution. The salt solutions were filtered through a 0.22-μm Millipore filter prior to use. The mother liquor solutions were then dialyzed for at least 4 weeks against the respective solvents to obtain the same chemical potential. Precautions were taken to prevent evaporation of the solvent during dialysis. The dialyzed polymer solutions were subsequently diluted with dialyzate to a series of concentrations ranging from 10 to 500 μg/mL. They were then centrifuged (7000 rpm) for 4 h before use in light-scattering experiments. Optical clarity of the solutions was assured by direct observation of the light beam within the solution as well as by constant readings on the channel monitor. The scattered intensities at different angles were simultaneously measured and analyzed by an IBM computer using Dawnflow software supplied by the manufacturer.

The differential refractive index, Δn, was measured on all light-scattering solutions at 25 $\pm$ 0.1°C using a Brice-Phoenix differential refractometer. The light source was a mercury-vapor lamp fitted with a filter to isolate the 632.8 nm emission line. The specific refractive index increment, dn/dc, was obtained from the slope of the linear regression line of a Δn versus concentration plot.

Light-scattering data were evaluated by the Zimm technique [14]. A computer program was developed in this laboratory in order to generate the Zimm plot and to obtain the most probable location of the subsequent extrapolated straight lines ($\theta = 0$ and $C = 0$).

RESULTS AND DISCUSSION

Ampholytic Ionomer Syntheses

The ampholytic ionomers prepared in this study were obtained by solution polymerization in water employing varying concentrations of MPTMA/AMPS or METMA/MES to acrylamide. The concentrations used are reported in Table 1, and the resulting mol% ion-pair comonomer contents in the ionomers are presented in Table 2. It is interesting to note from Table 2 that the ampholytic acrylamide ionomers synthesized had larger amounts of ion-pair comonomers than had originally existed in the feed. This circumstance is probably related to a higher radical reactivity of the ion-pair comonomers relative to acrylamide in the concentration ranges studied.

For the ionomers prepared, the elemental analyses revealed an excess of hydrogen and oxygen, which was most likely a result of water retention. Infrared spectra of these materials revealed no indication of imide formation [15, 16].

TABLE 1. Preparation of Ampholytic Ionomers

Sample	AAm, g	Ion pair g	Ion pair mol%	Volume, mL	ACVA, μmol/L	Temperature, °C	Time, min	Conversion, %
				MPTMA/AMPS				
1	20.03	0.36	0.33	200	128	50	120	9.80
2	25.36	1.13	0.80	200	118	50	120	6.42
3	5.29	0.59	1.97	100	214	50	180	34.00
4	2.27	0.66	5.02	50	49	50	240	52.12
				METMA/MES				
5	12.59	0.26	0.40	180	521	50	60	31.91
6	12.13	0.63	1.00	180	515	50	75	34.04
7	11.67	1.10	1.80	180	511	50	90	31.30
8	11.14	1.65	2.80	180	521	50	110	30.46

TABLE 2. Composition of Ampholytic Acrylamide Ionomers

Sample	Ion pair in feed, mol%	Elemental analysis, %				Ion pair in ionomer,[a] mol%
		C	H	N	S	
MPTMA/AMPS						
1	0.33	48.23	7.28	18.63	0.35	0.80
2	0.80	48.93	7.37	18.31	0.62	1.47
3	1.97	48.38	7.50	17.56	1.24	3.14
4	5.02	49.25	7.73	16.33	2.26	6.47
METMA/MES						
5	0.40	50.36	6.97	18.76	0.46	1.06
6	1.00	49.99	7.01	16.98	0.71	1.68
7	1.80	49.88	7.02	16.19	1.35	3.42
8	2.80	49.51	7.18	14.18	2.31	6.50

[a]Based on sulfur content.

These ampholytic ionomers were also characterized by ^{13}C-NMR measurements at 90°C with deuterium oxide as the solvent. Figure 1 illustrates the spectrum of an acrylamide METMA/MES ionomer with 6.5 mol% ionic content. It is apparent that besides three main peaks due to acrylamide moieties, many small resonances attributed to METMA/MES moieties, whose chemical shifts are identical to those for the homocopolymer of METMA/MES [8], are also detected. As in the case of neutral polyacrylamide, the methine and methylene resonances show some resolution, which may result from partial overlapping of the 10 possible pentad and the six possible tetrad peaks. Unfortunately, as mentioned by Inoue et al. [17], the splitting of these resonances still cannot give rise to any conclusion on the tacticity of these polymers. On the other hand, there are no discernible peaks due to methine or carbonyl carbons of acrylic acid moieties, as found in the case of partly hydrolyzed polyacrylamide [18], implying the absence of any carboxylic acid groups caused by pendent group hydrolysis.
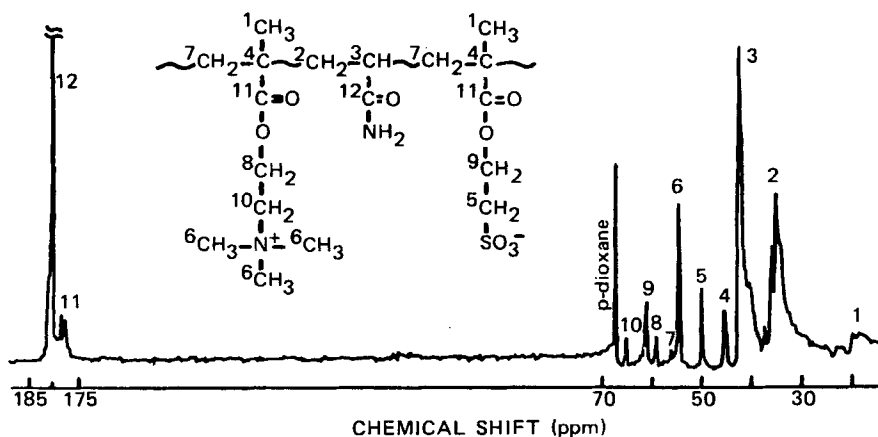
FIG. 1. ^{13}C-NMR spectrum of an acrylamide METMA/MES ionomer (Sample 8) in D_2O at 90°C.

The ^{13}C-NMR spectrum of an acrylamide MPTMA/AMPS ionomer containing 6.47 mol% ion-pair comonomer displayed a behavior similar to that of the 6.5 mol% ionic content acrylamide METMA/MES ionomer.

Semiconcentrated Solution Viscosity (Brookfield)

Semiconcentrated solution viscosity for all ionomer samples was studied as a function of shear rate ($\dot{\gamma}$, s^{-1}), ionic content, and salt concentration. It was found that all copolymer samples behaved in a similar fashion in deionized water as well as in solutions of various salt concentrations. Figure 2 is an illustration of viscosity dependence on shear rate for acrylamide MPTMA/AMPS ionomer samples in deionized water. The viscosity decreased with increasing amount of ion-pair MPTMA/AMPS in the ionomers. These samples also displayed a non-Newtonian, pseudoplastic character, i.e., a decrease in viscosity with increasing shear rate.

The pseudoplastic behavior can be evaluated by a power-law model of Ostwald-de Waele [19]:

$$\eta = m\dot{\gamma}^{n-1}, \tag{1}$$

where η is viscosity, $\dot{\gamma}$ is shear rate (s^{-1}), and m is a constant. The exponent n is a measure of the non-Newtonian behavior (pseudoplasticity) of a fluid
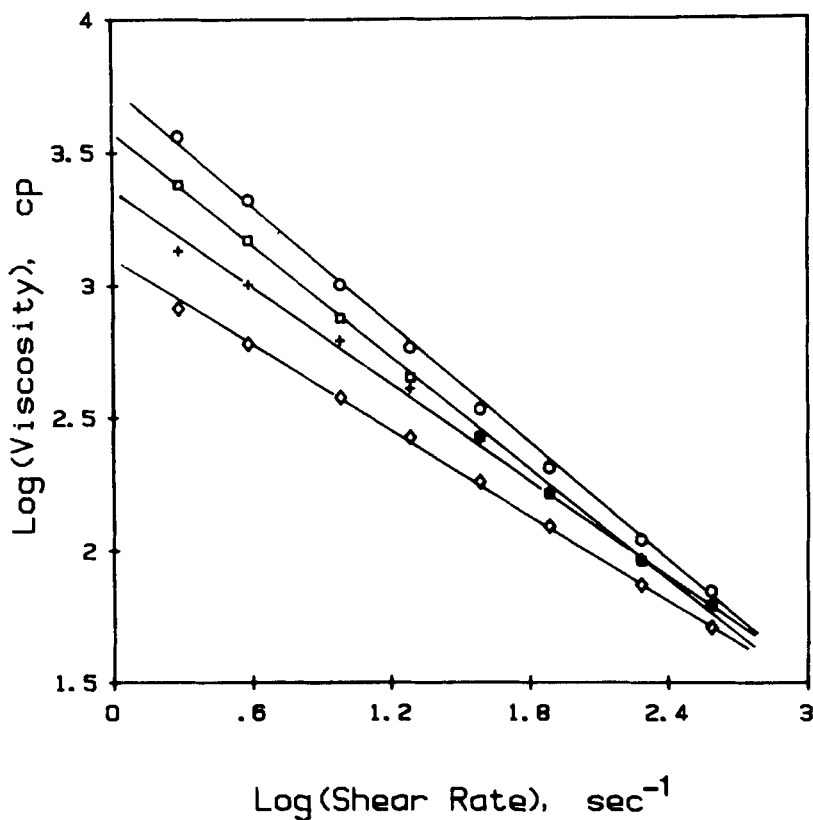
FIG. 2. Log-log plot of viscosity as a function of shear rate for acryl-amide MPTMA/AMPS ionomer of different ionic contents in deionized water at 25± 0.1°C: (○) 0.80 mol%, (□) 1.47 mol%, (+) 3.14 mol%, (◇) 6.47 mol%.

system and can be determined from the double logarithmic dependence of the viscosity on the shear rate, as shown in Fig. 2. Clearly, when $n = 1$, the value of m is the Newtonian viscosity, and if $n < 1$, the fluid is said to be pseudoplastic. Therefore, the values of m and n for acrylamide MPTMA/AMPS ionomers in deionized water as well as in different salt solutions were calculated by a curve fitting analysis using plots similar to those shown in Fig. 2, and the results are summarized in Table 3.

The viscosity dependence on shear rate for the acrylamide METMA/MES ionomers in water as well as in salt solutions was found to resemble the vis-

TABLE 3. Parameters for the Power-Law Model $\eta = m\dot{\gamma}^{n-1}$ for Acrylamide MPTMA/AMPS Ionomers[a]

Sample	Ion-pair MPTMA/AMPS mol%	Deionized water	NaCl, M		
			1.0	2.0	3.0
1	0.80	$m = 5606$	$m = 5702$	$m = 6196$	$m = 8581$
		$n = 0.250$	$n = 0.242$	$n = 0.240$	$n = 0.225$
2	1.47	$m = 3687$	$m = 4897$	$m = 6397$	$m = 4976$
		$n = 0.299$	$n = 0.274$	$n = 0.256$	$n = 0.293$
3	3.14	$m = 2181$	$m = 1804$	$m = 1865$	$m = 2181$
		$n = 0.407$	$n = 0.424$	$n = 0.421$	$n = 0.414$
4	6.47	$m = 1222$	$m = 774$	$m = 604$	$m = 766$
		$n = 0.472$	$n = 0.562$	$n = 0.591$	$n = 0.570$

[a] 1% (w/v) solutions in deionized water and in salt solutions at $25 \pm 0.1^{\pi}C$.

cosity behavior found for the acrylamide MPTMA/AMPS ionomers. Figure 3 is a representative plot of viscosity versus shear rate for the acrylamide METMA/MES ionomers in deionized water. These copolymers also exhibited pseudo-plastic character in salt solutions. The n and m values for these polymers were also calculated from a curve-fitting analysis, and the data are summarized in Table 4.

These results showed that the n values increased as the amount of ion-pair incorporated in the ionomers increased for either poly(acrylamide MPTMA/AMPS) or poly(acrylamide METMA/MES), whereas the opposite was found for the m constants. For example, in deionized water, m and n were found to be 5606 and 0.250, respectively, for Sample 1 containing 0.80 mol% MPTMA/AMPS, whereas for Sample 4 with 6.47 mol% ionic content, m and n were 1222 and 0.472, respectively. Similarly, for acrylamide METMA/MES ionomers in deionized water, m and n were found to be 3621 and 0.337, respectively, for Sample 5 containing 1.06 mol% METMA/MES, and 130 and 0.824, respectively, for Sample 8 containing 6.50 mol% ion-pair. The same was also observed for the polymers at various salt concentrations.

The increase in the n value with increasing content of ion-pair, giving a more Newtonian fluid, could be related to greater intramolecular/intermolec-

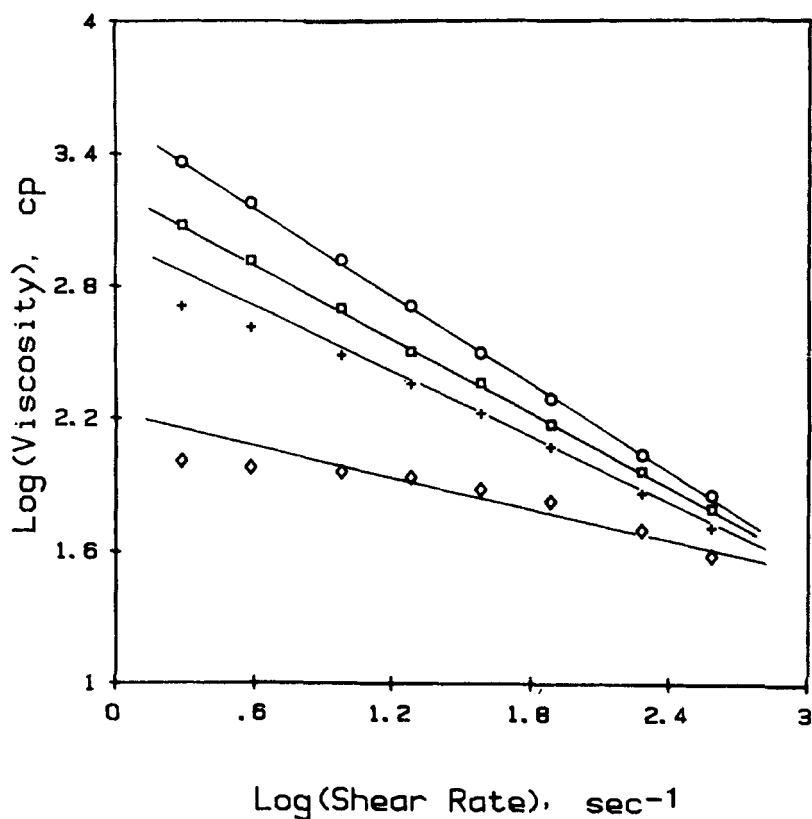FIG. 3. Log-log plot of viscosity as a function of shear rate for acrylamide METMA/MES ionomers of different ionic contents in deionized water at 25 ± 0.1°C: (O) 1.06 mol%, (□) 1.68 mol%, (+) 3.42 mol%, (◊) 6.5 mol%.

ular ionic interactions between oppositely charged pendent groups, which would presumably lead to greater compaction and smaller shear dependence effects. Clough et al. [13] reported higher cluster formation with increasing amount of ionic groups in the case of styrene MPTMA/AMPS ionomers. A similar situation may exist in this case.

Although an exact meaning of the constant m in the power-law model is still unknown, it is the general belief that m is somehow related to the viscosity of the solution [20, 21]. Thus, the decrease found in m as the ionic content increased indicates the decrease in the viscosity of the polymer solu-

TABLE 4. Parameters of the Power-Law Model $\eta = m\dot{\gamma}^{n-1}$ for Acrylamide METMA/MES Ionomers[a]

Sample	Ion-pair METMA/MES, mol%	Deionized water	NaCl, M		
			1.0	2.0	3.0
1	1.06	$m = 3621$	$m = 2624$	$m = 2712$	$m\ 3080$
		$n = 0.337$	$n = 0.382$	$n = 0.380$	$n = 0.366$
2	1.68	$m = 1742$	$m = 906$	$m = 1146$	$m = 1279$
		$n = 0.440$	$n = 0.532$	$n = 0.499$	$n = 0.490$
3	3.42	$m = 763$	$m = 329$	$m = 359$	$m = 439$
		$n = 0.562$	$n = 0.669$	$n = 0.661$	$n = 0.631$
4	6.50	$m = 130$	$m = 60$	$m = 80$	$m = 122$
		$n = 0.824$	$n = 0.832$	$n = 0.837$	$n = 0.815$

[a]1% (w/v) solutions in deionized water and in salt solutions at $25 \pm 0.1°C$.

tions. This agrees with the experimental findings (Figs. 2 and 3). The decrease in the viscosity with increasing ionic content may be related to a more compact structure, which reduces the solute-solvent interaction, or the ionomers of high ionic content are lower in molecular weight.

When the viscosity of the ampholytic ionomers in solutions of varied salt concentrations was studied, it was surprisingly found that added electrolyte had no significant effect for acrylamide MPTMA/AMPS ionomers. Interestingly, however, for acrylamide METMA/MES ionomers the salt effect was significantly different. These results are illustrated in Figs. 4 and 5 for 0.80 and 6.47 mol% MPTMA/AMPS-containing ionomers, respectively, and in Figs. 6 and 7 for a 1.06 mol% and a 6.50 mol% METMA/MES-containing ionomers, respectively. The salt effect might be related to the conformational changes of the polymers in salt solutions. It was reported that the polyampholytes take an expanded conformation in salt solutions [2, 6, 8, 9, 22, 23]. Thus, the addition of salt may have loosened the compact structure of the ionomers with a concomitant expansion in the ampholytic portion of the polymer chain. As a result, more charged sites were exposed, which again raised the possibility of ionic interactions as well as chain entanglements, and these eventually maintained the viscosity. The initial decrease in the viscosity
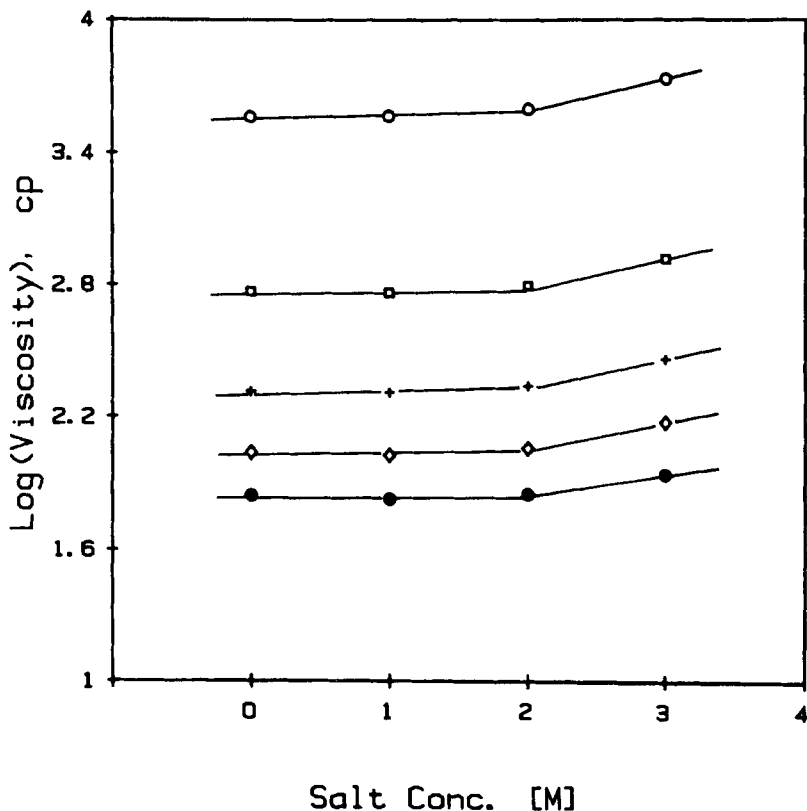
FIG. 4. Viscosity as a function of salt concentration for an acrylamide MPTMA/AMPS ionomer of 0.80 mol% ionic content at $25 \pm 0.1°C$ and at shear rates: (O) 1.92 s^{-1}, (□) 19.20 s^{-1}, (+) 76.80 s^{-1}, (◊) 192.0 s^{-1}, (●) 384.0 s^{-1}.

with increasing added electrolyte for METMA/MES-containing ionomers, especially for 6.50 mol% ionic content, might be due to breaking of a greater agglomerated structure resulting from hydrophobic association between the methacryloyl residues.

Dilute-Solution Viscosity

In dilute solution, both acrylamide ionomer systems, i.e., acrylamide MPTMA/AMPS and acrylamide METMA/MES, demonstrated a significant
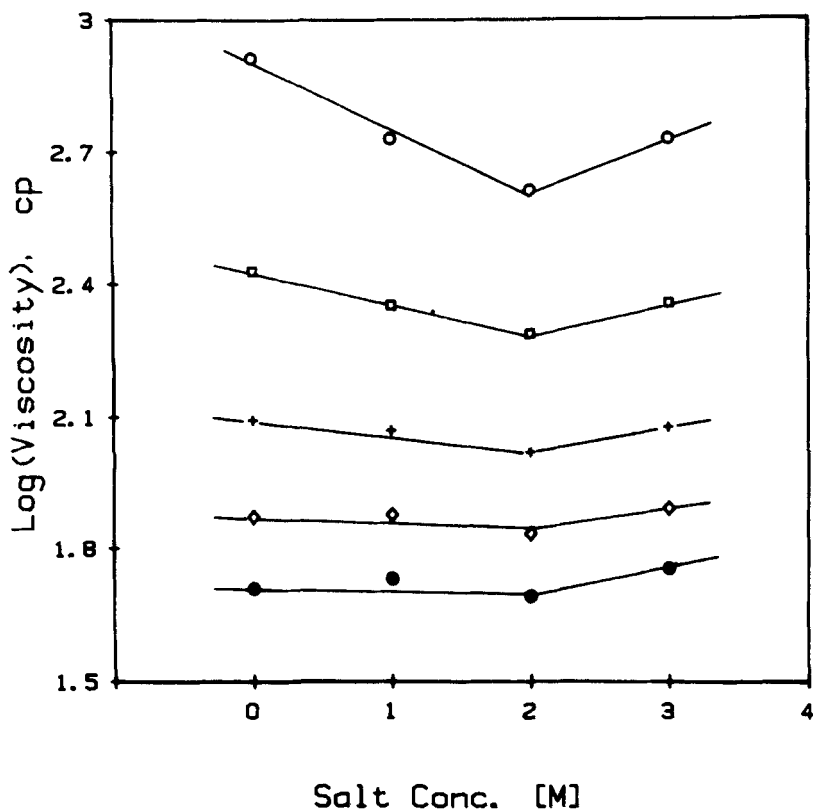
Salt Conc. [M]

FIG. 5. Viscosity as a function of salt concentration for an acrylamide MPTMA/AMPS ionomer of 6.47 mol% ionic content at $25 \pm 0.1°C$ and at shear rates: (O) 1.92 s^{-1}, (□) 19.20 s^{-1}, (+) 76.80 s^{-1}, (◊) 192.0 s^{-1}, (●) 384.0 s^{-1}.

pseudoplasticity even at very high salt concentration. However, the pseudo-plastic behavior of these ampholytic polymers gradually decreased, in general, with decreasing polymer concentration and increasing salt concentration. A typical plot of relative viscosity as a function of shear rate for a sample of ionomer, Sample 2 (Table 2), in deionized water is shown in Fig. 8.

In order to correct for the effect of shear rate in the estimation of viscosity parameters, particularly the intrinsic viscosity, $[\eta]$, which is related to the hydrodynamic volume of the polymer in solution [24], the relative viscosity
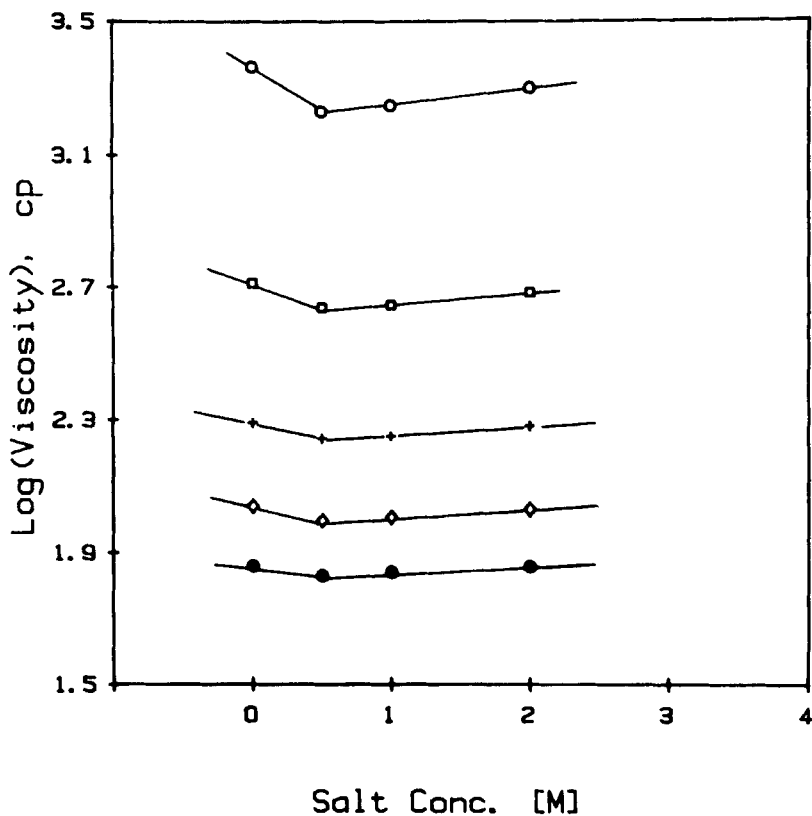
FIG. 6. Viscosity as a function of salt concentration for an acrylamide METMA/MES ionomer of 1.06 mol% ionic content at $25 \pm 0.1°C$ and at shear rates: (○) 1.92 s^{-1}, (□) 19.20 s^{-1}, (+) 76.80 s^{-1}, (◇) 192.0 s^{-1}, (●) 384.0 s^{-1}.

data were extrapolated to zero shear rate for each concentration (Fig. 8). The zero shear rate relative viscosity data, $(\eta_r)_{\dot{\gamma}=0}$, thus obtained were treated by the well-known Huggins equation [25]:

$$(\eta_r)_{\dot{\gamma}=0} - 1 = (\eta_{sp})_{\dot{\gamma}=0} = [\eta]_{\dot{\gamma}=0}C + k'[\eta]^2_{\dot{\gamma}=0}C^2. \qquad (2)$$

The zero shear rate intrinsic viscosity, $[\eta]_{\dot{\gamma}=0}$, was obtained from the extrapolation of the plot of reduced viscosity, $(\eta_{sp}/C)_{\dot{\gamma}=0}$, versus concentration as the
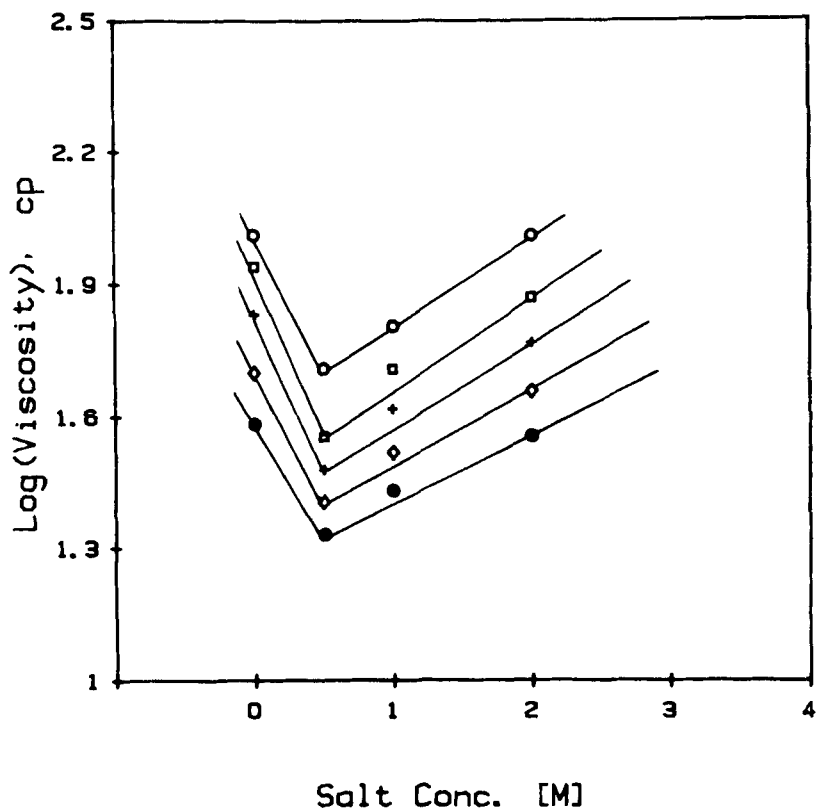
FIG. 7. Viscosity as a function of salt concentration for an acrylamide METMA/MES ionomer of 6.50 mol% ionic content at $25 \pm 0.1°C$ and at shear rates: (O) 1.92 s^{-1}, (□) 19.20 s^{-1}, (+) 76.80 s^{-1}, (◊) 192.0 s^{-1}, (●) 384.0 s^{-1}.

intercept on the viscosity axis. An illustration of this treatment is shown in Fig. 9.

To study the influence of ionic content of the ampholytic polymer on the dilute-solution viscosity parameters with a minimum aggregation effect, the viscosity measurements for both polymer systems were carried out in 3.0 M aqueous NaCl solution. The results are given in Tables 5 and 6. For the acrylamide MPTMA/AMPS ionomer system, with the exception of one sample (Sample 3), the charge density in the polymer did not have a significant influ-
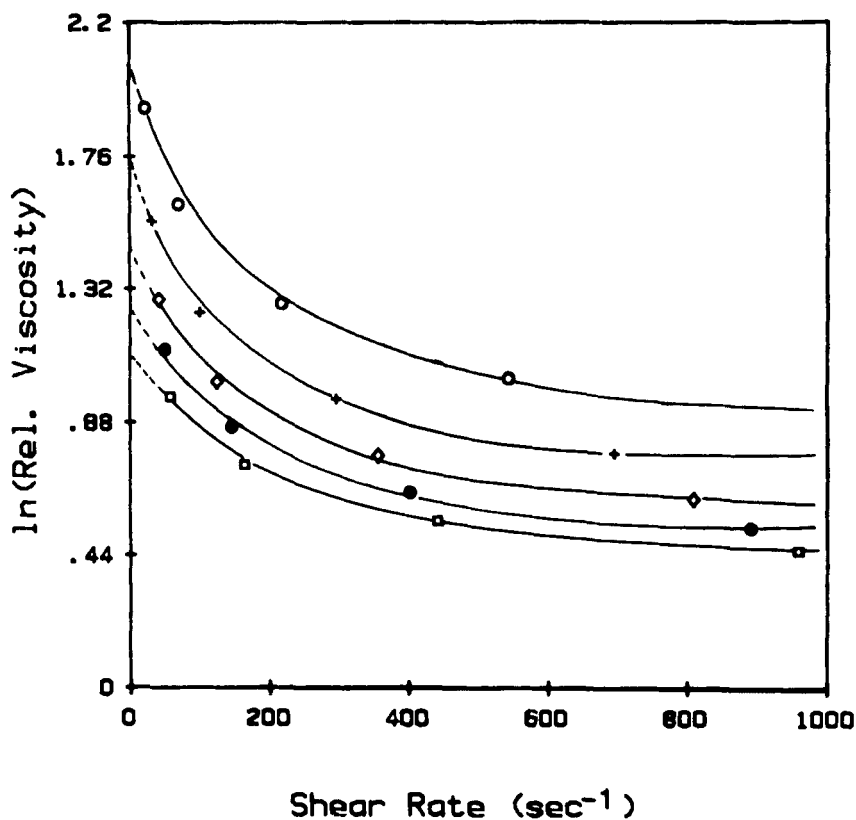
FIG. 8. The plot of relative viscosity as a function of shear rate for an acrylamide MPTMA/AMPS ionomer of 1.47 mol% ionic content in deionized water at $25 \pm 0.1°C$ and at polymer concentrations of (○) 0.037 g/dL, (+) 0.025 g/dL, (◇) 0.018 g/dL, (⊕) 0.015 g/dL, and (□) 0.012 g/dL.

ence on the zero shear rate intrinsic viscosity (Table 5). On the other hand, for acrylamide METMA/MES ionomers, the higher charge density in the polymer drastically influenced the intrinsic viscosity of the polymer (Table 6). This suggests that acrylamide METMA/MES ionomers were either substantially lower in molecular weight or of a compact structure resulting from hydrophobicity of the diester moieties.

The dilute solution viscosity behavior of Sample 2 (Table 2) in solutions of varied salt concentration are summarized in Table 7 and plotted in Fig. 10. It was found that after the initial decrease in $[\eta]_{\dot{\gamma}=0}$, further addition of salt had
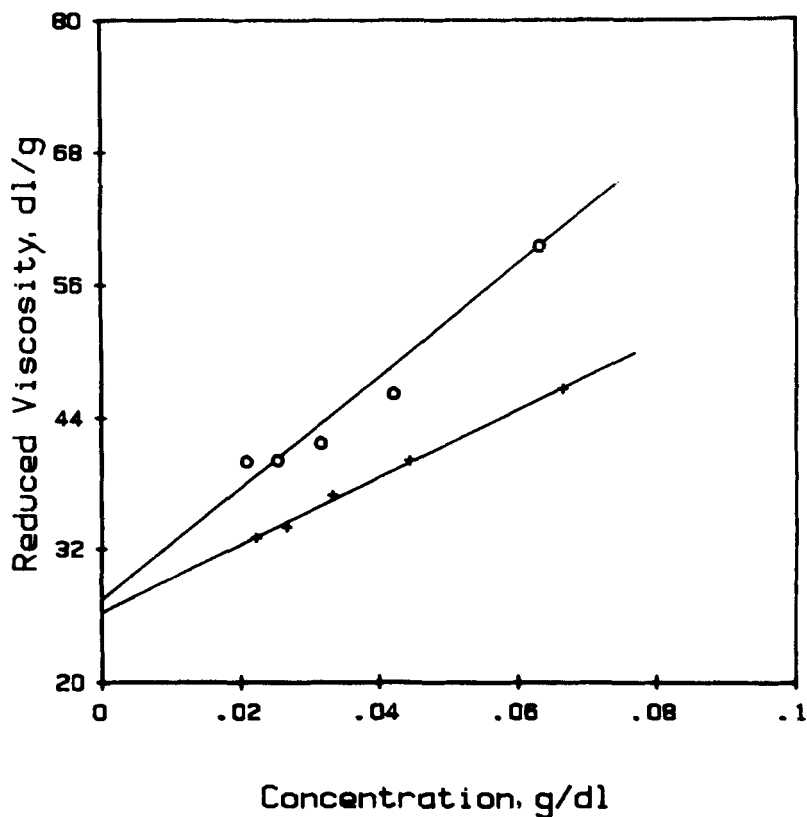
FIG. 9. Huggins plot for an acrylamide MPTMA/AMPS ionomer (Sample 2) in salt solutions: (○) 1.0 M NaCl, (+) 4.0 M NaCl.

no significant effect on it. In order to minimize or eliminate the effects of any systematic errors in the data, ratios of the intrinsic viscosities (water/salt solution) as a function of salt concentration are plotted in Fig. 11. Evidently, very little reduction in the hydrodynamic volume resulted in 5.0 M NaCl concentration compared to 1.0 M NaCl. This behavior may be rationalized on the basis of ampholytic chain expansion in the presence of salt, as described in relation to the semiconcentrated viscosity studies. A similar behavior was observed for a neutral polyacrylamide in salt solutions [26], and the results were interpreted as an expanded hydrodynamic volume due to rearrangements of the hydrogen bonds within the solution.

TABLE 5. Dilute-Solution Viscosity Data for Acrylamide MPTMA/AMPS Ionomers of Various Ionic Contents[a]

Sample	Ion-pair MPTMA/AMPS, mol%	$[\eta]_{\dot{\gamma}=0}$, dL/g	k'	Correlation coefficient
1	0.80	20.50	2.84	1.00
2	1.47	23.52	0.62	1.00
3	3.14	14.00	1.11	1.00
4	6.47	20.73	0.26	1.00

[a]In 3.0 M aqueous NaCl solution at 25 ± 0.1°C.

TABLE 6. Dilute-Solution Viscosity Data for Acrylamide METMA/MES Ionomers of Various Ionic Content[a]

Sample	Ion-pair METMA/MES mol%	$[\eta]_{\dot{\gamma}=0}$, dL/g	k'	Correlation coefficient
5	1.06	12.93	0.52	0.98
7	3.42	6.51	0.28	0.97
8	6.50	2.48	0.75	1.00

[a]In 3.0 M aqueous NaCl solution at 25 ± 0.1°C.

TABLE 7. Dilute-Solution Viscosity Data for an Acrylamide MPTMA/AMPS Ionomer of 1.47 mol% Ionic Content at Various Salt Concentration[a]

[NaCl], M	$[\eta]_{\dot{\gamma}=0}$, dL/g	k' [b]	Correlation coefficient
0.1	171.65	0.02	0.95
1.0	28.31	0.69	0.97
2.0	25.86	0.66	0.96
3.0	23.52	0.62	1.00
4.0	26.73	0.41	1.00
5.0	22.83	0.38	1.00

[a]At 25 ± 0.1°C.
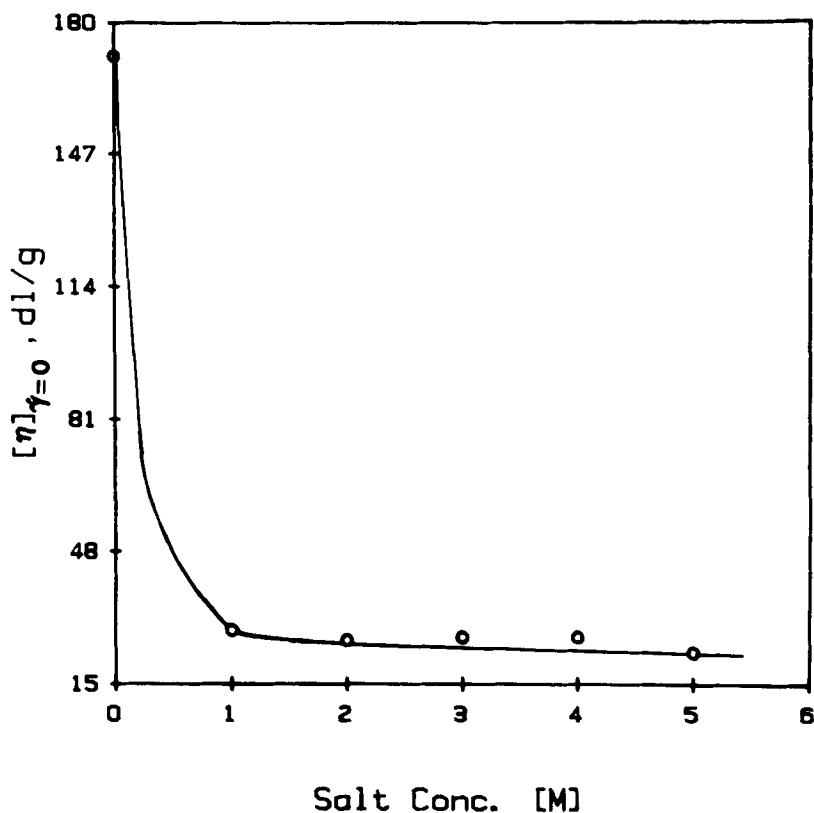[b]For a polymer in a good solvent, k' is expected to be 0.30 [25].

FIG. 10. The zero shear rate intrinsic viscosity, $[\eta]_{\dot{\gamma}=0}$, as a function of salt concentration for an acrylamide MPTMA/AMPS ionomer (Sample 2) at $25 \pm 0.1°C$.

It can also be noted from Table 7 that the Huggins constant, k', decreased gradually with increasing salt concentration. This is understandable since the addition of salt can loosen the compact structure which resulted from the inter- and intramolecular ionic interactions, and thus, the polymer can behave more freely in salt solutions. In other words, the higher the salt concentration, the better the solvation of the polymers. This is also supported by the relatively poor correlation coefficients obtained for the linear relationships of the reduced viscosity with polymer concentration in deionized water as well as in 1.0 and 2.0 M NaCl solutions (Table 7).
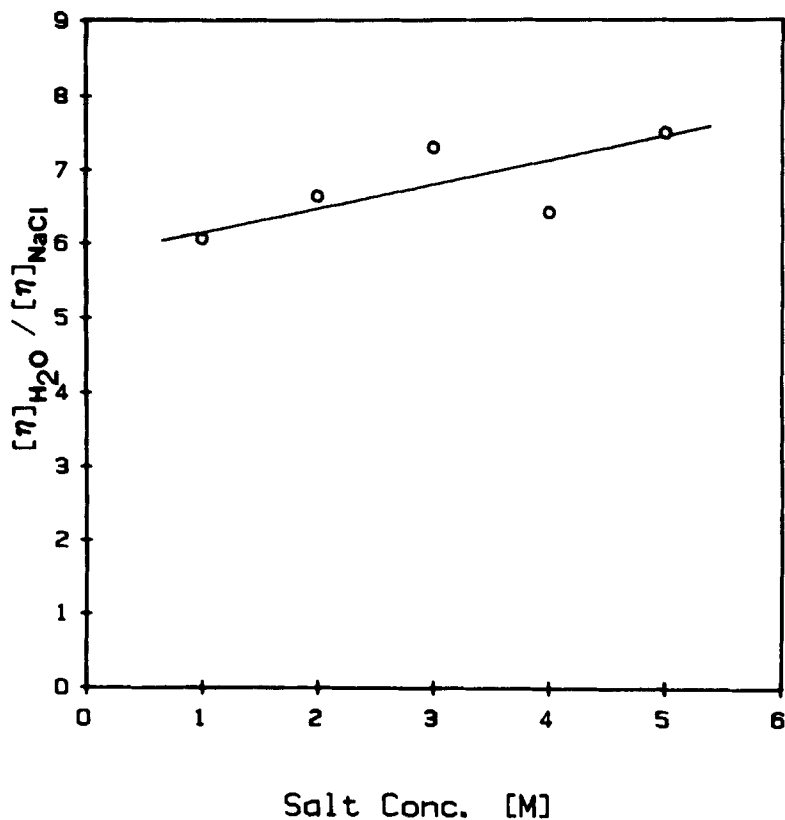
FIG. 11. The intrinsic viscosity ratio (water/salt solution) as a function of salt concentration for an acrylamide MPTMA/AMPS ionomer (Sample 2) at $25 \pm 0.1°C$.

Light-Scattering Studies

To supplement the viscosity studies, investigation of molecular parameters of these ionomer systems by light scattering was undertaken. Light-scattering studies were conducted at similar chemical potential (see Experimental Section) for the ionomers in salt solution. It was reported that, under this condition, light-scattering data can be evaluated by the Zimm technique which is very sensitive to such structural changes as intra- and/or intermolecular association [27-29].
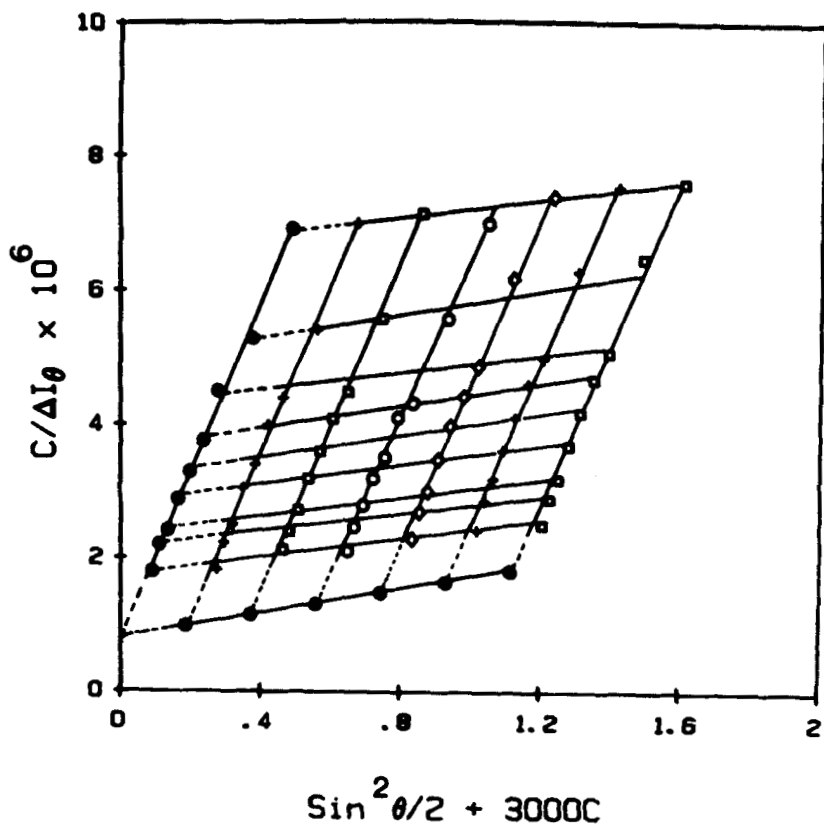
FIG. 12. Zimm plot for an acrylamide MPTMA/AMPS ionomer (Sample 2) in 3.0 M NaCl solution.

The intensities of scattered light were initially measured at 15 different angles ranging from 35 to 123°. The Zimm plots constructed exhibited curvatures beyond 90° scattering angles. However, the data up to 90° gave a reasonably linear plot. Figure 12 shows the Zimm plot up to 90° obtained for Sample 2 in 3.0 M NaCl solution, as an illustration. Though all ionomer samples of both systems were soluble in deionized water, molecular parameters could not be determined in water solution because the light-scattering data yielded a severely twisted Zimm plot owing, presumably, to the formation of aggregates [9, 29, 30].

TABLE 8. Molecular Parameters of Acrylamide MPTMA/AMPS Ionomers Obtained in 3.0 M NaCl Solution

Sample	Ion-pair MPTMA/AMPS, mol%	$\bar{M}_w \times 10^{-6}$	$A_2 \times 10^4$, mL·mol/g^2	R_g, Å	$[\eta]_{\dot{\gamma}=0}$, dL/g
1	0.80	15.00	2.53	3312	20.50
2	1.47	9.97	1.65	2706	23.52
3	3.14	4.00	3.51	2222	14.00
4	6.47	14.18	1.04	3583	20.73

Curvatures at higher scattering angles (>90°) for the solutions of polyacrylamide and acrylamide copolymers have also been observed by other investigators [31-35]. Francois et al. [31] showed that the curvatures at higher angles in the Zimm plot were due to excluded-volume effects and not to the presence of larger aggregates or extraneous floating debris in the light-scattering solutions. Kulkarni and Gundiah [35] as well as Orofino and Flory [36], who observed similar curvatures in the Zimm plots, used data at lower scattering angles for the meaningful evaluation of the weight-average molecular weight, $\bar{M}_w$, the second virial coefficient, A_2, and the radius of gyration, R_g, of the macromolecules. The values of the apparent $\bar{M}_w$, A_2, and R_g reported in this investigation were similarly calculated by using the data at lower scattering angles (<90°).

Tables 8 and 9 summarize the light scattering results for both ionomer systems in 3.0 M NaCl solution. The data appear to be consistent with the dilute-solution viscosity data. The amount of ionic content in the polymers had an

TABLE 9. Molecular Parameters of Acrylamide METMA/MES Ionomers Obtained in 3.0 M NaCl Solution

Sample	Ion-pair METMA/MES, mol%	$\bar{M}_w \times 10^{-6}$	$A_2 \times 10^4$, mL·mol/g^2	R_g, Å	$[\eta]_{\dot{\gamma}=0}$, dL/g
5	1.06	13.50	1.71	2787	12.93
7	3.42	1.74	2.53	1410	6.51
8	6.50	1.00	7.02	1125	2.48

TABLE 10. Molecular Characteristics of 1.46 mol% MPTMA/AMPS-Containing Acrylamide Ionomer at Various NaCl Concentrations

[NaCl], M	$\bar{M}_w \times 10^{-6}$	$A_2 \times 10^4$, mL·mol/g^2	R_g, Å	$[\eta]_{\dot{\gamma}=0}$, dL/g
1.0	14.40	0.20	2779	28.31
2.0	10.94	2.01	2846	25.56
3.0	9.97	1.65	2706	23.52
4.0	9.25	2.32	3074	26.73
5.0	5.07	3.29	2342	22.83

effect on molecular weight. The apparent molecular weight decreased first with increasing ionic content and then again increased with further increase in ionic content for acrylamide MPTMA/AMPS ionomers. On the other hand, for acrylamide METMA/MES ionomers, the apparent molecular weight decreased drastically with increasing amount of ionic contant. The reasons for these somewhat different effects are not presently known.

The second virial coefficients, A_2, for both polymer systems were found to be of the same order of magnitude as those reported for a neutral polyacrylamide [37] and for ion-containing acrylamide copolymers [34]. The radii of gyration, R_g, of these ionomers, however, were relatively high compared to other polymers of similar molecular weight in good solvents [34], reflecting the extended conformation of the ionomer chain in salt solution.

To clarify the salt effect, Sample 2 (Table 2) was studied in solutions of varied salt concentrations, and the light-scattering results are shown in Table 10. As the salt concentration is increased, the molecular weight decreases, while the second virial coefficient increases and the radius of gyration remains essentially unaffected. The decrease in molecular weight with increasing added electrolyte may be attributable to the dissociation of agglomerated structures that are present due to intermolecular ionic association in the low ionic strength medium. The increase in A_2 with increasing salt concentration indicates increased polymer-solvent interaction, such as has been observed with other ampholytic polymers [3, 9, 38].

Figure 13 shows that the radius of gyration remained unaffected by increasing salt concentration. This observation appears to confirm the ampholytic chain expansion in salt solution. Thus, with increasing salt concentration, chain expansion compensates for the radius of gyration being reduced
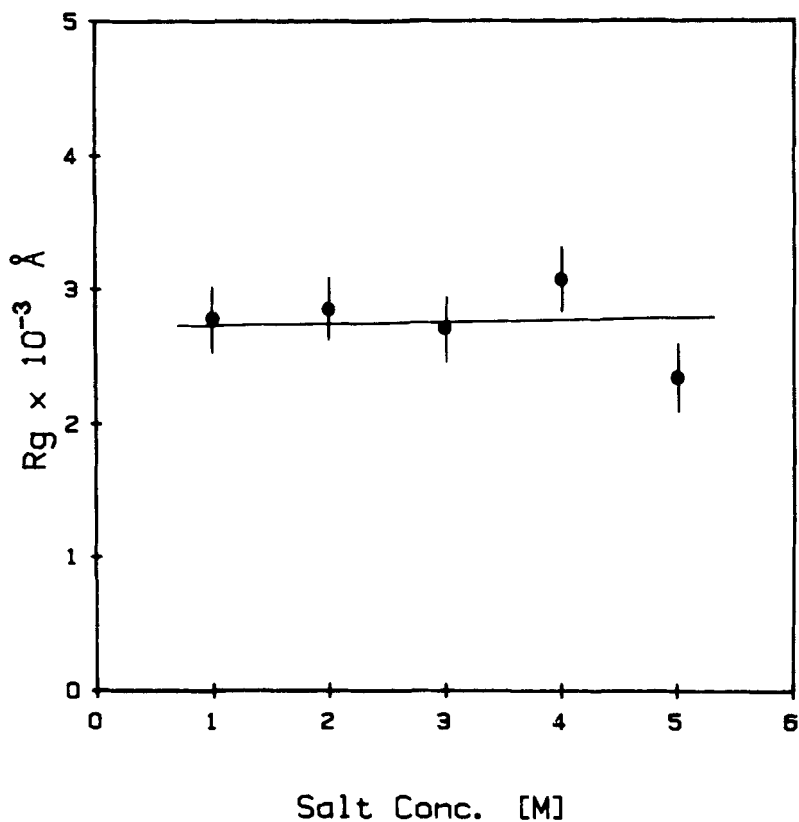
FIG. 13. Radius of gyration as function of salt concentration for an acryl-amide MPTMA/AMPS ionomer.

with decreasing molecular weight. This is in contrast to a cationic [34] or an anionic [39] acrylamide copolymer, in both of which the radius of gyration decreased with increasing added electrolytes.

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