

# Water-Soluble Copolymers. VI. Dilute Solution Viscosity Studies of Random Copolymers of Acrylamide with Sulfonated Comonomers

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## Synopsis

Dilute solution viscosity of a series of random copolymers of acrylamide (AM) with sodium-2-acrylamido-2-methylpropane sulfonate (NaAMPS) and with sodium-2-sulfoethylmethacrylate (NaSEM) has been studied using a four-bulb shear dilution capillary viscometer. The hydrodynamic volume of the copolymers in aqueous media was determined as a function of salt concentration, temperature, shear rate, and time. A linear relationship was observed between the intrinsic viscosity  $[\eta]_0$  and the reciprocal of the square root of ionic strength in sodium chloride solutions, with salt concentrations varying from 0.043M to 0.257M. Negative temperature coefficients for  $[\eta]_0$  indicate a decrease in the hydrodynamic volume of the ionic polymer molecules with increasing temperature. The relative zero-shear-intrinsic-viscosity change in distilled water to 0.257M sodium chloride aqueous media is used to elucidate viscosity-structure relationships. A maximum value is reached for this parameter at a composition of about 30 mol % of ionic comonomers for AM-NaAMPS and AM-NaSEM copolymer series.

## INTRODUCTION

In recent years an increasingly large number of synthetic water-soluble polymers have become available for a wide range of potential applications including use as displacement fluids in enhanced oil recovery.<sup>1,2</sup> The copolymers of acrylamide with sulfonated comonomers represent a group of strong polyelectrolytes and are of special interest in application to enhanced oil recovery. Szabo<sup>3</sup> recently compared a series of mobility control agents including copolymers of acrylamide (AM) with sodium-2-acrylamido-2-methylpropane sulfonate (NaAMPS). These copolymers were rated highly on the basis of cost, flow resistance, and adsorption properties. Brennan and Jennings<sup>4</sup> reported that sulfonated copolymers have better solubility in divalent salt solutions and also improved degradation resistance. However, the effectiveness of these polymers is not easily predicted due to the complexities encountered during use and the lack of adequate macromolecular characterization. Many fundamental questions remain to be answered concerning relationships between molecular structure and flow properties of these aqueous polymer solutions.<sup>2</sup>

Although substantial thermodynamic and viscosity data have been reported for potassium salts of poly(vinylsulfonate)<sup>5</sup> and poly(styrenesulfonate),<sup>6</sup> the sodium salt of poly(styrenesulfonate),<sup>7</sup> and various salts of poly(2-acrylamido-2-methylpropane sulfonate),<sup>8,9</sup> very little work has been published on sulfonated copolymers. In a previous paper,<sup>10</sup> we reported the synthesis and molecular

TABLE I  
Structural Data for the Copolymers of Acrylamide (AM) with Sodium-2-Acrylamido-2-Methylpropane Sulfonate (NaAMPS)

Sample no.	Composition <sup>a</sup>		Blockness <sup>b</sup>		Alternation, <sup>b</sup> AM-NaAMPS	Mean sequence length <sup>b</sup>		$\mu_{AM}/\mu_{NaAMPS}$
	Mol % AM	Mol % NaAMPS	AM-AM	NaAMPS-NaAMPS		$\mu_{AM}$	$\mu_{NaAMPS}$	
AMPS-1-5	90.5	9.5	82.2	1.2	16.6	9.0	1.1	8.2
AMPS-2-5	81.0	19.0	64.1	2.1	33.8	4.6	1.1	4.2
AMPS-3-5	72.1	27.9	50.0	5.7	44.3	3.1	1.2	2.6
AMPS-7-5	34.3	65.7	8.2	39.6	52.2	1.4	2.1	0.7
AMPS	—	100	—	100	—	—	$\infty$	0

<sup>a</sup> From elemental analysis.

<sup>b</sup> Statistically calculated from reactivity ratios.<sup>10</sup>

structure studies of copolymers of AM with NaAMPS and sodium-2-sulfoethylmethacrylate (NaSEM). Here, we wish to discuss some studies of the dilute solution viscosity behavior of these copolymers as a function of factors known to affect the hydrodynamic volume of polyelectrolyte molecules; that is, the ionic character (charge density), the polymer concentration, and the nature and concentration of added salts.

A subsequent paper will be concerned with the analysis of the intrinsic viscosity on the basis of the excluded volume theory and the wormlike chain model.<sup>11</sup>

## EXPERIMENTAL

**Materials.** Copolymers of acrylamide (AM) with sodium-2-sulfoethylmethacrylate (NaSEM) and sodium-2-acrylamido-2-methylpropane sulfonate (NaAMPS) were prepared at 30°C in aqueous solution using potassium persulfate as the initiator. Details of the synthesis, purification, and characterization procedures have been reported previously.<sup>10</sup>

Reagent grade sodium chloride and calcium chloride from J. T. Baker Co. were redried at 100°C for 1 day and used without further purification. All aqueous salt solutions were prepared using distilled water.

**Characterization.** The copolymer composition was determined from elemental analysis, infrared spectroscopy, and <sup>13</sup>C NMR. Micro- and overall

TABLE II  
Structural Data for the Copolymers of Acrylamide (AM) with Sodium-2-Sulfoethylmethacrylate (NaSEM)

Sample no.	Composition <sup>a</sup>		Blockness <sup>b</sup>		Alternation, <sup>b</sup> AM-NaSEM	Mean sequence length <sup>b</sup>		$\mu_{AM}/\mu_{NaSEM}$
	Mol % AM	Mol % NaSEM	AM-AM	NaSEM-NaSEM		$\mu_{AM}$	$\mu_{NaSEM}$	
K-16-5	84.4	15.6	71.8	3.0	25.2	6.8	1.3	5.2
K-6-5	70.5	29.5	51.1	10.1	38.8	3.5	1.6	2.2
K-17-5	53.9	46.1	31.0	23.3	45.7	2.6	2.1	1.2

<sup>a</sup> From elemental analysis.

<sup>b</sup> Statistically calculated from reactivity ratios.<sup>10</sup>

TABLE III  
Number-Average Molecular Weights and Second Virial Coefficients for AM-NaSEM and AM-NaAMPS Copolymers

Sample no.	$\bar{M}_n$ ( $\times 10^{-6}$ g/mol)	$A_2$ ( $\times 10^4$ ml-mol/g <sup>2</sup> )
K-16-5	$0.78 \pm 0.04$	11.20
K-6-5	$0.69 \pm 0.03$	10.40
K-17-5	$0.47 \pm 0.03$	7.70
AMPS-1-5	$1.11 \pm 0.05$	6.23
AMPS-2-5	$1.08 \pm 0.06$	4.75
AMPS-3-5	$0.92 \pm 0.06$	3.97
AMPS-7-5	$0.80 \pm 0.04$	3.78
AMPS	$0.76 \pm 0.03$	3.66

structure (Tables I and II) were calculated statistically as reported in the previous paper of this series.<sup>10</sup>

Number average molecular weights and second virial coefficients (Table III) of the copolymers were measured with a Knauer Membrane Osmometer in aqueous 0.257M NaCl solutions at 30°C. A B-19 type membrane from Arro Laboratories, Inc., was used for the measurement of osmotic pressures.

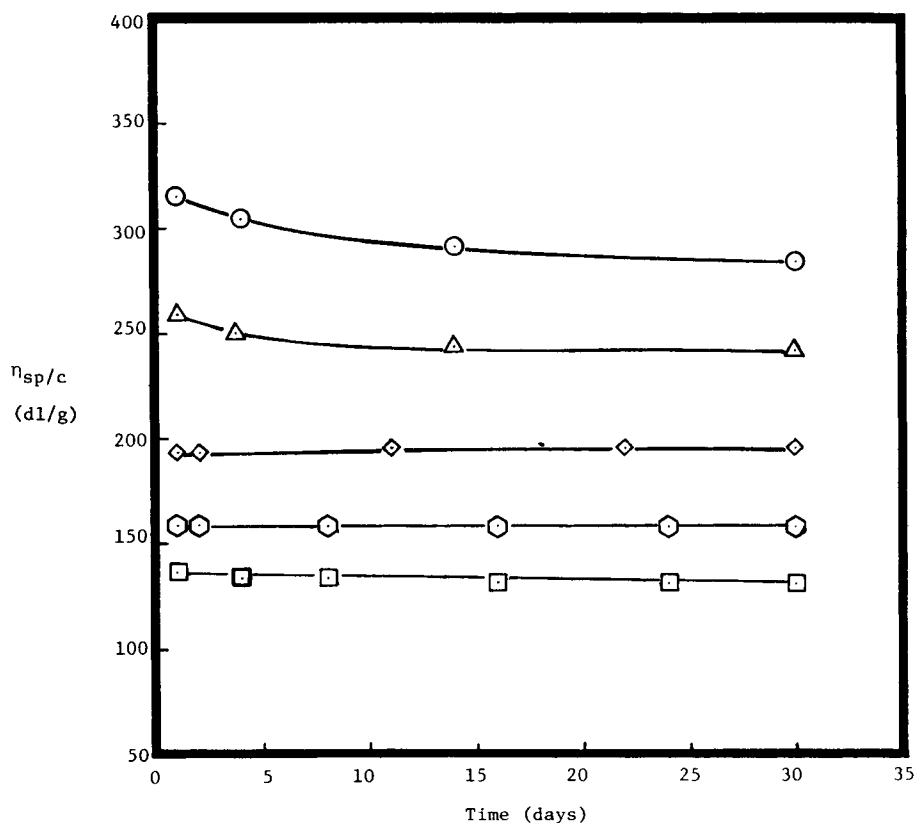


Fig. 1. Dependence of reduced viscosity  $\eta_{sp}/c$  of AM-NaAMPS and AM-NaSEM copolymers in water on time ( $T = 30^\circ\text{C}$ ; polymer concentration = 0.05 g/dL): (○) K-16-5; (△) K-17-5; (◇) AMPS-1-5; (⊙) AMPS-7-5; (□) AMPS.

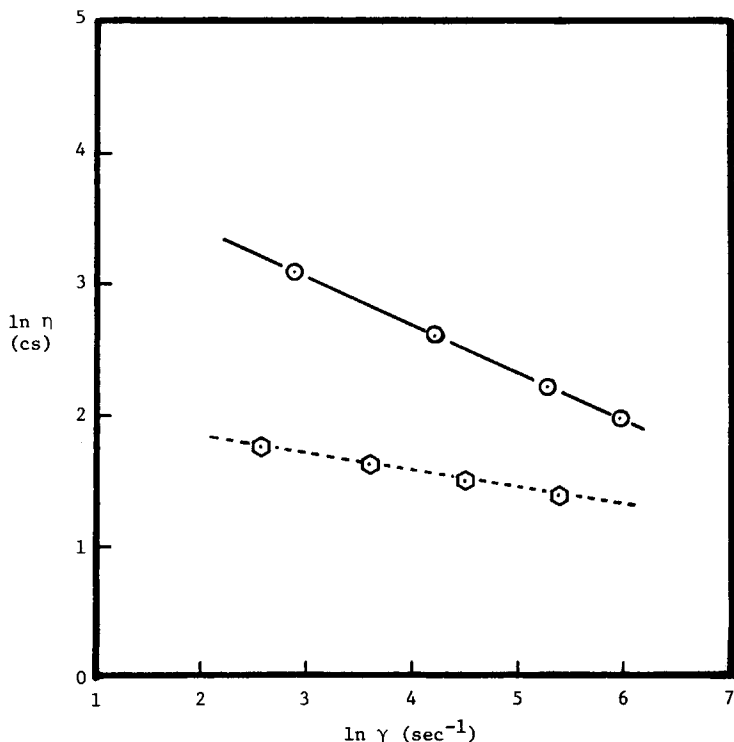


Fig. 2. Dependence of  $\ln \eta$  on  $\ln \gamma$  for AMPS (---) and for copolymer AMPS-1-5 (—) in 0.043M NaCl solution.

**Preparation of Solutions.** A series of stock solutions of sodium chloride in water ranging in salt concentrations from 0.0428M to 0.2570M, a 0.0857M calcium chloride solution (ionic strength = 0.2570), and a series of mixed NaCl/CaCl<sub>2</sub> solutions with total ionic strength 0.2570 were prepared by dissolving the appropriate amount of salt in water in a volumetric flask. Weighed quantities of the polymers were dissolved in the salt solutions in volumetric flasks at low shear rate.

**Viscosity Measurements.** Solution viscosities were measured in Cannon-Ubbelohde four-bulb shear dilution capillary viscometers (size 50, 100, and 150). The correction for kinetic energy was negligible.<sup>12</sup> Since absolute values were not essential for the analysis involved in this study, we neglected the density of the polymer solutions involved. The apparent viscosity  $\eta$  (also referred to as "kinematic viscosity") can then be related to the flow time  $t$  by a simplified equation<sup>12</sup>:

$$\eta = C_1 t \quad (1)$$

where  $C_1$  is the viscometer constant. The shear rate at the wall of the capillary,  $\gamma$ , was calculated from the following equation<sup>13,14</sup>:

$$\gamma = C_2/t \quad (2)$$

where  $C_2$  is the shear rate constant of each bulb. The viscometers used in this study were calibrated by Cannon Instrument Company.

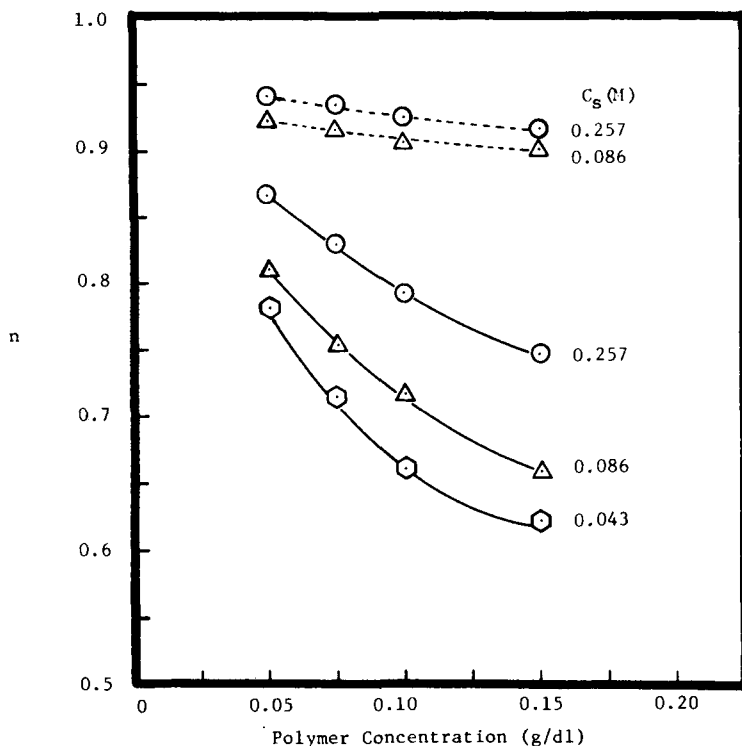


Fig. 3. Dependence of power law parameter  $n$  on the polymer concentration for AMPS (----) and for copolymer AMPS-1-5 (—) at different sodium chloride concentrations  $C_s$ .

Viscosity measurements of the polymer solutions were performed at different temperatures in water and aqueous salt solutions of various ionic strengths. Intrinsic viscosities  $[\eta]$  were obtained in the usual way by extrapolation of both the reduced viscosity  $\eta_{sp}/c$  and the inherent viscosity  $(\ln \eta_r)/c$  to infinite dilution according to<sup>15</sup>

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c \quad (3)$$

or

$$(\ln \eta_r)/c = [\eta] + k''[\eta]^2c \quad (4)$$

where  $k'$  is the Huggins constant and  $k''$  is the Kraemer constant.

## RESULTS AND DISCUSSION

### Aging Effect

Solution instability, also called the aging effect, appears experimentally as a decrease of solution viscosity and a loss of flocculation activity with time. This behavior has been observed for a number of water soluble polymers like polyacrylamides<sup>16-18</sup> and hydrolyzed polyacrylamides.<sup>19,20</sup> In this study it was observed that only the AM-NaSEM copolymers showed a slight decrease in pure water in the reduced viscosity with time (Figure 1). This decrease amounts to

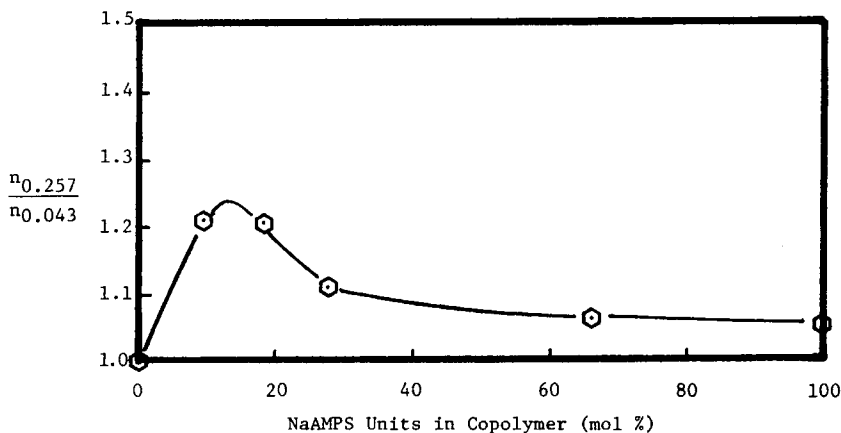


Fig. 4. Effect of copolymer composition on the power law parameter ratio,  $n_{0.257}/n_{0.043}$ , at 30°C (polymer concentration = 0.15 g/dL).

about 6–8% after 30 days, after which approximately the same value of  $\eta_{sp}/c$  will be reached. On the other hand, the homopolymer NaAMPS and the AM–NaAMPS copolymers show negligible aging behavior in water (<3%) (Fig. 1).

It is also of great interest to test the aging effect in the presence of a low molecular weight electrolyte such as NaCl. In 0.257M sodium chloride solution the viscosity decrease within 30 days is negligible (<2%) for all copolymers. This may indicate that addition of low molecular weight electrolyte reduces the time dependent viscosity decrease for AN–NaSEM copolymers.

Kulicke and Kniewske<sup>20</sup> have recently concluded, based on light scattering measurements, that the viscosity loss observed in solutions of hydrolyzed polyacrylamides cannot be explained by chain degradation, but may be caused by a conformational change of single macromolecules involving a cooperative effect of loosening and combining of hydrogen bonds. A similar behavior may be assumed for the AM–NaSEM copolymers in aqueous solutions. In general, viscosity stabilization can be observed after about 30 days for these polymer solutions.

### Effect of Shear Rate

A knowledge and control of the pseudoplastic nature of the water-soluble polymer solutions is extremely important because of the shear rates encountered by the injection fluids in enhanced oil recovery. At high shear rate conditions, as they exist near the well bore, the lower viscosity of pseudoplastic solutions results in less fluid flow resistance and thus less power is required for the injection of such solutions into a reservoir. Away from the well bore, small average shear rates ( $1\text{--}10\text{ s}^{-1}$ )<sup>21</sup> experienced in the reservoir by the polymer solutions would cause an increase in the fluid viscosity. High values of fluid viscosity in the reservoir are desirable because the polymer solution's displacement of oil is more efficient.

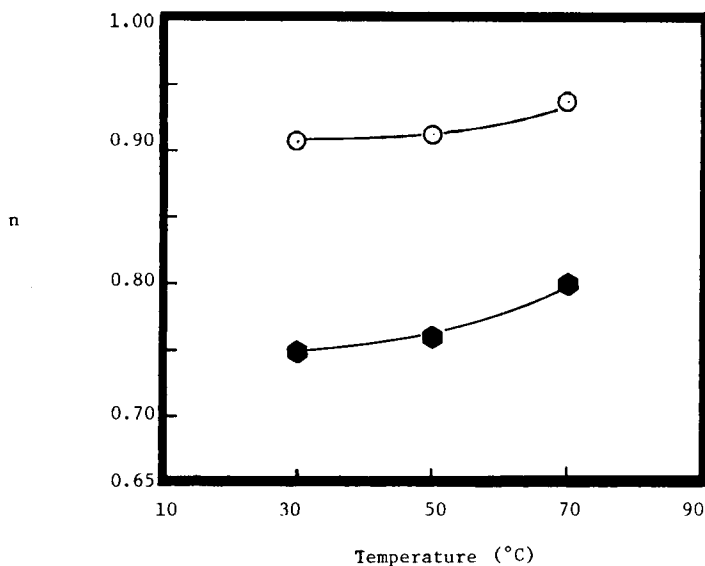


Fig. 5. Dependence of the power law parameter  $n$  on temperature for copolymers K-16-5 (○) and AMPS-1-5 (●) (polymer concentration = 0.15 g/dL).

The viscosity at different shear rates was studied as a function of the polymer concentration, salt concentration, and temperature. Using the simple “power law” model for pseudoplastic flow,

$$\eta = K \cdot \gamma^{n-1} \quad (5)$$

the exponent  $n$ , which is a measure of the non-Newtonian behavior of a fluid system, can be determined from the double logarithmic dependence of the viscosity  $\eta$ , on the shear rate  $\gamma$  (Fig. 2);  $K$  is a constant. In the Newtonian range,  $n$  is equal to 1 and for pseudoplastic fluids  $n$  is less than 1. Figure 3 represents some typical values of  $n$  for the NaAMPS homopolymer and an AM–NaAMPS copolymer sample as a function of polymer and NaCl concentration. The pseudoplastic behavior of these ionic copolymers increases in general with increasing polymer and decreasing salt concentration.

In order to show the dependence of the exponent  $n$  on the content of ionic groups in the copolymer and to minimize or eliminate the effect of the different molecular weights of the samples on  $n$ , the ratios ( $n_{0.257}/n_{0.043}$ ) of  $n$  in 0.257M aqueous NaCl solutions to  $n$  in 0.043M aqueous NaCl solution are used.

Results obtained from homopolyacrylamides of various molecular weights ( $M = 700,000$ – $5,000,000$ ) have shown that  $n$  is insensitive to changes in salt concentration within the limits of error.<sup>22</sup> The resulting  $n$  ratio is therefore unity for homopolyacrylamides and independent of the molecular weight of the sample. Figure 4 shows the effect of copolymer composition for the AM–NaAMPS copolymers on this  $n$  ratio. An increase in this ratio demonstrates a decrease in pseudoplastic behavior upon addition of salt to an aqueous polymer solution. A maximal decrease in pseudoplastic behavior is reached by copolymers with about 15 mol % of sulfonate groups in the polymer chain.

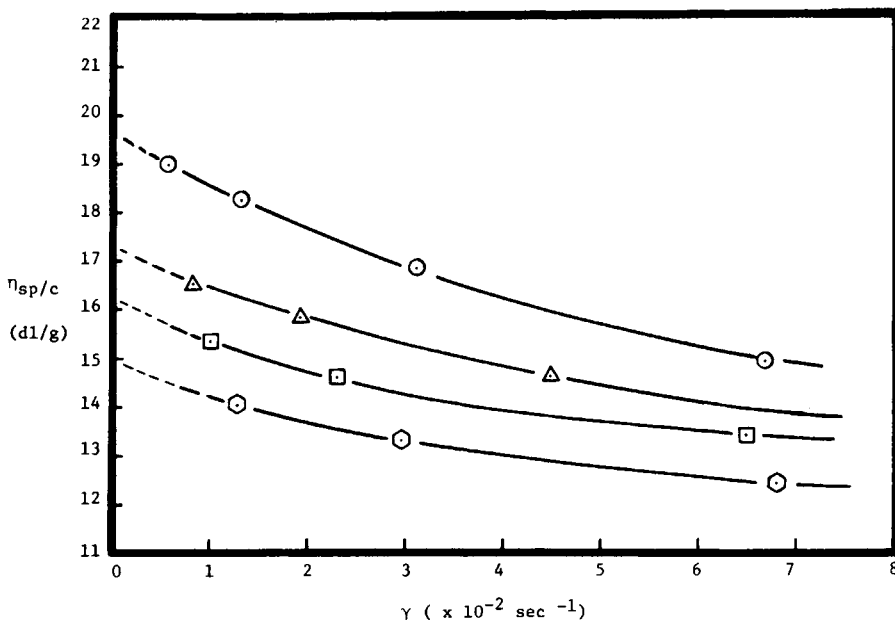


Fig. 6. Reduced viscosity for copolymer sample K-16-5 in 0.257M NaCl solution as a function of shear rate at 30°C. Polymer concentration: (○) 0.150 g/dL; (Δ) 0.100 g/dL; (◻) 0.075 g/dL; (◊) 0.050 g/dL.

The power law parameter  $n$  increases in general, approaching the Newtonian range, with increasing temperature as Figure 5 demonstrates for an AM-NaSEM and an AM-NaAMPS copolymer sample.

The significant pseudoplasticity of these solutions is also demonstrated by some typical viscosity data in Figure 6. In order to correct for the effect of shear rate in the estimation of the intrinsic viscosity, and in the absence of low-shear-rate data, the reduced viscosity data were extrapolated to zero shear rate<sup>13</sup> and the value of  $\eta_{sp}/c$  at this limit was obtained for each concentration. Plots of  $\eta_{sp}/c$  and  $(\ln \eta_r)/c$  vs. the concentration  $c$  (dL/g) (Fig. 7) were extrapolated to zero concentration according to eqs. (3) and (4) to obtain values for the intrinsic viscosities at zero shear rate,  $[\eta]_0$ . Figure 8 and Table IV clearly show the effect of shear rate on the intrinsic viscosity  $[\eta]$  and the Huggins constant  $k'$ . It was observed that  $[\eta]$  and  $k'$  increased with decreasing shear rate for all polymer solutions investigated.

### Effect of Ionic Strength, Temperature, and Composition on the Intrinsic Viscosity

The viscosities of the ionic copolymer solutions are strongly influenced by the addition of salts. A marked contraction of the polyelectrolyte coils occurs which is reflected in decreased intrinsic viscosity values.

The intrinsic viscosities may be related to the hydrodynamic volume of the polymer molecules by the Flory-Fox equation,<sup>23,24</sup> assuming nondraining, random coil character:

$$[\eta]_0 = \Phi_0 \langle (\bar{r}^2)^{3/2} \rangle_n / \bar{M}_n \quad (6)$$



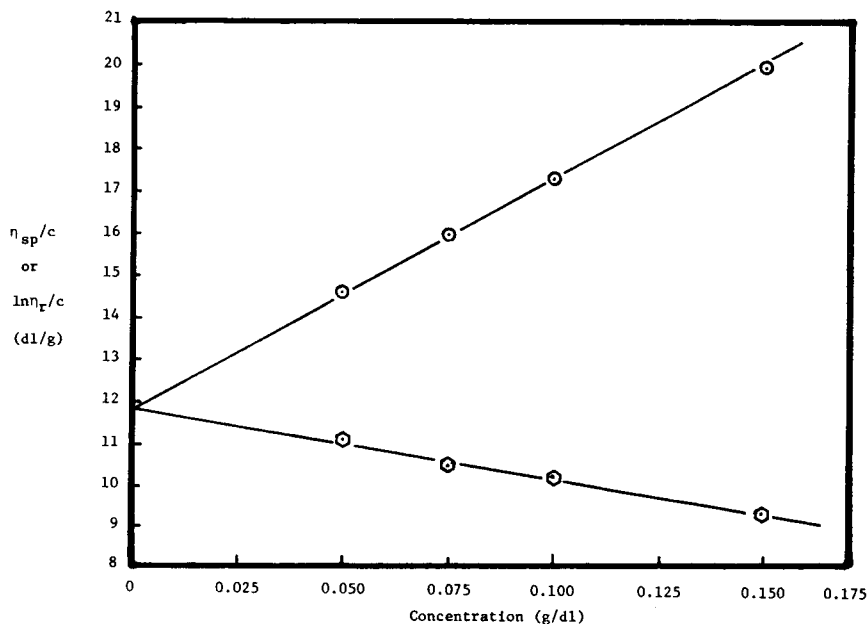


Fig. 7. Huggins ( $\odot$ ) and Kraemer ( $\ominus$ ) plots for K-16-5 copolymers in 0.257M NaCl solution at zero shear rate (temperature = 30°C).

where  $\Phi_0$  is the universal constant of the Flory theory,  $\langle(\bar{r}^2)^{3/2}\rangle_n$  is the number-average of the 1.5 power of the mean square end-to-end distance and  $\bar{M}_n$  is the number-average molecular weight. Values for the hydrodynamic volume parameter  $\langle(\bar{r}^2)^{3/2}\rangle_n$  of the synthesized copolymers in deionized water and

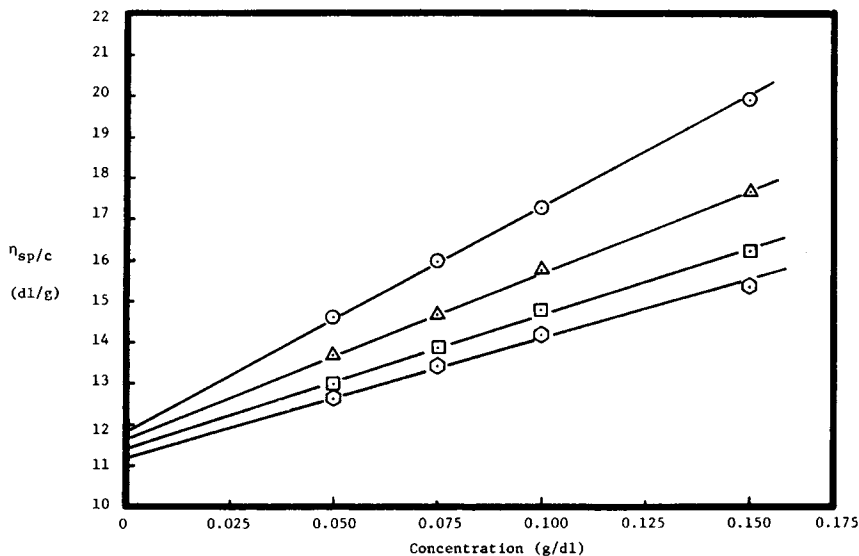


Fig. 8. Reduced viscosity concentration curves for K-16-5 copolymers in 0.257M NaCl solution at different shear rates (temperature = 30°C). Shear rate: ( $\odot$ ) 0 s<sup>-1</sup>; ( $\Delta$ ) 200 s<sup>-1</sup>; ( $\square$ ) 400 s<sup>-1</sup>; ( $\ominus$ ) 600 s<sup>-1</sup>.

TABLE IV  
Dependence of Intrinsic Viscosity and Huggins Constant on Shear Rate in 0.257M NaCl Solution at 30°C

Sample	$\gamma$ (s <sup>-1</sup> )	$[\eta]$ (dL/g)	$k'$
K-16-5	600	11.2	0.22
K-16-5	400	11.4	0.26
K-16-5	200	11.5	0.31
K-16-5	0	11.8 <sup>a</sup>	0.37 <sup>a</sup>
AMPS-1-5	300	25.5	0.14
AMPS-1-5	150	27.5	0.20
AMPS-1-5	50	28.5	0.33
AMPS-1-5	0	29.5 <sup>a</sup>	0.41 <sup>a</sup>

<sup>a</sup> From extrapolation to zero shear rate.

0.257M NaCl solution are given in Table V. The same value for the Flory constant  $\Phi_0 = 2.87 \times 10^{21}$  was adopted here for the calculations, due to a present lack of knowledge of the variation of  $\Phi$  with copolymer composition. Values of  $\Phi$  reported<sup>25,26</sup> for polyelectrolyte solutions are smaller than the value derived by Flory for nondraining coils. Therefore, it is important to bear in mind that the values given for  $\langle (\bar{r}^2)^{3/2} \rangle_n$  in Table V are merely lower bounds for the true values of  $\langle (\bar{r}^2)^{3/2} \rangle_n$ , which might actually be much larger, especially with distilled water as solvent. The relative change of the molecular size parameters with copolymer composition will be discussed later in this section.

The zero shear rate intrinsic viscosity,  $[\eta]_0$ , is experimentally found to be roughly linear with respect to the reciprocal square root of the ionic strength ( $1/\sqrt{I}$ ) of sodium chloride solutions (Figs. 9 and 10), where the ionic strength  $I$  of the aqueous salt medium is defined by

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (7)$$

In this equation  $m_i$  represents the molal concentration of ion species  $i$  with electrochemical valence  $z_i$ . Fisher, Sochor, and Tan<sup>8</sup> reported a similar linear relationship for the homopolymer NaAMPS in aqueous sodium chloride solutions. Such a linear relationship between  $[\eta]$  and  $I^{-1/2}$  [eq. (8)] in which  $[\eta]_\infty$

TABLE V  
Molecular Size Parameters for Copolymers of AM-NaAMPS and AM-NaSEM in Distilled Water and 0.257M NaCl at 30°C

Sample	Solvent: H <sub>2</sub> O		Solvent: 0.257M NaCl	
	$[\eta]_0$ (dL/g)	$\langle (\bar{r}^2)^{3/2} \rangle_n$ ( $\times 10^{-10} \text{ \AA}^3$ )	$[\eta]_0$ (dL/g)	$\langle (\bar{r}^2)^{3/2} \rangle_n$ ( $\times 10^{-10} \text{ \AA}^3$ )
K-16-5	310	8.2	11.8	0.32
K-6-5	320	7.7	9.4	0.23
K-17-5	215	3.52	7.4	0.12
AMPS-1-5	330	12.8	29.5	1.14
AMPS-2-5	340	12.8	23.0	0.87
AMPS-3-5	400	12.8	13.2	0.42
AMPS-7-5	335	9.3	12.8	0.36
AMPS	260	6.9	9.5	0.25

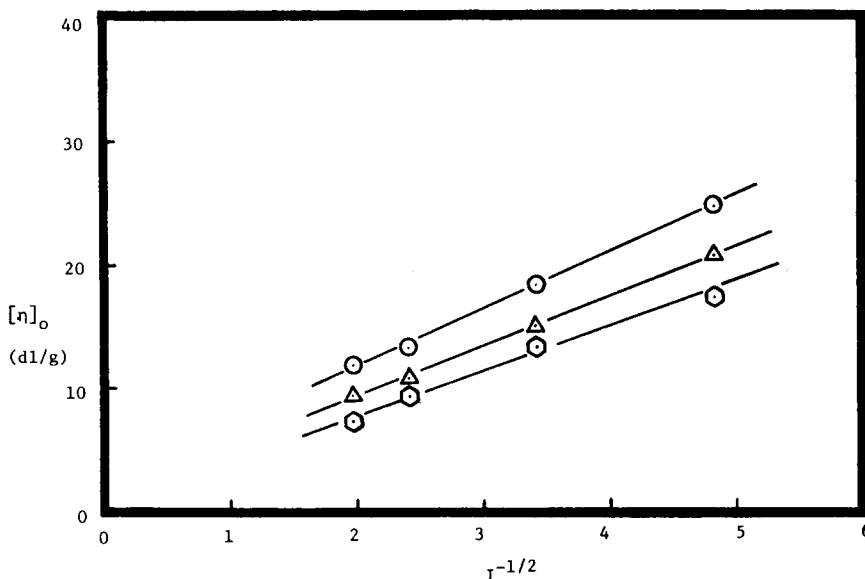


Fig. 9. Zero shear intrinsic viscosity of AM-NaSEM copolymers as a function of (ionic strength) $^{-1/2}$  in aqueous NaCl solutions: (○) K-16-5; (△) K-6-5; (○) K-17-5.

is the hypothetical intrinsic viscosity of the polyelectrolyte in an infinitely concentrated salt solution

$$[\eta] = [\eta]_{\infty} + \text{const}/I^{1/2} \quad (8)$$

has been reported for a large number of systems by several authors.<sup>27-29</sup> Our observations, as shown in Figures 8 and 9, further substantiate the experimental findings for copolymers of acrylamide with the sulfonated comonomers, NaSEM and NaAMPS.

The Huggins constant  $k'$  decreased with increasing concentration of added salt. Some typical results are given in Table VI. This is understandable since the polyelectrolyte molecule should be more extended in 0.043M than in 0.257M NaCl and dilution has a smaller effect on the viscosity of a more coiled molecule.

The addition of divalent gegenions to the sulfonated copolymers does not lead to precipitation as often observed in the case of polyacrylates,<sup>16</sup> but to a stronger viscosity decrease than in monovalent salt solutions.

Figure 11 demonstrates the effect of the fraction of divalent gegenions in a salt mixture of NaCl and CaCl<sub>2</sub> on  $[\eta]_0$  of two AM-NaAMPS copolymers at constant ionic strength  $I = 0.257$ . A decrease in  $[\eta]_0$  is observed with increasing divalent gegenion concentration.

These salt effects on the viscosity can be rationalized by increased shielding of the ionized sulfonate groups from one another by the gegenions or, alternatively, by a change in the water structure due to binding of the gegenions to individual groups causing a volume change.<sup>30</sup> Additionally, conformational fluctuations, due to changes in hydrogen bonding can influence the viscosity behavior.

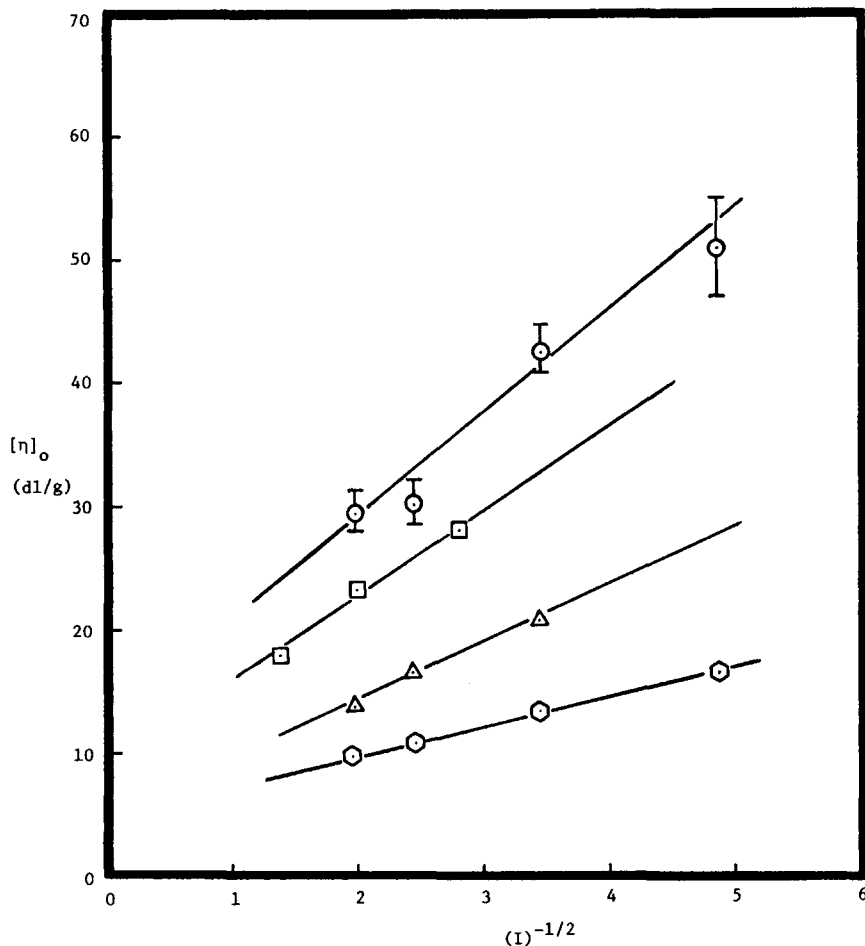


Fig. 10. Zero shear intrinsic viscosity of AM-NaAMPS copolymers as a function of (ionic strength)<sup>-1/2</sup> in aqueous NaCl solutions: (○) AMPS-1-5; (◻) AMPS-2-5; (△) AMPS-3-5; (○) AMPS.

TABLE VI  
Viscosity Parameters for Copolymers K-16-5 and AMPS-1-5 in Sodium Chloride Aqueous Solution at 30°C

Sample no.	Solvent	$[\eta]_0^a$	$k'^b$
K-16-5	0.257M NaCl (aq)	11.8 ± 0.5	0.37 ± 0.03
K-16-5	0.086M NaCl (aq)	17.5 ± 0.7	0.42 ± 0.04
K-16-5	0.043M NaCl (aq)	23.5 ± 1.0	0.46 ± 0.04
AMPS-1-5	0.257M NaCl (aq)	29.5 ± 1.0	0.41 ± 0.05
AMPS-1-5	0.086M NaCl (aq)	42.5 ± 2.0	0.54 ± 0.05
AMPS-1-5	0.043M NaCl (aq)	51.0 ± 3.5	0.70 ± 0.08

<sup>a</sup> Value derived from extrapolation to zero shear rate.

<sup>b</sup>  $k'$  = Huggins constant.

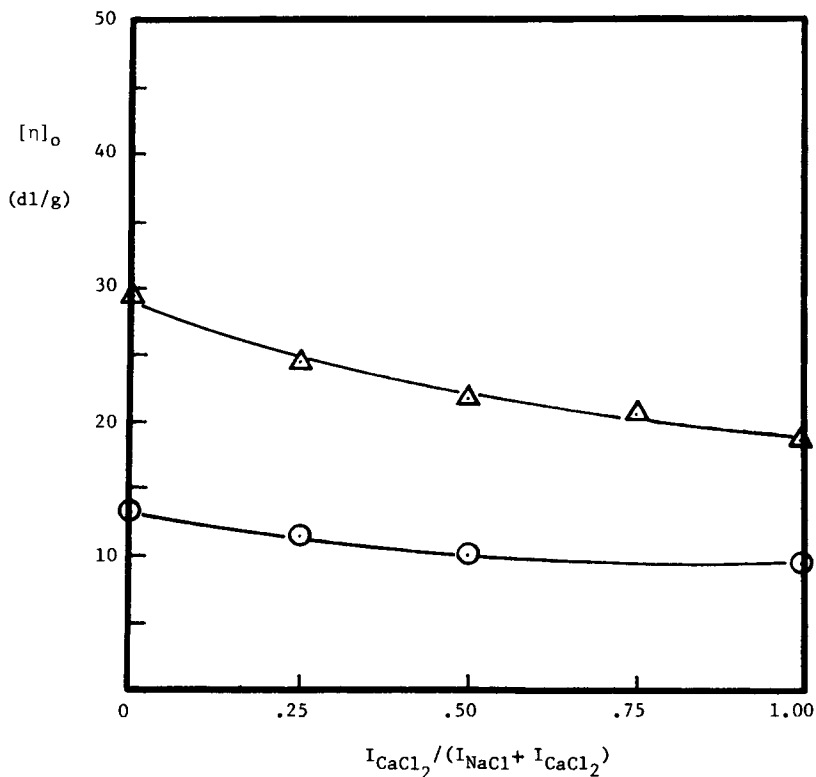


Fig. 11.  $[\eta]_0$  as a function of  $I_{CaCl_2}/(I_{NaCl} + I_{CaCl_2})$  at  $I_{total} = 0.257$ ;  $T = 30^\circ C$ . ( $\Delta$ ) AMPS-1-5; ( $\odot$ ) AMPS-3-5.

Intrinsic viscosities in  $0.257M$  aqueous NaCl solutions are plotted against temperature in Figure 12 for some copolymer samples. A logarithmic ordinate scale has been used for convenience. The temperature coefficients of  $[\eta]_0$  for the range  $30\text{--}70^\circ C$  are listed in Table VII. They are almost an order of magnitude greater than those observed for other polymers in good solvents. The latter seldom exceed  $\pm 0.02\%$  per degree in magnitude.<sup>24</sup> (In poor solvents they are strongly positive.) The decrease in  $[\eta]_0$  with temperature indicates a decrease in the hydrodynamic volume of the polymer molecules with increasing temperature. This behavior is mainly due to solvent effects on  $[\eta]_0$ , which are attributable to changes in the molecular expansion brought about by solvent action.

Since both molecular weight and composition are variables in the copolymers, the ratio of the intrinsic viscosity in distilled water to that in  $0.257M$  aqueous NaCl solution was chosen to study the effects of copolymer composition and microstructure on the hydrodynamic volume and therefore on the viscosity. By working with ratios it is hoped to minimize or eliminate the effects of any systematic errors in the absolute values.

Ratios of the intrinsic viscosities for the discussed copolymers are presented in Figure 13 as a function of the mol % of sulfonate units. Evidently, a maximum

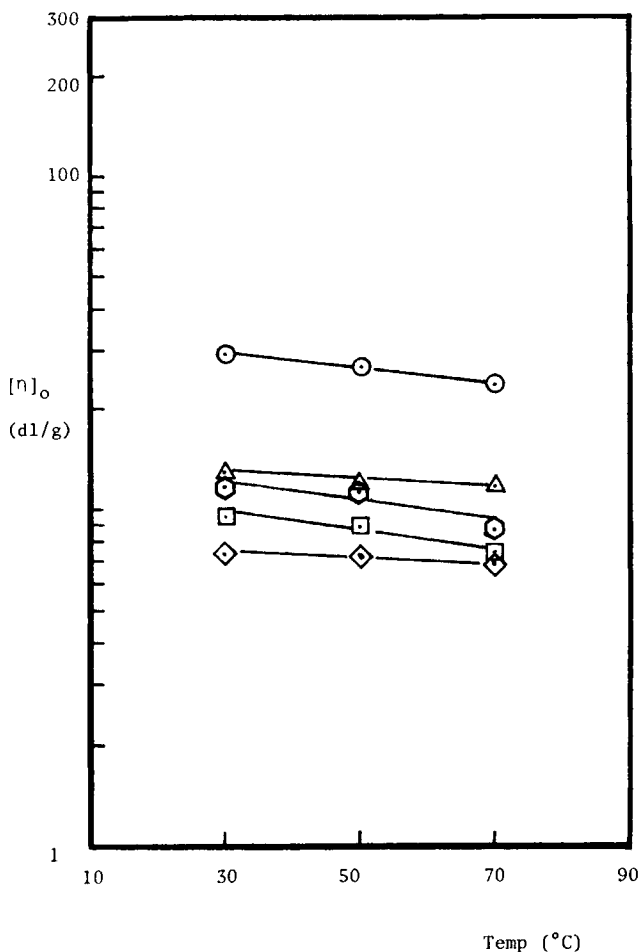


Fig. 12. Zero shear intrinsic viscosity in aqueous 0.257M NaCl solution as a function of temperature. Copolymer samples: (○) AMPS-1-5; (△) AMPS-3-5; (⊙) K-16-5; (□) AMPS; (◇) K-17-5.

value is reached for the ratio at a composition of about 30 mol % of sulfonate units. Above this value this parameter becomes very weakly dependent on the polyelectrolyte charge density. Similar results were also obtained for hydrolyzed polyacrylamide samples.<sup>31</sup> Apparently, the viscosity loss in brine increases

TABLE VII  
Temperature Coefficients of Intrinsic Viscosity

Sample	$-(d \ln[\eta]_0/dT) \times 10^2$ (°C <sup>-1</sup> )
AMPS-1-5	0.53
AMPS-3-5	0.30
AMPS	0.58
K-16-5	0.56
K-17-5	0.11

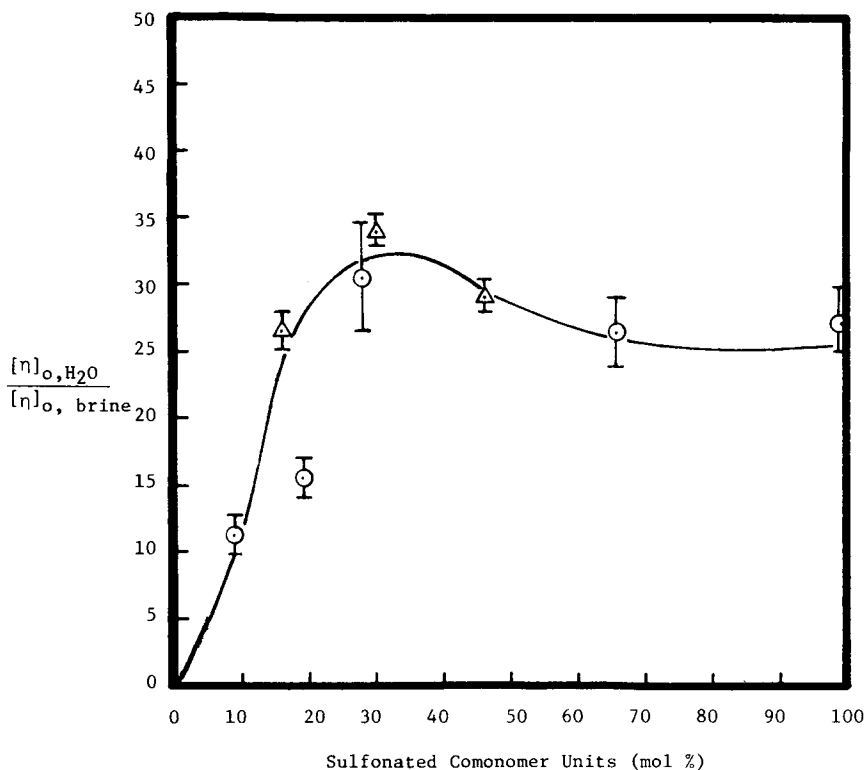


Fig. 13. Compositional effect on zero shear intrinsic viscosity ratio at 30°C: ( $\Delta$ ) AM-NaSEM copolymers; ( $\odot$ ) AM-NaAMPS copolymers.

strongly up to 30 mol % ionic units and stays almost constant with increasing polyelectrolyte charge density above this value.

In order to characterize the monomer sequence distribution (microstructure) and its influence on the dilute solution viscosity, the mean lengths of the closed monomer sequences (mean sequence lengths)  $\mu_{AM}$  and  $\mu_{sulfonate}$  have been calculated from reactivity ratios<sup>10,32</sup> and are listed for the AM-NaAMPS and AM-NaSEM copolymers in Tables I and II, respectively. Figure 14 shows the effect of the ratio of the mean sequence lengths  $\mu_{AM}/\mu_{sulfonate}$  on the intrinsic viscosity ratio. The hydrodynamic volume of homo-NaAMPS in 0.257M NaCl-brine decreases roughly by a factor of 30 in comparison to the hydrodynamic volume in distilled water. Evidently, there is not much change in the intrinsic viscosity ratio by increasing the mean sequence length ratio from 0 to about 3 acrylamide units per sulfonate unit. Increasing the latter to about 5 acrylamide units per sulfonate unit causes a relatively steep decrease in the salt sensitivity of the viscosity of AM-NaAMPS copolymer solutions which is followed by a weakly declining trend as  $\mu_{AM}/\mu_{sulfonate}$  increases further. A comparison with the AM-NaSEM copolymer data shows that the latter has intrinsic viscosity ratios which lie slightly above the values for the AM-NaAMPS samples and decrease less in the range from  $\mu_{AM}/\mu_{sulfonate} = 3-5$ . In order to prepare a sulfonated acrylamide copolymer with lower salt sensitivity, the mean sequence length ratio  $\mu_{AM}/\mu_{sulfonate}$  should be above 4 for NaAMPS as comonomer, and

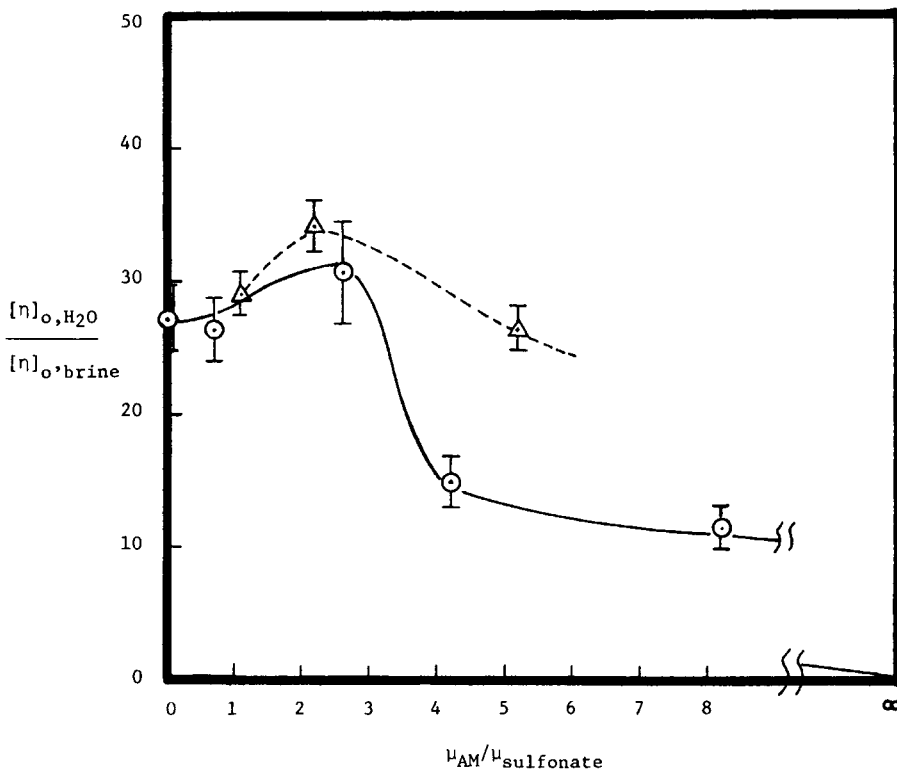


Fig. 14. Effect of the ratio of the mean sequence lengths,  $\mu_{AM}/\mu_{sulfonate}$ , on the zero shear intrinsic viscosity ratio at 30°C: ( $\Delta$ ) AM-NaSEM copolymers; ( $\circ$ ) AM-NaAMPS copolymers.

probably above 8 for NaSEM as comonomer. For  $\mu_{AM}/\mu_{sulfonate}$  ratios below 3 acrylamide units per sulfonated unit, the salt sensitivity of the polyelectrolyte solutions is higher, but rather insensitive with variations in the block size of the NaAMPS sequences. The significance of the microstructure of these model copolymers on the excluded volume of the macromolecules, and the persistence length will be further discussed in a subsequent paper.

## CONCLUSIONS

The viscosity of dilute aqueous solutions of the synthesized sulfonate-containing copolymers was found to follow typical polyelectrolyte behavior. High viscosities and pseudoplastic behavior are observed in distilled water. Addition of salts reduced viscosity to varying degrees depending upon copolymer microstructure. High salt sensitivity was found for copolymers with more than 30 mol % of sulfonate units and a mean sequence length ratio of less than 3 acrylamide units per sulfonated unit; the hydrodynamic volume of the copolymers in brine decreased roughly by a factor of 30 in comparison to the hydrodynamic volume in distilled water.

In order to prepare a sulfonated acrylamide copolymer with low salt sensitivity, the mean sequence length ratio should be above 4 acrylamide units per NaAMPS unit and above 8 acrylamide units per NaSEM unit. The viscosity aging for these



copolymers was found to be negligible for AM–NaAMPS copolymers and small in comparison to hydrolyzed polyacrylamides for the AM–NaSEM copolymers. The copolymers showed significant negative temperature coefficients for the intrinsic viscosity, indicating a decrease in the hydrodynamic volume with temperature.

From a practical point of view it is preferable to use samples with high sulfonate content for salt-free environments because the macromolecules will be more extended. When the concentration of salts is high, it is obvious that samples with low sulfonate content must be used. The facility with which these copolymers can be tailored includes them as excellent candidates for use in a variety of field conditions such as those encountered in enhanced oil recovery.

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### APPENDIX: NOMENCLATURE

$c$	polymer concentration (g/dL)
$C_1$	viscometer constant
$C_2$	viscometer shear rate constant
$I$	ionic strength, defined by eq. (7)
$k'$	Huggins constant
$k''$	Kraemer constant
$K$	power law constant
$m$	molal concentration (mol/1000 g solvent)
$M$	molar concentration (mol/L)
$\bar{M}_n$	number average molecular weight (g/mol)
$n$	power law exponent
$(\bar{r}^2)$	mean square end-to-end distance, Å
$t$	time (s)
$T$	temperature (°C)
$z$	electrochemical valence
$\gamma$	shear rate (s <sup>-1</sup> )
$\eta$	kinematic viscosity (cS)
$\eta_r$	relative viscosity
$\eta_{sp}$	specific viscosity
$[\eta]$	intrinsic viscosity (dL/g)
$\mu$	mean sequence length
$\Phi_0$	universal constant of Flory viscosity theory (dL/mol-cm <sup>3</sup> )
AM	acrylamide
AM–NaAMPS	random copolymers of AM with NaAMPS
AM–NaSEM	random copolymers of AM with NaSEM
NaAMPS	sodium-2-acrylamido-2-methylpropane sulfonate
NaSEM	sodium-2-sulfoethylmethacrylate

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