Water-soluble polymers: 33. Ampholytic terpolymers of sodium 2-acrylamido-2-methylpropanesulphonate with 2-acrylamido-2-methylpropanedimethylammonium chloride and acrylamide: synthesis and aqueous-solution behaviour

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Synthesis and viscometric studies of a series of moderate-to-low charge-density terpolymers of acrylamide (AM) with sodium 2-acrylamido-2-methylpropanesulphonate (NaAMPS) and 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) have been conducted. Plots of apparent viscosity *versus* polymer concentration revealed critical overlap concentrations (C^*) in the range 0.10–0.14 g dl^{-1}. The dependence of the reduced viscosity of the terpolymers on temperature was minimal, with only a slight decrease in viscosity observed with increasing temperature. Reduced viscosity was shown to be a function of polymer composition, charge distribution and molecular weight of the terpolymers. The low-to-moderate charge-density terpolymers of NaAMPS with AMPDAC displayed viscosities over 100% greater than the high charge-density copolymers. The superior viscometric characteristics of the terpolymers became more evident as the polymer concentration approaches C^*.

(**Keywords: synthesis; water-soluble polymers; terpolymers; viscosity; solution behaviour**)

INTRODUCTION

Water-soluble polymers are used in a number of applications, including enhanced oil recovery, drag reduction and absorbency, in which electrolyte tolerance is necessary for efficient performance. Polyampholytes have received relatively little attention despite their potential in such applications. These polymers offer unique properties as a result of ionic interactions, both intra- and intermolecular in nature, which affect hydrodynamic volume. Polyampholytes differ from conventional polyelectrolytes in that they contain both positive and negative charges distributed in some fashion along the polymer backbone.

Salamone *et al.* reported the synthesis of polyampholytes derived from cationic–anionic monomer pairs[1]. High charge-density copolymers with 1:1 molar ratios of the respective comonomers displayed viscosity behaviour in salt solution unlike that of normal polyelectrolytes. Later, the same group reported the spontaneous polymerization of several ion-pair comonomers[2,3]. The viscosities of the copolymers increased with potassium chloride concentration. Several studies have also been conducted on aliphatic and aromatic sulphobetaine polyampholytes, which incorporate positive and negative charges within the mer unit. Several of these inner salt polymers possess hydrogel characteristics. Peiffer and Lundberg recently reported the importance of incorporating non-charged monomers into ampholytic polymers for optimum viscosity behaviour[4].

Series of high charge-density copolymers of 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) with sodium 2-acrylamido-2-methylpropanesulphonate (NaAMPS) have been studied previously in our laboratories[5,6]. The solution properties of these polymers are determined by a number of parameters including charge type and distribution, polymer microstructure, molecular weight, hydrophobic/hydrophilic balance, solvent type, pH and ionic strength. Intramolecular ionic interactions dominate solution behaviour of copolymers with 1:1 molar compositions of AMPDAC and AMPS respectively.

In this work we report the synthesis and viscometric characterization of a series of low-to-moderate charge-density ampholytic terpolymers of AMPDAC, NaAMPS and acrylamide (AM). These have been synthesized and characterized with the goal of elucidating on a molecular level the effects that dictate macroscopic solution properties.

EXPERIMENTAL

Materials and monomer synthesis

2-Acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) was synthesized as previously described[7]. AMPDAC was converted to the base, 2-acrylamido-2-methylpropanedimethylamine (AMPDA) prior to purification. AMPDAC was found to be prone to spontaneous polymerization if stored in the acid form. To accomplish the deprotonation, AMPDAC was placed

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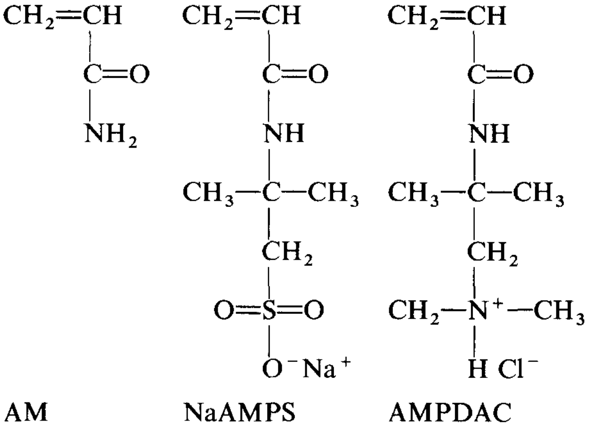
in a large excess of water followed by the addition of NaOH to attain a pH of 12. The uncharged AMPDA was then extracted with a three-fold excess of methyl ethyl ketone (MEK) and isolated by rotary evaporation of the MEK. The crude AMPDA was then recrystallized twice from MEK prior to use (m.p. = 61–63°C). Analysis calculated (for $C_9H_{18}N_2O$) C 63.49, H 10.65, N 16.46%; found C 63.42, H 10.27, N 16.58%. I.r.: N–H, 3270 cm^{-1}; C=C–H, 2980 cm^{-1}; aliphatic C–H, 2880 cm^{-1}; C=O, 1660 cm^{-1} (s), 1550 cm^{-1} (m); tertiary amine, 1160 cm^{-1}.

2-Acrylamido-2-methylpropanesulphonic acid (AMPSA) was obtained from Fluka Chemical Co. and recrystallized three times from a mixture of dry methanol and 2-propanol followed by vacuum drying at room temperature prior to use. A decomposition temperature of 185°C was observed for AMPSA. Acrylamide (AM) was obtained from Aldrich Chemical Co. and recrystallized twice from acetone followed by vacuum drying at room temperature prior to use (m.p. 83°C).

Polymer synthesis

The syntheses of terpolymers of 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) with sodium 2-acrylamido-2-methylpropanesulphonate (NaAMPS) and acrylamide (AM) (1), the ADASAM series, were conducted via free-radical initiation in water at 30°C employing potassium persulphate as the free-radical initiator. The total monomer concentration in each reaction was held constant at 0.45 M. The reaction mixture was diluted with two to four volumes of deionized water followed by precipitation into three volumes of reagent-grade acetone while stirring. A typical *FT*i.r. spectrum for ADASAM 15–15 is as follows: amide I, 1665 cm^{-1}; amide II, 1548 cm^{-1}; C–H stretch 2936–2984 cm^{-1}; asymmetrical CH_3 bending, 1453 cm^{-1}; geminal dimethyl groups, 1390 and 1370 cm^{-1}; S=O stretch, 1043 and 1200 cm^{-1}; ammonium ion N–H stretch, 3066 cm^{-1}; tertiary amine salt, 2752 cm^{-1}; N–H broad, 3400 to 3300 cm^{-1}.



(1)

$$CH_2{=}CH{-}C({=}O){-}NH_2 \qquad CH_2{=}CH{-}C({=}O){-}NH{-}C(CH_3)_2{-}CH_2{-}S({=}O)_2{-}O^-Na^+ \qquad CH_2{=}CH{-}C({=}O){-}NH{-}C(CH_3)_2{-}CH_2{-}N^+H(CH_3)_2\,Cl^-$$

Compositional studies

Terpolymer compositions for the ADASAM series were determined by elemental analysis for carbon, nitrogen and sulphur using the equations:

$$\mathrm{C}\,(\%)/12.01 = 7A + 9B + 3C \tag{2}$$

$$\mathrm{N}\,(\%)/14.01 = 1A + 2B + 1C \tag{3}$$

$$\mathrm{S}\,(\%)/32.06 = 1A \tag{4}$$

A, *B* and *C* represent the number of moles of NaAMPS, AMPDAC and AM, respectively, in a normalized weight of sample, e.g. 100 g. After determining *A*, *B* and *C* using matrix algebra, compositional data (mol%) were calculated using the equations:

$$\text{NaAMPS (mol\%)} = \frac{A}{A+B+C} \times 100 \tag{5}$$

$$\text{AMPDAC (mol\%)} = \frac{B}{A+B+C} \times 100 \tag{6}$$

$$\text{AM (mol\%)} = \frac{C}{A+B+C} \times 100 \tag{7}$$

Molecular-weight studies

Light scattering studies were performed on a Chromatix KMX-6 low-angle laser light scattering spectrophotometer utilizing a 2 mW He–Ne laser operating at 633 nm. All measurements were conducted at 25°C in 1.0 M aqueous NaCl solutions at a pH of 7.0. For quasielastic light scattering a Brookhaven BI-2030, 128-channel digital correlator was used in conjunction with the KMX-6. Multiple sample times were used to extend the range and accuracy of the autocorrelation function, which was evaluated via the method of cumulants[8].

Viscometric analysis

Aqueous stock solutions of NaCl (0.085, 0.140, 0.257 and 0.514 M) were prepared. Stock polymer solutions were prepared by dissolving the required quantity of polymer in each type of salt solution. Typical stock concentrations were 0.25 $g\,dl^{-1}$ for salt solutions and 0.13 $g\,dl^{-1}$ for pure water. The polymers were dissolved by slowly rotating solution vials in a manner such that shear degradation was avoided.

Solution viscosities were determined using a Contraves LS-30 Low Shear Rotational Rheometer. Measurements of the apparent viscosity at shear rates of 1.75 s^{-1} were used in conjunction with solvent viscosities to calculate reduced viscosities. Intrinsic viscosities were calculated using the Huggins equation. Precautions were taken to ensure that data used in the calculation of intrinsic viscosities were from the region of concentration below the critical overlap concentration, i.e. $[\eta]_0 C < 1$.

RESULTS AND DISCUSSION

Previous work in our laboratories[5,6] revealed that the NaAMPS/AMPDAC pair form interesting copolymers whose properties depend upon composition, pH and ionic strength of the aqueous solvent. For example, copolymers with 1:1 molar composition of NaAMPS:AMPDAC in the feed show maximum viscosity under high salt conditions and collapsed structures in pure water. Conventional polyelectrolyte behaviour is obtained at comonomer compositions with a large excess of either AMPDAC or NaAMPS. Copolymers intermediate in composition (e.g. 40–45 mol% AMPDAC) exhibit properties consistent with the operation of both repulsive and attractive ionic interactions.

In this study we sought to enhance terpolymer viscosity (or hydrodynamic volume) in salt solutions by introducing the hydrophilic acrylamide comonomer with the NaAMPS/AMPDAC pair. Such enhancement could be of great utility when designing high-viscosity and superabsorbent polymers. Important contributions of each monomer are as follows: (a) acrylamide—hydrophilic,

Table 1 ADASAM series: elemental analysis data

Sample name	C (%)	N (%)	S (%)
ADASAM 0.5–0.5	47.23	17.83	0.60
ADASAM 2.5–2.5L[a]	45.00	16.02	1.17
ADASAM 2.5–2.5	45.17	16.04	1.20
ADASAM 5–5L	44.73	15.11	1.86
ADASAM 5–5	46.52	15.69	2.06
ADASAM 10–10L	45.47	13.97	3.21
ADASAM 10–10	40.00	12.46	3.24
ADASAM 15–15L	46.06	13.32	4.05
ADASAM 15–15	45.97	13.37	3.98
ADASAM 5–10L	43.03	13.85	3.14
ADASAM 5–10	46.12	14.91	3.22
ADASAM 10–5L	45.27	14.70	2.16
ADASAM 10–5	40.27	12.91	2.13

[a] L denotes low conversion

Table 2 ADASAM series: reaction parameters[a] and terpolymer compositions

Sample name	Feed composition (AMPDAC: NaAMPS:AM)	Terpolymer composition[b] (AMPDAC: NaAMPS:AM)
ADASAM 0.5–0.5	0.5:0.5:99.0	1.0:1.5:97.5
ADASAM 2.5–2.5L[c]	2.5:2.5:95.0	5.2:3.4:91.4
ADASAM 2.5–2.5	2.5:2.5:95.0	5.4:3.4:91.2
ADASAM 5–5L	5:5:90	8.6:5.8:85.6
ADASAM 5–5	5:5:90	8.2:6.2:85.6
ADASAM 10–10L	10:10:80	11.1:12.6:76.3
ADASAM 10–10	10:10:80	10.7:12.6:76.7
ADASAM 15–15L	15:15:70	20.1:15.9:64.0
ADASAM 15–15	15:15:70	19.5:15.5:65.0
ADASAM 5–10L	5:10:85	8.2:10.7:81.1
ADASAM 5–10	5:10:85	8.3:10.2:81.5
ADASAM 10–5L	10:5:85	13.3:8.2:78.5
ADASAM 10–5	10:5:85	12.6:7.2:80.2

[a] pH = 6.0; $T = 30°C$; total monomer concentration = 0.45 M; $[K_2S_2O_8] = 4.5 \times 10^{-4}$ M

[b] Determined via elemental analysis for carbon, nitrogen and sulphur

[c] L denotes low conversion

high rate constant for polymerization in water; (b) NaAMPS—high reactivity, good hydrolytic stability due to the geminal dimethyl groups, ionization even at low pH values; (c) AMPDAC—hydrophilic, stabilized by geminal dimethyl groups, a 'matched' monomer for pairing with NaAMPS.

The polymers were prepared by separately placing a specified quantity of each monomer in deionized water followed by the addition of the corresponding inorganic salt, after which the solutions were mixed and eventually initiated. This procedure is analogous to that used for the copolymerization of AMPDAC with NaAMPS[4], with the exception that acrylamide was added.

Composition studies

Terpolymer compositions for the AMPDAC–NaAMPS–AM (ADASAM series) were calculated using elemental analysis for carbon, nitrogen and sulphur (*Table 1*). Terpolymer feed and compositional data are illustrated in *Table 2* along with the reaction conditions. The numbers following 'ADASAM' represent the mole per cent of AMPDAC and NaAMPS, respectively, in the terpolymer feed. For example, ADASAM 5–10 represents a terpolymer that included 5% AMPDAC, 10% NaAMPS and 85% AM in the reaction feed.

Molecular-weight studies

Weight-average molecular weights, second virial coefficients, degrees of polymerization (*DP*) and intrinsic viscosities in 1.0 M NaCl are listed for the ADASAM terpolymer series in *Table 3*. In general, as the ionic character of the terpolymers increases, the molecular weights increase from 1.0×10^6 to 12.0×10^6.

Light scattering (*Table 3*) and compositional data (*Table 2*) indicate that increasing the content of AMPDAC in the polymer causes a reduction in molecular weight, whereas increasing the amount of NaAMPS in the polymer results in an increase in molecular weight. ADASAM 15–15 displays a maximum in molecular weight of 12×10^6 g mol^{-1} because NaAMPS apparently propagates faster and/or causes less chain transfer than AMPDAC. The minimum in molecular weight for the series is exhibited by ADASAM 0.5–0.5, which is composed of the fewest number of charged mers.

The molecular weight does not solely influence the properties of the polymers, however. It is significant that the sample that displays the largest viscosity, ADASAM 5–5, possesses neither the highest molecular weight nor the greatest *DP*. Also, the sample that displays the greatest molecular weight, ADASAM 15–15, exhibits an intrinsic viscosity much less than most of the other polymers. This limited observation suggests that solution behaviour is influenced by copolymer compositional effects on solvation and molecular weight.

Quasielastic light scattering data, which include diffusion coefficients and mean hydrodynamic diameters, are given in *Table 4* along with values for degrees of polymerization and intrinsic viscosities in 1.0 M NaCl.

Table 3 ADASAM series: low-angle laser light scattering data[a]

Sample name	$M_w \times 10^{-6}$ (mol^{-1})	$A_2 \times 10^4$ (ml mol g^{-2})	$DP_w \times 10^{-4}$	$[\eta]^b$ (dl g^{-1})
ADASAM 0.5–0.5	1.03	–	13.8	1.79
ADASAM 2.5–2.5	7.40	2.93	88.3	14.7
ADASAM 5–5	8.77	9.27	95.1	17.5
ADASAM 10–10	7.57	2.87	71.8	14.1
ADASAM 15–15	12.0	2.78	98.3	8.31
ADASAM 5–10	10.5	2.43	107	15.6
ADASAM 10–5	3.75	–	37.7	7.19

[a] pH = 7.0; $T = 25°C$; [NaCl] = 1.0 M

[b] pH = 7.0; $T = 25°C$; [NaCl] = 1.0 M; via Contraves LS-30 Low Shear Rotational Rheometer

Table 4 ADASAM series: quasielastic light scattering data[a]

Sample name	$DP_w \times 10^{-4}$	$[\eta]^b$ (dl g^{-1})	$D_0 \times 10^8$ (cm^2 s^{-1})	d_0 (Å)
ADASAM 0.5–0.5	1.38	1.79	1.82	2560
ADASAM 2.5–2.5	8.83	14.6	1.67	2790
ADASAM 5–5	9.51	17.5	1.74	2680
ADASAM 10–10	7.18	14.1	1.52	3070
ADASAM 15–15	9.83	8.31	1.57	2970
ADASAM 5–10	10.7	15.55	1.10	4240
ADASAM 10–5	3.77	7.19	1.76	2650

[a] pH = 7.0; $T = 25°C$; [NaCl] = 1.0 M

[b] pH = 7.0; $T = 25°C$; [NaCl] = 1.0 M; via Contraves LS-30 Low Shear Rotational Rheometer

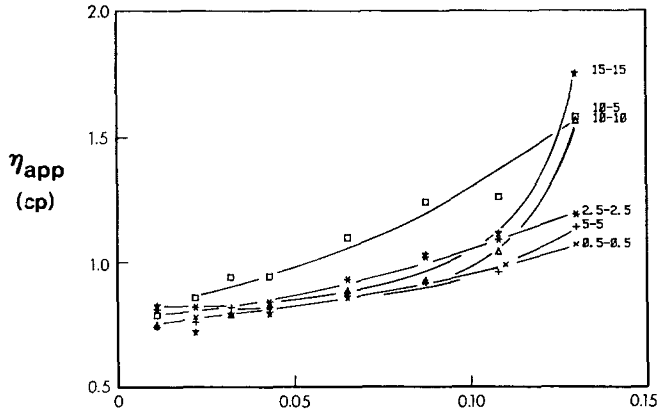


Figure 1 Effect of polymer concentration on the apparent viscosity of ADASAM series of terpolymers in pure water at a temperature of 30°C, a shear rate of 1.75 s^{-1} and a pH of 7

The diffusion coefficients do not vary greatly from sample to sample. The calculated hydrodynamic diameters reflect the viscosity trends of the samples, with three exceptions: ADASAM 2.5–2.5, 5–5 and 10–10 exhibit hydrodynamic diameters smaller than those measured by rotational viscometry.

Viscometric studies

The viscosity of low charge-density polyampholytes at concentrations below the critical overlap concentration (C^*) should be largely determined by intramolecular charge–charge associations and solvation. As the polymer concentration approaches C^*, the viscosity should change as a result of intermolecular associations. Ionic interactions above and below C^* would be expected to be strong in low ionic strength solutions and weak (due to charge shielding) at high ionic strength. For sufficiently hydrated systems, intramolecular charge interactions dominate solution behaviour as charge density increases, polymer concentration decreases and hydrodynamic volume decreases. For the ADASAM copolymers, hydrophobic interactions can play significant roles depending on polymer concentration and ionic strength.

Ageing studies. Previous studies in our laboratories have shown the importance of conducting solution studies after a sufficient ageing period. Apparent viscosity was monitored for each sample of the ADASAM series in deionized water and in 0.257 M NaCl. Although the viscosities of some samples, particularly those in pure water, fluctuated a great deal over the first 15 days, constant values were reached within 30 days. Apparently, intra- and intermolecular ion pairing and hydrogen bonding require significant periods of time to reach equilibrium.

Effects of copolymer concentration. Apparent viscosity is plotted against polymer concentration for each of the synthesized terpolymers in deionized water at 30°C and a shear rate of 1.75 s^{-1} (*Figure 1*). In general, those samples containing the greatest number of charged groups display the highest viscosities, particularly in the region of chain overlap (C^*). Terpolymers containing small concentrations of charged groups display behaviour that is similar to that of homopolyacrylamide. Apparently the charge density must reach a critical level in order to cause significant intermolecular ionic association. *Figure 2* depicts increasing apparent viscosity observed with increasing polymer concentration for ADASAM 5–10. This sample exhibits viscosities in pure water much greater than the other terpolymers, probably due to the charge imbalance in favour of NaAMPS. Copolymers of NaAMPS with AM are known to have large viscosities in pure water, especially at low NaAMPS compositions, due to charge–charge repulsion.

ADASAM 10–5 exhibits a viscosity among the lowest of the polymers since its molecular weight is reduced by the presence of a relatively large amount of AMPDAC (*Table 3*). Incorporation of the cationic AMPDAC monomer does not seem to increase hydrodynamic volume to the same extent as incorporation of the anionic NaAMPS monomer. AMPDAC is a good chain-transfer agent since it possesses abstractable hydrogen atoms on the carbons adjacent to the electron-rich amine nitrogen. These data are in agreement with viscosity and molecular-weight data of copolymers of AMPDAC with NaAMPS[5,6].

Apparent viscosity is plotted as a function of polymer concentration for each of the synthesized terpolymers in 0.257 M NaCl at 30°C and a shear rate of 1.75 s^{-1} (*Figure 3*). The moderate salt concentration allows sufficient shielding of charges to result in the reduction of viscosity of ADASAM 5–10 within the range of the other polymers. Terpolymers containing 10 mol% or greater of AMPDAC

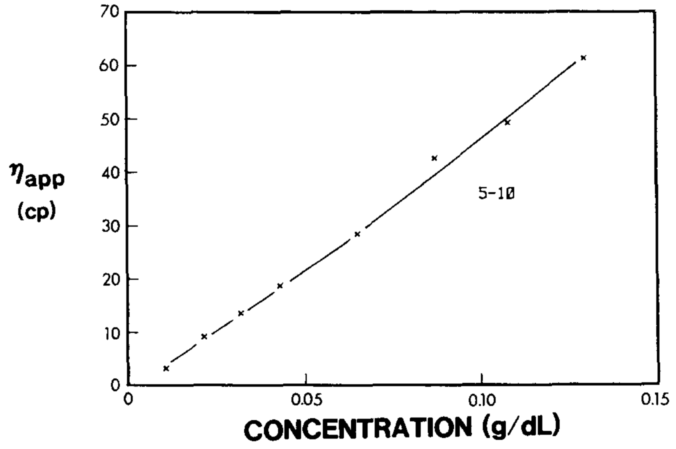


Figure 2 Effect of polymer concentration on the apparent viscosity of ADASAM 5–10 in pure water at a temperature of 30°C, a shear rate of 1.75 s^{-1} and a pH of 7

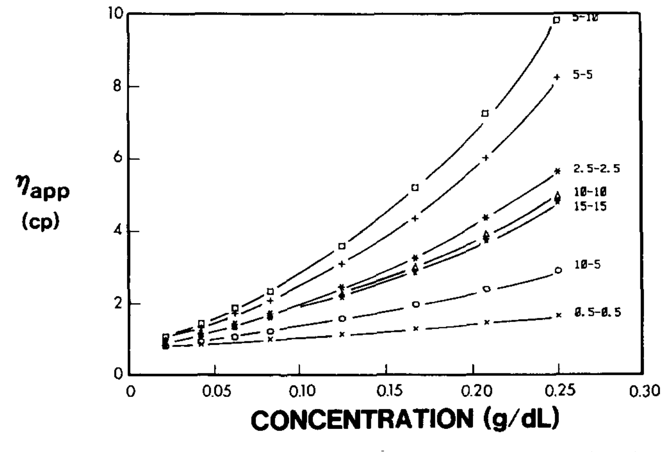


Figure 3 Effect of polymer concentration on the apparent viscosity of ADASAM series of terpolymers in 0.257 M NaCl at a temperature of 30°C, a shear rate of 1.75 s^{-1} and a pH of 7

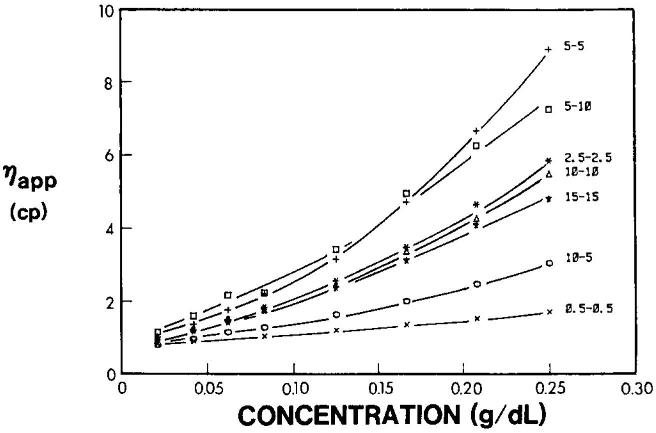


Figure 4 Effect of polymer concentration on the apparent viscosity of ADASAM series of terpolymers in 0.514 M NaCl at a temperature of 30°C, a shear rate of $1.75\,\mathrm{s}^{-1}$ and a pH of 7

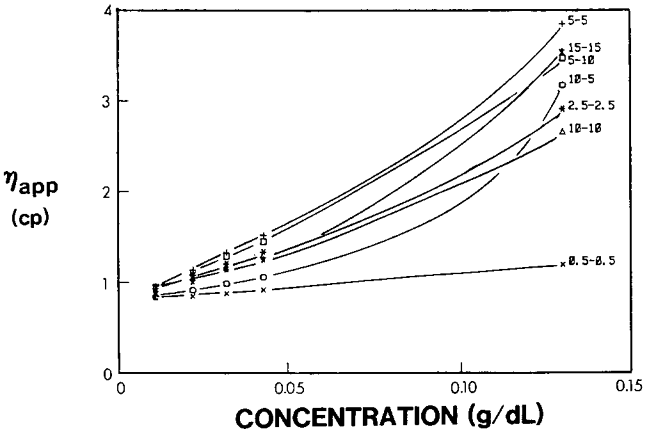


Figure 5 Effect of polymer concentration on the apparent viscosity of ADASAM series of terpolymers in 1 M NaCl at a temperature of 30°C, a shear rate of $1.75\,\mathrm{s}^{-1}$ and a pH of 7

in the feed display viscosities that are among the lowest under these conditions.

ADASAM 0.5–0.5 apparently has too few charged groups to affect its solution properties relative to polyacrylamide. ADASAM 2.5–2.5 and 5–5 exhibit intermediate viscosities since the charge density is large enough to warrant some intermolecular interaction but not so large that intramolecular interaction and a reduction in molecular weight adversely affect viscosity.

At NaCl concentrations of 0.514 and 1 M (*Figures 4* and *5*), ionic shielding results in the collapse of ADASAM 5–10 to the point that ADASAM 5–5 possesses a greater viscosity in the higher polymer concentration range. The fact that ADASAM 5–5 displays enhanced viscosities over 2.5–2.5 and 0.5–0.5 is attributed to a combination of molecular weight and the attainment of an optimum charge density for ionic interactions.

It is significant that the terpolymers of the ADASAM series display viscosities over 100% greater than the AMPDAC–NaAMPS (ADAS) high charge-density copolymers previously reported[5,6]. The superior viscometric characteristics of the ADASAM terpolymers are especially evident as the polymer concentrations approach C^*. The primary reason for the contrast in behaviour is the increased degree of intermolecular *versus* intramolecular ionic interaction possible for the low-to-moderate charge-density terpolymers. This observation lends support to the findings of other researchers, who have compared the properties of low charge-density polyampholytes to high charge-density ampholytic copolymers[4].

Effects of ionic strength. In order to assess clearly the effects of ionic strength, plots of reduced viscosity *versus* concentration were constructed for ADASAM samples in five NaCl solutions and in deionized water. For the terpolymers with balanced compositions, ADASAM 5–5, 10–10 and 15–15, reduced viscosities increased throughout the polymer concentration range ($0.04–0.25\,\mathrm{g\,dl^{-1}}$) with increasing NaCl concentrations (*Figures 6–8*). The intrinsic viscosities also increased with increasing NaCl concentration (*Figure 9*). The figures clearly demonstrate that intramolecular ionic interactions in water decrease hydrodynamic volume. As the salt concentration increases, the charged groups along the polymer chain are shielded, allowing some chain expansion.

As previously discussed, ADASAM 5–10 behaves differently from the other terpolymers because it possesses an overall polyelectrolyte character and a high molecular weight. Reduced and intrinsic viscosities decrease with increasing NaCl concentration. Conventional polyelectrolytes behave in this manner due to charge shielding of repulsive ionic interactions along the polymer chain.

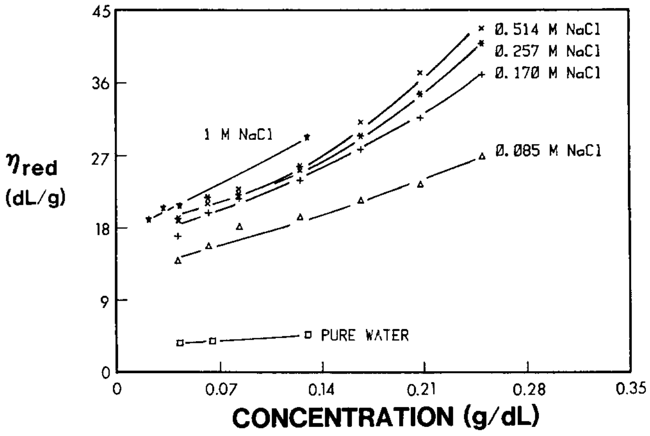


Figure 6 Effect of polymer concentration on the reduced viscosity of ADASAM 5–5 in pure water and NaCl solutions ranging from 0.085 to 1 M at a shear rate of $1.75\,\mathrm{s}^{-1}$, a temperature of 30°C and a pH of 7

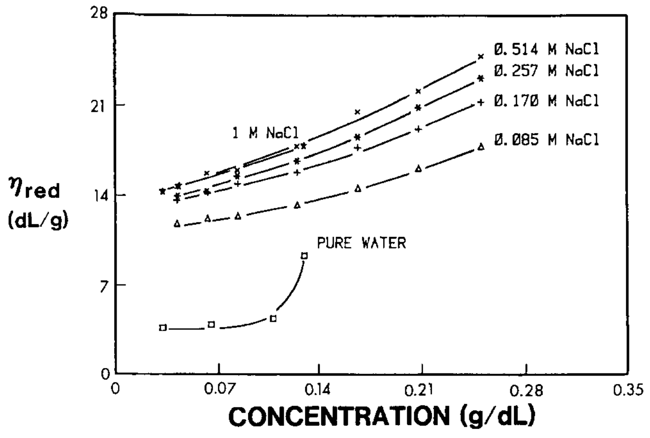


Figure 7 Effect of polymer concentration on the reduced viscosity of ADASAM 10–10 in pure water and NaCl solutions ranging from 0.085 to 1 M at a shear rate of $1.75\,\mathrm{s}^{-1}$, a temperature of 30°C and a pH of 7

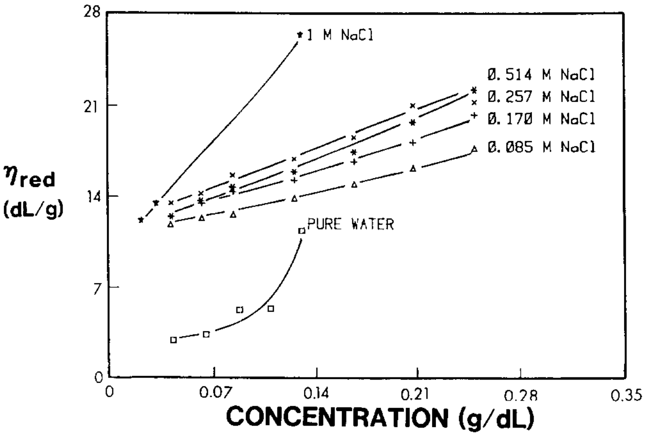


Figure 8 Effect of polymer concentration on the reduced viscosity of ADASAM 15–15 in pure water and NaCl solutions ranging from 0.085 to 1 M at a shear rate of 1.75 s^{-1}, a temperature of 30°C and a pH of 7

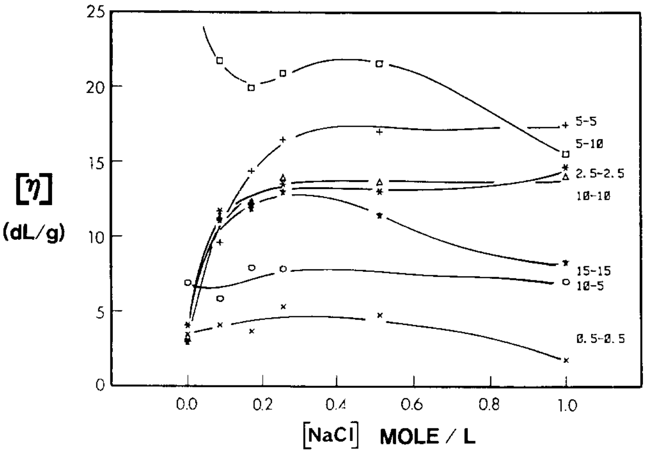


Figure 9 Effect of polymer concentration on the intrinsic viscosity of ADASAM series at a shear rate of 1.75 s^{-1}, a temperature of 30°C and a pH of 7

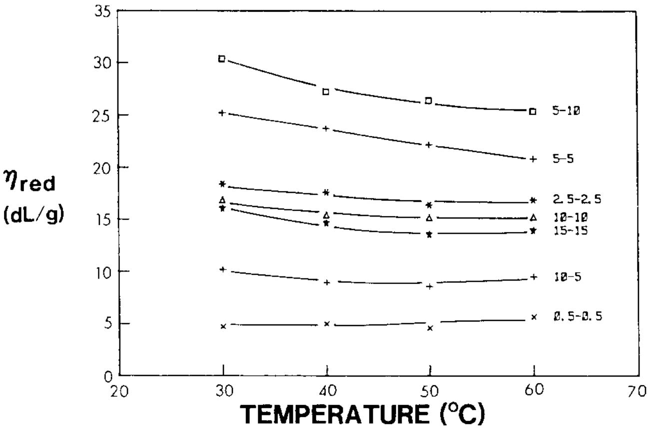


Figure 10 Effect of temperature on the reduced viscosity of ADASAM series at a polymer concentration of 0.1 g dl^{-1}, a shear rate of 1.75 s^{-1} and a pH of 7

Effects of temperature. Figure 10 illustrates the effects of temperature on the reduced viscosity of the terpolymers at a shear rate of 1.75 s^{-1} and a polymer concentration of 0.1 g dl^{-1}. The effect of temperature on the reduced viscosity of the terpolymers is minimal in the range 30–60°C.

Effects of shear rate. The effects of shear rate on the apparent viscosity of ADASAM 5–5, 15–15 and 5–10 were investigated in pure water and 0.257 M NaCl, and at both low and high polymer concentrations. The shear rates ranged from 1.75 to 128.5 s^{-1} with a temperature of 30°C, and pH of 7. In *Figure 11*, the behaviour of the terpolymers is shown at 0.033 g dl^{-1} in pure water. While ADASAM 5–5 and 15–15 exhibit low viscosity and Newtonian behaviour over the shear rate range, ADASAM 5–10 displays high viscosity and pseudoplastic behaviour. At approximately the same polymer concentration, 0.042 g dl^{-1}, but in 0.257 M NaCl, the polymers behave quite differently (*Figure 12*). ADASAM 5–10 no longer displays pseudoplastic behaviour. In fact, viscosity behaviour over the entire shear-rate range is similar to that of ADASAM 5–5. Interestingly, the viscosity of ADASAM 15–15 falls below that of 5–5; a very slight increase in the apparent viscosity is observed at low shear rates followed by a gradual decrease.

Figure 13 illustrates the effect of shear rate on viscosity of the three samples in pure water at a polymer concentration of 0.13 g dl^{-1}. Analogous behaviour to that shown in *Figure 11* is observed with a decrease in viscosity for ADASAM 5–10 and relatively low and constant viscosities for ADASAM 5–5 and 15–15 over

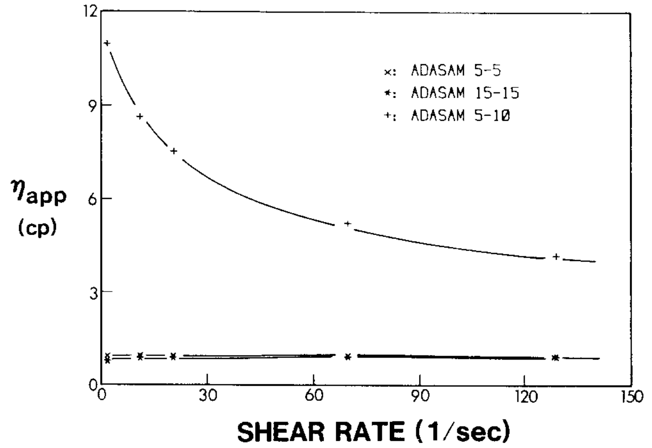


Figure 11 Effect of shear rate on the apparent viscosity of ADASAM 5-5, 15-15 and 5-10 in pure water at 30°C, a pH of 7 and a polymer concentration of 0.033 g dl^{-1}

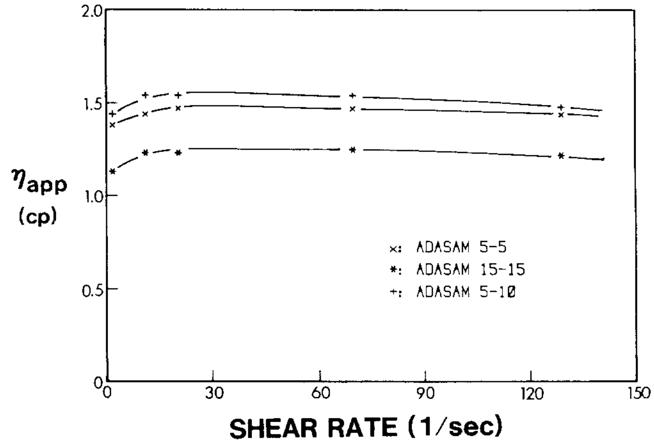


Figure 12 Effect of shear rate on the apparent viscosity of ADASAM 5-5, 15-15 and 5-10 in 0.257 M NaCl at 30°C, a pH of 7 and a polymer concentration of 0.042 g dl^{-1}

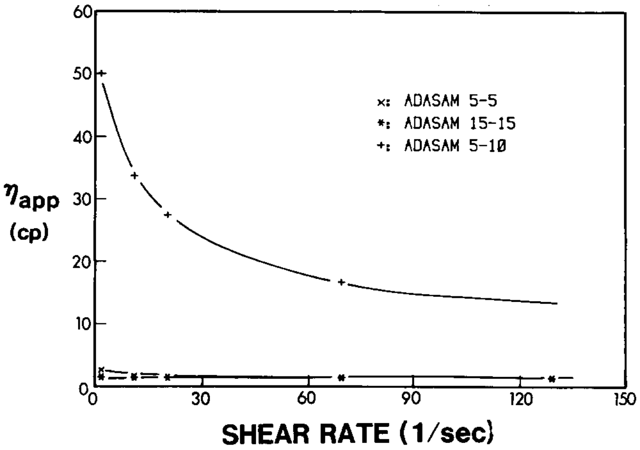


Figure 13 Effect of shear rate on the apparent viscosity of ADASAM 5–5, 15–15 and 5–10 in pure water at 30°C, a pH of 7 and a polymer concentration of 0.013 g dl^{-1}

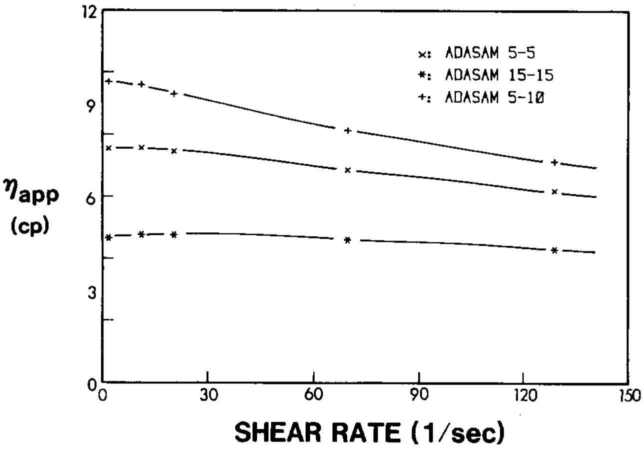


Figure 14 Effect of shear rate on the apparent viscosity of ADASAM 5–5, 15–15 and 5–10 in 0.257 M NaCl at 30°C, a pH of 7 and a polymer concentration of 0.025 g dl^{-1}

the range of shear rates. The absolute magnitudes of the viscosities are, of course, larger for the polymers in *Figure 13* than in *Figure 11*, owing to an increase in polymer concentration. *Figure 14* shows the behaviour of the terpolymers in 0.257 M NaCl at a polymer concentration of 0.25 g dl^{-1}. ADASAM 5–5 and 5–10 display slight decreases in viscosity with increasing shear rate, while 15–15 remains constant.

In general, shear-rate data indicate that terpolymers nearly balanced in charge display Newtonian or only slight pseudoplastic behaviour in deionized water and sodium chloride solutions at low and high polymer concentrations. The terpolymer that is predominantly anionic, i.e. ADASAM 5–10, displays pseudoplastic behaviour in pure water and essentially constant viscosity in salt solutions.

CONCLUSIONS

Terpolymers of 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) with sodium-2-acrylamido-2-methylpropanesulphonate (NaAMPS) and acrylamide (AM) were prepared under conditions analogous to those of the AMPDAC–NaAMPS copolymers previously reported[5]. A slight tendency for preferential incorporation of AMPDAC over NaAMPS was observed.

Molecular-weight studies indicate that terpolymers with more AMPDAC than NaAMPS have reduced degrees of polymerization. Solution properties are dependent on molecular weight but compositional effects predominate. Viscosity in electrolyte solutions can be maximized by choosing appropriate feed compositions. For example, ADASAM 5–5 possesses sufficient charge density and hydrodynamic volume to exhibit desirable viscosification properties over a wide range of solution ionic strengths.

ADASAM 5–10 displays solution viscosity behaviour similar to conventional polyelectrolytes since this terpolymer has an overall negative charge along the backbone. However, the remainder of the terpolymers exhibit solution viscosity behaviour similar to that of higher charge-density polyampholytes.

The variance of solution viscosity of the terpolymers to changes in temperature is not significant due to the fact that the charge density of the terpolymers is small. An increase in temperature does not result in the disruption of a large number of ionic interactions.

ADASAM 5–5 and 15–15 have viscosities in pure water and 0.257 M NaCl that are essentially invariant to changes in shear rate for dilute polymer concentrations. ADASAM 5–10 exhibits pseudoplastic nature in pure water and Newtonian behaviour in 0.257 M NaCl at dilute polymer concentrations. The viscosities of the former samples are much lower than those of the latter. In more concentrated solutions, the viscosities are much higher across the shear-rate range for ADASAM 5–5 and 15–15, especially in the presence of NaCl. The ADASAM 5–10 sample displays slightly lower viscosities in concentrated solutions than in dilute solutions. However, concentrated solutions of this polymer in pure water maintain high viscosities due to the polyelectrolyte effect.

The incorporation of acrylamide as a non-ionic comonomer allows the formation of terpolymers with larger degrees of polymerization than copolymers of AMPDAC and NaAMPS. Such copolymers display solution behaviour reflective of intramolecular ionic interactions. Attractive rather than repulsive interactions become more noticeable as the copolymers near equimolar composition. Low-to-moderate charge-density terpolymers of AMPDAC with NaAMPS and acrylamide have viscosities 100% greater than high charge-density copolymers[6]. The superior viscometric characteristics of the ADASAM terpolymers are especially evident as the polymer concentration approaches C^*. The primary reason for the contrast in behaviour is the increased degree of intermolecular *versus* intramolecular ionic interaction. The terpolymers are affected to a lesser extent than the high charge-density copolymers by changes in temperature since there are fewer ionic interactions disrupted in the former. The co- and terpolymers display similar shear behaviour.

Drag reduction behaviour of the terpolymer series is under study and will be reported in a future paper.

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