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Water-Soluble Copolymers. 29. Ampholytic Copolymers of Sodium 2-Acrylamido-2-methylpropanesulfonate with (2-Acrylamido-2-methylpropyl)dimethylammonium Chloride: Solution Properties

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ABSTRACT: Dilute solution properties of copolymers of (2-acrylamido-2-methylpropyl)dimethylammonium chloride (AMPDAC) with 2-acrylamido-2-methylpropanesulfonate (NaAMPS) have been studied as a function of composition, temperature, time, pH, and added electrolytes. Phase-separation and potentiometric studies have also been performed. The AMPDAC–NaAMPS copolymers decrease in molecular weight with increasing AMPDAC content. Typical polyelectrolyte behavior was observed for copolymers containing small amounts of either monomer. However, copolymers containing nearly equimolar amounts of the two monomers displayed a minimum in viscosity in pure water and a maximum in viscosity in concentrated salt solutions. The viscosity behavior as a function of composition was found to parallel microstructural features of the copolymers.

Introduction

Ordinary polyelectrolytes exhibit large solution viscosities relative to nonionic polymers as a result of repulsive interactions of groups with like ionic charges along the polymer chain. The ionic repulsive forces increase hydrodynamic volume of anionic or cationic polyelectrolytes, particularly in aqueous solutions of low ionic strength. An increase in salt concentration shields ionic charges which lessens the repulsive forces among the charges. Consequently, the hydrodynamic volumes of the macromolecules decrease as does the viscosity of the solution. Such behavior is considered normal for ordinary anionic or cationic polyelectrolytes.

Recently we have initiated studies of copolymers containing both positive and negative charges distributed along the chain. Related polymers have been examined by several groups and are reported to exhibit unusual solution behavior when compared to that of conventional polyelectrolytes.[1-3] In this work we report the solution properties of fully characterized ampholytic copolymers prepared from structurally homologous monomers. Sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) was copolymerized with (2-acrylamido-2-methylpropyl)dimethylammonium chloride (AMPDAC) as described in the previous paper of this series.

Experimental Section

Materials. Copolymers of AMPDAC with NaAMPS were prepared at 30 °C in aqueous solution at a pH of 6.0 by using potassium persulfate as the free radical initiator. Details of the synthesis, purification, and structural characterization of this series of polymers have been reported in the previous paper.

Structural Characterization. Molecular weights were determined by using low-angle laser light scattering. The copolymer compositions were determined from elemental analysis and ^{13}C NMR data. Elemental analysis data were further utilized to calculate reactivity ratios and various microstructural statistics (see Tables I and II from the preceding paper in this issue).

Viscosity Measurements. Aqueous stock solutions of NaCl (0.085, 0.140, 0.257, and 0.514 M) were prepared by dissolving the appropriate amount of salt in deionized water in volumetric flasks. 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 for salt solutions and 0.13 g/dL 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 by using a Cannon-Ubbelhode four-bulb shear dilution capillary viscometer (size 100). The shear rate constants and viscometer constants were provided by the manufacturer. Apparent viscosities at four shear rates, corresponding to the four bulbs, were extrapolated to zero shear allowing for the calculation of the zero-shear reduced viscosity. Reduced viscosities over four concentrations were then used, along with the Huggins equation, to extrapolate to infinite dilution to obtain zero-shear intrinsic viscosities, $[\eta]_0$.[4] Precautions were taken to assure that data used in the calculation of intrinsic viscosities were from the region of concentration below the critical overlap concentration, i.e., $[\eta]_0 C < 1$. Solution viscosities were also determined by using a Contraves LS-30 low shear rotational rheometer at copolymer concentrations in the semidilute region. The viscosities obtained from rheometry at 2 s^{-1} were compared to zero-shear data obtained via four-bulb viscometry.

Potentiometry Measurements. All measurements of pH were made at 25 ± 0.05 °C by using a Corning 130 pH–mV meter with an Orion pH electrode. The meter was calibrated by using a two-point calibration method. Copolymer concentrations were 0.15 g/dL with a minimal volume variation resulting from addition of the titrant. Titrations were performed on polymer dissolved in pure deionized water and 0.36 M potassium chloride to assess the effects of charge shielding of the ionic groups. Standard acid and base solutions less than 0.1 M in concentration were prepared as titrants. The titrations were conducted under nitrogen atmosphere.

Due to the complex nature of the polymers under study, no attempts were made to extract pK values although definite trends may be observed for the titration curves as shown in Figures 14 and 15.

Turbidimetry Measurements. Calcium chloride solutions were prepared gravimetrically and the concentrations verified by refractive index measurements. Polymer solutions of 0.15 g/dL were prepared by dissolving the appropriate amount of polymer in pure water followed by addition of a specified volume of calcium chloride solution. Precautions were taken to prevent evaporation of water during these studies.

A phototurbidimeter was employed for measuring the critical phase separation temperature of the polymers. A sample of polymer solution (30–36 mL) was stirred by a magnetic stirrer and heated at less than 1 °C/min. A thermometer was used to monitor the temperature to within ±0.1 °C. A decrease in the transmittance of light was used to identify the onset of polymer precipitation. The cloud point (critical temperature) was taken as the average temperature at which precipitation was first observed.

Results and Discussion

The primary objective of this study of the ADAS copolymers is to relate structural parameters to solution behavior. Therefore, we proceeded with a stepwise investigation for a selected copolymer series of molecular structure, molecular weight, counterion type and frequency, polymer concentration, ionic strength, and phase behavior.

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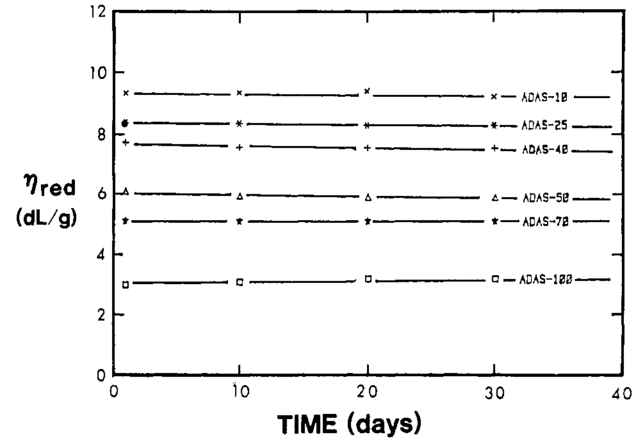

Figure 1. Aging of ADAS polymers in 0.257 M NaCl at 30 °C and pH 7.

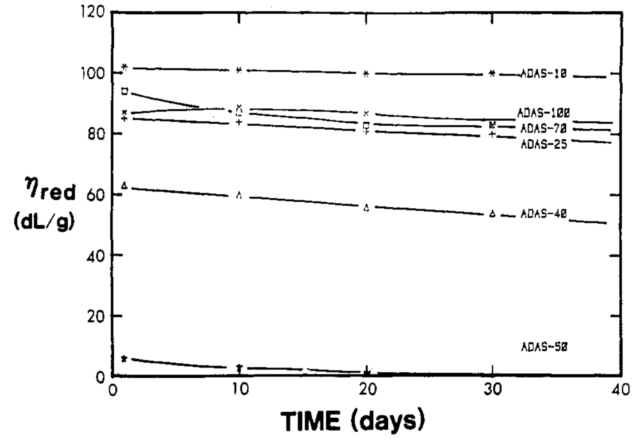

Figure 2. Aging of ADAS polymers in type 1 water at 30 °C and pH 7.

Aging Effects. The viscosities of many polyelectrolyte solutions show an initial increase during dissolution followed by a gradual decrease with time. These changes have been observed for polyacrylamide and numerous acrylamide copolymers and are thought to be the result of variations in hydrogen bonding and solvation. Such changes will eventually lead to the most thermodynamically stable polymer conformation and the viscosity will be constant with time. Sufficient aging time must therefore be allowed before conducting solution studies in a meaningful way.

The aging effects for the *AMPDAC*–Na*AMPS* copolymers (the acronym "ADAS" has been given to this series of copolymers) were studied utilizing a size 100 Cannon-Fenske capillary viscometer at 30 °C and a pH of 7.0. The polymer concentrations in 0.257 M NaCl and pure water were 0.25 and 0.13 g/dL, respectively.

A plot of reduced viscosity versus time for the series of copolymers in 0.257 M NaCl is shown in Figure 1. The numbers appearing after the name "ADAS" (e.g., ADAS-40) correspond to the mole percent of AMPDAC in the monomer feed. Copolymer compositions are given in Table I of the preceding paper of this issue. Polymers of the ADAS series showed no change in viscosity with time in 0.257 M NaCl. Figure 2 shows the effect of time on the reduced viscosity of the copolymers in pure water. Some of the polymer samples displayed a slight decrease in viscosity with time. Consequently, our studies were usually conducted at some finite electrolyte concentration.

In the case of ADAS-50, which corresponds to a monomer feed ratio of 1:1, the reduced viscosity decreased from a low value of about 7.0 cP to less than 1.0 cP within 30 days. This high charge density copolymer contains essentially an equimolar amount of oppositely charged mer units in the polymer; apparently a collapse of the coil with time is due to attractive interactions. Interestingly, the coil does not collapse to the point that the polymer precipitates from solution but results in an extremely low viscosity polymer solution in pure water. ADAS-50* displayed analogous aging characteristics. It is significant that the polymers do remain in solution in contrast to the behavior reported for other polyampholytes.[1-3]

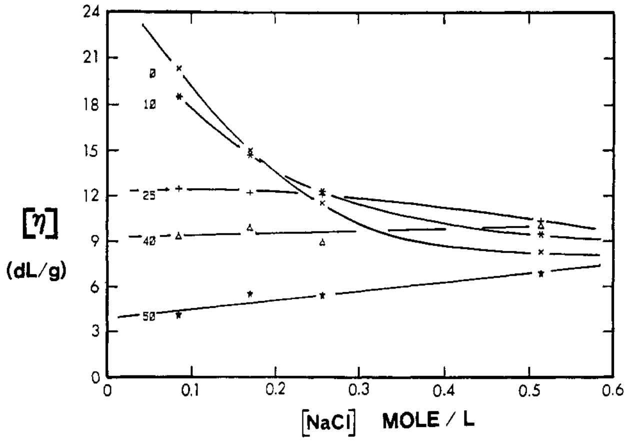

Figure 3. Effect of NaCl concentration on the zero-shear intrinsic viscosity of ADAS polymers at 30 °C and pH 7.

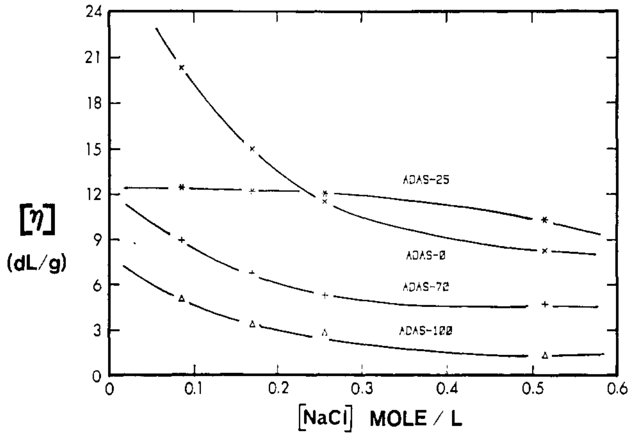

Figure 4. Effect of NaCl concentration on the zero-shear intrinsic viscosity of ADAS polymers at 30 °C and pH 7.

Effects of Added Electrolytes. The effects of added electrolytes on the intrinsic viscosity of the copolymers are shown in Figures 3 and 4. ADAS-0, the homopolymer of NaAMPS, displays typical polyelectrolyte behavior with increasing NaCl concentration. Analogous behavior is observed for ADAS-10, which contains 10 mol % AMPDAC in the feed, although the decrease in the viscosity with ionic strength is less pronounced.

Copolymers ADAS-25 through ADAS-50 display behavior which is atypical of ordinary polyelectrolytes; the viscosities of solutions of ADAS-25 and ADAS-40 are essentially invariant with changes in ionic strength while the ADAS-50 solution actually increases in viscosity upon the addition of electrolytes. This behavior is likely due to the shielding of the ionic charges along the polymer chain resulting in the disruption of positive–negative charge attractions allowing coil expansion by enhanced solvation.

Such behavior has been observed by other researchers studying high charge density polyampholytes containing approximately equimolar amounts of mer units. In particular, Peiffer and Lundberg[1] and Salamone et al.[2,3] noted that the solution behavior of high charge density ampho-

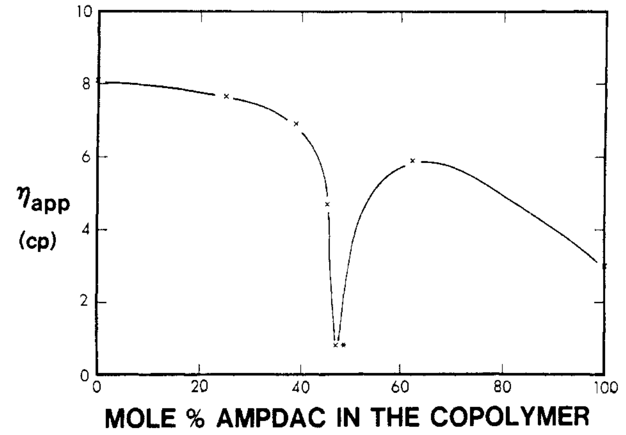

Figure 5. Effect of copolymer composition of the apparent viscosity of ADAS polymers in type 1 water at 30 °C (polymer concentration = 0.03 g/dL, shear rate = 100 s^{-1}, pH 7).

Table I
ADAS Series Low-Angle Laser Light Scattering Data[a]

sample	mole % AMPDAC copolymer	$10^{-6}M_w$, g mol^{-1}	10^4A_2, mL mol g^{-2}	$10^{-4}\,\overline{DP}_w$	$[\eta]$,[b] dL g^{-1}
ADAS-0	0.0	8.47	1.38	3.70	6.73
ADAA-10	25.1	9.46	1.58	4.24	8.01
ADAS-25	38.9	7.73	1.84	3.52	10.11
ADAS-40	45.0	7.55	1.22	3.46	9.75
ADAS-50	46.9	2.66	4.47	1.22	9.26
ADAS-70	63.4	2.68	2.30	1.25	5.95
ADAS-100	100.0	1.60	2.89	0.774	1.36

[a] pH 7.0; T = 25 °C; [NaCl] = 1.0 M. [b] pH 7.0; T = 25 °C; [NaCl] = 1.0 M; via Contraves low shear LS-30 rotational rheometer.

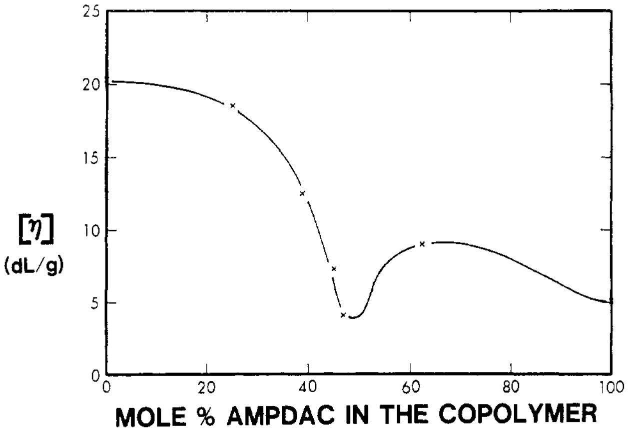

Figure 6. Effect of copolymer composition on the zero-shear intrinsic viscosity in 0.085 M NaCl at 30 °C and pH 7 for ADAS polymers.

lytic copolymers is controlled by intramolecular ionic interactions between oppositely charged groups. We concur with these observations and note that effects of added electrolytes on hydrodynamic volume for nonstoichiometric copolymers are reasonably predictable in dilute solution. Under those conditions in which intramolecular ionic interactions predominate, HDV is controlled by competitive (a) attraction of unlike macroions and (b) repulsion by like macroions. Addition of simple electrolytes effectively reduces both types of interaction by charge masking. For polyampholytes with balanced stoichiometry (a) predominates and addition of salt allows chain expansion. At intermediate feed ratios the relative effects of salt on (a) and (b) must be assessed. At feed ratios far away from stoichiometric balance, (b) predominates and typical polyelectrolyte behavior is observed with addition of salt. It should be noted that the relative sensitivity of the ampholytic copolymers to salt addition is also a function of hydration, chain stiffness, and pK of the charged functional group and its distance from the backbone.

Samples containing excess AMPDAC units in the copolymer again display typical polyelectrolyte behavior with the addition of inorganic electrolytes (Figure 4). Solution behavior of ADAS-70 is more representative of classical polyelectrolyte.

Effects of Copolymer Composition. The effect of copolymer composition on the zero-shear intrinsic viscosity of each copolymer was studied in low (0.085 M) and high (0.514 M) concentration NaCl solutions. The effect of copolymer composition on the apparent viscosity was studied in deionized water as well.

The apparent viscosities of copolymers of the ADAS series are plotted as a function of mole percent AMPDAC (Figure 5). The viscosities in pure water were determined at 30 °C and a polymer concentration of 0.03 g/dL. Graphical interpolation to a shear rate of 100 s^{-1} yielded the values shown in the plot. The most obvious feature of this figure is that the viscosity decreases sharply as the mole percent of AMPDAC in the copolymer approaches approximately 50%. This behavior is explained by attractive mer interaction as the copolymer mole ratio approaches unity.

Aside from the trough region in the apparent viscosity curve, the general trend is a decrease in viscosity with increasing AMPDAC incorporation. This behavior can be explained in terms of the weight-average molecular weights of the samples (Table I). With the exception of ADAS-10, which possesses a slightly greater molecular weight than ADAS-0, the molecular weight of the copolymers decreases with increasing mole percent of AMPDAC in the copolymer. The decrease in molecular weight is thought to be due to the presence of abstractable hydrogen atoms on the carbon atoms α to the tertiary ammonium group.

The zero-shear intrinsic viscosity is plotted against mole percent AMPDAC in the copolymer at a NaCl concentration of 0.085 M (Figure 6). The behavior is similar to that in water (Figure 5), except that the minimum in viscosity in the region of 50 mol % is less pronounced. In Figure 7, the zero-shear intrinsic viscosity is plotted versus mole percent AMPDAC in the copolymer at a NaCl concentration of 0.514 M. The trough region, which was present in pure water and 0.085 M NaCl studies, is absent in the high salt concentration plot. Inorganic ions shield the charges along the polymer chain to such an extent that intramolecular ionic associations contribute much less to a decrease in the hydrodynamic volume and viscosity of the copolymers. Polymer hydration is much more effective. ADAS-50* displays similar viscosity behavior in each environment to that of ADAS-50. Highly alternating polymers are formed in both cases during polymerization.

In Figure 7 the viscosities in 0.514 M NaCl follow the molecular weight trend (Table I) except for the two copolymers containing 25 and 40 mol % AMPDAC in the feed. On the basis of molecular weight alone, these two samples should exhibit viscosities below that of ADAS-0, the homopolymer of NaAMPS. Therefore, the viscosity of the copolymers must depend upon some additional parameter other than molecular weight.

ABA triads (Table II, preceding paper in this issue), where A represents NaAMPS and B represents AMPDAC, seem to relate to viscosity in the ADAS series. The maximum number of B-centered triads, among the synthesized polymers, occurs at an AMPDAC feed composition of about 25 mol %. A slightly reduced number of triads is seen for ADAS-40 which contains about 48 mol

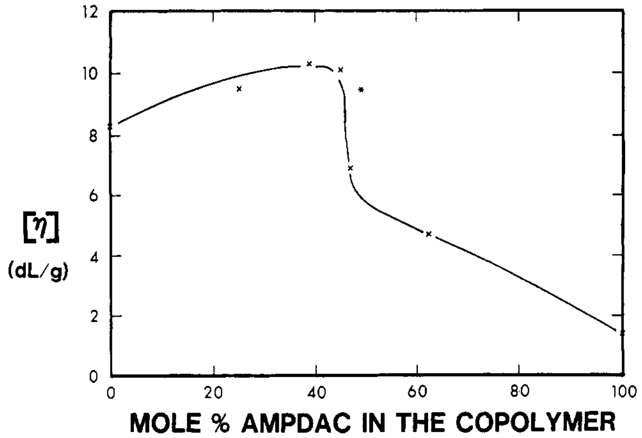

Figure 7. Effect of copolymer composition on the zero-shear intrinsic viscosity in 0.514 M NaCl at 30 °C and pH 7 for ADAS polymers.

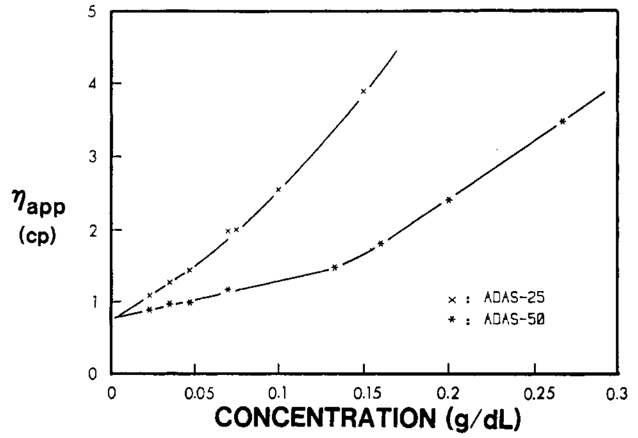

Figure 8. Effect of copolymer concentration on the apparent viscosity of ADAS-25 and ADAS-50 in 0.085 M NaCl at 30 °C, pH 7, and a shear rate of 1.97 s^{-1}.

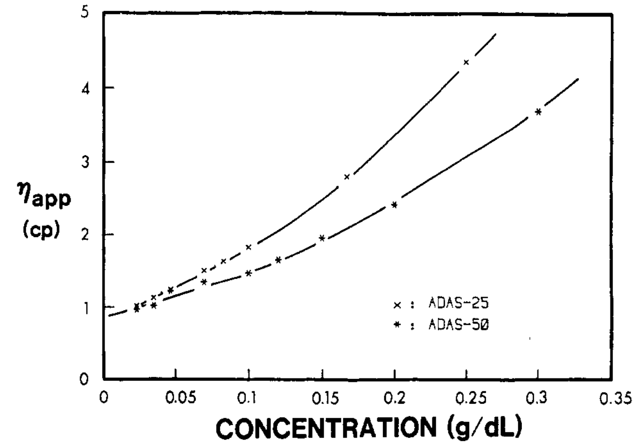

Figure 9. Effect of copolymer concentration on the apparent viscosity of ADAS-25 and ADAS-50 in 0.514 M NaCl at 30 °C, pH 7, and a shear rate of 1.97 s^{-1}.

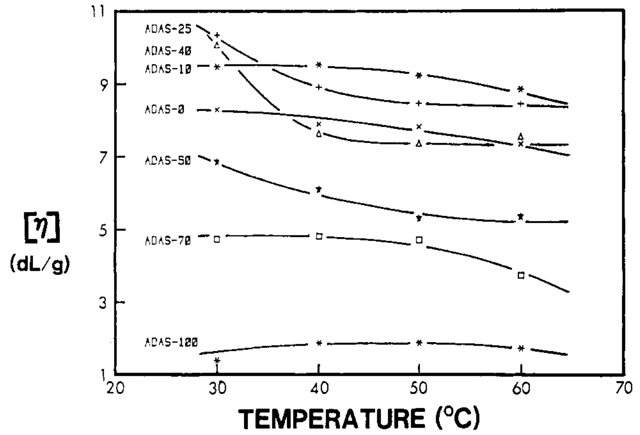

Figure 10. Effect of temperature on the zero-shear intrinsic viscosity of ADAS polymers in 0.514 M NaCl at pH 7.

% AMPDAC in the copolymer. The sharp loss in viscosity at about 50 mol % is due to the decrease in molecular weight observed for those samples containing greater than 40 mol % AMPDAC in the feed, i.e., ADAS-50, ADAS-70, and ADAS-100.

In further consideration of the effect of microstructure on viscosity, the number of BABAB pentads are presented in Table II of the preceding paper. The copolymer containing the largest number of this type of pentad corresponds to that with the minimum viscosity in pure water, ADAS-50. As the number of B-centered BABAB pentads increases the viscosity decreases.

Interestingly, aside from molecular weight, the viscosity behavior of the copolymers seems to depend on the number of alternating B-centered triads and pentads. Due to the slight difference in the reactivity ratios of the two monomers, 0.22 for NaAMPS and 0.31 for AMPDAC, the frequency of B-centered ABA triads and BABAB pentads does not exactly coincide. The viscosity trend in high salt coincides with the number of ABA triads. The segmental extension of the chain is influenced to a greater extent in pure water than in salt water. Hence, ionic effects are operative at a greater length along the chain in pure water than in 0.514 M NaCl.

Effects of Copolymer Concentration. The effects of copolymer concentration on the zero-shear apparent viscosity of ADAS-25 and ADAS-50 were investigated in low (0.085 M) and high (0.514 M) concentration NaCl solutions. Plots of zero-shear apparent viscosity versus copolymer concentration for the two samples in 0.085 M NaCl are shown in Figure 8. A change in the slope of the curve is observed at a lower concentration for ADAS-25 than for ADAS-50, indicating that ADAS-25 possesses a critical overlap concentration, *C**, less than that of ADAS-50. The difference in hydrodynamic volume of the two copolymers is a result of the enhanced molecular weight and the decreased probability of intramolecular ionic interaction for ADAS-25 relative to ADAS-50.

The viscosity behavior of ADAS-25 and ADAS-50 in 0.514 M NaCl as a function of polymer concentration is shown in Figure 9. The linearity of the curves relative to Figure 8 indicates that ionic effects are less pronounced due to shielding of the charges along the chain. Again, electrostatic shielding contributes to the similarity of the viscosity behavior of ADAS-25 and ADAS-50 in high salt concentration solutions. The region of chain overlap is similar for the two copolymers in high salt solution.

Effects of Temperature. The effects of temperature on the zero-shear intrinsic viscosity of the ADAS copolymers in 0.514 M NaCl are demonstrated in Figure 10. Homopolymers and copolymers composed of small amounts of either monomer essentially retain their viscosities through 60 °C. However, copolymers containing intermediate amounts of either monomer experience about a 20% reduction in viscosity from 30 to 60 °C. Interestingly, the trend in viscosity as a function of temperature is related to the number of B-centered triads. The maximum in positive–negative ionic interactions occurs with the maximum in the number of B-centered triads. An increase in temperature is known to result in the disruption of ionic interactions.

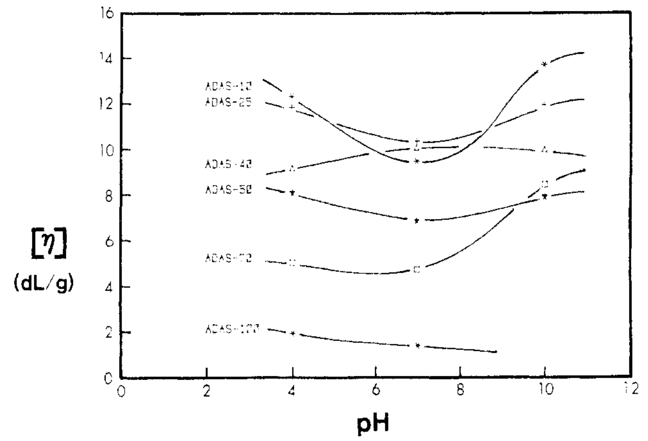

Figure 11. Effect of pH on the zero-shear intrinsic viscosity of ADAS polymers in 0.514 M NaCl at 30 °C.

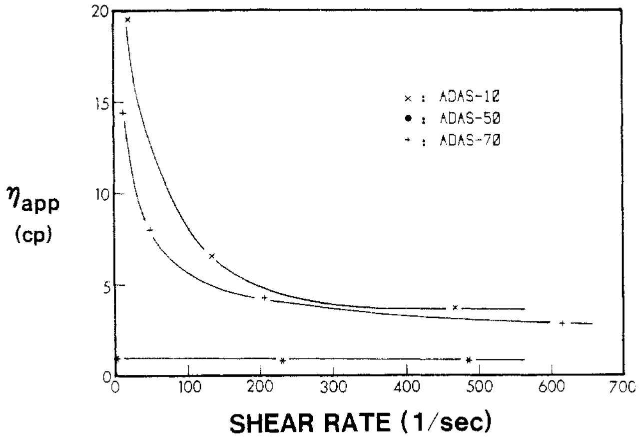

Figure 12. Effect of shear rate on the apparent viscosity of ADAS-10, ADAS-50, and ADAS-70 in type 1 water at 30 °C, pH 7, and a polymer concentration of 0.03 g/dL.

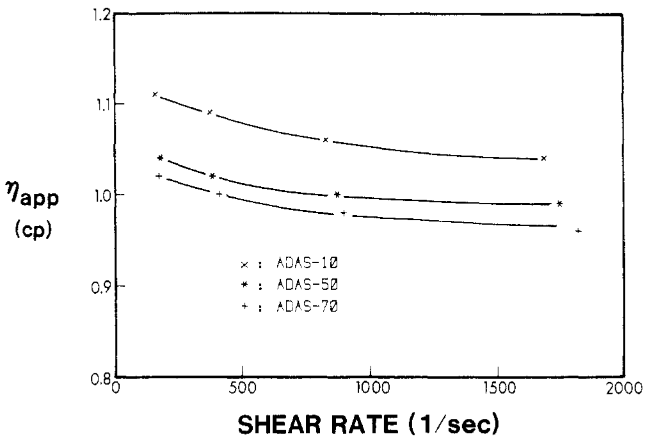

Figure 13. Effect of shear rate on the apparent viscosity of ADAS-10, ADAS-50, and ADAS-70 in 0.257 M NaCl at 30 °C, pH 7, and a polymer concentration of 0.035 g/dL.

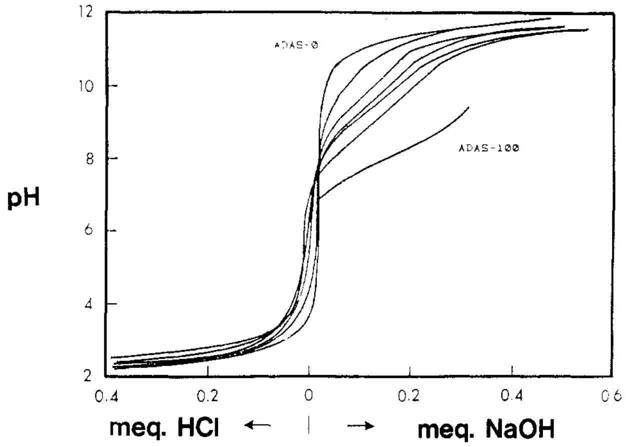

Figure 14. Potentiometric titration curves for ADAS polymers in 0.36 M KCl at 25 °C.

Effects of pH. A study of the effects of changes in pH on solution viscosity in 0.514 M NaCl at 30 °C was conducted. Measurements were made at pH values of 4, 7, and 10 as shown in Figure 11. For those samples containing an excess of either monomer, a minimum in viscosity was observed at a pH of 7. Samples containing nearly equimolar amounts of the constituents show little viscosity dependence on pH. At the extremes of pH, the AMPDA–AMPS associations are disrupted relative to at neutral pH. Another interesting observation is that the viscosities at pH 4 are less than those at pH 10. This may indicate that the NaAMPS unit is a more efficient viscosifier then the AMPDAC unit.

Effects of Shear Rate. The effects of shear rate on the apparent viscosity of three of the ADAS polymers in pure water and 0.257 M NaCl have been investigated. ADAS-10, ADAS-50, and ADAS-70 represent samples containing an excess of NaAMPS, an equimolar concentration of the two monomers, and an excess of AMPDAC, respectively.

Figure 12 shows the effect of shear rate at pH 7 on the apparent viscosity of the three polymers in pure water at concentration of 0.03 g/dL. The shear rate range extends from 0 to approximately 600 s^{-1}. ADAS-10 and ADAS-70 display pseudoplastic behavior. Their viscosities decrease with increasing shear rate from 0 to about 200 s^{-1}. ADAS-10 is, in effect, an anionic polyelectrolyte which incorporates about 43 mol % AMPDA-AMPS repeat units. ADAS-70 is, in effect, a cationic polyelectrolyte which consists of about 73 mol % AMPDA-AMPS repeat units. In contrast, the apparent viscosity of ADAS-50 is invariant, and very small, over the entire shear rate range due to the large number of AMPDA–AMPS units (94 mol %). The large number of intramolecular attractive interactions results in the collapse of ADAS-50 such that the macromolecule displays newtonian-like viscosity characteristics in this polymer concentration range. Compact, less hydrated molecules are less prone to elongational effects during flow.[5]

Figure 13 shows the effect of shear rate at pH 7 on the apparent viscosity of the three polymers in 0.257 M NaCl. The shear rate range extends from 0 to approximately 1800 s^{-1}. In this case, ADAS-10, ADAS-50, and ADAS-70 display low degrees of shear thinning. The viscosity of ADAS-50 is between those of ADAS-10 and ADAS-70. Evidently the presence of NaCl shields the charges of ADAS-50, allowing the molecule to become more chain extended and hydrated.

Potentiometry Studies. p*K* studies of the ADAS polymers are difficult due to the long time required for organization of the chains with changes in pH. Hence, true p*K* values were not determined due to the inability to detect end points. Nonetheless, some qualitative information may be extracted from the titration curves which appear in Figure 14 for 0.36 M KCl solutions and Figure 15 for pure water solutions. Only minor differences in the respective potentiometry curves appear in the acidic regions of the figure. The curves in Figures 14 and 15 correspond to increasing amounts of AMPDAC in the copolymer with decreasing pH. ADAS-0 is represented by the upper curve and ADAS-100 is represented by the lower curve. The intermediate curves correspond to increasing

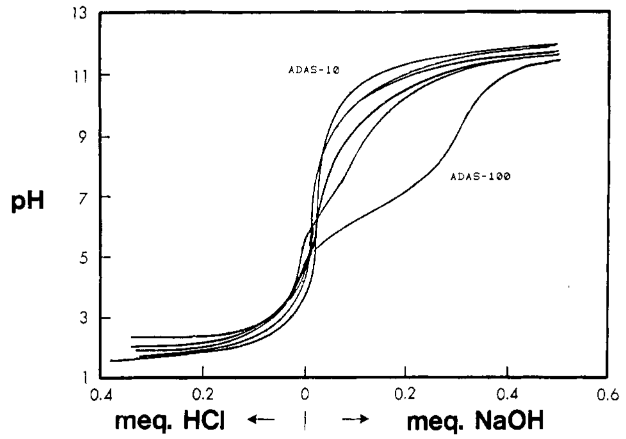

Figure 15. Potentiometric titration curves for ADAS polymers in type 1 water at 25 °C.

incorporation of AMPDAC in the copolymer. The p*K* appears to decrease with increasing AMPDAC incorporation in the copolymer. The decrease in the p*K* can be explained in terms of positive–positive charge interaction. As the mole percent of AMPDAC increases in the copolymer, AMPDAC units are forced to occupy positions adjacent to each other along the chain. Stabilization of the positive charge is accomplished by deprotonation of the adjacent tertiary ammonium chloride to form the amine. Previous studies conducted in our laboratories have shown that an AMPDAC monomer possesses a p*K* of about 10.4 while the homopolymer of AMPDAC has a p*K* of about 7.0.

Figure 15 depicts the potentiometric titration curves of the ADAS copolymers in pure water. Behavior analogous to that in salt water is observed, i.e., the slopes in the p*K* region of the curves decrease with increasing incorporation of AMPDAC.

Turbidimetry Studies. Turbidimetry studies were conducted for the ADAS copolymers in the presence of calcium chloride. Investigations were conducted to detect phase separation up to 100 °C. However, as expected, the ADAS copolymers did not phase separate within the temperature range investigated. Although anionic polyelectrolytes such as sodium acrylate are known to phase separate in the presence of divalent ions, sulfonates are much more stable.[6-11] Copolymers of NaAMPS with acrylamide, for example, do not phase separate with increasing temperature in $CaCl_2$ at temperatures up to 100 °C.[12]

Conclusions

Copolymers of *A*MP*D*AC with Na*A*MP*S* display interesting solution properties. Aging studies of the ADAS copolymers reveal essentially an invariance of viscosity with time in pure water and 0.257 M NaCl solutions. Copolymers containing small amounts of either monomer exhibit typical polyelectrolyte behavior as a function of added electrolytes. However, copolymers containing nearly an equimolar amount of oppositely charged mer units in the polymer display viscosities which are either invariant or increase with NaCl concentration. Also, copolymers containing nearly equimolar amounts of the two mer units exhibit low viscosities in pure water but intermediate viscosities in 0.514 M NaCl. The viscosity behavior as a function of copolymer composition parallels the number of ABA triads in 0.514 M NaCl and the number of BABAB pentads in pure water. The composition and properties of a polymer prepared in the absence of inorganic electrolytes, ADAS-50*, are essentially the same as those of a polymer prepared in the presence of an equimolar amount of counterions, ADAS-50. The ADAS-50 copolymer displays newtonian behavior in pure water, while the copolymers with unbalanced charges exhibit pseudoplastic behavior. In 0.257 M NaCl, all copolymers are pseudoplastic.

Potentiometric titration of copolymer solutions in pure water and 0.36 M KCl indicates a decrease in p*K* of the AMPDAC amine with increasing incorporation in the copolymer due to deprotonation of the ammonium salt. Little change in p*K* of the ADAS sulfonate is observed due to the high acidity of the copolymer. Turbidimetric measurements demonstrate that the copolymers are resistant to phase separation in the presence of calcium chloride up to temperatures of 100 °C.

The dilute solution behavior of the ADAS copolymers depends upon intramolecular ionic interactions in addition to parameters such as molecular weight. These high charge density ampholytic copolymers are subject to dramatic changes in hydrodynamic volume as dictated by factors which influence intramolecular ionic association including copolymer composition and microstructure, ionic shielding effects caused by solvated electrolytes, temperature, and pH.

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Registry No. (AMPDAC)(NaAMPS) (copolymer), 111255-99-3; NaCl, 7647-14-5.

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