Water-Soluble Copolymers. 68. Polyelectrolytes of *N*-Vinylformamide with Sodium 3-Acrylamido-3-methylbutanoate, Sodium 2-Acrylamido-2-methylpropanesulfonate, and Sodium Acrylate: Solution Behavior

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ABSTRACT: Dilute solution properties of copolymers of *N*-vinylformamide (NVF) with sodium 3-acrylamido-3-methylbutanoate (NaAMBA), sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS), and sodium acrylate (NaA) of known molecular weight and compositions have been studied in regard to added cosolutes, pH, and temperature. Phase separation studies have also been performed. All copolymers display typical polyelectrolyte behavior as observed by a reduction in viscosity in the presence of added electrolytes. Copolymers from all three series display losses of viscosity in the presence of urea at pH = 8.5. With the exception of a few copolymers of NVF with NaA (AAVF-100, -82, and -49), all copolymers investigated exhibit no phase separation in the presence of calcium chloride at 25 °C. Copolymers of NVF with NaAMPS (PSVF series) are soluble throughout the pH range investigated, while most copolymers from the BAVF and AAVF series phase separate as the pH of the aqueous medium is lowered. At low pH, phase separation at the lower critical solution temperature is observed for the BAVF series. Conversely, the phase separation of the AAVF copolymers is representative of an upper critical solution temperature and is affected by the presence of added cosolutes such as sodium chloride and urea.

Introduction

Water-soluble polymers with sulfonate or carboxylate functionality have commercial utility in a number of applications.[1−3] The sulfonate group is a weak base and remains charged throughout the useful pH range from ≈2 to 12. Counterion binding along the polyelectrolyte chain is less site specific for sulfonate groups than that observed with carboxylates.[4−6] The degree of ionization, number of ionic sites, and distance from the polymer backbone influence rheological properties, phase behavior, and responsiveness to pH and electrolyte changes.

In this work, we investigate the solution properties of copolymers of *N*-vinylformamide (NVF) with sodium 3-acrylamido-3-methylbutanoate (NaAMBA), sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS), and sodium acrylate (NaA). In-depth synthesis and structural characterization are reported in the accompanying paper of this series.[18]

Experimental Section

Materials. Copolymers of NVF with NaAMBA, NaAMPS, and NaA were prepared at 45 °C in aqueous solution at pH = 8.5 using 2,2′-azobis(*N,N*′-dimethyleneisobutyramidine) dihydrochloride.[18] All other materials were used as received.

Copolymer Characterization. The copolymer compositions were determined from ^{13}C NMR data. Molecular weights were determined by using low-angle laser light scattering. These procedures and values are reported in the accompanying paper in this series.[18]

Viscosity Measurements. Aqueous stock solutions of electrolytes and urea were prepared in deionized water. Stock polymer solutions were prepared at a concentration of 0.3 g/dL and pH = 8−8.5. Care was taken to avoid excessive shear during the dissolution of the polymers to limit degradation. Dilutions were performed isoionically and solutions allowed to age 2−3 weeks. Viscosity measurements were performed with a Contraves LS-30 rheometer at 25 °C and a shear rate of 6 s^{-1}. Duplicate runs were conducted and reproducibility was found to be within ±3−7%, dependent on the magnitude of the viscosity values. Unless otherwise stated, all viscosity measurements were performed at pH of 8.3−8.5. Precautions were taken to ensure that the data used in the calculation of the intrinsic viscosities were from the region of concentration below the critical overlap concentration. Intrinsic viscosities were evaluated using the Huggins equation.

Turbidimetry. The cloud points were obtained using a Brinkmann PC 800 colorimeter with a 620 nm light filter. The sample of polymer solution (15 mL) was stirred by a magnetic stirrer and was heated slowly by an air-heating system. A thermometer immersed in the solution was used to determine the temperature at which the phase transition occurred. pH values were adjusted by adding a concentrated HCl or NaOH solution via a microliter syringe. Samples were equilibrated for 5 min at low pH values to limit the possibility of hydrolysis. Reported values were taken when the transmittance was approximately 50%. The values reported are accurate to within ±0.8 °C and ±0.1 pH unit.

Results and Discussion

Polyelectrolytes (Figure 1) comprised of NVF with the comonomers NaA, NaAMBA, and NaAMPS have been prepared with microstructural control. These copolymer series, designated AAVF, BAVF, and PSVF, respectively, have been extensively characterized as to microstructure, overall composition, molecular weight, and extent of polymer−solvent interaction. Representative compositions and molecular weights are shown in Table 1. The numbers following the acronym represent the mol % of the anionic comonomer found in the final copolymer.

Effects of Polymer Concentration. The effects of polymer concentration on the apparent viscosity for the BAVF, PSVF, and AAVF copolymer series are shown in Figures 2−4. The measurements were conducted at pH = 8.5 and hence almost all of the anionic comonomers should be neutralized. Because of the polyelec-

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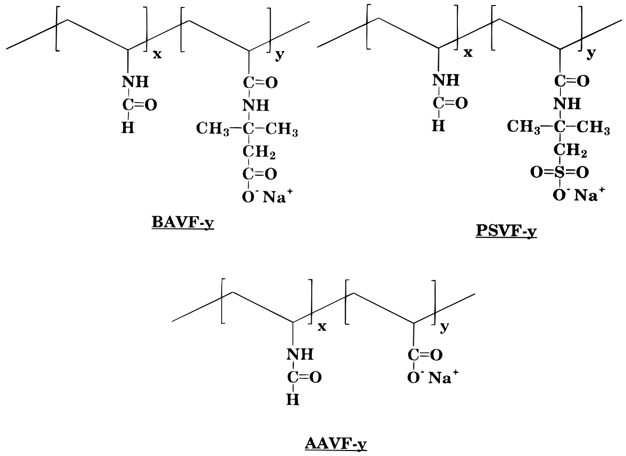

Figure 1. Copolymers of *N*-vinylformamide with sodium 3-acrylamido-3-methylbutanoate (BAVF series), sodium 2-acrylamido-2-methylpropanesulfonate (PSVF series), and sodium acrylate (AAVF series).

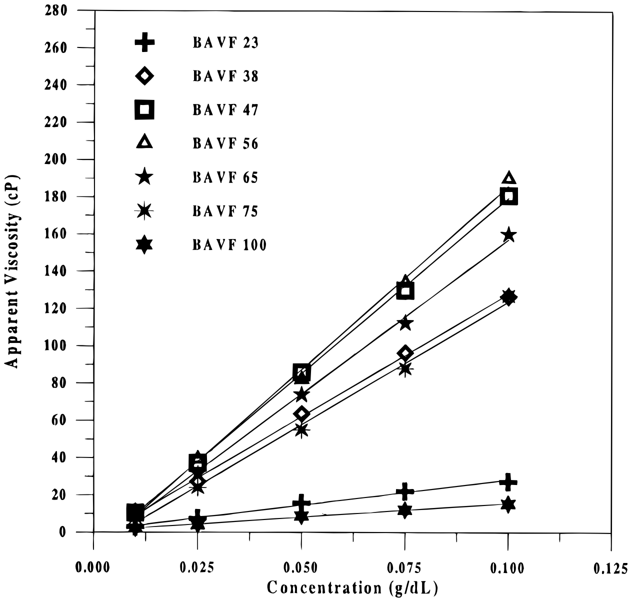

Figure 2. Effect of polymer concentration on the apparent viscosity for the BAVF copolymer series.

Table 1. Molecular Weight and Second Virial Coefficient Data for Copolymers of NVF with NaAMBA, NaAMPS, and NaA

sample	NVF found[a] (mol %)	$M_w \times 10^{-6}$	$A_2 \times 10^4$ (mL·mol/g^2)	DP × 10^{-4}
BAVF 38	62.0	2.4	4.0	2.0
PSVF 40	60.0	2.6	12.0	1.9
BAVF 56	44.0	6.8	2.8	4.9
PSVF 56	44.0	7.5	1.0	4.7
AAVF 62	38.0	3.9	5.1	4.6

[a] Determined from ^{13}C NMR.

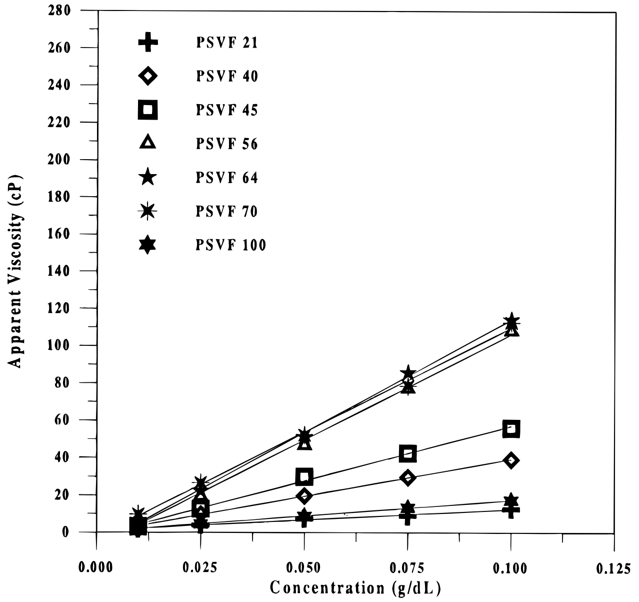

Figure 3. Effect of polymer concentration on the apparent viscosity for the PSVF copolymer series.

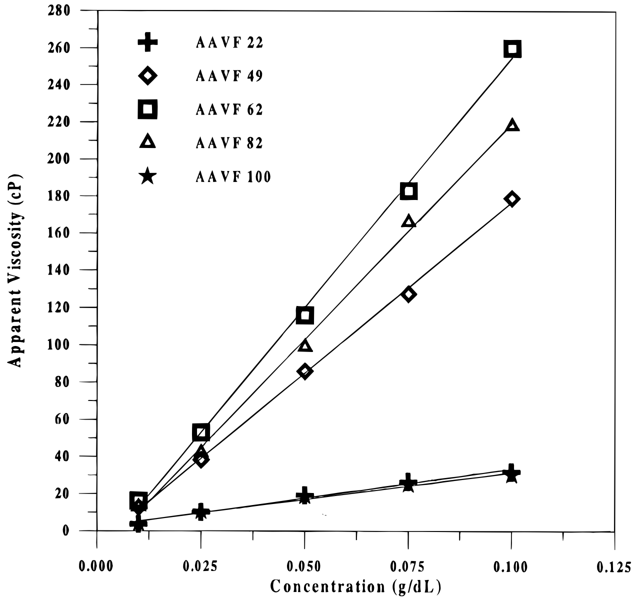

Figure 4. Effect of polymer concentration on the apparent viscosity for the AAVF copolymer series.

trolytic nature of the copolymers, relatively high apparent viscosities are observed at low polymer concentration due to Coulombic repulsions between the anionically charged comonomers.

An interesting trend is also noted for all three copolymer series. The homopolyelectrolytes (BAVF-100, PSVF-100, and AAVF-100) and the copolymers containing the lowest incorporation of charged comonomers (BAVF-23, PSVF-21, and AAVF-22) consistently exhibit the lowest apparent viscosities. Previously, we have found that for similar polyelectrolytes incorporating AM instead of NVF the copolymers always yielded higher viscosity values than the homopolyelectrolytes. Furthermore, for the AM copolymers, the highest viscosity values were obtained when there was ≈10−35 mol % incorporation of either NaAMBA[7,8] or NaAMPS,[9] while for AM−NaA copolymers,[10] 50 mol % NaA incorporation yielded the highest viscosity. For the NVF copolymers, those containing a slight molar excess of the anionic comonomer (ca. 60 mol %) attain the highest apparent viscosity. This behavior results from numerous factors which affect the hydrodynamic volume, including molecular weight, mol % of anionic comonomer, and the extent of hydration of the polymer coil. Additionally, intramolecular hydrogen bonding of adjacent mer units can stiffen the polymer backbone, resulting in a larger hydrodynamic volume. This has been previously observed for copolymers of AM and NaA.[13−15] Another effect which influences solvation of polyelectrolytes is that of counterion condensation, which effectively neutralizes a portion of the anionic charge, thereby reducing charge repulsion effects. Intramolecular hydrogen bond-

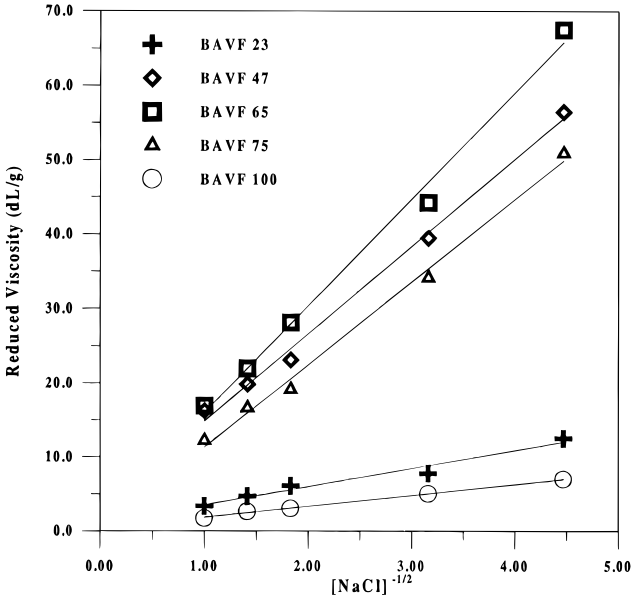

Figure 5. Reduced viscosity as a function of the inverse square root of ionic strength for the BAVF copolymer series ($C_p = 0.1$ g/dL).

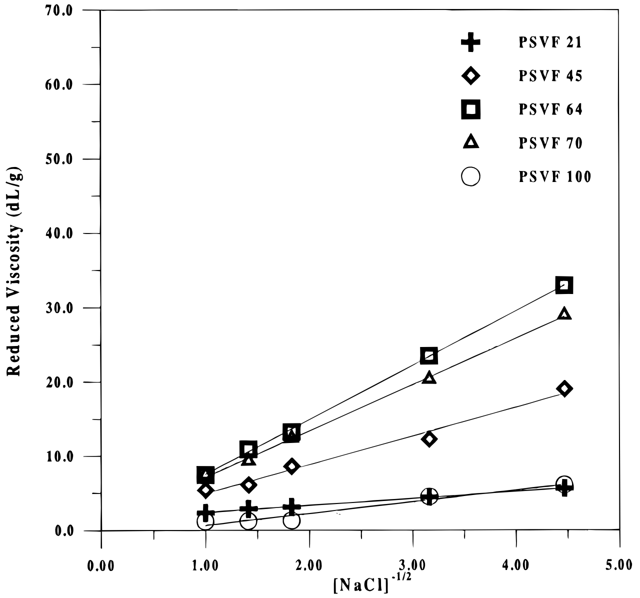

Figure 6. Reduced viscosity as a function of the inverse square root of ionic strength for the PSVF copolymer series ($C_p = 0.1$ g/dL).

ing, counterion condensation, and charge−charge repulsions are stronger with the AAVF series, in which the anionic group is closer to the macromolecular backbone.

Effects of Added Electrolytes. The effects of sodium chloride on the reduced viscosity were also examined and displayed in Figures 5−7. Polyelectrolyte behavior is observed as evidenced by the linear dependence of the reduced viscosity as a function of the inverse square root of ionic strength. As the concentration of electrolyte is increased (from right to left in the figures), the Debye−Hückel reciprocal screening length decreases. This, in turn, leads to a screening of the electrostatic repulsions along the polyelectrolyte, which, in turn, allows the polymer chain to acquire a more random coil-like configuration. Furthermore, by examining the magnitude of the slopes in the figures, the extent of conformational change induced by the addition of electrolytes can be assessed. Higher slope values indicate that the polymer coil is more susceptible to undergo conformational changes as the concentration of electrolyte is increased. From the figures, the copolymers incorporating the carboxylate group exhibit higher slopes than the sulfonate copolymers and may be indicative of enhanced counterion binding. Other factors which affect the hydration and conformation of the coil, such as the degree of hydrophobicity and steric repulsions, are also likely operative. The effects of polymer composition on the reduced viscosity follow similar trends as mentioned earlier. Namely, the copolymers with approximately 40−80 mol % of charged comonomer maintain higher viscosities even in the presence of electrolytes. This behavior still prevails in 1.0 M NaCl, conditions in which polymer conformation is only negligibly influenced by charge−charge repulsions.

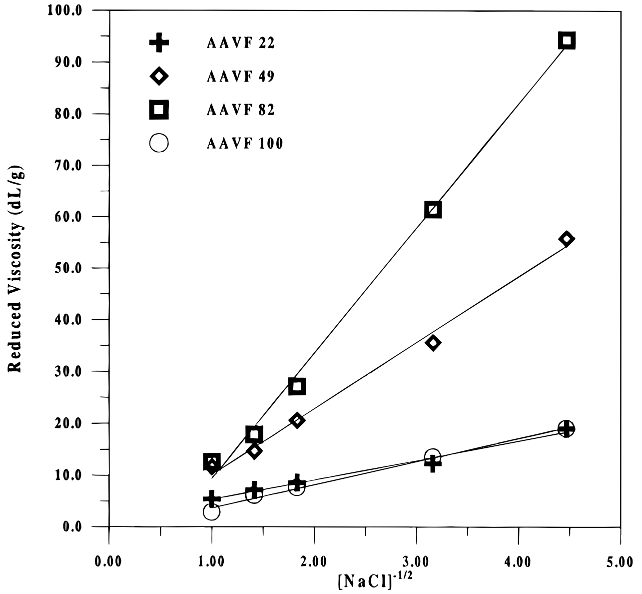

Figure 7. Reduced viscosity as a function of the inverse square root of ionic strength for the AAVF copolymer series ($C_p = 0.1$ g/dL).

Effects of the Nature of the Anionic Comonomer. In an effort to gain an understanding of the influence of the nature of the anionic comonomer on the solution behavior, viscosity studies were conducted on BAVF-38 and -56, PSVF-40 and -56, and AAVF-62. Since these pairs possess similar degrees of polymerization and essentially equivalent molar compositions of charged species, structure/property comparisons may be made. Molecular weight values and degrees of polymerization are shown in Table 1.

The apparent viscosities of the copolymers in deionized water at pH = 8.5 are shown in Figure 8. AAVF-62 has the highest apparent viscosity followed by BAVF-56 and PSVF-56. The ionic groups of AAVF are closer to both the polymer backbone and adjacent anionic groups compared to the BAVF and PSVF series. The forces resulting from charge−charge repulsions therefore cause a greater extension of the polymer backbone and subsequently larger hydrodynamic volumes. For the BAVF and PSVF copolymers, the charged centers are farther removed from the backbone and more conformational side chain motion allows charge−charge repulsions to be diminished. The BAVF copolymers consistently display higher viscosities than the PSVF copolymers. The difference between the two copolymers is the nature of the anionic species, BAVF possessing a carboxylate group and PSVF possessing a sulfonate

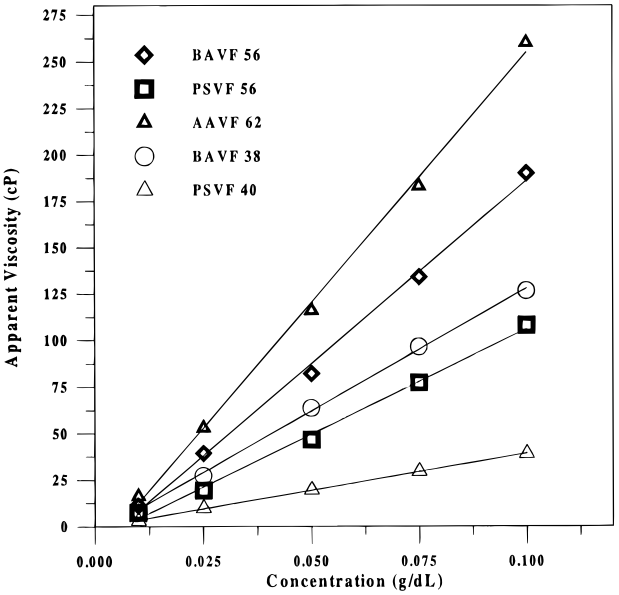

Figure 8. Effect of polymer concentration on the apparent viscosity for the selected copolymers.

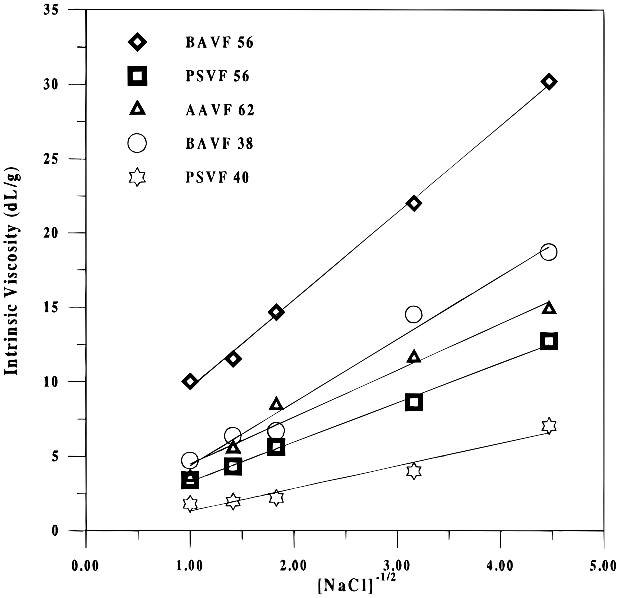

Figure 9. Intrinsic viscosity as a function of the inverse square root of ionic strength for the selected copolymers.

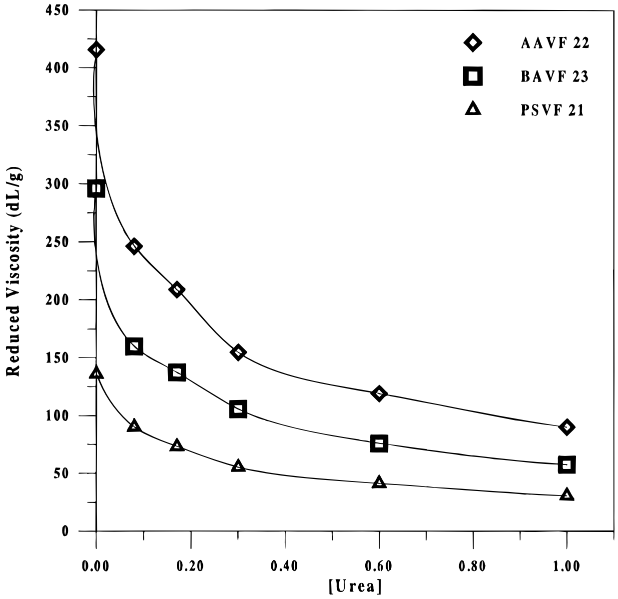

Figure 10. Effect of urea concentration on the reduced viscosity for the selected copolymers ($C_p = 0.025$ g/dL).

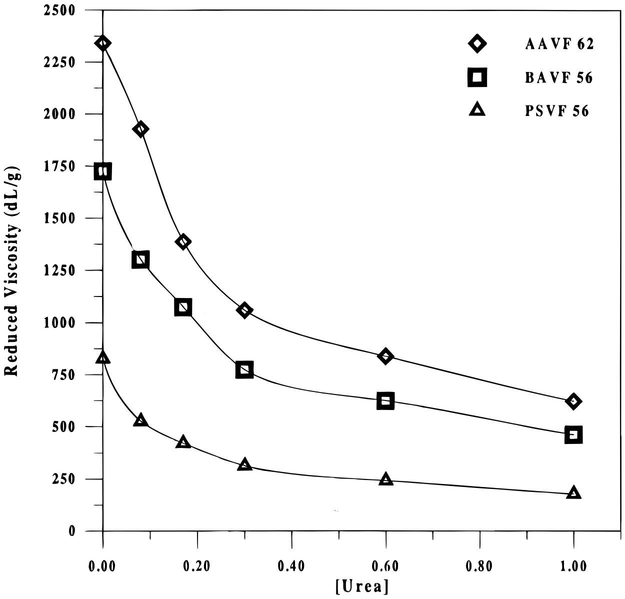

Figure 11. Effect of urea concentration on the reduced viscosity for the selected copolymers ($C_p = 0.025$ g/dL).

group. Past studies in our laboratories have shown similar behavior for copolymers of acrylamide with NaAMBA and NaAMPS.[7-12] In those studies, the copolymers containing the NaAMBA comonomer exhibited higher viscosities than those with NaAMPS. This behavior was attributed to both intramonomer and intermonomer hydrogen bonding between the carboxylate moiety and the acrylamido moieties. The carboxylate group is a stronger base than the sulfonate group and should therefore be a stronger hydrogen bond acceptor. Other factors such as enhanced solvation of the carboxylate group as compared to the sulfonate group and differing degrees of polarizability of the two groups may also be operative.

Figure 9 shows the effect of sodium chloride on the intrinsic viscosities of BAVF-38 and -56, PSVF-40 and -56, and AAVF-62. As before, there is a linear dependency of the intrinsic viscosity on the inverse square root of ionic strength. The BAVF copolymers exhibit higher slopes and therefore experience more conformational changes as the concentration of electrolytes is increased. Furthermore, the BAVF copolymers display an enhanced viscosity compared to the PSVF copolymers while the AAVF copolymer exhibits behavior intermediate to the BAVF and PSVF series. Similar trends have previously been observed for AM copolymers with NaAMPS and NaAMBA in the presence of electrolytes. Enhanced chain stiffness caused by hydrogen-bonding interactions may, in part, reflect the observed differences in salt response.

Effects of Urea. The effects of urea on the solution behavior of the copolymers were examined in the absence of added electrolytes, and the results are shown in Figures 10−12. Interestingly, urea has the same effect as small-molecule electrolytes, that is a reduction in the reduced viscosity as concentration is increased The dramatic loss of hydrodynamic volume implies a decrease in the solvent/polymer interaction as opposed to a shielding effect as is the case for added electrolytes. Whether this effect is due to specific interactions of urea

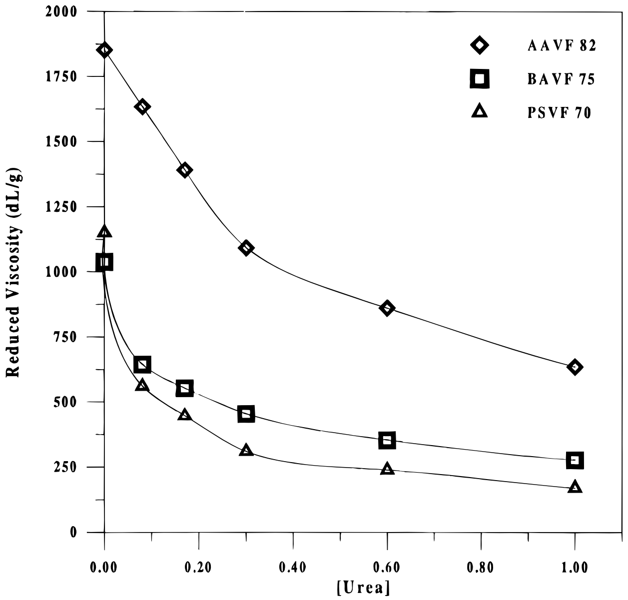

Figure 12. Effect of urea concentration on the reduced viscosity for the selected copolymers (C_p = 0.025 g/dL).

with the polymer and/or a result of the perturbation of the water structure cannot be decisively concluded by viscosity studies alone. It should also be noted that this phenomenon is observed for all three copolymer series, thus implying that the results are independent of the structure of the anionic comonomer and the mol % incorporated into the copolymer.

Phase Behavior. Many polymers possessing anionic moieties are known to undergo phase separation in the presence of divalent electrolytes such as calcium chloride and magnesium chloride.[4−6,11] This phenomenon is attributed to a strong site binding of the anionic moieties with divalent cations. The effects of calcium chloride as well as changes in the pH of the aqueous medium have been assessed for the BAVF, PSVF, and AAVF copolymer series.

1. Effects of Calcium Chloride. The phase behavior of the AAVF, BAVF, and PSVF copolymers in the presence of calium chloride was studied at 25 °C and at polymer concentrations of 0.2 g/dL at pH = 8.5. The behavior of the AAVF copolymer series is similar to that of copolymers of acrylamide and sodium acrylate. In the presence of calcium chloride, all of the copolymers, with the exception of AAVF-21, phase separate. The BAVF and PSVF copolymers, however, are soluble in the presence of calcium chloride (0−2 M) at 25 °C. Similar phase stability for copolymers of acrylamide with NaAMBA in the presence of calcium chloride has previously been reported by our group.[7] It is also noted that both BAVF-100 and BAVF-75 undergo phase separation at higher temperatures. For example, BAVF-75 in the presence of 0.1 M $CaCl_2$ exhibits a lower critical solution temperature (LCST) of 86 °C, while BAVF-100 exhibits a LCST of 76 °C. In the presence of 0.3 M $CaCl_2$, the LCST for BAVF-75 falls to 82 °C while the LCST for BAVF-100 falls to 71 °C. For copolymers containing 65 mol % or less of NaAMBA, no phase separation was observed in 0.3 M $CaCl_2$ up to 100 °C. The PSVF copolymers were stable in the presence of $CaCl_2$ at all temperatures. The differences in the solubility behavior between the BAVF and PSVF copolymer series may be attributed to the stronger affinity for the calcium ion of the carboxylate group compared to the sulfonate group.

2. Effects of pH. The phase behavior of the copolymers was also examined as a function of pH in deionized water at 25 °C and a polymer concentration of 0.05 g/dL. To limit hydrolysis, the lowest pH value examined was approximately 1. The PSVF copolymers were soluble over the entire pH range examined (pH 1−11). This behavior is directly attributable to the weak basicity of the sulfonate groups which are essentially disassociated at this pH value. In contrast, with the exception of BAVF-23, all of the BAVF copolymers phase separate at a critical pH value dependent on the mol % NaAMBA incorporated into the copolymers. For instance, BAVF-100 phase separates as the pH approaches 5.4 while BAVF-38 does not precipitate until the pH approaches 3.4. The phase separation may be explained by the fact that as the pH is lowered, more NaAMBA comonomer units will be progressively protonated and thus rendered nonionic. As this occurs, the polymer becomes more hydrophobic; at a critical pH value, the polymer phase separates. Besides the mol % NaAMBA incorporated into the copolymer, the transition is also affected by changes in the aqueous media, such as ionic strength and temperature. For example, at pH = 3.0, a heterogeneous solution of BAVF-38 becomes homogeneous as the temperature is lowered to 11 °C. This behavior, similar to that observed for poly(N-isopropylacrylamide), is representative of a LCST.

The phase behavior of the AAVF series is also dependent on polymer composition and temperature. AAVF-100 was not examined as the solution behavior of poly(acrylic acid) is well documented.[1] At 25 °C, AAVF-82 precipitates as the pH approaches 2.3 while AAVF-62 precipitates as the pH approaches 2.7. AAVF-40 and AAVF-22 do not precipitate under these conditions. The effect of temperature on the phase stability of the AAVF copolymers was studied at pH = 2. With the exception of AAVF-22, which remains homogeneous between 0 and 100 °C, all copolymers exhibit an upper critical solution temperature (UCST) in contrast to the BAVF copolymers. The upper critical solution temperatures at pH = 2 for AAVF-82, -62, and -40 are 38, 42, and 19 °C, respectively. When the samples are heated above their respective temperatures, the copolymer resolubilizes and one phase results. In contrast to the BAVF series, which phase separates because of hydrophobic interactions, the hydrogen-bonding interaction between the carboxylic acid and the formamide group in the AAVF series is responsible for phase separation. Insolubility in aqueous solution as a result of hydrogen bonding has been cited previously for numerous interpolymer complexes as well as copolymers of acrylic acid and acrylamide.[16,17] The effects of sodium chloride and urea on the UCST of AAVF-62 were also examined, and the results are shown in Figure 13. The presence of sodium chloride, which slightly enhances water structure, increases the UCST of AAVF-62. In contrast, urea, which disrupts water structure, decreases the UCST of AAVF-62. This behavior is a result of solvent perturbation in the presence of the added cosolute, which, in turn, affects the polymer−solvent interaction.

Conclusions

The solution behavior of copolymers of NVF with NaA, NaAMBA, and NaAMPS has been investigated as a function of pH, added electrolytes, and temperature. Polyelectrolyte behavior is observed for all three copolymer series. In deionized water, copolymers containing approximately 60 mol % of the anionic comonomer

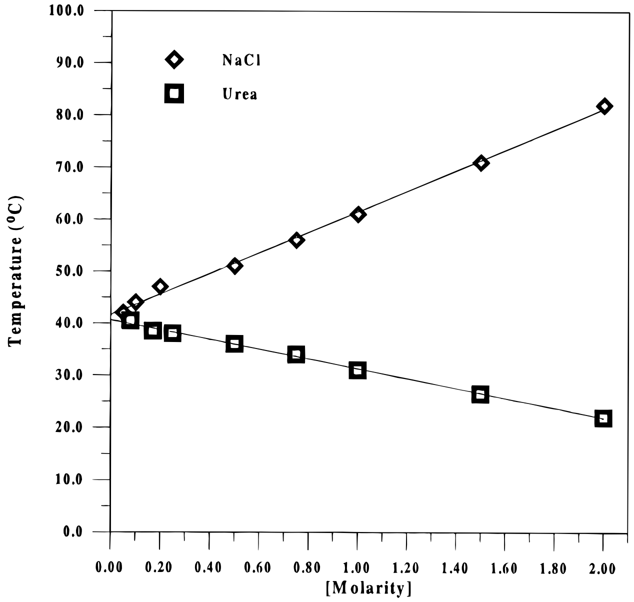

Figure 13. Effect of sodium chloride and urea concentration on the upper critical solution temperature (UCST) for AAVF-62 (C_p = 0.1 g/dL).

exhibit the highest viscosities. Furthermore, the closer the charged group is spatially located to the polymer backbone, the higher the viscosity. The nature of the anionic species of the comonomer also affects the solution behavior as evidenced by the enhanced viscosity of the BAVF series versus the PSVF series at pH = 8.5. The addition of electrolytes to all three copolymer series causes a marked reduction in viscosity due to shielding effects. Urea also induces a reduction in the hydrodynamic volume of the copolymers. The PSVF series is stable in the presence of calcium chloride and with changes in pH of the aqueous media due to the weak basicity of the sulfonate group. For the BAVF series, copolymers containing 75 mol % or more of NaAMBA phase separate in the presence of calcium chloride at elevated temperatures. In addition, BAVF copolymers containing 38 mol % or more of NaAMBA phase separate at a critical pH value, dependent on the amount of NaAMBA incorporated into the copolymer. AAVF copolymers also phase separate in the presence of calcium chloride and at lower pH values, dependent on the mol % of NaA in the copolymer. At pH = 2, AAVF copolymers exhibit a UCST which is influenced by added cosolutes.

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