Water-Soluble Copolymers. 52. Sodium-23 NMR Studies of Ion-Binding to Anionic Polyelectrolytes: Poly(sodium 2-acrylamido-2-methylpropanesulfonate), Poly(sodium 3-acrylamido-3-methylbutanoate), Poly(sodium acrylate), and Poly(sodium galacturonate)

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ABSTRACT: ^{23}Na NMR studies of counterion relaxation behavior in the presence of added electrolytes have been performed to determine the relative binding affinities of Na^+, K^+, Mg^{2+}, and Ca^{2+} ions to the homopolymers of poly(sodium acrylate) (NaAA), poly(sodium 2-acrylamido-2-methylpropanesulfonate) (NaAMPS), and poly(sodium 3-acrylamido-3-methylbutanoate) (NaAMB). The addition of Mg^{2+} and Ca^{2+} to the biopolymer poly(sodium galacturonate) (NaGAL) was also investigated. Addition of salts yielded the order of binding $Ca^{2+} > Mg^{2+} > K^+ \approx Na^+$ for NaAA and NaAMB and $Ca^{2+} \approx Mg^{2+} > K^+ > Na^+$ for NaAMPS. Significant differences in the ^{23}Na NMR behavior for NaAA are observed for added Mg^{2+} and Ca^{2+} and were interpreted in terms of hydration of the polyelectrolyte near phase separation, although a conformational change cannot absolutely be ruled out. Differences observed upon addition of Mg^{2+} and Ca^{2+} in the NaGAL system are discussed in relation to the "egg-box" model of Ca^{2+} binding to NaGAL. Viscosity profiles for each of the polymers with the above cations are related to the NMR data. Phase-separation studies on NaAMB demonstrate increased hydrophobicity of the polymer in the presence of excess Ca^{2+}.

Introduction

The behavior of uncharged polymers and polyelectrolytes in the presence of simple electrolytes is a subject of continuing research in our laboratory. The large viscosity losses and, ultimately, phase separation of anionic polyelectrolytes by a divalent cation are due to the strong chelating effect that reduces hydrodynamic volume and solvation. Sufficient inter- and intramolecular binding occurs to reduce the hydration of the polymer to a critical point at which phase separation occurs. The maintenance of viscosity in high concentrations of electrolytes is critical for application of polymers in areas such as enhanced oil recovery, drag reduction, and controlled release. Synthetic efforts have resulted in polymer systems that maintain viscosity in the presence of both monovalent and divalent ions and do not phase separate readily.[1-5] An increased understanding of the ion-binding and phase-separation phenomena of these polymers is necessary for tailoring polymer systems for use in areas where high salt concentrations adversely affect performance.

The viscosity behavior and phase stability of polyelectrolytes in the presence of excess salts have been extensively studied.[1-14] Poly(acrylates)[6-8] and hydrolyzed poly(acrylamide) (HPAM)[1,9-11] exhibit large viscosity losses and may phase separate in the presence of divalent counterions such as Mg^{2+}, Ca^{2+}, and Ba^{2+}. Poly(sodium acrylate) (NaAA) precipitates from solution when the concentration of divalent counterion (Mg^{2+}, Ca^{2+}, Ba^{2+}) reaches a critical value relative to the number of anionic sites available (approximately 0.8 on an equivalent basis).[6] Macroscopic solution properties (viscosity, phase separation) of poly(vinylsulfonate) (PVS) are dependent on the nature of the counterion species.[13,14]

Copolymers of acrylamide with sodium 2-acrylamido-2-propanesulfonate (NaAMPS)[1,3,4] and 3-acrylamido-3-methylbutanoic acid (NaAMB) maintain viscosity in high concentrations of divalent salts and do not phase separate in the presence of Ca^{2+} at temperatures up to 100 °C (polymer structures are shown in Figure 1).[3,4] However, unlike NaAMPS, the NaAMB homopolymer will phase separate at temperatures above 70 °C in high concentrations of $CaCl_2$.[3] The amount of Ca^{2+} necessary to precipitate NaAMB far exceeds the stoichiometric concentration required to bind to all of the anionic sites. This difference has been attributed to a weaker binding of the divalent ion to the sulfonate moiety in NaAMPS and the possibility of intramolecular ion complexation of the divalent ion to the pendent NaAMB side chain, preventing formation of insoluble ionic bonds.[4]

The subject of this work was to investigate homopolymers of NaAA, NaAMB, and NaAMPS to determine the relative binding characteristics of cations, Na^+, K^+, Mg^{2+}, and Ca^{2+} and to elucidate structural influence on macroscopic solution behavior (i.e., viscosity and phase separation). In particular, we wished to ascertain differences in binding characteristics of carboxylate or sulfonate functional groups near to or removed from the polymer backbone. Comparison of the behavior among homopolymers of NaAA, NaAMB, and NaAMPS has thus been made. ^{23}Na nuclear magnetic resonance (NMR) relaxation rate studies have been performed on these polymers both with and without added electrolytes. ^{23}Na NMR measurements of poly(sodium galacturonate) (NaGAL) with added Mg^{2+} and Ca^{2+} are also included since specific differences in the binding of ions are known to occur. Viscosity profiles of NaAMB and NaAMPS in the presence of each of the salts are presented as well as phase behavior studies on NaAA and NaAMB.

The ^{23}Na relaxation rates for the polyion systems studied in this work have been employed to yield correlation times, τ_c, by employing a theoretical estimate for the fraction of bound monovalent ions, P_b, in the presence of excess divalent ions. Correlation times were then utilized to obtain values for the quadrupolar coupling constant, χ. Values for P_b for Na^+ in the presence of excess divalent ions were determined using the Manning two-variable

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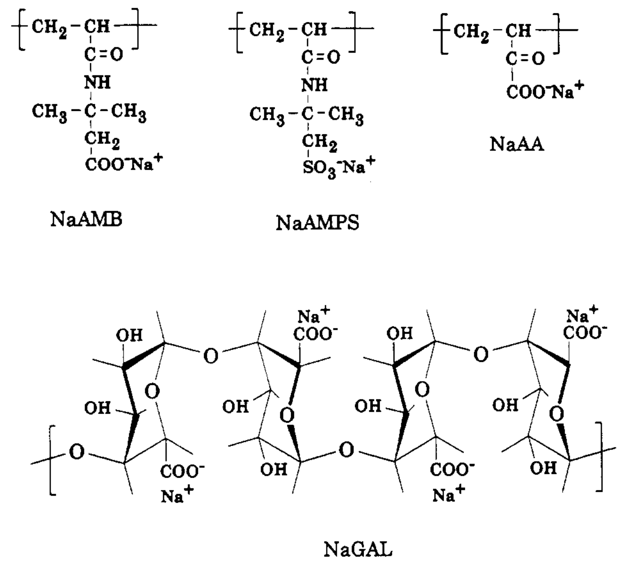

Figure 1. Structures for NaAMB, NaAMPS, NaAA, and NaGAL.

theory,[15] which has been demonstrated to be qualitatively descriptive of the fraction of ions bound in the presence of divalent ions.[19-21]

Background

Manning's treatment of polyelectrolyte behavior is based on the reduction of the dimensionless linear charge density, ξ, to $\xi_{crit} = 1$ by "condensation" of sufficient numbers of counterions according to (1)

$$\xi = \frac{\alpha e^2}{\epsilon k T l} \quad (1)$$

where ϵ is the dielectric of the medium (78.54 for water), α is the degree of ionization, and l is the charge separation along the backbone. For polyelectrolytes prepared from vinyl monomers, $l = 0.25$ nm, leading to the value of 2.85 for ξ. The fraction of counterions bound to poly(sodium acrylate) (NaAA) is predicted to be 65%.[15] For a divalent ion ($z = 2$) such as Ca^{2+}, the fraction of bound ions is predicted to be much higher (82% on an equivalent basis). However, this approach cannot account for differences in the residence times of Na^+ ions at the polyion surface, and treatment of the dielectric constant at the polyion surface has been questioned.[16] Although Manning's approach has been very successful in many respects, ^{23}Na NMR studies have observed counterion–polymer interactions inconsistent with the theory.[17] In some cases, changes in counterion relaxation behavior as a function of the degree of ionization and concentration are better modeled using the Poisson–Boltzmann "cell" model.[18] However, for cases of added salt, solutions to the Poisson–Boltzmann equation require numerical analysis. Again, the treatment of dielectric constant is likely insufficient.

Kwak and co-workers[19-21] have used Manning's two-variable theory as a theoretical basis for predicting the binding of divalent ions to biopolymers such as dextran sulfate[19] and heparin[20] and the synthetic polymers (carboxymethyl)cellulose[21] and poly(styrenesulfonate)[21] in mixed electrolyte systems. The activity coefficients of Mg^{2+} and Ca^{2+} were determined by a dye-fluorescence technique, and their binding behavior was studied as a function of ionic strength. The ion-binding effects for dextran sulfate indicated that, in general, Ca^{2+} ions had a greater affinity for the polymer and their behavior was better described by the model than Mg^{2+} ions under similar conditions.[19] This work also revealed that the ionic strength dependence of the degree of binding was determined by the nature of the added monovalent ion, Na^+ or K^+. In a similar study,[21] the binding of Ca^{2+} to poly(galacturonate) (pectin) was found to be much stronger than that predicted on the basis of Manning's theory. In contrast, the theory was very successful for binding of Mg^{2+} and Ca^{2+} to poly(styrenesulfonate) where no specificity between the ions was observed.[21]

Ion association and changes in water structure surrounding the polyelectrolyte upon binding have been investigated by dilatometry,[13,22,23] refractive index studies,[24] sound–velocity measurements,[25,26] and determination of activity coefficients.[19-21,28-30] Specific ion effects have been observed in viscosity[14] and volume changes for different ions.[13,22,23,27] The dehydration of Mg^{2+} and Ca^{2+} ions upon binding to NaAA indicates that Ca^{2+} ion forms intimate ion pairs with NaAA, while Mg^{2+} does not.[25,26]

The gelling behavior of several naturally-occurring polysaccharides in the presence of Ca^{2+} has been extensively studied.[31-35] The so-called egg-box model of binding has been reported for the carrageenans, alginates, and pectins.[31] In this model, the gelation of certain polysaccharides in the presence of Ca^{2+} initially proceeds through the formation of dimers in which Ca^{2+} ions are sandwiched between the helical polysaccharide chains.[32-34] The Ca^{2+} ions are tightly bound and cannot be removed even during extensive dialysis against high concentrations of monovalent salts.[32,33] A number of studies have shown that the amount of Ca^{2+} bound to the dimers is approximately 50% of the stoichiometric amount of carboxylate groups present.[32,33] As the amount of Ca^{2+} is increased, the ions bind to the exposed carboxylate groups on the dimers until nearly 100% of the stoichiometric requirement of carboxylate groups is fulfilled; at this point an extensive gel network forms.[32] The gelation occurs with a number of divalent ions including Ba^{2+}, Sr^{2+}, Cu^{2+}, Cd^{2+}, and Ca^{2+} but not with Mg^{2+}. This is reportedly due to the small size of Mg^{2+} and its inability to fit within the interstices of the polysaccharide chains.[35]

^{23}Na NMR and Polyelectrolytes. ^{23}Na nuclei are well suited for the study of cation-binding behavior to electrolytes due to a 100% natural abundance and a high magnetogyric ratio that allow observation by NMR. The sodium ion has a spin $^3/_2$ nucleus in which relaxation is dominated by quadrapolar effects in solution. The relaxation rates, R_1 and R_2, are sensitive to changes that affect the overall motion in solution and to electric field gradients (efg) about the nuclei. ^{23}Na relaxation rate measurements and chemical shift values thus provide a means for investigation of cation binding to polyelectrolytes[17,36-45] and observation of conformational changes that may occur as the degree of ionization along the polymer backbone increases.[41,43,46,47]

The results for ^{23}Na NMR relaxation studies have generally been interpreted using a two-site model for the observed line widths or relaxation rates.[17,36,41,43] The two-site model is justified when the exchange rate for the Na^+ nuclei between the polyanion and bulk solution is faster than the NMR observation time, usually the case for the sodium salts of polyanions. The observed relaxation rates are, therefore, an average of the relaxation rates for the unbound fraction (P_F) or free sodium nuclei and the fraction of ions bound (P_b) to the polymer,

$$R_{1,obs} = P_F R_{1,F} + P_b R_{1,b} \quad (2)$$

$$R_{2,obs} = P_F R_{2,F} + P_b R_{2,b} \quad (3)$$

The magnitude of the relaxation rate depends on the strength of the efg experienced by the sodium nuclei at the polyion surface, the lifetime of the Na^+ at the site, and the number of sodium nuclei that are bound.[42] The longitudinal and transverse relaxation rates generally display single-exponential behavior of the intensity of the NMR signal (M_{obs}) as a function of t, the relaxation delay.

$$M_{L,obs}(t) - M_{L,0} = (M_L(0) - M_{L,0}) \exp(-R_1 t) \quad (4)$$

$$M_{T,obs}(t) = M_T(0) \exp(-R_2 t) \quad (5)$$

This is a result of the rapid motion and reorientation of the sodium nuclei such that $\omega\tau_c < 0.25$ and, consequently, $R_1 = R_2$. Under conditions of fast exchange and $\omega\tau_c > 1.5$,[42] R_1 is no longer equal to R_2, and the relaxation rates become biexponential decays of the intensity of the NMR transition and the relaxation delay, t.[48]

$$M_{L,obs}(t) = M_L(0)\ 0.6 \exp(-R_{2f}t) + M_L(0)\ 0.4 \exp(-R_{2s}t) \quad (6)$$

Here R_{2f} and R_{2s} refer to the fast and slow components of the relaxation decay. In practice, only the transverse relaxation has been observed to display significant biexponential decay, with the longitudinal relaxation having single-exponential behavior.[44,47] When $0.25 < \omega\tau_c < 1.5$, the biexponential behavior is diminished but the relaxation rates are approximately exponential with $R_1 \neq R_2$. Under these conditions, τ_c can be obtained from the ratio of R_1 to R_2.[36,47]

$$R_1 = (1 - P_b)R_{1,F} + \frac{2P_b\pi^2\chi^2\tau_c}{5}\left(\frac{0.2}{1 + \omega^2\tau_c^2} + \frac{0.8}{1 + 4\omega^2\tau_c^2}\right) \quad (7)$$

$$R_2 = (1 - P_b)R_{2,F} + \frac{P_b\pi^2\chi^2\tau_c}{5}\left(0.6 + \frac{1}{1 + \omega^2\tau_c^2} + \frac{0.4}{1 + 4\omega^2\tau_c^2}\right) \quad (8)$$

$$\Delta\left(\frac{R_1}{R_2}\right) = \frac{R_1 - P_F R_{1,F}}{R_2 - P_F R_{2,F}} = \frac{\dfrac{1.6}{1 + 4\omega^2\tau_c^2} + \dfrac{0.4}{1 + \omega^2\tau_c^2}}{0.6 + \dfrac{0.4}{1 + 4\omega^2\tau_c^2} + \dfrac{1}{1 + \omega^2\tau_c^2}} \quad (9)$$

As τ_c becomes larger and $\omega\tau_c$ exceeds 1.5, the biexponential relaxation is pronounced and τ_c may be found from the ratio of R_{2s} to R_{2f}.[47]

$$R_{2f} = (1 - P_b)R_{2,F} + \frac{P_b\pi^2\chi^2\tau_c}{5}\left(1 + \frac{1}{1 + \omega^2\tau_c^2}\right) \quad (10)$$

$$R_{2s} = (1 - P_b)R_{2,F} + \frac{P_b\pi^2\chi^2\tau_c}{5}\left(\frac{1}{1 + \omega^2\tau_c^2} + \frac{1}{1 + 4\omega^2\tau_c^2}\right) \quad (11)$$

$$\Delta\left(\frac{R_{2f}}{R_{2s}}\right) = \frac{R_{2f} - P_F R_{2,F}}{R_{2s} - P_F R_{2,F}} = \frac{1 + \dfrac{1}{1 + \omega^2\tau_c^2}}{\dfrac{1}{1 + \omega^2\tau_c^2} + \dfrac{1}{1 + 4\omega^2\tau_c^2}} \quad (12)$$

The correlation time, τ_c, is determined by employing a theoretical estimate for P_b[47] or by assuming $P_F > P_b$.[41] Once τ_c is known, $P_b\chi^2$, the product of P_b and χ, the quadrapolar coupling constant, may be determined. χ is a measure of quadrapolar interactions and is proportional to the magnitude of the efg experienced by the counterion nuclei. The determination of χ requires independent knowledge of P_b. Using theoretical estimates for P_b, χ has been found to range from 35 to 700 kHz,[36,37] although some researchers have reported higher values.[49] The value of the quadrapolar coupling constant is expected to increase as the strength of binding increases[36] and higher values (1.2 MHz) have been attributed to site binding of the sodium counterion to anionic sites on heparin.[49] Grasdalen and Kvam reported χ values of 440 and 770 kHz for poly(mannuronate) and poly(guluronate), respectively, although these higher values could not be absolutely ascribed to site binding.[36]

Lindman and co-workers[41] used ^{23}Na NMR to identify an increased affinity of potassium over sodium in solutions of multichain chondroitin sulfate (CS) at low pH. A more rapid decrease in the transverse relaxation rate of sodium ions upon addition of a particular competing cation is interpreted as an increased affinity compared to Na^+. This behavior has been employed to rank relative binding affinities of Na^+ and K^+ to solutions of CS. However, addition of calcium to a multichain CS caused a sharp increase in R_2 which has been interpreted as either a change in the polymer conformation or an aggregation of individual polymer chains.[41] Similar behavior has been observed for addition of Mg^{2+} to vascular connective tissue and is ascribed to a conformational change in the polyelectrolyte in the presence of Mg^{2+}.[43] The concentration dependence of R_2 in PMA[47] and increases in the sodium counterion line width upon storage of poly(guluronate)[36] solutions have been attributed to aggregation phenomena.

Recently, Spencer et al. have conducted several studies employing ^{23}Na NMR to determine relative binding stengths of various ions with a number of polymer systems.[17,38–40] Solutions of PVS[39] and PSS[17] were found to bind the counterions in order of preference of $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. However, polyelectrolytes, such as NaGAL and NaAA, containing carboxylate moieties indicated no preference for any of the monovalent ions studied. The Poisson–Boltzmann "cell" model was found to be predictive of the binding behavior of Mg^{2+} in NaGAL, NaAA, and sodium malonate solutions.[17,38–40]

Experimental Section

Materials. 2-Acrylamido-2-methylpropanesulfonate (AMPS) was washed repeatedly with 2-propanol to remove impurities and vacuum dried at 30 °C before use. All salts (KCl, NaCl, $CaCl_2$, $MgCl_2$, $Mg(NO_3)_2$, and $Ca(NO_3)_2$) were 99.98% purity or greater and were purchased from Aldrich Chemical Co. Potassium persulfate was obtained from Aldrich Chemical Co. and was recrystallized in water prior to use. 3-Acrylamido-3-methylbutanoic acid (AMB) was synthesized via a Ritter reaction using acrylonitrile and 3,3-dimethylacrylic acid in the presence of water and excess sulfuric acid.[50] Poly(galacturonic acid) (MW between 25 000 and 50 000) was purchased from Fluka.

Polymer Synthesis. Polymers of NaAA, NaAMB, or NaAMPS were prepared at a concentration of 0.45 M by free-radical initiation in water at 30 °C using potassium persulfate. After dissolution of the monomer, the pH of the solution was adjusted to 9 by addition of NaOH to insure that the monomer was present in the ionized form (NaAMB and NaAMPS). Excess NaOH was used in the polymerization of NaAA to minimize chain end repulsion to yield a higher MW. The mixture was purged with nitrogen for 20 min before initiation with an appropriate amount of potassium persulfate (0.1 mol %). After 4–6 h, the reaction mixture was diluted with 2–4 volumes of H_2O followed by precipitation of the polymer in reagent-grade acetone while stirring. The polymer was washed repeatedly with excess acetone and vacuum dried at 40 °C before dissolution into H_2O. The aqueous polymer solution was dialyzed in water for 1 week before freeze-drying. The polymer was vacuum dried at 40 °C overnight and stored under desiccant. Polymer conversions were approximately 50%. The molecular weights of NaAMB and NaAMPS homopolymers were approximately 3 × 10^6.[51] The viscosity-average MW of the NaAA homopolymer was estimated from the Mark–Houwink parameters to be approximately 6 × 10^5.

Poly(sodium galacturonate) (NaGAL) was prepared by neutralization with NaOH to pH 7.7. Dialysis was performed to remove excess salt.[35] Given the temporal nature of gel formation,[34] Ca^{2+}/NaGAL solutions were allowed at least 30 min to reach equilibrium and were checked at regular intervals over the course of 24 h for changes in the ^{23}Na relaxation rates.

NMR, Viscosity, and Phase Separation Measurements. Sodium NMR measurements were conducted at 25 °C with a Bruker MSL-400 operating at 105.6 MHz for ^{23}Na nuclei. The glass cylinders supporting the transmitter/receiver coils were replaced with Teflon counterparts to minimize signal interference from sodium borosilicate glass. Teflon NMR tube liners from Wilmad Glass Co. were used in place of glass NMR tubes. Longitudinal relaxation rates (R_1) were measured using the inversion–recovery method. All curves were observed to be single-exponential decays and were fit to (8) using the Bruker SIMFIT program. Transverse relaxation rates (R_2) were measured (nonspinning) using the Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence and were fit to (5) and (6). Since no previous criteria have been established for the determination of the onset of biexponential relaxation behavior, we have arbitrarily chosen a cutoff for the onset of biexponentiality as being the point where the error of the fit of (5) exceeded that of (6) by 10%. The transverse relaxation rates are the average of three separate determinations. Error bars on the plots represent a 95% confidence level.

All polymers were vacuum-dried overnight at 40 °C prior to use. Salts were vacuum-dried at 80 °C and 5 Torr pressure before use. Polymer solutions were prepared at 0.1 g/dL concentration with 5% D_2O to provide a frequency lock. The polymer concentration was chosen for these studies to provide a good signal-to-noise ratio with a reasonable number of scans and a reasonably low solution viscosity. Solution volumes for the NMR measurements were 4 mL. Salt solutions were prepared at concentrations between 0.25 and 1 M to cover a range of cation/polymer ratios on an equivalent basis. The maximum volume addition to a polymer solution was 200 μL. Addition of an equivalent amount of H_2O to a control polymer solution resulted in no change in the relaxation rate of the Na^+ ions due to dilution effects. R_1 and R_2 measurements on similar concentrations of NaCl solutions were found to have values of 17.3 and 30.3 s^{-1}, respectively, and were employed in all calculations involving R_1 and R_2. The relaxation rates for the monomers NaAA, NaAMB, and NaAMPS were also measured and were close to those values for sodium chloride. The natural line width of a sodium counterion is 16.7 s^{-1}, and this value is used in all calculations involving R_{2s} and R_{2f}.[47] All calculations and curve fitting were performed with the commercial software program Mathcad. The experimental errors on the plots are the errors about the mean at the 95% confidence level.

Viscosity measurements were conducted on a Cannon–Fenske capillary viscometer at 25 °C and a polymer concentration of 0.1 g/dL. Polymer solutions were aged for at least 1 month prior to measurement. Phase-separation studies were performed on a Brinkmann PC-800 colorimeter using solutions identical to those employed in the viscosity measurements.

Results and Discussion

^{23}Na NMR. Interpretation of the ^{23}Na NMR measurements requires the condition of fast exchange such that the observed relaxation rates are an average of the bound and unbound Na^+ ions (two-site model). This was verified as an increase in R_{2s} with the reciprocal of temperature (Figure 2), as described by Grasdalen and Kvam,[36] and has been reported for a number of polyelectrolytes.[36,37,44,47] The relaxation data are plotted versus the ratio of the number of equivalents of added salt to the number of charged polymer sites.

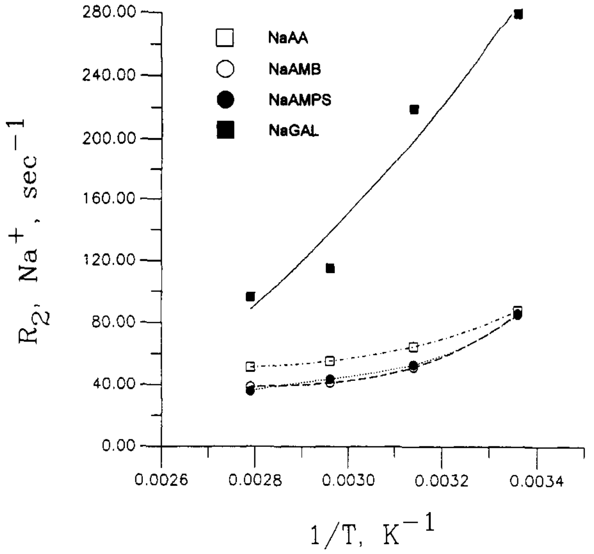

Figure 2. Slow component of the relaxation rate, R_{2s}, of NaAA, NaGAL, NaAMB, and NaAMPS as a function of temperature at a polymer concentration of 0.1 g/dL.

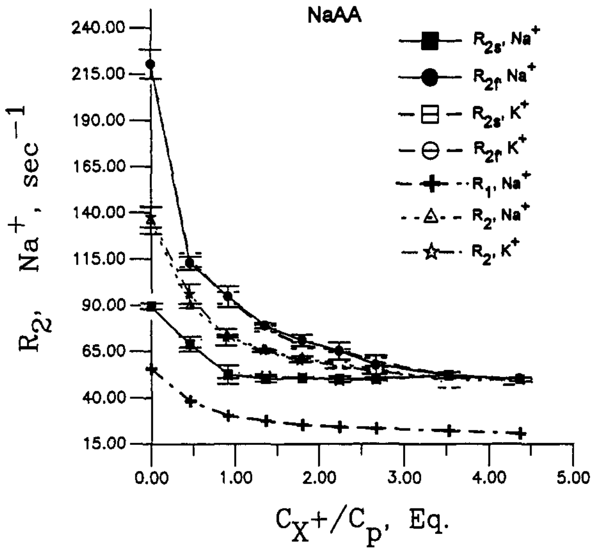

Figure 3. Longitudinal (R_1) and transverse (R_{2s} and R_{2f}) relaxation rates of NaAA with increasing Na^+ and K^+ concentration. The polymer concentration is 0.1 g/dL.

Biexponential relaxation rates were observed to be time-dependent in solutions of NaAA, NaAMB, and NaAMPS, with R_{2f} decreasing slightly to a constant value over the course of approximately 1 month. This behavior is reminiscent of the time dependency in the viscosity of NaAMB[2] and is consistent with initial clustering of polymer chains upon dissolution that slowly deaggregate. Polymer solutions, stored in polypropylene containers to eliminate the possibility of Na^+ ions diffusing into the solutions from glass, behaved the same as those stored in glass containers. The increase in biexponential relaxation ($\Delta R_2 = R_{2f} - R_{2s}$) with decreasing polymer concentration for NaAA correlated with that predicted by Halle et al.[37] ΔR_2 with no added salt is approximately 140 Hz for the polymer concentration (0.011 M) employed in this work.[37]

The behavior of R_2 for sodium counterions with NaAA in the presence of added Na^+ and K^+ is shown in Figure 3. The effect of added Na^+ on R_1 is also shown. The R_1 data for K^+ and the single-exponential fits to the transverse relaxation are not presented to avoid confusion on the plots. The R_1 data for K^+ are nearly identical to those for Na^+. The experiments by Leyte and co-workers demonstrated that the biexponential behavior of sodium poly-

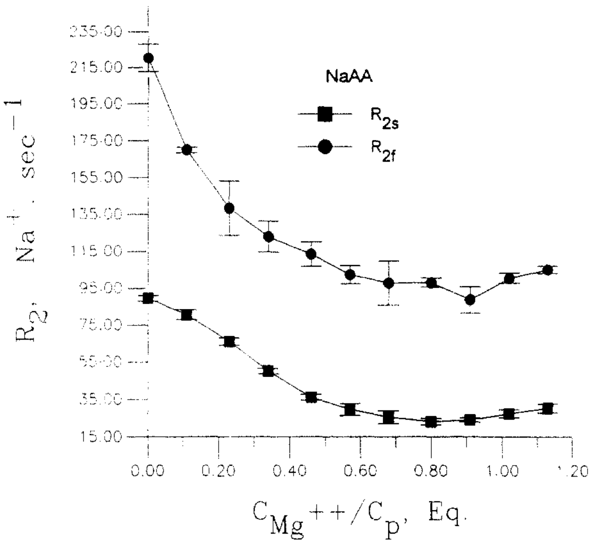

Figure 4. Transverse (R_{2s} and R_{2f}) relaxation rates of NaAA with increasing Mg^{2+} concentration. The polymer concentration is 0.1 g/dL.

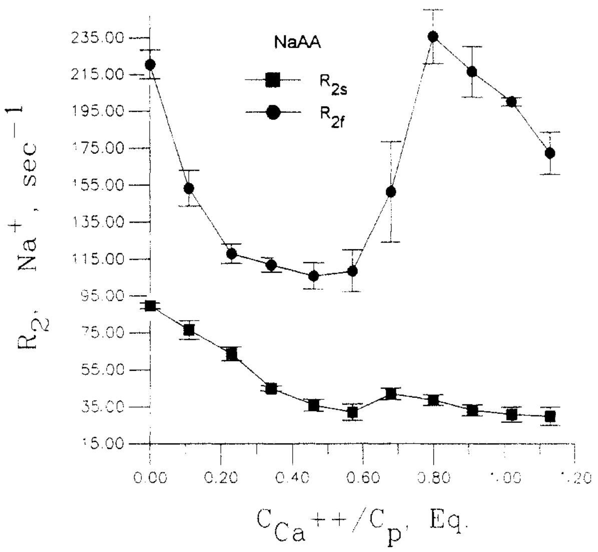

Figure 5. Transverse (R_{2s} and R_{2f}) relaxation rates of NaAA with increasing Ca^{2+} concentration. The polymer concentration is 0.1 g/dL.

(styrenesulfonate) (NaPSS) diminished as the concentration of added NaCl increased to approximately twice the polymer concentration.[37,44] In Figure 3, R_{2f} and R_{2s} reach similar values at $C_{salt}/C_p \approx 3$. Biexponential relaxation of NaAA with added Na^+ and K^+ is nearly identical, indicating similar binding of the ions to NaAA.

In Figure 4, the relaxation rates are plotted as the concentration of Mg^{2+} ion increases. R_{2s} and R_{2f} decrease gradually to $C_{Mg^{2+}}/C_p \approx 0.8$; above this value a slight increase in the relaxation rates is observed and the polymer precipitates from solution. In Figure 5, both relaxation rates initially decrease with added Ca^{2+} as observed with Mg^{2+}. However, at $C_{Ca^{2+}}/C_p \approx 0.8$, a sharp rise in R_{2f} occurs. This increase in R_{2f} occurs just prior to the Ca^{2+} concentration that causes phase separation of the polymer from solution, as measured from turbidimetry (see Table 1). There is also a small increase in R_{2s} prior to phase separation. If the increase in the biexponential relaxation behavior were due solely to aggregation, the R_2 behavior would be similar for Mg^{2+} and Ca^{2+}. These data suggest that a conformational transition or rearrangement of the polymer chains occurs upon binding of Ca^{2+}; such an event is not observed with Mg^{2+}. The biexponential relaxation persists at phase separation for both divalent ions, indicating that a significant amount of Na^+ is bound to the chain in the presence of excess divalent salt.

The changes in R_{2s} and R_{2f} with added salt for the individual polymers NaAMB and NaAMPS are shown in Figures 6–9. Again, as in Figure 3, the R_1 data for K^+ and the single-exponential fits to the transverse relaxation data are not presented. In Figure 6, R_{2f} exhibits a more negative slope in the presence of K^+ than Na^+ for NaAMPS. This behavior demonstrates that K^+ is binding tighter to NaAMPS than Na^+. Literature precedent for this has been reported for sulfonated polyelectrolytes such as PSS[17] and PVS.[39] In Figure 7, Mg^{2+} and Ca^{2+} behave similarly upon binding to NaAMPS, indicating a lack of specificity.

Table 1. Turbidimetry of NaAA (% Transmittance)

C_{salt}/C_p	Mg^{2+}	Ca^{2+}	C_{salt}/C_p	Mg^{2+}	Ca^{2+}
0	100	100	0.75	100	100
0.25	100	100	0.8	99.4	99.6
0.5	100	100	0.85[a]	95.6	95.3

[a] Solutions visibly cloudy.

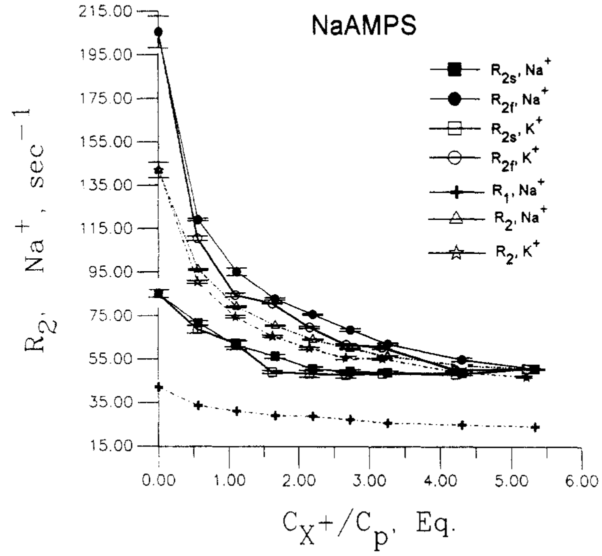

Figure 6. Longitudinal (R_1) and transverse (R_{2s} and R_{2f}) relaxation rates of NaAMPS with increasing Na^+ and K^+ concentration. The polymer concentration is 0.1 g/dL.

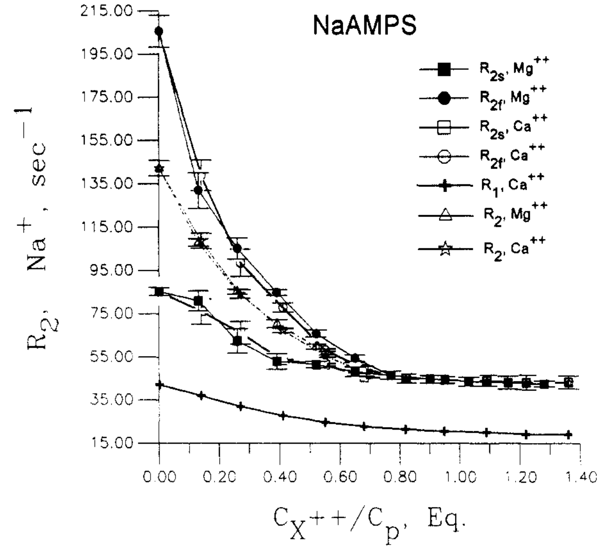

Figure 7. Longitudinal (R_1) and transverse (R_{2s} and R_{2f}) relaxation rates of NaAMPS with increasing Mg^{2+} and Ca^{2+} concentration. The polymer concentration is 0.1 g/dL.

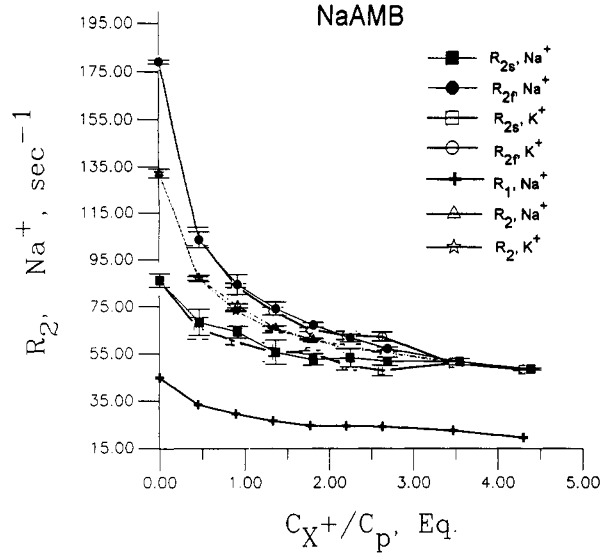

Figure 8. Longitudinal (R_1) and transverse (R_{2s} and R_{2f}) relaxation rates of NaAMB with increasing Na$^+$ and K$^+$ concentration. The polymer concentration is 0.1 g/dL.

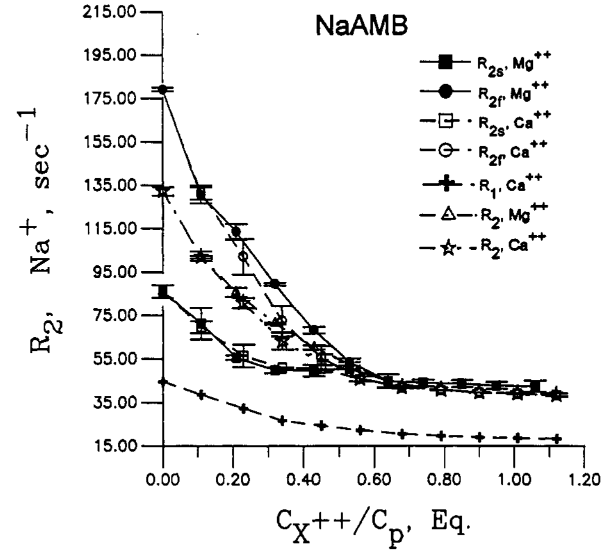

Figure 9. Longitudinal (R_1) and transverse (R_{2s} and R_{2f}) relaxation rates of NaAMB with increasing Mg^{2+} and Ca^{2+} concentration. The polymer concentration is 0.1 g/dL.

The binding of Na$^+$ and K$^+$ to NaAMB is presented in Figure 8. The behavior of R_{2s} and R_{2f} is nearly identical for these ions. Figure 9 depicts the effect of addition of Mg^{2+} and Ca^{2+} on the transverse relaxation rate behavior of NaAMB. The decrease in R_{2f} is greater for Ca^{2+} than for Mg^{2+}, indicating a slight preference for Ca^{2+} binding to NaAMB. At the higher C_{salt}/C_p ratios, R_2 values are slightly smaller in the presence of Ca^{2+} as compared to Mg^{2+}.

In Figure 10, $P_b\chi^2$ for NaAA is plotted as a function of C_{salt}/C_p for Ca^{2+}. Values of $P_b\chi^2$ have been calculated using (12) with a theoretical estimate for P_b to determine τ_c; (11) is used to determine χ. Manning's two-variable theory[15] has been employed for estimation of the fraction of bound sodium ions with increasing concentration of divalent ions. Although Manning's theory is reported to be inconsistent in regard to the concentration dependence of the ^{23}Na relaxation rates for polyelectrolytes,[36] the two-variable theory has been successfully employed for predicting P_b in some polyelectrolytes, based on activity coefficients.[21] Also included in Figure 10 are estimates for the upper and lower limits for the fraction of sodium ions bound assuming P_b is, for a lower limit, $0.2 - C_{salt}/C_p$ with the lowest possible value of $P_b = 0.01$. The upper limit of binding is chosen to be $P_b = 0.8 - C_{salt}/C_p$ with the lowest value of $P_b = 0.1$. These limits are independent of any theories and represent reasonable estimates for the upper and lower values of P_b over the course of this experiment.

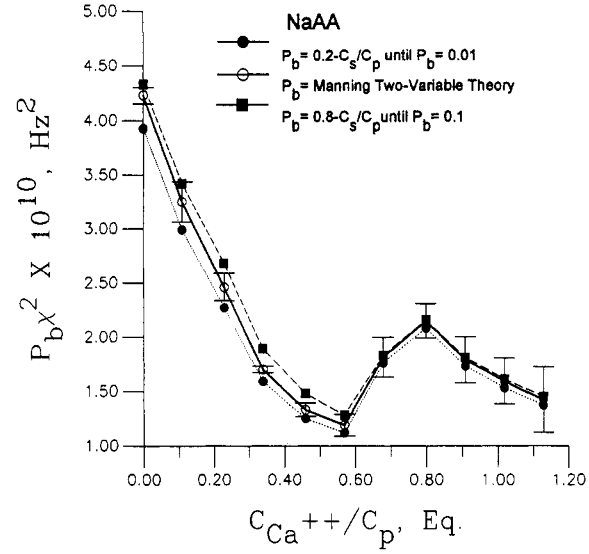

Figure 10. $P_b\chi^2$ for NaAA with increasing Ca^{2+} concentration. Reasonable limits for P_b are used to provide a boundary of solutions for $P_b\chi^2$. Manning's "two-variable" theory has been employed to provide specific values of P_b. The polymer concentration is 0.1 g/dL.

An increase in $P_b\chi^2$ is observed with increasing Ca^{2+} near phase separation, suggesting either a sudden increase in P_b or χ. In Figure 11, $P_b\chi^2$ values for NaAA with Mg^{2+} and Ca^{2+} are shown using the Manning prediction for P_b. An increase in $P_b\chi^2$ is not observed in the presence of Mg^{2+} below $C_{Ca^{2+}}/C_p \approx 0.8$. The maximum limits of $P_b\chi^2$ for Mg^{2+} range from 0.68 ($P_b = 1$) to 1.44 × 10^{10} Hz^2 ($P_b = 0$) for $C_{Mg^{2+}}/C_p = 0.8$. The experimentally observed value of $P_b\chi^2$ for Ca^{2+} of approximately 2 × 10^{10} Hz^2 cannot be accounted for by changes in P_b alone since the P_b value for Na$^+$ at $C_{Ca^{2+}}/C_p$ of 0.8 would have to nearly triple to yield the observed values of $P_b\chi^2$. Even at the unreasonable limits of $P_b = 0$ and 1, the magnitude of $P_b\chi^2$ observed for Ca^{2+} cannot be attained using (12), without significant changes in χ over $C_{Ca^{2+}}/C_p$ values of 0.6–0.8 in the NaAA/Ca^{2+} system.

Previous literature studies have shown that Mg^{2+} does not bind as strongly as Ca^{2+} to NaAA and that the hydration sphere of Mg^{2+} is less perturbed on binding.[6,25,26] A less hydrated coil in the presence of Ca^{2+} would result in a lower local dielectric constant and a concomitant increase in χ for the sodium ions that remain bound within the polymer domain. However, a conformational change of NaAA in the presence of Ca^{2+} near phase separation that affects the τ_c values cannot be ruled out.

Measured values of the quadrapolar coupling constant, χ, as function of $C_{Ca^{2+}}/C_p$ yield some insight into solution behavior. As shown in Figure 1, NaAMB and NaAMPS have identical structural components except for the carboxylate and sulfonate moieties, respectively. For NaAA, the carboxylate moiety is located closer to the backbone. For Manning's two-variable theory, values for P_b for each of these polymers would be identical for a given $C_{Ca^{2+}}/C_p$ value. Using such an assumption, Figure 12 was constructed from (8) for NaAMB and NaAMPS and (11) for NaAA.

Several features of this plot should be addressed. First of all, only slight differences in χ are exhibited by NaAMB

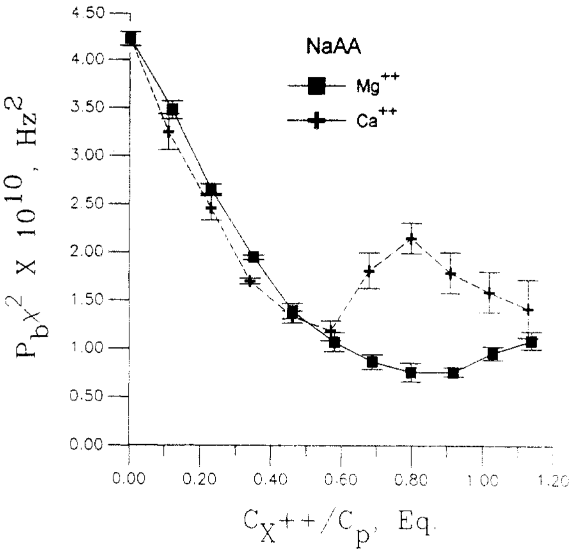

Figure 11. $P_b\chi^2$ for NaAA with increasing Mg^{2+} and Ca^{2+} concentrations using the Manning prediction for the fraction of bound ions. The polymer concentration is 0.1 g/dL.

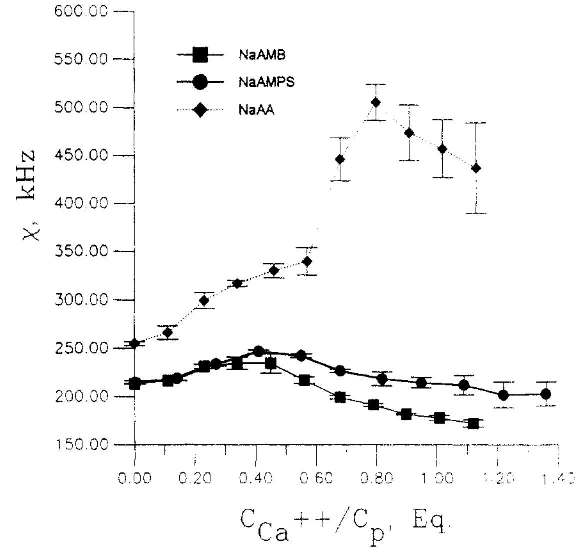

Figure 12. Values of χ for NaAA, NaAMB, and NaAMPS with increasing Ca^{2+} concentration. The Manning prediction is employed for estimation of P_b. The polymer concentration is 0.1 g/dL.

and NaAMPS. χ values above $C_{Ca^{2+}}/C_p > 0.4$ diverge to a small but significant degree. This is consistent with a slightly stronger binding of Ca^{2+} to the carboxylate units on NaAMB as compared to the sulfonate units on NaAMPS. However, experiments with Ca^{2+} selective electrodes at $C_{Ca^{2+}}/C_p = 1$ yielded P_b values for Ca^{2+} of 0.71 and 0.66 in 0.36 M KCl for NaAMB and NaAMPS, respectively.[4,52] Since values of χ in Figure 12 were constructed from $P_b\chi^2$ data, differences in behavior of NaAMB and NaAMPS may actually reflect differences in P_b.

A second striking feature in Figure 12 is the rapid increase in χ for $C_{Ca^{2+}}/C_p$ values of 0.6–0.8 for NaAA. As discussed previously, the magnitude of this increase cannot be accounted for by changes only in P_b and must be due to changes in χ. A third feature is the lack of change in χ over the range of $C_{Ca^{2+}}/C_p$ values for both NaAMB and NaAMPS as compared to NaAA. In the former cases, it is likely that little conformational change occurs, while in the latter, dramatic molecular structural changes probably ensue with a maximum in χ at $C_{Ca^{2+}}/C_p = 0.8$ at phase separation. Note that no such increase is observed for Mg^{2+} (Figure 11). The increased magnitude of χ for NaAA compared to NaAMB and NaAMPS is consistent with an increased local dielectric constant with ionic sites tethered away from the more hydrophobic backbone in the latter systems. In addition, χ values calculated from biexponential relaxation rates (eqs 11 and 12) have been previously reported to yield higher values for χ compared to those obtained from R_1 and R_2 (eqs 8 and 9).[47]

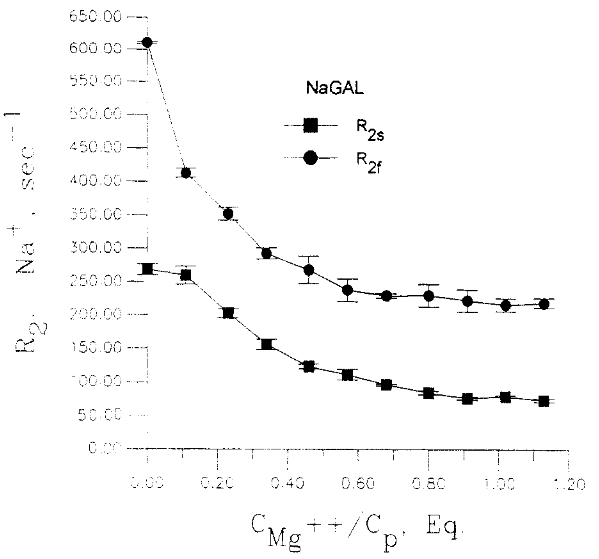

Figure 13. Transverse (R_{2s} and R_{2f}) relaxation rates of NaGAL with increasing Mg^{2+} concentration. The polymer concentration is 0.1 g/dL.

In Figure 13, the relaxation rates for NaGAL are plotted as a function of increasing Mg^{2+}. Both R_{2s} and R_{2f} follow a smooth decrease that levels out at higher $C_{Mg^{2+}}/C_p$ values. This is similar to the behavior observed for NaAA. The decrease in both relaxation rates is due to a smaller fraction of Na^+ ions binding to the polyelectrolyte as the concentration of the divalent ion increases. The relaxation rates reach a constant value as the bound Na^+ ions are replaced by Mg^{2+}. However, the biexponential relaxation behavior would be expected to diminish if all of the Na^+ ions were no longer associated with the NaGAL chain. Thus, a significant number of the Na^+ ions appear to be associated in some fashion with the chain even though sufficient numbers of Mg^{2+} ions are present to bind all of the carboxylate sites.

In Figure 14, the transverse relaxation rates of the Na^+ counterions are plotted as a function of increasing Ca^{2+} concentration. The behavior is markedly different from that observed for added Mg^{2+} ions. R_{2f} increases while R_{2s} decreases up to $C_{Ca^{2+}}/C_p \approx 0.4$–$0.5$, at which point R_{2f} begins to decrease in a fashion similar to R_{2s}. At $C_{Ca^{2+}}/C_p > 1$, both relaxation rates drop precipitously, indicating a sharp decrease in the amount of Na^+ that is bound to NaGAL. This behavior can be rationalized in terms of the egg-box model proposed by Rees and co-workers for poly(galacturonic acid).[37] As the concentration of Ca^{2+} ions increases up to $C_{Ca^{2+}}/C_p \approx 0.5$, bound Na^+ ions are replaced and R_{2s} decreases. The increase in R_{2f} is probably due to the dimerization of the NaGAL chains which effectively dilutes the polyelectrolyte in the solution. The decrease in concentration from 0.0046 to 0.0023 M has been predicted to increase ΔR_2 by approximately 210 Hz.[37] Assuming the two-site model with $R_{2,obs} = R_{2f}$ and using $P_b = 0.26$[47] to find $R_{2b} = 2245$ Hz (eq 3), the decrease in R_{2f} due to displacement of half of the bound Na^+ ions ($P_b = 0.13$) is approximately 320 Hz. The decrease in R_{2f} due to a lower fraction of bound Na^+ would be nearly offset

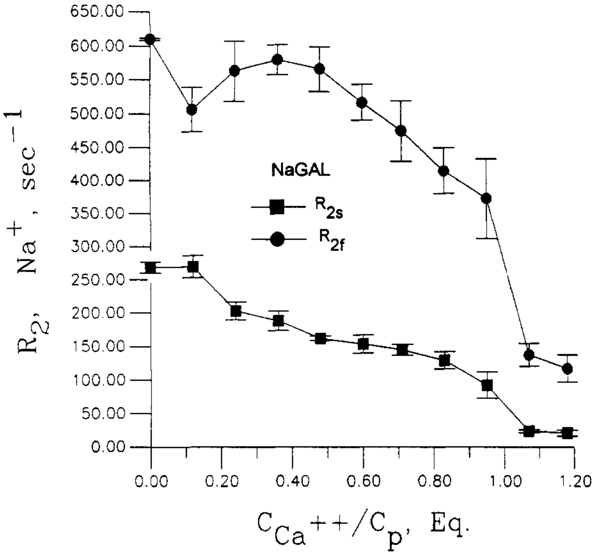

Figure 14. Transverse (R_{2s} and R_{2f}) relaxation rates of NaGAL with increasing Ca^{2+} concentration. The polymer concentration is 0.1 g/dL.

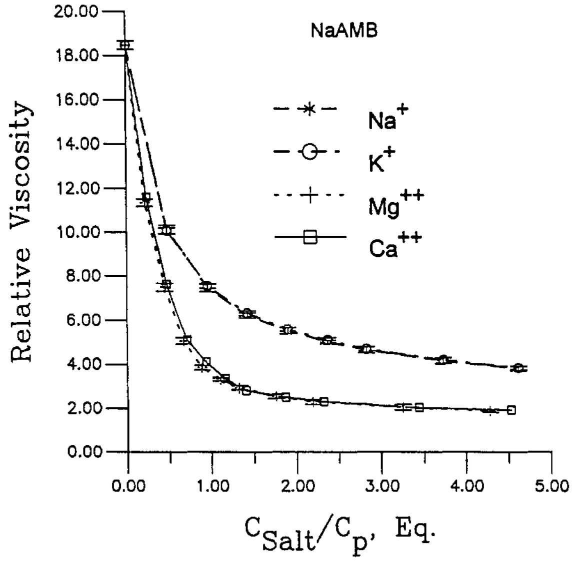

Figure 15. Dependence of the relative viscosity of NaAMPS with increasing concentration of Na^+, K^+, Mg^{2+}, and Ca^{2+}. The polymer concentration is 0.1 g/dL.

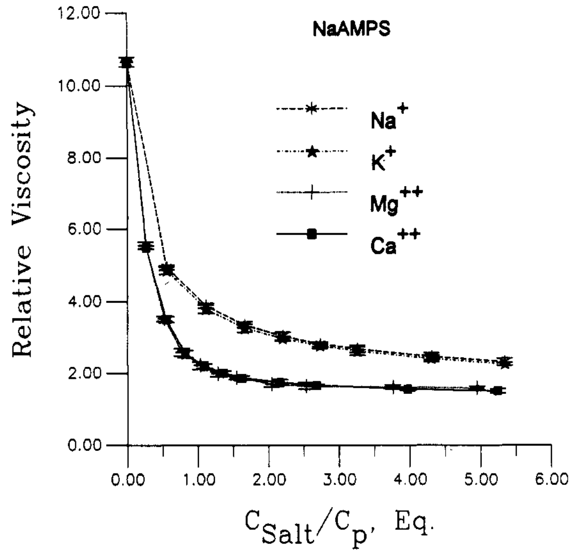

Figure 16. Dependence of the relative viscosity of NaAMB with increasing concentration of Na^+, K^+, Mg^{2+}, and Ca^{2+}. The polymer concentration is 0.1 g/dL.

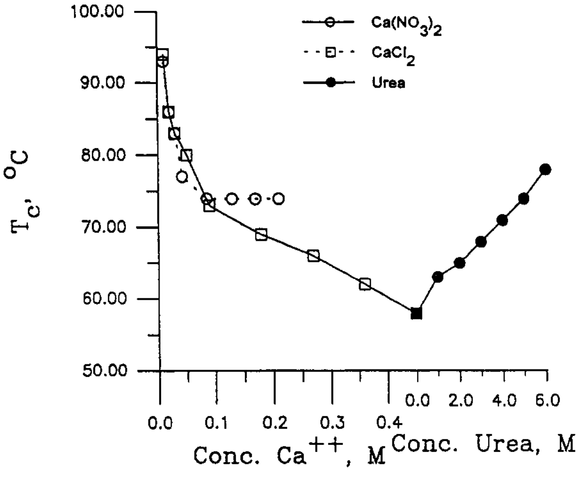

Figure 17. Dependence of the phase-separation temperature, T_c, of NaAMB with $CaCl_2$ and $Ca(NO_3)_2$. The increase in T_c after addition of urea to NaAMB/$CaCl_2$ is also depicted. The polymer concentration is 0.1 g/dL.

by the increase in ΔR_2 due to dimerization. When the concentration of Ca^{2+} ions increases beyond $C_{salt}/C_p \approx 0.5$, both relaxation rates should decrease; the bound Ca^{2+} ions approach the stoichiometric number of carboxylate moieties, expelling Na^+ ions from the network and thus causing a sharp drop in the relaxation rates. Consistent with experimental results from the Mg^{2+}/NaGAL system, a significant fraction of Na^+ apparently remains bound (evidenced by the persistence of the biexponential relaxation at $C_{salt}/C_p \approx 1$).

Viscosity and Phase Separation. In Figures 15 and 16, the relative viscosities versus C_{salt}/C_p (Na^+ and Ca^{2+}) are presented for NaAMB and NaAMPS, respectively. The relative viscosities of the polymers differ due to a slightly higher molecular weight and a higher repeat unit concentration for the NaAMB homopolymer. In both figures, the viscosity is reduced dramatically with increasing C_{salt}/C_p and nearly level above $C_{salt}/C_p \approx 1$ for added Mg^{2+} and Ca^{2+}. This behavior parallels the NMR results which indicate that, at higher C_{salt}/C_p ratios, the divalent ions replace most of the Na^+ ions. Since addition of more divalent ion does not reduce the viscosity beyond a residual relative value, the remaining hydrodynamic volume is likely due to hydration of polymer segments not involved in ion binding. In contrast, NaAA precipitates from solution when a critical ratio of added divalent ion (Mg^{2+}, Ca^{2+}, and Ba^{2+}) to the number of anionic sites is reached.[13]

Phase-separation studies of NaAMB in the presence of divalent salts were conducted in an effort to clarify the mechanism for phase separation of this polyelectrolyte. $CaCl_2$ causes precipitation of NaAMB homopolymer at high temperatures; $MgCl_2$ does not.[51] Addition of $Mg(NO_3)_2$, $MgSO_4$, and $MgCl_2$ to a 0.1 g/dL solution of NaAMB results in no precipitation of the polymer from solution. Addition of $Ca(NO_3)_2$ and $CaCl_2$ has different effects on the phase-separation temperature (T_c) of NaAMB as shown in Figure 17. $CaCl_2$ depresses T_c to a larger degree (salting out) than $Ca(NO_3)_2$. This is the expected behavior when hydrophobic interactions influence the phase separation.[53-55] The dependence of the T_c with added urea at constant $CaCl_2$ is also shown in Figure 17. Urea is a known water-structure breaking agent and causes a disruption of hydrophobic bonding in aqueous systems.[56] The increase in T_c with increasing urea concentration also suggests that hydrophobic effects play a role in the phase-separation mechanism in NaAMB.

Conclusions

The differences in the phase-separation behavior of NaAMB and NaAMPS in the presence of Ca^{2+} have been previously attributed to a weaker binding of the ion to the polymer sites and are consistent with the ^{23}Na NMR results presented here. A faster decrease for R_{2f} and $P_b\chi^2$ values is observed for added Ca^{2+} as compared to Mg^{2+} in NaAA; thus, the relative ion affinity is $Ca^{2+} > Mg^{2+} > Na^+ \approx K^+$. An increase in χ is demonstrated for NaAA in the presence of Ca^{2+} near phase separation. The ^{23}Na NMR relaxation measurements of NaGAL in the presence of Mg^{2+} indicate simple exchange of Mg^{2+} for Na^+ at the anionic sites. However, addition of Ca^{2+} to NaGAL solutions results in complex relaxation rate behavior consistent with an interpretation based on the egg-box model. For NaAMB, the order is the same as that for NaAA with a slight preference for Ca^{2+} over Mg^{2+}. For NaAMPS, the order of binding is $Ca^{2+} \approx Mg^{2+} > K^+ > Na^+$.

The NMR studies performed here cannot distinguish between intra- and intermer complexation of divalent ions to the side chains of NaAMB. However, the estimated χ values suggest that the lack of phase separation of NaAMB and NaAMPS as compared to NaAA is related to differences in affinities of ions for the respective polymers.

The turbidimetric studies illustrate the effects of hydrophobicity in phase separation. It appears that χ increases in a more hydrophobic environment (see the following paper[57]) and the relationships between the local dielectric constant and ion binding are important in phase separation. In the studies performed on NaAA, the changing local environment experienced by the Na^+ ion may be observed by following changes in χ with added Ca^{2+}. In NaAMB and NaAMPS, the anionic groups are decoupled from the backbone and may allow the bound Na^+ ions to experience a region of higher dielectric constant. No such dramatic changes in χ are observed with added divalent ions for these systems probably because spacing allows additional conformational freedom of the side chains.

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