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# Water-Soluble Copolymers. XX. Copolymers of Acrylamide with Sodium 3-(N-Propyl)Acrylamido-3-Methylbutanoate: Solution Properties

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## ABSTRACT

Dilute solution properties of copolymers of acrylamide (AM) with sodium 3-(N-propyl)acrylamido-3-methylbutanoate (NaPAMB) of known molecular weight have been studied as a function of composition, temperature, time, pH, and added electrolytes. Phase separation and potentiometric studies have also been performed. The AM-NaPAMB copolymers possess lower molecular weights and solution viscosities than the AM-NaAMB copolymers. In addition, the AM-NaPAMB polymers exhibit moderate viscosity-temperature coefficients and poor salt tolerance. These polymers undergo phase separation in the presence of divalent cations as a function of temperature. The observed properties can be related to the steric and hydrophobic effects caused by the presence of the n-propyl substituent at the amide nitrogen.

## INTRODUCTION

In our continuing efforts to develop model water-soluble polymers of acrylamide for use as viscosity-modifying agents, we have reported the synthesis, characterization, and solution properties of copolymers

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of acrylamide with comonomers which were carboxylated analogs of sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) [1-4]. In the preceding paper of this series we reported the synthesis and structural characterization of copolymers of acrylamide with sodium 3-(N-propyl)acrylamido-3-methylbutanoate (NaPAMB). We now report the characterization and solution properties of the AM-NaPAMB copolymers. Previously the effects of an $\alpha$-methyl substituent on the backbone were assessed [3, 4]. In this study we assess the effects of an n-propyl substituent at the amide nitrogen. The resulting polymers maintain their polyelectrolyte behavior while possessing a much more hydrophobic character. These effects are compared to the previously reported systems.

## EXPERIMENTAL

### Materials

Copolymers of acrylamide (AM) with sodium 3-(N-propyl)acrylamido-3-methylbutanoate (NaPAMB) were prepared at 30°C in aqueous solution at a pH of 9 using potassium persulfate as the initiator. Details of the synthesis, purification, and characterization procedures were reported in the previous paper. The polymers were freeze-dried and stored in a vacuum desiccator until used.

Reagent grade sodium chloride from J. T. Baker Co. was used without purification. Calcium chloride from J. T. Baker Co. was dissolved in water, filtered, and dried at 175°C prior to use. All aqueous salt solutions were prepared using deionized water.

### Characterization

The copolymer compositions of all polymers were determined from elemental analysis and $^{13}C$ NMR. Microstructures (Table 1) were calculated using the statistical method described in the previous paper [5].

### Viscosity Measurements

Stock solutions of sodium chloride (0.043, 0.086, 0.257, and 0.514 M NaCl) were prepared by dissolving the appropriate amount of salt in deionized water in volumetric flasks. The required quantities of the dry copolymers were then dissolved in the salt solutions.

Solution viscosities were measured in a Cannon-Ubbelohde four-bulb shear dilution capillary viscometer (Size 100). The shear rate constants and viscometer constants were provided by the manufac-

TABLE 1. Structural Data for the Copolymers of Acrylamide (AM) with Sodium 3-(N-Propyl)Acrylamido-3-Methylbutanoate (NaPAMB)

| | Composition, mol%[a] | | Blockiness, mol%[b] | | Alternation, mol%[b] | Mean sequence length | |
|---|---|---|---|---|---|---|---|
| Sample | AM | NaPAMB | AM-AM | NaPAMB-NaPAMB | AM-NaPAMB | $\mu_{AM}$ | $\mu_{NaPAMB}$ |
| PAMB-10-1 | 91.38 | 8.62 | 83.1 | 0.3 | 16.6 | 11.3 | 1.0 |
| PAMB-25-1 | 80.64 | 19.36 | 63.1 | 1.8 | 35.1 | 4.4 | 1.1 |
| PAMB-40-1 | 68.96 | 31.04 | 43.4 | 5.5 | 51.1 | 2.7 | 1.2 |
| PAMB-60-1 | 53.50 | 46.50 | 22.5 | 15.5 | 62.0 | 1.8 | 1.5 |

[a] From elemental analysis.
[b] Statistically calculated by reactivity ratios.

turer. The Carreau model [6] was used to obtain zero-shear viscosities by extrapolation of apparent viscosities to zero-shear rate. The Huggins equation [7] was then used to obtain zero-shear intrinsic viscosities, $[\eta]_0$, by extrapolation of the reduced viscosity, $\eta_{sp}/c$, to infinite dilution.

### Turbidimetry Measurements

The turbidimetric method used to study the phase separation of these copolymers and the apparatus required for the measurements have been previously reported [2, 4, 8, 9]. Calcium chloride solutions were prepared gravimetrically, and the concentrations were verified by refractive index measurements. Polymer solution concentrations were 1.5 g/L. Salt concentrations were varied by addition of solid salt for higher concentrations or known amounts of salt solution for lower concentrations. Water lost by evaporation during the experiment was replaced.

### Potentiometry Measurements

The procedure utilized in these studies for the potentiometric measurements was reported previously [2, 4, 8, 10]. Measurements were made by using a Corning 130 pH-mV meter with an Orion pH electrode at a constant temperature of 25 ± 0.05°C.

Polymer concentrations were 1.5 g/L. Each sample was titrated at constant ionic strength (0.36 M KCl) and with no ionic strength adjustment ($H_2O$). The titrations were conducted under nitrogen atmosphere with dilute standardized acid solutions ($<$ 0.1 M). The degree of ionization ($\alpha$) was measured as reported previously [2, 8, 10]. The dissociation constants ($pK_a$) were calculated by using the modified Henderson-Hasselbalch equation [11]. The values reported are apparent $pK_a$ values.

## RESULTS AND DISCUSSION

### Aging Effects

In order to properly assess the effects of added electrolytes, copolymer composition, temperature, and pH on the solution behavior of the AM-NaPAMB polymers, aging studies were first conducted. The effects of aging are seen in an initial viscosity increase during dissolution followed by a gradual decrease in measured viscosity as a function of time. Such an aging effect has been observed for aqueous solutions of polyacrylamide [12] and partially hydrolyzed polyacrylamide [13], and may be attributed to conformational changes resulting from changes in inter- and intrachain hydrogen bonding.

The aging effects for the AM-NaPAMB polymers were studied by utilizing a Size 100 Cannon-Fenske capillary viscometer at 30°C. Figure 1 shows the aging effect for the polymers in deionized water. The reduced viscosities of the polymers decreased sharply over the 30-day aging period; however, the most dramatic decrease occurred within the first 2 weeks. The percent loss in viscosity increased with increasing NaPAMB content in the polymer, and ranged from 35% for PAMB-10-2 (8.8 mol% NaPAMB) to 90% for the NaPAMB homopolymer. The nature of the NaPAMB comonomer increases the possibility of hydrophobic interactions, resulting in a polymer with a smaller hydrodynamic size.

Figure 2 shows the aging effect on the polymers in 0.257 M NaCl solutions. The viscosity decreases were less over the 30-day aging period, ranging from 23% for PAMB-10-2 to 40% for the NaPAMB homopolymer. The presence of salt apparently stabilizes the changes on the polymer, preventing some major conformational and/or hydrogen bonding changes; however, the hydrophobicity of the NaPAMB comonomer is still a driving force for changes in chain geometry which leads to a diminished hydrodynamic volume as a function of time.

## Effects of Added Electrolytes

The effects of added sodium chloride on the zero-shear intrinsic viscosities of the AM-NaPAMB polymers are shown in Fig. 3. As expected, plots of $[\eta]_0$ vs $I^{-1/2}$ were found to be linear [14, 15]. The viscosities were found to decrease with increasing NaCl concentration due to shielding of ionic charges along the polymer chain. PAMB-10-2, which contains 8.8 mol% NaPAMB, exhibited the greatest degree of salt tolerance with a viscosity decrease of about 47% over the studied range of salt concentrations.

The remaining copolymers and the homopolymer showed viscosity decreases of 60-70% over the studied range of salt concentrations. A comparable copolymer of AM with sodium 3-acrylamido-3-methylbutanoate (NaAMB) containing about 8 mol% NaAMB exhibited a viscosity decrease of 24% over the same range of salt concentrations [2]. It may therefore be concluded that increasing the hydrophobicity of the comonomers tends to increase the salt sensitivity of the resultant copolymers by promoting tighter coil formation in salt solutions.

## Effects of Copolymer Composition

The effects of copolymer composition on the zero-shear intrinsic viscosities of the AM-NaPAMB polymers in 0.514 M NaCl and on the apparent viscosities of the polymers in deionized water are shown in

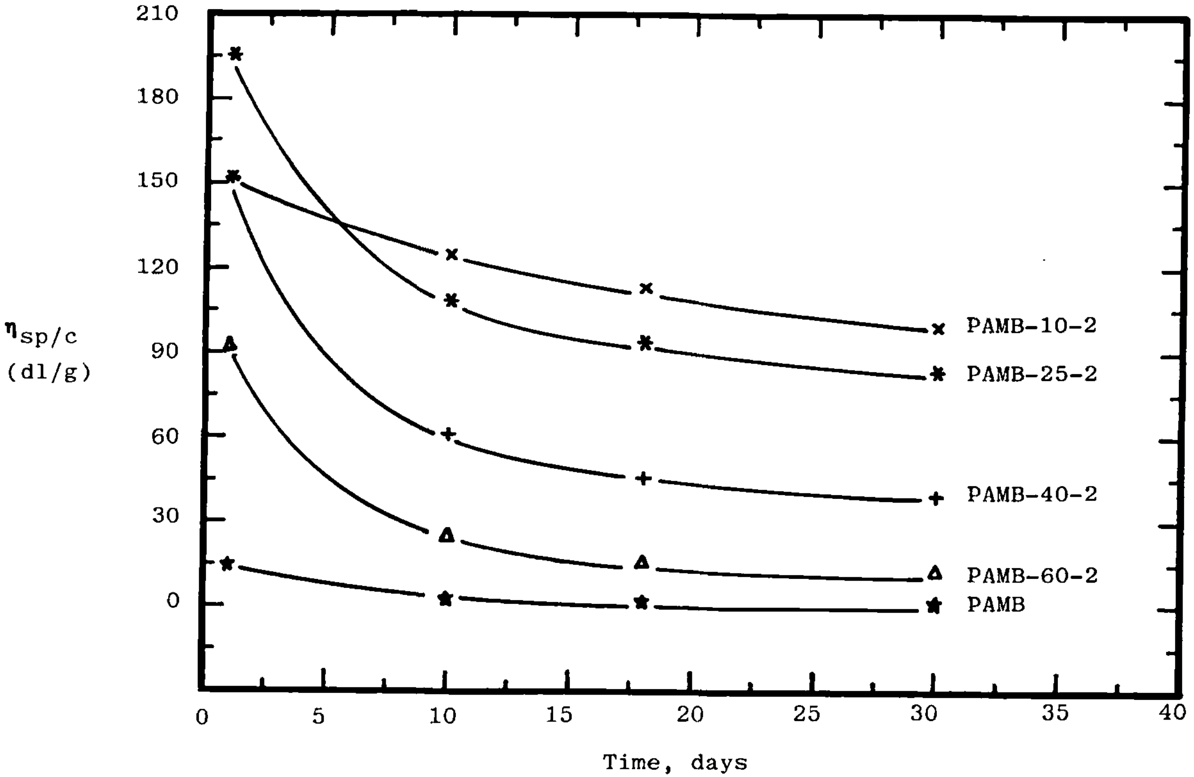

FIG. 1. Aging of AM-NaPAMB copolymers and NaPAMB homopolymer in deionized water at 30°C.

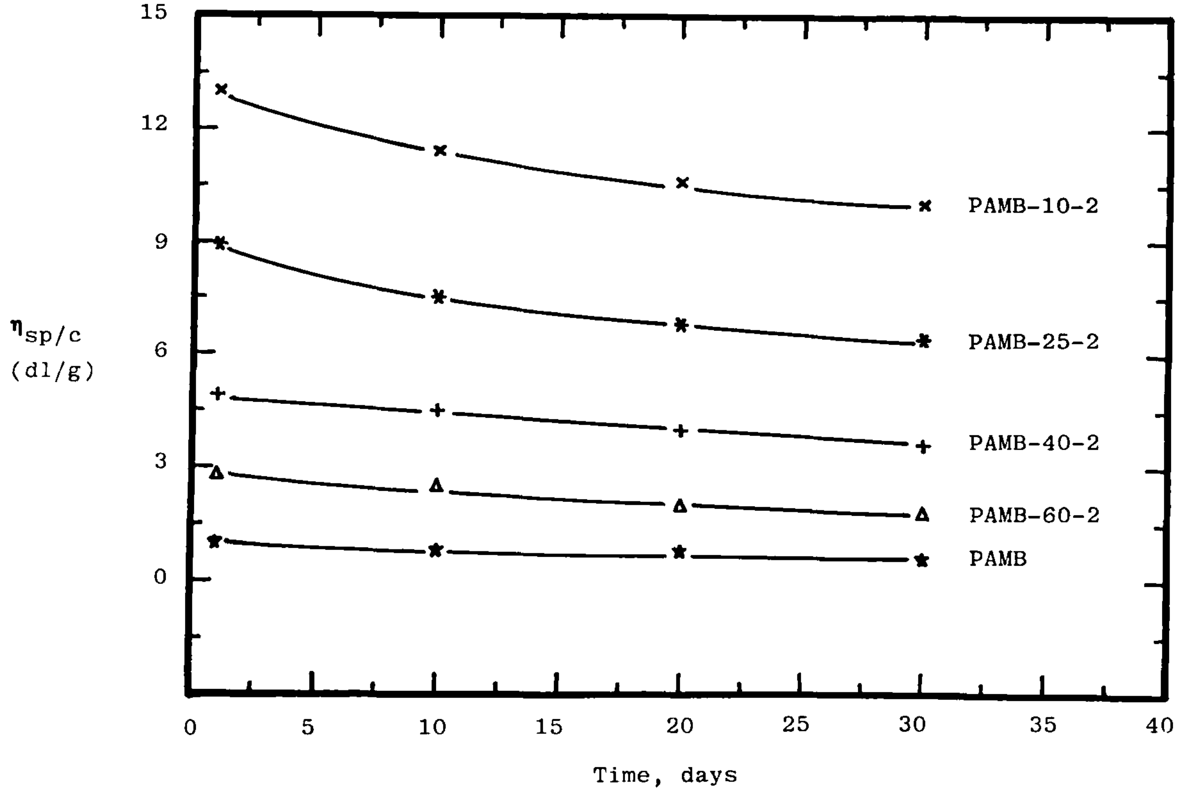

FIG. 2. Aging of AM-NaPAMB copolymers and NaPAMB homopolymer in 0.257 M $NaCl_{(aq)}$ at 30°C.

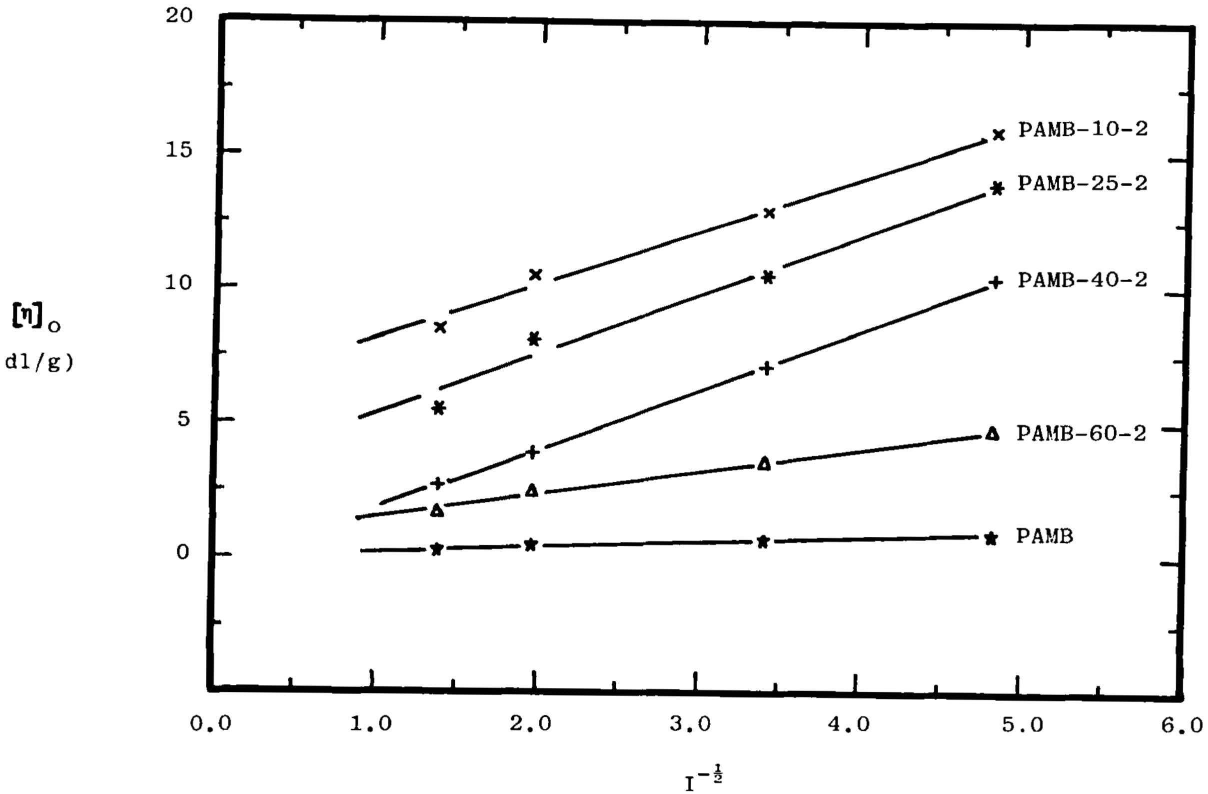

FIG. 3. Zero-shear intrinsic viscosities of the AM-NaPAMB polymers as a function of (ionic strength NaCl)$^{-1/2}$ at 30°C.

Figs. 4 and 5, respectively. The zero-shear intrinsic viscosities of the polymers in 0.514 M NaCl decrease with increasing NaPAMB content; however, the molecular weight also decreases with increasing NaPAMB content. It is therefore difficult to assess the relative contributions of molecular weight and composition on the viscosities in salt solutions.

It was not possible to obtain intrinsic viscosities for the AM-NaPAMB polymers in deionized water by extrapolation to zero shear rate due to the overwhelming polyelectrolyte effect. However, a comparison of viscosities at 100 $s^{-1}$ and a polymer concentration of 0.03 g/dL was made. PAMB-10-2 exhibited the highest viscosity, but also possessed the highest molecular weight. The copolymer containing 32.5 mol% NaPAMB (PAMB-40-2) exhibited nearly the same viscosity as the copolymer containing 20.5 mol% NaPAMB (PAMB-25-2), although the former possessed a molecular weight about 60% lower than the latter. The relatively large hydrodynamic size of PAMB-40-2 in pure water may be attributed to an optimum in charge density as predicted by the Manning theory [16].

## Effects of Temperature

The effects of temperature on the zero-shear intrinsic viscosities of the AM-NaPAMB polymers in 0.257 M NaCl are shown in Fig. 6. The zero-shear intrinsic viscosities of the polymers were found to decrease with increasing temperature, indicating a decrease in the hydrodynamic volume of the polymer molecules. Furthermore, the percent viscosity loss increased with increasing NaPAMB content in the polymer. Conformational and solvent associational changes occurring as a function of temperature may provide for increased hydrophobic interactions, resulting in a diminished hydrodynamic size in the NaPAMB copolymers.

## Effects of pH

Table 2 illustrates the dependence of the intrinsic viscosities on pH for the copolymers of AM with NaPAMB. The zero-shear intrinsic viscosities increased with increasing pH due to an increasing degree of ionization of the carboxylate groups, leading to more extended chain structures because of electrostatic repulsions. PAMB-40-2 and PAMB-60-2, which contain 32.5 and 53.4 mol% NaPAMB, respectively, precipitated at a pH of about 5.5 since enough of the carboxylated monomer was in the acid form to render the polymer insoluble.

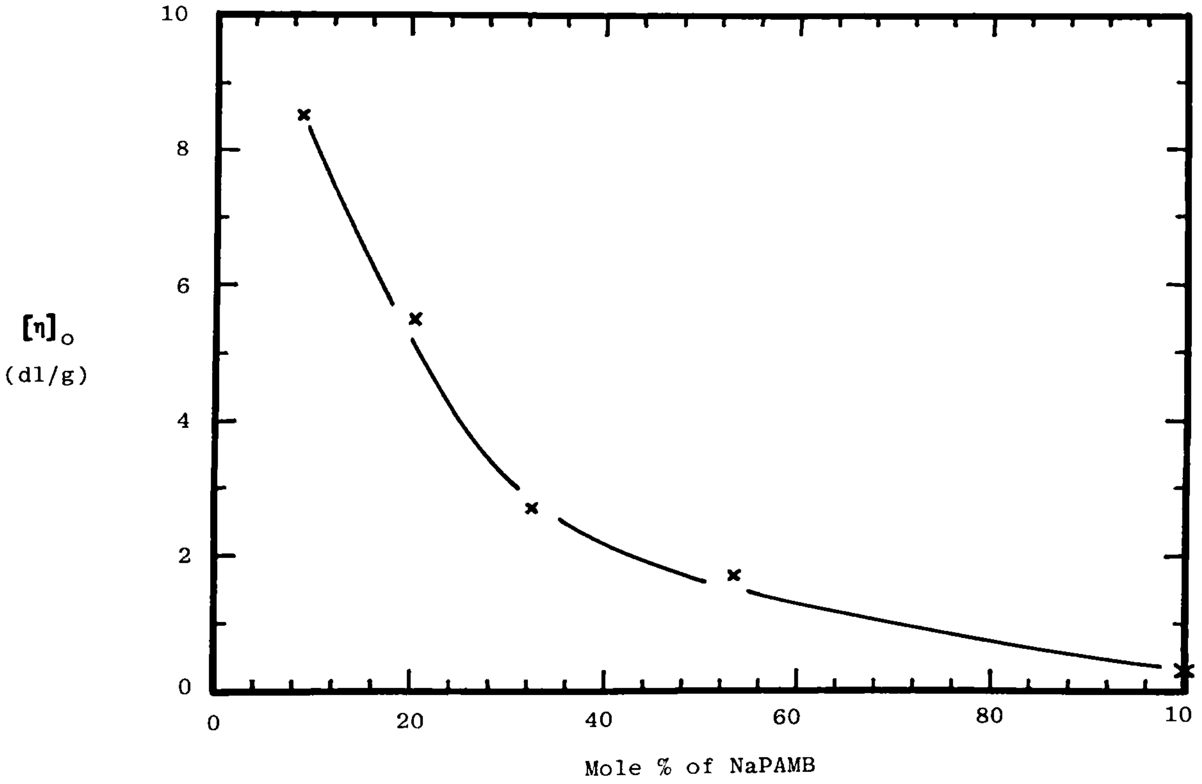

FIG. 4. Compositional effect on the zero-shear intrinsic viscosities of AM-NaPAMB polymers in 0.514 M $NaCl_{(aq)}$ at 30°C.

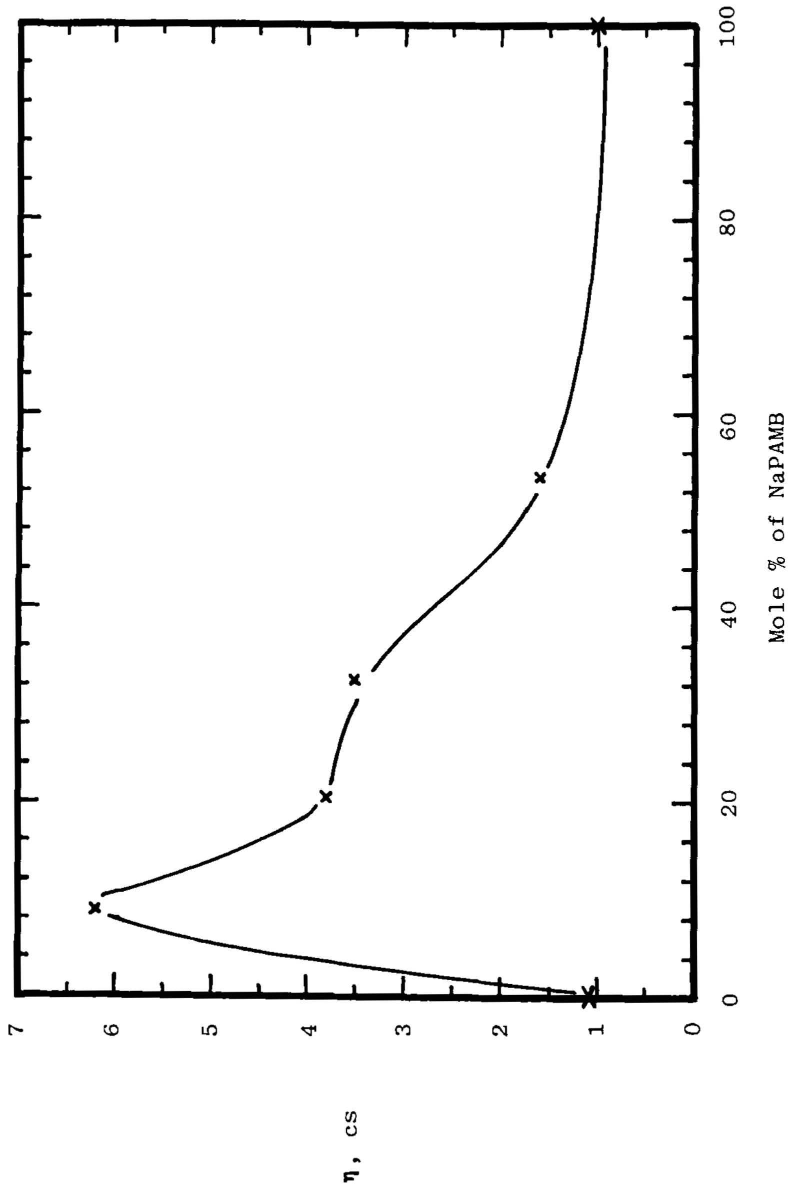

FIG. 5. Compositional effect on viscosity in deionized water at 30°C for AM-NaPAMB polymers (polymer concentration = 0.03 g/dL, shear rate = 100 $s^{-1}$).

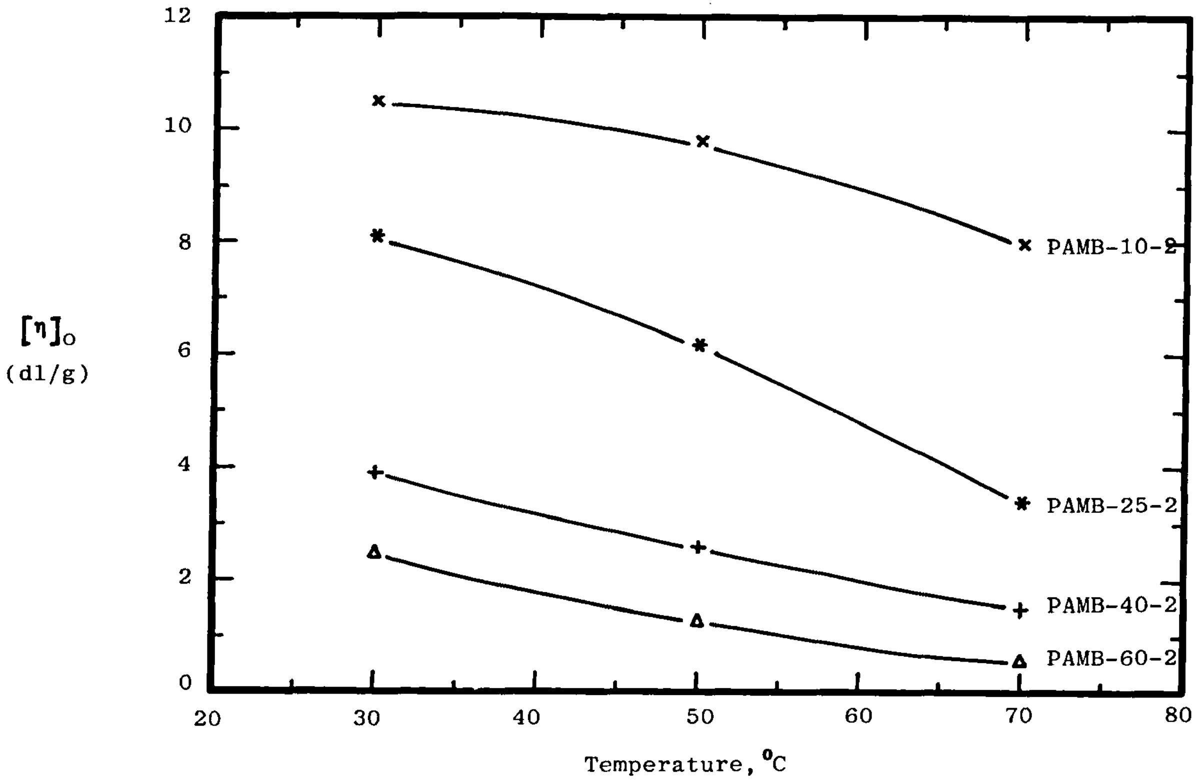

FIG. 6. Effect of temperature on the zero-shear intrinsic viscosities of AM-NaPAMB copolymers in 0.257 M $NaCl_{(aq)}$.

TABLE 2. Zero-Shear Intrinsic Viscosity Data for Copolymers of Acrylamide (AM) with Sodium 3-(N-Propyl)Acrylamido-3-Methylbutanoate (NaPAMB) in 0.514 M NaCl Solutions of Various pH Values at 30°C

| Sample | NaPAMB, mol% | pH | $[\eta]_0$, dL/g |
|---|---|---|---|
| PAMB-10-2 | 8.8 | 5 | 3.6 |
| | | 6 | 7.7 |
| | | 8 | 8.5 |
| PAMB-25-2 | 20.5 | 5 | 1.4 |
| | | 6 | 4.2 |
| | | 8 | 5.5 |
| PAMB-40-2 | 32.5 | 5 | [a] |
| | | 6 | 1.9 |
| | | 8 | 2.7 |
| PAMB-60-2 | 53.4 | 5 | [a] |
| | | 6 | 1.1 |
| | | 8 | 1.7 |

[a] Insoluble.

## Turbidimetry

The PAMB copolymers and homopolymer were found to display phase separation in the presence of $CaCl_2$ as a function of temperature. These results are shown in Fig. 7.

The phase separation curves appear at lower temperatures with increasing NaPAMB content, with PAMB-10, having 8% NaPAMB units, and PAMB-25, having 20% NaPAMB units, remaining soluble in $CaCl_2$ solutions up to 100°C. PAMB-40 and PAMB-60 show phase separation at low $CaCl_2$ concentrations, but are more stable in solution than copolymers of acrylamide and sodium acrylate with comparable copolymer compositions [8, 9]. The NaPAMB homopolymer solutions act similarly to a homopolymer solution of sodium acrylate, being very unstable even at low $CaCl_2$ concentrations.

Other copolymers of acrylamide with structures analogous to NaPAMB have been reported to be very stable in aqueous calcium chloride solutions, showing no phase separation up to 100°C. These include poly(acrylamide-co-sodium 2-acrylamido-2-methylpropanesulfonate) (NaAMPS) [9], poly(acrylamide-co-sodium 3-acrylamido-3-methylbutanoate) (NaAMB) [2], and poly(acrylamide-co-sodium 3-methacrylamido-3-methylbutanoate) (NaMAMB) [4]. The NaPAMB copolymers and homopolymer bind $Ca^{2+}$ ions more tightly since their

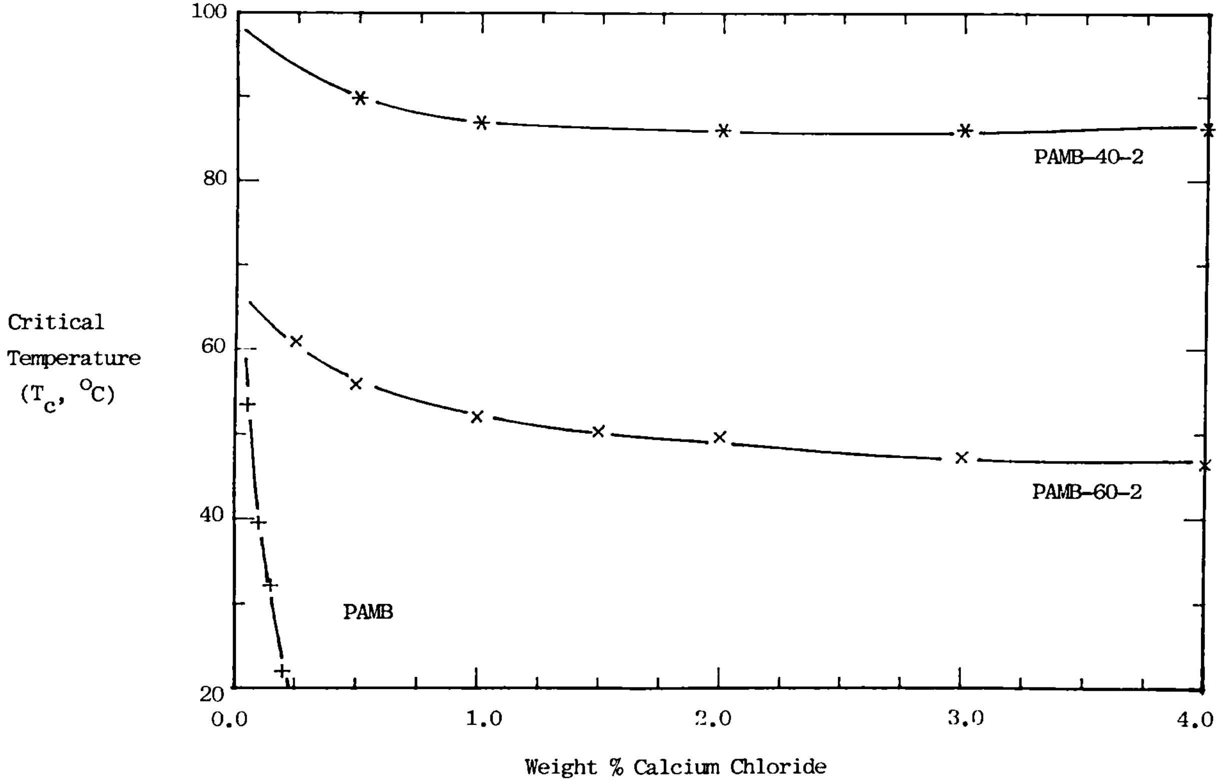

FIG. 7. Phase separation behavior of AM-NaPAMB polymers; no phase separation for PAMB-10-2 and PAMB-25-2.

TABLE 3. Dissociation Constants of the PAMB Series by the Modified Henderson-Hasselbalch Equation[a]

| | $H_2O$ | | | 0.36 M KCl | | |
|---|---|---|---|---|---|---|
| Sample | $pK_a$ | $\Delta pK_a$ | n | $pK_a$ | $\Delta pK_a$ | n |
| PAMB-10 | 5.70 ± 0.04 | 0.10 | 0.9 | 5.25 ± 0.04 | 0.14 | 0.9 |
| PAMB-25 | 6.00 ± 0.05 | 0.05 | 1.0 | 5.42 ± 0.04 | 0.12 | 0.9 |
| PAMB-40 | 6.22 ± 0.04 | 0.19 | 1.3 | 5.49 ± 0.05 | 0.16 | 1.0 |
| PAMB-60 | 6.56 ± 0.05 | 0.13 | 1.3 | 5.84 ± 0.05 | 0.26 | 1.0 |
| PAMB-homo | 7.51 ± 0.06 | 0.18 | 1.4 | 6.31 ± 0.06 | 0.24 | 1.0 |

[a] All correlation coefficients are 0.99.

conjugate bases are stronger, as shown by the potentiometric results. Because the amide group in the NaPAMB unit is fully substituted (as compared to the above systems which possess secondary amides), the stabilization caused by the hydration of the amide group is not possible. This increases the amount of intermolecular binding of calcium and increases precipitation of the copolymers.

## Potentiometry

Table 3 shows data from the potentiometric titrations of the PAMB series. These are calculated from the modified Henderson-Hasselbalch equation. The results indicate that the carboxylate ions on the NaPAMB units are destabilized by the greater hydrophobicity of the NaPAMB unit. The resulting $pK_a$ values are higher than those previously reported for copolymers of AM with NaAMB [2] and NaMAMB [4].

The copolymers show a general trend of increasing $pK_a$ value with increasing NaPAMB content. The increase in $pK_a$ with increasing charge density is expected as the increased charge repulsion destabilizes the charged groups of the NaPAMB units. This trend can be observed in pure water solutions by observing the increase in the Henderson-Hasselbalch n values. By contrast, the n values in 0.36 M KCl are approximately 1.0, a result of the charge shielding caused by the added electrolyte.

Plots of $pK_a$ as a function of the degree of ionization $\alpha$ are shown for the NaPAMB copolymers in 0.36 M KCl in Fig. 8. The hydrophobic

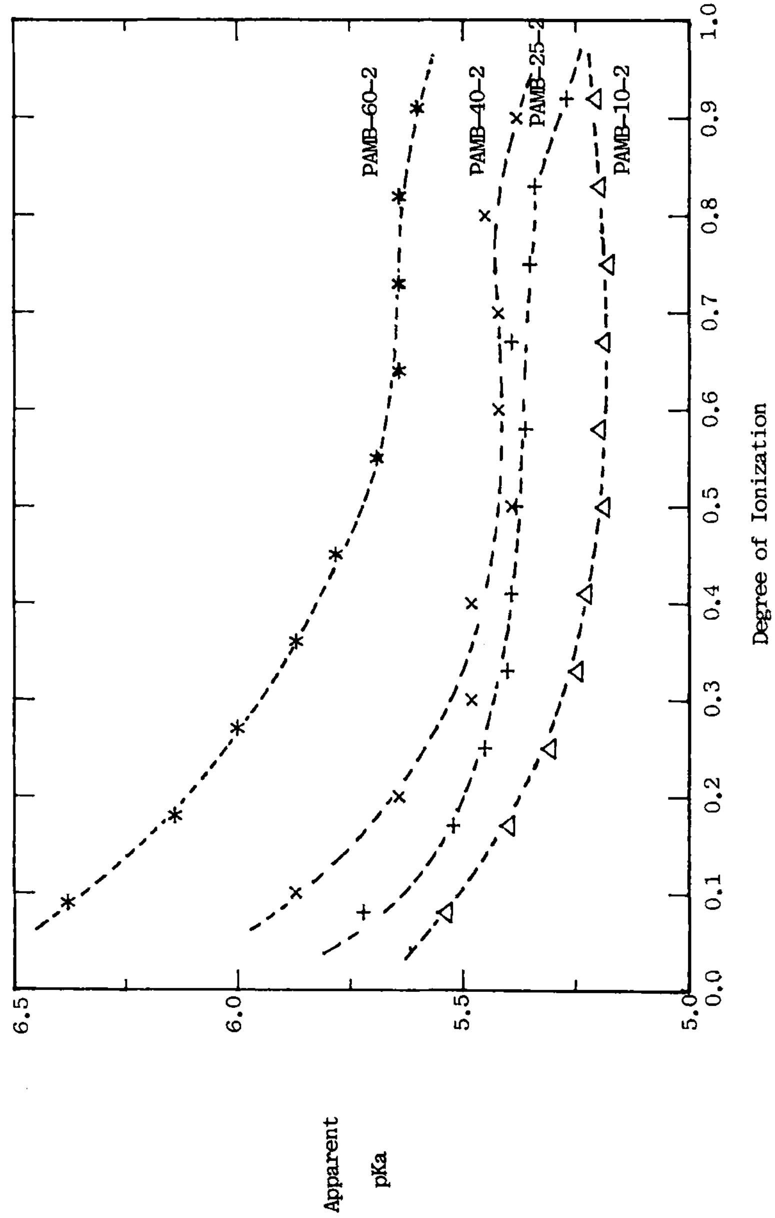

FIG. 8. $pK_a$ versus $\alpha$ plots for copolymers of AM with NaPAMB in 0.36 M KCl.

effects of the NaPAMB units can be observed by studying the changes in $pK_a$ with changes in the degree of ionization. At low $\alpha$ values, when the NaPAMB units are in the protonated form, the $pK_a$ values are much higher due to the greater hydrophobic nature and the decreased solubility of the polymers. As $\alpha$ increases, the polymer becomes more soluble as more of the acid groups become ionized. At $\alpha = 0.5$, the $pK_a$ values level off and remain constant as $\alpha$ is increased to 1.0.

The same effects are seen in the copolymers in $H_2O$ solutions, but to a lesser extent (Table 3). The aqueous salt solutions are worse solvents for the hydrophobic NaPAMB polymers. The poorer polymer-solvent interactions can be observed by studying the conformational changes caused by changes in the degree of ionization. Larger values of $\Delta pK_a$ are found in the 0.36 M KCl solutions than in the $H_2O$ samples which is opposite of the normally observed trend. Thus, in 0.36 M KCl solution as $\alpha$ approaches 0, the hydrophobic groups interact in order to enhance their stability. This is evidenced by the fact that the NaPAMB polymers are insoluble in aqueous solvents when $\alpha = 0$. As the acid groups are ionized, the NaPAMB units become more hydrophilic, allowing the polymer chains to uncoil into a more extended conformation as the polymer-solvent interactions become more favorable. This macromolecular conformational change greatly affects the local environment of the NaPAMB units, which causes significant changes in the observed $pK_a$ values.

## CONCLUSIONS

The increased hydrophobicity of the AM-NaPAMB copolymers (relative to AM-NaAMB and AM-NaMAMB polymers) significantly affects the observed solution properties. The AM-NaPAMB copolymers and the NaPAMB homopolymer were found to undergo large, time-dependent viscosity reductions due to hydrophobic interactions. Furthermore, the increased hydrophobicity of the comonomers accounts for the increased salt sensitivity; for example, PAMB-10-2 (8.8 mol% NaPAMB) showed a 47% viscosity decrease over the studied range of ionic strengths, while a NaAMB copolymer containing 8 mol% NaAMB lost only 24% of its viscosity over the same range. The NaPAMB copolymer exhibited viscosity decreases with increasing temperature and decreasing pH.

The turbidimetric and potentiometric properties were also significantly affected by the hydrophobic character of the AM-NaPAMB polymers. The NaPAMB homopolymer and the AM-NaPAMB copolymers exhibited higher $pK_a$ values than the NaAMB or NaMAMB polymers. The higher $pK_a$ values of the NaPAMB polymers promote increased binding of divalent cations. As a result of this increased binding, the AM-NaPAMB polymers undergo increased phase separation relative to NaAMB and NaMAMB copolymers.

As shown by the viscometric, turbidimetric, and potentiometric data, the hydrophobicity of the studied copolymers is an important factor. The solution properties are also dependent upon other local interactions specified by copolymer microstructure such as hydrogen-bonding and steric effects.

## ACKNOWLEDGMENT

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