Polymer Compatibility and Interpolymer Association in the Poly(acrylic Acid)–Polyacrylamide–Water Ternary System

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Synopsis

Polyacrylamide and poly(acrylic acid) form a water-insoluble phase when solutions of the two having concentrations that are not too low are mixed. The insoluble complex contains nearly stoichiometric 1 : 1 ratios of acrylamide and acrylic acid. The phase behavior of the ternary system was studied as a function of the degree of neutralization, α, of poly(acrylic acid). The complex is not formed when α is high. The formation of the complex was studied by measurement of pH increases observed when poly(acrylic acid) was titrated with polyacrylamide to infer a degree of linkage, θ, between the two polymers. A Hill plot of the data showed that the association was cooperative when the molecular weight was high.

INTRODUCTION

There is increasing interest in characterizing the association of complementary macromolecules which form interpolymer complexes in solution. The complexes have been reported[1] to have two conformations using a scheme (Scheme 1) where interacting fragments are either side groups or part of the backbone:
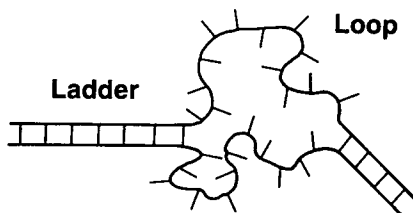
Scheme 1

Klenina and Fain[2] have observed that poly(acrylic acid) and polyacrylamide are incompatible in water and aqueous salt solutions. The precipitate or gel phase that forms above critical concentrations of the polymers was found to have nearly 1 : 1 stoichiometry.

We wish to report a series of investigations in which we attempted to understand the association between these polymers, whether association oc-

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curs for compositions in the single phase region of the ternary diagram and why there is a difference between the position of the phase boundary in the presence of different dissolved salts.

EXPERIMENTAL

Materials

Two PAA samples were used in these studies, both were commercial products from Rohm and Haas Chemical Co. A-1 was an atactic product provided as a 27.0% active ingredient aqueous solution. It was determined to have a molecular weight (M_n) of 27,000 and (M_w/M_n) of 6.2, by GPC. A-3 was an atactic product provided as a 27.0% solution with a molecular weight of 132,000 and (M_w/M_n) of 4.1.

Three PAM samples were used in these studies. The first, designated PAM-A, was synthesized at 50°C with potassium persulfate initiator. It had an intrinsic viscosity of 10.2 $\pm$ 0.4 dL/g and a Huggins constant of 0.5 $\pm$ 0.1 in 0.34M NaCl. It contained less than 1 mol % hydrolyzed groups, determined by titration. The second, PAM-B, synthesized under the same conditions except for the presence of 50 wt % isopropanol, had an intrinsic viscosity of 0.3 $\pm$ 0.05 dL/g in 0.3M NaCl. The third, PAM-C, was a commercial product of the American Cyanamid Co., Cyanamer P-250. It is a mixture of PAM, water, and sodium sulfate in the ratio 0.838 : 0.092 : 0.07, by weight, where the PAM was 3.7% hydrolyzed. Its intrinsic viscosity was 7.1 dL/g in 0.5M NaCl.

Lithium, potassium, and tetraethylammonium chloride salts were commercial materials used without further purification. Lithium chloride was purum p.a. grade reagent from the Fluka Chemical Co. Potassium chloride was Ultrex grade material from J. T. Baker Co. Tetraethylammonium chloride hydrate was reagent grade material from Aldrich Chemical Co.

Methods

Polymer phase compositions were assessed by a combination of differential refractometry[‡] and potentiometric titration or gravimetry and titration. Refractive index increments were measured on a Wood RF-600 differential refractometer at 546 nm and 25°C using KCl solutions for standardization. Acid–base titrations and pH measurements were performed under nitrogen on a Metrohm 636 Autotitrator at 25°C.

Viscosity measurements were conducted on a Contraves Low Shear vicometer at a shear rate of 1.3 s^{-1} at 25°C. Solutions and mixtures were prepared with gentle mixing and no exclusion of air.

RESULTS AND DISCUSSION

Polycarboxylic acids associate with proton acceptor polymers in aqueous solution and their ternary mixtures undergo phase separation with the formation of nearly stoichiometric hydrogen-bonded complex coacervates.[4] The

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[‡]Refractive index increments were determined to be 0.187 mL/g for polyacrylamide and 0.156 for poly(acrylic acid) at 546 nm, 25°C in water. The PAM values with Ref. 3.
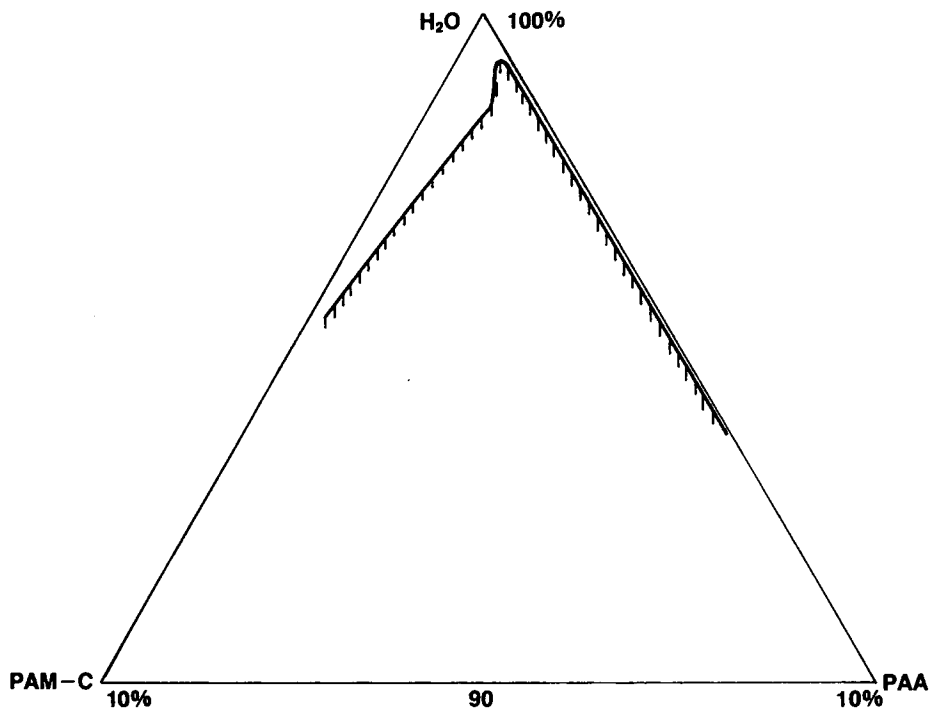
Fig. 1. The ternary phase diagram for polyacrylamide (PAM-C) and poly(acrylic acid) (A-3) in water. The hatched portion marks the region of insoluble complex formation.

association is often cooperative, since it requires higher molecular weight polymer.[5] It is also strongly dependent on the degree of neutralization of the polymer acid, since phase separation only occurs at low pH values.[6,7]

Figure 1 displays the ternary diagram for the A-3–PAM-C–H$_2$O system revealing the formation of a gel-like phase at compositions where PAA exceed about 0.25% in > 1.0% PAM mixtures. The high purity PAM, PAM-A, was similarly used in a study of the phase behavior of the system by cloud point determination. Figure 2 provides two ternary diagrams for three sets of mixtures which include 0.1M dissolved salt. The phase boundary is indistinguishable for the systems containing LiCl and KCl, but the ternary mixture containing 0.1M TEA$^+$Cl$^-$ has increased polymer compatibility, i.e., the position of the phase boundary is lowered away from the solvent vertex. This solubility enhancement is ascribed to a counterion effect on PAA ionization and neutralization. PAA is the traditional model for the treatment of polycarboxylic acid dissociation, where rather than being a constant independent of concentration and cations, the pK$_A$ is defined as

$$pK_A = pH - \log(\alpha_T/1 - \alpha_T),$$

where α_T is the total degree of neutralization. The pH of pure PAA solutions fits the line described by pH = (4.6 + p[PAA])/2 and, further, the pK$_A$ of PAA in a titration mixture varies as the degree of neutralization increases.
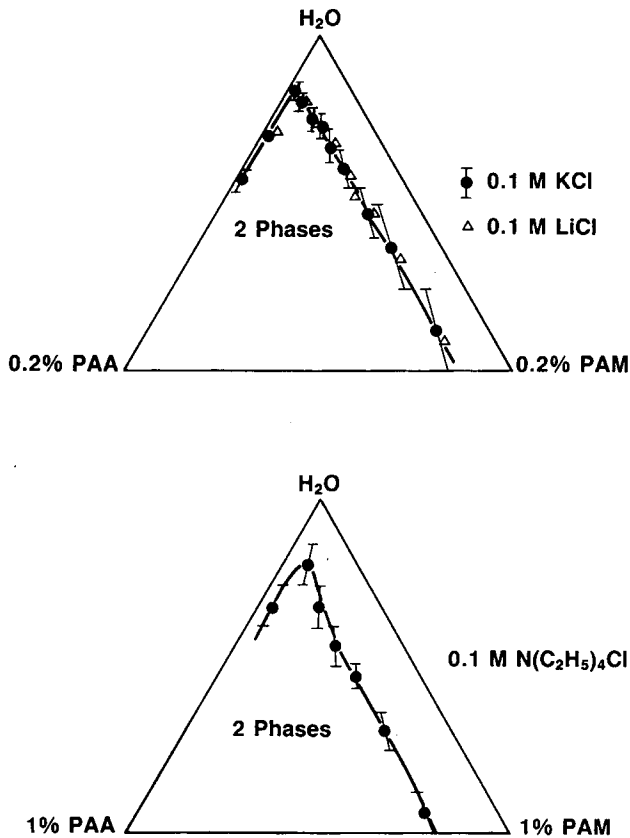
Fig. 2. A comparison of the ternary phase diagrams for poly(acrylic acid) (A-3) and poly-acrylamide (PAM-A) in $0.1M$ solutions of either KCl, LiCl, or tetraethylammonium chloride.

This is interpreted as due to an increase in the electrostatic charge on the polyanion chain.

In media containing LiCl and KCl, the cations can effectively shield the polyanion charge. Cations with large surface-to-charge ratios, like TEA^+, do not shield the electrostatic field as well. Correspondingly, PAA has a higher pH at each degree of neutralization in TEA^+Cl^-, revealing a higher degree of ionization. The cation influence on the phase diagram then correlates to different pH behaviors and can be interpreted as revealing interpolymer association differences between PAA and PAM in the solutions.

Figure 3 reveals analytical results on a series of precipitate phases, each separated from ternary mixtures whose compositions were in the two-phase region of Figure 1. Although the mixture compositions varied from 1.2 to 4.0, and the solubility of each polymer in water was not exceeded, the gel phases resolved to approximately 1:1 complexes of PAA and PAM, as previously reported.[2]

Figure 4 shows the comparison of the ternary diagrams for compositions, where the PAA was successively partially neutralized to 3 and 5% by KOH.
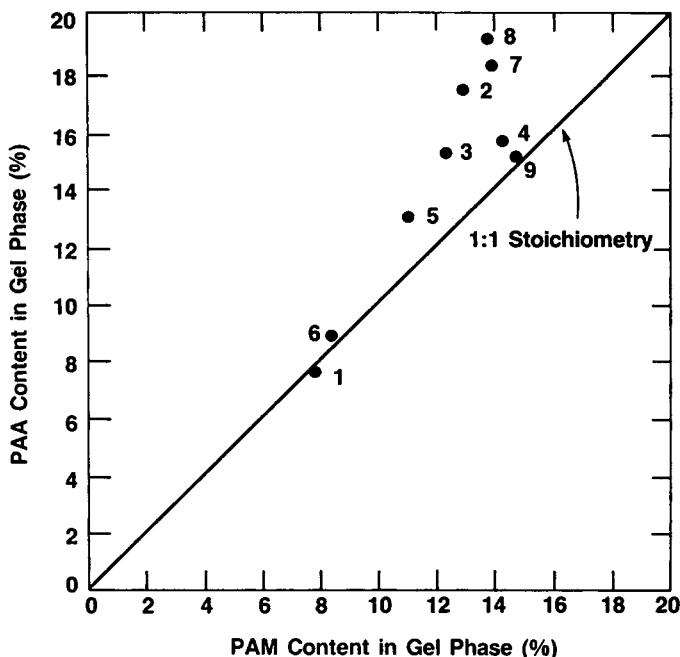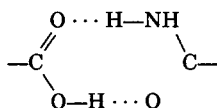
Fig. 3. The composition of the insoluble gel complex using PAM-C and A-3 in water, when the initial compositions of the mixtures were varied. Polymer ratio (eq_{PAA}/eq_{PAM}): (1) 2.2; (2) 4.3; (3) 1.2; (4) 1.3; (5) 1.5; (6) 2.8; (7) 3.7; (8) 4.0; (9) 1.7.

The higher the degree of neutralization, the greater the compatibility between the two polymers.

Interpolymer association resulting from mixing specific ratios of complementary polymers can be characterized by analyzing the pH values of single phase mixtures. Table I summarizes representative data for a series of solutions with the same PAA concentration which show that the pH rises for mixtures with increasing PAM concentration. However, potentiometric titrations on each sample revealed no PAA neutralization by PAM. Thus, the carboxylic acid protons of PAA are involved in the formation of the complex with PAM. This is consistent with the proposed structure linked by hydrogen bonds,

$$
\begin{array}{c}
O \cdots H\text{—}NH \\
\parallel \qquad\qquad \backslash \\
\text{—}C \qquad\qquad C\text{—} \\
\backslash \qquad\qquad\quad \\
O\text{—}H \cdots O
\end{array}
$$

Osada[8] has developed a model that describes this hydrogen bond association between polymers using pH to quantify their degree of linkage. PAA, being a weak acid with a dissociation constant K, at concentration c_0, gives a concentration of hydrogen ions of

$$[H^+] = (K \cdot c_0)^{1/2} \tag{1}$$

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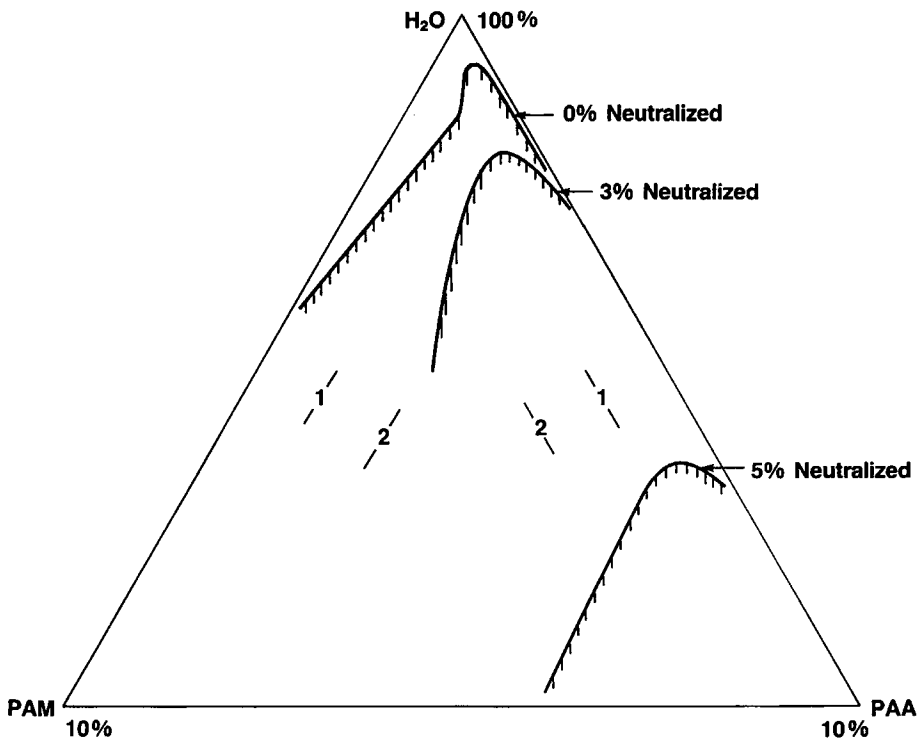

Fig. 4. The ternary diagrams (PAM-C and A-3) when the poly(acrylic acid) was partially preneutralized with KOH.

when $K \ll c_0$. In the presence of hydrogen-bond associating polymer, the concentration of free carboxylic acid sites is reduced to c, where $c_0 > c$ and the number of equilibrium sites not available to solvent is $\theta \cdot c_0$, where

$$\theta = \frac{c_0 - c}{c_0} = 1 - \left(\frac{[H^+]}{[H^+]_0} \right)^2 \qquad (2)$$

is the degree of linkage between the polymers. Figure 5 displays the dependence of θ on the polymer ratio (PAM)/(PAA) for two polymer pairs. Both

TABLE I

Representative Measurements of Poly(acrylic acid) (A-3)–Polyacrylamide (PAM-C)–Water at 25°C, Concentration A-3 = 0.25%

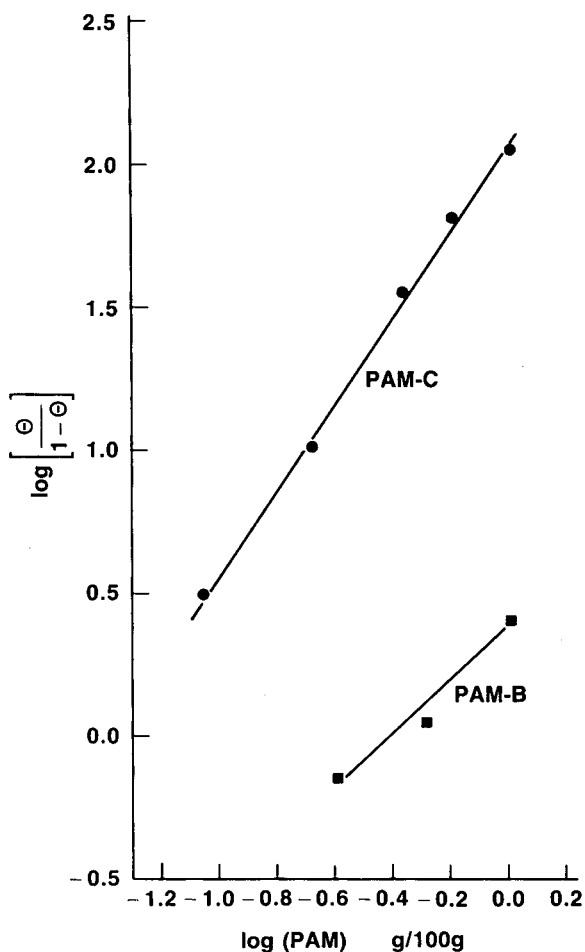| Solution compositions (PAM/PAA)	Solution properties	
	pH	η (cP)
0.0	3.14	1.05
0.36	3.37	1.77
0.88	3.58	5.92
1.8	3.82	15.4
2.6	3.96	37.8

Fig. 5. The degree of linkage, θ, of the two polymers as a function of the ratio of the polyacrylamide to the poly(acrylic acid) concentrations. In both curves the concentration of PAA (A-3) was 0.25%. The upper curve used PAM-C and the lower curve PAM-B. The latter has the lower molecular weight.

ternary systems used 0.25% PAA, but differed in the molecular weight of the PAM. The results suggest that there is a higher degree of association with the PAA–PAM pair of higher molecular weight. This molecular weight effect has been reported by previous workers on a number of similar polymer pairs. Figure 6 displays the result of a similar study, using an even higher molecular weight PAM. This ternary system also used 1/10 the PAA concentration as was used in Figure 5 and a supporting electrolyte, $0.1N$ KCl. Strikingly, the degree of linkage behavior is quite similar to the lower molecular mass pair shown in Figure 5.

The difference in the θ plots of Figures 5 and 6 arises because PAA, being a weak acid, ionizes more when it is diluted in solution, according to

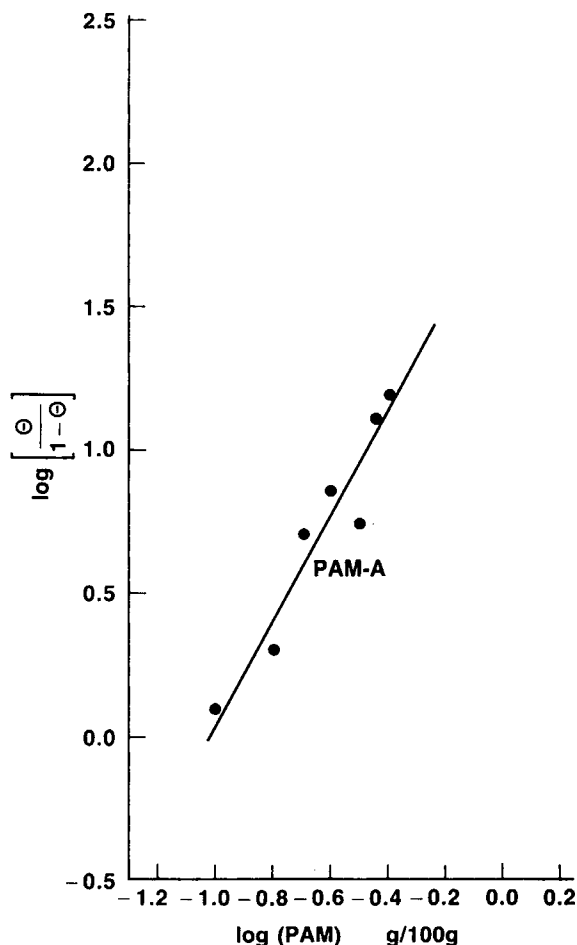$$\alpha_T = (K/[\text{PAA}])^{1/2} \qquad (3)$$

Fig. 6. The degree of linkage plot obtained using PAM-A and A-3. The polyacrylic acid concentration was 0.025%.

where α_T is the total degree of neutralization and K is the ionization constant for acrylic acid. Thus, under the conditions used to plot Figure 6, $\alpha = 0.27$, and it is only 0.08 for the conditions in Figure 5. For these calculations a value of 4.6 was used for pK.

Another approach for treating the pH data can give some insight into the cooperativity of the macromolecular association for the different molecular weight pairs. In dilute solutions where the degree of linkage is not near the extremes of 0 and 1, the interpolymer association can be written

$$\text{PAA} + n\text{PAM} \rightarrow \text{PAA} \cdot n\text{PAM} \tag{4}$$

with a stability constant K_a (g/100 g) representing (fraction of sites associated)/(fraction of sites free), where

$$K_a = \frac{[\text{PAA} \cdot n\text{PAM}]}{[\text{PAA}][\text{PAM}]^n} = \frac{1}{[\text{PAM}]^n} \cdot \frac{\theta}{1-\theta} \tag{5}$$
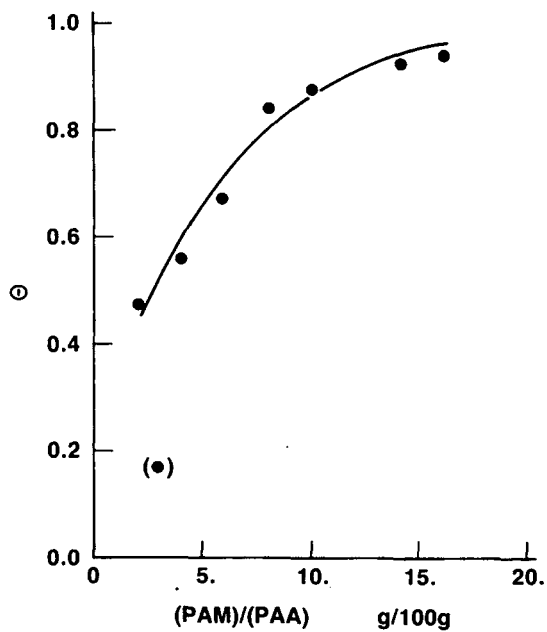
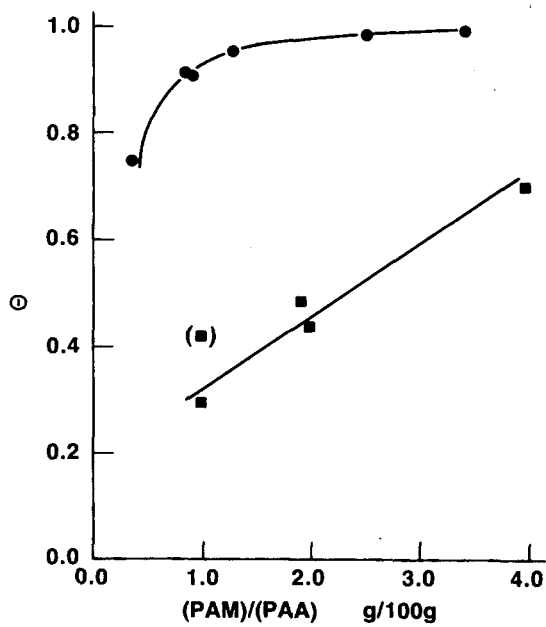Fig. 7.   Hill plot of the data in Figure 6.

Fig. 8.   Hill plot of the data in Figure 5.

then

$$\log \frac{\theta}{1 - \theta} = \log K_a + n \log[\text{PAM}] \qquad (6)$$

and a plot of $\log \theta/(1 - \theta)$ vs. $\log(\text{PAM})$ giving $n > 1$ will indicate cooperative interaction. Higher degrees of cooperativity are indicated by higher n values. Figure 7 displays the pH data of Table I and Figure 5 in a Hill plot which yields values of 1.6 and 10^2 for n and K_a, respectively, for the A-3–PAM-C pair. The lower molecular mass pair, A-1–PAM-B, gives values of 0.9 and 2.5, respectively. Figure 8 presents the data for the A-3–PAM-A pair, indicating cooperative interaction for this pair with $n = 2.5$ and $K_a = 10^2$.

CONCLUSIONS

This paper describes the importance of pH and molecular weight above 10^5 on interpolymer complexes of PAA and PAM. At very low concentrations ($< 0.1\%$), ternary mixtures are soluble since a high fraction of the acid groups dissociate. At concentrations 0.1 to 0.5% of polymer in ternary mixtures, polymers associate and modify solution properties. At concentrations exceeding 1% polymer, phase separation occurs. For a representative set of compositions, a 1 : 1 stoichiometry was found.

The behavior of soluble ternary mixtures is described by their pH. For mixtures containing the same PAA concentration, higher PAM concentrations gave higher pH. This indicates the binding of a larger fraction of acrylic acid sites. An analysis of the data was shown to give interpolymer complex stability constants and to suggest cooperativity in polymer pairs which included higher molecular weight polymers.

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