

# Viscometric Investigation of the Poly(Acrylic Acid)–Polyacrylamide Interpolymer Association

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## SYNOPSIS

A viscometric approach to the formation of interpolymer complexes between a polyelectrolyte, polyacrylic acid, and a non-ionic polymer, polyacrylamide, is investigated. The following method compares the reduced viscosity of the polymer mixture with an "ideal" value which results from the additivity of the reduced viscosities of the two components taking into account the polyelectrolyte effect of polyacrylic acid. This reveals the formation of a compact complex or gel-like interpolymer association which depends on the polymer mixture composition. Both the influence of the degree of polyacrylic acid neutralization and of the presence of a salt on the interpolymer association are also studied.

## INTRODUCTION

Viscometric methods have frequently been employed in the investigation of polymer mixture compatibility<sup>1–5</sup> and in characterizing the association of macromolecules forming interpolymer complexes in solutions.<sup>6–10</sup> The additivity of the specific, reduced, or intrinsic viscosities<sup>1,4,6</sup> of two polymers has been used as a criterion of their compatibility or association. A positive deviation from a linear dependence of the specific, reduced, or intrinsic viscosity of a dilute solution of a mixture of two polymers on its composition shows a good compatibility of the polymer pair or a gel-like association, while a negative deviation shows a poor compatibility or, sometimes, the formation of a compact interpolymer complex.

It is known that polyacrylic acid (PAA) forms polymer complexes with polybases such as polyethyleneoxide (PEO), polyvinylpyrrolidone (PVP), or polyacrylamide (PAAm).<sup>9–12</sup> These complexes may have a compact or a gel-like structure.<sup>9</sup>

In this work we have investigated the PAA–PAAm interpolymer association in dilute solution in water by measuring the reduced viscosity of the polymer mixture  $(\eta_{sp}/c)_m$ , as a function of its composition at constant total concentration  $c$ . The re-

duced viscosity of the polymer mixture without interaction between PAA and PAAm was calculated from the equation

$$(\eta_{sp}/c)_m = w_1(\eta_{sp1}/c_1) + w_2(\eta_{sp2}/c) \quad (1)$$

where 1 is PAA and 2 is PAAm,  $c$  is the total polymer concentration,  $w_1$  and  $w_2$  are the weight fractions of the two polymers in the mixture,  $\eta_{sp2}/c$  is the reduced viscosity of PAAm at concentration  $c$ , and  $\eta_{sp1}/c_1$  is the reduced viscosity of PAA at the different concentrations  $c_1$  at which it exists in the different compositions of the polymer mixture. In order to calculate the "ideal" curve by the above equation we have experimentally measured the reduced viscosity of pure PAAm at concentration  $c$  and the reduced viscosity of pure PAA at the different concentrations  $c_1$ . This treatment provides an "ideal" curve for the reduced viscosity of the polymer mixture as a function of its composition which presents an upward curvature (Fig. 1, dashed line) relatively to the straight line (dotted line) which represents the weight average of the reduced viscosities of the two pure components at concentration  $c$  and which is in general acceptable as an ideal curve for the reduced viscosity of a mixture of two nonionic polymers. In our system one of the two polymers, PAA, is a polyelectrolyte and as a result its reduced viscosity increases considerably with a decrease in its concentration (polyelectrolyte effect). This behavior

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of PAA has obliged us to propose eq. (1) by which the influence of the polyelectrolyte effect in the reduced viscosity of the polymer mixture has been taken into account.

We consider that the reduced viscosity–composition curve determined by eq. (1) adequately expresses the ideal behavior of the mixture. Any deviation of the experimental results from this curve would be a manifestation of special interactions between the two polymers.

The above method has proven useful in the characterization of the interactions between PAA and PAAm. The influence of the degree of neutralization,  $\alpha$ , of PAA and the presence of a salt, NaCl, on these interactions have also been investigated.

## EXPERIMENTAL

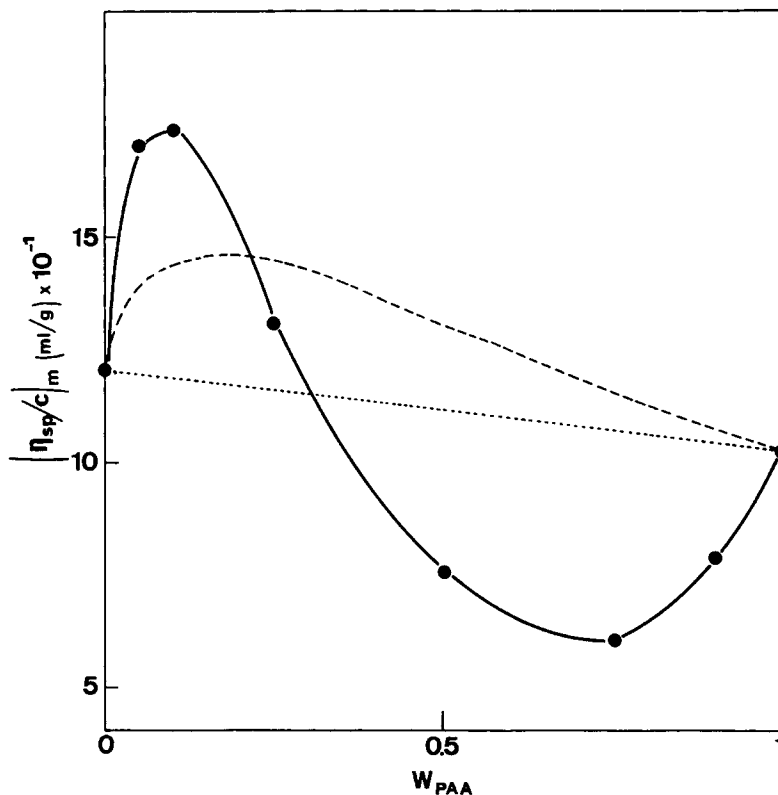
The PAAm sample was synthesized in a water–methanol mixture 50% by volume with hydrogen

peroxide as initiator<sup>13</sup> at 50°C. It was reprecipitated from a water solution by methanol and dried under vacuum for two days at 35°C. Its molecular mass has been determined viscometrically in water<sup>14</sup> and has been found to equal 148,000.

The PAA sample used was a solution 25% in water of Polysciences. This was purified by ultrafiltration and freeze dried. Its molecular weight has been determined viscometrically in NaBr 0.5 M after 100% neutralization<sup>15</sup> by NaOH 1.0 M and has been found to equal 130,000.

Water used for the preparation of the solutions was de-ionized by an ion-exchange resin and then purified by a Millipore Norganic cartridge equipped with a 0.45  $\mu\text{m}$  filter.

The polymer solutions were prepared 24 h before viscosity measurements, which were performed at 30°C with an automated viscosity measuring system, AVS 310 Schott–Geräte, equipped with an Ubbelohde-type viscometer. The concentration of the solutions was always  $8.5 \times 10^{-3} \text{ g/cm}^3$ .



**Figure 1** Variation of the reduced viscosity  $(\eta_{sp}/c)_m$ , of the polymer mixture PAAm–PAA in solution in water as a function of its composition,  $W_{\text{PAA}}$ . The concentration is  $8.5 \times 10^{-3} \text{ g/cm}^3$ . The composition of the mixture is expressed as the weight fraction and almost coincides with the molar fraction because the molar masses of the repeating units of the two polymers are almost the same (PAA 73, PAAm 72). (—) experimental results; (---) results according to eq. (1) “ideal curve.”

## RESULTS AND DISCUSSION

Figure 1 presents the viscometric behavior of the mixture PAA-PAAm in solution in water as a function of its composition. The dashed line has been determined according to eq. (1). The dashed line deviation from linearity expresses the influence of the polyelectrolyte effect on the reduced viscosity of the polymer mixture and we consider this curve a good approximation to the "ideal" viscometric behavior of the polymer mixture. The positive deviation of the experimental curve (solid line) with respect to the calculated curve implies a gel-like interpolymer association of the polymer mixture poor in PAA ( $W_{\text{PAA}} < 0.20$ ), while the negative deviation implies the formation of a compact complex when the polymer mixture is rich in PAA ( $W_{\text{PAA}} > 0.20$ ). The minimum of this curve shows the predominant formation of a compact complex at a PAA-PAA<sub>m</sub> molar ratio of 2 : 1. We have to point out here that the viscometric investigation reveals a gel-compact complex transition of the ternary system PAA-PAA<sub>m</sub>-H<sub>2</sub>O. This transition separates the reduced viscosity-composition diagram in two regions, one hydrophilic region where the polymer mixture appears an expansion of its hydrodynamic volume ( $W_{\text{PAA}} < 0.20$ ), and another hydrophobic region where the polymer mixture appears a compact complex conformation ( $W_{\text{PAA}} > 0.20$ ). In the hydropho-

bic region the ternary system tends to be separated into two phases by precipitation of the polymer mixture. This behavior has been certified by the observation of a slight turbidity of the solutions in this composition region by a small lowering of the temperature and it is consistent with phase separation results recently reported.<sup>12</sup>

The viscometric behavior of PAA-PAAm in water-NaCl solution  $1.00 \times 10^{-2} M$  presented in Figure 2 shows a dramatical reduction of the gel-like interpolymer association region and an enlargement of the compact complex conformation region (compare with Fig. 1). It is obvious that the presence of the salt favors the hydrophobicity of the polymer mixture. This behavior could be explained by the cation shielding of the polyacid negative charge due to its dissociation. This counter-ion shielding causes a contraction of the PAA coil, therefore, the gel-like interpolymer association is not favored.

It is of interest to study the influence of the degree of neutralization of PAA on the viscometric behavior of the mixture. As seen from Figure 3 a slight neutralization of the polyacid ( $\alpha = 0.75\%$ ) is enough to eliminate the compact complex region and to expand the gel-like interpolymer association region in the whole composition range. The same behavior, characteristic of a gel-like interpolymer association, is observed also at any degree of neutralization of the polyacid studied in this work (2%, 5%, and 10%).

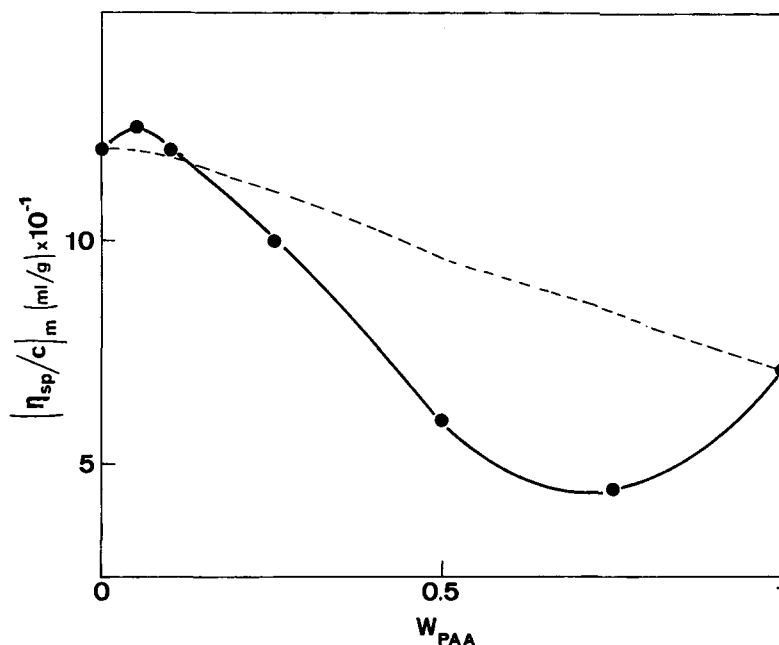
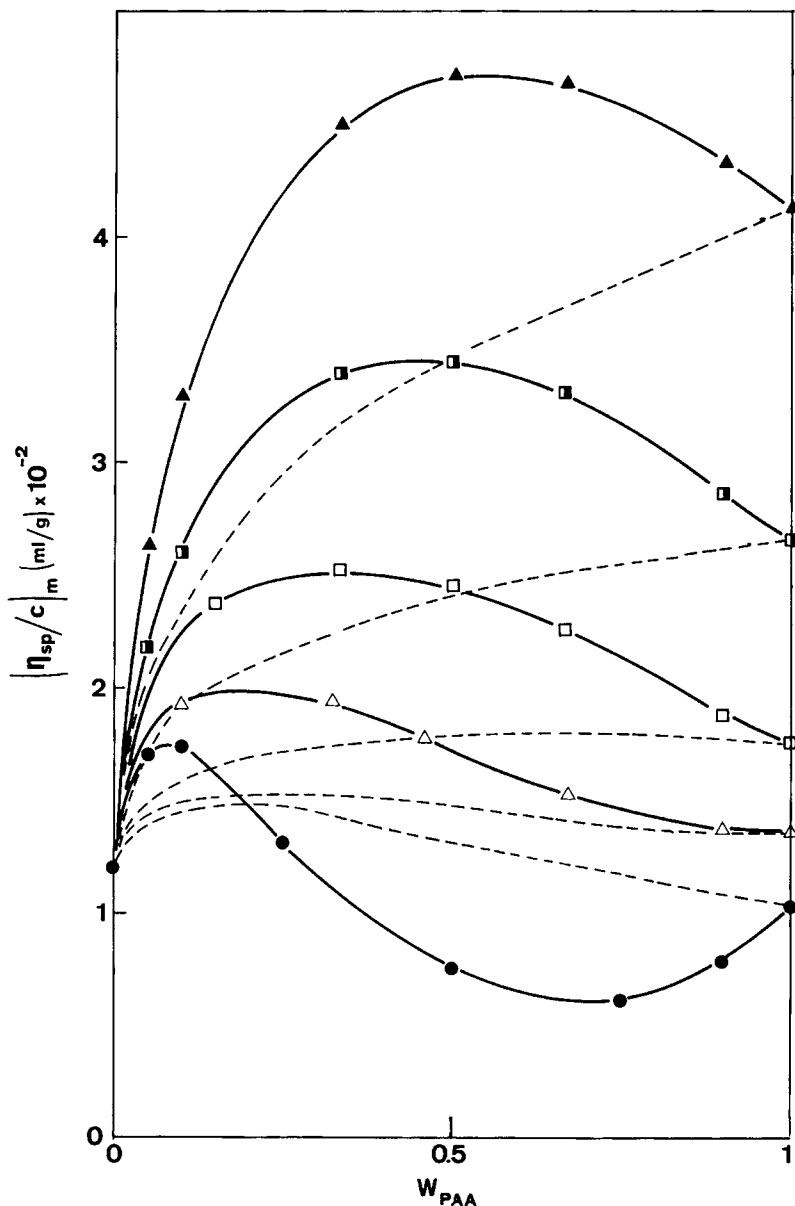


Figure 2 Variation of  $(\eta_{sp}/c)_m$  of PAAm-PAA in solution in water-NaCl  $1.00 \times 10^{-2} M$  as a function of  $W_{\text{PAA}}$ . (—) experimental; (---) "ideal."

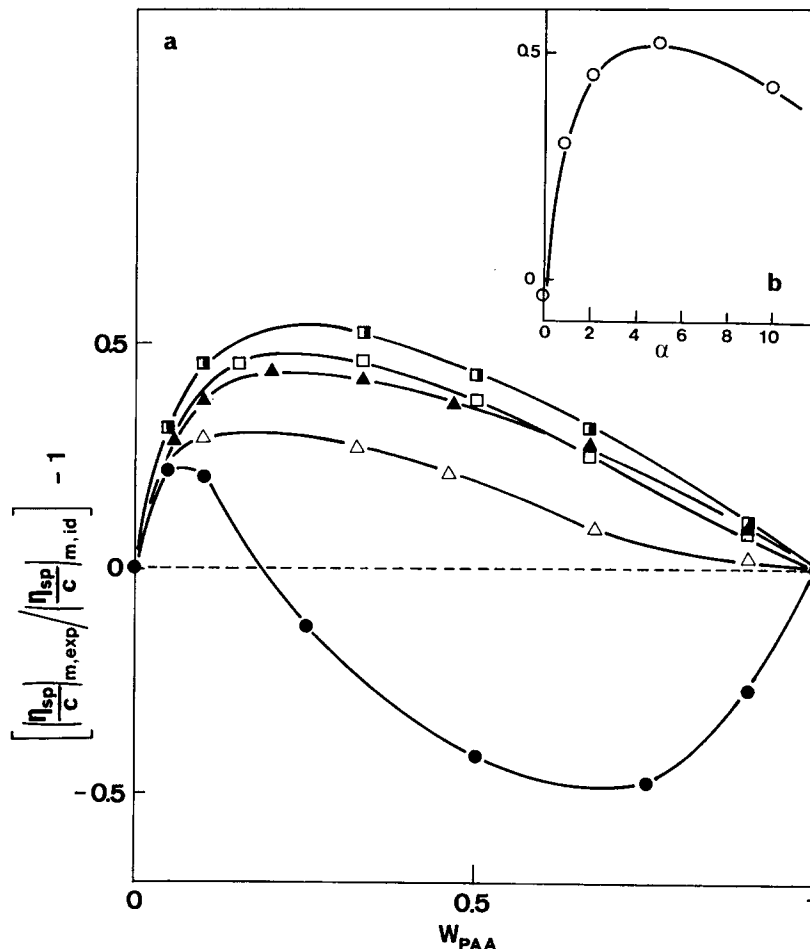


**Figure 3** Variation of  $(\eta_{sp}/c)_m$  of PAAM-PAA in solution in water as a function of  $W_{PAA}$  for different degrees of neutralization. ( $\bullet$ )  $\alpha = 0.00\%$ ; ( $\Delta$ )  $\alpha = 0.75\%$ ; ( $\square$ )  $\alpha = 2.0\%$ ; ( $\blacksquare$ )  $\alpha = 5.0\%$ ; and ( $\blacktriangle$ )  $\alpha = 10\%$ . (—) experimental; (---) "ideal."

In order to examine the influence of the degree of neutralization on the deviation of the reduced viscosity of the polymer mixture from the ideal behavior predicted by eq. (1), we have plotted the relative deviation  $\left[ \left( \frac{\eta_{sp}}{c} \right)_{m,exp} / \left( \frac{\eta_{sp}}{c} \right)_{m,id} \right] - 1$  as a function of the composition of the polymer mixture [Fig. 4(a)]. The considerably negative deviation for  $\alpha = 0$  at a composition  $W_{PAA} > 0.20$  is rapidly converted to a positive deviation by a small partial neutralization of PAA ( $\alpha = 0.75\%$ ). We also note that

for each degree of neutralization, a maximum relative deviation is observed around the composition region  $W_{PAA} = 0.20$ . This deviation as a function of the degree of neutralization ( $\alpha$ ) is illustrated in Figure 4(b) showing a maximum at  $\alpha = 5\%$ . This behavior indicates that the gel-like complex formation is favored by the expansion of the polyacid coil but it is not favored by the decrease of the carboxylic units which are the functional groups responsible for the interpolymer association.

Finally the influence of a salt, NaCl  $1.00 \times 10^{-2}$



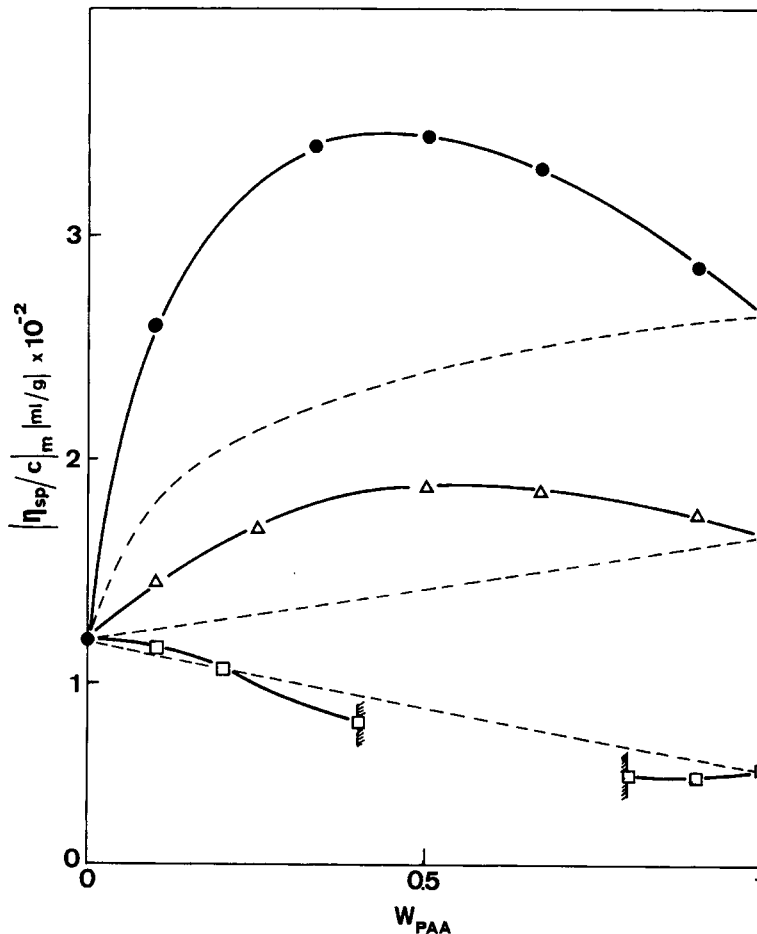
**Figure 4** (a) Variation of the relative deviation,  $\left[ \frac{(\eta_{sp}/c)_{m,exp}}{(\eta_{sp}/c)_{m,id}} \right] - 1$  of PAAm-PAA in solution in water as a function of  $W_{PAA}$  for different degrees of neutralization. Points as in Figure 3. (b) Variation of  $\left[ \frac{(\eta_{sp}/c)_{m,exp}}{(\eta_{sp}/c)_{m,id}} \right] - 1$  at  $W_{PAA} = 0.20$  as a function of the degree of neutralization,  $\alpha$ .

$M$  and  $1.00 \times 10^{-1} M$ , on the viscometric behavior of the mixture containing partially neutralized PAA ( $\alpha = 5\%$ ) is presented in Figure 5. As we can see, the deviation of  $(\eta_{sp}/c)_m$  (comparison between ideal and experimental) in the presence of salt is drastically decreased until elimination. This decrease is probably due to the shrinkage of the polyelectrolyte chain in the presence of salt and to the prevailing of hydrophobic forces which favor the precipitation of a compact complex. Indeed, precipitation occurs in the mixture composition region  $0.40 < W_{PAA} < 0.80$ , when the concentration of NaCl is  $1.00 \times 10^{-1} M$ . This behavior is consistent with recent phase separation results,<sup>16</sup> according to which a polyelectrolyte-non-ionic polymer pair behaves like

a two non-ionic polymer pair in the presence of a salt.

## CONCLUSIONS

Complex formation between PAA and PAAm has been viscometrically studied by a thorough comparison with an experimentally determined "ideal" viscometric behavior of the polymer mixture. Depending on the composition of the polymer mixture, the two polymers form a gel-like or a compact complex. A slight neutralization of the polyacid ( $\alpha = 0.75\%$ ) is enough to inhibit the formation of the compact complex and to induce a gel-like interpolymer association which is favored at  $\alpha = 5\%$ . This gel-like complex is depressed to a compact form by the presence of a salt (NaCl).



**Figure 5** Variation of  $(\eta_{sp}/c)_m$  of PAAm-PAA in solution. (●) in water, ( $\Delta$ ) in NaCl  $1.00 \times 10^{-2} M$ ; and ( $\square$ ) in NaCl  $1.00 \times 10^{-1} M$  as a function of  $W_{PAA}$ . PAA is 5% neutralized. (—) experimental; (---) "ideal."

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