

## **Influence of denaturing agents on macromolecular coil dimensions of polyacrylamides in diluted aqueous solutions**

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### Summary

A viscosimetric method was used to investigate the intramolecular association in diluted aqueous solution of two polyacrylamides. The concentration at which only intramolecular association take place were obtained from temperature effect on  $[\eta]$ . Addition of kalium iodide, a hydrogen bond breaker, increased  $[\eta]$ . As salt concentration was higher  $[\eta]$  became greater, proving that some part of intramolecular hydrogen bonds was broken. The values of  $[\eta]$  in 1 N salt solutions were in the order:  $\text{HPO}_4^{2-} < \text{H}_2\text{O} < \text{Br}^- < \text{NO}_3^- < \text{I}^- = \text{BrO}_3^- < \text{ClO}_3^- = \text{SCN}^-$ . The dependence of the reduced viscosity at a constant concentration of 0.05 % polyacrylamide for the above mentioned salts, as well as for isopropyl alcohol, isobutyl alcohol, glycerine, urea, hydroxylamine hydrochloride, sodium acetate and sodium carbonate on additive concentration has been determined. The slopes of these diagrams were positive for hydrogen bond breakers and negative for hydrogen bond makers, showing that the first increased the macromolecular coil dimensions, whereas the last decreased them.

### Introduction

Polyacrylamides (PAAM) are linear chain molecules capable of hydrogen bonding through the amide groups in aqueous solutions. This could happen both intra- and intermolecularly, similar to those presumed to be involved in the case of proteins. Such investigations, apart from the knowledge of interactions between polymers carrying hydrogen bond forming groups and small molecules, may shed some light on protein interactions.

Specific volumes and endothermic heat of dilution data (1), as well as NMR ones (2), suggest that PAAM segments prefer contact with water to contact with other polymer segments, the amide group of the polymer being hydrated to a similar extent as that of small amides (3). The water molecules, hydrogen bonded to one amide group, dimerize, trimerize, etc. acting as a bridge linking two amide groups together.

The hydrodynamic properties of polymer solutions are very sensitive to macromolecular coil dimensions and intermolecular associations. As the degree of intermolecular association or coil dimensions increase the intrinsic viscosity  $[\eta]$  and reduced viscosity  $\eta_{sp}/c_2$  of polymer solutions will increase and vice versa.

In the present paper the results of viscosimetric investigation on diluted aqueous solutions of two polyacrylamides are presented. The reality of intramolecular association among amide groups in such solutions was proved by the addition of denaturing agents as urea, glycerine, isopropyl alcohol, isobutyl alcohol, hydroxylamine hydrochloride and some salts which have the ability to brake or to make the hydrogen bonds of water.

### Experimental Part

Two unhydrolysed polyacrylamides were used: one obtained by solution polymerization, viscosity-average molecular weight  $\bar{M}_v = 4.40 \times 10^6 \text{ g.mol}^{-1}$ , and the other one obtained by inverse emulsion polymerization,  $\bar{M}_v = 5.18 \times 10^6 \text{ g.mol}^{-1}$ .  $\bar{M}_v$  were determined with an Oa-type Ubbelohde viscometer having  $k = 0.004887$ , in 1 N sodium nitrate aqueous solution at  $30^\circ\text{C}$ , according to the relation (4):

$$[\eta] = 1.34 \times 10^{-3} \bar{M}_v^{0.57} \quad (1)$$

applicable for  $7 \times 10^5 < \bar{M}_v < 1.2 \times 10^7$ . All the viscosimetric measurements were made using the same viscometer. The temperature of the viscometer bath was  $30 \pm 0.05^\circ\text{C}$ , excepting for the intrinsic viscosity in water at  $20 \pm 0.05$  and  $40 \pm 0.05^\circ\text{C}$ .

For a constant concentration of 0.05 % PAAM the dependence of reduced viscosity on additive concentration  $c_2$  was determined for the following added substances: isopropyl and isobutyl alcohols, glycerine, urea, hydroxylamine hydrochloride, sodium bromide, sodium iodide, sodium nitrate, sodium chlorate, calcium chlorate, sodium bromate, kalium thiocyanate, sodium acetate, and sodium hydrogen phosphate. All the above substances were p. a. grade reagents, used without further purification. The solutions were used freshly prepared, to prevent fungus formation.

The PAAM solutions suffering the aging phenomenon, they were used about a week after complete dissolution. The flow times were measured with an accuracy of  $\pm 0.1$  s and were corrected for kinetic energy.

### Results and Discussion

Macromolecules are isolated from each other if PAAM solutions are diluted enough and the intramolecular association prevails. In such solutions reduced viscosity can be expressed in terms of polymer concentration  $c_2$ , according to the well known Huggins relationship:

$$\eta_{sp}/c_2 = [\eta] + K_H [\eta]^2 c_2, \quad (2)$$

where  $K_H$  is Huggins constant. The value of  $[\eta]$  is a measure of the shape and size of the individual polymer molecules, whereas the slope  $K_H [\eta]^2$  depends on solvent and is a measure for the strength of the solvation, i.e. for the degree of solvation.

High  $[\eta]$  values are not always a consequence of large molecular weights: they can also result from a high value of the

slope and the exponent of the viscosity equation, i.e. the result of loose coiling of the molecules. The slope is taken as a measure of the energetic interaction between the molecule and the solvent.

The presence of intramolecular bonds might be expected to change not only the size, but also the shape and the distribution of the segments about the center of gravity. The fact that the coil expansion of PAAM is satisfactorily represented by the Flory-Fox model of coil expansion (5), which considered the segments statistically distributed about this center, might be considered as an evidence that the formation of an intramolecular bond involved only the formation of small ring in the chain. Such intramolecular hydrogen bonds, between groups close to each other in the chain only, have been demonstrated for polymers carrying similar groups in solvents of lower dielectric constant (6). Thus, intramolecular hydrogen bonding would have the effect only of shortening the PAAM molecule and its linear and coiling character is maintained.

The concentration at which only intramolecular association take place can be obtained from the temperature effect on the viscosities of PAAM aqueous solutions: the increase of reduced viscosity and  $[\eta]$  with temperature is an evidence for intramolecular association; if the opposite is true, the association is intermolecular. Both the reduced viscosities and  $[\eta]$  of aqueous PAAM solutions increased on heating from 20 to 30 and to 40°C, as figure 1 shown, as a result of intramolecular hydrogen bonds breaking, so that the association is intramolecular only for concentration up to 0.1%. An exception has been registered for 0.1 % solution at 20°C: the point fall off the straight line and is equal to that of 40°C. Consequently, in 0.1 % solution at 20°C PAAM associates both inter- and intramolecularly.

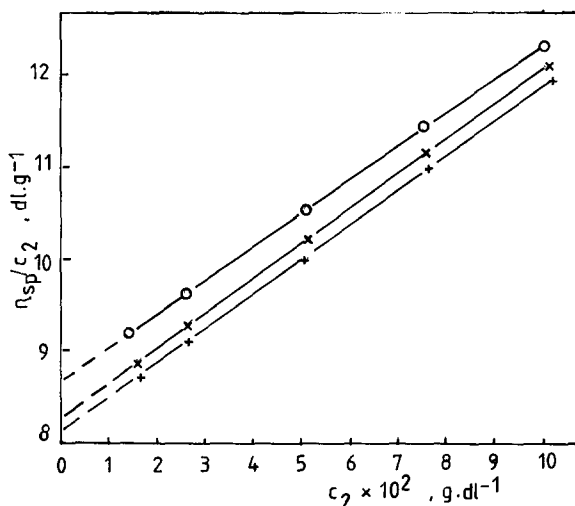


Figure 1. Effect of temperature on the reduced viscosity of aqueous PAAM solutions plotted vs. concentration: + - 20°C; x - 30°C; o - 40°C.

Amide groups being linked together by hydrogen bonds through water molecules, the addition of some substances which have the ability to break or to make the hydrogen bonds of water will have a similar effect on intramolecular hydrogen bonds of PAAM and this will affect the macromolecular coil dimensions.

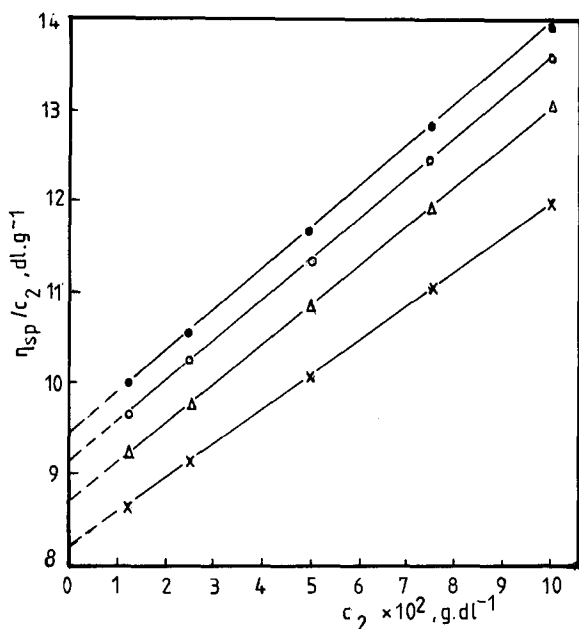


Figure 2. Effect of potassium iodide concentration on intrinsic viscosity of PAAM: x - 0;  $\Delta$  - 0.5; o - 1.0; · - 1.5 N.

Addition of potassium iodide, known as a hydrogen bond breaker (7-11), has led to an increase of  $[\eta]$  with salt concentration  $c_2$  (figure 2). The slopes of the straight lines also increased, as can be seen from figure 2, proving that salt solutions become better solvents as  $c_2$  raised.

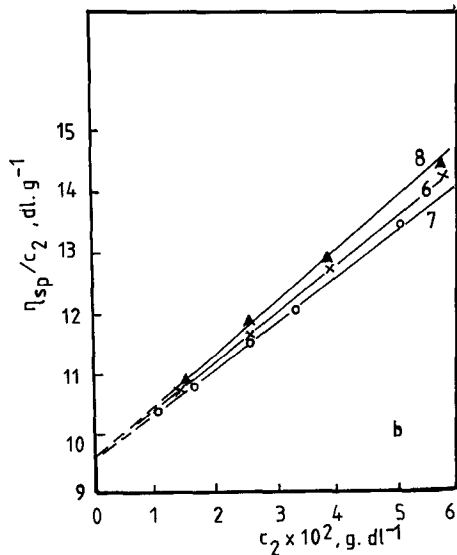
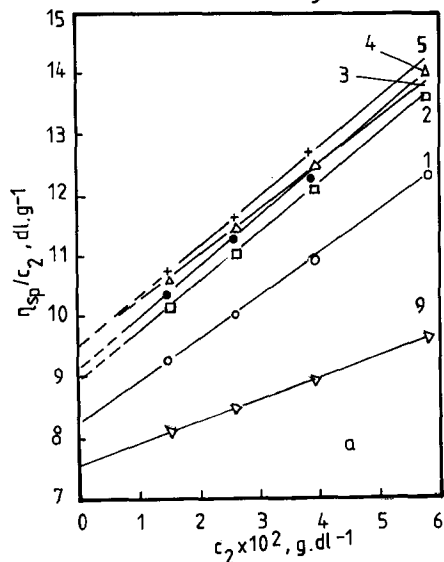


Figure 3. Intrinsic viscosities in 1 N salt solution: 1 -  $H_2O$ ; 2 -  $NaBr$ ; 3 -  $NaNO_3$ ; 4 -  $NaI$ ; 5 -  $NaBrO_3$ ; 6 -  $NaClO_3$ ; 7 -  $Ca(ClO_3)_2$ ; 8 -  $KSCN$ ; 9 -  $Na_2HPO_4$ .

It is well established that the anions make or brake the hydrogen bonds of water in salt solutions. The values of  $[\eta]$  were determined in 1 N salt solutions (figure 3a,b) and they were found to increase as follows:  $\text{HPO}_4^{2-} < \text{H}_2\text{O} < \text{Br}^- < \text{NO}_3^- < \text{I}^- = \text{BrO}_3^- < \text{ClO}_3^- = \text{SCN}^-$ , the same series as the series of solution listed in order of decreasing average strength of water-water hydrogen bonds found from IR and NMR measurements for the same ionic strength (11). That also indicate that intramolecular hydrogen bonds are responsible for the macromolecular coil dimensions increase. Sodium and calcium chlorate gave the same value for  $[\eta]$ , proving that the cation play no prominent part in hydrogen bond braking or making.

The effect of the anion  $\text{HPO}_4^{2-}$  on the hydrogen bonds of water was not found in the literature. The experiment show that the addition of sodium hydrogen phosphate favours PAAM precipitation in the final stage of inverse emulsion polymerization. Its effect is indeed to decrease the intrinsic viscosity comparing to that in water, which proves that macromolecular coils became more compact as a result of more intramolecular hydrogen bonds. In the same time, the relative viscosity of sodium hydrogen phosphate aqueous solutions increased very much when its concentration is raised.

The slopes of the straight lines  $\eta_{sp}/c_2 = f(c_3)$  become higher as the ability of the anion to decrease the hydrogen bonds of water increase and vice versa, which demonstrate that salt solutions are better solvents for PAAM.

Plotting  $\eta_{sp}/c_2$  in terms of kalium iodide concentration for a constant concentration of polymer, as well as  $[\eta]$  (figure 4), it can be seen that the curve for the intrinsic viscosity lies almost paralel with those for 0.025 and 0.05 %.

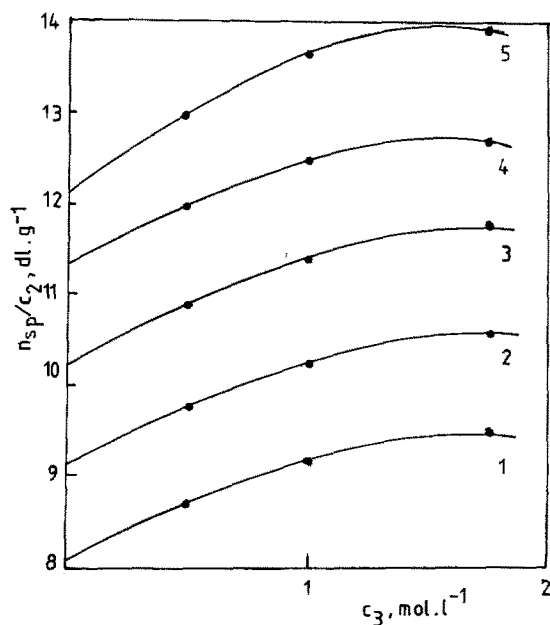


Figure 4. Dependence of  $\eta_{sp}/c_2$  on kalium iodide concentration on a constant concentration of PAAM: 1 - 0; 2 - 0.025; 3 - 0.05; 4 - 0.075; 5 - 0.1 %.

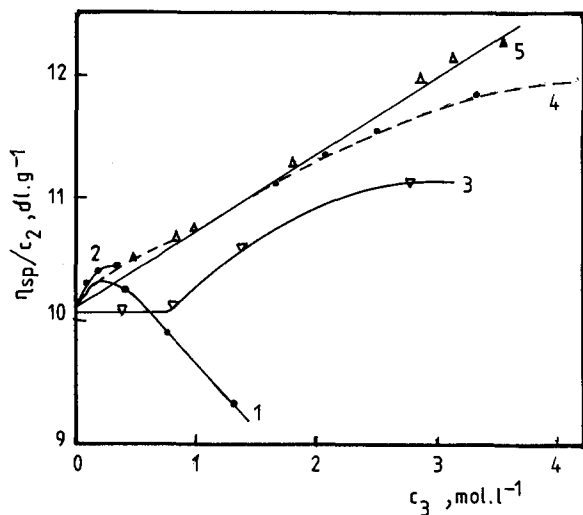


Figure 5. Effect of additive concentration on  $\eta_{sp}/c_2$ : 1 - isopropyl alcohol; 2 - isobutyl alcohol; 3 - glycerine; 4 - urea; 5 - hydroxylamine hydrochloride.

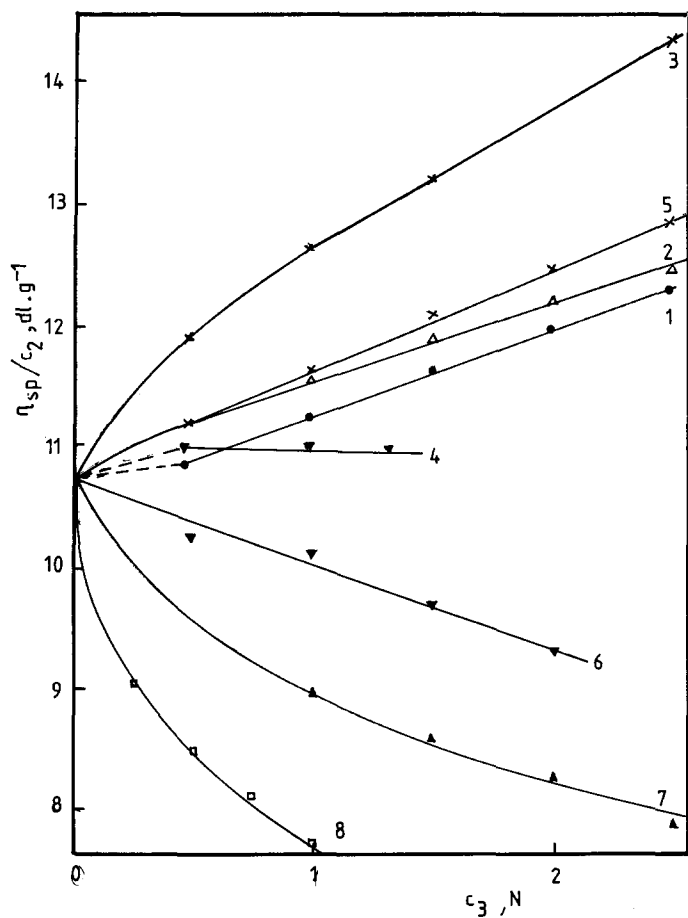


Figure 6. Effect of salt concentration on  $\eta_{sp}/c_2$ : 1 - NaBr; 2 - NaI; 3 - NaClO<sub>3</sub>; 4 - NaBrO<sub>3</sub>; 5 - KSCN; 6 - Na<sub>2</sub>CO<sub>3</sub>; 7 - CH<sub>3</sub>COONa; 8 - Na<sub>2</sub>HPO<sub>4</sub>.

It follows that the dependence of  $[\eta]$  on salt concentration is properly represented by the variation of reduced viscosity for 0.025 and 0.05 % PAAM. Thus, the concentration of 0.05 % was selected to follow the dependence of macromolecular coil dimensions on the added substance concentration,  $c_2$ .

The change of reduced viscosity in terms of additive concentration is represented in figures 5 and 6. As can be seen, isopropyl alcohol first increases the macromolecular coil dimensions, up to a concentration of  $0.25 \text{ mol.l}^{-1}$  (about 3 %) and then decrease them (figure 5, curve 1); isobutyl alcohol produces an increase of the reduced viscosity for all the concentration available (isobutyl alcohol is soluble in water up to a concentration of  $0.33 \text{ mol.l}^{-1}$  or 3 %) (figure 5, curve 2). Glycerine increases reduced viscosity beginning from about  $0.85 \text{ mol.l}^{-1}$ , urea and hydroxylamine hydrochloride had hydrogen bond breaker character for all the used concentrations.

The dependence on salt concentrations had a positive slope for hydrogen bond breaker salts (figure 6, curves 1-5) and a negative one for hydrogen bond maker salts: sodium acetate (curve 7), known as a hydrogen bond maker for water (11), sodium hydrogen phosphate (curve 8) and sodium carbonate (curve 6) which were observed to have a hydrogen bond maker character.

The above described phenomena are important in PAAM dissolution, precipitation, efficiency as a drag reducer, and prevention of solution aging.

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