# Conformation of Polyacrylamide in Aqueous Solution with Interactive Additives and Cosolvents

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**ABSTRACT:** The viscosity of polyacrylamide (PAM) dilute aqueous solutions with NaCl, glucose, and SDS as additives was measured by Ubbelohde viscometry. There was linear relationship between reduced viscosity vs. PAM concentration in aqueous solutions. The Huggins constant $k$ and intrinsic viscosity $[\eta]$ were used to study the conformation of the polymer chains and the degree of polymer–solvent interaction. In addition, the viscosity of diluted PAM solutions in water with acetone, ethanol, DMF, and ethylene glycol as cosolvent was measured. It was found that the polymer chain conformation contracted as the acetone, ethanol, and DMF cosolvent composition ratio increased, but there was no distinguishing difference between water–ethylene glycol compositions. The solution properties of PAM were used to estimate the swelling properties of PAM gel in the same external conditions, as gel is formed by crosslinking of linear polymer. In good solvent the polymer chain should be expanded, and gel is expected to have large swelling ratio. In water cosolvent systems, when the linear polymer chain underwent coil–globule transition, PAM gel should have volume phase transition under corresponding external conditions. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3122–3129, 2003

**Key words:** water–soluble polymers; viscosity; hydrogels; swelling

## INTRODUCTION

Hydrogels are three-dimensional networks that can absorb a large amount of water and swell,[1] while the swelling ratio ranges from 10–20% to 100 times of weight of gel itself. Under certain conditions, such as when additives are present,[2–4] cosolvent composition is changed,[5,6] or temperature[7] and pH[8] become different, the gels change in volume. Sometimes the change is smooth, but sometimes it happens step-like, which means the gels undergo volume phase transition, and the polymer chain conformation undergoes coil (swollen state) to globule (collapsed state) transition.[5,9,10] The transition is reversible, which was first observed at 1979.[11] Since then, this phenomenon has been studied extensively. The external conditions include ionic strength and salt species, pH, temperature, cosolvent composition, and hydrolysis time.[12,13] The volume phase transition is applied to smart gels, which are mainly used for controlled release, waste water treatment, and oil recovery.

Hydrogels are formed by crosslinking of water–soluble linear polymers, so the properties of linear polymer solutions can be used to estimate the gel properties. Viscosity measurement is a traditional method used to study the interactions between polymer molecules and solvent. In dilute solution of a simple binary system, Huggins constant $k$ and intrinsic viscosity $[\eta]$ can be obtained.[14] Huggins constant $k$ is used to predict the degree of interaction between polymer and solvent. In a good solvent, $k$ value is less than 0.5, while in poor solvent, $k$ is larger than 0.6–0.8 (when the unit of concentration is g/dL).[15,16] The $[\eta]$ value shows molecular size and conformation, it increases when intermolecular interaction increases, and decreases when intramolecular interaction increases.[17] From studying the viscosity of a linear polymer in a variety of solutions, the solvent quality and polymer conformation can be deduced. The polymer chains expand (coil conformation) in a good solvent and contract (globular conformation) in a poor one. As a result, the swelling ability of a hydrogel can be estimated in these corresponding solutions, because expanded chains lead to swell and contracted chains lead to collapse contrarily.

Polyacrylamide (PAM) is one of the most important nonionic water–soluble polymers. One of its applications is to form SDS–PAM gel to determine the molecular weight of polypeptides.[18,19] Other applications include detergent,[20] waste–water treatment, biomedical applications,[21] and as a flocculant in paper manufacture. Hydrophobic modified[22–24] or ionic–monomer copolymerized[25] PAM are also applied extensively in cosmetics, paints, and oil recovery. From a scientific point of view, these kinds of polymer have

**TABLE I**
**The Huggins Constant $k$ and intrinsic viscosity $[\eta]$ Values of PAM in NaCl, Glucose, and SDS Aqueous Solutions**

| SDS | | | Glucose | | | NaCl | | |
|---|---|---|---|---|---|---|---|---|
| C (g/L) | $[\eta]$ (dL/g) | $k$ | C (g/L) | $[\eta]$ (dL/g) | $k$ | C (g/L) | $[\eta]$ (dL/L) | $k$ |
| 0 | 0.1101 | 0.99 | 0 | 0.1101 | 0.99 | 0 | 0.1101 | 0.99 |
| 0.1 | 0.0965 | 0.752 | 0.65 | 0.106 | 0.712 | 3.3 | 0.0904 | 0.94 |
| 0.8 | 0.1028 | 0.653 | 5 | 0.1036 | 0.727 | 11 | 0.1015 | 0.757 |
| 2.8 | 0.1176 | 0.412 | 16 | 0.1008 | 0.728 | 52 | 0.1111 | 0.568 |
| 3.0 | 0.1122 | 0.469 | 24 | 0.0984 | 0.764 | 99 | 0.1204 | 0.469 |
| 4.0 | 0.1073 | 0.564 | | | | | | |
| 6.0 | 0.1042 | 0.657 | | | | | | |

already been used to study volume phase transition. In this article, PAM is studied under various external conditions: aqueous solutions with NaCl, glucose, sodium dodecylsulfate (SDS) as additives, and cosolvents mixed by water and the second solvent. The second solvent refers to acetone, ethanol, dimethylformamide (DMF), or ethylene glycol (EG), and cosolvents refer to water–acetone, water–ethanol, water–DMF, and water–EG mixture, respectively. Through a viscosity study of these solutions, conformational changes are obtained, and the results will be used to predict the properties of PAM gel under these external conditions.

## EXPERIMENTAL

### Materials

Polyacrylamide 50%(w/w) water solution, with molecular weight of 10,000 g/mol and density of 1.189 g/mL, was purchased from Aldrich Company. NaCl, (D+)glucose, SDS, acetone, ethanol, DMF, and EG were all laboratory grade and used as received.

### Solvent preparation

NaCl, glucose, and SDS additives were dissolved in water with a variety of concentrations (the concentrations are listed in Table I).

Acetone, ethanol, DMF, and EG were mixed with water respectively to form cosolvents systems. The volume composition of water : second solvent ranged from 10 : 0 (pure water), 8 : 2 (the second solvent 0.2),

6 : 4 (the second solvent 0.4), 4 : 6 (the second solvent 0.6), 2 : 8 (the second solvent 0.8), to 0 : 10 (the pure second solvent). Where the first number is for water volume, and the second is for the second solvent volume.

### Solution preparation

The PAM pure water solution was diluted from the concentrated stock solutions.

Acetone was used to precipitate PAM from the stock solution, and PAM was dried to constant weight. The dried PAM was dissolved in NaCl, glucose, and SDS aqueous solutions, and the dried PAM was placed into cosolvents to obtain the solubility, which is listed in Table II. The PAM concentration was controlled within 0–6.5 g/dL.

### Measurement of viscosity

A Ubbelohde viscometer was used to measure the relative viscosity of the solutions. The symbol $\eta$ refers to as the viscosity of solution, $\eta_0$ refers to the viscosity of the solvent, $t$ is the efflux time of solution, and $t_0$ is the efflux time of solvent. The temperature was controlled at 25°C. The related definitions are as follow:

$$\text{Specific viscosity: } \eta_{sp} = (t - t_0)/t_0 \qquad (1)$$

$$\text{Reduced viscosity: } \eta_{red} = \eta_{sp}/c \qquad (2)$$

$$\text{Intrinsic viscosity: } [\eta] = (\eta_{sp}/c)_{c=0} \qquad (3)$$

**TABLE II**
**Solubility of PAM in Water-*co*-Solvents Systems**

| The second solvent volume fraction[a] | Acetone | Ethanol | DMF | EG |
|---|---|---|---|---|
| 0.2 | dissolved | dissolved | dissolved | dissolved |
| 0.4 | Turbid solution | dissolved | dissolved | dissolved |
| 0.6 | Turbid solution with droplet | Turbid solution with droplet | Turbid solution with droplet | dissolved |
| 0.8 | Clear liquid with droplet | undisolved | Clear liquid with droplet | dissolved |
| 1 | undissolved | undissolved | undissolved | dissolved |

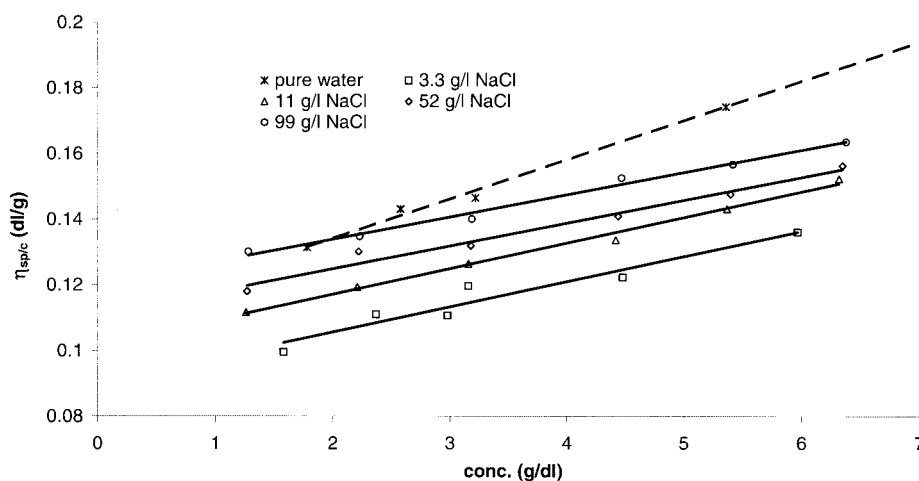[a] The number listed in the table are the volume fraction of the second solvent.

**Figure 1** Reduced viscosity vs. concentration of PAM in NaCl aqueous solutions.

and Huggins equation is:

$$\eta_{sp}/c = [\eta] + k[\eta]^2 c \qquad (4)$$

where $k$ is the Huggins constant. For a linear relationship between reduced viscosity and concentration, the $k$ is the slope and $[\eta]$ is the intercept of the curve.

## RESULTS AND DISCUSSION

### PAM in NaCl solutions

Figure 1 shows that the reduced viscosity of PAM increases as NaCl concentration increases. This behavior is quite different from polyelectrolytes in salt solutions.[26–28] Usually, the viscosity of polyelectrolyte solutions decreases at low salt concentration because of the screening effect, then it increases after the salt concentration increases to a certain level. After this salt concentration, the net electrostatic interaction between polymer chains begins to increase. Because

PAM is a nonionic polymer, NaCl interacts with it in a different way. PAM has two structure components: the nonpolar hydrocarbon chain and the polar amide group. NaCl has a salting-out effect on nonpolar chains and salting-in effect on amide groups. As amide groups have a dielectric constant much higher than that of water, amide group should be salted-in, and when exposed to more water, and this makes the polymer chain more expanded.[29,30]

Although PAM is easily dissolved in pure water, the $k$ value of water solution is 0.99, which means water is not a thermodynamically good solvent for PAM. From Table I, it can be seen that when the concentration of NaCl increased, the $k$ value decreased, and the $[\eta]$ value increased, which suggests that PAM chains become more expanded in higher concentrations of NaCl solution. When NaCl was highly concentrated (NaCl 99 g/L), the NaCl solution became a good solvent for PAM (the $k$ value was 0.469). The ion–permanent dipole interaction between NaCl and amide
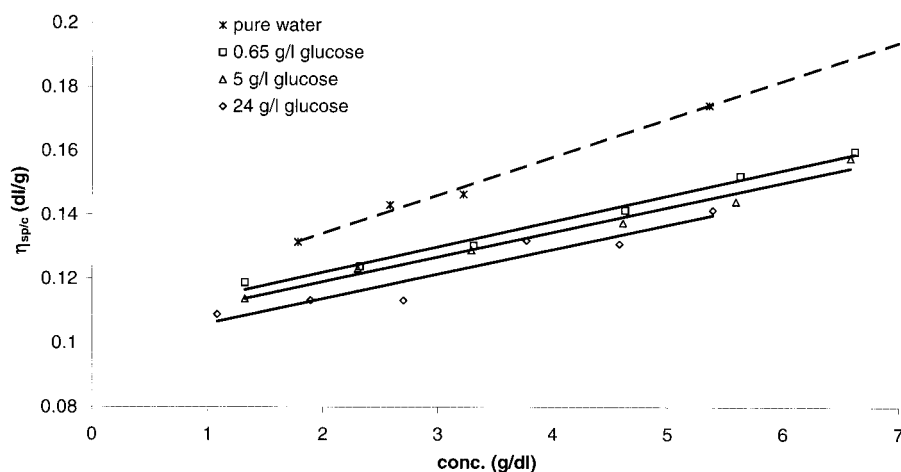


**Figure 2** Reduced viscosity vs. concentration of PAM in glucose aqueous solutions.
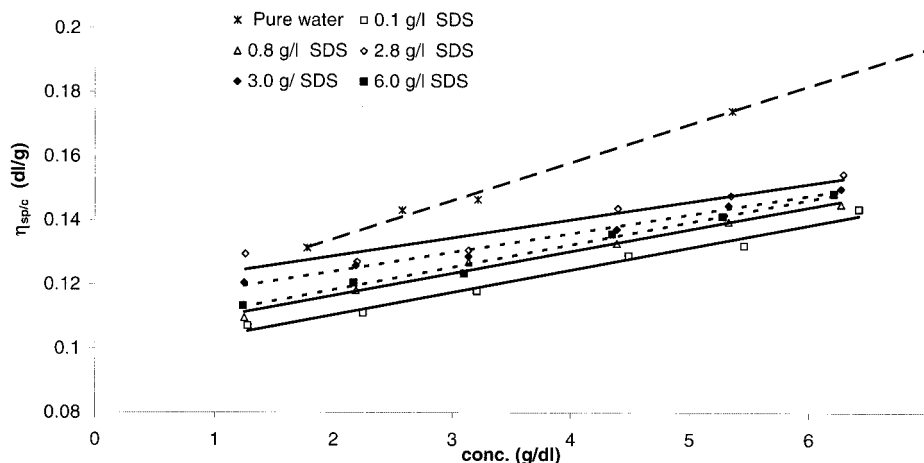
**Figure 3**  Reduced viscosity vs. concentration of PAM in SDS aqueous solutions.

groups makes the polymer chains more expanded than in pure water, and higher ionic strength improves such interactions, allowing polymer chains to expand further. These results suggest that a PAM gel should have a larger swelling ratio in concentrated NaCl solution than in pure water. This viscosity behavior confirms that PAM has a high saline tolerance.

## PAM in glucose solutions

Contrary to that found in NaCl solutions, the reduced viscosity of PAM decreased moderately as glucose or SDS concentration increased, which is shown on Figures 2 and 3. Glucose molecules have many hydroxy groups, and water has hydrogen bonding interactions with hydroxy groups and amide groups. As the hydrogen bonding interaction between glucose and water is stronger than that of between amide and water, PAM chains become less exposed to water. PAM intramolecular interactions increased when more glucose molecules were added into water. The $k$ and $[\eta]$ values of glucose solutions are listed in Table I, all the $k$ values of PAM solutions are greater than 0.6, which suggest that glucose solutions are poor solvents for PAM. From Figure 4, it can be seen that $[\eta]$ decreased as the glucose concentration increased, the glucose solution became a poorer solvent for PAM at higher glucose concentrations, but the influence of concentration was as not significant.

## PAM in SDS solutions

The SDS solutions were good solvents for PAM compared with pure water, as shown in Table I and Figure 3, as all $k$ values were smaller than that of pure water. It was reported that insoluble uncharged poly(vinyl-alcohol) could be solubilized in SDS solutions.[31] Both cases show that SDS can improve the solvent quality

for nonionic water–soluble polymers. SDS is an amphophilic molecule with ionic head group and long hydrophobic hydrocarbon chain. When SDS is mixed with an uncharged polymer, the hydrophobic group can associate with the polymer chain, resulting in increased repulsion between ionic head groups, so the solubilization of polymer is increased, which means that water became a good solvent for the uncharged polymer after adding SDS.[31,32]

Although the interaction between SDS and PAM is reported to be very weak,[31] it is observed (Figure 4) in this case that the reduced viscosity of PAM increased with the increased SDS concentration until a maximum value was experienced, followed by a decrease
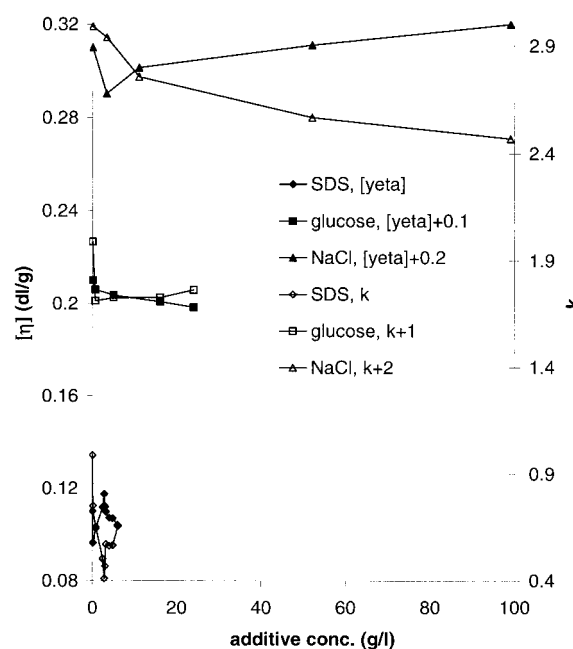


**Figure 4**  Huggins constant $k$ and intrinsic viscosity $[\eta]$ values of PAM aqueous solution vs. additive concentration.
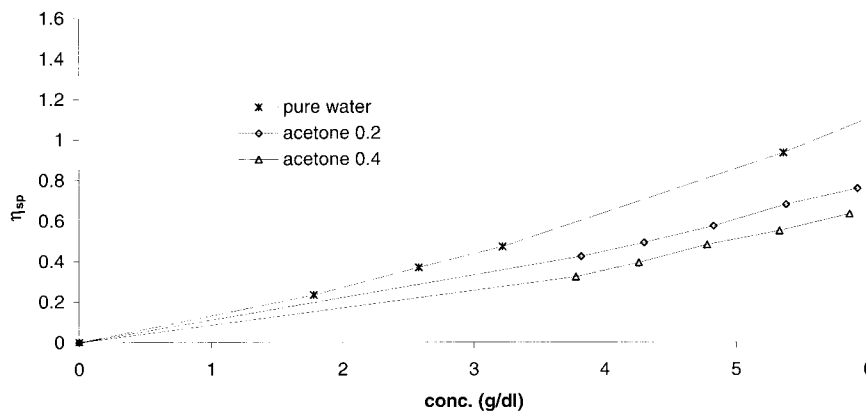
**Figure 5**   Specific viscosity vs. PAM concentration in water–acetone cosolvent system.
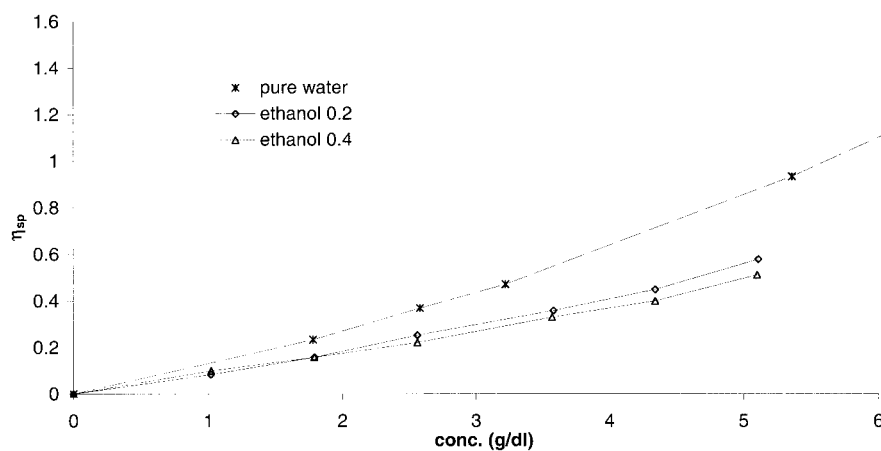


**Figure 6**   Specific viscosity vs. PAM concentration in water–ethanol cosolvent system.
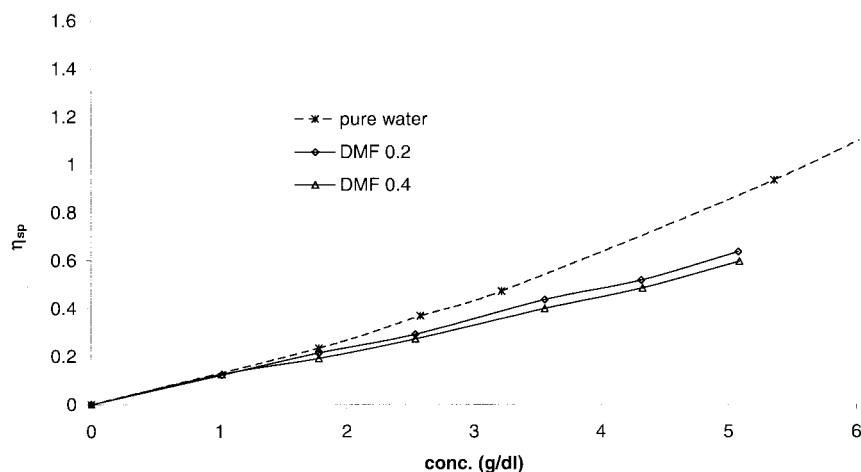


**Figure 7**   Specific viscosity vs. PAM concentration in water–DMF cosolvent system.

with further SDS concentration increase. When the reduced viscosity was a maximum, the maximum $[\eta]$ and minimum $k$ were obtained. At this condition, the SDS concentration was between 2.8–3.0 g/L, while the reported theoretical critical micelle concentration (CMC) of SDS is 2.9 g/L.[33] This viscosity study shows

that PAM molecules are most expanded at the CMC of SDS. A possible interpretation is that the polymer expanded when it was mixed with SDS, but after the SDS concentration reached its CMC, the hydrophobic interaction of surfactant tails would compact the polymer chain, so the polymer could not expand further.
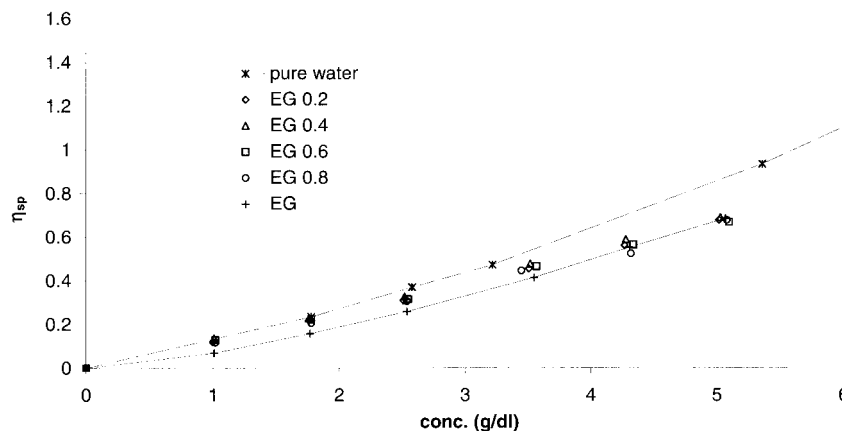
**Figure 8** Specific viscosity vs. PAM concentration in water–EG cosolvent system.

There is a balance between SDS redistribution along polymer chain and polymer reconformation.

### PAM in water–acetone, water–ethanol, and water–DMF cosolvents

There is no linear relationship between reduced viscosity and concentration of the ternary system containing polymer, water, and the second solvent. However, Figures 5–7 all show similar results that, when the second solvent composition was increased, the specific viscosity of PAM decreased, indicating that intramolecular interactions increased. Increased intramolecular interaction resulted in the polymer chains contracting, and finally the polymer precipitated from the cosolvents. The solubility of PAM in cosolvents, which is shown in Table II, confirmed the results. It is proposed that the polymer chains undergo a coil-to-globule transition when the second solvent composition increases, although these results can not determine whether the process is smooth or step like.

As the polymer chain conformation undergoes a coil-to-globule transition, the PAM gel should undergo a volume phase transition when the secondary solvent composition increases. Whether the phase transition is continuous or discrete depends on ionisation,[5,9] molecular rigidity,[10] or other factors. External conditions include temperature, pH, ion strength, solvent composition, light, and electric field. The discrete transition is a critical phenomenon of gels, and it has extensive applications.

There are four fundamental interactions of the volume phase transition: Van der Waals, hydrophobic, hydrogen bonding, and electrostatic.[1] For three cosolvent systems, water–acetone, water–ethanol, and water–DMF, the probable reasons for the transition are different. For the water–acetone system, increasing acetone composition can increase polymer–polymer Van der Waals attractive interactions, while for the water–ethanol system, increasing ethanol can increase intrachain interaction by hydrogen bonding. For the water–DMF system, the reason is complicated and not understood from the current results.

### PAM in water–EG cosolvents

The viscosity behavior of water–EG cosolvents (Figure 8) was different from the other three cosolvents systems, which can be seen in Figure 9. Water has a strong interaction with acetone, ethanol, and DMF. The maximum relative viscosity was obtained at nearly 6 : 4 volume fraction, and these three cosolvents systems were similar. It is suggested that near the 6 : 4 volume fraction, complexes were formed between water and the second solvents. Then the complexes interacted with PAM. In EG, the molecules were bonded strongly by intermolecular hydrogen bonding, causing a high relative viscosity compared with pure water. After adding water into EG, the relative viscosity decreased very quickly, as the hydrogen bonding interaction between EG molecules was diluted by water. It is suggested that water and EG interact with PAM by hydrogen bonding separately. Both water and EG can dissolve PAM, and there is no distinguishing difference of PAM chain conformation between different EG fractions (Fig. 8). It seems that the conformation of PAM chain in water is slightly more expanded than that in EG, as shown on Table II and Figure 8. Contact angle and surface tension measurement will be used to further study PAM solutions. This method can separate the difference between different EG compositions.

### CONCLUSIONS

The viscosity of PAM solutions was used to study conformation change and the interaction between polymer and solvent.
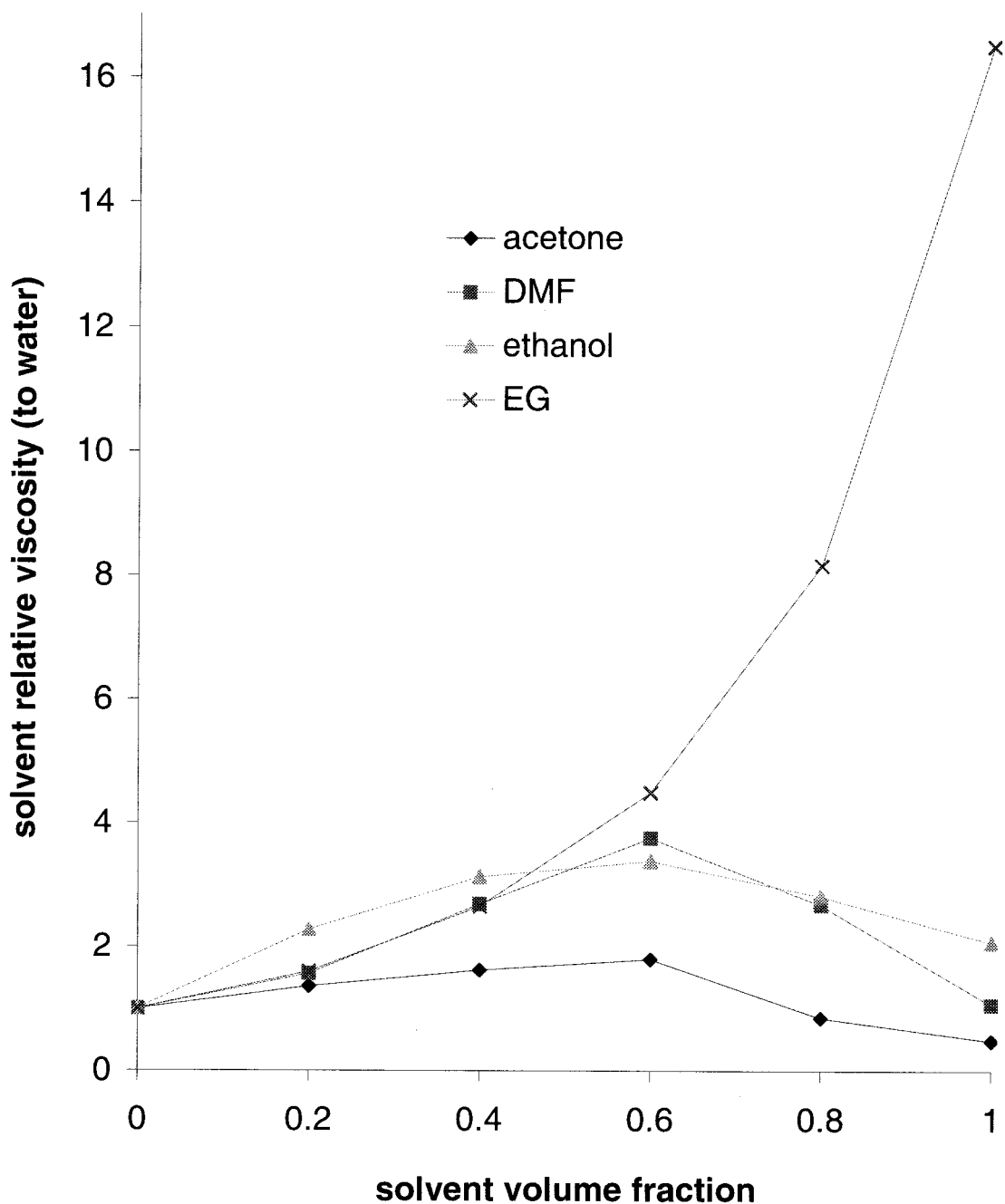
**Figure 9** Cosolvent relative viscosity (compared with pure water) vs. the second solvent volume fraction (pure water viscosity is defined as 1).

In aqueous solutions, three different additives had different influences on PAM conformation, (1) the conformation of PAM in concentrated NaCl aqueous solution was very expanded, and polymer chains became more expanded as the NaCl concentration increased. (2) The PAM polymer chains contracted in glucose aqueous solutions, especially at higher glucose concentration. (3) SDS aqueous solutions were good solvents for PAM compared with pure water. The SDS hydrophobic chains were associated with polymer chains, which caused the hydrophilic head

groups to repel each other, and this increased the solubility of PAM. The PAM chains expanded to a maximum at the SDS critical micelle concentration.

For water–acetone, water–ethanol, and water–DMF cosolvent systems, the polymer chains underwent a coil–globule transition when the second solvent volume fraction increased. This suggests that there will be volume phase transition for PAM gels under similar conditions. The polymer chains were slightly more expanded in pure water than in pure EG. The chain expansion in water–EG cosolvents did not show any

distinguishing difference with variations of EG compositions.

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