

Solubility Study of Polyacrylamide in Polar Solvents

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ABSTRACT: Contact angles and surface tension data were measured to obtain the surface tension components of polyacrylamide (PAM). According to Van Oss, Chaudhury, and Good (VCG) theory, the surface tension components were used to calculate the PAM solubility in five different polar solvents: water, ethylene glycol (EG), acetone, ethanol, and dimethyl formamide (DMF). It was found that PAM had a monopolar surface nature, which resulted in polymer dissolution in water. The solubility of PAM in water was greater than in EG, but PAM was solvophobic in the other three solvents. For PAM, water, and the second solvent (cosolvent) ternary system, the solubility of PAM could not be calculated directly. Surface tension was used as an index of polarity for cosolvent systems (the mixture of water and the

second solvent). The cosolvent polarity decreased when the composition of the second solvent increased. PAM would be dissolved in the cosolvent when the system's polar contribution was greater than the apolar contribution. The apparent surface tension of PAM aqueous solutions was not sensitive enough to show polymer conformation changes when additive concentrations were changed. The solubility of PAM in binary polar solvent systems or ternary cosolvent systems was used to estimating the swelling properties of a PAM hydrogel under corresponding external conditions. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1493–1499, 2004

Key words: water-soluble polymers; hydrogels; hydrophilic polymers; swelling; surfaces

INTRODUCTION

Water-soluble polymers can form hydrogels after crosslinking. The hydrogel is usually insoluble, but can absorb considerable water and swell. The swelling ratio is measured by mass or volume change, which is a macroscopical property. But on the other hand, the swelling ratio strongly depends on the intrinsic properties of corresponding linear polymer, such as solubility and conformation. High solubility and expanded conformation in certain solvents lead to a high swelling ratio. In this article, we use the intrinsic property—solubility—to predict the swelling behavior of a PAM hydrogel. As this study has rarely done before, it gives a new point of view for understanding of macroscopical behavior. Also, from a practical point of view, a polymer solution can be used to study gel properties instead of gel preparation.

There are three different categories of solubility: dissolved, partly (slightly) dissolved, and undissolved (precipitated). The solubility is normally referred to as the mass of solute that can be dissolved in a certain amount of solvent at a particular temperature and pressure. For macromolecules, this concept does not

completely explain solubility because of their complexity.

The second understanding of solubility is referred to as a thermodynamic force in a binary system. Solubility is the free energy change per unit area when molecules of 1 (the solute) are initially present in phase 2 (the solvent), with an effectively infinite layer of phase 2 separating two surfaces of phase 1. The free energy change is ΔG_{121} .¹ There is relationship between the first qualitative understanding of solubility and the second thermodynamic understanding of solubility. When $\Delta G_{121} \gg 0$, solute 1 is solvophilic for solvent 2, and solute 1 will be dissolved in solvent 2; when $\Delta G_{121} \approx 0$, solute 1 is slightly dissolved in solvent 2; when $\Delta G_{121} \ll 0$, solute 1 is solvophobic for solvent 2, and solute 1 will not be dissolved in solvent 2. The value of ΔG_{121} quantitatively indicates the degree of solvophilicity or solvophobicity.² A gel in a solvophilic solvent should have larger swelling ratio than in a solvophobic solvent.

In 1986, Van Oss, Chaudhury, and Good (VCG) introduced a method to calculate the value of ΔG_{121} . According to the VCG theory, $\Delta G_{121} = -2\gamma_{12}$, where γ_{12} is the interfacial surface tension between phase 1 (solute) and phase 2 (solvent).^{3,4} Using this method, VCG calculated the solubility of many water-soluble materials, and in particular, biopolymers such as proteins and polysaccharides. They also used this method to estimate the miscibility of organic solvents and water.⁴

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In this article, the VCG method is used to study the solubility of polyacrylamide (PAM), which is one of most important water-soluble polymers, in five pure polar solvents. The solvents include acetone, ethanol, dimethylformamide (DMF), ethylene glycol (EG), and water. For PAM, water and a second solvent (which is miscible with water) ternary system, the free energy is difficult to calculate, so another approach is required. The surface tension will be used as an index of polarity for water–acetone, water–ethanol, water–DMF, and water–EG cosolvent systems. From the polarity comparison, the “cosolvency power” will be inferred. Cosolvency power⁵ means the dissolving capacity of a cosolvent for PAM. The apparent surface tension of PAM in aqueous solutions with NaCl, glucose, and sodium dodecylsulfate (SDS) as additives will also be measured. By studying the solubility of the linear polymer, the swelling property of a gel can be estimated. Although the theory and practical method are based on previous work by VCG, the aim of the article is used to explain the gel swelling behavior from a new point of view.

THEORY

Surface tension component

According to the surface tension component theory, the components of surface tension are additive. After 1987, VCG developed an advanced approach to suggest that a nonionic surface consists of two contributions: one is γ^{LW} , and the other is γ^{AB} . The γ^{LW} corresponds to Lifshitz–van der Waals interactions, comprising dispersion, dipolar, and induction forces, and the γ^{AB} is an acid–base interaction, comprising all of the electron donor–accepter interactions, such as hydrogen bonding.^{3,6} For substance i , γ_i^{AB} is defined as:

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+ \gamma_i^-} \quad (1)$$

where γ_i^+ stands for an electron–acceptor parameter, and γ_i^- for an electron–donor parameter. The total surface tension of substance i is:⁷

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} = \gamma_i^{LW} + 2\sqrt{\gamma_i^+ \gamma_i^-} \quad (2)$$

When a given substance i only manifests a γ_i^+ or only a γ_i^- parameter, it is called a monopolar substance. A monopolar material can strongly interact with polar substances (such as water and other polar solvents), and they mutually repel, leading to dissolution in the polar solvent. According to the VCG theory, most water-soluble polymers are monopolar substances, and they manifest a γ_i^- value.⁴

Surface tension component measurement

According to the VCG surface tension component theory, a complete Young–Dupre equation for a certain solid–liquid systems can be written as:^{6,8}

$$(1 + \cos\theta)\gamma_L = 2(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+\gamma_L^+} + \sqrt{\gamma_S^-\gamma_L^-}) \quad (3)$$

for a certain solid S , the three parameters γ_S^{LW} , γ_S^+ , and γ_S^- can be determined by measurement of the contact angle of three liquids for which the parameters γ_L^{LW} , γ_L^+ , and γ_L^- are known.

These three liquids should be polar liquids with different parameters, or one apolar liquid for which the γ_L^+ and γ_L^- contribution are zero and two polar liquids with different parameters.

Solubility calculation

The interaction between two molecules or particles of the same substance 1, immersed or dissolved in liquid 2 is given by:⁴

$$\Delta G_{121} = -2\gamma_{12} \quad (4)$$

Therefore, the interfacial tension of solute 1 and solvent 2 can be used to determine the solubility of solute 1 in solvent 2.

For two completely miscible materials, the interfacial tension is not directly measurable, but it can be calculated from the individual surface tension components:⁹

$$\gamma_{12} = (\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}})^2 + 2(\sqrt{\gamma_1^+ \gamma_1^-} + \sqrt{\gamma_2^+ \gamma_2^-} - \sqrt{\gamma_1^+ \gamma_2^-} - \sqrt{\gamma_1^- \gamma_2^+}) \quad (5)$$

For two completely immiscible materials (or any given solid–liquid system), the interfacial tension can be determined directly by contact angle measurement:⁸

$$\gamma_{SL} = \gamma_S - \gamma_L \cos\theta \quad (6)$$

Solvent polarity

There are a few physical quantities used as an index of polarity; these include dielectric constant, solubility parameter, interfacial tension, surface tension, partition coefficient, and hydrogen bonding donor densities.⁵ Here, the polarity is defined as relative polar contribution to total surface tension γ_{rel}^{AB} , as the total surface tension of substance i is the sum of an apolar contribution γ_i^{LW} and a polar contribution γ_i^{AB} .

$$\gamma_{rel}^{AB} = \gamma^{AB} / \gamma = 1 - (\gamma^{LW} / \gamma) = 1 - \gamma_{rel}^{LW} \quad (7)$$

The γ_{rel}^{LW} can be calculated by using a contact angle measurement. When a solid surface is totally apolar, $\gamma_S = \gamma_S^{LW}$, $\gamma_S^+ = \gamma_S^- = 0$, then eq. (3) is simplified to:^{10–12}

TABLE I
Solubility of PAM in the Cosolvents

	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	Undissolved	Clear liquid with droplet	Dissolved

The numbers listed in the table are the volume fraction of the second solvent.

$$(1 + \cos\theta)\gamma_L = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} \quad (8)$$

The solid surface tension γ_S^{LW} , the contact angle θ , and total liquid surface tension γ_L can be used to determine the apolar contribution of the liquid, γ_L^{LW} . Then γ_{rel}^{AB} is calculated by eq. (7).

EXPERIMENTAL

Materials

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

A film of an Engage POE (polyolefin elastomer), obtained from DuPont-Dow Company, was prepared by extrusion of pellets and was used as an apolar solid surface to determine the polarity of the cosolvent systems. Diiodomethane (DIM), glycerol, and water were used for the contact angle measurement, and were all of analytical grade and used as received.

Cosolvents and PAM aqueous solution preparation

The second solvent refers to acetone, ethanol, DMF, and EG, and they were mixed with water to form the cosolvent systems, respectively. The volume composition of water : second solvent ranged from 10 : 0 (pure water), 8 : 2 (second solvent 0.2), 6 : 4 (second solvent 0.4), 4 : 6 (second solvent 0.6), 2 : 8 (second solvent 0.8) to 0 : 10 (pure second solvent). The solubility of PAM in these cosolvents is listed in Table I.

Acetone was used to precipitate PAM from the stock solution and then it was dried to constant weight under vacuum. Dried PAM was dissolved in NaCl, glucose, and SDS aqueous solutions. The concentra-

TABLE II
Contact Angles (θ) of Three Solvents
on the PAM Surface

	DIM	Glycerol	Water
PAM	27.22	20.64	23.6

tion of PAM solutions was controlled to within 0–20 g/dL. PAM water solutions were prepared by diluting the concentrated stock solutions.

PAM surface preparation

PAM solution was dropped onto a glass slide, then the slide was placed on a spin coating machine to spin a thin smooth PAM layer on the slide.

The slides with a PAM layer were placed on a warm hot plate to evaporate the water. After evaporation, the slides were stored in desiccator for later use.¹³

Apolar surface preparation

Engage POE was used as an apolar solid surface to determine the polarity of the cosolvent systems. The POE pellets were extruded to form a smooth thin film. The thin film was bonded to glass slides using adhesive tape, and cleaned with acetone before using.

Contact angle measurement

The contact angles were measured by the sessile drop method^{14,15} using a Contact Angle System (OCA20) from Particle and Surface Science Pty Ltd.

DIM, glycerol, and water were spread onto the PAM surface. Every contact angle was measured 15 times, the average value was taken as the result, and they are listed in Table II. Surface tension components of these three liquids are listed in Table III. The surface tension components of PAM were calculated by eq. (3), and the result is shown in Table III.

TABLE III
Surface Tension Components of PAM
and the Four Solvents (mJ/m²)

	γ	γ^{LW}	γ^+	γ^-
PAM	62.33	45.32	1.88	38.56
Water ^a	72.8	21.8	25.5	25.5
DIM ^a	50.8	50.8	0	0
Glycerol ^a	64	34	3.92	57.4
EG ^a	48	29	3.0	30.1

^a Ref. 9.

TABLE IV
Apparent Surface Tension (γ_L) of Cosolvents (mJ/m²) and their Contact Angles (θ) on the Apolar Surface

Second solvent volume fraction	Acetone		Ethanol		DMF		EG	
	θ	γ_L	θ	γ_L	θ	γ_L	θ	γ_L
0.2	80.00	48.24	80.00	36.71	93.22	58.61	95.26	65.72
0.4	70.13	37.78	64.28	31.03	86.12	53.18	92.00	60.34
0.6	55.18	31.55	57.1	29.69	76.86	48.15	88.3	55.82
0.8	43.55	26.92	47.69	29.77	66.71	42.69	85.7	52.85
1.0		25		21		37		48

DIM was spread on the surface of the POE film to determine its surface tension. Water–acetone, water–ethanol, water–DMF, water–EG cosolvents were dropped onto the apolar POE surface. The contact angles were averaged from 15 measurements, and the results are listed in Table IV.

Apparent surface tension measurement

The apparent surface tension was measured by the suspended drop method using the OCA20 instrument.

The apparent surface tension of cosolvents was measured five times, and the average values are listed in Table IV. The apparent surface tension of PAM aqueous solutions with NaCl, glucose, and SDS as additives were measured.

Cosolvent polarity

The apparent surface tension and contact angle of cosolvents on an apolar surface are listed in Table IV. The results were used to calculate the cosolvent polarity according to eqs. (7) and (8). The apolar contribution and polarity of the cosolvents are listed in Table V.

RESULTS AND DISCUSSION

PAM monopolar nature

PAM is generally accepted as a hydrophilic polymer. Quantitatively measuring the hydrophilicity has never been done before, according to our knowledge. There are three parameters that are quantitative expressions of hydrophilicity or hydrophobicity.¹⁶ (1) One is the

free energy of interfacial interaction, ΔG_{iwi} (substance i and water), and this will be discussed later. (2) Another is the free energy of adhesion for formation of the i –water interface, ΔG_{iw}^{adh} , and it is equivalent to the free energy of hydration of substance i in a two-phase system. (3) The third one is the value of γ^- , that is a semiquantitative indicator of the degree of hydrophilicity. The higher the value γ^- , the higher will be the degree of hydrophilicity. To obtain the γ^- value, the PAM surface tension components have to be determined, and these were calculated from the contact angle measurements.

As DIM has the highest value of γ^{LW} and zero contribution from γ^+ and γ^- among the solvents for which surface tension components were known, DIM is taken to measure the γ^{LW} of the solid surface. The γ^{LW} of PAM is 45.32 mJ/m² according to this measurement. For the two polar solvents, each of the total surface tensions must be larger than 45.32 mJ/m², which keeps $\cos\theta$ within 0–1, so that the value of θ is measurable. Only three solvents were available to fit this criteria: water, glycerol, and formamide.¹⁰ Here, water and glycerol were chosen, the contact angles were measured immediately after the drop stopped advancing. The contact angles for three solvents (DIM, water, and glycerol) on PAM are listed in Table II, and the surface tension components of PAM, DIM, water, and glycerol are listed in Table III. Even a very small difference in contact angle measurement can result in a great variation in the calculation of the surface tension components, so an average of 15 measurements was used to determine the contact angles.

The results in Table III show that for PAM, the value of $\gamma^- \gg \gamma^+$, which means PAM is a monopolar

TABLE V
Apolar Contribution γ^{LW} (mJ/m²) and the Polarity γ_{rel}^{AB} of the Cosolvents

Second solvent volume fraction	Acetone		Ethanol		DMF		EG	
	γ^{LW}	γ_{rel}^{AB}	γ^{LW}	γ_{rel}^{AB}	γ^{LW}	γ_{rel}^{AB}	γ^{LW}	γ_{rel}^{AB}
0.2	21.67	0.55	12.54	0.66	20.68	0.65	24.08	0.63
0.4	17.31	0.54	13.38	0.57	21.78	0.59	22.91	0.62
0.6	16.60	0.47	14.18	0.52	23.60	0.51	22.32	0.60
0.8	14.57	0.46	16.76	0.44	23.98	0.44	21.81	0.59

TABLE VI
 ΔG_{121} Values for PAM in Five Different
 Polar Solvents (mJ/m²)

	Water	EG	Acetone	Ethanol	DMF
PAM	8.56 [eq.(5)] 8.76 [eq.(6)]	-2.58	-74	-84	-50

material, of which most are water soluble. The strength of a monopole is expressed by δ , $\delta = \sqrt{\gamma_s^- / \gamma_w^-}$, where γ_w^- is the water's electron-donor parameter, which is 25.5 mJ/m². The δ must have a minimum value of 1.055 for repulsion to occur, which means that γ^- must be greater than 28.3 mJ/m².⁴ A compound with γ^+ between 0–1 mJ/m² and $\gamma^- > 28.3$ mJ/m² is genuinely hydrophilic. (Although for PAM, $\gamma^+ = 1.88$ mJ/m², which is slightly greater than 1 mJ/m², PAM is still a hydrophilic material.) The total surface tension of PAM is 62.33 mJ/m², which was calculated by eq. (2). The surface tension components confirmed the PAM hydrophilic monopolar nature.

When a monopolar material is immersed in water, its molecules will tend to repel each other, and this finally leads to dissolution. For a crosslinked gel, the repellency can lead to swelling. The γ^- value can be used to compare the hydrophilicity of different water-soluble polymers. For example, the γ^- value of polyvinylpyrrolidone (PVP) is 29.7 mJ/m²,¹⁶ for polyethylene glycol (PEO) it is 64 mJ/m²,^{4,16} and for PAM it is 38.56 mJ/m² according to our calculations. Therefore, the hydrophilicity of PAM is better than PVP, but not as good as PEO.

Solubility of PAM in pure polar solvents

The value of ΔG_{iwi} can be used to express the hydrophilicity of substance i . Similarly, the value of ΔG_{121} can be used to express the solvophilicity of substance 1 in solvent 2. Here, substance 1 was always PAM, and solvents range from water to acetone, ethanol, DMF, and EG. As PAM is miscible with water and EG, the solubility of PAM in water and EG was calculated according to eq. (4) and (5). The water–PAM interfacial force could also be calculated according to eq. (6), using the contact angles from Table II. PAM is immiscible with acetone, ethanol, and DMF. The solubility of PAM in these three solvents was calculated according to eqs. (4) and (6). All of the θ values of acetone, ethanol, and DMF on a PAM surface were taken as 0, because the surface tension of these three solvents was too small, they could not form drops on the PAM surface. The surface tension components of water and EG are listed in Table III. The apparent surface tension of acetone, ethanol, and DMF is listed in Table IV.

The calculated values of ΔG_{121} for PAM in the different five solvents are listed in Table VI. The value of

ΔG_{121} for EG is slightly below 0; however, the PAM is still miscible in EG. (For example, the ΔG_{121} value for agarose–water is -4.2 mJ/m², although agarose can be dissolved in water at an elevated temperature, but becomes a gel at low temperature; for glycerol–formamide ΔG_{121} is -1.2 mJ/m², and the two solvents are still miscible.)⁴ By comparison of the value of ΔG_{121} , it can be seen that the solvophilicity of PAM in water is greater than in EG. From these calculations, we can deduce that a PAM gel would have a greater swelling ratio in water than in EG. Previously, the conformation study by the viscosity measurement of PAM diluted water and EG solutions showed that the PAM chains in water was more extended than in EG, which means that a PAM gel should swell more in water than in EG.¹⁷ This solubility and viscosity study provided the same conclusion from a different point of view. The values of ΔG_{121} for acetone, ethanol, and DMF were much smaller than 0, so it can be concluded that the PAM molecules cannot repel each other in these three solvents; there would be no swelling when PAM gel is placed in these three solvents.

Cosolvent polarity

For the ternary systems, VCG used the symbol ΔG_{132} to show the free energy change, which means polymer 1 and 2, dissolved in solvent 3 (two solutes and one solvent); and $\Delta G_{132} = \gamma_{12} - \gamma_{13} - \gamma_{23}$. When $\Delta G_{132} > 0$, mixing will be favored, and when $\Delta G_{132} < 0$, phase separation will occur.¹⁸ In our case, the ternary systems are that polymer is dissolved in cosolvents (one solute and two solvents). This is more complicated because: (1) the two solvents can interaction with each other to form a complex; (2) the two solvent fractions could change, and that can cause the polarity and the apparent surface tension of the cosolvent systems to change. Under this situation (ternary system containing two solvents and one solute), the ΔG_{132} value is not suitable to provide the free energy change. Another approach must be used.

In the pharmaceutical industry, organic solvents are often used to enhance the solubility of drugs in aqueous solutions.^{5,19,20} The effect on the water solubility of organic compounds of adding one or more completely water-miscible organic cosolvent is defined as cosolvency. Decreasing the polarity of a cosolvent would be favorable for hydrophobic solutes, and increasing the polarity would be favorable for hydrophilic solutes. The cosolvent polarity is used as an index of the cosolvency. If a hydrophilic material has a monopolar nature, it will repel other like molecules more strongly when the polarity becomes higher, and the repulsion results in dissolution. Instead of using total surface tension as index of polarity,⁵ here we use γ_{rel}^{AB} [see eq. (7)] as index of solvent polarity, and this

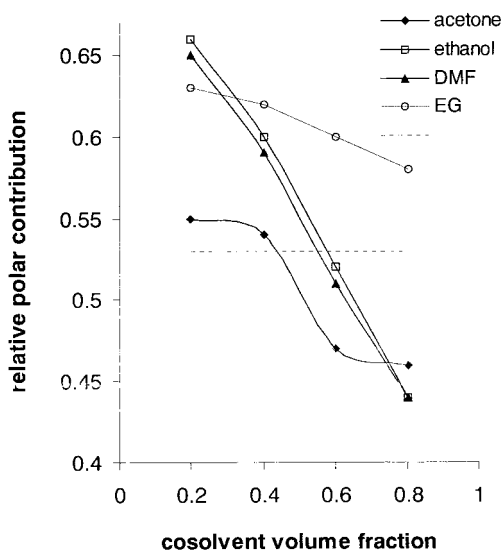


Figure 1 The polarity (γ_{rel}^{AB} , relative polar contribution) of the cosolvents vs the volume fraction of the second solvent.

value is more reasonable, because it shows the relative polar contribution to total surface tension.

The POE surface tension only has a contribution from γ^{LW} , and the value was determined by contact angle measurement. DIM drops on the POE surface were used for the measurement, as DIM also only had a contribution from γ^{LW} . The contact angle θ was 45, and γ^{LW} of POE is 37 mJ/m² from eq. (8). By measuring the apparent surface tension of a cosolvent and its contact angle on the POE apolar surface, the apolar surface tension component of this liquid was calculated using eq. (8). Then the polarity of the liquid was obtained according to eq. (7). The results are listed in Table V. Figure 1 shows the polarity of the cosolvents vs the second solvent volume fraction. Combining the solubility results in Table I, it shows that when the polarity of the cosolvent is larger than about 0.50–0.53 (while for a liquid, the polar contribution is greater than the apolar contribution), then the repulsion of PAM molecules is greater than the attraction, and this results in dissolution. The higher the polarity, the higher will be the solubility of the hydrophilic solute. Notice that the polarity of all the EG cosolvents is larger than 0.53. There are only slight differences between EG fractions, which suggests that the solubility will increase slightly when the EG fraction decreases. Previously, viscosity measurements were used to compare the polymer chain conformations; however, this method did not show the slight differences.¹⁷ Figure 1 also demonstrates that the acetone cosolvents have the smallest polarity compared with the other three cosolvents. Therefore, acetone will be the best precipitant for PAM.

When a hydrophilic material is immersed in water, there are two different interactions with water: (1)

hydrophobic interaction, which is caused by the free energy of cohesion of water due to hydrogen bonding, and this interaction is always attractive;²¹ (2) hydrophilic interaction, which is caused by a net negative interfacial tension, although under these conditions, the system has a thermodynamically unstable interface, so repulsion occurs until the interfacial tension becomes zero.¹⁶ Only when the repulsion overcomes the attraction will dissolution occur. Similarly, when a material is immersed in a solvent, the solvophobic interactions and solvophilic interactions coexist, the material cannot be dissolved in this solvent if the solvophobic interaction is great enough. For PAM immersion in a cosolvent, because PAM is hydrophilic to water, but solvophobic to the second solvent (acetone, ethanol, or DMF), when the second solvent composition is increased, the total solvophobic interaction would finally overcome the hydrophilic interaction and precipitation will occur. For water–EG cosolvent systems, as PAM was solvophilic to both water and EG, the repulsion will always be stronger than the attraction, so PAM can be dissolved in these cosolvent systems, regardless of the second solvent composition.

Apparent surface tension of aqueous solutions

Apparent surface tension is a sensor of surface activity. When a substance with surface activity is absorbed into to a liquid surface, the apparent surface tension of the liquid will decrease until the substance reaches saturation on the surface. For a polymer, when it has larger molecules or it has a more expanded conformation, it will be absorbed less on the surface, then the surface tension will decrease less compared with a smaller or more compacted molecule.²² Therefore, surface tension measurements can be used to characterize the molecular size or conformational change of a polymer.

In these experiments, PAM was dissolved in aqueous solutions with NaCl, glucose, and SDS as additives. When the concentration of additive changed, the polymer conformation also changed. Unfortunately, surface tension measurements were not sensitive enough to quantitatively measure this change. Previously viscosity measurements were used, and they showed that the PAM conformation changed when the concentration of additive changed.¹⁷

CONCLUSIONS

The swelling property of PAM gel was studied from a new point of view—solvophilicity. Based on VCG method and theory, the solubility of PAM in certain solvents was studied, and it was found that:

1. The water-soluble polymer PAM has a monopolar surface nature. According to contact angle measurements and calculations, the electron-do-

nor parameter was greater than the electron acceptor parameter. The molecules will repel each other in polar solutions, resulting in dissolution. Swelling property of gel is caused by the hydrophilicity of corresponding linear polymer.

2. For PAM–solvent binary systems, the free energy change, ΔG_{121} , was used to quantitatively indicate the solvphilicity or solvphobicity of PAM in five different pure polar solvents. It was found that the PAM solvphilicity for water was higher than EG, but it was solvphobic for acetone, ethanol, and DMF. Therefore, a PAM gel would have a greater swelling ratio in water than in EG, and there would be no swelling in acetone, ethanol, and DMF.
3. For PAM and cosolvent ternary systems, the relative polar contribution of γ_{rel}^{AB} surface tension was used as an index of polarity for the cosolvent systems. It was found that when the polarity of a cosolvent was greater than 0.50–0.53, the monopolar PAM will be dissolved in that cosolvent system. For higher polarity, the solubility of PAM will be greater. For the water–EG system, the solubility will slightly decrease as the EG composition increased. Acetone was the best precipitant for PAM compared with the three other polar solvents.
4. The measurement of apparent surface tension for PAM aqueous solutions was not sensitive enough to show the polymer conformation change.

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