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Swelling behavior of strong polyelectrolyte poly(*N*-*t*-butylacrylamide-co-acrylamide) hydrogels

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Abstract

Temperature-sensitive ionic hydrogels based on *N*-*t*-butylacrylamide (TBA), acrylamide (AAm), 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) and *N*,*N*′-methylenebis(acrylamide) (BAAm) monomers were prepared. The molar ratio of TBA to the monomers AAm and AMPS was fixed at 60/40, while the AMPS content of the hydrogels was varied. The elastic modulus of the hydrogels was in the range of 347–447 Pa, much lower than the modulus of PAAm or poly(*N*-isopropylacrylamide) hydrogels due to the reduced crosslinking efficiency of BAAm in TBA/AAm copolymerization. The hydrogels exhibited swelling–deswelling transition in water depending on the temperature. Increasing ionic group (AMPS) content resulted in shifting of the transition temperature interval in which the deswelling takes place. The higher the ionic group content, the broader the temperature interval at the phase transition. Ionic hydrogels exhibited first-order reentrant conformational transitions in ethanol–water and in dimethylsulfoxide (DMSO)–water mixtures. The higher the ionic group content of the hydrogels the narrower the ethanol (or DMSO) range in which the reentrant phenomena occur. By taking into account the difference of the solvent mixture composition inside and outside the gel, the equilibrium swelling theory provided a satisfactory agreement to the experimental swelling data of the hydrogels immersed in the solvent mixtures.

Keywords: 2-acrylamido-2-methylpropane sulfonic acid sodium salt; *N*-*t*-butylacrylamide; Swelling; Temperature-sensitive hydrogels; Transitions

1. Introduction

Temperature-sensitive polymer–solvent systems have received considerable attention due both to fundamental and technological interests [1]. The temperature sensitivity of polymer solutions or polymeric gels is associated with the temperature dependence of hydrogen bonding and hydrophobic interactions [2]. At lower temperatures, water molecules in the vicinity of hydrophobic polymer chains are highly hydrogen bonded. Since these hydrogen bonding interactions lower the free energy of mixing considerable, the polymer chains dissolve or swell in water at low temperatures. At higher temperatures, the hydrogen bonds weaken; the contact between water and hydrophobic surfaces, i.e., the hydrophobic interaction increases [3]. As a result, on heating a polymer solution or a polymer gel, a transition from swollen to collapsed state occurs at a critical temperature.

Poly(*N*-isopropylacrylamide) (PNIPA) gel is a well known temperature-sensitive gel exhibiting volume phase transition at approximately its lower critical solution temperature (LCST), i.e., at 34 °C [4,5]. Below this temperature, the gel is swollen and it shrinks as the temperature is raised. The modification of the LCST of temperature-sensitive gels is of primary interest [6–11]. A decrease in the LCST can be achieved by increasing the hydrophobicity of the network chains.

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Recently, we investigated a series of hydrogels based on *N-t*-butylacrylamide (TBA) and acrylamide (AAm) monomers of various molar ratios [12]. It was shown that the hydrogels with 40–60% TBA by mole exhibit temperature sensitivity. While for the 60% TBA gel, the temperature interval for the deswelling transition was in the range from 10 to 28 °C, for the 40% TBA gel, the deswelling started at around 20 °C and continued until the onset of the hydrolysis of the network chains at 64 °C. In all the TBA/AAm hydrogels, however, the volume phase transitions took place in a broad range of temperature and, it was not as sharp as what it was in PNIPA gels. According to the swelling theories, a discontinuous (first-order) volume phase transition in polymer networks can be achieved by decreasing the initial monomer concentration of the gel forming system and/or by introduction of charged groups into the network chains [2,13]. In the present work, we decreased the initial monomer concentration and also included a strong electrolyte ionic comonomer, 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS), into the TBA/AAm comonomer mixture. The free radical crosslinking copolymerization reactions of TBA, AAm, AMPS and the crosslinker *N,N′*-methylenebis(acrylamide) (BAAm) were carried out in *t*-butanol–water mixture (1:1 by volume) as the polymerization solvent in the presence of potassium persulfate as the initiator. In this way, a series of poly(*N-t*-butylacrylamide-co-acrylamide) (abbreviated henceforth as TBA/AAm) hydrogels with various charge densities was prepared and their swelling degrees in water at various temperatures were determined.

Swelling behavior of hydrogels in solvent mixtures is also of considerable interest to many applications of membranes, including drug delivery and pervaporation. Hydrophobically modified hydrogels are known to exhibit reentrant phenomena in solvent mixtures, in which the hydrogels first deswell but then reswell if the solvent composition is continuously varied [14–18]. Here, we also investigated the swelling behavior of strong polyelectrolyte TBA/AAm hydrogels in water–DMSO and in water–ethanol mixtures; the observed phenomena were explained within the framework of the equilibrium swelling theories.

2. Experimental

2.1. Materials

AAm (Merck) was crystallized from acetone/ethanol mixture (70/30 by volume) below 30 °C. TBA (Fluka), BAAm (Merck) and potassium persulfate (KPS, Merck) were used as received. 2-acrylamido-2-methylpropane sulfonic acid (Merck) was crystallized from boiling methanol. It was neutralized with NaOH and a stock solution was prepared containing 0.966 M AMPS. Distilled and deionized water and reagent-grade solvents *t*-butanol, dimethylsulfoxide (DMSO), and ethanol were used without further purification.

2.2. Synthesis of hydrogels

In our previous work, TBA/AAm hydrogels were prepared in methanol as the polymerization solvent using 2,2′-azobisisobutyronitrile (AIBN) as the initiator [12]. The initial monomer concentration was 20 w/v%. As pointed out in the Section 1, in order to induce a discontinuous volume change during the phase transition in gels, we decreased here the monomer concentration from 20 to 5 w/v% and included the ionic comonomer AMPS into the monomer mixture. At this monomer concentration, however, preliminary experiments showed no gel formation in methanol. A set of experiments was carried out to find the optimum reaction condition. Several solvents including methanol, ethanol, *t*-butanol, 2-isopropanol, as well as their mixtures with water were tested. Complete monomer conversions and reproducible results were obtained in *t*-butanol–water mixture (1:1 by volume) using KPS as the initiator. Compared to AIBN, KPS was found to be successful to initiate and to complete the reactions at 50 °C. The following synthesis parameters were fixed throughout this study while the ionic group (AMPS) content of the hydrogels was varied between 0 and 2 mol%:

[TBA]/[AAm + AMPS]	60/40
[BAAm]/[TBA + AAm + AMPS]	1/80
[KPS]/[TBA + AAm + AMPS]	1/500
The total monomer concentration	5 w/v%
Polymerization temperature	50 °C
Polymerization time	24 h

To illustrate the synthetic procedure, we give details for the preparation of the hydrogel with 1 mol% AMPS in the monomer feed composition.

TBA (0.359 g), AAm (0.130 g), AMPS stock solution (0.049 mL), BAAm (0.0091 g), and KPS (0.0025 g) were dissolved in *t*-butanol–water mixture to give a total volume of 10 ml. After bubbling nitrogen for 15 min, the solution was poured into several glass tubes of about 5 mm internal diameters and about 15 cm long. The glass tubes were then sealed, immersed in a thermostated water bath at 50 ± 0.2 °C and the polymerization was conducted for 24 h. Homologous series of hydrogels were prepared in this way allowing variation of the AMPS content of the monomer mixture.

After polymerization, the reaction was stopped by cooling the reaction mixture in an ice-water bath. The crude hydrogels, 5 mm in diameter, were freed from the glass tubes and they were cut into samples of about 10 mm length. Each sample was placed in an excess of water, and water was replaced many times. The hydrogels after extraction were carefully deswollen in acetone. The hydrogel samples were then dried at room temperature under vacuum to constant weight. Dilution degree of the hydrogels after preparation q_F was calculated as

$$q_F = \frac{m_0}{m_{dry}} \tag{1}$$

where m_0 and m_{dry} are the weights of the hydrogel after preparation and after drying, respectively. The volume fraction of the crosslinked polymer after gel preparation v_2^0 relates to the dilution degree q_F through the equation:

$$v_2^0 = \left(1 + \frac{(q_F - 1)\rho}{d_1}\right)^{-1} \tag{2}$$

where ρ and d_1 is polymer and the solvent (*t*-butanol-water 1:1) densities. The q_F and v_2^0 values of the hydrogels with 0.5–2 mol% AMPS are collected in Table 1. Note that the non-ionic TBA/AAm hydrogel was very soft and sticky so that a few drops of methanol have to be added on the gel samples after their preparation to separate them from the glass surface. Therefore, q_F of the non-ionic gels cannot be determined.

2.3. Swelling measurements

After crosslinking copolymerization, the initial diameters of the gel samples D_0 were measured by a calibrated digital compass. Then, each sample was placed in an excess of solvent or solvent mixture at a given temperature. In order to reach the equilibrium degree of swelling, the hydrogels were immersed in solvents for at least one week during which solvent was replaced every other day; the swelling equilibrium was tested by weighing the samples, or by measuring their diameters. To achieve good precision, three measurements were carried out on samples of different length taken from the same gel. The equilibrium volume swelling ratio of the hydrogels with respect to the after preparation state V/V_0 (volume of swollen gel/volume of the gel after preparation) was calculated as

$$V/V_0 = \left(\frac{D}{D_0}\right)^3 \tag{3}$$

where D is the diameter of hydrogels after equilibrium swelling in solvent. The standard deviations of the measured swelling ratios were less than 10% of the mean.

Table 1
The characteristic data of the hydrogels

AMPS (mol%)	q_F	v_2^0	G$_0$ (Pa)	N
0.5	12.7	0.053	347	20 900
1.0	12.0	0.057	382	20 400
1.5	11.1	0.061	403	20 700
2.0	9.6	0.071	447	21 700

q_F = dilution degree of the hydrogels after preparation (mass of gel after preparation/mass of dry gel), v_2^0 = volume fraction of the crosslinked polymer after gel preparation, calculated using Eq. (2) with $d_1 = 0.89$ g/ml, and $\rho = 1.35$ g/ml (the density of PAAm), G_0 = elastic modulus of gels after their preparation, N = number of segments between two successive crosslinks of the network.

2.4. Mechanical measurements

Uniaxial compression measurements were performed on hydrogels after their preparation. All the mechanical measurements were conducted in a thermostated room of 23 ± 0.5 °C. The stress–strain isotherms were measured by using an apparatus described before [19]. The measurements were conducted up to about 15% compression. The elastic modulus G_0 after gel preparation was determined from the slope of linear dependence [20]:

$$f = G_0(\lambda - \lambda^{-2}) \tag{4}$$

where f is the force acting per unit cross sectional area of the undeformed gel specimen, and λ is the deformation ratio (deformed length/initial length). From the repeated measurements, the standard deviations in the G_0 value were less than 3%. For a homogeneous affine network of Gaussian chains, the elastic modulus of gels G_0 is related to the network crosslink density by [20,21]

$$G_0 = (NV_1)^{-1} RT v_2^0 \tag{5}$$

where N is the number of segments between two successive crosslinks, V_1 is the molar volume of a segment, which is taken as the molar volume of water (18 ml/mol), R and T are in their usual meanings. The elastic moduli of the hydrogels together with their crosslink densities in terms of N are shown in columns 4 and 5 of Table 1.

3. Results and discussion

A series of TBA/AAm hydrogels was prepared at various charge densities between 0 and 2 mol%. The hydrogels with >2 mol% AMPS were too weak to withstand the mechanical and the swelling measurements. As seen in Table 1, the volume fraction of crosslinked polymer after gel preparation v_2^0 slightly increases with AMPS% from 0.053 to 0.071. The elastic moduli G_0 of the hydrogels are in the range of 347–447 Pa, also slightly increasing function of AMPS%. From G_0 and v_2^0 values together with Eq (5), the number of segments between two successive crosslinks was calculated as $N = 20\,900 \pm 560$ for all the hydrogels (Table 1). Assuming that all the crosslinker (BAAm) molecules formed effective crosslinks in the network, the chemical crosslink density N_{chem} can be calculated using the equation $N_{\mathrm{chem}} = 0.5\overline{V}_{\mathrm{r}}/(XV_1)$ where X is the crosslinker ratio (molar ratio of crosslinker to monomer) and $\overline{V}_{\mathrm{r}}$ is the average molar volume of polymer repeat unit. Using $X = 1/80$, $V_1 = 18$ ml/mol, and $\overline{V}_{\mathrm{r}} = 77.5$ ml/mol, N_{chem} was calculated as 172. The difference between the effective and chemical crosslink densities indicates that 99% of the crosslinker BAAm were wasted during the crosslinking copolymerization, probably due to the cyclization and multiple crosslinking reactions [22]. This amount of wasted BAAm is much higher than that found in the crosslinking polymerization of AAm or *N*-isopropylacrylamide monomers [23,24].

In Fig. 1, the swelling ratio V/V_0 of the hydrogels in water at 23 °C is plotted as a function of their ionic group (AMPS%) contents. For comparison, the swelling ratios of PNIPA and PAAm hydrogels having similar chemical crosslink densities were also included in the figure. The data for PNIPA and PAAm gels were taken from the literature [23,24]. As expected, the swelling ratio increases with AMPS% due to the simultaneous increase of the mobile counterion (Na^+) concentration inside the gel because of the condition of electroneutrality. The concentration difference of Na^+ between the inside and the outside of the gel creates an additional osmotic pressure that swells the gel. Fig. 1 also shows that the rate of increase of the equilibrium swelling ratio with the AMPS% is much more rapid in TBA/AAm hydrogels than in PNIPA or PAAm hydrogels. This is a result of the reduced crosslinking efficiency of BAAm in the TBA/AAm copolymerization. Indeed, the elastic moduli of TBA/AAm hydrogels are 347–447 Pa, compared to 3000–6000 Pa reported for PAAm and PNIPA hydrogels of the same polymer and crosslinker concentrations [23,24].

Fig. 2 shows the temperature influence on the swelling behavior of TBA/AAm hydrogels of various AMPS content. The gel samples were left at least 5 days at a given swelling temperature to reach the true swelling or shrinking equilibrium. The swelling data were recorded during both heating and cooling processes. The swelling curves obtained during the heating process can also be reproduced during the cooling process. The swelling data of the non-ionic TBA/AAm hydrogel prepared at $v_2^0 = 0.25$ were also included in the figure for comparison. It is seen that the gels are swollen at low temperatures while they are collapsed at high temperatures. Although the decrease of v_2^0 from 0.25 to 0.05 increased the extent of volume change during the phase transition, the volume changes still occur over a wide range of temperature, even in case of ionic gels. One can also see that increasing ionic group content results in shifting of

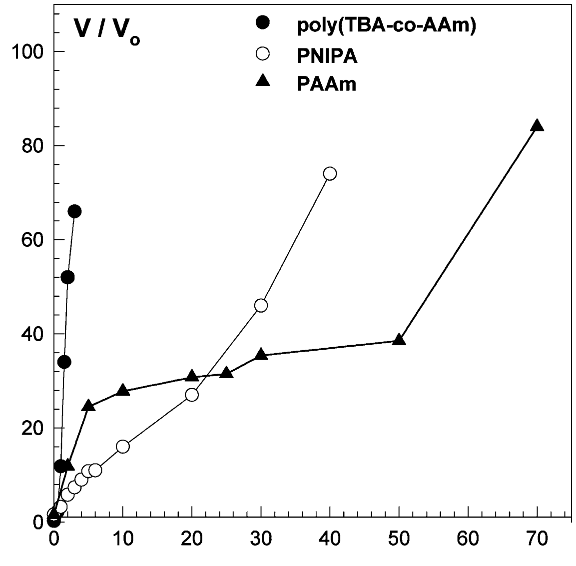

Fig. 1. The equilibrium volume swelling ratios of the hydrogels V/V_0 in water shown as a function of their AMPS contents. (●) TBA/AAm hydrogels, the monomer concentration (c) = 5 w/v%, the crosslinker ratio (molar ratio of crosslinker to monomer, X) = 1/80. (▲) PAAm hydrogels, $c = 5$ w/v%, $X = 1/82$. (○) PNIPA hydrogels, $c = 8$ w/v%, $X = 1/85 - 1/126$. The data for PAAm and PNIPA gels were taken from the literature [23,24]. The curves only show the trend of data.

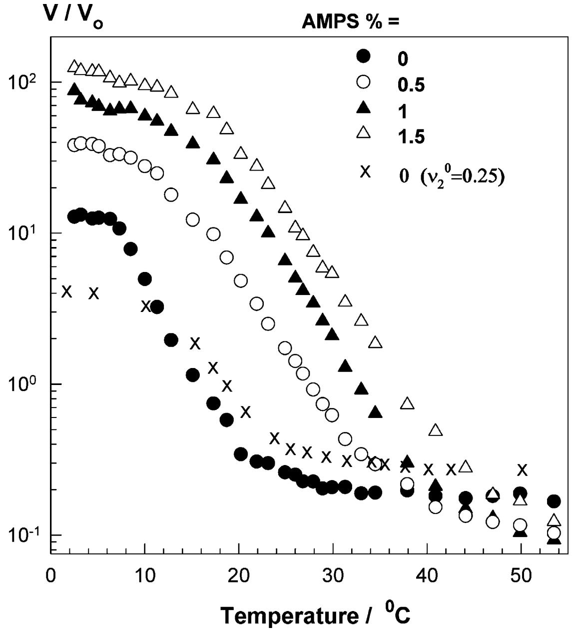

Fig. 2. The equilibrium volume swelling ratios of the hydrogels V/V_0 in water shown as a function of the temperature. The AMPS contents of the hydrogels are indicated in the figure. The swelling data for the non-ionic hydrogel prepared at $v_2^0 = 0.25$ were taken from the literature [12].

the transition temperature interval in which the deswelling takes place. For example, the temperature intervals for the deswelling transition are in the range 8–22 °C and 15–46 °C for the hydrogels with 0 and 1.5 mol% AMPS, respectively. Thus, as the ionic group content is increased, the temperature interval at the phase transition becomes even broader. This result contradicts the prediction of the theories because the osmotic pressure of the counterions should induce discontinuous volume change in ionic gels. This unusual feature, which has not been reported before for temperature-sensitive hydrogels, can be explained with the heterogeneity in the molecular-level chemical composition of the network chains. Although the overall composition of the network chains is equal to the monomer feed composition, TBA and AAm segments may distribute along the network chains heterogeneously due to the different solubilities of the monomers [12]. TBA-rich network chains will undergo the phase transition earlier, i.e., at lower temperatures than the other chains. According to this picture, the network chains will shrink gradually depending on their composition, which will alter the overall dimension of the gel sample continuously. The broadening of the temperature interval at the phase transition on rising AMPS% also supports this explanation.

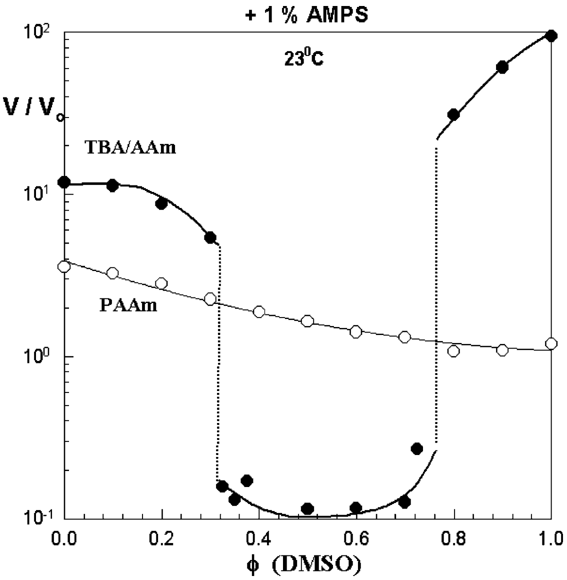

Fig. 3. The equilibrium volume swelling ratios of the hydrogels V/V_0 in DMSO–water mixtures shown as a function of the DMSO volume fraction ϕ in the solution. The filled and open symbols represent the data of TBA/AAm and PAAm hydrogels, respectively, both with 1 mol% AMPS. The solid curves show the trend of data. The dotted vertical lines illustrate the phase transition regions.

The swelling measurements were also carried out in DMSO–water, and ethanol–water mixtures at 3 and 23 °C. The results are collected in Figs. 3–5 as the dependence of the gel volume on the volume fraction of the cosolvent in the external solution ϕ. The solid curves only show the trend of data. The dotted vertical lines illustrate the phase transition regions. It is seen that all the TBA/AAm hydrogels exhibit reentrant conformational transitions in these solvent mixtures. In Fig. 3, the swelling behavior of a TBA/AAm gel in DMSO–water mixtures is compared with that of a PAAm gel, both with 1 mol% AMPS. The TBA/AAm gel first deswells slightly with increasing ϕ from 0 to 0.30. If ϕ crosses 0.30, the gel undergoes a first-order collapse transition and remains in the collapsed state up to $\phi = 0.73$. If ϕ is further increased, the gel undergoes a first-order recollapse transition and remains in the swollen state up to $\phi = 1$. Thus, in this ternary system, an insolubility gap exists between $\phi = 0.30$ and 0.73, in which both water and DMSO separate out of the network phase. In contrast to the TBA/AAm gel, PAAm gel slightly deswells on increasing the DMSO concentration in the external solution. This demonstrates that the *t*-butyl groups on the network chains are responsible for the observed reentrant phenomena of the hydrogel in DMSO–water mixtures. As seen in Fig. 3, the volume of TBA/AAm gel in pure DMSO is about 100-fold larger than that of the PAAm gel, indicating that the incorporation of TBA segments on the network chains creates attractive interactions between the network segments and DMSO. Thus, water and DMSO taken separately are good solvents for TBA/AAm network. However, in mixtures, the attractive water–DMSO interactions seem to dominate over water–TBA/AAm or DMSO–TBA/AAm interactions so that the gel deswells in DMSO–water mixtures.

Figs. 4 and 5 illustrate the effect of the ionic group content of the hydrogels on their swelling behavior in DMSO–water and in ethanol–water mixtures, respectively. The measurements were carried out at 3 and 23 °C. The shaded areas in the figures show the collapsed regions. In uncharged gels, the reentrant phase transitions occur smoothly, while in ionic gels, they occur rapidly as first-order phase transitions. The higher the ionic group content of the hydrogels the narrower the DMSO range in which the reentrant phenomena occur. On the other hand, the non-ionic gel, which is in collapsed state in water at 23 °C, remains in the collapsed state up to a critical DMSO or ethanol content above which it undergoes a swelling transition.

Comparison of Figs. 4 and 5 also shows that both the collapse and recollapse transitions occur earlier, if DMSO is replaced with ethanol. This is also illustrated in Fig. 6 showing V/V_0 versus ϕ plots for the hydrogel with 0.5 mol% AMPS immersed in ethanol–water and in DMSO–water mixtures. The variation of the reentrant phase transition regions depending on the type of the solvent can be explained with the higher extent of hydrogen bonding interactions between ethanol and water

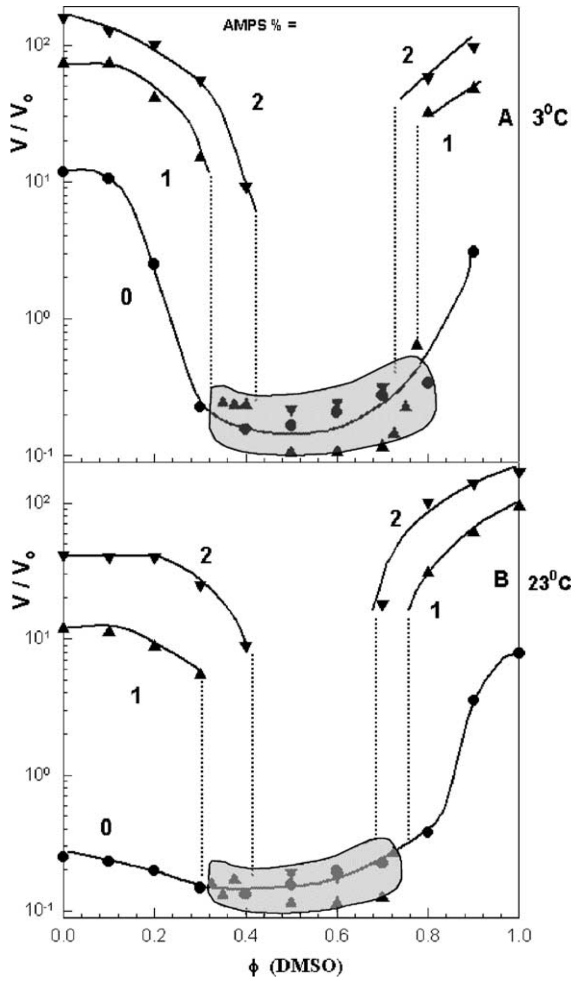

Fig. 4. The swelling ratios of the hydrogels V/V_0 in DMSO–water mixtures shown as a function of the DMSO volume fraction ϕ in the solution. The AMPS contents of the hydrogels are indicated in the figure. The swelling temperature: 3 °C (A) and 23 °C (B).

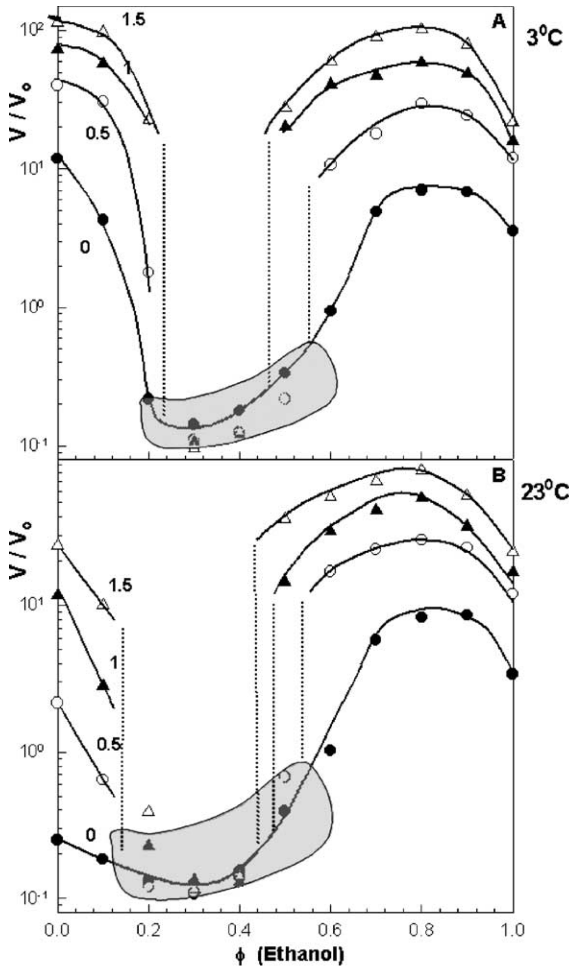

Fig. 5. The swelling ratios of the hydrogels V/V_0 in ethanol–water mixtures shown as a function of ethanol volume fraction ϕ in the solution. The AMPS contents of the hydrogels are indicated in the figure. The swelling temperature: 3 °C (A) and 23 °C (B).

compared to those between DMSO and water. The hydrogen bonding solubility parameters for ethanol and DMSO are 19.4 and 10.2 MPa$^{1/2}$, respectively, indicating that ethanol forms more hydrogen bonds with water than DMSO [25]. When water is mixed with ethanol, heat evaluation and a large decrease in entropy are observed suggesting the mixing process leads to degradation of the ordered water clusters and to the formation of more hydrogen bonds in the mixtures as compared with either liquid alone [26]. In the presence of a hydrophobic polymer such as the TBA/AAm hydrogel, water molecules form clusters around the hydrogel due to the hydrophobic interaction. When ethanol is added to water, ethanol molecules like to stay in the solution due to the strong interaction between ethanol and water which reduces the gel swelling. The decrease in the gel swelling will increase the intramolecular hydrophobic interactions of the *t*-butyl groups, which may promote further shrinkage of the TBA/AAm gel. On the other hand, at high ethanol concentration ϕ, attractive polymer–ethanol interactions dominate over the ethanol–water interactions due to the increased number of contacts between ethanol molecules and TBA segments. As a result, ethanol enters into the gel phase and results in gel swelling. As the ethanol concentration ϕ is decreased, water–ethanol interactions start to dominate so that the gel deswells. Thus, the competing attractive interactions between water–ethanol (DMSO) and polymer–ethanol (DMSO) result in the reentrant conformational transitions in the network. This mechanistic picture explains the phenomena shown in Figs. 3–5.

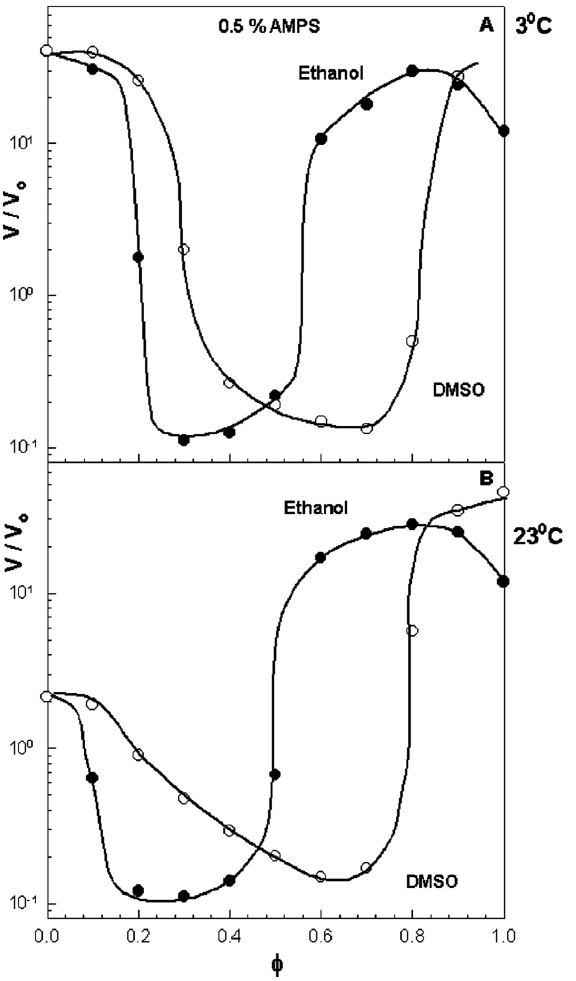

Fig. 6. Comparison of the swelling behavior of the hydrogels in ethanol–water and DMSO–water mixtures. The swelling temperature: 3 °C (A) and 23 °C (B).

To analyze the volume phase transition of gels in solvent mixtures, a single liquid approximation has often been used. In this approximation, the composition of the solvent mixture is assumed to be identical inside and outside the gel. However, phase transitions can be described more accurately by taking into account the difference of the solvent mixture compositions inside and outside the gel phase. In the following paragraphs, we consider a gel system consisting of three components i; two liquid components ($i = 1$ for water, and $i = 3$ for DMSO or ethanol) and a polymer segment ($i = 2$). Let the number of segments on the component i be x_i. The interactions between the components i and j are represented by the interaction parameter χ_{ij} ($i \neq j$, $\chi_{ij} = \chi_{ji} x_i / x_j$). Each of the network chains is assumed to have N segments from which f_i fraction carries charged groups. We also assume that the gel is a highly dilute solution so that the electrostatic interaction between the charged groups is neglected. We consider that the gel is immersed into an infinite volume of liquid mixture so that the composition of the liquid mixture outside the gel is fixed.

The free energy change ΔG in this process can be written as a sum of three terms [21], $\Delta G = \Delta G_{\mathrm{m}} + \Delta G_{\mathrm{el}} + \Delta G_{\mathrm{ion}}$, where ΔG_{m} is the free-energy change of mixing; ΔG_{el}, the free energy change due to the elastic deformation of the network chains, and ΔG_{ion}, the free energy change due to the non-equal distribution of mobile counterions between the inside and outside the gel. These terms are given by Eqs. (6)–(8) [21]:

$$\Delta G_{\mathrm{m}} = RT\left(\sum_{i=1}^{3} n_i \ln v_i + \sum_{i=1}^{3} n_i v_j \chi_{ij}\right) \quad (i < j) \tag{6}$$

$$\Delta G_{\mathrm{el}} = (3/2) V_{\mathrm{P}} \left(\frac{RT}{N V_1}\right)\left(\alpha^2 - 1 - \ln \alpha\right) \tag{7}$$

$$\Delta G_{\mathrm{ion}} = RT f_i \frac{v_2}{v_1} n_1 \ln(f_i v_2) \tag{8}$$

where n_i is the moles of the species i; v_i, its volume fraction, V_{P} and V_1 are the volumes of polymer network and the segment, respectively; α is the linear swelling ratio with respect to the after-synthesis-stage of the gel, i.e., $\alpha = (v_2^0/v_2)^{1/3}$; R, the gas constant; and T, the temperature. Summing up of Eqs. (6)–(8) and differentiating with respect to the number of moles of the components i yield the following equation for the excess chemical potential of the component i in the gel phase ($\Delta\mu_i^{\mathrm{gel}}$):

$$\begin{aligned}\frac{\Delta\mu_i^{\mathrm{gel}}}{x_i RT} &= x_i^{-1} \ln v_i + x_i^{-1}(1 - v_i) - \sum_{j=1}^{3} v_j / x_j \\ &\quad + x_i^{-1} \sum_{j=1}^{3} \chi_{ij} v_j \sum_{j=1}^{3} v_j - x_j^{-1} \chi_{jk} v_j v_k \\ &\quad + \left(\frac{\partial \Delta G_{\mathrm{el}}}{\partial n_i}\right)_{T,P,n_j} + \left(\frac{\partial \Delta G_{\mathrm{ion}}}{\partial n_i}\right)_{T,P,n_j} \\ &\quad (i,j,k = 1,2, \text{ and } 3;\ j,k \neq i;\ j < k)\end{aligned} \tag{9}$$

The chemical potential of the components i in the solution ($\Delta\mu_i^{\mathrm{sol}}$) can be obtained from Eq. (9) as

$$\begin{aligned}\frac{\Delta\mu_i^{\mathrm{sol}}}{x_i RT} &= x_i^{-1} \ln v_i' + x_i^{-1}(1 - v_i') + x_i^{-1} \chi_{ij} (1 - v_i')^2 \\ &\quad (i,j = 1 \text{ and } 3;\ j \neq i)\end{aligned} \tag{10}$$

where the symbols with a prime denote the concentrations in the external solution ($v_1' + v_3' = 1$). The state of equilibrium swelling of the hydrogel in the solvent mixture is obtained when each of the solvent components are in thermodynamic equilibrium with those outside. This equilibrium state is described by the equality of the chemical potential of the components in both phases. Thus, at swelling equilibrium, we have:

$$\Delta\mu_i^{\text{gel}} = \Delta\mu_i^{\text{sol}} \quad (i = 1 \text{ and } 3) \tag{11}$$

Combining Eqs. (9)–(11), setting $x_2 = \infty$ for the polymer network, and since v_3' is equal to ϕ in our experiments, we obtained the following two equations describing the thermodynamic equilibrium condition of an ionic gel immersed in a solvent mixture:

$$\ln\left(\frac{1 - v_2 - v_3}{1 - \phi}\right) + (v_2 + v_3 - \phi) - (v_3 - \phi)/y + \chi_{12}v_2^2 + \chi_{13}(v_3^2 - \phi^2) + (\chi_{12} + \chi_{13} - \chi_{23})v_2v_3 + N^{-1}v_2(\alpha^2 - 0.5 - f_i) = 0 \tag{12}$$

$$-\ln\left(\frac{1 - v_2 - v_3}{1 - \phi}\right) + (1/y)\ln(v_3/\phi) - 2\chi_{13}(v_3 - \phi) - (\chi_{12} + \chi_{13} - \chi_{23})v_2 = 0 \tag{13}$$

where y is the ratio of the molar volumes of the liquid components, $y = x_3/x_1$. The equilibrium concentrations (v_2 and v_3) in the gel phase can be obtained by solving Eqs. (12) and (13) for a given composition ϕ of the external liquid mixture. When multiple sets of solutions are obtained for a given value of ϕ, we considered the solution that gives the minimum value of $\Delta\mu_2^{\text{gel}}$ in Eq. (9) as a stable point. If two sets of solutions give the same value of $\Delta\mu_2^{\text{gel}}$, the stable equilibrium curve changes discontinuously, implying that the gel will undergo a phase transition.

The parameters required for the solution of Eq. (12) and (13) for the swelling degree of the hydrogels ($V/V_0 = v_2^0/v_2$) and for the cosolvent concentration inside the gel v_3 are: v_2^0, N, y, and χ_{ij}. Both v_2^0 and N were determined experimentally (Table 1). The values $v_2^0 = 0.05$ and $N = 2.1 \times 10^4$ were used for the present simulation. The binary interaction parameters χ_{ij} between the polymer network and the solvents were evaluated from the swelling ratios of the hydrogels in pure solvents. Following values were found: $\chi_{12} = 0.44$ (at 3 °C), and 0.58 (at 23 °C), $\chi_{23} = 0.147$ and 0.100 for ethanol and DMSO, respectively. From the molar volumes of the solvents, y was calculated as 3.3 and 4, for ethanol and DMSO, respectively.

After finding these parameters, the equations contain one unknown parameter, the interaction parameter χ_{13} between the solvents. Reported values for χ_{13} provided poor agreement with the experimental data, indicating that the extent of the interactions between the solvents is influenced by the presence of a third hydrophobic component [26]. Therefore, Eqs. (12) and (13) were solved for χ_{13} as a function of ϕ in order to reproduce the experimental swelling data of non-ionic gels in solvent mixtures. The calculated values of χ_{13} at 3 °C are shown in Fig. 7 plotted as a function of the cosolvent concentration in the solution ϕ. The shape of the dependence of χ_{13} on ϕ quantifies the mechanistic picture explained above. In both solvent mixtures, χ_{13} first decreases with ϕ attaining a minimum at $\phi = 0.3$ and 0.4 for ethanol and DMSO, respectively, but then increases at higher values of ϕ. Thus, addition of one of the cosolvents into water, or water into the cosolvent results in attractive interactions, which are stronger than the interactions existing in pure solvents. The decrease of χ_{13} with ϕ is much more rapid in water–ethanol than in water–DMSO system, demonstrating the stronger interactions between water and ethanol.

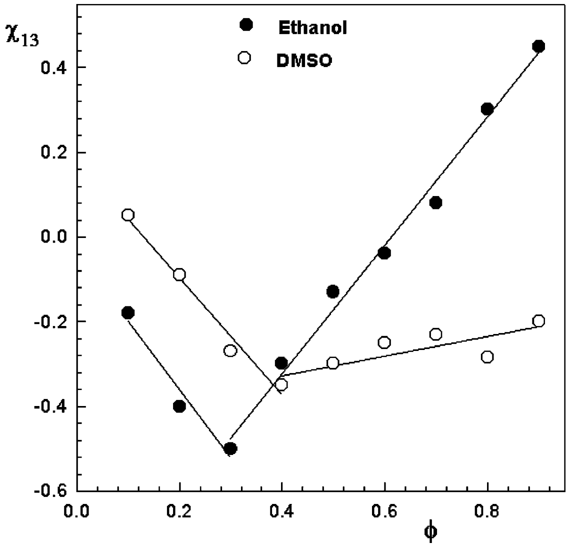

Fig. 7. The interaction parameter χ_{13} for water–ethanol and water–DMSO mixtures plotted against the volume fraction of ethanol (or DMSO) in the mixture.

The solid lines in Fig. 7 are the linear best fits to the data points below and above the minimum. Using these χ_{13} versus ϕ relations, we calculated the swelling ratio of the hydrogels of various charge densities f_i in solvent mixtures. The calculation results for ethanol–water system are shown in Fig. 8. The experimental data for the non-ionic gel are also shown in the figure by the symbols. It is seen that, after taking into account the concentration dependent χ_{13} parameter, the theory predicts what we observed experimentally (Figs. 4 and 5). The counterions inside the gel are responsible for the first-order collapse and recollapse transitions of the hydrogels in solvent mixtures. As the charge density f_i is increased, the reentrant transition occurs in a narrower range of ethanol concentration. The dashed curve in Fig. 8 was calculated for $f_i = 0$ and $\chi_{12} = 0.58$, i.e., for the swelling equilibrium of the non-ionic gel in ethanol–water mixture at 23 °C. In accord with the experimental observation, the gel is collapsed in water at 23 °C and remains in this state up to $\phi = 0.4$. If ϕ is further in-

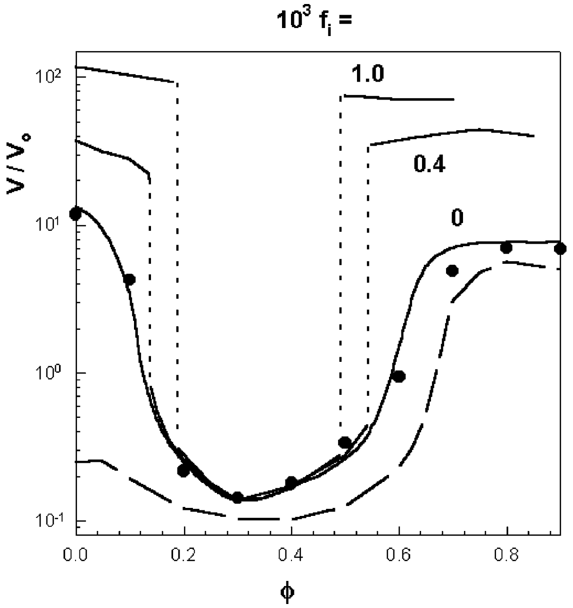

Fig. 8. The equilibrium volume swelling ratios of the hydrogels V/V_0 in ethanol–water mixtures shown as a function of the ethanol volume fraction in the solution ϕ. The experimental data points for the non-ionic TBA/AAm hydrogel are shown by symbols. The curves were calculated using Eqs. (12) and (13). The dotted lines represent the phase transition regions. The ionic group contents f_i used in the calculations are indicated in the figure. Calculations were for 3 °C (solid curves) and 23 °C (dashed curve).

creased, the gel undergoes a smooth swelling transition due to the attractive polymer–ethanol interactions represented by χ_{23}.

Fig. 9 shows the volume fraction of ethanol in the gel phase v_3 plotted as a function of its volume fraction in the external solution ϕ. Calculations were for 3 °C. The dotted line in the figure represents the relation $v_3 = \phi$. Thus, along this line the solvent composition inside the gel is equal to that in the solution. At low or high concentrations of ethanol ($\phi < 0.10$ or $f > 0.65$), v_3 is almost equal to ϕ; thus, the solvent compositions inside and outside the gel are almost equal, so that the gels are swollen in the solvent mixtures (Fig. 8). However, between $\phi = 0.10$ and 0.65, ethanol concentration in the gel v_3 becomes smaller than that in the solution ϕ. The concentration difference ($v_3 - \phi$) creates an osmotic pressure compressing the gel. Between $\phi = 0.10$ and 0.65, $v_3 - \phi$ changes continuously in non-ionic gels. However, for ionic gels, $v_3 - \phi$ exhibits discontinuity at $\phi = 0.185$ and 0.495, which results in the first-order reentrant phenomena in the solvent mixtures (Fig. 8).

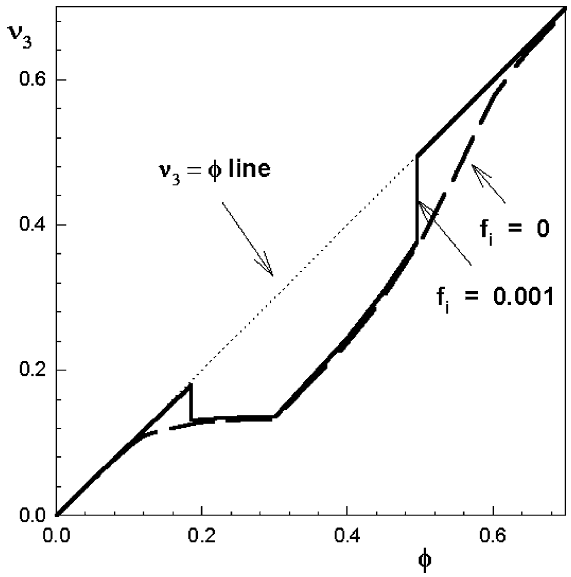

Fig. 9. The volume fraction of ethanol in the gel phase v_3 plotted as a function of its volume fraction in the external solution ϕ. Calculations were for 3 °C. The ionic group contents f_i used in the calculations are indicated in the figure. The dotted line represents the relation $v_3 = \phi$.

The results show that Eqs. (12) and (13) describe semi-quantitatively the swelling behavior of the gels in solvent mixtures. In fact, the agreement between the experimental data and the theory can further be improved if (a) a ternary interaction parameter is introduced into the swelling equations [26], and (b) the variation of the effective network charge density depending on the dielectric constant of the solvent mixture is taken into account [27,28]. Moreover, the introduction of the non-Gaussian statistics to describe the swelling behavior of highly swollen gels provides a better fit at high swelling ratios [23]. However, these improvements increase the number of parameters required for the simulation. The simple theory used here shows that the competing attractive interactions between water–ethanol (DMSO) and polymer–ethanol (DMSO), represented by χ_{13} and χ_{23} parameters, respectively, are responsible for the reentrant phase transition in TBA/AAm hydrogels immersed in solvent mixtures.

4. Conclusions

Temperature-sensitive ionic hydrogels based on TBA, AAm, AMPS and BAAm monomers were prepared. The molar ratio of TBA to the monomers AAm and AMPS was fixed at 60/40, while the AMPS content was varied. The elastic modulus of the hydrogels was in the range of 347–447 Pa, much lower than the modulus of PAAm or PNIPA hydrogels due to the reduced crosslinking efficiency of BAAm in TBA/AAm copolymerization. The hydrogels exhibited swelling–deswelling transition in water depending on the temperature. Increasing AMPS content resulted in shifting of the transition temperature interval in which the deswelling takes place. The higher the ionic group content, the broader the temperature interval at the phase transition. This result can be explained with the heterogeneity in the molecular-level chemical composition of the network chains. Ionic hydrogels exhibited first-order reentrant conformational transitions in ethanol–water and in DMSO–water mixtures. The higher the ionic group content of the hydrogels the narrower the ethanol (or DMSO) range in which the reentrant phenomena occur. By taking into account the difference of the solvent mixture composition inside and outside the gel, the equilibrium swelling theory provided a satisfactory agreement to the experimental swelling data of the hydrogels immersed in the solvent mixtures. The theory indicates that the competing attractive interactions between water–ethanol (DMSO) and polymer–ethanol (DMSO) are responsible for the reentrant phase transition in TBA/AAm hydrogels immersed in solvent mixtures.

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