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Reentrant conformation transition in poly(*N*,*N*-dimethylacrylamide) hydrogels in water–organic solvent mixtures

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Abstract

Conformational changes in poly(*N*,*N*-dimethylacrylamide) (PDMA) networks swollen in aqueous solutions of organic solvents are studied both experimentally and theoretically. PDMA hydrogels of various charge densities were prepared by free-radical crosslinking copolymerization. Swelling behavior of the hydrogels was investigated in aqueous organic solvent mixtures as functions of solvent species and the concentration. With increasing volume fraction ϕ of acetone, tetrahydrofuran, or 1,4-dioxane in the aqueous solution, PDMA hydrogels exhibit reentrant conformation transition. During this transition, the gel first deswells in the range of ϕ between 0.4 and 0.9, and then rapidly reswells if ϕ is monotonically increased. The reswelling of the collapsed PDMA gel occurs in a narrow of ϕ above $\phi = 0.97$. It was shown that the reentrant transition in PDMA gels requires moderate hydrogen bonding organic solvents, so that the hydrophobic interactions between PDMA and the organic solvent dominate the swelling process. The results were interpreted using the theory of equilibrium swelling. The interaction parameters in the gel system as well as the partition parameter of the organic solvent between the gel and the solution phases were calculated.
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Keywords: Hydrogels; Reentrant transition; Hydrophobic interactions

1. Introduction

Swelling behavior of hydrogels in solvent mixtures is of considerable interest to many applications of membranes, including drug delivery and pervaporation. Recently, a phenomenon called reentrant swelling transition was observed in hydrophobically modified hydrogels immersed in aqueous solutions of organic solvents or linear polymers [1,2]. In such a transition, the gel first collapses then reswells if a particular external parameter such as the organic solvent or linear polymer concentration is continuously varied. Reentrant phase transitions were observed in poly(*N*-isopropylacrylamide) (PNIPA) hydrogels in aqueous solutions of dimethylsulfoxide (DMSO) [2,3], methanol [4], ethanol [4], as well as in aqueous solutions of poly(ethylene glycol)s of various molecular weights [5–8]. Recently, it was shown that solutions and gels of poly(*N*,*N*-dimethylacrylamide) (PDMA) exhibit reentrant transitions in water–acetone and water–dioxane mixtures [9]. Moreover, hydrogels based on *N*-*t*-butylacrylamide (TBA)

and acrylamide (AAm) monomers with 40–60% TBA by mole also exhibit reentrant transitions in water–DMSO and water–ethanol mixtures [10,11].

Since the reentrant phenomenon is not observable in polyacrylamide (PAAm) hydrogels or in hydrogels containing less than 40% TBA, hydrophobic interactions are mainly responsible for the reentrant transition behavior of the hydrogels. Although the hydrophobic interactions have long been considered to play a dominant role in the formation of biological structures, the mechanism of the hydrophobic effect is still under debate [12,13]. Therefore, hydrophobically modified hydrogels in solvent mixtures form a simple model system to understand the origin of hydrophobic interactions.

Here, we investigated the conformational changes in PDMA networks swollen in aqueous solutions of various organic solvents. For this purpose, a series of PDMA hydrogels was prepared by free-radical copolymerization of *N*,*N*-dimethyla-crylamide (DMA) monomer and *N*,*N'*-methylenebis(acryla-mide) (BAAm) crosslinker. 2-Acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) and acrylic acid (AAc) were used as the ionic comonomer in the hydrogel preparation. The solvent specificity for the PDMA gel transition was correlated with the relative magnitude of hydrogen bonding, polar and hydrophobic interactions in the gel system. Moreover, the observed reentrant transition phenomena in water–dioxane,

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water–acetone, and water–tetrahydrofuran (THF) mixtures were explained within the framework of the equilibrium swelling theories.

2. Experimental section

2.1. Materials

N,N-dimethylacrylamide (DMA, Fluka), acrylamide (AAm, Merck), *N,N'*-methylenebis(acrylamide) (BAAm, Merck), ammonium persulfate (APS, Merck), and *N,N,N',N'*-tetra-methylethylenediamine (TEMED) were used as received. Acrylic acid (AAc, Fluka) was distilled under a reduced pressure of 10 mmHg to remove its inhibitor. 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 acetone, THF, 1,4-dioxane (dioxane), methanol, ethanol, 1-propanol, *t*-butanol, and DMSO were used without further purification. APS and TEMED stock solutions were prepared by dissolving 0.080 g APS and 0.250 ml TEMED separately in 10 ml of water.

PDMA hydrogels were prepared by free-radical cross-linking copolymerization of DMA and BAAm in aqueous solution at 5 °C in the presence of 3.51 mM APS initiator and 0.25 v/v% TEMED accelerator. For the preparation of ionic PDMA hydrogels, AMPS or AAc was used as the ionic comonomer during the gel preparation. The initial concentration of the total monomers was 5.1 w/v%. The crosslinker ratio X (mole ratio of the crosslinker BAAm to the monomers DMA+AAc or AMPS) was fixed at 1/83. To illustrate the synthetic procedure, we give details for the preparation of a non-ionic hydrogel.

APS stock solution (1.0 ml), DMA (0.50 ml), BAAm (9.37 mg) and water (7.50 ml) were mixed in a 10 ml graduated flask. After bubbling nitrogen for 15 min, TEMED stock solution (1.0 ml) was added to the mixture. The solution was then poured into several glass tubes of 4.5–5 mm internal diameters and about 100 mm long. The glass tubes were sealed, immersed in a thermostated water bath at 5 °C and the polymerization was conducted for one day.

For comparison, polyacrylamide (PAAm) hydrogels were also prepared under the same experimental condition except that AAm monomer instead of DMA was used in the gel preparation.

2.2. PDMA network concentration at the stage of gel preparation

The degree of dilution of the networks after their preparation was denoted by ν_2^0, the volume fraction of crosslinked polymer after the gel preparation. In order to determine ν_2^0, PDMA hydrogels after preparation were first swollen in water to extract non-polymerizable or soluble components and then dried to constant mass. ν_2^0 was

calculated as

$$\nu_2^0 = \left[1 + \frac{(q_F - 1)\rho}{d_1}\right]^{-1} \tag{1}$$

where q_F is the dilution degree after the gel preparation (mass of gel after preparation/mass of dried gel), ρ is the polymer density (1.21 g/ml) and d_1 is the solvent density (1.00 g/ml). The determination of ν_2^0 gave a value of $\nu_2^0 = 0.056 \pm 0.005$ for all the hydrogels of various charge densities.

2.3. Swelling measurements in solvents and in solvent mixtures

The hydrogels in the form of rods of about 4 mm in diameter were cut into samples of about 10 mm length. Then, each sample was placed in an excess of solvent or solvent mixture at 24 ± 0.5 °C. In order to reach swelling equilibrium, the hydrogels were immersed in solvent for at least 2 weeks replacing the solvent or the solvent mixture every other day. The swelling equilibrium was tested by measuring the diameter of the gel samples. To achieve good precision, three measurements were carried out on samples of different length taken from the same gel. The linear swelling ratio D/D_0 was determined by measuring the diameter of the hydrogel samples after equilibrium swelling D and after synthesis D_0 by a calibrated digital compass (Mitutoyo Digimatic Caliper, Series 500, resolution: 0.01 mm). The normalized volume of the equilibrium swollen hydrogels V_{eq} (volume of equilibrium swollen gel/volume of the gel just after preparation) was calculated as

$$V_{eq} = \left(\frac{D}{D_0}\right)^3 \tag{2}$$

For the ionic gels, the swelling measurements were carried out gravimetrically due to the deformation of the gel samples during their deswelling period under poor solvent condition. For this purpose, the weight of the hydrogels equilibrium swollen in solvent mixtures was measured after blotting the excess surface solvent. The normalized weight swelling ratio of the hydrogels with respect to their swelling ratio in water, m_{rel}, was calculated as:

$$m_{rel} = \frac{m}{m_w} \tag{3}$$

where m and m_w are the masses of the equilibrium swollen gel sample in a solvent mixture and in water, respectively.

2.4. Mechanical measurements

Uniaxial compression measurements were performed on gels just after their preparation. All the mechanical measurements were conducted in a thermostated room of 24 ± 0.5 °C. The stress–strain isotherms were measured by using an apparatus previously described [14]. The elastic modulus G_0

was determined from the slope of linear dependence [15]:

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

where f is the force acting per unit cross-sectional area of the undeformed gel specimen, and α is the deformation ratio (deformed length/initial length). For a network of Gaussian chains, the elastic modulus G_0 of gels after preparation state is related to the number of segments between two successive crosslinks N by [15,16]:

$$G_0 = A(NV_1)^{-1}RT\nu_2^0 \tag{5}$$

where V_1 is the molar volume of segment, which is taken as the molar volume of water (18 ml/mol), the front factor A equals to 1 for an affine network and $1-2/\phi$ for a phantom network, where ϕ is the functionality of the crosslinks, R and T are in their usual meanings.

3. Results and discussion

3.1. Swelling behavior in solvent mixtures

PDMA hydrogels of various charge densities were prepared at a fixed crosslinker ratio of $X = 1/83$. The initial monomer concentration was kept as 5.1 w/v%. In Fig. 1(A), the equilibrium swelling ratio V_{eq} of the hydrogels in water is shown as a function of the ionic comonomer concentration (AMPS or AAc mol%) in the feed. As expected, the swelling ratio increases as the ionic comonomer content of the hydrogel increases. This is a consequence of the osmotic pressure exerted by the counterions of AMPS and AAc units in the network chains. This osmotic pressure increases as the concentration of the counterions increases. Moreover, Fig. 1(B) showing the elastic modulus G_0 of gels after preparation as functions of AMPS and AAc mol% indicates that G_0 is about 5 ± 0.5 kPa, only slightly dependent on the gel charge density [17]. Using the G_0 and ν_2^0 values of the hydrogels together with Eq. (5), one may calculate the number of segments N between two successive crosslinks of the hydrogels. The results for affine network model ($A = 1$) gave a value of $N = 1600 \pm 260$ for all the hydrogel samples.
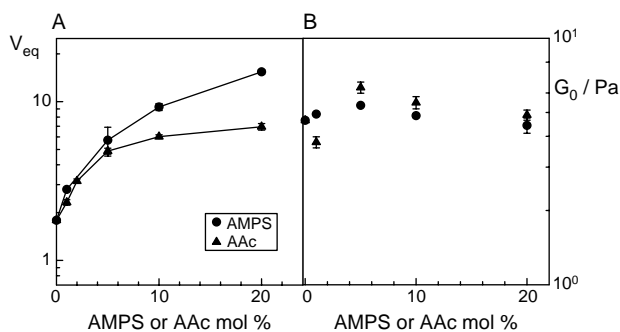

Fig. 1. The equilibrium swelling ratio V_{eq} of the hydrogels in water (A) and the modulus of elasticity G_0 just after the hydrogel preparation (B) are shown as a function of the ionic comonomer concentration (AMPS or AAc mol%) in the feed.
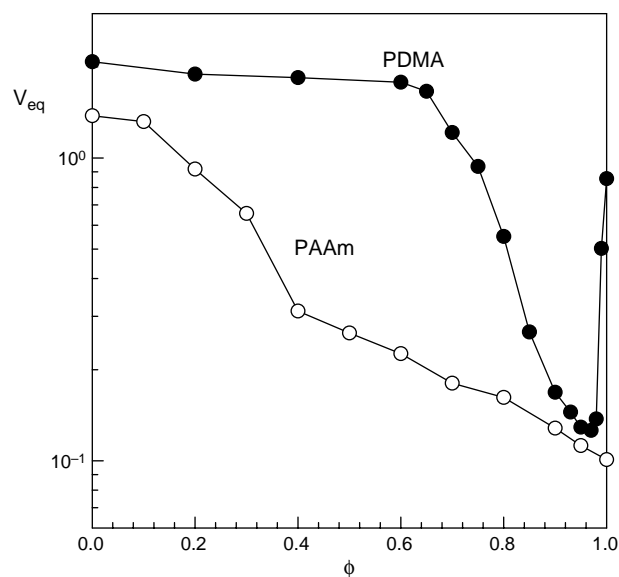

Fig. 2. The equilibrium swelling ratio V_{eq} of PDMA (filled symbols) and PAAm hydrogels (open symbols) shown as a function of the acetone volume fraction ϕ in the external aqueous solution.

The filled symbols in Fig. 2 show the equilibrium swelling ratio V_{eq} of the non-ionic PDMA gel in water–acetone mixtures plotted as a function of the acetone volume fraction ϕ in the external solution. For comparison, the swelling behavior of the non-ionic PAAm gel is also shown in the figure by the open symbols. As ϕ is increased, PAAm gel undergoes a deswelling transition and finally attains a collapsed state in pure acetone with a volume $V_{eq} \cong 10^{-1}$. In contrast, PDMA gel first remains in the swollen state up to $\phi = 0.65$. As ϕ crosses 0.65, the gel exhibits a reentrant transition in which the gel first deswells up to $V_{eq} \cong 10^{-1}$, then rapidly reswells if ϕ is monotonically increased. The reswelling of the collapsed PDMA gel occurs in a narrow of ϕ above $\phi = 0.97$.

Since the only difference between the PDMA and PAAm gels is the existence of the methyl groups in PDMA networks, the results indicate that the hydrophobic interactions are responsible for the reentrant conformation transition in PDMA gels immersed in acetone–water mixtures. As can be seen from Fig. 2, the volume of PDMA gel in acetone ($\phi = 1$) is about 10 fold larger than that of PAAm gel. This means that the incorporation of the methyl groups on the network chains creates attractive hydrophobic interactions between PDMA segments and acetone molecules. Furthermore, as evidenced from the large swelling ratio of PDMA gel in water, DMA segments and water molecules also attract each other due to the hydrogen bonding interactions. Thus, water and acetone molecules taken separately are good solvents for PDMA network. However, in mixtures with a ϕ value between 0.65 and 1, the attractive water–acetone interactions together with the intramolecular hydrophobic forces within the PDMA network seem to dominate over the water–PDMA or acetone–PDMA interactions. As a result, in this range of ϕ, addition of acetone to water or water to acetone decreases the solvent content of the gel so that the gel contracts and attains a minimum volume at $\phi = 0.97$ (Fig. 2).
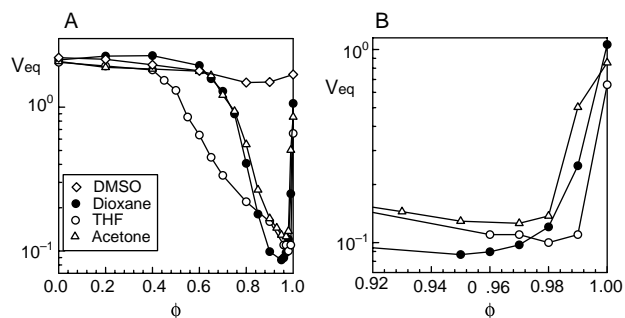
Fig. 3. (A) The equilibrium swelling ratio V_{eq} of PDMA hydrogels shown as a function of the organic solvent volume fraction ϕ in the external aqueous solution. The organic solvents used are indicated in the figure. (B) shows the magnified observation of the high ϕ range of (A).

The experimental evidence of hydrogen bonding and hydrophobic interactions in solutions and gels of poly(*N*-monoalkylacrylamide) as well as in poly(*N,N*-dialkylacrylamide) has been reported before by using a variety of techniques [18–22]. Maeda et al. showed by IR spectroscopy that most of the C=O groups of poly(*N,N*-diethylacrylamide) (PDEA) in water or in water/methanol mixture are associated with water and methanol molecules through hydrogen bonds, even above the lower critical solution temperature (LCST) [22]. Although the ethyl groups of PDEA are also hydrated below the LCST, upon phase transition, most of these groups are dehydrated and associate through hydrophobic interaction [22].

To understand the relative magnitude of the intermolecular forces responsible for the reentrant conformation transition in gels, we investigated the swelling behavior of non-ionic PDMA gels in various organic solvent–water mixtures. The results are collected in Figs. 3 and 4. Fig. 3(A) shows the volume V_{eq} of PDMA gels plotted against the volume fraction
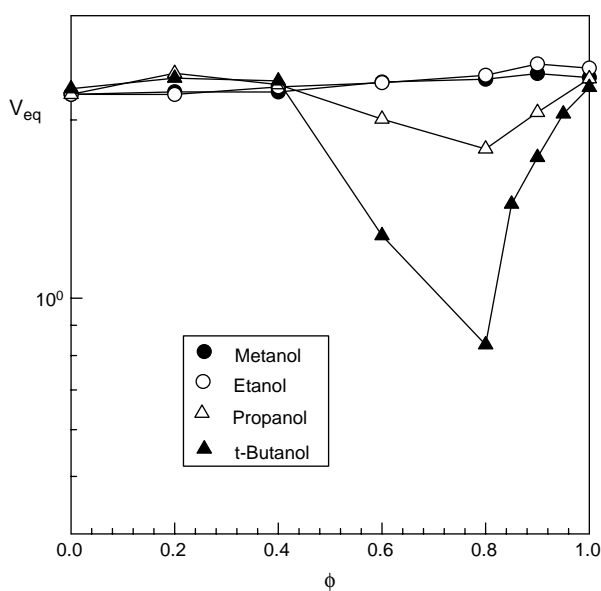
ϕ of DMSO, dioxane, and THF in the external aqueous solution. For comparison, the data obtained in acetone–water mixtures are also included in the figure. Except the DMSO–water system, all the organic solvent–water mixtures induce strong reentrant transitions in PDMA gels. Deswelling of the gel starts at ϕ between 0.4 and 0.65 while the reswelling of the collapsed gel occurs at ϕ values close to unity. Fig. 3(B) showing the magnified observation of the high ϕ range of Fig. 3(A) indicates that the reswelling mainly occurs above $\phi = 0.97$–0.99. Thus, addition of a small amount of water into one of these organic solvents induces a collapse transition in PDMA gel. These results also suggest that the trace amount of water existing in these organic solvents can be determined by monitoring the volume change of PDMA gels.

The swelling behavior of non-ionic PDMA gels in aqueous solution of various alcohols is shown in Fig. 4. In methanol or ethanol solutions, the gel remains in the swollen state over the entire range of ϕ. The reentrant transition in gels appears in aqueous solutions of 1-propanol and *t*-butanol. Fig. 5 shows the effect of the charge density on the swelling behavior of PDMA
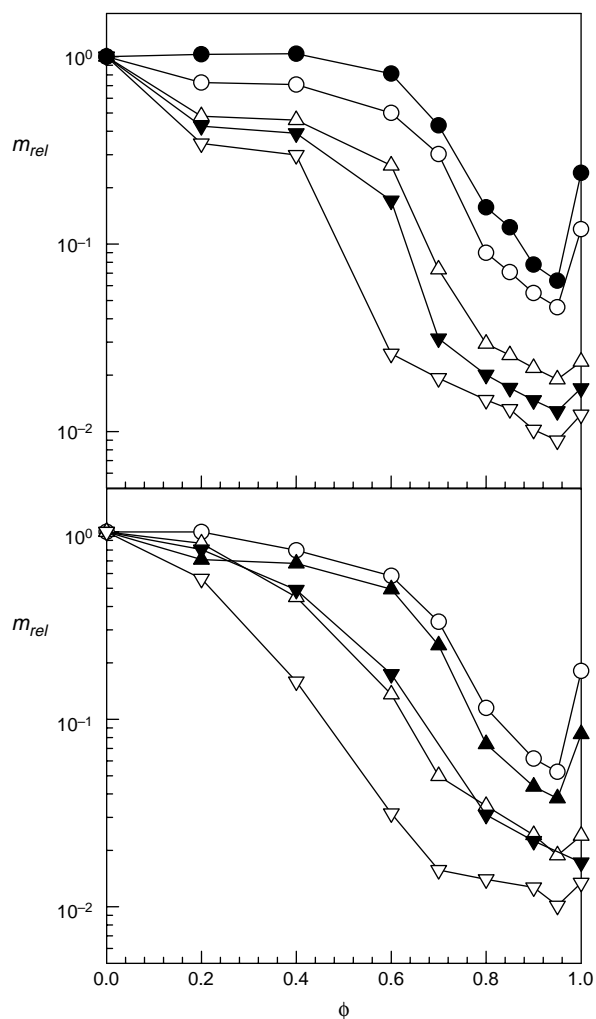

Fig. 4. The equilibrium swelling ratio V_{eq} of PDMA hydrogels shown as a function of the alcohol volume fraction ϕ in the external aqueous solution. The alcohols used are indicated in the figure.

Fig. 5. The relative weight swelling ratio m_{rel} of ionic PDMA hydrogels shown as a function of acetone volume fraction ϕ in the external aqueous solution. The ionic comonomer used in the hydrogel preparation is AMPS (A) and AAc (B). AMPS or AAc mol% = 0.5 (●), 1 (○), 2 (▲), 5 (△), 10 (▼), and 20 (▽).

gels in acetone–water mixtures. Here, the relative weight swelling ratio m_{rel} of gels of various charge densities is plotted against the acetone volume fraction ϕ in the external solution. AMPS and AAc were used as the ionic comonomer in the hydrogel preparation. It is seen that the acetone concentration ϕ required for the deswelling transition shifts to smaller values while the reswelling transition becomes weaker as the gel charge density is increased. The reentrant transition gradually disappears and becomes a deswelling transition at high charge densities.

In order to understand the effect of the solvent specificity on the reentrant transition in PDMA gels, the solubility parameters provide an easy numerical method of predicting the extent of interactions in the system components. According to the Hildebrand theory, the properties of solvents are classified in terms of the solubility parameter δ [23]. A more detailed solubility parameter approach proposed by Hansen separates the solubility parameter into components due to dispersion forces δ_d, polar forces δ_p, and hydrogen bonding interactions δ_h [24]. The literature data [25] indicate that the polar and the hydrogen bonding components of the solubility parameter values vary considerable depending on the type of the organic solvent used in the swelling tests. For example, δ_p decreases from 12.3 to 5.7 Mpa$^{1/2}$ as the number of carbon atoms of the alcohols increases from one to four. Thus, according to the experimental results in Fig. 4, decreasing the polarity of the alcohols increases the extent of reentrant transition of PDMA gels in aqueous alcohol solutions.

In the following, the extent of the reentrant transition is represented by V_{min}, which is the minimum volume of PDMA gel recorded in a given water–organic solvent mixture. Thus, the lower V_{min}, the larger the volume change in the water–organic solvent mixture, the larger the extent of reentrant transition. Fig. 6(A) shows V_{min} plotted against the hydrogen bonding component of the solubility parameter δ_h of the organic solvent. As δ_h decreases, the gel passes to a more collapsed state in the water–organic solvent mixture. Thus, acetone, THF, or dioxane forming moderate hydrogen bonds in

the mixtures with water compared to alcohols and DMSO induce a strong reentrant conformation transition in PDMA gels. In Fig. 6(B), V_{min} is plotted against the normalized swelling ratio V_{solv} of PDMA gel in the pure organic solvent. It is seen that V_{min} decreases with decreasing swelling ratio of gel in the organic solvent. Thus, strong attractive interactions between the organic solvent and PDMA network represented by a high value of V_{solv} prevents the reentrant transition in PDMA gels. Reentrant transition requires weak attractive interactions between PDMA network and the organic solvent.

The results thus suggest that a reentrant conformation transition in PDMA gel requires a moderate hydrogen bonding organic solvent so that hydrophobic interactions dominate the swelling behavior of gels in the organic solvent. This condition facilitates the movement of the individual organic solvent molecules through the network and results in the observed large volume change in PDMA gels. It should be noted that, although PDMA hydrogels remain in the swollen state in aqueous solutions of methanol or ethanol, PNIPA as well as TBA/AAm hydrogels exhibit strong reentrant conformation transitions in these solvent mixtures [4,10,11]. It seems that due to the less hydrophobic character of PDMA compared to PNIPA and TBA/AAm networks, less hydrogen bonds are needed between the organic solvent and water for the observation of a reentrant phenomenon in PDMA networks.

The following mechanistic picture explains the phenomena shown in Figs. 2–5: The organic solvents acetone, THF, and dioxane are attracted by water through the hydrogen–bonding interactions. These organic solvents are also attracted by the PDMA gel due to the hydrophobic interactions between the methyl groups of PDMA and the methyl or methylene groups of the organic solvent. The competing weak interactions between organic solvent–water and organic solvent–PDMA network results in reentrant swelling behavior of the hydrogel. Thus, when the organic solvent is added to water, organic solvent molecules like to stay in the solution due to the interaction between organic solvent and water, which reduces the gel swelling. The decrease in the gel swelling will increase the intramolecular hydrophobic interactions of the methyl groups of PDMA, which may promote further shrinkage of the PDMA gel. Furthermore, at high values of ϕ, the attractive PDMA–organic solvent interactions dominate over the organic solvent–water interactions due to the increased number of contacts between organic solvent molecules and PDMA segments. As a result, organic solvent enters into the gel phase and results in gel swelling.

Moreover, in case of ionic PDMA gels, the swelling behavior in water–organic solvent mixtures is closely related with the ion pair formation. As is well known, the fraction of ions forming ion pairs in the gel strongly depends on the dielectric constant of the gel phase [26,27]. The formation of ion pairs is more pronounced for solutions with a lower solvent dielectric constant ε. A decrease in ε increases the probability of ionpairing and results in the deswelling of the gel. Because ε of acetone is 21 compared to the value of $\varepsilon = 80$ for water, the counterions that are free in water bind tightly in the acetone environment to the AMPS or AAc units to form ion pairs. Thus,
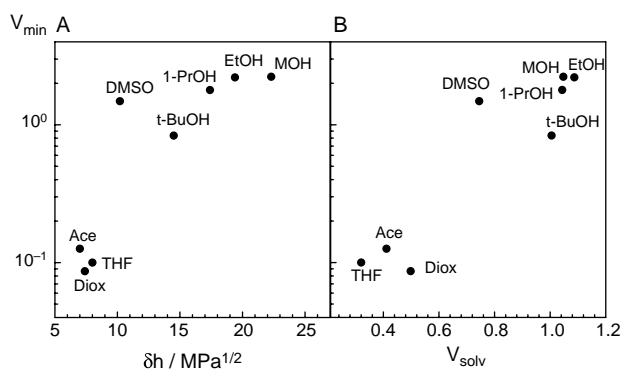

Fig. 6. (A) The minimum gel volume V_{min} recorded in a given organic solvent–water mixture is shown as a function of the hydrogen bonding component of the solubility parameter δ_h of the organic solvent. (B) V_{min} is plotted against the normalized swelling ratio V_{solv} of PDMA gels. V_{solv} is the ratio of the equilibrium swelling ratio of PDMA gel in the organic solvent to that in water. MOH, methanol; EtOH, ethanol; 1-PrOH, 1-propanol; t-BuOH, t-butanol; Ace, acetone; Diox, 1,4-dioxane.

ionic PDMA gels deswell with increasing acetone content in the solution so that the reentrant transition gradually becomes a deswelling transition at high AMPS or AAc contents (Fig. 5).

3.2. Interaction parameters and the partition of the organic solvent between the gel and solution phases

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 the organic solvent) 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 $\chi_{ij}(i \neq j,$ $\chi_{ij} = \chi_{ji}(x_i/x_j))$. Each of the network chains is assumed to have N segments. 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 two terms [16], $\Delta G = \Delta G_m + \Delta G_{el}$, where ΔG_m is the free-energy change of mixing and ΔG_{el} is the free energy change due to the elastic deformation of the network chains. These terms are given by Eqs. (6) and (7) [16]:

$$\Delta G_m = RT\left(\sum_{i=1}^{3} n_i \ln v_i + \sum_{i=1}^{3} n_i v_j \chi_{ij}\right) \quad (6)$$

$(i < j)$

$$\Delta G_{el} = \left(\frac{3}{2}\right) V_P\left(\frac{RT}{NV_1}\right)(\alpha^2 - 1 - \ln \alpha) \quad (7)$$

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; and α is the linear swelling ratio with respect to the after-synthesis-stage of the gel, i.e. $\alpha = (v_2^0/v_2)^{1/3}$. Summing up of Eqs. (6) and (7), 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 ($\Delta\mu_i^{gel}$):

$$\frac{\Delta\mu_i^{gel}}{x_i RT} = x_i^{-1}\ln v_i + x_i^{-1}(1 - v_i) - \sum_{j=1}^{3} v_j/x_j$$

$$+ x_i^{-1}\sum_{j=1}^{3}\chi_{ij}v_j\sum_{j=1}^{3}v_j - x_j^{-1}\chi_{jk}v_j v_k + \left(\frac{\partial \Delta G_{el}}{\partial n_i}\right)_{T,P,n_j} \quad (8)$$

$(i,j,k = 1, 2, \text{and } 3; j,k \neq i; j < k)$.

The chemical potential of the components i in the solution ($\Delta\mu_i^{sol}$) can be obtained from Eq. (8) as:

$$\frac{\Delta\mu_i^{sol}}{x_i RT} = x_i^{-1}\ln v_i' + x_i^{-1}\left(1 - v_i'\right) + x_i^{-1}\chi_{ij}\left(1 - v_i'\right)^2 \quad (9)$$

$(i,j = 1 \text{ and } 3; j \neq i)$

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:

$$\Delta\mu_i^{gel} = \Delta\mu_i^{sol} \quad (i = 1 \text{ and } 3) \quad (10)$$

Combining Eqs. (8)–(10), 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 a non-ionic gel immersed in a solvent mixture:

$$\ln\left(\frac{1 - v_2 - v_3}{1 - \phi}\right) + (v_2 + v_3 - \phi) - (v_3 - \phi)/y + \chi_{12}v_2^2$$
$$+ \chi_{13}(v_3^2 - \phi^2) + (\chi_{12} + \chi_{13} - \chi_{23})v_2 v_3$$
$$+ N^{-1}v_2(\alpha^2 - 0.5) = 0 \quad (11)$$

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

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. (11) and (12) for a given composition ϕ of the external liquid mixture. In the following, the calculation results of v_3 are presented in terms of the organic solvent partition parameter φ,

$$\varphi = \frac{v_3}{\phi(1 - v_2)} \quad (13)$$

which is the ratio of the organic solvent concentration inside the gel to that in the external solution. Thus, $\varphi = 1$ means that the organic solvent concentration in the gel is equal to that in the solution, while $\varphi = 0$ means total exclusion of the organic solvent molecules from the polymer network.

The parameters required for the solution of Eqs. (11)–(13) were evaluated as follows: Both v_2^0 and N were determined experimentally. The values $v_2^0 = 0.056$ and $N = 1.6 \times 10^3$ were used for the present simulation. The interaction parameters χ_{12} between the PDMA network and water was recently evaluated as $\chi_{12} = 0.48 + 0.33v_2$ [28]. The interaction parameters χ_{23} between the PDMA network and the organic solvent was calculated from the swelling ratios of the hydrogels in pure organic solvents (Figs. 2–4) together with the following equation:

$$\ln(1 - v_2) + v_2 + y\chi_{23}v_2^2 + yN^{-1}v_2(\alpha^2 - 0.5) = 0 \quad (14)$$

The values found were $\chi_{23} = 0.124, 0.107, 0.116,$ and 0.114 for acetone, dioxane, THF, and DMSO, respectively. From the molar volumes of the solvents, y was calculated as 4.1, 4.7, 4.5, and 3.9 for acetone, dioxane, THF, and DMSO, respectively.

After finding these parameters, the equations contain three unknown parameters: the polymer concentration in the gel phase v_2, the partition parameter φ, and the interaction
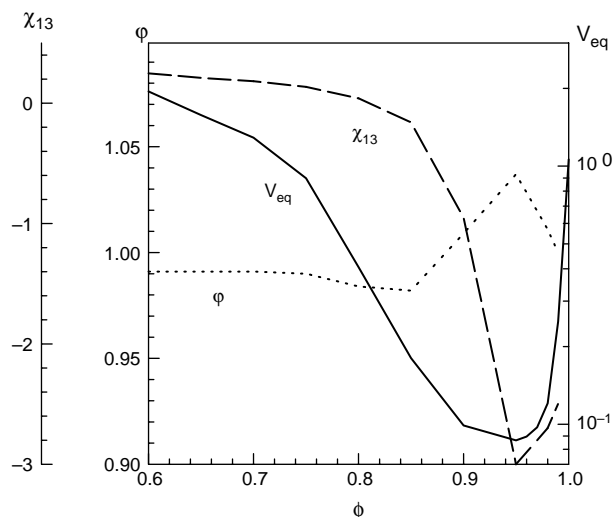
Fig. 7. Interaction parameter between water and dioxane χ_{13} (dashed curve) and the partition parameter φ of dioxane between the gel and the solution phases (dotted curve) shown as a function of dioxane concentration ϕ in the external solution. For comparison the experimental gel volume V_{eq} vs. ϕ dependence is also shown in the figure by the solid curve. Calculations were using the Eqs. (11)–(13).

parameter χ_{13} between the organic solvent and water. Therefore, Eqs. (11)–(13) were solved for χ_{13} and φ as a function of ϕ in order to reproduce the experimental polymer concentrations ν_2 ($\nu_2 = \nu_2^0 / V_{eq}$) of non-ionic gels in solvent mixtures.

Fig. 7 shows the calculated values of χ_{13} (dashed curve) and φ (dotted curve) plotted as a function of the dioxane volume fraction ϕ in the external solution. For comparison the experimental gel volume V_{eq} vs. ϕ dependence is also shown in the figure by the solid curve. Depending on the value of ϕ, three different regimes can be distinguished from Fig. 7:

1. Between $\phi = 0.60$ and 0.85, both the partition parameter φ and χ_{13} are decreasing functions of ϕ. Thus, the fraction of dioxane molecules penetrating into the PDMA network decreases as ϕ is increased. This is due to the predominant attraction of dioxane by water molecules locating in the external solution, which lowers both the swelling degree V_{eq} and the partition parameter φ.
2. Between $\phi = 0.85$ and 0.95, χ_{13} rapidly decreases while the partition parameter φ increases, i.e. the solution inside the gel is enriched by dioxane as ϕ is increased. The opposite behavior of the partition parameter φ in this regime is due to the collapsed state of PDMA gel. High polymer segment concentration inside the gel together with the high dioxane concentration in the external solution increases the number of contacts between PDMA and dioxane so that dioxane molecules reenter the collapsed gel phase. The reentrance of dioxane molecules into the gel network, however, does not suffice to swell the gel due to the strong water–dioxane attractions represented χ_{13}, which still dominate the swelling process.
3. For $\phi > 0.95$, the collapsed gel starts to swell again due to the favorable PDMA–dioxane interactions now dominating

the swelling process. Thus, in this regime, the gain in energy due to the increased number of contacts between PDMA and dioxane exceeds the attraction forces between water and dioxane. As a result, χ_{13} increases on rising ϕ so that the volume of the network increases. At the same time, φ decreases again and approaches to unity due to the increase of the gel volume that facilitates the penetration of both water and dioxane molecules into the gel network.

It should be noted that, in case of PNIPA and TBA/AAm networks, the increase of the partition parameter φ in the second regime is accompanied with the gel swelling [2–8,10,11]. As a result, the reswelling of the collapsed PNIPA or TBA/AAm gels occurs at a much lower concentration of the organic solvent than the PDMA gels do. Thus, in the presence of these more hydrophobic networks, the reentrance of the organic solvent into the network and the associated energy gain compensate more than the water–organic solvent attractions so that the volume of the network
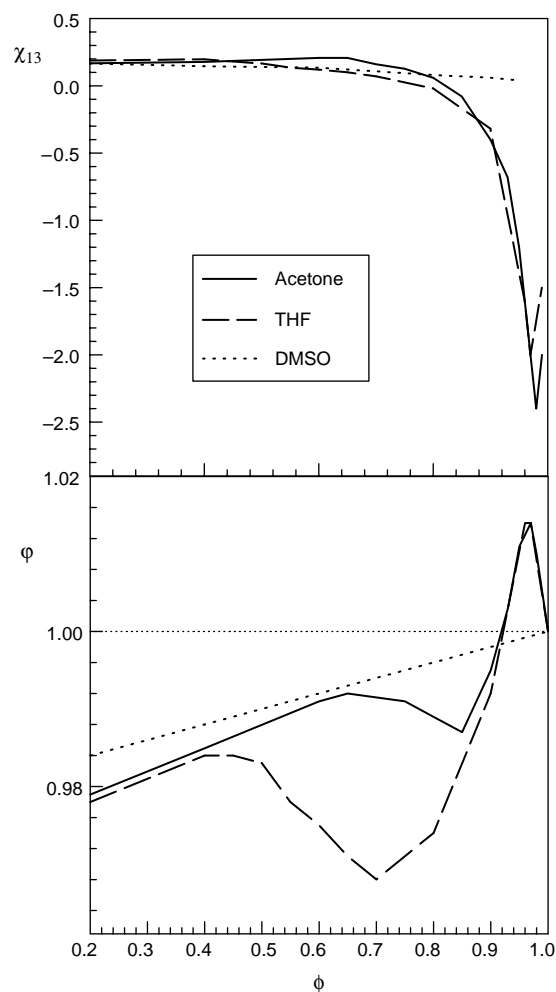

Fig. 8. Interaction parameter between water and the organic solvent χ_{13} (A) and the partition parameter φ of the organic solvent between the gel and the solution phases (B) shown as a function of the organic solvent concentration ϕ in the external solution. Calculations were using the Eqs. (11)–(13). The organic solvents are indicated in the figure. The thin dotted line in (B) represents the relation $\varphi = 1$.

increases in the second regime. However, due to the less hydrophobicity of PDMA network, a much higher organic solvent concentration is required to reswell the gel. This is the main characteristic of PDMA networks.

Calculated values of χ_{13} and φ for PDMA gels in aqueous solutions of acetone, THF, DMSO, are shown in Fig. 8 as a function of ϕ. Except the DMSO–water system, the shape of the dependence of χ_{13} and φ on ϕ is similar to that shown in Fig. 7 and quantifies the mechanistic picture explained in the previous section. Organic solvent molecules flow from the solution to the gel phase or vise versa depending on ϕ and results in the reentrant transition in PDMA gels. However, in DMSO–water mixtures, χ_{13} does not change much with ϕ so that the gel remains in the swollen state over the whole range of ϕ. Moreover, the φ ratio for this system remains below unity due to the conformational entropy of DMSO molecules. Since the penetration of DMSO with a size of $y = 3.9$ is accompanied by a loose of entropy of the DMSO molecules, DMSO concentration in the solution remains always higher than its concentration in the gel solution.

It should be noted that respective calculations using Eqs. (11)–(13) over the entire range of ϕ give single set of solutions for the composition of the PDMA gel immersed in the solvent mixtures. This implies that the conformational changes in PDMA networks occur continuously in the present solvent mixtures.

4. Conclusions

Swelling behavior of PDMA hydrogels in water–organic solvent mixtures was investigated as functions of the solvent species and the volume fraction of the organic solvent ϕ in the external solution. The results show that PDMA hydrogel has a tendency to reentrant transition in aqueous solutions of acetone, dioxane and THF; that is, the gel first collapses then reswells if the organic solvent concentration is continuously varied. It was shown that the reswelling of the collapsed gel occurs at ϕ values close to unity. Due to this feature of PDMA gels, they can be used to determine the trace amount of water in the organic solvents. It was also shown that the observation of a reentrant conformation transition in PDMA gels requires moderate hydrogen bonding organic solvents so that the hydrophobic interactions dominate the swelling behavior of gels in the organic solvent. The results were interpreted using

the theory of equilibrium swelling. Calculations show that, due to the less hydrophobic character of PDMA compared to PNIPA or TBA/AAm networks, a much higher organic solvent concentration is required for the observation of a reentrant transition in PDMA hydrogels.

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