Measurement and Correlation of the Swelling Pressure of *N*-Isopropylacrylamide Gel

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ABSTRACT: Swelling pressures of *N*-isopropylacrylamide gels of various cross-linking densities were measured from their swollen state to shrunken state by swelling the gels in polymer aqueous solutions whose concentrations were adjusted to show the desired osmotic pressures. The swelling pressures of the gels were determined to be equal to the osmotic pressure of the aqueous solution in which the gel was swollen. The measured swelling pressures were in the range 0–6000 Pa. It was found that the binodal curve of the gel–gel transition of *N*-isopropylacrylamide gels, which was estimated from the measured swelling pressure data, was similar to that in liquid–liquid equilibria of poly(*N*-isopropylacrylamide) aqueous solutions, especially in the vicinity of a critical region (namely near its lower critical solution temperature, LCST). The parameters of the prediction model proposed by Hooper *et al.* were fitted to the measured swelling pressure data of the gels of various cross-linking densities and applied to the calculation of the swelling equilibria of the gels. The calculation results were in good agreement with the experimental data, suggesting that the addition of the mixing and elastic contributions in osmotic pressure of the gel could be a useful assumption for the prediction of swelling equilibria of the gel, i.e., that the nature of the gel could be approximately expressed by means of its elasticity.

Introduction

Hydrogels swollen in an aqueous solution sometimes exhibit a discontinuous volume change in response to changes in environmental conditions such as temperature, solvent composition, pH, etc. This phase change has been denoted the volume phase transition or gel–gel transition of gels.[1]

It is well-known that polymers of *N*-isopropylacrylamide (NIPA) show lower critical solution temperature (LCST) behavior in water[2] and its gels have a volume phase transition at about 34 °C in water[3] (the volume decreases at temperatures higher than 34 °C). This feature of the NIPA gel has attracted much attention and has been studied by many researchers from both experimental and theoretical points of views.[4–7] These previous works on NIPA gels and poly-NIPA aqueous solutions focused mostly on the swelling behavior of the gel and revealed that strong, oriented interactions such as hydrogen bonding and/or hydrophobic hydration are important in the transition.

A number of thermodynamic models have been proposed for hydrogels. However, most of them are not able to describe the quantitative phase behavior of NIPA gels and poly-NIPA aqueous solutions since they were based on random-mixing polymer solution models (e.g. Flory–Huggins theory[8]) which do not account for orientation interactions. Recently, some lattice models have been proposed to account for hydrogen bonding or orientation interactions and succeeded in representing the swelling behavior of NIPA gels.[9–12]

According to the thermodynamics, swelling equilibria between a gel and solution must satisfy the following criteria:

$$\mu_i^{gel} = \mu_i^{ex.sol} \quad (1)$$

i.e.

$$\pi^{gel} = \pi^{ex.sol}$$

where μ_i is the chemical potential of the i-component and π is the osmotic pressure of the gel or the external solution. The swelling pressure (the osmotic pressure) of nonionic gels, π, is generally described as a sum of two contributions: the contribution due to polymer/solvent mixing and the contribution due to the elasticity.[8,12] Although this addition is an assumption that has not been theoretically justified, all prediction models proposed for gels adopt this assumption. According to the addition of the two contributions, the parameters in the mixing contribution of the models are usually determined from data for the corresponding polymer solutions because they represent the interactions between solvent and polymer chains in gels and the elasticity can be treated to come from the cross-linking in gels. In other words, the parameters in the mixing term of the prediction models for gels have been determined by using polymer solution data, which is numerous compared with the swelling equilibrium data of gels.

Swelling equilibrium provides generally only one composition (e.g. volume fraction) of a gel at $\pi^{gel} = 0$, since most of the swelling equilibrium experiments are carried out at a condition where the osmotic pressure of external solution is zero ($\pi^{ex.sol} = 0$). Therefore from swelling equilibrium data only, it is difficult to examine the functional form of the prediction model, in which the swelling pressure is usually presented as a function of temperature and composition. However, swelling pressure data obtained by measuring the swelling volume under given osmotic pressures, can provide much information on the pressure–temperature–volume relationships. This feature of swelling pressure is considered to be very useful

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for examining the applicability of the prediction model to the swelling equilibrium calculation for the gel. However, few reports on the swelling pressure of gels have been published so far.

Horkay *et al.*[13,14] measured swelling pressures and the shear modulus of vinyl acetate gels in toluene and acetone solutions of known amounts of poly(vinyl acetate) whose osmotic pressure was available. With the experimental data, they discussed the assumption for the addition of the mixing and elastic contributions and concluded that the assumption was questionable. However, the formulas of the mixing and elastic terms used in their work were very simple and their data were limited to those only in the swollen state.

In this study, we measured the swelling pressure of NIPA gels of various cross-linking densities from swollen to shrunken states in aqueous solutions of poly(ethylene glycol) (PEG) according to the method of Horkey *et al.*[13] The osmotic pressure data of aqueous solutions of PEG were reported in a previous paper.[15] The lattice model proposed by Hooper *et al.*,[10] which was originally proposed by Prange *et al.*[9] and is capable of representing the liquid–liquid equilibria for polymer aqueous solutions including the LCST behavior of poly-NIPA aqueous solutions, was used for the calculation of swelling equilibria of the NIPA gels. The additivity assumption of the mixing and elastic contribution is examined by comparing the experimental data to the calculated swelling pressure and equilibria for NIPA gels of various cross-linking densities.

Experimental Section

Sample Preparation. Sample gels were prepared via a radical polymerization according to the method by Hirotsu *et al.*[5] The NIPA monomer, provided by Eastman Kodak Co., was purified by recrystallization from benzene/*n*-hexane mixtures. The purified NIPA monomer and *N,N'*-methylenebis(acrylamide) (BIS), cross-linking reagent, were dissolved in water containing an initiator, K_2SO_4. To the solution, accelerator *N,N,N',N'*-tetramethylenediamine was added. The reaction was carried out in capillary tubes of 1.65 mm diameter at 0 °C. The concentration of NIPA was kept to 0.7 M while the molar ratio of NIPA/BIS was varied as 0.04, 0.02, 0.01, 0.005, and 0.0025.

Measurements. The swelling pressure was measured according to the method by Horkay *et al.*[13] The NIPA gel was swollen in the PEG aqueous solutions whose PEG concentrations were in the range 0.5–2.5 wt % at 5–32 °C. PEG was provided from Tosoh Co. and its weight averaged molecular weight M_w was 520 000.

After attaining the swelling equilibrium, the diameter, d, of the gel was measured by calibrated scale photography.[7] As a reference volume we adopted the volume, V_0, when the gel was synthesized in a capillary tube of 1.65 mm, d_0. The swelling ratio of the gel, V/V_0, was calculated from d and d_0 by the following equation:

$$(V/V_0) = (d/d_0)^3 \tag{2}$$

The swelling pressure of the gel was determined to be equal to the osmotic pressure of an external aqueous solution of PEG after confirming that the PEG chain could not enter the inside of the gel by comparing the measured diameter of the gel with that of the gels enclosed by a semipermeable membrane.

The osmotic pressure of the aqueous solutions of PEG were measured by a membrane osmometer and reported in a previous paper.[15]

Results and Discussion

Figure 1 shows a plot of swelling pressures vs swelling ratio that were measured at various temperatures for the NIPA gel where the BIS/NIPA ratio was 0.0025. The fluctuation of the data is due to the experimental errors

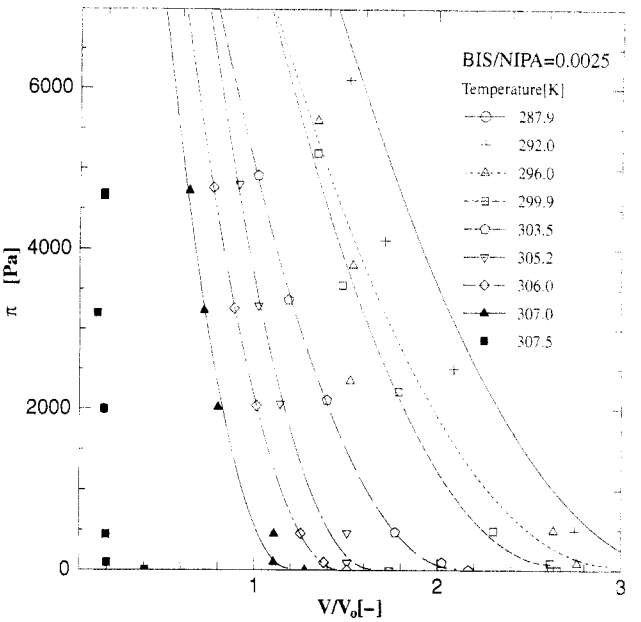

Figure 1. Measured swelling pressures for a NIPA gel (BIS/NIPA = 0.0025). Symbols denote the measurement values. Lines are smooth curves of the measurement data.

in measuring the osmotic pressure of the external solutions and the swelling volume of the gel. The volume of the gel in the swollen state at lower temperatures was strongly affected by the osmotic pressure of the external solution. At higher temperatures, however, the volume of the gel was relatively insensitive to increases in the osmotic pressure of the external solution. In other words, the small volume change at higher temperature required a high swelling pressure for the gel. Similar results were obtained for the swelling pressure of other gels having different BIS/NIPA ratios.

By interpolation of these swelling pressure data, the data could be transformed into the temperature and swelling volume of the gels for a given swelling pressure. The swelling curves obtained at various BIS/NIPA ratios are shown in Figure 2a–e. In the shrunken state, the swelling volume of the gel hardly changes with swelling pressure. The volume phase transition was observed for all the gels and the transition temperature was almost constant at ca. 34 °C for all the gels within experimental error (a slight decrease in the transition temperature was observed with an increase in the swelling pressure). Whereas the magnitude of volume change at the transition was strongly dependent on the BIS/NIPA ratio, i.e., cross-linking density of the gel, it became larger as the cross-linking density of the gel decreased. The effect of the swelling pressure on the swelling equilibrium was significant for the gels with lower cross-linking density.

The locus of the transition points of a gel with swelling pressure can be considered to correspond to the binodal curve in gel–gel equilibria of the gel. The binodal curves, estimated from the swelling pressure data of the NIPA gel, were found to be of the LCST type and very flat in temperature–volume (concentration) coordinates around its critical point, which may be coincident with the fact that the coexistence curve of a poly-NIPA aqueous solution is very flat around its LCST.[2] It should be noted that this finding is experimental evidence indicating the similarity in phase equilibrium between a gel and its corresponding polymer solution.

The prediction model by Hooper *et al.*[10] was adopted for calculating swelling pressures and swelling equilibria of the gels in this work. The model is expressed as follows:

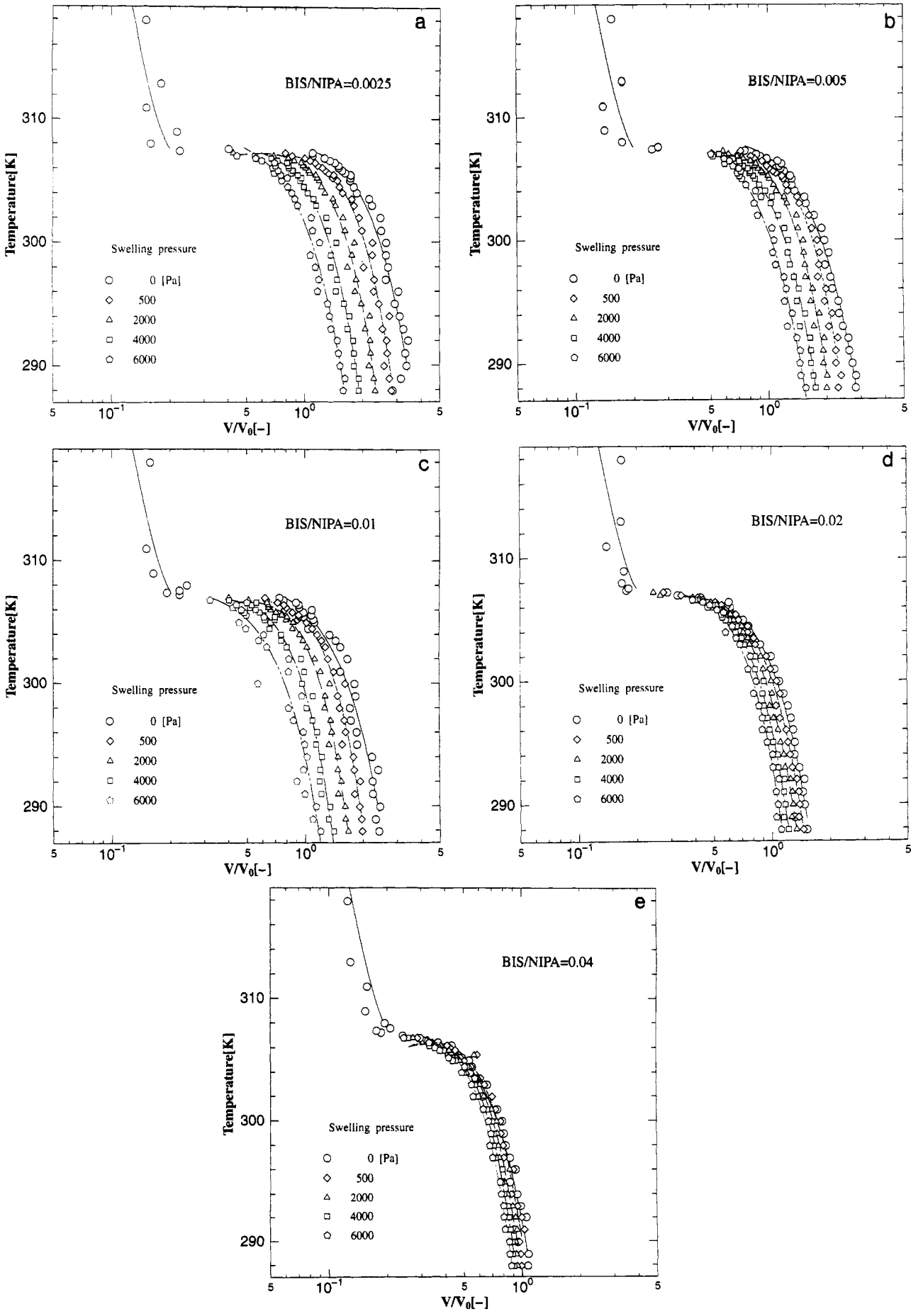

Figure 2. Swelling equilibria for NIPA gels under various swelling pressures: (a) BIS/NIPA = 0.0025; (b) BIS/NIPA = 0.005; (c) BIS/NIPA = 0.01; (d) BIS/NIPA = 0.02; (e) BIS/NIPA = 0.04.

$$\pi = \pi_{\text{mixing}} + \pi_{\text{elastic}}$$

$$\pi_{\text{mixing}} = -\frac{RT}{\nu_1}\left[\ln \phi_1 + \phi_2 - \frac{1}{2}z_1^a q_1 \ln\frac{[\Gamma_{11}^{aa}]_{\text{pure}}}{[\Gamma_{11}^{aa}]_{\text{mix}}} - \frac{1}{2}z_1^\beta q_1 \ln\frac{[\Gamma_{11}^{\beta\beta}]_{\text{pure}}}{[\Gamma_{11}^{\beta\beta}]_{\text{mix}}} - \frac{1}{2}z_1^D q_1 \ln\frac{[\Gamma_{11}^{DD}]_{\text{pure}}}{[\Gamma_{11}^{DD}]_{\text{mix}}}\right] \quad (3)$$

$$\pi_{\text{elastic}} = -\frac{RT}{\nu_1}\left(\frac{\phi_2^0}{2x_c}\right)\lambda^{-1}[1 + K(\lambda,\kappa)]$$

$$\lambda = \left(\frac{\phi_2^0}{\phi_2}\right)^{1/3} \qquad \kappa = \frac{1}{4}P\phi_2^0 x_c^{1/2}$$

$$\frac{[\Gamma_{ij}^{kl}]^2}{[\Gamma_{ii}^{kk}][\Gamma_{jj}^{ll}]} = \exp[-2\omega_{ij}^{kl}/kT]$$

where ϕ_1 and ϕ_2 are volume fractions of the solvent and gel, respectively, q_1 is the surface area fraction of solvent, z_1 is the coordination number of solvent, ϕ_2^0 is the volume fraction fo the gel at its preparation, x_c is the average number of segments per network chain, P is a dimensionless number related to constraints of the junction fluctuation κ, and Γ is a nonrandom factor of the mixing of the solvent and polymer chains in the gel. The mixing term was the formula proposed for the prediction of phase equilibria for polymer solutions by Prange *et al.*[9] based on Guggenheim's quasichemical equilibrium approximation,[16] which accounts for hydrogen bonding by distinguishing between the interaction sites. Superscripts, α, β, and D denote the hydrogen-bond donor site, hydrogen-bond acceptor site, and dispersion-force interaction site, respectively. The elastic term, π_{elastic}, adopts the formula by Erman and Flory,[17] in which the contributions from junction fluctuations between phantom and affine networks are involved. $K(\lambda,\kappa)$ is a parameter given by Erman and Flory. The interaction parameters, ω_{ij}'s, in the mixing term can be determined by fitting the experimental data for polymer solutions.

Firstly, we predicted the swelling equilibria of the NIPA gels by Hooper's model using the interaction parameters, ω_{ij}'s, determined from the osmotic pressure data of poly-NIPA aqueous solutions in our previous paper. The values used are presented in Table 1. The volume fraction of the gel at the preparation, ϕ_2^0, was estimated to be 0.07 from the synthesis condition of the gel. Other parameters were evaluated from the experimental conditions. The determined x_c for the NIPA gels of different BIS/NIPA ratios are listed in Table 1. The assumptions and parameters presented by Prange *et al.*[9] and Hooper *et al.*[10] were also adopted in our calculations.

$$\omega_{ij}^{\alpha\beta} = \omega_{ji}^{\alpha\beta} \qquad \omega_{ij}^{\alpha D} = \omega_{ij}^{\beta D} \qquad i, j = 1, 2$$

$$\omega_{ii}^{\alpha\beta}/k = \omega_{jj}^{\alpha\beta}/k = -200.0 \text{ K}$$

$$Z^\alpha + Z^\beta + Z^D = 10 \qquad Z^\alpha_{\text{water}} = Z^\beta_{\text{water}} = 2$$

$$Z^\alpha_{\text{NIPA}} = Z^\beta_{\text{NIPA}} = 1.1$$

$$P = 3.0$$

The prediction results are shown by dotted lines in Figure 3 for the swelling equilibria of the NIPA gel of BIS/NIPA = 0.01. The agreement between the calculated and experimental swelling curves is not satisfactory. The calculated values exhibit a continuous volume change,

Table 1. Parameters Determined for Eq 3 from Experimental Data

BIS/NIPA	$\omega_{ij}^{\alpha\beta}/k$ [K]	$\omega_{ij}^{D\,a}/k$ [K]	ω_{ij}^{D}/k [K]	x_c^b
0.0025	−812.5	−119.2	254.7	71.37
0.005	−814.0	−120.3	256.3	140.7
0.01	−815.2	−118.8	256.7	278.6
0.02	−810.7	−119.5	254.0	542.5
0.04	−809.9	−122.1	255.0	1082
for all the gels	−812.9	−122.5	256.4	
for polymer sol[a]	−1545.2	−133.7	834.6	

[a] Determined from the osmotic pressure data.[15] [b] Evaluated from the experimental conditions.

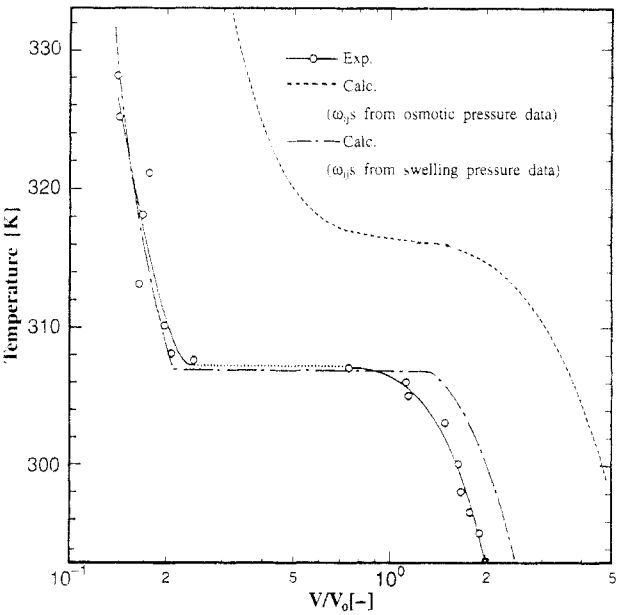

Figure 3. Comparison between the experimental and calculated swelling equilibria in pure water for a NIPA gel of BIS/NIPA = 0.01.

while the experimental ones exhibit a discontinuous transition. The possible reasons for this are as follows: (i) wrong formula in the mixing term; (ii) wrong formula in the elastic term; (iii) wrong parameter values for ω_{ij}'s in the mixing term. Since discussion about (i) and (ii) was difficult at the present stage, we made an attempt to examine the parameter values for ω_{ij}'s. In calculations, the parameter values were assumed to be valid at the concentrations corresponding to the polymer solution in the NIPA gel swollen in aqueous solution. However, it was found that the polymer concentration of the osmotic pressure data used to determine the interaction parameters in the previous work was very dilute (less than 2.5 wt %) compared with that in the gel swollen in aqueous solution. We determined the interaction parameters in eq 3 by fitting to the swelling pressure data measured in this work. The fitting method used was the hybrid method.[18] The parameters determined for the gel at various BIS/NIPA ratios are presented in Table 1.

The calculated swelling ratios of the NIPA gel (BIS/NIPA = 0.01) with these newly determined parameters are shown by the dash-dotted line in Figure 3. The calculations could represent the swelling behavior of the NIPA gel. Similarly to this figure, good agreement between the calculated and experimental swelling equilibria was obtained for the NIPA gel of other BIS/NIPA ratios, as shown in Figure 4a,b with the new parameter values. After adjusting the parameter values, we found that the values were almost same for all the gels regardless of their cross-linking densities (BIS/NIPA ratios). This finding suggests

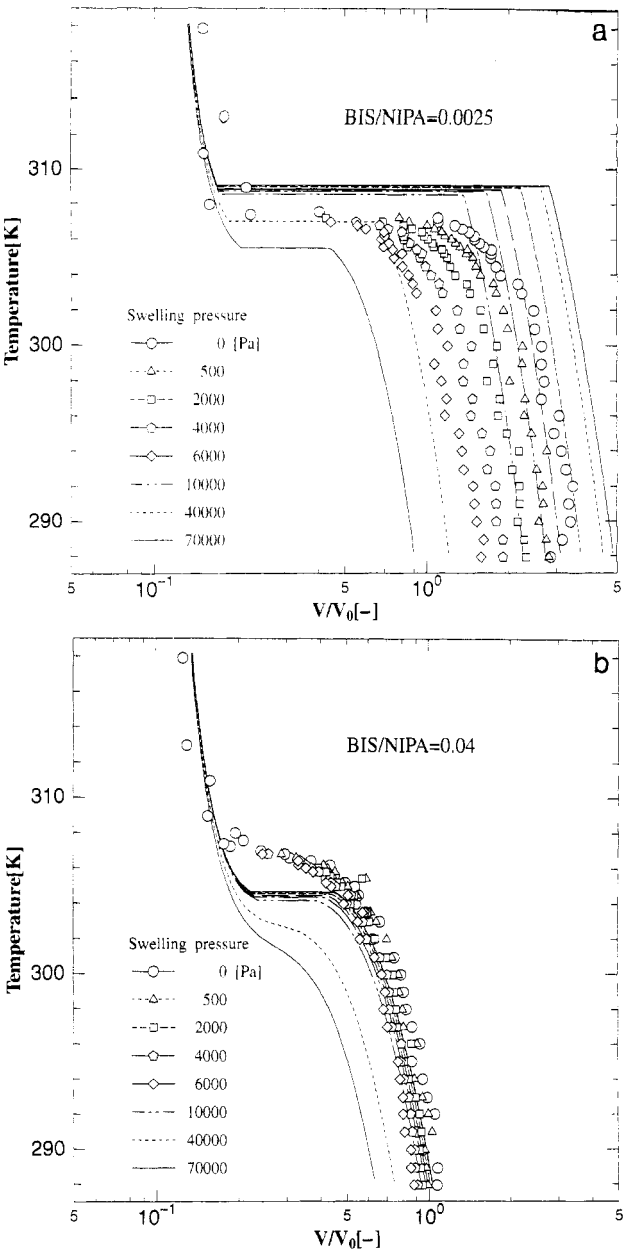

Figure 4. Comparison between the experimental and calculated swelling equilibria for a NIPA gel under various swelling pressures: (a) BIS/NIPA = 0.0025; (b) BIS/NIPA = 0.04. Symbols denote the experimental values and lines are calculated values.

that the effect of cross-linking density on swelling pressure was almost successfully represented by the formula (Erman–Flory equation) adopted for the elastic osmotic pressure of the gel. Next we tried to evaluate one set of parameter values for all the NIPA gels used in this work by using all the swelling pressure data.

The obtained values are also tabulated in Table 1. The calculated swelling equilibria of the gels of different cross-linking densities at zero swelling pressure are presented in Figure 5. Although small deviations between the calculated and experimental values were observed, the calculations could represent the behavior of the swelling equilibria for these gels, especially the effect of cross-linking density on the swelling equilibria. Namely, one can find that the binodal curve of the gel is the LCST type and that the transition temperature of the gel is not strongly dependent on the cross-linking density of the gel while the magnitude of volume change at the transition decreases with the increase in the BIS/NIPA ratio.

On the basis of these results, it might be noted that the addition of the mixing and elastic contribution is a useful

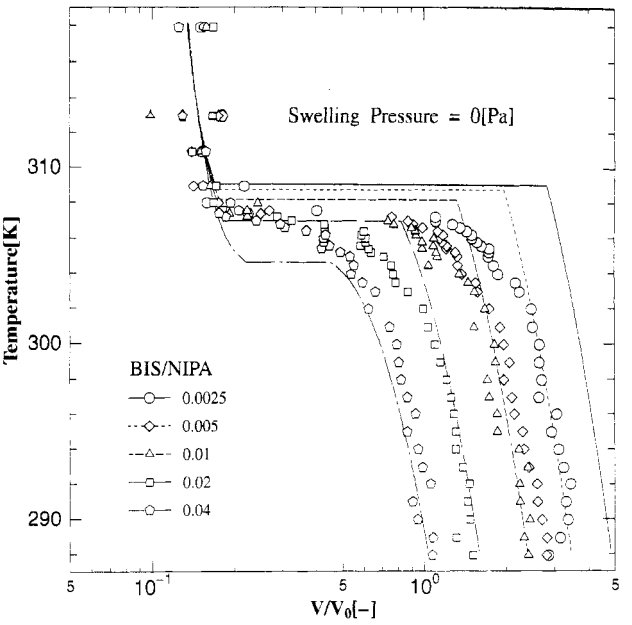

Figure 5. Comparison between the experimental and calculated swelling equilibria for a NIPA gels of various cross-linking densities at zero swelling pressure. The same interaction parameters were used for all the gels.

assumption in calculating the osmotic pressure of gels swollen in solution within the experimental conditions in this work.

Conclusion

The swelling pressures of NIPA gels were measured from the swollen state to the shrunken state. The measurement data revealed that the binodal curve in the gel–gel transition of the NIPA gel was the LCST type and similar to that in liquid–liquid equilibria of poly-NIPA aqueous solutions, especially its flatness in the vicinity of the critical region.

The prediction model proposed by Hooper *et al.* could represent the swelling equilibria under various swelling pressures when the parameters in the mixing term of the model were determined by fitting to the swelling pressure data measured in this work. The obtained parameter values were found to be close for all gels regardless of cross-linking densities. This finding seems to suggest that the cross-linking of the gels has a small effect on the mixing of solvent and gel networks, namely that the interaction between the solvent and polymer chains in the gel can be evaluated independently of the elasticity originating from a gel. For further investigation, we determined a single set of values for the interaction parameters in the model from all the swelling pressure data and applied the parameter values to the calculation of the swelling equilibria of all the gels. The agreement between the calculated and experimental swelling equilibria was fairly good, and the calculation could represent the effect of cross-linking density on the swelling equilibria of the gel. On the basis of these calculation results, we have confirmed that the addition of the mixing and elastic contributions in osmotic pressure of the gel is a reasonable assumption in calculating the swelling equilibria of gels.

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Notation

d = diameter of the gel
d_0 = diameter of the gel at preparation (=1.65 mm)
$K(\lambda,\kappa)$ = parameter given by Erman and Flory
k = Boltzmann constant
P = dimensionless number
q = surface area fraction
V/V_0 = swelling ratio of the gel
ν_1 = molar volume of the solvent
z = coordination number (=10)

Greek Letters

ϕ = volume fraction
ϕ_2^0 = volume fraction of the gel at preparation (=0.07)
Γ = nonrandom factor of mixing
κ = a measure of the constrains on the junction fluctuation
μ = chemical potential of the i-component
π = osmotic pressure
ω_{ij} = interaction parameter in eq 3
x_c = average number of segments per network chain

Subscripts

1 = solvent
2 = polymer (gel)

Superscripts

0 = reference state (~sample preparation)
α = hydrogen-bond donor site
β = hydrogen-bond acceptor site
D = dispersion-force interaction site

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