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Contributions to the thermodynamics of polymer hydrogel systems

Éder D. Oliveira, Antônio F.S. Silva, Roberto F.S. Freitas*

Laboratory of Gels and Polymers, Department of Chemical Engineering, School of Engineering, Federal University of Minas Gerais, Rua Espírito Santo, Lab 601, Belo Horizonte, Minas Gerais 30160-030 Brazil

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Abstract

In this work, an extended version of a quasichemical thermodynamic model is presented. The swelling behavior of crosslinked acrylamide polymer gels and N-substituted derivatives, such as *N*-isopropylacrylamide and *N-tert*-butylacrylamide has been compared to predictions from such model which takes into account the specific hydrogen bonding interactions encountered in these systems. The calculated volume transition temperature of the poly(*N*-isopropylacrylamide) gel is 0.8 °C lower than the experimental value and the predicted solvent volume fraction in the collapsed and swollen gel states are about 2% larger than the corresponding experimental data measured at the transition point. Applying the same energy parameters obtained from regressing poly(*N*-isopropylacrylamide) gel swelling pressure data, the model has also been capable to correctly represent the major features found in the swelling behavior of linear poly(*N-tert*-butylacrylamide) and poly(*N-tert*-butylacrylamide) gels, after the model parameters that characterize the molecular structure were changed in accord to each polymer repetitive unit.

Keywords: Quasichemical thermodynamic model; Thermoreversible hydrogel; Poly(*N*-isopropylacrylamide)

1. Introduction

Poly(*N*-isopropylacrylamide) (PNIPA) exhibits a well-known lower critical solution temperature (LCST) in water [1], i.e. phase separation occurs on increasing temperature. Similarly, PNIPA gels undergo a considerably abrupt volume phase transition at around 32–34 °C in water [2, 3]. While theoretical aspects correlating the coil-to-globule transition of linear chains with the unusual discontinuity of volume transition in gels have been the subject of extensive discussions [4–6], the potential technological use of PNIPA gels associated with their particular structure and thermodynamic behavior has attracted the interest of many research groups. PNIPA gels and their derivatives have been tested for many different applications, including concentration of macromolecular solutions [7,8], column packing materials for chromatography [9], drug delivery systems [10] and cell culture substrata [11]. The utility of gels lies on their elastic properties, mass transfer characteristics, and swelling behavior—principally, responses to physicochemical stimuli [3,12,13].

PNIPA gel can display either continuous or discontinuous volume change depending on the system composition, network crosslink density and ionization degree [3,12–15]. It is generally believed that the LCST behavior of PNIPA in aqueous solutions is strongly related to the destabilization of hydrogen bonds between water molecules and amide groups with increasing temperature, probably induced by the presence of the hydrophobic isopropyl group and backbone [14–17]. Thermodynamically, the mixing process at low temperatures is favored by the formation of hydrogen bonds, which lead to a large negative enthalpy of mixing. However, despite the moderate gain in compositional entropy resulting from the mixing process, hydrogen-bonded molecules acquire a very low orientation entropy [18]. Phase separation occurs with increasing temperature due to the more unfavorable entropy contribution to the free energy [14–21].

Due to this fact, some thermodynamic models have been proposed to incorporate the influence of hydrogen bonding and describe the phase behavior of these systems. Prange and collaborators [21], for instance, extended Guggenheim's [22] quasi-chemical partition

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* Corresponding author. Tel.: +55-31-3238-1780; fax: +55-31-3238-1789.

E-mail addresses: freitas@deq.ufmg.br (R.F.S. Freitas), eder@deq.ufmg.br (E.D. Oliveira), fabrica@belquimica-fob.com.br (A.F.S. Silva).

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function with three categories of interaction sites: hydrogen-bond donors, hydrogen-bond acceptors, and dispersion force contact sites. The resulting model is able to describe the major features of LCST behavior in aqueous solutions of linear polymers and polymer gels using the same set of temperature-independent parameters [21]. The model can also be promptly extended to apply to copolymer containing systems. Other available models for polymer hydrogels often require parameters that are different from those applied to the linear polymer solutions [23,24]. A few other models indirectly introduce the influence of hydrogen bond interaction. For instance, Painter et al. [25] also attempted to introduce the effects of hydrogen bonding on the hydrogel thermodynamic properties. The extent of the hydrogen bonding is quantified by an equilibrium constant, which must be determined from experimental data. The influence of polymer–water interactions on the gel phase transition is introduced through a function of experimentally determined chemical potential for water molecules in a model proposed by Sasaki and Maeda [26]. Lele et al. [27,28], used an extended version of Sanchez and Lacombe's [29] theory that includes hydrogen-bonding effects. Different from the approach of Prausnitz and co-workers [21], a temperature-dependent interaction parameter is used to describe the observed volume transition of poly(*N*-isopropylacrylamide) gels on increasing the temperature [27,28]. Alternatively, Hino and Prausnitz [30] have proposed a model that extends Flory–Huggins theory [31] by considering Flory's interaction parameter as a product of a temperature and a composition-dependent term. The temperature-dependent contribution accounts for the effects of specific interactions such as hydrogen bonding. One of the advantages of this model is its similarity to the classical Flory–Rehner theory for hydrogels [31] but the specific oriented interactions are bundled into a pair of interaction-dependent parameters. Finally, Chun and Kim [32] modified UNIQUAC model [33] using scaling concepts to represent polymer–water interactions in PNIPA hydrogel systems. Other models have been suggested that do not take hydrogen bonding as the main mechanism for hydrogel collapsing but their molecular interaction parameters are empirically defined and their roles are difficult to be completely determined. Therefore, without clear evidence that the specific interactions do not play an important role in the hydrogel swelling behavior [20,34].

In the present work, an extended version of the oriented quasichemical approach proposed by Prange et al. [21] is presented. It is, then, correlated to swelling pressure data of a poly(*N*-isopropylacrylamide) gel. The model is also tested to determine if it can describe the major changes in the gel swelling behavior that takes place as a result of modifications in the chemical structure of the acrylamide-based polymer.

2. Theory

2.1. Equilibrium swelling and critical phenomena in gels

In principle, the swelling behavior of gels can be determined from thermodynamic statistical models. The approach, used by almost all models, is based on Flory–Rehner hypothesis [31] that the mixing Gibbs energy of a nonionic system, ΔG, is resultant of independent mixing, ΔG_m, and elastic, ΔG_{el}, contributions:

$$\Delta G = \Delta G_m + \Delta G_{el} \tag{1}$$

or in terms of the chemical potential of the species, μ_i :

$$\Delta\mu_i = \Delta\mu_{i,m} + \Delta\mu_{i,el} \tag{2}$$

where $\Delta\mu_i$ represents the difference between the chemical potential of the *i*th-component in the gel, μ_i, and in the state of reference, usually taken as the pure component at the same temperature and pressure of the system, μ_i^0. In Eqs. (1) and (2), it is assumed that the presence of crosslinks does not affect the polymer interactions with the solvent and other solutes.

The general thermodynamic conditions for the existence of critical phenomena in gels were later derived by Hasa et al. [35,36] as well as Erman and Flory [37]. By using a concentration-dependent interaction parameter, a elastic contribution from the constrained-junction theory, and ideal osmotic effects, Erman and Flory [37] showed that the presence of charged groups in the network facilitates the occurrence of first-order transitions-in agreement to the results obtained by Hasa and co-workers using an earlier elasticity theory [35,36]. However, heat-induced discrete phase transition was observed in neutral poly(*N*-isopropylacrylamide) gels [3,14].

The equilibrium condition for the solvent in the gel and external solution is represented by the equation [21,31,35–37]:

$$\Delta\mu_1 = -\pi v_1 = 0 \tag{3}$$

whereπ denotes the osmotic pressure and v_1 the molar volume of the solvent.

Conditions for the coexistence of two gel phases, in a pure solvent, one swollen with composition $\phi_2{}'$ and the other collapsed with composition $\phi_2{}''$ are determined by [21,31,35–37]

$$\Delta\mu_1(\phi_2{}') = \Delta\mu_1(\phi_2{}'') \tag{4a}$$

$$\Delta\mu_2(\phi_2{}') = \Delta\mu_2(\phi_2{}'') \tag{4b}$$

The condition given by Eq. (4b) is usually replaced by the Maxwell construction [35–37]:

$$\int_{\phi_2{}''}^{\phi_2{}''} \frac{\Delta\mu_1}{\phi_2^2}\,\mathrm{d}\phi_2 = 0 \tag{5}$$

For a given pressure, the phase transition temperature for a gel in equilibrium with a pure solvent is the one for which Eqs. (4a) and (5) are satisfied.

2.2. Polymer solution theory: mixing of flexible chains

According to Prange et al. [21], a quasichemical partition function can be applied to represent the thermodynamic mixing properties of homopolymer aqueous systems considering that each molecule or polymer segment may possess three energetically types of contact sites. The sites are divided in hydrogen-bond donating sites (α-site), hydrogen-bond accepting sites (β-site), and sites which interact through dispersion forces (D-site). The partition function can be readily extended to further consider molecules containing different types of segments or copolymers. For a system formed by a solvent (component 1), containing a k-distinct segment, and a polymer network (component 2) with a l-type segment (copolymer), the hydrogen-bond effects on the thermodynamic potentials can be introduced through nonrandom-factors, $\Gamma_{ij}^{S_iS_j}|_{kl}$. These factors represent the ratio between the number of $S_i - S_j$ contact pairs (S_i and $S_j = \alpha$, β, or D), involving a k-type segment of a molecule i and the l-segment of a molecule j, and the number of $S_i - S_j$ contact pairs involving the former segments of each molecule in a completely random mixture. The mixing contribution to the solvent chemical potential can be represented by the equation:

$$\Delta\mu_{1,\mathrm{m}} = RT\left[\ln\phi_1 + \phi_2 - \sum_{k=1}^{m_1}\frac{1}{2}q_1(\rho_1|k)(z_1^{\alpha}|k)\ln\frac{\Gamma_{11}^{\alpha\alpha}|_{kk_\mathrm{p}}}{\Gamma_{11}^{\alpha\alpha}|_{kk_\mathrm{m}}} - \sum_{k=1}^{m_1}\frac{1}{2}q_1(\rho_1|k)(z_1^{\beta}|k)\ln\frac{\Gamma_{11}^{\beta\beta}|_{kk_\mathrm{p}}}{\Gamma_{11}^{\beta\beta}|_{kk_\mathrm{m}}} - \sum_{k=1}^{m_1}\frac{1}{2}q_1(\rho_1|_k)(z_1^{\mathrm{D}}|_k)\ln\frac{\Gamma_{11}^{\mathrm{DD}}|_{kk_\mathrm{p}}}{\Gamma_{11}^{\mathrm{DD}}|_{kk_\mathrm{m}}}\right] \tag{6}$$

where $\rho_1|k$ is the number fraction of a k-type segment present in the solvent, m_1 and m_2 are the number of different type of segments forming the solvent and the polymer, respectively,ϕ_1 is the solvent volume fraction, andϕ_2 is the polymer volume fraction of the gel. Subscripts p and m refer to pure and mixture states, respectively. Besides, a kth-segment of a given molecule can interact through$z_1^{\alpha}|_k$ hydrogen-bond donating sites, $z_1^{\beta}|_k$ hydrogen-bond accepting sites, and $z_1^{\mathrm{D}}|_k$ sites interacting through dispersion forces. The total coordination number of the lattice is $z = z_i^{\alpha}|_k + z_i^{\beta}|_k + z_i^{\mathrm{D}}|_k$, usually taken to be 10 [21].

Following Guggenheim's [22] quasichemical method for a N-component system, the nonrandom factors are related through quasichemical equations of the form:

$$\frac{(\Gamma_{ij}^{S_iS_j}|_{kl})}{(\Gamma_{ii}^{S_iS_i}|_{kk})(\Gamma_{jj}^{S_jS_j}|ll)} = \exp\left(-\frac{2w_{ij}^{S_iS_j}|_{kl}}{k_\mathrm{B}T}\right) \tag{7}$$

where k_B is the Boltzmann constant and $w_{ij}^{S_iS_j}|_{kl}$ are the exchange energy for a $S_i - S_j$ pair (S_i and $S_j = \alpha, \beta$, or D, $1 \le i \le N$, $1 \le j \le N$, $1 \le k \le m_i$, and $1 \le l \le m_j$). The nonrandom factors are also constrained by contact-site balance equations that, for hydrogel systems, can be written as

$$\sum_{j=1}^{N}\sum_{l=1}^{m_j}(\rho_j|_l)(\phi_j^{\alpha}|_l)\Gamma_{ij}^{S_i\alpha}|_{kl} + \sum_{j=1}^{N}\sum_{l=1}^{m_j}(\rho_j|_l)(\phi_j^{\beta}|_l)\Gamma_{ij}^{S_i\beta}|_{kl} + \sum_{j=1}^{N}\sum_{l=1}^{m_j}(\rho_j|_l)(\phi_j^{\mathrm{D}}|_l)\Gamma_{ij}^{S_i\mathrm{D}}|_{kl} = 1 \tag{8}$$

where $1 \le i \le N$, $S_i = \alpha$, β, or D, $\phi_j^{\alpha}|_l = (z_j^{\alpha}|_l/z)\phi_j$, $\phi_j^{\beta}|_l = (z_j^{\beta}|l/z)\phi_j$, $\phi_j^{\mathrm{D}}|_l = (z_j^{\mathrm{D}}|l/z)\phi_j$.

2.3. Elasticity of polymer networks

An expression for the elastic contribution to the chemical potential of the solvent in a tetra-functionally crosslinked gel can be obtained from rubber elasticity theories [31, 37–41]. Traditionally, the equation proposed by Flory and Rehner [31] for a network that deforms affinely has been widely applied [21,31,37–41]:

$$\Delta\mu_{i,\mathrm{el}} = RT\rho_x\frac{v_1}{v_\mathrm{u}}\phi_{2\mathrm{o}}\left[\left(\frac{\phi_2}{\phi_{2\mathrm{o}}}\right)^{1/3} - \frac{\phi_2}{2\phi_{2\mathrm{o}}}\right] \tag{9}$$

where ρ_x is the number of elastically effective network chains per unit volume of the dry gel, v_1 and v_u are the molar volume of the solvent and the monomer unit, respectively, and $\phi_{2\mathrm{o}}$ is the gel polymer volume fraction at the unperturbed state, usually approximated to the gel synthesis state.

More recent theories try to overcome some limitations presented by Flory–Rehner equation such as the assumption of infinite extendibility of the polymer chains [37,41] or problems to represent the transition from phantom to affine elastic behavior in gels as they collapse [39,40]. For simplicity, Eq. (9) is used to represent the elastic contribution to the chemical potential in the present work.

2.4. Evaluation of exchange energy parameters and calculation of gel swelling degree

In the simplest case, the description of the swelling behavior of a homopolymer gel in a conventional solvent ($N = 2$, $m_1 = m_2 = 1$, and $\rho_1|m_1 = \rho_2|m_2 = 1$), 21 nonrandom factors are needed. Thus, 21 nonlinear algebraic equations, fifteen quasichemical equations, Eq. (7), and six contact-site balance equations, Eq. (8), must be solved numerically to determine the nonrandom factors used in the model. Additionally, the exchange energy parameters must be determined by fitting experimental gel swelling data. Following Prange and collaborators [21], three exchange energy adjustable parameters are necessary to represent the phase behavior of a homopolymer network in equilibrium with a solvent. An additional simplification consists in fixing the value of the pure component hydrogen-bonding exchange energy, $w_{ii}^{\alpha\beta}/k_B = -200.0$ K.

To determine the parameters, the SIMPLEX method [42] has been applied to minimize a conventional objective function constituted by the sum of quadratic residuals, formed by the difference between the theoretical and experimental osmotic pressures, which must be null in the equilibrium (Eq. (3)) [31,35–37]. The model was adjusted to fit Eq. (3) to a predetermined range of polymer volume fraction ($0.040 \leq \phi_2 \leq 0.250$), displayed by poly(*N*-isopropylacrylamide) 8 × 1 gel (PNIPA 8 × 1). The first digit denotes the mass of monomer and crosslinker in 100 ml of water, the second the percentage of crosslink agent in the total mass [3,14]. It is important to stress that the model adjustable parameters have been found by minimizing the sum of solvent chemical potential residuals or swelling pressure, instead of a direct fitting to experimental gel volumetric degree of swelling. This imposes a more strict comparison between the theory and experimental gel volume data since the parameters fitted to the swelling pressure must also correctly describe the volumetric degree of swelling afterwards. The regressing of the model to PNIPA 8 × 1 swelling data is a nonlinear process that requires the solution of the algebraic equation system for each set of parameters tested. The process is repeated until the objective function is minimized. The transition temperature and equilibrium swelling degree for the gel in expanded and collapsed states can be determined by numerically solving the algebraic nonlinear equations together with Eqs. (3), (4a) and (5).

Besides the adjusted parameters, the model also contains structural parameters that depend upon the molecular structure of the polymer and solvent as well as the gel synthesis conditions. In Table 1, it is displayed the structural parameters used to represent PNIPA 8 × 1 gel, poly(*N-tert*-butylacrylamide) 8 × 1 gel (PTBA 8 × 1), and poly(acrylamide) 8 × 1 gel (PAA 8 × 1). They were obtained from the chemical structure of monomers and solvent as well as the conditions used to prepare a perfect PNIPA 8 × 1 gel as indicated by Prange et al. [21]. PTBA 8 × 1 and PAA 8 × 1 gels are similar to PNIPA 8 × 1 gel but with different capabilities to interact through hydrogen bonds. Their swelling behavior was simulated to test the ability of the model to predict (altering only hydrogen bond structural parameters for each network) the major features of the swelling equilibrium in gel systems similar to PNIPA but which present very distinct expansion behavior.

Table 1
Structural parameters of water and acrylamide based hydrogels

Substance	Structural parameter					
	ρ_x	v_i, (cm^3/mol)^a	z_i^{α}	z_i^{β}	z_i^{D}	ϕ_{2o}
Water	–	18.02	2.0^b	2.0^b	6.0^b	–
PNIPA 8 × 1 gel	0.017^b	102.76	1.1^b	1.1^b	7.8^b	0.07^b
PTBA 8 × 1 gel	0.017^b	119.80	1.0^c	1.0^c	8.0^c	0.07^b
PAA 8 × 1 gel	0.017^b	67.48	2.0^c	2.0^c	6.0^c	0.07^b

[a] Based on experimental molar volumes at 25 °C and 1.0 atm.

[b] Based on Ref. [21].

[c] Modification of PNIPA z_i^{α}, z_i^{β}, and z_i^{D} values based on group contribution methods [21].

3. Experimental

Synthesis and experimental swelling data of PNIPA 8 × 1 and 10 × 1 gels are described in the literature [3,14, 15]. Similar procedures and methods were applied in the preparation of PTBA 10 × 1 and PAA 10 × 1 gels and determination of their swelling behavior as a function of temperature [14,15]. Spinodal critical equilibrium data for PNIPA 10 × 1 gel were obtained from light scattering measurements reported elsewhere [43].

4. Results and discussion

4.1. Poly(N-isopropylacrilamide) swelling behavior

In Table 2, the fitted values of the model interaction parameters are shown along with the fixed value of the pure component hydrogen-bonding exchange energy. The exchange energies for hydrogen-bonding site contacts (α–β) are negative reflecting their favorable formation from an energy standpoint. The dispersion exchange energies (D–D) between unlike molecules are generally positive since, as predicted by quantum mechanical methods, such interactions between unlike molecules are less favorable than the average of interactions between like molecules. The last type of exchange energies describing α–D or β–D type of site contacts are negative because of their favorable interactions, relative to α–α or β–β contacts [21]. The values of exchange energies presented in Table 2 are not identical to those obtained by Prange and co-workers after fitting linear poly(*N*-isopropylacrylamide) two-phase liquid equilibrium data [21], but have the same order of magnitude and relative sign. Inomata and Saito [44] also found that correlation of swelling pressure data from PNIPA gel will result in a different set of parameters relative to the correlation of osmotic pressure data from linear PNIPA aqueous solutions. Such differences may be due to limitations of the model as well as those related to the validity of Flory–Rehner's hypothesis [45]. In spite of the differences, parameters fitted to the linear polymer–liquid

Table 2
Exchange energies for PNIPA 8 × 1 gel equilibrated with water

$w^{\alpha\beta}_{(11\text{ or }22)}/k_B$ (K)	w^{DD}_{12}/k_B (K)	$w^{\alpha\beta}_{12}/k_B$ (K)	$w^{D(\alpha\text{ or }\beta)}_{12}/k_B$ (K)
−200.0	314.1	−1302.9	−236.9

phase equilibrium data represent the features of PNIPA gel behavior semi-quantitatively [21].

Using the exchange energies based on the fitting of swelling pressure data, PNIPA 8 × 1 gel swelling behavior can be simulated. Fig. 1 shows the coexistence curve for the gel with pure solvent (solid line) along with experimental data for PNIPA 8 × 1 gel (squares), the binodal or coexistence curve for two gel phases (broken line), and the spinodal curve for the gel–solvent system (dotted line). These curves were obtained from the solution of the model and by applying thermodynamic equilibrium and stability criteria aforementioned. The predicted gel transition temperature (305.6 K) is 0.8 degree lower than the observed collapse temperature (306.4 K). Concomitantly, the calculated volume fraction of solvent in the gel at the swollen state (0.947) is about 1.5% larger than the observed value (0.933) while the calculated value for the collapse state (0.769) is approximately 2.5% bigger than the experimental data (0.750). The binodal and spinodal curves divide the figure into regions corresponding to stable (s), metastable (m), and unstable (u) states. A characteristic feature for polymer gels is an unstable region ($\partial \mu_1 / \partial \phi_1 < 0$) at high concentration of solvent or high degree of swelling. This instability is caused by the elastic force contributions to the chemical potential of the solvent that impede the polymer dissolving completely [21,35–37]. Since a solvent and two gel phases in equilibrium contain only one degree of freedom, the phase transition temperature can be displaced along the binodal curve as pressure is changed and the phase transition becomes continuous [46]. At temperatures below the transition point, the model has only one stable phase solution, corresponding to the coexistence of a swollen gel with the solvent. At temperatures above the transition, a collapsed gel phase will coexist with the solvent in equilibrium. For a given pressure, the gel will display a unique transition temperature. Fig. 1 shows also two-phase liquid equilibrium data for linear PNIPA (circles) [1]. Near the region of the lower critical solution temperature ($\phi_1 = 0.84$, $T = 304.2$ K) the calculated binodal curve (estimated gel critical point: $\phi_1 = 0.846$, $T = 302.9$ K) follows the behavior observed in the experimental data. In analogy and complement to findings from the correlation to liquid–liquid equilibrium data [21], the model is also able to describe the major features of LCST behavior in aqueous solutions of linear polymers using the same set of temperature-independent parameters obtained from polymer gel data fitting. At last, experimental spinodal data (triangles) from light scattering measurements [43] in a denser PNIPA 10 × 1 gel (transition temperature: 307.5 K) are included for completeness. The calculated curve is shifted in relation to experimental data due to differences in gel composition, experimental uncertainties related to the determination of critical properties, and model limitations. However, the model is capable to qualitatively represent the gel behavior at unstable critical states.

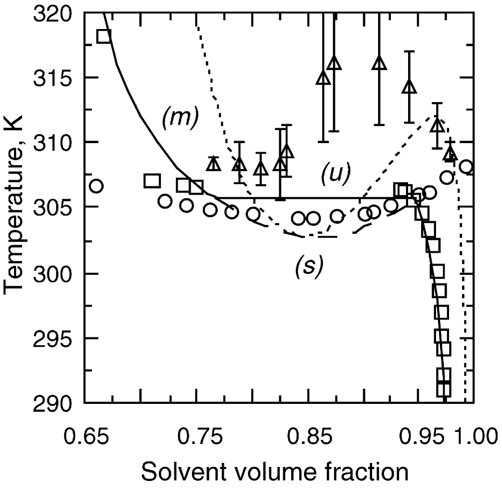

Fig. 1. Phase diagram for poly(*N*-isopropylacrylamide) in water. Square, circle, and triangle symbols represent experimental equilibrium data for 8 × 1 gel [3,14], linear two-phase liquid polymer equilibrium points [1], and spinodal critical data for 10 × 1 gel [43], respectively. Solid and dotted lines describe coexistence and spinodal curves from the model, respectively. Broken line corresponds to binodal curve for the coexistence of swollen and collapsed gel phases. The curves divide the diagram into areas corresponding to stable (s), metastable (m), and unstable (u) states.

Fig. 2 shows the experimental and theoretical results for PNIPA 8 × 1 gel in terms of the volume swelling degree for a wide range of collected data. Besides the aforementioned lower transition temperature, the experimental results show that PNIPA 8 × 1 gel expansion tends to an asymptotic value with decreasing temperature that is not observed in the predicted swelling—it is larger than the observed values at low temperatures. These deviations are due to the assumption that the elastic contribution to the solvent chemical potential can be represented by Eq. (9). It is has been determined that the Flory–Rehner equation only partially describes the elastic behavior of collapsed gel phases which, in turn, result in predicted phase transition temperatures lower than those observed experimentally [30,39,40].

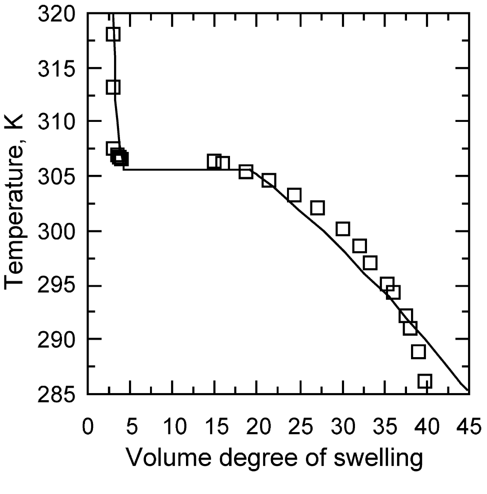

Fig. 2. Swelling of poly(*N*-isopropylacrylamide) 8 × 1 gel in water. Symbols represent experimental data. Solid line is predicted behavior from the model.

Additionally, the distribution of the chains in the gel are assumed to be Gaussian which admits an infinite extendibility of the polymer chains that cannot be reached for real systems. This introduces a significant error at high degrees of swelling in which the chains reach their extension limit [38,41]. Despite its simplicity, Eq. (9) is still useful for testing the model performance in a first depiction of the thermoresponsive PNIPA gel swelling behavior as well as those of other acrylamide-based gels, which display significantly different capabilities to interact through hydrogen bonds.

4.2. Poly(N-tert-butylacrilamide) and poly(acrylamide) swelling behavior

Altering the polymer structural parameters, based only upon the monomer molecular structure, PTBA 8 × 1 and PAA 8 × 1 gel swelling behavior can be obtained-applying the same exchange energy values found for PNIPA 8 × 1 gel. Table 3 displays the calculated and experimental swelling degree for these gels at different temperatures. The predicted swelling behavior agrees with experimental observations showing that PAA gels remain expanded in the tested range of temperature, while PTBA gels in water display a volume swelling degree similar to the collapsed PNIPA 8 × 1 gel, independent of temperature. The model describes correctly such features found in the swelling behavior of these gels. In the case of PTBA gel, it can be observed that the decrease in hydrogen bond connection sites (larger influence of dispersion forces as a result) because of larger steric hindrance of *tert*-butyl side-groups takes the gel to remain always in the collapsed state. On the other hand, for PAA gels, the greater number of hydrogen bonding sites available to interact with water and the smaller influence of unfavorable dispersion interaction result in the suppression of the phase transition, retaining the gel always expanded. These results are in agreement with the observed and other reported behavior for such systems [2,14]. As observed, the hydrogen bond mechanism, originally suggested by Hirschfelder and collaborators [19] can physically represent the swelling behavior of acrylamide-based hydrogel systems and the quasichemical thermodynamic model is able to account for the specific molecular interactions present in these systems, without introducing any empirical correlation.

Table 3
Volumetric swelling degree of PTBA and PAA gels

Temperature (K)	PTBA gel volume degree of swelling		PAA gel volume degree of swelling	
	Theoretical[a]	Experimental[a]	Theoretical[a]	Experimental[a]
285	1.73	2.47	173	149
305	1.71	1.98	161	148
315	1.71	1.88	156	148

[a] Calculated values for 8 × 1 gels. Experimental data obtained from 10 × 1 gels.

5. Conclusions

The oriented quasichemical thermodynamic model, with exchange energy parameters obtained from the regression of swelling pressure data or solvent chemical potential difference, can correctly depict the swelling behavior of PNIPA gel. It represents correctly the competition between hydrogen bonding and dispersion forces that take to the transition from less entropic swollen gel phases to more entropic collapsed gel states, displaying a phase transition temperature similar to LCST found in analogous linear polymer solutions. The energy parameters obtained from fitting the experimental data have magnitudes and signs consistent with the model physical premises. Deviations observed in relation to the experimental data are mainly related to the simplicity of the Gaussian approach used to represent the elasticity of the gel. The model has also been capable to represent PTBA and PAA gel swelling behaviors, after the model structural parameters were changed in accord to the molecular structure of their repetitive units—applying the same energy parameters obtained from adjusting PNIPA gel swelling pressure data. A stricter test of the theory will come from comparison to swelling data of copolymer gels, which have started to receive more attention [28]. For these future applications, it is important to address two of the model major problems: the estimation of the exchange energies directly from experimental data, at least partially, and the reduction of its number of equations. The former can be more easily approached if it is recognized that energy parameters used to correlate experimental data are relative, that is, they do not represent the molecular interaction absolutely. This permits that the adjusted parameters be only indicative of the signs and magnitudes of the interactions, with respect to values fixed or directly correlated to experimental data [47,48]. The latter restriction will require a simplification of the quasichemical equations.

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References

[1] Heskins M, Guillet JE. J Macromol Sci 1968;A2(8):1441–55.
[2] Hirokawa Y, Tanaka T. J Chem Phys 1984;81:6379–80.
[3] Freitas RFS, Cussler EL. Chem Engng Sci 1987;42:97–103.

[4] Tiktopulo EI, Bychkova VE, Ricka J, Ptitsyn OB. Macromolecules 1994;27:2879–82.
[5] Wu C, Zhou S. Macromolecules 1997;30:574–6.
[6] Wu C. Polymer 1998;39:4609–19.
[7] Freitas RFS, Cussler EL. Separ Sci Technol 1987;22:911–9.
[8] Jin MR, Wu CF, Lin PY, Hou W. J Appl Polym Sci 1995;56:285–8.
[9] Kanazawa H, Kashiwase Y, Yamamoto K, Matsushima Y, Kikushi A, Sakurai Y, Okano T. Anal Chem 1997;69:823–30.
[10] Chung JE, Yokoyama M, Yamato M, Aoyagi T, Sakurai Y, Okano T. J Controlled Release 1999;62:115–27.
[11] Okano T, Yamada N, Okuhara M, Sakai H, Sakurai Y. Biomaterials 1995;16:297–303.
[12] Gehrke SH. Adv Polym Sci 1993;110:81–97.
[13] Gehrke SH. In: Amidon GL, Lee PI, Topp EM, editors. Transport processes in pharmaceutical sciences. New York: Marcel Dekker; 2000. p. 473–546.
[14] Freitas RFS. Extraction with and phase behavior of temperature-sensitive gels. PhD Thesis, University of Minnesota, Minneapolis; 1986.
[15] Oliveira ED. Estudo das Propriedades e do Comportamento de Fases de Géis Termossensíveis. MSc Dissertation, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brazil; 1992.
[16] Schild HG, Tirrel DA. J Phys Chem 1990;94:4352–6.
[17] Ramon O, Kesselman E, Berkovici R, Cohen Y, Paz Y. J Polym Sci Part B 2001;39:1665–77.
[18] Walker JS, Vause CA. Sci Am 1987;256(5):90–8.
[19] Hirschfelder J, Stevenson D, Eyring H. J Chem Phys 1937;5:896–912.
[20] Otake K, Inomata H, Konno M, Saito S. J Chem Phys 1989;91:1345–50.
[21] Prange MM, Hooper HH, Prausnitz JM. AIChE J 1989;35:803–13.
[22] Guggenheim EA. Proc Roy Soc London 1944;A183:213–27.
[23] Hirotsu S, Hirokawa Y, Tanaka T. J Chem Phys 1987;87:1392–5.
[24] Inomata H, Nagahama K, Saito S. Macromolecules 1994;27:6459–64.
[25] Painter PC, Graft J, Coleman MM. J Chem Phys 1990;92:6166–74.
[26] Sasaki S, Maeda H. Phys Rev E 1996;54(3):2761–5.
[27] Lele AK, Karode SK, Badiger MV, Mashelkar RA. J Chem Phys 1997;107:2142–8.
[28] Varghese S, Lele AK, Mashelkar RA. J Chem Phys 2000;112:3063–70.
[29] Sanchez IC, Lacombe RH. Macromolecules 1978;11:1145–56.
[30] Hino T, Prausnitz JM. Polymer 1998;39(14):3279–83.
[31] Flory PJ. Principles of polymer chemistry. Ithaca: Cornell University Press; 1953. Chapters 11–13.
[32] Chun SW, Kim JD. Kor J Chem Engng 2002;19(5):803–7.
[33] Abrams DS, Prausnitz JM. AIChE J 1975;21:116–26.
[34] Marchetti M, Prager S, Cussler EL. Macromolecules 1990;23:1760–5.
[35] Hasa J, Ilavsky M, Dusek K. J Polym Sci Polym Phys Ed 1975;13:253–62.
[36] Ilavsky M. Polymer 1981;22(7):1687–91.
[37] Erman B, Flory PJ. Macromolecules 1986;19:2342–53.
[38] Treloar LRG. The physics of rubber elasticity, 3rd ed. London: Oxford at the Claredon Press; 1975. Chapter 6.
[39] Birshtein TM, Pryamitsyn VA. Macromolecules 1991;24:1554–60.
[40] Grosberg AY, Kuznetsov DV. Macromolecules 1992;25:1970–9.
[41] Erman B, Mark JE. Structures and properties of rubberlike networks. New York: Oxford University Press; 1997. Chapters 3–6.
[42] Nelder JA, Mead R. Comput J 1965;7:308–13.
[43] Sousa RG, Freitas RFS. Polímeros: Ciência e Tecnologia 1995;3:32–7.
[44] Inomata H, Saito S. Fluid Phase Equil 1993;82:291–302.
[45] Vilgis TA, Sommer J-U, Heinrich G. Macromol Symp 1995;93:205–12.
[46] Lee KK, Marchetti M, McHugh MA, Cussler EL. Chem Engng Sci 1990;45:766–7.
[47] Madden WG, Pesci AI, Freed KL. Macromolecules 1990;23:1181–91.
[48] Kenkare NR, Hall CK, Khan SA. J Chem Phys 2000;113:404–18.