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A thermodynamic model of phase transition of poly (N-isopropylacrylamide) hydrogels in ionic solutions

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ABSTRACT

Submerged in an aqueous solution of sodium chloride (NaCl), a poly(N-isopropylacrylamide) (PNIPAM) hydrogel can be in one of two phases: swollen phase and collapsed phase. We measure the equilibrium volume of the hydrogel as a function of temperature T and ionic concentration y. The hydrogel is in the swollen phase when T and y are low, and is in the collapsed phase when T and y are high. We develop a thermodynamic model in which the free energy is a function of volume, temperature, and ionic concentration. The free energy also contains several adjustable parameters, which we best-fit to the experimental data of volume as a function of T and y. For a given pair of T and y, the free energy is a function of volume. This function has a single minimum for some pairs of (T, y), but two minima and a maximum for other pairs of (T, y). In the former, the single minimum corresponds to either a swollen or a collapsed state. In the latter, the lower minimum corresponds to a state of equilibrium, the higher minimum corresponds to a metastable state, and the maximum corresponds to an unstable state. When the two minima are equal, the hydrogel undergoes phase transition. The condition of phase transition is represented as a curve on the (T, y) plane. The thermodynamic model represents the experimental data well.

1. Introduction

This paper considers a hydrogel in which a three-dimensional polymer network is aggregated with aqueous solutions. In contact with an aqueous solution, the hydrogel can swell or deswell, in response to change in temperature (Li et al., 2019; Pelton, 2000; Tang et al., 2021) and concentration of solutes (Hong et al., 2010; Li et al., 2019; Tanaka et al., 1980). Here we focus on a poly(N-isopropylacrylamide) (PNIPAM) hydrogel in equilibrium with an aqueous solution of sodium chloride (NaCl). In an aqueous solution of fixed ionic concentration y, the hydrogel deswells and reduces volume V as temperature T increases (Fig. 1a). The hydrogel undergoes a phase transition at a temperature, at which the volume of the hydrogel jumps (Hirokawa and Tanaka, 1984). The transition temperature decreases as the ionic concentration increases (Park and Hoffman, 1993). The condition of phase transition is represented by a curve on the (T, y) plane (Fig. 1b). The hydrogel is in the "swollen phase" below the curve, and in the "collapsed phase" above the curve. A PNIPAM hydrogel in equilibrium with pure water has been described using a thermodynamic model in which the free energy is a function of volume and temperature (Cai and Suo, 2011). Here we extend this model to include the effect of ions. The model consists of the free energy as a function of volume, temperature, and ionic concentration. The free energy also contains several adjustable parameters, which we best-fit to experimental data available in the literature and newly obtained in this work.

The phase transition has been interpreted in terms of molecular processes. A PNIPAM chain contains both amide group, CO=NH, and isopropyl group, $CH(CH_3)_2$. The former is hydrophilic, and the latter hydrophobic. At a low temperature in pure water, the amide group forms hydrogen bonds with water molecules. These water molecules also form hydrogen bonds with other water molecules, despite the presence of the isopropyl group, so that the hydrogel imbibes a large amount of water (Fig. 2a) (Lin et al., 1999; Ono and Shikata, 2006). At a high temperature in pure water, the amide groups form hydrogen bonds between themselves, leaving the isopropyl groups to repel water, so that the hydrogel imbibes a small amount of water (Fig. 2b). In an ionic solution, ions polarize water molecules and destabilize the hydrogen bonds between water and amide, again leaving the isopropyl groups to repel water, so that the hydrogel also imbibes a small amount of water (Fig. 2c) (Zhang et al., 2005).

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2. Experiments

We synthesize PNIPAM hydrogels as follows (Fig. 3). N-isopropylacrylamide (NIPAM; Aladdin, I106818) (5.6 g) is dissolved in deionized water (50 g). N,N′-methylenebisacrylamide (MBAA; Aladdin, M104022) (0.23 g), N,N,N′,N′-tetramethylethylenediamine (TEMED; Sigma-Aldrich, T9281) (0.02 mL) and ammonium persulfate (APS; Aladdin, A112447) (10 mg) are added as crosslinker, accelerator, and initiator. All chemicals are purchased and used without further purification. The solution is poured into a reaction vessel made of two parallel glass sheets separated by a 2 mm thick silicone spacer. The thermally initiated radical polymerization is carried out at 15 °C for 24 h. After the polymerization, the hydrogel is extensively washed with deionized water, and then punctured into cylindrical samples of diameter 10 mm and thickness 2 mm.

The samples of hydrogel are immersed in aqueous solutions of sodium chloride of various concentrations at various temperatures for at least 48 h to reach equilibrium. Define the swelling ratio by $J = V/V_0$, where V_0 is the volume of the dry polymer network, and V is the volume of the hydrogel in equilibrium with the ionic solution. The swelling ratio is measured as a function of temperature and ionic concentration, $J(T, y)$, as follows. After reaching equilibrium, the sample is taken out of water, blotted with tissue paper to remove excessive water on the surface, and then weighed on an analytical scale with an accuracy of 10^{-4} g to obtain the mass of sample, m_{gel}. Another prepared sample of the same size without immersing in the solution sodium chloride is freeze-dried for 24 h in a lyophilizer (FD-1A-80, Boyikang Inc.) and weighed to obtain the mass of the dry network m_{dry}. The swelling ratio is calculated by

$$J = 1 + \frac{\left(m_{gel} - m_{dry}\right)/\rho_{solution}}{m_{dry}/\rho_{PNIPAM}} \tag{1}$$

where the density of solution $\rho_{solution}$ is interpolated from the tabulated data of NaCl solutions in literature (Arps, 1953); and the density of PNIPAM is $\rho_{PNIPAM} = 1.1$ g/cm^3 (Heskins and Guillet, 1968). Each data point is the average from the measurements of three samples.

In each run of the experiment, a sample of the hydrogel is kept at an ionic solution of a fixed concentration at a fixed temperature. The experiment results in an equilibrium volume of the hydrogel. The experiment is repeated for many values of T and y. The measured swelling ratios are plotted in the J-T plane (Fig. 4). Our own data complement the experimental data reported in literature with the same recipe of hydrogel (Park and Hoffman, 1993). The swelling ratio decreases as the ionic concentration increases or as the temperature increases. When the hydrogel is immersed in pure water ($y = 0$), the swelling ratio is $J = 14.24$ at $T = 277.15$ K and changes to $J = 1.52$ at $T = 308.15$ K. The hydrogel is transparent at 304.15 K and opaque at 308.15 K. Thus, we can determine the phase transition temperature at $y = 0$ is in the range of 303.15 K ~ 308.15 K, which is consistent with those reported in literature (Suzuki et al., 1999). When the hydrogel is immersed in an ionic solution with $y = 1$ M, the swelling ratio changes from 6.79 to 2.33 in the small temperature range, 288.15 K ~ 293.15 K, which indicates the phase transition temperature falls within this range. The existence of 1 M sodium chloride lowers the phase transition temperature of PNIPAM hydrogel by about 10 K. In the J-T plane, we can determine the phase transition temperature and study the effect of ions on the phase transition temperature. The same experimental data are also plotted in the J-y plane (Fig. 5). In the J-y plane, we can determine the phase transition concentration and study the effect of temperature on the phase transition concentration. The two figures represent temperature and concentration on equal footing.

3. Thermodynamic model

We now develop a thermodynamic model to describe the PNIPAM hydrogel in ionic solutions of various concentrations at various temperatures. The model extends an existing one that describes the PNIPAM hydrogels in pure water at various temperatures (Cai and Suo, 2011).

A unit cube of a dry polymer network is taken as the reference state. Submerged in a solution of ionic concentration y at temperature T, the polymer network swells into a gel of volume J. The free energy of the gel is a function of three independent variables, $W(J, T, y)$. Following Flory and Rhener, we write the function as a sum (Flory and Rehner, 1943):

$$W(J, T, y) = W_{stretch}(J, T) + W_{mix}(J, T, y) \tag{2}$$

where $W_{stretch}$ comes from the entropy of elasticity of the polymer network, and W_{mix} comes from the entropy and energy of mixing of the polymer network and solution. The two functions take the following forms (Flory, 1941):

$$W_{stretch} = \frac{1}{2}NkT\left(3J^{\frac{2}{3}} - 3 - 2logJ\right), \tag{3}$$

$$W_{mix} = \frac{kT}{\Omega}\left[(J-1)log\left(1-J^{-1}\right) + \chi\left(1-J^{-1}\right)\right]. \tag{4}$$

where N is the number of polymer chains per unit volume in the dry network, kT is the temperature in the unit of energy, $\Omega = 3 \times 10^{-29}$ m^3 is the volume of a water molecule, and χ is a dimensionless measure of the energy of mixing.

In general, the free energy of the gel is a function of the ionic concentration of the gel rather than the ionic concentration of the external solution. Consider that the PNIPAM gel is electrically neutral, and the

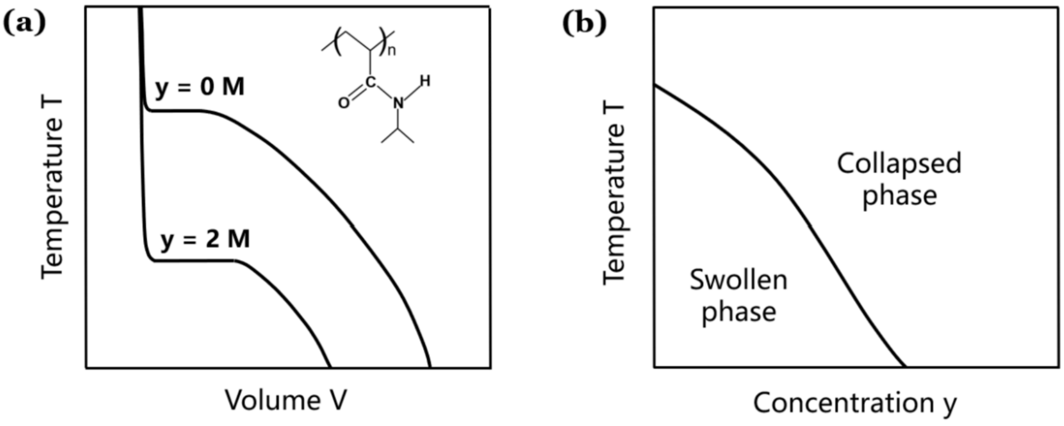

Fig. 1. A poly(N-isopropylacrylamide) (PNIPAM) hydrogel in an ionic solution can be in one of two phases, swollen phase and collapsed phase. (a) The volume of the hydrogel is a function of temperature T and ionic concentration y. In a phase transition, the volume of the hydrogel jumps at a pair of (T, y). (b) The condition for phase transition is a curve on (T, y) plane.

external solution is dilute in ionic concentration. The ionic concentration is taken to be unchanged when the external solution enters the gel. Following the theory of polyelectrolyte hydrogels (Marcombe et al., 2010), we can derive that when the gel equilibrates with the external solution, the ionic concentration of the gel is equal to the ionic concentration of the external solution, and thus the following equation holds

$$\frac{\partial W(J,T,y)}{\partial J}=0 \tag{5}$$

The interaction parameter χ captures the energy of mixing. Here we assume that χ is affected by the ions, as well as the water molecules and temperature, χ (J, T, y). Following Huggins, we write the dependence on J in the following form (Huggins, 1964):

$$\chi=\chi_0+\chi_1 J^{-1} \tag{6}$$

In the previous study of PNIPAM hydrogel swelling in pure water, χ_0 and χ_1 are taken to be linear functions of temperature (Cai and Suo, 2011). As discussed above, the ions in the solution affect the hydrophilicity of the polymer in a similar manner as temperature. Therefore, we assume that the ions and temperature affect the interaction parameter χ in the following form:

$$\chi_0=\alpha_1+\alpha_2 T+\beta_1 y, \tag{7a}$$

$$\chi_1=\alpha_3+\alpha_4 T+\beta_2 y. \tag{7b}$$

The condition of equilibrium (6) becomes

$$N\Omega\left(J^{-\frac{1}{3}}-J^{-1}\right)+log\left(1-J^{-1}\right)+J^{-1}+(\alpha_1+\alpha_2 T+\beta_1 y-\alpha_3-\alpha_4 T-\beta_2 y)J^{-2}+2(\alpha_3+\alpha_4 T+\beta_2 y)J^{-3}=0. \tag{8}$$

Thus, the model has a total of seven adjustable parameters α_1, α_2, α_3, α_4, β_1, β_2 and $N\Omega$.

4. Results and discussions

The seven adjustable parameters are best-fit to the experimental data. When the uncrosslinked PNIPAM chains are mixed with pure water, $y=0$, the contribution of elasticity, $N\Omega\left(J^{-\frac{1}{3}}-J^{-1}\right)$, drops from (8). This specialized equilibrium condition has been used to fit to the experiment data of the solution of uncrosslinked polymer chains and pure water, resulting in the following values (Afroze et al., 2000):

$$\alpha_1=-12.947,\alpha_2=0.04496K^{-1},\alpha_3=17.92,\alpha_4=-0.0569K^{-1}. \tag{9}$$

We adopt these values in this work.

When a crosslinked PNIPAM network is submerged in pure water, $y=0$, Eq. (8) retains the contribution of elasticity, $N\Omega\left(J^{-\frac{1}{3}}-J^{-1}\right)$. This equation is used to fit parameter $N\Omega$ as follows. When the polymer network is submerged in pure water, we measure the volume of the hydrogel as a function of temperature, giving the J-T function for $y=0$ (Fig. 4). Using the least-square method, we best-fit (8) to the measured J-T function under the condition $y=0$, giving

$$N\Omega=0.04. \tag{10}$$

When the samples of the hydrogel are in equilibrium with ionic solutions of various concentrations at various temperatures, the experimentally measured function J (T, y) is used to fit the two remaining

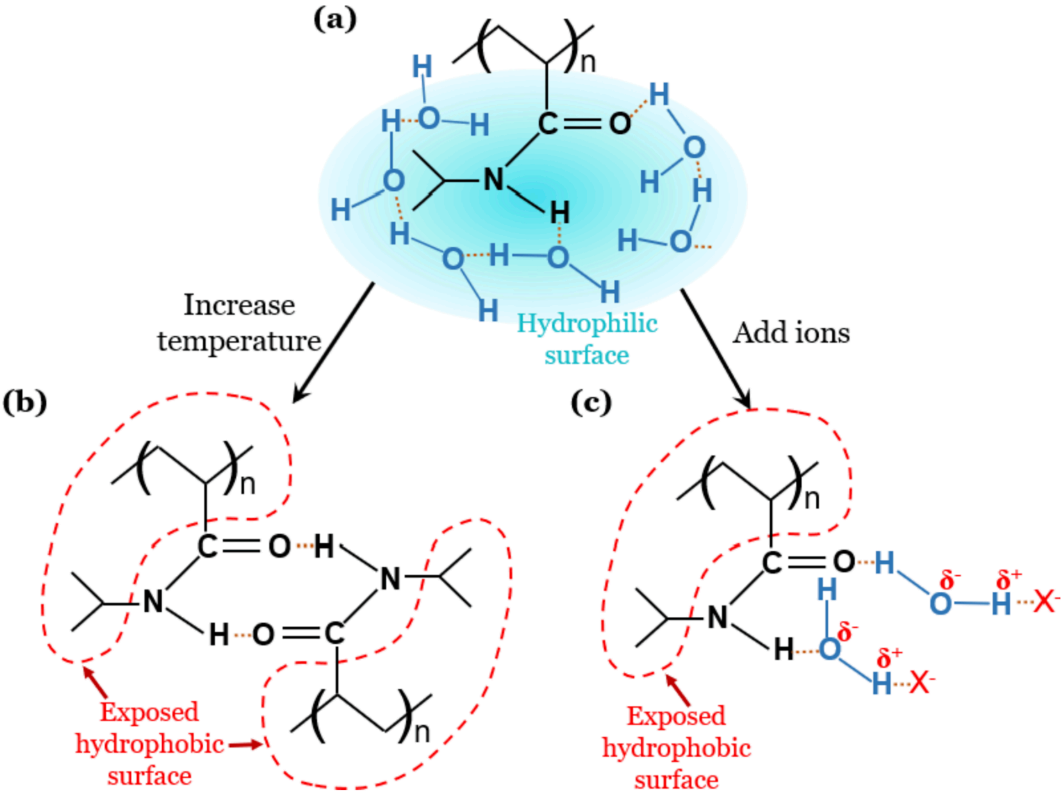

Fig. 2. Molecular mechanisms for the effect of temperature and ions on the volume of PNIPAM hydrogel. (a) At a low temperature in pure water. (b) At a high temperature in pure water. (c) In an ionic solution.

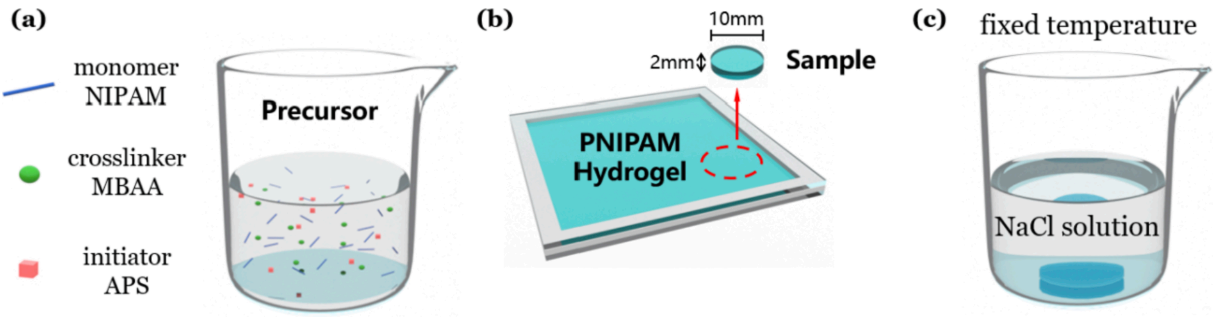

Fig. 3. Experimental procedure. (a) The precursor is an aqueous solution of NIPAM monomer, MBAA crosslinker, and APS initiator. (b) The PNIPAM hydrogel is cast in a mold of thickness 2 mm. The as-prepared hydrogel is punctured into cylindrical samples of diameter 10 mm. (c) The samples are immersed in an aqueous solution of sodium chloride at a fixed temperature to reach equilibrium.

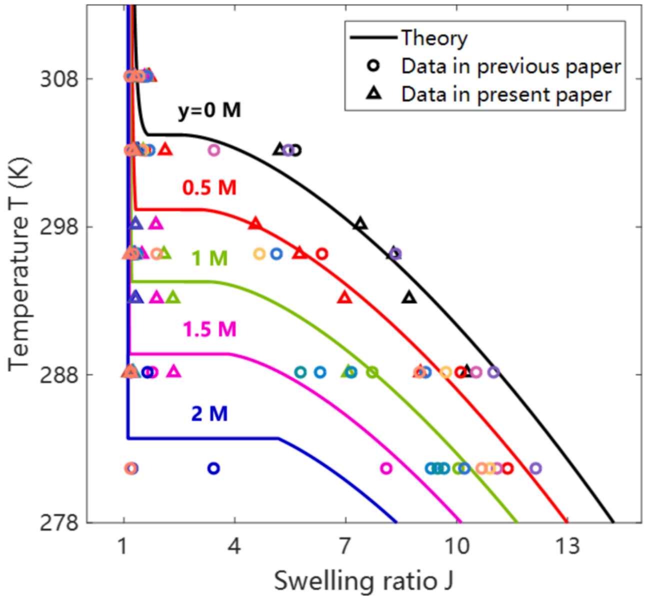

Fig. 4. The swelling ratio of a hydrogel in sodium chloride solutions of various concentrations at several temperatures is plotted in the *J*-*T* plane. Triangles represent the data obtained in this paper, and circles represent the data obtained in a previous paper (Park and Hoffman, 1993). The curves represent the thermodynamic model.

parameters, β_1 and β_2. Observe that (8) is linear in β_1 and β_2. Upon fitting the equation to the experimental data using the least square method, we obtain that

$$\beta_1 = 0.5172M^{-1}, \beta_2 = -0.3349M^{-1}. \tag{11}$$

We next examine the conditions of phase transition. At any fixed ionic concentration, the condition of equilibrium (8) generates a N-shaped curve on the *J*-*T* plane (Fig. 6a). At low *T*, *T* is a monotonic function of *J*, and the hydrogel is in the swollen phase. At high *T*, *T* is also a monotonic function of *J*, and the hydrogel is in the collapsed phase. At an intermediate interval of *T*, *T* is not a monotonic function of *J*, so that each value of *T* corresponds to three values of *J*. At a temperature in this interval, the hydrogel undergoes phase transition. For PNIPAM gels, the experimentally observed volume–temperature curve upon heating often differs from that upon cooling (Linden et al., 2004). This can be interpreted from Fig. 6(a) that, if temperature is controlled to continuously increase, the swelling ratio will reach the peak of the curve and snap-through; while if temperature is controlled to continuously decrease, the swelling ratio will reach the valley of the curve and snap-back. The metastable state at intermediate ionic concentration and temperature are usually not observed. The loading hysteresis is commonly observed in the phenomenon of phase transition (Lu et al., 2016). Similarly, at any fixed temperature, the condition of equilibrium (8) generates a N-shaped curve on the plane of swelling ratio and ionic concentration (Fig. 6b). The hydrogel is in the swollen phase when the ionic concentration is low, and in the collapsed phase when the ionic concentration is high. At an intermediate ionic concentration, the hydrogel undergoes phase transition.

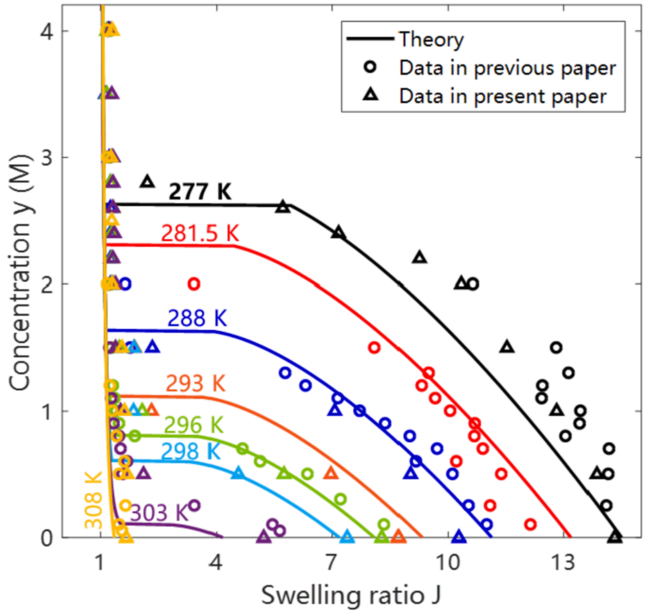

Fig. 5. The swelling ratio of PNIPAM hydrogel in sodium chloride solution of various ionic concentrations at several temperatures plotted in the *J*-*y* plane.

To determine the exact temperature at which the hydrogel undergoes phase transition, we plot the free energy function *W* (*J*, *T*, *y*) as a function of *J* for several fixed values of *T*. For example, consider a polymer network submerged in a solution of $y = 1$ M (Fig. 6c). At a low temperature $T = 288$ K, the free-energy function *W* has a single minimum at a large swelling ratio, corresponding to a state of equilibrium, a swollen state. At a high temperature $T = 296$ K, the free-energy function *W* has a single minimum at a small swelling ratio, corresponding to another state of equilibrium, a collapsed state. At a temperature in an intermediate interval, the free energy function *W* has two minima and one maximum. Of the two minima, the lower one corresponds to a state of equilibrium, and the higher one corresponds to a metastable state. The maximum corresponds to an unstable state. The two minima of *W* are equal at a particular temperature, at which the hydrogel undergoes phase transition. For fixed *T* and *y*, the swelling ratios for the two minima, a swollen state and a collapsed state, are determined by

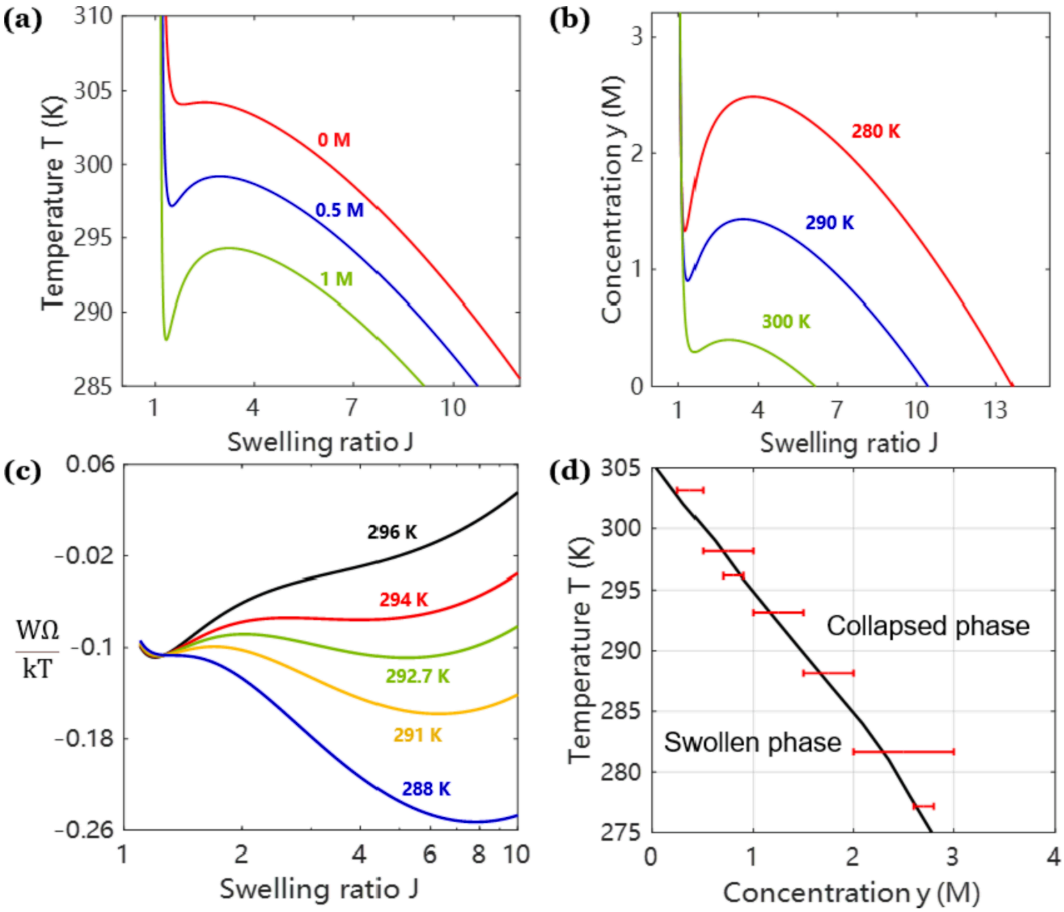

Fig. 6. Conditions for phase transition. (a) The condition of equilibrium, Eq. (8), is plotted on the J-T plane for several ionic concentrations. (b) The condition of equilibrium, Eq. (8), is plotted on the J-y plane for several temperatures. (c) The normalized free energy of gel as a function of swelling ratio plotted at several temperatures ($y = 1$ M). (d) On the temperature-concentration plane, the condition for the phase transition is a curve. Also included are the experimental data. Each segment represents the sudden drop in concentration at a fixed temperature.

$$\left\{\frac{\partial W(J,T,y)}{\partial J}\right\}_{swollen} = 0, \tag{12}$$

$$\left\{\frac{\partial W(J,T,y)}{\partial J}\right\}_{collapsed} = 0. \tag{13}$$

The swollen state and the collapsed state coexist in equilibrium when the two minima of the free energy function $W(J, T, y)$ equal:

$$\{W(J,T,y)\}_{swollen} = \{W(J,T,y)\}_{collapsed} \tag{14}$$

Given an ionic concentration, y, the three Eqs. (12)-(14) solve the transition temperature, T, and the swelling ratios of the two states in equilibrium, $J_{swollen}$ and $J_{collapsed}$.

Repeat the above procedure for various values of ionic concentration y, we obtain the transition temperature T as a function of ionic concentration y (Fig. 6d). Under the curve, the hydrogel is in the swollen phase. Above the curve, the hydrogel is in the collapsed phase. On the same T-y plane, we also plot experimental data as follows. In the experiment, the hydrogel is transparent in the swollen phase, and opaque in the collapsed phase. At a fixed temperature, the experiment is conducted at a discrete set of ionic concentrations. On the T-y plane, we plot the highest concentration when the hydrogel is transparent and the lowest ionic concentration when the hydrogel is opaque. The transition concentration falls at a point in a segment between the two concentrations. The curve predicted from the model agrees well with the experimental data. This agreement is also evident when we add the transition temperatures predicted by the model as horizontal segments on the plane of temperature and swelling ratio (Fig. 4). Similarly, we add the transition ionic concentrations predicted by the model as horizontal segments on the plane of ionic concentration and swelling ratio (Fig. 5).

The developed thermodynamic model describes the free swelling behavior of PNIPAM hydrogels under the coupled influence of ionic concentration and temperature. It has the potential to assist the design of PNIPAM-based materials in field of soft robotics and biomedical applications, such as morphing materials (Li et al., 2019), soft actuators (Tian et al., 2017) and wound dressings (Blacklow et al., 2019; Gao et al., 2021).

5. Concluding remarks

We develop a thermodynamic model for PNIPAM hydrogels submerged in aqueous solutions of NaCl. When a hydrogel equilibrates in a solution of a fixed ionic concentration at a fixed temperature, we measure the volume of the hydrogel. Our data complement those existing in literature. In equilibrium, the hydrogel can be in one of two phases, the swollen phase and the collapsed phase. We model this thermodynamic system with the free energy as a function of volume, temperature, and ionic concentration. The free energy contains seven adjustable parameters, which we best-fit to all available experimental data of volume as a function of temperature and ionic concentration. For a given pair of temperature and ionic concentration (T, y), the free energy is a function of volume. This function has a single minimum for some pairs of (T, y), but two minima and a maximum for other pairs of (T, y). In the former, the single minimum corresponds to either a swollen or a collapsed state.

In the latter, the lower minimum corresponds to a state of equilibrium, the higher minimum corresponds to a metastable state, and maximum corresponds to an unstable state. When the two minima are equal, the hydrogel undergoes phase transition. The condition of phase transition is represented as a curve on the plane of temperature and ionic concentration. The thermodynamic model represents the experimental data well.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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