



# Molecular thermodynamic model for swelling behavior and volume phase transition of multi-responsive hydrogels

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## ABSTRACT

A new molecular thermodynamic model for swelling behavior and volume phase transition of multi-responsive hydrogels was developed. The swelling behavior of hydrogels results from three contributions, the mixing of polymer network and solvent, the elasticity of polymer network and the ionic effect containing Donnan equilibrium of ions distributed inside and outside hydrogels and electrostatic interactions between the charges carried by the polymer network and the counter ions. Two kinds of model parameters are included; they are the interaction energy parameters between polymer network and solvent or between the two solvents, and a size parameter which is the molecular mass of the network between two cross-linking points. They should be determined from the experimental swelling curves of hydrogels. It is shown that this model can describe the swelling behavior and volume phase transitions of pH-sensitive and ion-sensitive hydrogels by using fewer model parameters comparing with other models. The different swelling behaviors such as shrinking at low pH and swelling at high pH, swelling at low pH and shrinking at high pH, shrinking at middle pH and swelling at both low pH and high pH, the swelling behaviors of pH- and temperature-sensitive hydrogels or temperature- and solvent-sensitive hydrogels, can be satisfactorily described.

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## 1. Introduction

Hydrogels are a kind of soft materials with three-dimensional network structure composed of water and polymer. Almost all the organisms in nature are composed of hydrogels. The bean curd, jelly and contact lenses in daily life are also hydrogels. The three-dimensional network might be a permanent structure formed by covalent bond or a reversible structure by electrovalent bond or secondary bond. Hydrogels will swell due to the solvent entering or shrink due to the solvent escaping by the external stimuli (such as temperature, pH, ionic strength, and composition of solvent, etc.). Volume phase transition phenomena can be found in some hydrogels. On this occasion, the volume of hydrogels will change drastically with only a small change of external conditions. Because of this special property, hydrogels can be widely used in drug controlled release systems [1–3], immobilized enzyme [4], sensors [5,6], materials extraction [7,8] and so on. As examples: Zhang et al. [9] synthesized pH/temperature-responsive hydrogels composed of comb-type grafted cationic poly(*N*-isopropylacrylamide-co-*N*,*N*-dimethylamino ethyl methacrylate), which exhibits a much rapid deswelling rate in response to a pH increases from 2.0 to 11.0. The

model drug Vitamin B<sub>12</sub> can be rapidly released from the hydrogels with simultaneous temperature and pH stimuli. Shin et al. [10] demonstrated an inverse opal hydrogel pH sensor. The response time for pH change is 12 s for pH 5–6, which is 100 times faster than that of the previously reported inverse opal pH sensors [11]. Kioussis et al. [12] prepared poly(allyl amine) hydrochloride hydrogels which can adsorb the nutrient anion from aquaculture wastewater. Results showed that 99% of PO<sub>4</sub><sup>3-</sup>, 70% of NO<sub>3</sub><sup>-</sup> and 95% of SO<sub>4</sub><sup>2-</sup> can be removed at maximum. The PO<sub>4</sub><sup>3-</sup> diffusion coefficient is found to decrease slightly with increasing pH. You et al. [13] synthesized a series of core-shell pH-responsive hydrogels with homogeneously dispersed, biologically inert, highly conductive gold (Au) nanoparticles as cores. The conductivity of these smart hybrid materials can be reduced with the decrease of pH due to the increase of the volume, which may be used to sense physiological changes related to disease pathology.

Quantitatively describing and predicting the swelling behavior and volume phase transition properties is an important research area of hydrogels. Many contributions have devoted to the mechanism of swelling and volume phase transition. Otake et al. [14] investigated the mechanism of temperature-induced phase transition by differential scanning calorimetry. They found that the strong hydrogen bonding between the acylamide groups and water molecules makes the water molecules combined around the acylamide groups forming a water cage structure around the

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hydrophobic groups when the temperature is lower than LCST. When the temperature is higher than LCST, some hydrogen bonding breaks, the hydrogen bonding interaction weakens and the interactions between hydrophobic groups become dominant, which leads to an entropy-driven hydrogels collapse. Feil et al. [15] studied the mechanism of the effect of charges of polymer network on the swelling behavior of hydrogels. With the increase of the charges of polymer network, the amount of hydrophobic groups reduces and the hydrophilicity of the polymer increases. The LCST of hydrogels increases due to the strong interactions between water and charged groups fixed on the polymer network. Oyen et al. [16] simulated the swelling behavior of polymer network and predicted the effect of temperature and pressure on the swelling rate. Yin et al. [17] simulated the volume phase transitions in highly-charged crosslinked polyelectrolyte network by molecular dynamics method. They found that the discontinuous volume phase transition is dependent on the electrostatic interactions and the counterion excluded-volume entropy. Later this group [18] studied the effect of ion strength on the interactions between polymer network and solvent and studied the effect of interactions on the swelling rate. Results show that the higher ion strength the weaker interactions, which leads to the collapse of hydrogels. Those investigations show that the volume change of hydrogels due to the external environmental stimuli is closely related with the change of interaction between polymer network and solvent and the change of charges fixed on the polymer network under different environmental conditions. The change of interactions and charges is related with hydrophilicity and dissociation of groups.

Some researchers try to develop molecular thermodynamic models to quantitatively describe the swelling behaviors and volume phase transition phenomena of hydrogels. Flory [19] predicted the existence of volume phase transition as early as in 1953. The starting point of the model is the equality of the chemical potentials inside and outside the hydrogel. The chemical potential inside the hydrogel is composed of two contributions, the mixing of polymer network and solvent and the elasticity of polymer network. The former can be calculated by the Flory–Huggins theory and the latter is similar to the deformation of rubber, which can be calculated by the affine model. The volume phase transition phenomenon is dominated by the incompatibility between the solvent and polymer inside the hydrogels. Since Flory, some similar models have been developed by following this idea but with different models for mixing contribution and elastic contribution. Marchetti et al. [20,21] developed a compressible lattice model by introducing free volume as a third pseudo-component into the binary mixture of solvent and polymer to calculate the mixing contribution. Theoretically, this model can describe the effect of pressure on the swelling behavior and volume phase transition of hydrogels. By using a new interpolated affine model for the elastic contribution, a semi-empirical thermodynamic model was established by Prausnitz et al. [22]. Lele et al. [23,24] developed an extended lattice-fluid hydrogen-bond (LFHB) model by combining the free energy of affine deformation of elastic network with the free energy of mixing given by LFHB model. This model not only describes the volume phase transition of hydrogels but also quantitatively calculates the free and bound water content of polymer network. Oliveira et al. [25] presented a new quasichemical thermodynamic model by combining the oriented quasichemical thermodynamic model which takes into account the specific hydrogen bonding interactions between different components in hydrogels and Flory–Rehner model for affine deformation network. When some groups fixed on the polymer network carry charges due to dissociation, the pH of solution, the kind and concentration of electrolyte will affect the swelling behavior and volume phase transition of hydrogels. To quantitatively describe the swelling behavior and volume phase transition of those pH-/ion-sensitive hydrogels, electrostatic interactions

arising from the dissociation of polymer network are key factors. When the amount of charge carried by polymer network is smaller, the effect of ion can be regarded as the disturbances to a neutral network. In this case, due to the longer average distance and the smaller electrostatic repulsion interaction between ions, the penetration of counter ions based on Donnan effect [26] is particularly important. Based on this idea, Tanaka et al. [27] established a partial ionic hydrogel model based on the Flory close-packed lattice theory. The volume phase transition of ion-sensitive hydrogels was described from the perspective of osmotic pressure. Siegel et al. [28] and Peppas et al. [29] also developed a molecular thermodynamic model of hydrophobic cationic copolymer gels, respectively. Based on a semi-empirical lattice model and the Donnan theory, Hooper et al. [30] described the swelling behavior of ionized gels. Nieves et al. [31] established a model for cationic polyelectrolyte hydrogels and had a good correlation between the charge of the hydrogel network and its size. Then they also modified this model [32] and studied the effect of salt concentration on the swelling of polyelectrolyte hydrogels [33]. The model developed by Chan et al. [34] could better describe the swelling ratio of pH and ion-sensitive hydrogels in which the Flory–Huggins parameter in the mixing contribution term is regarded as a function of ionic strength. Nevertheless, there exist not only small free molecular ions but also macromolecular ions fixed on polymer network when hydrogels reach equilibrium. The electrostatic repulsion interaction between macromolecular ions and the electrostatic attraction interaction between macromolecular ions and small molecular ions can not be ignored. In this case, Hasa et al. [35,36] established a model for anionic polyelectrolyte hydrogels based on the electrostatic free energy of polyelectrolyte solution proposed by Katchalsky et al. [37] and explored the effect of model parameters on the swelling behavior and volume phase transition. A similar molecular thermodynamic model has been developed by Lu et al. [38] and has been used to correlate the swelling ratio of hydrogels at different pH. Hoare et al. [39] established a swelling model of functional microgels. In this model, the ionic term includes not only the contribution of Donnan equilibrium and that of the electrostatic repulsion interaction but also the contribution due to the electrostatic attraction interaction between macromolecular ion and the counter ion.

All these models mentioned above can only describe the effect of one or two environmental condition change on the swelling behavior and volume phase transition of hydrogels, the model which can describe various different kinds of environmental responsive is rare. In our previous work [40], a molecular thermodynamic model for temperature-sensitive hydrogels based on a closed packed lattice model for polymer solution developed by Yang et al. [41–43] and the elastic free energy based on the Gaussian chain model has been developed. This model has been further extended to temperature- and solvent-sensitive hydrogels [44] based on a multi-component lattice model for polymer solution [45] and has been used to describe the effect of temperature and composition of mixed solvent on the swelling behavior and volume phase transition. Satisfactorily correlated results were obtained. In this work, based on these two models, a new molecular thermodynamic model for describing the swelling behavior and volume phase transition of multi-responsive hydrogels was developed by considering the concentration gradient of small ions, the dissociation equilibrium of polymer and the electrostatic interaction. This model can describe not only the swelling behavior and volume phase transition of temperature-/solvent-sensitive hydrogels but also that of various kinds of pH-sensitive hydrogels. Such as the swelling behavior of hydrogels which shrinks at low pH and swells at high pH, which swells at low pH and shrinks at high pH, and which shrinks at middle pH and swells both at low pH and high pH. In addition, this model can describe the swelling behavior of

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