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A molecular thermodynamic model for temperature- and solvent-sensitive hydrogels, application to the swelling behavior of PNIPAm hydrogels in ethanol/water mixtures

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ABSTRACT

The swelling curves of poly-N-isopropylacrylamide (PNIPAm) hydrogels in ethanol/water mixtures were determined. A molecular thermodynamic model for swelling behavior of temperature- and solvent-sensitive hydrogels in solvent mixtures was developed by integrating a modified multiple lattice model developed previously for the mixing term and the Flory's Gaussian chain model for the elastic term. Three energy parameters and one volume parameter are included in this model for gel/ solvent mixtures systems. Three of the four parameters can be determined from the swelling behavior of hydrogels in pure solvents. The energy parameter measuring the interaction between the two solvents is adjustable and expressed as a quadratic form of the inverse temperature. The calculated results for the swelling curves of PNIPAm hydrogels in ethanol/water mixtures at different temperatures are in good agreement with the experiments. In addition, the equilibrium concentrations of solvent mixtures inside and outside hydrogels can be predicted by this model, which is important for the application of hydrogels.

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1. Introduction

A hydrogel is a hydrophilic network able to absorb big quantities of water without dissolving due to chemical or physical crosslinking. The swelling ratio of hydrogels changes in response to external stimulus such as temperature, pressure, solvent, ionic strength of solution and pH, etc., therefore, they are usually called the intelligent or smart materials. Poly-N-isopropylacrylamide (PNIPAm) hydrogel is a typical temperature-sensitive hydrogel. It shows a volume phase transition behavior near 32 °C, where the swelling ratio of PNIPAm hydrogels alters greatly with a small change of temperature.

Hydrogels have received increasing attention due to its potential applications in many areas such as chemical separation, drug transfer and release, chemical machine, chemical switch, sensors, artificial muscles and so on. Hsiue et al. (2002) successfully developed the controlled release of ophthalmic agents for glaucoma therapy based on PNIPAm hydrogels. Results of the animal experiments showed that the decreased-pressure response of the formulation was lasted six-fold longer than that of the traditional ophthalmic drops. Brugger et al. (2008) found that the temperature-and pH-responsive hydrogel of poly(N-isopropylacrylamide)-co-

methacrylic acid can be used as stimuli-sensitive stabilizers for emulsions. The emulsions were stable at high pH and low temperature, but instable at low pH and high temperature. Wang et al. (2009) synthesized a temperature- and pH-responsive hydrogel of poly(N-isopropylacrylamide)-co-poly[2-methacrylic acid 3-(biscarboxymethylamino)-2-hydroxypropyl ester] (PNIPAM-co-PMACHE) which could be used as a reaction medium and the Pd catalyst support for Suzuki and Heck reactions. They found that Suzuki and Heck reactions were accelerated due to the highly enriched reactants and Pd catalysts inside the hydrogel. The PNIPAM-co-PMACHE hydrogel/Pd composite was easily recovered and reused since the hydrogel/Pd composite could reversibly swell and deswell. Ju et al. (2008) synthesized a temperature-sensitive and ion-recognition hydrogel of poly(N-isopropylacrylamide-co-benzo-18-crown-6-acrylamide) (PNIPAM-co-PBCAm). When BCAm receptors in the hydrogel captured Ba2+, the lower critical solution temperature (LCST) of (PNIPAM-co-BCAm) hydrogel increased. Whereas BCAm receptors captured Cs⁺, the LCST shifted to a lower temperature. It could be used in drug controlled-release systems or biomedical fields. Hua et al. (2008) studied a molecularly imprinted gel (MIP) for selective recognition of bovine serum albumin (BSA). Results showed that the volume of the MIP as well as the ability of MIP to recognize the target protein could be controlled by external stimuli such as temperature and ionic strength.

Theoretically, since the pioneer work of Tanaka and his coworkers (Hirotsu et al., 1987) many researchers have paid

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attention to the development of the molecular thermodynamic model at molecular level to quantitatively describe swelling behaviors of hydrogels. When pure solvent and polymer form hydrogels, Gibbs free energy changes, which usually contains two parts: the mixing Gibbs free energy of pure solvent and polymer and the elastic Gibbs free energy of gel network. Besides, to describe the swelling behavior caused by external stimuli except temperature, other changes of Gibbs free energy should be considered. Then the change of Gibbs free energy can be expressed as:

$$\Delta G = \Delta G_{mix} + \Delta G_{elas} + \Delta G_{other} \tag{1}$$

The phase behavior of thermo-sensitive hydrogels has been widely studied. Marchetti et al. (1990a, b) developed a compressible lattice model by introducing free volume as a third pseudocomponent in the binary mixture of solvent and polymer. The phase behavior such as near-critical lower consolute boundaries. low-temperature upper consolute boundaries and closed-loop miscibility gaps can be predicted. By using a new interpolated affine model for the elastic term, a semi-empirical thermodynamic model was established by Hino and Prausnitz (1998) to predict the volume phase transition of neutral and weakly charged hydrogels. Considering the hydrogen bonding, Lele et al. (1997) developed an extended lattice-fluid hydrogen-bond(LFHB) model by adding the free energy of affine deformation of elastic network based on LFHB model. Oliveira et al. (2004) presented a quasichemical thermodynamic model, which explained the competition between hydrogen bonding and dispersion forces, leading to the transition from less entropic swollen gel phases to more entropic collapsed gel states. Recently, the swelling behavior of hydrogels in solvent mixtures were attracted more attentions. Xu et al. (2003a, b) observed the swelling behavior of a PNIPAm hydrogel in ethanol/water mixtures at 25 °C. A thermodynamic model based on the UNIQUAC model with the "freevolume" contribution was applied to predict the swelling ratio of hydrogels. Jung et al. (2009) described the reentrant swelling behavior of a PNIPAm hydrogel in a water-N,N-Dimethylformamide(DMF) system using molecular interaction parameters obtained from closed-loop type LLE data for PNIPAm in a water-DMF system. Water-DMF mixtures were considered to be pseudo pure solvent in this model.

Recently, Huang et al. (2008) developed a new molecular thermodynamic model to describe the swelling behavior of thermo-sensitive hydrogels in single solvent which was based on the close-packed lattice model for polymer solutions by Yang et al. (2006a, b, c). The results of this model were in good agreement with the experimental data and the number of parameters of this model was the least.

In this work, a new molecular thermodynamic model which can be used to describe the swelling behavior of hydrogels in solvent mixtures has been established. The model is based on a modified multi-component lattice model developed by this group (Xin et al., 2008) and the Gaussian chain model by Flory (1953). The swelling behavior of PNIPAm hydrogels in ethanol/water mixtures and different temperatures were correlated. Particularly, the equilibrium concentrations of solvents inside and outside the PNIPAm hydrogels can be predicted.

2. Experiment

2.1. Material

N-isopropylacrylamide (NIPAm, 97%) was obtained by USA.MSDS; Ammonium persulfate (APS, 98%) was purchased from Lingfeng chemical reagent (Shanghai, China); N,N-Methyle-

nebisacrylamide (MBAAm, 98%), Tetramethylethylenediamine (TEMED, 98%) and ethanol were provided by Sinopharm Chemical Reagent (China).

2.2. Synthesis of PNIPAm hydrogel

2.0 g of NIPAm, 0.014 g of MBAAm, 0.06 g of APS and 2 drops of TEMED were dissolved together in 18 ml of deionized water. After the complete dissolution, the solvent mixtures were sealed into a glass tube. Copolymerization was performed for 24 h at room temperature. The obtained PNIPAm hydrogels were cut into pieces of about 0.25, 0.5 and 1.0 g. These hydrogels were immersed in the deionized water for 7 days to remove any residual materials with low molecular weight and the water-soluble linear polymers.

2.3. Swelling ratio measurements

PNIPAm hydrogels were dried by freeze drying for 8 days. Then the dried PNIPAm hydrogels were put into ethanol/water mixtures with different compositions for 7 days. The compositions of ethanol/water mixtures was 0.0, 0.1, 0.3, 0.4, 0.5, 0.6, 0.7, 0.9, 1.0(w/w) and the temperature was set in 30, 31, 32, 33, 34, 36 and 40 °C.

The equilibrium swelling ratio of PNIPAm hydrogels was calculated according to the measured weight of the swollen hydrogel (m_s) and that of the dried hydrogel (m_d) :

Swelling ratio =
$$\frac{m_s}{m_d}$$
 (2)

2.4. The composition of solvent mixtures inside PNIPAm hydrogels measurements

Firstly, the refractive index and density of prepared ethanol/ water mixtures were measured and two standard curves were obtained. Secondly, since the standard curve of the refractive index is a quadratic figure, the composition of solvent mixtures outside PNIPAm hydrogels could be determined via the refractive index when it is lower than 0.6. However, when the composition of solvent mixtures outside PNIPAm hydrogels is higher than 0.6, one value of refractive index corresponds to two different compositions of solvent mixtures. The additional measurement of density is adopted to decide the range of the composition of solvent mixtures, because the standard curve of density is a linearity figure. So the composition of solvent mixtures can be determined. Finally, using the material balance method we obtain the composition of solvent mixtures inside the PNIPAm hydrogels.

When the volume faction of ethanol outside PNIPAm hydrogels closes to 0.1, the swelling ratio is the lowest and the quantity of absorbed solvents is the least. The relative error of the volume fraction of ethanol inside PNIPAm hydrogels gets to the maximum, which can be calculated as:

$$\frac{\Delta\phi_{\text{inside}}}{\phi_{\text{inside}}} = \frac{|\Delta_{\text{error}}| \times 16.0}{\phi_{\text{inside}}} \times \frac{m_{\text{outside}}}{m_{\text{inside}}}$$
(3)

where $\Delta_{\rm error}$ is the apparatus error of refractometer, which is ± 0.0001 . $\phi_{\rm inside}$ is the volume fraction of ethanol inside hydrogels. $m_{\rm outside}$ and $m_{\rm inside}$ are the qualities of solvents outside and inside PNIPAm hydrogels. The 16.0 is the multiples when the refractive index transforms into the concentration, because the concentration changes 0.0016 when the refractive index changes 0.0001 based on the standard curve of the refractive index of prepared ethanol/water mixtures,. The maximum of the relative error is 19.56%. The relative errors of the rest data are less than 3% in general.

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