



Modeling non-electrolyte hydrogel swelling using the adjusted parameters from liquid-liquid equilibrium data of the linear polymer

A.S. Carvalhal^a, C.C. Santana^a, G.M.N. Costa^{b,*}, M. Embiruçu^b

^a Escola Politécnica (Polytechnique Institute), Universidade Federal da Bahia, Brazil

^b Programa de Engenharia Industrial (Industrial Engineering Program), Escola Politécnica (Polytechnique Institute), Universidade Federal da Bahia, Rua Prof. Aristides Novis, no 2, Federação, CEP: 40210-630, Salvador, Bahia, Brazil

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ABSTRACT

Hydrogels are tridimensional elastic hydrophilic cross-linked polymers with the ability to absorb water in a process called swelling. The Flory-Huggins (FH) theory can be applied to model hydrogel swelling with appropriate adjustments. In the literature the FH model parameter is directly estimated from experimental data on swelling. The target of this paper is to evaluate the effect of using parameters estimated from liquid-liquid equilibria of the linear polymer directly in the swelling modeling of the respective cross-linked polymer as these data can be easily found in literature. Three methods that use different equations for the FH parameter and two methods for the mechanical contribution are evaluated. These models were applied to the polymer poly(N-isopropylacrylamide), PNIPA, and compared in three swelling intervals: the volume contraction region; the transition temperature; and the region of volume expansion. The most relevant and important behaviors of each region are shown, analyzed and discussed.

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1. Introduction

The chemical nature of a hydrogel-forming polymer is one of its determining properties [1]. Hydrogels are tridimensional structures containing hydrophilic polymers with crosslink agents. The crosslink holds the polymeric chains together and prevents them from dissolving in the aqueous solution. As a result of the presence of hydrophilic groups, these polymeric structures can absorb hydrophilic solvents and their solutions. The quantity of absorbed liquid is often very large, reaching hundreds of times the mass of the dry gel [2].

Regarding the potential applications of hydrogels, there is a variety of different possible fields, such as: raw material for the manufacture of contact lenses [3]; substitutes for gauzes in wound treatment [3]; personal hygiene products [4,5]; agriculture (prevention of soil water loss) [6]; biomedicine [7], including reconstruction of injured human tissues [8]; and actuators [9]. Much attention has been given to stimuli responsive hydrogels. Among their applications site-specific drug delivery stands out. This technique is based on pH or temperature differences among different

regions of the human body. Using a hydrogel which is sensitive to these variables, it is possible to develop drug delivery systems that only release the active principle in specific regions of the human body [1]. Furthermore, due to the kinetics involved in the mass transfer between the hydrogel and the surroundings, the time taken for the drug to be fully released can also be controlled. Therefore, an understanding of the phase equilibrium and gel swelling kinetics as a function of these variables is critical.

In this paper we investigate only the temperature influence in thermo-responsive polymers, such as poly(-propylmethacrylamide), poly(N-n-diethylacrylamide), poly(N-vinylprolactam), poly(N-n-propylacrylamide) and poly(N-isopropylacrylamide). Among these temperature sensitive hydrogels, the most used is poly(N-isopropylacrylamide) (PNIPA), the classic example of non-ionic hydrogel with hydrophilic groups due to its biocompatibility and to the fact that it is particularly sensitive to temperatures close to the human body temperature [1], which makes the PNIPA a strong candidate when considering the application of the site-specific drug delivery technique. PNIPA contains hydrophobic groups in addition to the hydrophilic groups responsible for the swelling phenomenon. Therefore, aqueous PNIPA solutions with non-cross-linked polymers have a Lower Critical Solution Temperature (LCST) [10]. When the temperature is below

* Corresponding author.

E-mail address: gmeyberg@ufba.br (G.M.N. Costa).

the LCST, this polymer is soluble in water due to hydrogen bonds between the water molecules and the (C=O) and (N–H) groups in the polymer. However, when the temperature is above the LCST these specific interactions are weakened and the hydrophobic interactions between the isopropyl groups of the polymer prevail [11] and consequently there is a formation of two phases. Due to the lower miscibility between the polymer and the solvent with increasing temperature, the polymer absorbs less solvent. In certain cases, there is a transition temperature range where a sudden collapse of the polymer structure occurs. This transition temperature range can generally be observed in temperatures close to the LCST of the corresponding linear polymer [12]. The hydrogel swelling behavior, like in PNIPA, can be classified into three states: collapsed; transition; and swollen.

Although there are many works on hydrogel modeling in the literature [13–35], some research issues still remain open. In this work the Flory–Huggins (FH) model is used because of its simplicity, easy implementation and absence of comparisons between its various modifications in the literature [13–21]. Three different functions for the interaction parameter are evaluated: Qian et al. [16] model; Bae et al. [17] model; and the extended Flory–Huggins model [16,17] used by Hino and Prausnitz [18]. This choice was made based on the simplicity of the interaction parameter expression of these models. In these models the Flory interaction parameter is expressed as the product of two functions: one temperature-dependent; and the other composition-dependent. The parameters of these functions are obtained by fitting Liquid–Liquid Equilibrium (LLE) data of the linear polymer. Thus, a description of the gel behavior is made possible by the description of the linear polymer phase equilibrium. The decision to use LLE parameters for swelling modeling, rather than setting it up from experimental swelling data, is motivated by the fact that it is easier to obtain experimental LLE data of linear polymers in the literature. In other words, this approach simplifies and facilitates the description of the swelling behavior. In addition to the FH models for the mixing contribution, two mechanical contribution approaches are evaluated: the Flory and Rehner [36] model; and the Hino and Prausnitz [18] interpolated model.

2. Thermodynamic models

According to Hino and Prausnitz [18], for a polymer gel containing solvent and cross-linked polymer without electrolytes (therefore, without ionic contributions), the mixture Helmholtz free energy is given by:

$$\Delta A_{mix} = \Delta A^{mix} + \Delta A^{elas} \quad (1)$$

where ΔA_{mix} is the Helmholtz free energy, ΔA^{mix} is the mixing contribution and ΔA^{elas} is the contribution due to the network elasticity. Considering the mixing contribution given by Flory–Huggins [13] for a binary mixture:

$$\frac{\Delta A_{mix}}{k_B \cdot T} = n_1 \cdot \ln(\phi_1) + n_2 \cdot \ln(\phi_2) + \chi \cdot \phi_1 \cdot \phi_2 \quad (2)$$

where ΔA_{mix} is the mixing Helmholtz free energy, T is the temperature, k_B is the Boltzmann constant, and ϕ_1 , ϕ_2 , n_1 and n_2 are the volume fractions of the components and the number of moles, respectively. Subscripts 1 and 2 refer to the solvent and the polymer, respectively, and χ is the FH segmental interaction parameter. An equation widely used to calculate χ was proposed by Qian et al. [16] as a product of two terms, a function of temperature $D(T)$ and a function of concentration $B(\phi)$:

$$\chi(T, \phi) = D(T) \cdot B(\phi) \quad (3)$$

The estimation of Equation (3) parameters is done by fitting the liquid–liquid equilibrium of a solvent/(non-cross-linked) linear polymer binary system using the phase equilibrium criterion:

$$\mu_1^\alpha = \mu_1^\beta \quad (4)$$

$$\mu_2^\alpha = \mu_2^\beta \quad (5)$$

where μ is the chemical potential and the superscripts α and β refer to each liquid phase. The main objective of this paper is to describe the swelling of temperature-sensitive hydrogels by using three different equations for the FH χ parameter, and to analyze the influence of this parameter in the swelling calculation. Simple and successful models were selected that express the χ parameter as a product of a temperature-dependent function and a polymer concentration-dependent function to describe the swelling. Therefore, using Equation (3) for FH parameter description, the following equations are used to describe the binodal curve:

$$\begin{aligned} & \ln\left(\frac{1-\phi_2^\beta}{1-\phi_2^\alpha}\right) + (\phi_2^\beta - \phi_2^\alpha) \cdot \left(1 - \frac{r_1}{r_2}\right) + r_1 \cdot D(T) \cdot [B(\phi_2^\beta) \cdot (\phi_2^\beta) \\ & - B(\phi_2^\alpha) \cdot (\phi_2^\alpha)] \\ & = 0 \end{aligned} \quad (6)$$

$$\begin{aligned} & \ln\left(\frac{\phi_2^\beta}{\phi_2^\alpha}\right) + (\phi_2^\alpha - \phi_2^\beta) \cdot \left(1 - \frac{r_2}{r_1}\right) + r_2 \cdot D(T) \cdot \left[\phi_2^\beta \cdot (1 - \phi_2^\beta) \cdot B(\phi_2^\beta) \right. \\ & \left. - \phi_2^\alpha \cdot (1 - \phi_2^\alpha) \cdot B(\phi_2^\alpha) - \int_{\phi_2^\beta}^{\phi_2^\alpha} B(\phi) \cdot d\phi \right] \\ & = 0 \end{aligned} \quad (7)$$

where r_1 and r_2 are the relative molar volumes of each component.

As stated earlier, three different functions for the interaction parameter are evaluated: Qian et al. [16] [Equations (8) and (9)]; Bae et al. [17] [Equations 8 and 10]; and the extended Flory–Huggins model [16,17] used by Hino and Prausnitz [18] [Equations 10–13]. As previously shown in Equation (1), for the thermodynamic modeling of a polymer gel it is necessary to calculate the mechanical contribution ΔA^{elas} for the Helmholtz free energy. In this paper two mechanical models were selected: the first one is based on the theory of Flory and Rehner [36] and the ΔA^{elas} contribution is given by Equations (14) and (16); and the second model, called the interpolated mechanical model by Hino and Prausnitz [18], is given by Equations (15) and (16). Thus, using a combination of the three approaches selected to describe the FH interaction parameter [χ described by Equation (3), which use two functions for $D(T)$, Equations (8) and (11–13), and two functions for $B(\phi)$, Equations (9) and (10)] with the two approaches selected for the mechanical contribution [described by Equations (1), (14) and (16)–(16)], six different models are found to evaluate the temperature-sensitive hydrogel swelling. Table 1 summarizes these models and shows the equations and nomenclature adopted here.

The volume fraction resulting from the gel swelling in phase equilibrium, ϕ_2 , is determined by the following expression [18]:

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