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A new thermodynamic model of volume changes in temperature-sensitive polymer gels

D. Browarzik *

Martin-Luther University Halle-Wittenberg, Institute of Chemistry—Physical Chemistry, 06099 Halle, Germany

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ABSTRACT

In the classical swelling theory a polymer gel is a very (infinitely) large cross-linked polymer molecule that engages the solvent molecules. Here, a new swelling model is developed. Firstly, this model permits many cross-linked polymer molecules with finite molar mass instead of a single one. The gel formation is described by a huge number of consecutive swelling equilibria incorporating a solvent molecule by solvent molecule. Thus, the gel is a polydisperse mixture of cross-linked polymer molecules engaging different amounts of solvent. The polydispersity is expressed by a gel-distribution function, the width of which decreases with increasing molar mass of the cross-linked polymer. In the limit of infinite molar mass the new swelling theory is equivalent to the classical one. Secondly, different to the classical treatment, the polymer network is considered to be finitely extensible. Both theories are applied to hydrogels of poly(N-isopropylacrylamide). The mixing contribution of the Helmholtz energy is described by a modified Flory–Huggins expression, the parameters of which are fitted to cloud-point data of a solution of a linear poly(N-isopropylacrylamide). For the elastic contribution the phantom network theory is applied. The new model calculates the swelling degree as a function of temperature nearly perfect in comparison with the experimental data. The classical theory fails in the range of high swelling degrees. Furthermore, the classical treatment predicts a first-order transition between a swollen and a shrunken gel. The new model predicts also a sharp but continuous transition.

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1. Introduction

There are many theoretical and experimental studies considering the volume changes in temperature-sensitive polymer gels [1–17]. Usually, a gel phase is assumed to behave like a fluid engaged in an elastic structure, similarly to the treatment of an osmotic equilibrium. The elastic structure is formed by a cross-linked polymer molecule that is assumed to be infinitely large. The fundamental equations of phase equilibrium basing on this concept were outlined in detail by Maurer and Prausnitz [14] and by Hino and Prausnitz [15]. In theoretical treatment the Helmholtz energy is considered to be a sum of a mixing term and of an elastic term. In the case of charged polymer gels an electrostatic term has to be added. The mixing term, in the simplest case, can be taken from the Flory–Huggins lattice theory or of a modified version of that. Some authors take into account free volume contributions too [8,9,16–22]. There are a few expressions for the elastic term, e.g. the affine network theory of Flory [23] and the phantom network theory of James and Guth [24]. Some elastic models are discussed by

Gusler and Cohen [25]. The most extensively studied polymer gel is the poly(N-isopropylacrylamide) (PNIPAM) gel [3–13,15–22,26–31]. These are very different applications. So, some authors investigated the applicability of PNIPAM hydrogels for drug delivery purposes [26–30]. In the simplest case the swelling degree of PNIPAM in water is studied in dependence on temperature [3–13,15,16]. The investigations of Marchetti et al. [9] are particularly interesting. These authors presented the swelling degree in the temperature range of 280 K–313 K based on numerous experimental data. Near 306 K they found a first-order transition between a shrunken and a swollen gel. This transition temperature is not far away from the lower critical solution temperature (LCST) of an aqueous solution of linear PNIPAM. For description of the experimental data they combined a compressible lattice model and the phantom network theory [24]. Above 300 K (including the first-order transition) the calculated results agree very well with the experimental results. However, below 300 K the theory predicts the swelling degree too high. The poor description at low temperature (high swelling degree) results from the assumption of an infinite extensibility of the cross-linked chains.

In this paper a new swelling model is introduced. Here, there are many cross-linked polymer molecules engaging different amounts of solvent. The gel formation is described by a huge number of consecutive swelling equilibria. Here, solvent molecule by solvent molecule is incorporated until the upper limit of the extensibility of the network is

Abbreviations: PNIPAM, poly(N-isopropylacrylamide); LCST, lower critical solution temperature.

* Tel.: +49 345 5525828; fax: +49 345 55 27017.

E-mail address: dieter.browarzik@chemie.uni-halle.de.

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reached. In this way also in the low-temperature region a good description of the experimental swelling curve of Marchetti et al. [9] is possible.

2. Theory

2.1. Classical treatment

Let us consider a polymer gel that consists of a very large cross-linked polymer molecule B and the solvent A. Usually, in polymer thermodynamics because of the size differences of the molecules segment-molar quantities are considered. In this, the molecules are divided into segments of the same size and, the quantity is related to one mol of segments. Here, the solvent molecule is considered to be the reference segment. Firstly, we introduce the change ΔA_s of the segment-molar Helmholtz energy. The reference state of the change is the pure solvent A and the pure polymer B in a stress-free state. The segment-molar Helmholtz energy of the system is the sum of two contributions:

$$\Delta A_s = \Delta A_s^{mix} + \Delta A_s^{elast}. \tag{1}$$

The mixing part is given by:

$$\frac{\Delta A_s^{mix}}{RT} = (1 - \phi_B) \ln(1 - \phi_B) + \frac{A_s^E}{RT}. \tag{2}$$

Here, R is the universal gas constant, T is the temperature and ϕ_B is the volume fraction of the polymer (the quotient of the number of B-segments and of the number of all segments). $1 / \phi_B$ is proportional to the volume of the gel. The first term of Eq. (2) originates from the well-known Flory–Huggins equation. It describes the entropic effect at mixing of small A-molecules and large B-molecules in the framework of lattice model. Usually, there is still the Flory–Huggins term $(\phi_B / r_B) \ln \phi_B$. However, in classical treatment because of the large value of the segment number r_B this term is cancelled. A_s^E is the excess part of the segment-molar Helmholtz energy. This term describes the influence of the intermolecular interactions. Here, a simplified expression of the Koningsveld–Kleintjens model [32] is applied.

$$\frac{A_s^E}{RT} = \phi_B(1 - \phi_B)g_0 \left(1 + \alpha\phi_B + \frac{\beta}{T} \right). \tag{3}$$

There are the three fit parameters g_0 , α , and β . ΔA_s^{elast} is the elastic contribution of the segment-molar Helmholtz energy. In the framework of the phantom-network theory [24] this contribution is given by:

$$\frac{\Delta A_s^{elast}}{RT} = \frac{3}{4} \frac{\nu}{r_B} \phi_B \left[\left(\frac{\phi_{B0}}{\phi_B} \right)^{2/3} - 1 \right]. \tag{4}$$

Here, ν is the number of elastic chains (where a chain extends between two cross-linking positions) in a tetrafunctional network. ϕ_{B0} is the volume fraction in a stress-free state (corresponding to a “random walk configuration” of the network). In many cases the number of chains ν and the quantity ϕ_{B0} are not exactly known. Furthermore, the phantom-network model is based on some assumptions that are not quite accurate. Therefore, it seems useful to introduce the new parameter

$$B = \frac{1}{2} \frac{\nu}{r_B} \phi_{B0}^{2/3} \tag{5}$$

and, to consider B as a fit parameter. Combining Eqs. (1)–(5) the segment-molar Helmholtz energy reads:

$$\begin{aligned} \frac{\Delta A_s}{RT} = & (1 - \phi_B) \ln(1 - \phi_B) + \phi_B(1 - \phi_B)g_0 \left(1 + \alpha\phi_B + \frac{\beta}{T} \right) \\ & + \frac{3}{2} B \phi_B \left(\frac{1}{\phi_B^{2/3}} - \frac{1}{\phi_{B0}^{2/3}} \right). \end{aligned} \tag{6}$$

Knowing ΔA_s one can derive expressions for the segment-molar chemical potentials using:

$$\Delta \mu_{s,A} = \Delta A_s - \phi_B \left(\frac{\partial \Delta A_s}{\partial \phi_B} \right)_T; \quad \Delta \mu_{s,B} = \Delta A_s + (1 - \phi_B) \left(\frac{\partial \Delta A_s}{\partial \phi_B} \right)_T \tag{7}$$

In swelling equilibrium, the segment-molar chemical potential $\Delta \mu_{s,A}$ has to fulfil the equilibrium condition $\Delta \mu_{s,A} = 0$. This condition may be expressed by:

$$\ln(1 - \phi_B) + \phi_B + \phi_B^2 g_0 \left(1 - \alpha + 2\alpha\phi_B + \frac{\beta}{T} \right) + B \phi_B^{1/3} = 0. \tag{8}$$

In classical treatment, the gel consists of one very large polymer molecule with r_B segments and j solvent molecules. Then, the volume fraction ϕ_B of the polymer is given by $\phi_B = r_B / (r_B + j)$. Defining the swelling degree q by the ratio of the segment number of swollen gel, $r_B + j$, and of dried gel, r_B , one finds the simple relation:

$$q = 1 / \phi_B. \tag{9}$$

Eqs. (8) and (9) permit an explicit calculation of the temperature T if the swelling degree q is given. In this paper the swelling curves are presented as function $q(T)$.

There is also the possibility that a swollen and a shrunken gel are in equilibrium. Then the molar Helmholtz energy has to be equal in the both gel phases I and II. In terms of the segment-molar Helmholtz energy this means:

$$(\Delta A_s / \phi_B)^I = (\Delta A_s / \phi_B)^{II} \tag{10}$$

Considering a constant amount of polymer one can easily show that Eq. (10) is equivalent to:

$$\int_{\phi_B^I}^{\phi_B^{II}} \frac{\Delta \mu_{s,A}}{\phi_B^2} d\phi_B = 0. \tag{11}$$

In literature [14,15], often Eq. (11) is applied. However, Eq. (10) is more comfortable to derive the equilibrium condition. Based on Eqs. (6) and (10) the condition reads:

$$\begin{aligned} \ln \left(\frac{1 - \phi_B^{II}}{1 - \phi_B^I} \right) - \frac{\ln(1 - \phi_B^{II})}{\phi_B^{II}} + \frac{\ln(1 - \phi_B^I)}{\phi_B^I} + g_0 \left(1 - \alpha + \frac{\beta}{T} \right) (\phi_B^{II} - \phi_B^I) \\ + g_0 \alpha \left[(\phi_B^{II})^2 - (\phi_B^I)^2 \right] - \frac{3}{2} B \left[(\phi_B^{II})^{-2/3} - (\phi_B^I)^{-2/3} \right] = 0. \end{aligned} \tag{12}$$

One can also consider the linear form of the polymer B (without cross links). Then, the system solvent A + polymer B is a polymer solution instead showing swelling behavior. In Eq. (6) the last term (elastic

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