

A modeling study of the effect of environmental ionic valence on the mechanical characteristics of pH–electrosensitive hydrogel

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Abstract

A modeling study is presented to analyze the effect of the ionic valence of the environmental solution on the mechanical behavior of a smart hydrogel responding to the combined stimuli of pH and electric voltage when the hydrogel is immersed in a pH buffer solution subjected to an externally applied electric field. The study is conducted through the multi-effect-coupling pH–electric-stimuli model, which considers chemo-electromechanical coupled effects and incorporates a fixed charge density. The model is composed of nonlinear partial differential governing equations that are capable of predicting the responsive deformation of the hydrogel, the distribution of diffusive ionic species concentrations and the fixed charge density, as well as the electric potential in the whole computational domain covering the hydrogel and surrounding buffer solution. The one-dimensional steady-state simulation is conducted numerically to enable discussion of the influence of the ionic valence of the surrounding buffer solution on the distribution of diffusive ionic species concentrations and the mechanical deformation of the hydrogels subjected to the stimuli of the solution's pH combined with electric voltage. It is demonstrated that the hydrogel stiffness, fixed charge density and osmotic pressure depend on the equilibrium state of the hydrogel in different pH and ionic environments with monovalent–multivalent ion exchange under AN electric field.

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1. Introduction

Polyelectrolyte hydrogels are being used in an increasingly wide range of biomechanical and biosensory applications because of their relative low cost, good permeability, stimulus sensitivity, biocompatibility and biodegradability [1]. As is well known, the hydrogels are often stimulated by coupled environmental conditions [2,3]. Due to the relatively high concentrations of ionizable groups bound onto the polymeric crosslinked chains of the hydrogels, stimuli-sensitive hydrogels exhibit pH-responsive characteristics and also respond to electric stimulus simultaneously [4,5].

To date, numerous experimental studies have been conducted on the responsive characteristics of smart hydrogels to multiple environmental stimuli, such as solution pH

combined with an electric field. Probably the first example of the application of a pH–electrosensitive hydrogel is the poly(methylmethacrylate) (PMMA)–poly(acrylic acid) (PAA) hydrogel used for the development of an electrically controlled modulator of the solution pH [6]. A PAA hydrogel immersed in a basic solution subjected to a DC electric field was investigated at the phase transition point [7], where the hydrogel deformation was observed to be dependent on the concentrations of ionic species and the conformation of polymeric chains. It is well known that the volume of hydrogel in the swelling state could be several times that in the collapsed state, when a large force will be generated during phase transition. As a result, pH–electrosensitive hydrogels have been used in the design of actuators in drug delivery systems [8,9].

More and more studies have been carried out to further understand the equilibrium deformation behaviors of the interpenetrating polymer networks of hydrogels responsive

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to pH–electric combined stimuli, including the hyaluronic acid (HA)/poly(vinyl alcohol) (PVA) hydrogels, PMMA–PVA hydrogel, poly(2-acrylamido-2-methylpropane sulfonic acid)–HA hydrogels, PVA–PAA hydrogel and the PAA–poly(vinyl sulfonic acid) copolymer [5,10–13].

Many factors can have an effect on the degree of swelling of polyelectrolyte hydrogels. In addition to solution pH and the ionic strength of the swelling medium, the change in the valence of mobile ions can trigger a dramatic volume transition in polyelectrolyte hydrogels [14]. The phenomena may be explained by the monovalent–multivalent ion exchange taking place between the gel and solution phases. For a given pH and ionic strength, it was found that the extent of swelling in buffers with multivalent ions is lower than that in buffers with monovalent ions [15,16]. The increase in the counterion valence leads to a shift to smaller osmotic pressure owing to the smaller concentration difference between the hydrogel and the surrounding solution [17]. For studying the relation between the osmotic pressure and the volume transition of the hydrogels, it is very important to understand that monovalent–multivalent ion exchange plays a significant role in many physical and chemical processes in biological systems, such as nerve excitation and muscle contraction [18–21]. Moreover, the volume transition of the hydrogels stimulated by valence change may in turn affect the drug-releasing capacity of the hydrogel [22].

The effect of the multivalent ionic species, including monovalent and divalent ions, on the response of smart hydrogels has been investigated experimentally by many research groups [22–25], who have observed that the equilibrium swelling ratio decreases significantly as the valency of the counterion changes from 1 to 2. For example, Bajpai [23] reported that, when the electrolyte changes from NaCl to CaCl₂ at constant pH, temperature and ionic strength, the different polyelectrolyte hydrogels deswell in the range of 1.2–8.9%. In addition, the divalent cations Cu²⁺ [24], Mg²⁺ [25] and Ni²⁺ [22] also affect the degree of ionization or protonation of pH-sensitive hydrogels.

A search of the literature shows that the theoretical features of pH–electrosensitive hydrogels remain poorly understood. A few theoretical modeling studies have been reported [26–29], but they all have drawbacks. For example, Gu et al. [26] proposed a model for the analysis of the distribution of electric potential in tissue only, without considering the surrounding solution. Wallmersperger et al. [27] presented their model based on the linear elastic theory, which will be inaccurate when the hydrogels swell nonlinearly under higher electric voltage. In order to overcome these limitations, Tamagawa and Taya [30] investigated theoretically the distribution of mobile ions in amphoteric hydrogel, where a symmetrical profile was observed in a pH–electrosensitive hydrogel. When an electric field is applied, the distributive profiles of the mobile ionic concentrations in the cationic or anionic hydrogel become heterogeneous [31,32]. For modeling pH–electrosensitive hydrogels, the present authors developed the

multi-effect-coupling pH–electric-stimuli (MECpHe) model, which was validated by comparing the model simulation with published experimental measurements to ascertain the impact of the solution pH and an externally applied electric voltage on the deformation of the hydrogel and the distribution of ionic species, electric potential and fixed charge density in both the hydrogel and the surrounding solvent [33]. In a biomedical system based on pH–electrosensitive hydrogels, an important factor is the influence of the ionic strength of the surrounding solution on the response of the hydrogels. This was investigated with regard to the bending deformation of the hydrogels under the combined stimuli of solution pH and electric voltage [34]. In addition, as one of the most important material properties of smart hydrogels for controlling the swelling equilibrium, the effect of the initial fixed charge density on the swelling ratio of a microgel strip was also studied well under pH–electric combined stimuli [35].

However, this paper is an extension of the previous work based on the MECpHe model [33–35], in which we focus on the monovalent–multivalent ion exchange in the biological solution, and elucidate the effect of ionic valence on the distribution of diffusive ionic species concentrations and the deformation of the hydrogel when subjected to the combined stimuli of solution pH and electric voltage.

2. Theoretical formulation of MECpHe model

By the law of mass conservation, in a state of equilibrium, the change in the number of moles of diffusive species k in a specific volume can be characterized by the difference between the fluxes entering and leaving the reference volume. The Nernst–Planck type of continuity equations can thus be formulated in the undeformed configuration as [33,34]:

$$-\nabla_X \cdot N_k + J_{v_k} r = 0 \quad (k = 1, 2, \dots, N) \quad (1)$$

$$N_k = -JD_k C^{-1} \left[\nabla_X c_k + \frac{z_k F}{RT} c_k \nabla_X \psi \right] + c_k V \quad (2)$$

in which N_k , D_k , c_k , z_k and v_k are the Piola–Kirchhoff molar flux (mM s^{−1}), diffusivity tensor (m² s^{−1}), concentration (mM), valence number and stoichiometric coefficient in the chemical reaction for the k th diffusive ionic species ($k = 1, 2, \dots, N$), respectively. N is the number of total diffusive ionic species. X is the reference configuration, $J = \det(\mathbf{F})$, \mathbf{F} is the deformation gradient tensor and \mathbf{C}^{-1} is the inverse of the right Cauchy–Green tensor, where $\mathbf{C}^{-1} = \mathbf{F}^{-1} \mathbf{F}^{-T}$. V is the velocity of the solvent flow, r is the rate of chemical reaction that represents a source term and ψ is the electrostatic potential. F , R and T are the Faraday’s constant, universal gas constant and absolute temperature (K), respectively.

In this paper, it is assumed that the pore of the hydrogel is very small and that the smart hydrogel is placed in an unstirred solution in a vibration-free experimental microdevice, so that the diffusion dominates the flux transmis-

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