Modeling the effects of pH and ionic strength on swelling of anionic polyelectrolyte gels

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Abstract

A constitutive model is developed for the elastic response of an anionic polyelectrolyte gel under swelling in water with an arbitrary pH and an arbitrary molar fraction of dissolved monovalent salt. A gel is treated as a three-phase medium consisting of a solid phase (polymer network), solvent (water), and solute (mobile ions). Transport of solvent and solute is thought of as their diffusion through the polymer network accelerated by an electric field formed by mobile and fixed ions and accompanied by chemical reactions (dissociation of functional groups attached to polymer chains and formation of ion pairs between bound charges and mobile counter-ions). Constitutive equations are derived by means of the free energy imbalance inequality for an arbitrary three-dimensional deformation with finite strains. These relations are applied to analyze equilibrium swelling diagrams on poly(acrylic acid) gel, poly(methacrylic acid) gel, and three composite hydrogels under water uptake in a bath (i) with a fixed molar fraction of salt and varied pH, and (ii) with a fixed pH and varied molar fraction of salt. To validate the ability of the model to predict observations quantitatively, material constants are found by matching swelling curves under one type of experimental conditions and results of simulation are compared with experimental data in the other type of tests.

Keywords: polyelectrolyte gel, swelling, finite elasticity, constitutive modeling
1. Introduction

This paper deals with constitutive modeling and numerical simulation of the elastic behavior of polyelectrolyte gels under swelling in a water bath with an arbitrary pH and an arbitrary concentration of dissolved monovalent salts.

Hydrogels are three-dimensional networks of polymer chains linked by covalent bonds, physical cross-links, hydrogen bonds, van der Waals interactions, and crystallite associations [1]. When a dry gel is immersed into water, it swells retaining structural integrity and ability to withstand large deformations. The mechanical response of swollen gels has recently attracted substantial attention as these materials demonstrate potential for a wide range of smart applications including biomedical devices, drug delivery carriers, scaffolds for tissue engineering, filters and membranes for selective diffusion, sensors for on-line process monitoring, soft actuators, and optical systems [2–5].

Stimuli-sensitive gels form an important class of hydrogels whose equilibrium degree of swelling and kinetics of solvent uptake are strongly affected by temperature, pH, ionic strength, electric field, light, and enzymes [6–9]. In pH-responsive gels, functional groups are attached to main or side chains. When pH of water is altered, some of these groups are ionized. Depending on the charge of bound groups, anionic, cationic, and ampholytic polyelectrolyte (PE) gels are distinguished. This work focuses on water uptake by anionic gels whose functional groups dissociate into negative bound charges and positive mobile ions.

Comparison of swelling diagrams on neutral and PE gels in deionized water reveals that the latter (i) demonstrate faster kinetics of swelling, and (ii) their equilibrium water uptake exceeds that of neutral gels. A higher rate of solvent transport in PE gels is attributed to electroosmosis: an electric field formed by mobile ions accelerates their flow, which, in turn, induces an increase in diffusivity of water molecules with which these ions are associated. A larger equilibrium degree of swelling of PE gels is explained by two mechanisms: (i) development of ionic pressure (an excess pressure induced by the difference in concentrations of ions inside a specimen and in the water bath) and (ii) electrostatic interactions between bound charges. Although there are no doubts regarding the importance of both mechanisms [10], the latter is conventionally disregarded due to the lack of simple and reliable expressions for the energy of interaction between bound charges and polymer chains [11–14].

When a salt is immersed into the water bath, the equilibrium degree of swelling of a PE gel is strongly reduced. The concept of ionic pressure together with the Donnan equilibrium conditions explains qualitatively the decay in water uptake with molar fraction of salt, but fails to predict observations quantitatively [15]. Three additional mechanisms are suggested to ensure agreement with observations [12]: (i) condensation of mobile counter-ions around bound charges [16] that induces screening of electrostatic forces [17, 18], (ii) binding of mobile counter-ions with bound charges and formation of electrically neutral complexes (ion pairs) that lead to a decrease in concentration of charged groups distributed along polymer chains [18–21], and (iii) evolution of the chemical potential of solvent with concentration of mobile ions that causes changes in the Flory–Huggins parameter [22, 23].

The objective of this study is twofold: (i) to develop constitutive equations for the elastic behavior of PE gels and diffusion of solvent and solutes under arbitrary three-dimensional deformations accompanied by swelling, (ii) to apply these relations to the analysis of equilibrium swelling diagrams on PE gels immersed in water baths with various concentrations of salts.

Modeling and simulation of the mechanical response of pH-sensitive gels under three-dimensional deformations with finite strains has attracted substantial attention in the past decade when it has been confirmed by observations that their equilibrium water uptake is strongly
affected by constraints [24, 25]. Coupled equations for the elastic behavior and transport of solvent have recently been derived in [26–35] for PE gels and in [36, 37] for polyampholytic gels. The effect of ionic strength on swelling of pH-responsive gels was analyzed in [38–42], to mention a few.

The novelty of the proposed approach consists in the following. (i) Derivation of constitutive equations for the elastic response of and diffusion of solvent and solutes through a PE gel is grounded on the free energy imbalance inequality, which allows an analog of the Henderson–Hasselbach equation for degree of ionization of chains to be developed within a unified approach. (ii) Both ionic pressure and interaction between bound charges and polymer chains are taken into account to describe solvent uptake by a pH-responsive gel. (iii) Attachment of mobile counter-ions to bound charges and formation of neutral ion pairs is treated as the main mechanism for a decay in degree of swelling with ionic strength of solution. (iv) A PE gel is modeled as a three-phase medium consisting of a polymer network, solvent, and solutes. Its free energy density equals the sum of the specific free energies of non-interacting constituents, the energy of their interactions, and the energy of an electric field formed by mobile and immobilized ions. (v) Interactions between bound charges and the electric field is accounted for by presuming the reference (stress-free) state of the polymer network to evolve with degree of ionization of chains.

The exposition is organized as follows. Constitutive equations for a PE gel under an arbitrary three-dimensional deformation accompanied by swelling are developed in section 2 by means of the free energy imbalance inequality. To simplify these relations, a principle of electro-mechanical equivalence is introduced, which postulates that for each polymer network with bound charges, an equivalent non-charged network exists (whose reference state may differ from the reference state of the gel) such that stresses in these two networks coincide. Governing equations for equilibrium swelling of a PE gel are derived in section 3 with reference to the Donnan equilibrium conditions. These relations involve (in the simplest case) five material constants that are found in section 4 by fitting experimental swelling diagrams. The effect of geometrical constrains on swelling of pH-sensitive gels is analyzed numerically. Concluding remarks are formulated in section 5. Technical details of derivations are collected in appendices A and B.

2. Constitutive model

A PE gel is treated as a three-phase medium composed of a solid phase (covalently cross-linked network of polymer chains), solvent (water), and solutes (mobile ions). Transport of solvent and solutes is modeled as their diffusion through the network accompanied by chemical reactions (dissociation of functional groups attached to chains and formation of ion pairs between bound charges and mobile ions) and accelerated by an electric field formed by mobile and fixed ions.

2.1. Chemical reactions in the bath

Due to self-ionization of water in the bath

\[ 2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- , \]

(1)

it contains positively charged hydronium ions \(\text{H}_3\text{O}^+\) (hydroxide ions \(\text{H}^+\) associated with neutral water molecules) and negatively charged hydroxyl radicals \(\text{OH}^-\). Concentrations of positive and negative ions are characterized by
\[
\text{pH} = -\log[H^+], \quad \text{pOH} = -\log[OH^-],
\]
where \( \log = \log_{10} \), and \([H^+], [OH^-] \) stand for molar fractions of \( H^+ \), \( OH^- \) ions. In thermodynamic equilibrium, pH and pOH obey the equality
\[
\text{pH} + \text{pOH} = pK_w,
\]
where \( K_w \) denotes water ionization constant, and \( pK_w = -\log K_w \) with \( pK_w = 14 \) at room temperature. The electro-neutrality condition for deionized water reads \([H^+] = [OH^-] \), which, together with equation (3), implies that \( pH = 7 \).

To alter pH of water, hydrochloric acid or sodium hydroxide are conventionally added to the bath. To obtain acidic conditions with \( pH < 7 \), strong acid HCl is immersed that dissociates entirely into \( H^+ \) ions (associated with water molecules to form hydronium ions) and \( Cl^- \) ions
\[
H_2O + HCl \rightleftharpoons H_3O^+ + Cl^-.
\]
Given a molar fraction \( \theta_{HCl} \) of HCl, pH of water in the bath is calculated from the electro-neutrality condition \([H^+] = [OH^-] + [Cl^-] \). Bearing in mind that \([Cl^-] = \theta_{HCl} \) and using equations (2) and (3), we find that
\[
\theta_{HCl} = 10^{-pH} - 10^{\text{pOH} - pK_w}.
\]
Basic conditions in the bath with \( pH > 7 \) are reached when strong base NaOH is added which dissociates entirely into \( Na^+ \) ions (associated with water molecules) and \( OH^- \) ions
\[
H_2O + NaOH \rightleftharpoons Na^+H_2O + OH^-.
\]
For a given molar fraction \( \theta_{NaOH} \) of NaOH, pH of water in the bath is determined from the electro-neutrality condition \([H^+] + [Na^+] = [OH^-] \). Taking into account the equality \([Na^+] = \theta_{NaOH} \) and using equations (2) and (3), we obtain
\[
\theta_{NaOH} = 10^{\text{pH} - pK_w} - 10^{-pH}.
\]
To change ionic strength of water, a monovalent salt is immersed into the bath whose molar fraction \( \theta \) lies below its solubility threshold. For definiteness, we presume sodium chloride NaCl to be dissolved that dissociates into \( Na^+ \) ions (associated with water molecules) and \( Cl^- \) ions
\[
H_2O + NaCl \rightleftharpoons Na^+H_2O + Cl^-.
\]
When an anionic PE chain is immersed into deionized water, some functional groups attached to the chain dissociate, which results in formation of negative bound charges and positive mobile ions. Presuming bound charges to be monovalent, we model the ionization process as dissociation of carboxyl groups,
\[
H_2O + COOH \rightleftharpoons H_3O^+ + COO^-.
\]
Dissociation of functional groups in water with \( Na^+ \) ions is accompanied by the complexation reaction in which ionized carboxyl groups form ion pairs with sodium ions
\[
Na^+H_2O + COO^- \rightleftharpoons Na^+COO^- + H_2O.
\]
Denote by \( n_1 \) the number of non-ionized groups COOH, by \( n_2 \) the number of ionized groups COO\(^-\), by \( n_3 \) the number of ion pairs \( Na^+COO^- \), and by \( n = n_1 + n_2 + n_3 \) the entire number of functional groups per chain. The corresponding concentrations \( \beta_1, \beta_2, \beta_3 \) read
\[
\beta_1 = \frac{n_1}{n}, \quad \beta_2 = \frac{n_2}{n}, \quad \beta_3 = \frac{n_3}{n}.
\]
Degree of ionization $\alpha$ is defined as the ratio of the number of charged bound groups to the total number of functional groups per chain, $\alpha = \beta_2$, which, together with equation (11), yields
\[ \alpha = 1 - \beta_1 - \beta_3. \] (12)

Denote by $\bar{c}$, $\bar{c}_{H^+}$, $\bar{c}_{Na^+}$, $\bar{c}_{OH^-}$, $\bar{c}_{Cl^-}$ concentrations (number of species per unit volume) of water molecules, hydroxide ions, sodium cations, hydroxyl radicals and chloride ions in the bath. Molar fractions of ions are connected with their concentrations by the relations
\[ [H^+] = \kappa \frac{\bar{c}_{H^+}}{\bar{c}}, \quad [Na^+] = \kappa \frac{\bar{c}_{Na^+}}{\bar{c}}, \quad [OH^-] = \kappa \frac{\bar{c}_{OH^-}}{\bar{c}}, \quad [Cl^-] = \kappa \frac{\bar{c}_{Cl^-}}{\bar{c}}, \] (13)
where $\kappa = 1000/18$ stands for molarity of water. Combination of equations (2), (3) and (13) yields
\[ \frac{\bar{c}_{H^+}}{\bar{c}} = \frac{1}{\kappa} 10^{-\text{pH}}, \quad \frac{\bar{c}_{OH^-}}{\bar{c}} = \frac{1}{\kappa} 10^{\text{pH} - pKw}, \quad \frac{\bar{c}_{Na^+}}{\bar{c}} = \frac{1}{\kappa} [Na^+], \quad \frac{\bar{c}_{Cl^-}}{\bar{c}} = \frac{1}{\kappa} [Cl^-]. \] (14)

Under acidic conditions, when HCl and NaCl are dissolved in the bath, we conclude that
\[ [Na^+] = \theta. \] (15)

Under basic conditions, when NaOH and NaCl are added to the bath, which means that
\[ [Na^+] = \theta + \theta_{NaOH}, \] equation (7) implies that
\[ [Na^+] = \theta - 10^{-\text{pH}} + 10^{\text{pH} - pKw}. \] (16)

Ionic strength of the bath is calculated as
\[ I = \frac{1}{2} ([H^+] + [Na^+] + [OH^-] + [Cl^-]). \] (17)

Keeping in mind the electro-neutrality condition $[H^+] + [Na^+] = [OH^-] + [Cl^-]$, we find that
\[ I = [H^+] + [Na^+]. \] It follows from this relation and equation (2) that
\[ [Na^+] = I - 10^{-\text{pH}}. \] (18)

With reference to the conventional approach to the analysis of water uptake by PE gels, the bath is treated in what follows as an infinite reservoir containing solvent (water) and solutes (mobile ions) with fixed concentrations, self-ionization reaction (1) and dissociation reactions (4) and (6) are disregarded, and reactions (9) and (10) are modeled in the simplified manner (without account for association of mobile ions with water molecules)
\[ COOH \rightleftharpoons H^+ + COO^-, \quad Na^+ + COO^- \rightleftharpoons Na^+COO^-. \] (19)

2.2. Macro-deformation of a hydrogel

Macro-deformation of the gel coincides with deformation of the polymer network. For definiteness, the initial configuration is chosen to coincide with that of the undeformed dry specimen. Transformation of the initial state into the actual state is determined by the deformation gradient $\mathbf{F}$. The Cauchy–Green tensors for macro-deformation read
\[ \mathbf{B} = \mathbf{F} \cdot \mathbf{F}^T, \quad \mathbf{C} = \mathbf{F}^T \cdot \mathbf{F}, \] (20)
where the dot stands for inner product, and $^T$ denotes transpose.
The volume element in the actual configuration \( dv \) is expressed by means of the volume element in the initial configuration \( dV \) as
\[
dv = JdV, \tag{21}
\]
where
\[
J = \det F. \tag{22}
\]
The surface element \( nda \) with unit normal \( n \) in the actual configuration is connected with the surface element \( Nda \) with unit normal \( N \) in the initial configuration by the equation
\[
nda = JF^{-T} \cdot Nda = JN \cdot F^{-T}dA. \tag{23}
\]
Denote by \( C \) concentration of water molecules per unit volume in the initial configuration.

Disregarding volume changes in a hydrogel driven by the presence of mobile ions and adopting the molecular incompressibility condition, we write
\[
J = 1 + Cv, \tag{24}
\]
where the characteristic volume of a water molecule \( v \) is determined from the equality \( \tilde{c}v = 1 \).

Denote by \( C_{H^+}, C_{Na^+}, C_{OH^-}, \) and \( C_{Cl^-} \) concentrations of \( H^+, Na^+, OH^- \), and \( Cl^- \) ions per unit volume in the initial configuration. According to equation (21), concentrations of water molecules and mobile ions per unit volume in the actual configuration are given by
\[
c = \frac{C}{J}, \quad c_{H^+} = \frac{C_{H^+}}{J}, \quad c_{Na^+} = \frac{C_{Na^+}}{J}, \quad c_{OH^-} = \frac{C_{OH^-}}{J}, \quad c_{Cl^-} = \frac{C_{Cl^-}}{J}. \tag{25}
\]

Denote by \( M \) the number of chains per unit volume in the initial configuration, by \( C_b = Mn \) concentration of functional groups attached to chains, and by \( C_{b^2} = Mn^2 \) concentration of charged bound groups per unit volume in the initial configuration. It follows from equation (12) that
\[
C_{b^2} = (1 - \beta_1 - \beta_3)C_b. \tag{26}
\]

2.3. Electric field

Transport of mobile ions and deformation of the polymer network with charged groups attached to chains lead to formation of an electric field with electrostatic potential \( \Phi \). The electric field vectors, \( e \) and \( E \), in the actual and initial states are given by
\[
e = -\nabla\Phi, \quad E = -V_0\Phi, \tag{27}
\]
where \( \nabla \) and \( V_0 \) are the gradient operators in the actual and initial configurations. A gel is modeled as a linear dielectric material whose electric displacement vector in the actual state reads
\[
h = eE, \tag{28}
\]
where the electric permittivity \( \epsilon \) is presumed to be constant. It follows from equations (27) and (28) and the chain rule for differentiation
\[
V_0\Phi = V\Phi \cdot F = F^\dagger \cdot V\Phi \tag{29}
\]
that
\[
E = e \cdot F = F^\dagger \cdot e, \quad h = eE \cdot F^{-1} = eF^{-T} \cdot E. \tag{30}
\]
Let \( \Omega \) be an arbitrary domain with boundary \( \partial\Omega \) in the initial state. Their images upon transition into the actual configuration are denoted as \( \omega \) and \( \partial\omega \). The Gauss law for a dielectric
medium states that the flux of the electric displacement through a closed surface equals the sum of charges enclosed by this surface,
\[
\int_{\partial \omega} \mathbf{h} \cdot \mathbf{n} \, d\alpha = \int_{\omega} s \, dv,
\]
where \( s \) stands for charge density in the actual state. It follows from this relation and equations (21), (23) and (26) that
\[
\int_{\partial \alpha} \mathbf{j} \cdot \mathbf{F}^{-\top} \cdot \mathbf{N} \, d\alpha = \int_{\alpha} S \, dV, \tag{31}
\]
where charge density in the initial state \( S = s \) \( J \) is given by
\[
S = e[C_{H^+} + C_{N_d^2} - C_{OH^-} - C_{CT} - (1 - \beta_1 - \beta_3)C_b]. \tag{32}
\]
and \( e \) stands for the charge of electron. Applying the Stokes formula to equation (31) and introducing the nominal electric displacement
\[
\mathbf{H} = J\mathbf{F}^{-1} \cdot \mathbf{h} = J\mathbf{h} \cdot \mathbf{F}^{-\top}, \tag{33}
\]
we arrive at the equation
\[
V_0 \cdot \mathbf{H} = S. \tag{34}
\]
Equations (20), (30) and (33) imply that
\[
\mathbf{H} = eJ \mathbf{C}^{-1} \cdot \mathbf{E} = eJ \mathbf{E} \cdot \mathbf{C}^{-1}. \tag{35}
\]
Insertion of equations (32) and (35) into equation (34) results in the Poisson equation
\[
V_0 \cdot (eJ \mathbf{C}^{-1} \cdot V_0 \Phi) = -e[C_{H^+} + C_{N_d^2} - C_{OH^-} - C_{CT} - (1 - \beta_1 - \beta_3)C_b]. \tag{36}
\]
For an ideal dielectric that occupies a domain \( \Omega \) in the initial state and a domain \( \omega \) in the actual state, the energy of the electric field reads [43]
\[
\int_{\omega} \frac{\mathbf{h} \cdot \mathbf{h}}{2e} \, dv = \int_{\omega} \frac{1}{2eJ} \mathbf{H} \cdot \mathbf{C} \cdot \mathbf{H} \, dV,
\]
where we employed equations (20), (21) and (33). According to this equality, free energy density of the electric field formed by mobile ions and bound charges (per unit volume in the initial configuration) reads
\[
W_{el} = \frac{1}{2eJ} \mathbf{H} \cdot \mathbf{C} \cdot \mathbf{H}. \tag{37}
\]
For an arbitrary domain \( \Omega \), the work of the electric field (per unit time) is determined by [43]
\[
U_{el} = -\int_{\partial \Omega} \Phi \mathbf{H} \cdot \mathbf{N} \, d\alpha,
\]
where the superscript dot stands for the derivative with respect to time. Transforming the integral by means of the Stokes formula and using equations (27) and (34), we find that
\[
U_{el} = \int_{\Omega} (\mathbf{E} \cdot \mathbf{H} - \Phi \dot{S}) \, dV.
\]
It follows from this equality and equation (32) that the work of electric field (per unit volume in the initial configuration and unit time) is given by
\[
U_{el} = \mathbf{E} \cdot \mathbf{H} - e\Phi[C_{H^+} + C_{N_d^2} - C_{OH^-} - C_{CT} + (\beta_1 + \beta_3)C_b]. \tag{38}
\]
2.4. **Kinetic relations**

Denote by $\mathbf{J}$, $\mathbf{J}_{HH}$, $\mathbf{J}_{Na^+}$, $\mathbf{J}_{OH^-}$, $\mathbf{J}_{Cl^-}$ the flux vectors for solvent molecules and mobile ions in the initial configuration (numbers of species moving through unit area per unit time). Their counterparts in the actual configuration read $\mathbf{j}$, $\mathbf{j}_{HH}$, $\mathbf{j}_{Na^+}$, $\mathbf{j}_{OH^-}$, $\mathbf{j}_{Cl^-}$. Keeping in mind that $\mathbf{n} \cdot \mathbf{j} \, d\mathbf{a} = \mathbf{N} \cdot \mathbf{J} \, d\mathbf{A}$, we find from equation (23) that

$$
\mathbf{J} = \mathbf{J} \mathbf{F}^{-1} \cdot \mathbf{j}, \quad \mathbf{J}_{HH} = \mathbf{J} \mathbf{F}^{-1} \cdot \mathbf{j}_{HH}, \quad \mathbf{J}_{Na^+} = \mathbf{J} \mathbf{F}^{-1} \cdot \mathbf{j}_{Na^+}, \\
\mathbf{J}_{OH^-} = \mathbf{J} \mathbf{F}^{-1} \cdot \mathbf{j}_{OH^-}, \quad \mathbf{J}_{Cl^-} = \mathbf{J} \mathbf{F}^{-1} \cdot \mathbf{j}_{Cl^-}.
$$

(39)

The flux of solvent in the actual configuration is described by the relation

$$
\mathbf{j} = -\frac{D \mathbf{c}}{k_B T} \nabla \mu,
$$

(40)

where $T$ is the absolute temperature, $k_B$ is Boltzmann’s constant, $D$ is solvent diffusivity, and $\mu$ is chemical potential of water molecules in the gel. It follows from equations (25), (29), (39) and (40) that

$$
\mathbf{J} = -\frac{D \mathbf{c}}{k_B T} \mathbf{F}^{-1} \cdot \nabla \mu \mathbf{F}^{-1}.
$$

(41)

The mass conservation law for solvent reads

$$
\dot{C} = -\mathbf{V}_0 \cdot \mathbf{j}.
$$

(42)

Combination of equations (41) and (42) yields

$$
\dot{C} = \mathbf{V}_0 \cdot \left( -\frac{D \mathbf{c}}{k_B T} \mathbf{F}^{-1} \cdot \nabla \mu \mathbf{F}^{-1} \right).
$$

(43)

Denote by $\mu_{H^+}$, $\mu_{Na^+}$, $\mu_{OH^-}$, $\mu_{Cl^-}$ chemical potentials of mobile ions. Their flux vectors in the initial state are determined by analogy with equation (41),

$$
\mathbf{J}_{H^+} = -\frac{D_{H^+} C_{H^+}}{k_B T} \mathbf{F}^{-1} \cdot \nabla \mu_{H^+} \mathbf{F}^{-1}, \quad \mathbf{J}_{Na^+} = -\frac{D_{Na^+} C_{Na^+}}{k_B T} \mathbf{F}^{-1} \cdot \nabla \mu_{Na^+} \mathbf{F}^{-1}, \\
\mathbf{J}_{OH^-} = -\frac{D_{OH^-} C_{OH^-}}{k_B T} \mathbf{F}^{-1} \cdot \nabla \mu_{OH^-} \mathbf{F}^{-1}, \quad \mathbf{J}_{Cl^-} = -\frac{D_{Cl^-} C_{Cl^-}}{k_B T} \mathbf{F}^{-1} \cdot \nabla \mu_{Cl^-} \mathbf{F}^{-1},
$$

(44)

where $D_{H^+}$, $D_{Na^+}$, $D_{OH^-}$, $D_{Cl^-}$ stand for the corresponding diffusivities. The mass conservation laws for mobile ions are given by

$$
\dot{C}_{H^+} = -\mathbf{V}_0 \cdot \mathbf{J}_{H^+} + \Gamma_{H^+}, \quad \dot{C}_{Na^+} = -\mathbf{V}_0 \cdot \mathbf{J}_{Na^+} + \Gamma_{Na^+}, \\
\dot{C}_{OH^-} = -\mathbf{V}_0 \cdot \mathbf{J}_{OH^-}, \quad \dot{C}_{Cl^-} = -\mathbf{V}_0 \cdot \mathbf{J}_{Cl^-},
$$

(45)

where

$$
\Gamma_{H^+} = -\beta_1 C_b
$$

(46)

is the rate of production of $H^+$ ions induced by dissociation of non-ionized functional groups, and

$$
\Gamma_{Na^+} = -\beta_2 C_b
$$

(47)

is the rate of production of $Na^+$ ions driven by dissociation of ion pairs, see equation (19). Insertion of equation (44) into equation (45) implies that
\[
\dot{C}_{\text{H}^+} = V_0 \cdot \left( \frac{D_{\text{H}^+} C_{\text{H}^+}}{k_B T} \cdot \nabla (\mu_{\text{H}^+} \cdot F^{-1}) + \Gamma_{\text{H}^+} \right),
\]
\[
\dot{C}_{\text{Na}^+} = V_0 \cdot \left( \frac{D_{\text{Na}^+} C_{\text{Na}^+}}{k_B T} \cdot \nabla (\mu_{\text{Na}^+} \cdot F^{-1}) + \Gamma_{\text{Na}^+} \right),
\]
\[
\dot{C}_{\text{OH}^-} = V_0 \cdot \left( \frac{D_{\text{OH}^-} C_{\text{OH}^-}}{k_B T} \cdot \nabla (\mu_{\text{OH}^-} \cdot F^{-1}) \right),
\]
\[
\dot{C}_{\text{CT}^-} = V_0 \cdot \left( \frac{D_{\text{CT}^-} C_{\text{CT}^-}}{k_B T} \cdot \nabla (\mu_{\text{CT}^-} \cdot F^{-1}) \right).
\]

For an arbitrary domain \( \Omega \) with boundary \( \partial \Omega \), the work produced by transport of solvent and solutes per unit time reads [43]
\[
\mathcal{U}_{\text{def}} = - \int_{\partial \Omega} (\mu \mathbf{J} + \mu_{\text{H}^+} \mathbf{J}_{\text{H}^+} + \mu_{\text{Na}^+} \mathbf{J}_{\text{Na}^+} + \mu_{\text{OH}^-} \mathbf{J}_{\text{OH}^-} + \mu_{\text{CT}^-} \mathbf{J}_{\text{CT}^-}) \cdot \mathbf{N} d\mathbf{A}.
\]

Transforming the integral by means of the Stokes formula and using equations (42) and (45), we find that
\[
\mathcal{U}_{\text{def}} = - \int_{\Omega} \left( \mathbf{J} \cdot \nabla \mu + \mathbf{J}_{\text{H}^+} \cdot \nabla (\mu_{\text{H}^+} \cdot F^{-1}) + \mathbf{J}_{\text{Na}^+} \cdot \nabla (\mu_{\text{Na}^+} \cdot F^{-1}) + \mathbf{J}_{\text{OH}^-} \cdot \nabla (\mu_{\text{OH}^-} \cdot F^{-1}) + \mathbf{J}_{\text{CT}^-} \cdot \nabla (\mu_{\text{CT}^-} \cdot F^{-1}) \right) dV
\]
\[
+ \int_{\Omega} \left[ \mu \dot{\mathbf{C}} + \mu_{\text{H}^+} \dot{C}_{\text{H}^+} (\dot{\mathbf{C}}_{\text{H}^+} - \dot{\Gamma}_{\text{H}^+}) + \mu_{\text{Na}^+} \dot{C}_{\text{Na}^+} (\dot{\mathbf{C}}_{\text{Na}^+} - \dot{\Gamma}_{\text{Na}^+}) + \mu_{\text{OH}^-} \dot{C}_{\text{OH}^-} + \mu_{\text{CT}^-} \dot{C}_{\text{CT}^-} \right] dV.
\]

It follows from equations (46), (47) and (49) that the work produced by transport of solvent and solutes (per unit volume in the initial configuration and unit time) is given by
\[
u_{\text{def}} = \mu \dot{\mathbf{C}} + \mu_{\text{H}^+} \dot{C}_{\text{H}^+} (\dot{\mathbf{C}}_{\text{H}^+} - \dot{\Gamma}_{\text{H}^+}) + \mu_{\text{Na}^+} \dot{C}_{\text{Na}^+} (\dot{\mathbf{C}}_{\text{Na}^+} - \dot{\Gamma}_{\text{Na}^+}) + \mu_{\text{OH}^-} \dot{C}_{\text{OH}^-} + \mu_{\text{CT}^-} \dot{C}_{\text{CT}^-} \right) + \bar{u}_{\text{def}},
\]
\[

2.5. Kinematic relations

The reference configuration of the polymer network (in which stresses in chains vanish) is presumed to differ from the initial configuration. Transformation of the initial state into the reference state is described by the deformation gradient \( \mathbf{f} \). For an isotropic polymer network,
\[
\mathbf{f} = f \frac{1}{3} \mathbf{I},
\]
where \( f \) stands for the coefficient of volume expansion of the network driven by interaction between polymer chains and ionized functional groups, and \( \mathbf{I} \) is the unit tensor.

The deformation gradient for elastic deformation \( \mathbf{F}_e \) describes transformation of the reference configuration into the actual configuration. This tensor is connected with the deformation gradient for macro-deformation \( \mathbf{F} \) by the multiplicative decomposition formula
\[
\mathbf{F} = \mathbf{F}_e \cdot \mathbf{f}.
\]
Substitution of equation (52) into equation (53) implies that
\[ \mathbf{F} = \frac{1}{3} \mathbf{F}_c, \]  
(54)
According to equation (54), the coefficient of volume expansion \( f \) plays the same role as the coefficient of thermal expansion on the conventional theory of thermo-elasticity. The only difference between the two approaches is that the coefficient of thermal expansion characterizes volume changes driven by an increase in temperature, while \( f \) is responsible for evolution of the reference state caused by changes in degree of ionization of chains (this phenomenon was first accounted in [44] within the blob model for PE chains).

Differentiation of equation (54) with respect to time results in
\[ \mathbf{D} = \mathbf{D}_c + \frac{f}{3f} \mathbf{I}, \]  
(55)
where
\[ \mathbf{L} = \mathbf{F} \cdot \mathbf{F}^{-1}, \quad \mathbf{L}_c = \mathbf{F}_c \cdot \mathbf{F}_c^{-1}, \quad \mathbf{D} = \frac{1}{2}(\mathbf{L} + \mathbf{L}^T), \quad \mathbf{D}_c = \frac{1}{2}(\mathbf{L}_c + \mathbf{L}_c^T) \]  
(56)
stand for the velocity gradients and rate-of-strain tensors.

The Cauchy–Green tensors for elastic deformation are given by
\[ \mathbf{B}_c = \mathbf{F}_c \cdot \mathbf{F}_c, \quad \mathbf{C}_c = \mathbf{F}_c^T \cdot \mathbf{F}_c. \]  
(57)
The derivatives of the principal invariants \( J_{e1}, J_{e2}, J_{e3} \) of these tensors with respect to time read
\[ J_{e1} = 2 \mathbf{B}_c : \mathbf{D}_c, \quad J_{e2} = 2(J_{e1} \mathbf{I} - J_{e3} \mathbf{B}_c^{-1}) : \mathbf{D}_c, \quad J_{e3} = 2J_{e3} \mathbf{I} : \mathbf{D}_c, \]  
where the colon stands for convolution of tensors. Insertion of equation (55) into these relations implies that
\[ J_{e1} = 2 \mathbf{B}_c : \mathbf{D} = \frac{2f}{3f} J_{e1}, \quad J_{e2} = -2 \mathbf{B}_c^{-1} : \mathbf{D} J_{e3} \]
+ \[ \frac{2}{3f} \mathbf{I} : \mathbf{D} \]
\[ J_{e3} = 2 \left( \mathbf{I} : \mathbf{D} - \frac{f}{3f} \right) J_{e3}. \]  
(58)

2.6. Free energy density

For a gel (treated as a three-phase composite), the Helmholtz free energy \( \Psi \) (per unit volume in the initial configuration) equals the sum of six components: (i) the energy of solvent and solutes not interacting with each other and with the solid phase \( \Psi_1 \), (ii) the energy of the solid phase not interacting with solvent and solutes \( \Psi_2 \), (iii) the energy of mixing of the solid phase and water \( \Psi_3 \), (iv) the energy of mixing of water and mobile ions \( \Psi_4 \), (v) the energy of mixing of charged and non-charged functional groups distributed along polymer chains \( \Psi_5 \), and (vi) the energy of the electric field created by mobile ions and bound charges \( \Psi_{el} \),

\[ \Psi = \Psi_1 + \Psi_2 + \Psi_3 + \Psi_4 + \Psi_5 + \Psi_{el}. \]  
(59)
The specific energy density \( \Psi_1 \) is given by [34]
\[ \Psi_1 = \mu^0 C + \mu_{H^+} C_{H^+} + \mu_{Na^+} C_{Na^+} + \mu_{OH^-} C_{OH^-} + \mu_{Cl^-} C_{Cl^-}. \]  
(60)
where $\mu_0^0$, $\mu_{H^+}^0$, $\mu_{Na^+}^0$, $\mu_{OH^-}^0$, $\mu_{Cl^-}^0$ denote chemical potentials of non-interacting water molecules and mobile ions.

The free energy density of the polymer network not interacting with solvent and solutes reads

$$\Psi_f = W(J_{e1}, J_{e2}, J_{e3}, \alpha, f),$$

where $\Psi_f$ is the specific mechanical energy stored in chains. This quantity is treated as a function of the principal invariants of the Cauchy–Green tensor for elastic deformation (in accord with the conventional approaches in thermo-elasticity and elasto-plasticity), degree of ionization of chains $\alpha$ (that characterizes concentration of ionized functional groups), and coefficient of volume expansion of the network $f$ (that accounts for mutual displacements of bound charges).

The specific energies of mixing are determined by the conventional formulas

$$\Psi_3 = k_BT C \ln \left( \frac{C_v}{1 + C_v} + \frac{\chi}{1 + C_v} \right),$$

$$\Psi_4 = k_BT \left[ C_{H^+} \ln \left( \frac{C_{H^+}}{C_v} - 1 \right) + C_{Na^+} \ln \left( \frac{C_{Na^+}}{C_v} - 1 \right) + C_{OH^-} \ln \left( \frac{C_{OH^-}}{C_v} - 1 \right) + C_{Cl^-} \ln \left( \frac{C_{Cl^-}}{C_v} - 1 \right) \right],$$

$$\Psi_5 = k_BT C [\beta_1 \ln(1 + \beta_1 + \beta_3) - (1 - \beta_1 - \beta_3) \ln(1 - \beta_1 - \beta_3)],$$

where $\chi$ stands for the Flory–Huggins interaction parameter.

### 2.7. Free energy imbalance inequality

Under isothermal deformation with finite strains, the free energy imbalance inequality reads

$$\Psi - u_{\text{mech}} - u_{el} - u_{\text{diff}} - u_{\text{dis}} \leq 0,$$

where $u_{\text{mech}}$, $u_{el}$, $u_{\text{diff}}$, $u_{\text{dis}}$ are works (per unit volume in the initial state and unit time) produced by stresses, electric field, transport of solvent and solutes, and due to dissociation of functional groups and formation of ion pairs.

The mechanical work is determined by the conventional formula

$$u_{\text{mech}} = JT : D,$$

where $T$ is the Cauchy stress tensor. The works performed by the electric field and diffusion of solvent and solutes are given by equations (38) and (50), respectively. The work induced by dissociation of functional groups and formation of ion pairs reads

$$u_{\text{dis}} = -(\Delta \mu_1 \dot{\beta}_1 + \Delta \mu_3 \dot{\beta}_3) C_h,$$

where the constant $\Delta \mu_1$, $\Delta \mu_3$ stand for the excess chemical potentials of non-ionized functional groups and ion pairs with respect to the chemical potential of bound charges.

Equation (63) is satisfied when functions $C$ and $F$ are connected by the molecular incompressibility condition (24). To account for this dependence, we differentiate equation (24) with respect to time, use equation (A.6), and obtain

$$\dot{C}_v = JF : D = 0.$$
Multiplying this equality by an arbitrary function $\Pi$ and summing the result with equation (63), we arrive at
\[ \Psi = u_{\text{mech}} - u_{cl} - u_{\text{dif}} - u_{\text{din}} + \Pi(\dot{C}_V - J_1 : D) \leq 0. \] (66)
Differentiating equation (59) with respect to time and utilizing equations (37) and (60)–(62), we find that (appendix A)
\[ \Psi = 2(K_{\text{mech}} + K_{el}) : D + E \cdot H + \left[ W_{\text{dif}} - \left( \frac{2K}{3f} - W_f \right) \dot{f} \right] + \Theta C \dot{C} 
+ \Theta_{H^+} \dot{C}_{H^+} + \Theta_{Na^+} \dot{C}_{Na^+} + \Theta_{OH^-} \dot{C}_{OH^-} + \Theta_{CT^+} \dot{C}_{CT^+} + (\Theta \beta_1 + \Theta_3 \beta_3) C_b. \] (67)
where the coefficients are determined by equations (A.3), (A.9) and (A.10). Substitution of equations (38), (50), (64), (65) and (67) into equation (66) implies that
\[ 2(K_{\text{mech}} + K_{pol}) - J(T + \Pi) \] : $D + \left[ W_{\text{dif}} - \left( \frac{2K}{3f} - W_f \right) \dot{f} \right] + (\Theta C + \Pi v - \mu) \dot{C} 
+ (\Theta_{H^+} + \epsilon \Phi - \mu_{H^+}) \dot{C}_{H^+} + (\Theta_{Na^+} + \epsilon \Phi - \mu_{Na^+}) \dot{C}_{Na^+} 
+ (\Theta_{OH^-} - \epsilon \Phi - \mu_{OH^-}) \dot{C}_{OH^-} + (\Theta_{CT^+} - \epsilon \Phi - \mu_{CT^+}) \dot{C}_{CT^+} 
+ (\Theta_1 - \mu_{H^+} + \epsilon \Phi + \Delta \mu_1) \beta_1 C_b + (\Theta_3 - \mu_{Na^+} + \epsilon \Phi + \Delta \mu_3) \beta_3 C_b - \bar{u}_{\text{dif}} \leq 0. \] (68)
Using equation (51) and keeping in mind that $D$, $C$, $C_{H^+}$, $C_{Na^+}$, $C_{OH^-}$, $C_{CT^+}$, $\beta_1$, $\beta_3$ are now arbitrary functions, we conclude that equation (68) is fulfilled, provided that (i) the Cauchy stress tensor reads
\[ T = -\Pi I + \frac{2}{f} (K_{\text{mech}} + K_{el}). \] (69)
(ii) chemical potential of water molecules and mobile ions are given by
\[ \mu = \Theta_C + \Pi v, \quad \mu_{H^+} = \Theta_{H^+} + \epsilon \Phi, \quad \mu_{Na^+} = \Theta_{Na^+} + \epsilon \Phi, \quad \mu_{OH^-} = \Theta_{OH^-} - \epsilon \Phi, \quad \mu_{CT^+} = \Theta_{CT^+} - \epsilon \Phi, \] (70)
(iii) concentrations of non-ionized functional groups obey the equations
\[ \Theta_1 - \mu_{H^+} + \epsilon \Phi + \Delta \mu_1 = 0, \quad \Theta_3 - \mu_{Na^+} + \epsilon \Phi + \Delta \mu_3 = 0, \] (71)
and (iv) volume expansion for the polymer network is governed by the equation
\[ \left( \frac{2K}{3f} - W_f \right) \dot{f} = W_{\text{dif}}. \] (72)
To transform equation (69), we substitute equations (24), (A.3) and (A.9) into this relation and find that
\[ T = -\Pi I + \frac{2}{1 + Cv} \left[ W_1 B_e - J_2 W_2 B_e^{-1} + (J_2 W_2 + J_3 W_3) I \right] + T_M. \] (73)
where
\[ T_M = \frac{1}{c} \left[ (h \otimes h) - \frac{1}{2} (h \cdot h) I \right] \] (74)
stands for the Maxwell stress [45].

Insertion of equation (A.10) into equations (70) yields

$$\mu = \mu^0 + k_B T \left[ \ln \frac{C_v}{1 + C_v} + \frac{1}{1 + C_v} + \frac{x}{(1 + C_v)^2} + \frac{\Pi v}{k_B T} = \frac{C_{H^+} + C_{Na^+} + C_{OH^-} + C_{Cl^-}}{C} \right],$$

$$\mu_{H^+} = \mu_{H^+}^0 + k_B T \ln \frac{C_{H^+}}{C} + e\Phi,$$

$$\mu_{Na^+} = \mu_{Na^+}^0 + k_B T \ln \frac{C_{Na^+}}{C} + e\Phi,$$

$$\mu_{OH^-} = \mu_{OH^-}^0 + k_B T \ln \frac{C_{OH^-}}{C} - e\Phi,$$

$$\mu_{Cl^-} = \mu_{Cl^-}^0 + k_B T \ln \frac{C_{Cl^-}}{C} - e\Phi. \quad (75)$$

It follows from equations (71), (75) and (A.10) that

$$\ln \frac{\beta_1}{1 - \beta_1 - \beta_3} - \ln \frac{C_{H^+}}{C} + \ln K_i = 0, \quad \ln \frac{\beta_3}{1 - \beta_1 - \beta_3} - \ln \frac{C_{Na^+}}{C} + \ln K_j = 0, \quad (76)$$

where

$$K_i = \exp \left( \frac{\Delta \mu_i - \mu_{H^+}^0}{k_B T} \right), \quad K_j = \exp \left( \frac{\Delta \mu_j - \mu_{Na^+}^0}{k_B T} \right).$$

Resolving equation (76) with respect to $\beta_1$ and $\beta_3$, we obtain

$$\beta_1 = \left[ 1 + \frac{K_i C}{K_i C_{H^+}} \right]^{-1}, \quad \beta_3 = \frac{K_j C_{Na^+}}{K_i C_{H^+}} \left[ 1 + \frac{K_i C}{K_j C} \right]^{-1}. \quad (77)$$

Substitution of equation (77) into equation (12) yields

$$\alpha = K'_1 \left[ K'_1 + \frac{C_{H^+}}{K'_1 C_{Na^+}} + R \frac{C_{Na^+}}{C} \right]^{-1}, \quad (78)$$

where $K'_1 = K'_1$ stands for the acid dissociation constant, and $R = K_i/K_j$. Equation (78) provides an extension of the Henderson–Hasselbach equation that accounts for formation of ion pairs between mobile cations Na$^+$ and bound anions COO$^-$. Constitutive equations for a PE gel involve (i) stress–strain relations (73) and (74), (ii) equations (75) for chemical potentials of solvent and solutes, (iii) equations (46) and (47) for the rates of chemical reactions, (iv) equations (77) and (78) for concentrations of non-ionized functional groups and degree of ionization, and (v) equation (72) for the coefficient of inflation of the polymer network. These relations are accompanied by (i) the equilibrium equation for the Cauchy stress tensor, (ii) reaction-diffusion equations (43) and (48) for solvent and solutes, and (iii) equation (36) for the electrostatic potential.

### 2.8. Simplification of the model

Although the governing equations describe basic electro-mechanical processes in a PE gel under swelling, these relations appear to be overly complicated for practical applications. To simplify the model, we disregard the Maxwell stress (74) compared with the mechanical stress

$$T = -\Pi I + \frac{2}{1 + C_v} \left[ W_1 B_e - J_3 W_2 B_e^{-1} + (J_{e2} W_2 + J_{e3} W_3) I \right]. \quad (79)$$
Elementary estimates show that the characteristic Maxwell stress does not exceed $10^3$ Pa which is small compared with the characteristic elastic modulus of a hydrogel whose order is $10^5$ Pa.

To further simplify these relations, we introduce the principle of electro-mechanical equivalence and presume the existence of an equivalent non-charged polymer network with coefficient of volume expansion $f_{eq}(\alpha)$ and elastic energy $W_{eq}(J_{e1}, J_{e2}, J_{e3})$ such that the Cauchy stress in the real (partially ionized) network $T$ coincides with the Cauchy stress in the equivalent network

$$T_{eq} = -\Pi I + \frac{2}{1 + C_v}[W_{eq,1}B_1 - J_{e3}W_{eq,2}B_2^{-1} + (J_{e2}W_{eq,2} + J_{e3}W_{eq,3})I].$$

This approach allows (i) differential equation (72) to be excluded from consideration by replacing it with a phenomenological equation for the function $f_{eq}(\alpha)$, and (ii) conventional formulas to be employed for the elastic energy $W_{eq}$ instead of complicated expression (61) that depends on five arguments. With reference to this concept, we omit the subscript ‘eq’ in what follows, and calculate the Cauchy stress tensor by means of equation (79) with $W$ depending on the principal invariants $I_{en}$ only.

Finally, (i) the neo–Hookean formula is adopted for the strain energy density of the equivalent network

$$W = \frac{1}{2} G[(J_{e1} - 3) - \ln J_{e3}],$$

where $G$ stands for shear modulus, and (ii) coefficient of volume expansion of the equivalent network $f$ is presumed to increase linearly with concentration of bound charges

$$f = 1 + q_0 + q_1C_i\alpha,$$

where $q_0$ stands for degree of swelling of an as-prepared gel, and $q_1$ is a material constant.

The physical meaning of equation (80) was discussed in [46] where this formula was ‘re-derived’ within the concept of entropic elasticity by using the approach proposed in [47]. More sophisticated expressions for this function were developed in [48, 49].

3. Equilibrium swelling

We apply now the model to fit experimental swelling diagrams on anionic gels. With reference to [50], it is assumed that in a fully swollen gel, (i) concentrations of solvent and solutes are independent of spatial coordinates, and (ii) the electrostatic potential is independent of spatial coordinates, but adopts different values, $\Phi$ and $\bar{\Phi}$, in the gel and in the bath. The difference $\Phi - \bar{\Phi}$ characterizes strength of an electric double layer on the boundary of a sample (whose thickness is disregarded compared with the characteristic size of a specimen).

3.1. Donnan equilibrium

Under equilibrium conditions, chemical potentials of solvent and solutes in a gel and in the bath coincide

$$\mu = \bar{\mu}, \quad \mu_{H^+} = \bar{\mu}_{H^+}, \quad \mu_{Na^+} = \bar{\mu}_{Na^+}, \quad \mu_{OH^-} = \bar{\mu}_{OH^-}, \quad \mu_{Cl^-} = \bar{\mu}_{Cl^-},$$

where the bar denotes parameters of the bath. Substituting equations (75) and (78) into equation (82), we arrive at the equations (appendix B)
\[ X \left[ X - K_0 \frac{Q_b}{Q} \left( K_0 + \frac{10^{-pH} + R[Na^+]}{10^{-pH} + [Na^+]} X \right)^{-1} \right] = \frac{1}{\kappa^2} (10^{-pH} + [Na^+])^2, \quad (83) \]

\[
\ln \frac{Q}{1 + Q} + \frac{1}{1 + Q} + \frac{\chi}{(1 + Q)^2} + \frac{\Pi}{k_B T} - \frac{1}{X} \left( X - \frac{1}{\kappa} (10^{-pH} + [Na^+])^2 \right) = 0,
\]

where

\[ Q = C_v, \quad Q_b = C_{b,v}, \quad X = \frac{C_{H^+} + C_{Na^+}}{C}. \]

It follows from equation (24) that under unconstrained swelling, the deformation gradient for macro-deformation reads

\[ F = (1 + C_v) \frac{1}{3} I. \quad (85) \]

Substitution of equations (81) and (85) into equation (54) implies that

\[
F = \left( \frac{1 + C_v}{1 + q_0 + q_1 C_{b,v}} \right)^{\frac{1}{3}} I. \quad (86)
\]

It follows from equations (79) and (80) that

\[ T = -\Pi I + \frac{G}{1 + C_v} (B_b - I). \quad (87) \]

Insertion of equations (57) and (86) into equation (87) yields

\[ T = T I, \quad T = -\Pi + \frac{G}{1 + C_v} \left[ \left( \frac{1 + C_v}{1 + q_0 + q_1 C_{b,v}} \right)^{\frac{2}{3}} - 1 \right]. \]

Keeping in mind that \( T = 0 \) for a specimen with a traction-free boundary surface, we find that

\[ \Pi = \frac{G}{1 + C_v} \left[ \left( \frac{1 + C_v}{1 + q_0 + q_1 C_{b,v}} \right)^{\frac{2}{3}} - 1 \right]. \]

Combining this expression with equation (84) and setting

\[ g = \frac{G v}{k_B T}, \quad \bar{q} = q_1 C_{b,v}, \]

we find that

\[
\ln \frac{Q}{1 + Q} + \frac{1}{1 + Q} + \frac{\chi}{(1 + Q)^2} + \frac{g}{1 + Q} \left[ \left( \frac{1 + Q}{1 + q_0 + \bar{q} \alpha} \right)^{\frac{2}{3}} - 1 \right] \]

\[
- \frac{1}{X} \left( X - \frac{1}{\kappa} (10^{-pH} + [Na^+])^2 \right) = 0.
\]

Given pH and molar fraction of Na\(^+\) ions in the bath, equations (83) and (88) determine degree of swelling \( Q \) and concentration \( X \) of positively charged mobile ions. Degree of ionization of
chains $\alpha$ is given by equation (B.9). These relations involve seven material constants: (i) $g$ stands for the dimensionless elastic modulus, (ii) $Q_b$ is volume fraction of functional groups in the initial state, (iii) $K_a$ denotes their dissociation constant, (iv) $R$ is the ratio of dissociation constants for carboxyl groups and ion pairs, (v) $\chi$ is the Flory–Huggins parameter, and (vi) $q_0$, $\bar{q}$ describe evolution of the stress-free state of polymer chains induced by their ionization. To reduce the number of parameters in simulation, we set $q_0 = 0$ (the reference state of a gel with non-ionized functional groups coincides with its initial state) and $\chi = 0.4$ (water is treated as a poor solvent).

4. Numerical simulation

Our aim now is to compare experimental data in equilibrium swelling tests with predictions of the model and to assess the effect of geometrical constraints on solvent uptake by PE gels.

4.1. Comparison with observations

We focus on the study of equilibrium water uptake by PE gels for which swelling diagrams are provided simultaneously as functions of pH (for a fixed concentration of salt or ionic strength of solution) and molar fraction of salt $\theta$ (for a given pH). For each set of material parameters, equations (83) and (88) are solved numerically by the Newton–Raphson algorithm.

We begin with the analysis of observations on methacrylated dextran–acrylic acid (dextran–AAc) composite gels prepared by radical copolymerization at room temperature of dextran and AAc monomers in an aqueous solution by using ammonium peroxydisulfate (APS)
as an initiator and \( N, N', N'-\)tetramethylethylenediamine (TEMED) as an accelerator \([51]\).

In the first series of tests, dry samples were swollen in deionized water (\( \text{pH} = 7 \)) where various molar fractions \( \theta \) of NaCl salt were dissolved. In the other series of experiments, specimens were swollen in water baths with fixed molar fractions \( \theta = 5, 10, 100 \) mM of salt and varied pH (by insertion of HCl and NaOH). Observations in the first series of tests are depicted in figure 1 where equilibrium degree of swelling \( Q \) is plotted versus \( \theta \). Equilibrium swelling curves in the other series of experiments are reported in figure 2 where \( Q \) is depicted versus pH at various \( \theta \).

Adjustable parameters in the governing equations are found by matching observations in figure 1. With reference to \([20]\), we fix dissociation constant for acrylic acid \( \text{pK}_a = 4.6 \), where \( K_a = \kappa K_a \), and set \( Q_b = 1.0 \cdot 10^{-7} \). The dimensionless elastic modulus \( \varepsilon = 3.56 \cdot 10^{-3} \) is determined by fitting observations at high molar fractions of salt. Coefficients \( q = 2.55 \) and \( R = 4.0 \cdot 10^{-3} \) are calculated from the best-fit condition for the entire swelling diagram.

After determining material constants, equations (83) and (88) are solved numerically for equilibrium swelling of the gel in water baths with fixed concentrations of salt \( \theta \) and varied pH. The ability of the model to predict experimental data is illustrated in figure 2 where results of simulation are plotted together with experimental data.

Changes in degree of ionization of chains \( \alpha \) with molar fraction of salt \( \theta \) and pH of water bath are reported in figures 1 and 3. The following conclusions are drawn: (i) under swelling in a water bath with pH exceeding substantially \( \text{pK}_a \), \( \alpha \) reaches its maximum value at low concentrations of NaCl (\( \theta < 0.1 \) mM), decreases pronouncedly with \( \theta \) in the interval between 0.1 and 100 mM, and vanishes at higher molar fractions of salt, (ii) for a fixed \( \theta \), \( \alpha \) equals zero at low pH values, increases monotonically with pH, and reaches its ultimate value at pH exceeding 7, (iii) the ultimate degree of ionization for samples swollen in a water bath with immersed salt remains below unity and decreases strongly with \( \theta \).
Figure 3. Degree of ionization $\alpha$ versus pH of water baths with various molar fractions of salt $\theta$ mM. Solid lines: predictions of the model.

Figure 4. Degree of swelling $Q$ and degree of ionization $\alpha$ versus molar fraction of salt $\theta$ in a water bath with pH = 7. Circles: experimental data [52]. Solid lines: results of simulation.
To confirm these conclusions, we approximate observations on poly(acrylic acid) gel prepared by polymerization of AAc monomers in an aqueous solution at 60 °C by using \( N, N' \)-methylene-bis-(acrylamide) (BAAm) as a cross-linker, APS as an initiator, and TEMED as an accelerator [52]. Experimental data in two series of tests are reported in figures 4 and 5. In the first series (figure 4), dry samples were swollen in deionized water \((\text{pH} = 7)\) with various molar fractions \(\theta\) of NaNO\(_3\) salt. In the other series (figure 5), specimens were swollen in a water bath without salt whose pH was varied by immersion of HCl.

Material constants are determined by matching observations in figure 4. We use the same value of pKa as in figures 1 and 2, set \(Q_0 = 5.0 \cdot 10^{-8}\), determine elastic modulus \(g = 5.0 \cdot 10^{-2}\) by matching the data at high \(\theta\), and calculate \(\bar{\Delta} = 109.0, R = 1.0 \cdot 10^{-2}\) from the best-fit condition for the entire swelling curve. Afterwards, the governing equations are solved numerically for the conditions of the second series of tests. Results of simulation are compared with experimental data in figure 5.

In the analysis of observations reported in figures 1, 2, 4 and 5, material constants are found by fitting data in tests with varied molar fraction of salt \(\theta\) and applied to predict swelling curves in experiments with altered pH. To show that the same accuracy of prediction can be reached when adjustable parameters are determined by fitting experimental data in a test with varied pH (provided that the equilibrium degree of swelling \(Q\) is measured in the entire range of pH values), we focus on observations on poly(acrylamide–sodium acrylate) gel prepared by free-radical copolymerization of acrylamide and sodium acrylate monomers in aqueous solution at room temperature by using BAAm as a cross-linker, APS as an initiator, and sodium metabisulfite as an accelerator [53].

We begin with approximation of the equilibrium swelling diagram depicted in figure 6 where \(Q\) is plotted versus pH of a water bath without salt. In the fitting procedure, we set \(Q_0 = 2.0 \cdot 10^{-8}\), determine \(g = 0.1\) by matching data at low pH, and find pK\(_a\) = 6.4, \(\bar{q} = 31.5, R = 2.5 \cdot 10^{-4}\) from the best-fit condition for the entire curve.
Afterwards, the governing equations are solved for equilibrium swelling in a bath with pH = 7 and various molar fractions of salt θ. Results of simulation are depicted in figure 7 together with experimental data for equilibrium water uptake by the gel immersed in deionized water with dissolved NaNO₃ salt.

The following conclusions are drawn from figures 6 and 7: (i) an increase in pH of water under acidic conditions results in the growth of degree of swelling $Q$ and degree of ionization of chains $\alpha$, (ii) when pH changes under basic conditions, $Q$ and $\alpha$ remain constant until concentration of Na⁺ ions reaches its critical value, (iii) further growth of pH induces pronounced decays in $Q$ and $\alpha$ driven by formation of ion pairs, (iv) at very high pH values, all COO⁻ groups attached to chains form ion pairs with Na⁺ ions, degree of ionization $\alpha$ vanishes, and degree of swelling $Q$ coincides with that for a gel with non-charged functional groups.

To examine how evolution of $Q$ and $\alpha$ with pH is affected by molar fraction of salt θ, we analyze observations on carrageenan–acrylic acid copolymer gel. Samples (designated as KC-1 in [54]) were prepared by mixture of kappa carrageenan and acrylic acid aqueous solutions with addition of vinyltriethoxysilane as a cross-linker and potassium persulfate (KPS) as an initiator. Figures 8–10 report observations in three series of tests conducted at room temperature. In the first series, dry samples were immersed into water baths with various pH (without addition of salt) and allowed to swell until equilibrium (figure 8). In the other series, specimens were swollen in deionized water (pH = 7) with molar fractions of NaCl salt ranging from 0.05 to 1.0 M (figure 9). In the last series of experiments, water uptake was investigated in a buffer solution with θ = 25 mM and varied pH (figure 10).

As scatter of experimental data is noticeable, material constants are found by matching observations depicted in figures 8 and 9 simultaneously. We employ the same values of $pK_a$ and $Q_b$ as in figures 1 and 2, determine elastic modulus $g = 4.0 \cdot 10^{-2}$ by fitting the data at high
Afterwards, simulation of the governing equations is conducted for water uptake by the gel in the buffer solution. Predictions of the model are depicted in figure 10 together with observations.

Comparison of figures 8 and 10 implies that an increase in molar fraction of salt results in (i) a pronounced decay in degree of swelling $Q$ and degree of ionization $\alpha$ at all pH, and (ii) an increase in pH at which $Q$ and $\alpha$ decay under basic conditions.

The model is developed for equilibrium swelling of PE gels in a water bath with an arbitrary monovalent salt. To demonstrate that accuracy of predictions is independent of chemical composition of salt, experimental swelling diagrams are analyzed on poly(acrylic acid) gel. Specimens with a fixed average molecular weight between cross-links $M_c = 12,700$ were prepared by end-linking of poly(acrylic acid)-bis-(4-aminophenyl sulfide) with tris(4-isocyanato-phenyl) methane [55]. Observations in two series of tests at room temperature are presented in figures 11 and 12. In the first series, specimens were swollen in a water bath with a fixed molar fraction $\theta = 50$ mM of KCl salt, where pH was regulated by addition of HCl and KOH (figure 11). In the other series, equilibrium degree of swelling was measured on specimens immersed into deionized water (pH $= 7$) with various molar fractions (ranging from 10 to 150 mM) of dissolved KCl salt (figure 12).

Adjustable parameters in the governing equations are determined by fitting observations in figure 11. We set $pK_a = 4.6$, $Q_b = 1.0 \cdot 10^{-7}$ (the same values as in figures 1 and 2), find $g = 5.0 \cdot 10^{-3}$ by matching observations at low pH values, and calculate $\bar{q} = 110.0$, $R = 7.5 \cdot 10^{-4}$ from the best-fit condition for the entire swelling curve. Then equations (83) and (88)
are solved numerically for water uptake by the gel in deionized water with various molar fractions of dissolved salt, and results of simulation are reported in figure 12 together with experimental data. Comparison of figures 9 and 12 demonstrates that the accuracy of predictions of
equilibrium swelling diagrams by the model is independent of composition of monovalent salts.

To examine the difference between equilibrium swelling diagrams on PE gels immersed in water with a constant concentration of salt and with a constant ionic strength, we analyze observations on poly(methacrylic acid) (MAc) gel. Specimens were prepared by radical polymerization of MAc monomers in an aqueous solution at 60 °C by using BAAm as a cross-linker, and APS and KPS as initiators [56]. Two series of swelling experiments were performed at 37 °C. In the first series (figure 13), equilibrium degree of swelling was measured as a function of pH of a water bath with a fixed ionic strength $I = 0.2$ M (adjusted by dissolution of appropriate amounts of HCl). In the other series, equilibrium degree of swelling was measured on specimens immersed in deionized water with various ionic strengths. Keeping in mind that $I$ coincides practically with $\theta$ for deionized water, see equations (16) and (18), $Q$ is re-plotted versus $\theta$ in figure 14.

Adjustable parameters in the governing equations are found by matching experimental data in figure 13. We set $Q_b = 1.0 \cdot 10^{-7}$, find $g = 5.0 \cdot 10^{-3}$ by fitting observations at low pH, and calculate $pK_a = 5.4$, $\bar{q} = 85.0$, $R = 4.0 \cdot 10^{-5}$ from the best-fit condition for the entire swelling curve. Figure 13 demonstrates that $Q$ remains constant at high pH values (unlike the graphs in figures 6, 8, 10 and 11 that show a strong decay in $Q$ with pH). This difference is induced by the fact that under basic conditions, molar fraction of Na$^+$ ions increases with pH, see equation (16), when swelling occurs in a bath with a constant $\theta$ (this increase induces formation of ion pairs and decay in water uptake) and remains practically independent of pH, see equation (18), when experiments are conducted in a bath with a constant ionic strength $I$.

To demonstrate that the model with material constants determined by approximation of experimental data in figure 13 predicts adequately observations in swelling tests with various molar fractions of salt, simulation is conducted of the governing equations, and results of numerical analysis are depicted in figure 14 together with experimental data.

Figure 10. Degree of swelling $Q$ and degree of ionization $\alpha$ versus pH of a water bath with $\theta = 25$ mM. Circles: experimental data [54]. Solid lines: predictions of the model.
Figure 11. Degree of swelling $Q$ and degree of ionization $\alpha$ versus pH of a water bath with 50 mM of salt. Circles: experimental data [55]. Solid lines: results of simulation.

Figure 12. Degree of swelling $Q$ and degree of ionization $\alpha$ versus molar fraction of salt $\theta$ in a water bath with pH = 7. Circles: experimental data [55]. Solid lines: predictions of the model.
The following conclusions are drawn from figures 1–14: (i) the constitutive equations with only five adjustable parameters describe correctly experimental data in swelling tests with a fixed concentration of salt and varied pH and with a fixed pH and varied concentration of salt (or ionic strength), (ii) when material constants are determined by matching observations in one type of tests, the model predicts quantitatively experimental data in the other type of tests, (iii) for covalently cross-linked AAc gels and copolymer gels with AAc component, adjustable parameters adopt similar values ($g$ belongs to the interval between $5.0 \cdot 10^{-3}$ and $5.0 \cdot 10^{-2}$ depending on molar fraction of cross-linker, $q$ varies between 109.0 and 174.0 depending on average molecular weight between cross-links, and $R$ ranges from $7.5 \cdot 10^{-4}$ and $1.0 \cdot 10^{-2}$ depending on chemical composition of salt and concentration of AAc monomers).

4.2. Constrained swelling of PE gels

To evaluate the effect of constraints on equilibrium solvent uptake, results of simulation are compared for unconstrained and constrained swelling. Two types of constrained deformations are analyzed: (i) radial swelling of a cylinder with a fixed length, and (ii) swelling of a thin layer connected to a rigid substrate.

4.2.1. Swelling of a cylinder. We study solvent uptake by a cylindrical specimen immersed into a water bath and allowed to swell in the radial direction while positions of its ends are fixed [57, 58]. The deformation gradient for macro-deformation reads

$$F = e_1 \otimes e_1 + \lambda (e_2 \otimes e_2 + e_3 \otimes e_3),$$

(89)
where $e_m$ are unit vectors of a Cartesian frame ($e_1$ is directed along the axis of the cylinder). The coefficient of lateral expansion under swelling $\lambda$ is determined from equations (24) and (89),

$$\lambda = (1 + Cv)^{1/2}. \quad (90)$$

Substitution of equations (81), (89) and (90) into equation (54) implies that

$$E = \frac{1}{(1 + q_0 + q_1Cv\alpha)^{1/2}} \left[ e_1 \otimes e_1 + (1 + Cv)^{1/2}(e_2 \otimes e_2 + e_3 \otimes e_3) \right]. \quad (91)$$

It follows from equations (57), (87) and (91) that

$$T = T_1 e_1 \otimes e_1 + T_2(e_2 \otimes e_2 + e_3 \otimes e_3), \quad (92)$$

where

$$T_1 = -\Pi + G \frac{1}{1 + Cv} \left[ \frac{1}{(1 + q_0 + q_1Cv\alpha)^2} - 1 \right],$$

$$T_2 = -\Pi + G \frac{1 + Cv}{1 + Cv} \left[ \frac{1 + Cv}{(1 + q_0 + q_1Cv\alpha)^2} - 1 \right].$$

Bearing in mind that $T_2 = 0$ for a cylinder with the traction-free lateral surface, we find that
\[ \Pi = \frac{G}{1 + C_v} \left[ \frac{1 + C_v}{(1 + Q_0 + qC_s\alpha)^2} - 1 \right]. \]

Insertion of this expression into equation (84) results in

\[ \ln \frac{Q}{1 + Q} + \frac{1}{1 + Q} + \frac{\chi}{(1 + Q)^2} + \frac{g}{1 + Q} \left[ \frac{1 + Q}{(1 + Q_0 + qC_s\alpha)^2} - 1 \right] \]

\[ - \frac{1}{X} \left( X - \frac{1}{\kappa} \left( 10^{-pH} + [Na^+] \right) \right)^2 = 0. \quad (93) \]

4.2.2. Swelling of a thin layer. A thin gel layer grown on a rigid substrate is immersed into a water bath and allowed to swell along direction \( e_1 \) of its thickness, while in-plane deformation along the vectors \( e_2 \) and \( e_3 \) is restricted [59, 60]. According to equation (24), the deformation gradient for macro-deformation reads

\[ \mathbf{F} = (1 + C_v) e_1 \otimes e_1 + e_2 \otimes e_2 + e_3 \otimes e_3. \quad (94) \]

Equations (54), (81) and (94) imply that

\[ \mathbf{E} = \frac{1}{(1 + Q_0 + qC_s\alpha)} [(1 + C_v) e_1 \otimes e_1 + (e_2 \otimes e_2 + e_3 \otimes e_3)]. \quad (95) \]

It follows from equations (87) and (95) that the Cauchy stress tensor is given by equation (92) with

\[ T_1 = -\Pi + \frac{G}{1 + C_v} \left[ \frac{(1 + C_v)^2}{(1 + Q_0 + qC_s\alpha)^2} - 1 \right]. \]

\[ T_2 = -\Pi + \frac{G}{1 + C_v} \left[ \frac{1}{(1 + Q_0 + qC_s\alpha)^2} - 1 \right]. \]

The equilibrium equation and the traction-free boundary conditions at the faces of the layer imply that \( T_1 = 0 \). Combination of these equations results in

\[ \Pi = \frac{G}{1 + C_v} \left[ \frac{(1 + C_v)^2}{(1 + Q_0 + qC_s\alpha)^2} - 1 \right]. \]

Inserting this expression into equation (84), we arrive at

\[ \ln \frac{Q}{1 + Q} + \frac{1}{1 + Q} + \frac{\chi}{(1 + Q)^2} + \frac{g}{1 + Q} \left[ \frac{(1 + Q)^2}{(1 + Q_0 + qC_s\alpha)^2} - 1 \right] \]

\[ - \frac{1}{X} \left( X - \frac{1}{\kappa} \left( 10^{-pH} + [Na^+] \right) \right)^2 = 0. \quad (96) \]

To examine the influence of constraints on equilibrium swelling, Equations (83), (88), (93) and (96) are solved numerically for poly(acrylic acid) gel whose material parameters are determined by fitting observations in figure 4. Results of simulation are reported in figure 15.
(where $Q$ is plotted versus pH) and 16 (where this quantity is depicted versus concentration of salt $\theta$ in deionized water). Figure 15 demonstrates that in the interval of pH values between 3 and 12 where degree of ionization of chains is strongly affected by mobile ions, the presence of constraints induces a pronounced decay in equilibrium degree of swelling. For example, at pH = 7, $Q$ under unconstrained swelling exceeds that for a cylinder with a fixed length by a factor of 5 and $Q$ for a thin layer by a factor of 22. In the intervals of low (pH < 3) and high (pH > 12) pH values, where all functional groups attached to polymer chains are neutral, this difference becomes less pronounced. According to figure 16, the same relations between $Q$ under unconstrained and constrained swelling are fulfilled for water uptake in an aqueous solution of salt with concentrations $\theta$ below $10^{-3}$ M. The effect of constraints weakens with further increase in concentration of salt and becomes insignificant at $\theta > 1$ M. The data in figures 15 and 16 are in accord with the results of numerical simulation reported in [24, 25]: a novel phenomenon revealed in figure 15 is a decay in degree of swelling at high pH values driven by formation of ion pairs (this effect was disregarded in previous studies).

Results of numerical analysis for unconstrained swelling and swelling of a thin layer in solutions of salt in water with various pH are depicted in figure 17 where $Q$ is plotted versus $\theta$ for pH ranging from 3 to 9. This figure shows that (i) at all pH, degree of swelling $Q$ remains constant at $\theta < 1$ mM and decreases monotonically with $\theta$ at higher concentrations of salt; (ii) given $\theta$, degree of swelling increases with pH: this growth is pronounced at low $\theta$ and becomes negligible at $\theta > 0.1$ M; (iii) at $\theta < 0.01$ M, the presence of constraints induces a pronounced decay in water uptake.

Unlike previous models [24], equations (83), (88) and (96) with the material constants found by matching experimental data do not predict a non-monotonous dependence of $Q$ on $\theta$ at pH close to $pK_a$. Although a decay in $Q$ of a layer by two orders of magnitude caused by a decrease in concentration of salt from $10^{-3}$ to $10^{-5}$ M [24] has not yet been observed in
experiments, a weak decay in this quantity caused by a reduction of $\theta$ has been reported in tests on polymer brushes whose thickness diminishes by 10–20% [61, 62].

To demonstrate that this phenomenon can be described by the constitutive model, simulation is performed of the governing equations with $Q_b = 8.0 \cdot 10^{-7}$. We do not change material constants $g$, $R$, $pK_a$ and determine $q = 111.0$ from the best-fit condition for the data depicted in figure 4. Results of numerical analysis are presented in figures 18 and 19 where $Q$ and $\alpha$ are plotted versus $\theta$ for unconstrained water uptake and swelling of a thin layer. Figure 18 shows that under unconstrained swelling, $Q$ and $\alpha$ decrease with $\theta$ for all pH values. According to figure 19, under swelling of a thin layer, $Q$ and $\alpha$ decay with $\theta$ at pH far below and above $pK_a$ and demonstrate a non-monotonic behavior when pH is close to $pK_a$. Comparison of figures 17 and 19 shows that non-monotonicity of the diagram $Q(\theta)$ appears at relatively high concentrations of functional groups only.

5. Conclusions

A model is developed for the elastic response of and diffusion of solvent and solute through an anionic gel under swelling in a water bath with arbitrary pH and molar fraction of dissolved monovalent salt. A PE gel is treated as a three-phase continuum composed of a solid phase (polymer network), solvent (water), and solute (mobile ions). Transport of solvent and solute is thought of as their diffusion through the network accelerated by an electric field formed by mobile ions and bound charges and accompanied by chemical reactions (dissociation of functional groups attached to polymer chains and formation of ion pairs between bound charges and mobile counter-ions). Constitutive equations are derived by means of the free energy imbalance inequality for an arbitrary three-dimensional deformation with finite strains.
Figure 17. Degree of swelling $Q$ versus molar fraction of salt $\theta$ in water with various pH. Symbols: results of simulation for unconstrained swelling and swelling of a thin layer.

Figure 18. Degree of swelling $Q$ and degree of ionization $\alpha$ versus molar fraction of salt $\theta$ in water with various pH. Symbols: results of simulation for unconstrained swelling.
In the analysis of swelling of PE gels, both ionic pressure and interaction of bound charges with polymer chains are taken into account. To describe the latter phenomenon in a tractable way, the reference (stress-free) state of the network is presumed to differ from the initial state of a dry undeformed gel, and the coefficient of its volume expansion is treated as a linear function of degree of ionization of chains. A decay in degree of swelling of a gel with molar fraction of salt is explained by formation of neutral ion pairs between bound anions and mobile cations. This phenomenon is described by a novel version (78) of the Henderson–Hasselbach equation for degree of ionization of chains. With reference to the Donnan equilibrium conditions, governing equations (83), (88), (93) and (96) are developed for unconstrained and constrained swelling of PE gels.

An advantage of the constitutive model is that the influence of pH and molar fraction of salt on swelling of a PE gel is treated in a unified manner which does not require introduction of phenomenological relations for dissociation constant and the Flory–Huggins parameter in order to ensure agreement with experimental data.

The model is applied to study equilibrium water uptake by poly(acrylic acid) gel, poly(methacrylic acid) gel, and composite (dextran-AAc, carrageenan-AAc, and acrylamide-sodium acrylate) gels immersed into a water bath with varied pH and into a bath with a fixed pH and varied molar fraction of salt \( \theta \) (or ionic strength \( I \)). The main conclusion of this study is that observations in these tests are mutually dependent: when adjustable parameters in the governing equations are found by matching observations in one type of swelling tests, the model predicts correctly equilibrium water uptake in the other type of experiments.

Numerical analysis demonstrates the ability of the model to predict a strong decay in degree of swelling at high pH values, to account for the difference between equilibrium swelling

![Figure 19](image-url). Degree of swelling \( Q \) and degree of ionization \( \alpha \) versus molar fraction of salt \( \theta \) in water with various pH. Symbols: results of simulation for swelling of a thin layer.
diagrams under a fixed concentration of salt and a fixed ionic strength, and to describe weakly non-monotonic dependencies of water uptake on pH under constrained swelling.

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**Appendix A.**

Substitution of equations (60)–(62) into equation (59) implies that

$$
\Psi = \mu^0 C + k_b TC\left(\frac{C}{1 + C} + \frac{\chi}{1 + C} \right) + \mu^0 H^+ C_{H^+} + k_b TC_{H^+}\left(\ln \frac{C_{H^+}}{C} - 1 \right)
$$

$$
+ \mu^0 N_d C_{N_d} + k_b TC_{N_d}\left(\ln \frac{C_{N_d}}{C} - 1 \right) + \mu^0 OH^- C_{OH^-} + k_b TC_{OH^-}\left(\ln \frac{C_{OH^-}}{C} - 1 \right)
$$

$$
+ \mu^0 CL^- C_{CL^-} + k_b TC_{CL^-}\left(\ln \frac{C_{CL^-}}{C} - 1 \right) + k_b TC_N \beta_1 \ln \beta_1 + \beta_3 \ln \beta_3
$$

$$
+ (1 - \beta_1 - \beta_3) \ln(1 - \beta_1 - \beta_3)] + W + W_e\alpha. \tag{A.1}
$$

The derivative of equation (61) with respect to time reads

$$
W = W_{,1} J_{e1} + W_{,2} J_{e2} + W_{,3} J_{e3} + W_{,d}\alpha + W_{,f},
$$

where

$$
W_m = \frac{\partial W}{\partial J_m}, \quad W_\alpha = \frac{\partial W}{\partial \alpha}, \quad W_f = \frac{\partial W}{\partial f}.
$$

Insertion of equation (58) into this equality yields

$$
W = 2K_{\text{mech}} : D + W_{,d}\alpha - \left[\frac{2K}{3f} - W_f\right] f, \tag{A.2}
$$

with

$$
K_{\text{mech}} = W_{,1} B_1 - J_{e3} W_{,2} B_{e3}^{-1} + (J_{e2} W_{,2} + J_{e3} W_{,3}) I, \quad K = J_{e1} W_{,1} + 2J_{e2} W_{,2} + 3J_{e3} W_{,3}. \tag{A.3}
$$

Differentiation of equation (37) with respect to time implies that

$$
W_{e1} = \frac{1}{2eJ}\left(2H \cdot C \cdot H + H \cdot C \cdot H - \frac{f}{f} H \cdot C \cdot H\right)
$$

This relation together with equation (35) results in

$$
W_{e3} = E \cdot H + \frac{1}{2eJ}\left(H \cdot C \cdot H - \frac{f}{f} H \cdot C \cdot H\right). \tag{A.4}
$$

It follows from equations (20) and (56) that
\[ \dot{\mathbf{C}} = 2\mathbf{F}^T \cdot \mathbf{D} \cdot \mathbf{F}. \]

Combination of this equality with equation (35) yields

\[ \frac{1}{2eJ} \mathbf{H} \cdot \dot{\mathbf{C}} \cdot \mathbf{H} = \frac{1}{eJ} \mathbf{H} \cdot \mathbf{F}^T \cdot \mathbf{D} \cdot \mathbf{F} \cdot \mathbf{H} = \frac{J}{e} \mathbf{h} \cdot \mathbf{D} \cdot \mathbf{h} = \frac{J}{e} (\mathbf{h} \otimes \mathbf{h}) : \mathbf{D}, \quad (A.5) \]

where \( \otimes \) stands for tensor product. Keeping in mind that

\[ J = J \mathbf{I} : \mathbf{D} \quad (A.6) \]

and utilizing equation (20), we conclude that

\[ \frac{j}{2eJ^2} \mathbf{H} \cdot \dot{\mathbf{C}} \cdot \mathbf{H} = \frac{1}{2eJ} \mathbf{H} \cdot \mathbf{F}^T \cdot \mathbf{D} \cdot \mathbf{F} \cdot (\mathbf{H}(I : \mathbf{D})) = \frac{j}{2e} (\mathbf{h} \cdot \mathbf{h} I : \mathbf{D}). \quad (A.7) \]

Substitution of equations (A.5) and (A.7) into equation (A.4) implies that

\[ W_{el} = \mathbf{E} \cdot \mathbf{H} + 2K_{el} I : \mathbf{D}, \quad (A.8) \]

where

\[ K_{el} = \frac{j}{2eI} \left[ (\mathbf{h} \otimes \mathbf{h}) - \frac{1}{2} (\mathbf{h} \cdot \mathbf{h}) \mathbf{I} \right]. \quad (A.9) \]

Differentiating equation (A.1) with respect to time and using equations (A.2) and (A.8), we arrive at equation (67) with

\[ \Theta_C = \mu^0 + k_BT \left[ \ln \frac{C_v}{1 + C_v} + \frac{1}{1 + C_v} + \frac{X}{(1 + C_v)^2} - \frac{C_{H^+} + C_{Na^+} + C_{OH^-} + C_{Cl^-}}{C} \right], \]
\[ \Theta_{H^+} = \mu_{H^+}^0 + k_BT \ln \frac{C_{H^+}}{C}, \quad \Theta_{Na^+} = \mu_{Na^+}^0 + k_BT \ln \frac{C_{Na^+}}{C}, \]
\[ \Theta_{OH^-} = \mu_{OH^-}^0 + k_BT \ln \frac{C_{OH^-}}{C}, \quad \Theta_{Cl^-} = \mu_{Cl^-}^0 + k_BT \ln \frac{C_{Cl^-}}{C}, \]
\[ \Theta_1 = k_BT \frac{\beta_1}{1 - \beta_1 - \beta_3}, \quad \Theta_3 = k_BT \frac{\beta_3}{1 - \beta_1 - \beta_3}. \quad (A.10) \]

Appendix B.

Insertion of equation (75) into equation (82) implies that

\[ \ln \frac{C_{H^+}}{C} = \ln \frac{C_{H^+}}{\bar{e}} - \frac{e}{k_BT} (\Phi - \Phi), \quad \ln \frac{C_{Na^+}}{C} = \ln \frac{C_{Na^+}}{\bar{e}} - \frac{e}{k_BT} (\Phi - \Phi), \]
\[ \ln \frac{C_{OH^-}}{C} = \ln \frac{C_{OH^-}}{\bar{e}} + \frac{e}{k_BT} (\Phi - \Phi), \quad \ln \frac{C_{Cl^-}}{C} = \ln \frac{C_{Cl^-}}{\bar{e}} + \frac{e}{k_BT} (\Phi - \Phi). \quad (B.1) \]

where concentrations of water molecules and mobile ions in the bath in the initial configuration are replaced with their concentrations in the actual configuration. It follows from equation (B.1) that
\[
\begin{align*}
\frac{C_{\text{H}^+} C_{\text{OH}^-}}{C} &= \frac{\bar{e}_{\text{H}^+} \bar{e}_{\text{OH}^-}}{\bar{e}}, \\
\frac{C_{\text{Na}^+} C_{\text{OH}^-}}{C} &= \frac{\bar{e}_{\text{Na}^+} \bar{e}_{\text{OH}^-}}{\bar{e}}, \\
\frac{C_{\text{H}^+} C_{\text{CT}^-}}{C} &= \frac{\bar{e}_{\text{H}^+} \bar{e}_{\text{CT}^-}}{\bar{e}}, \\
\frac{C_{\text{Na}^+} C_{\text{CT}^-}}{C} &= \frac{\bar{e}_{\text{Na}^+} \bar{e}_{\text{CT}^-}}{\bar{e}}.
\end{align*}
\] (B.2)

Combination of equations (B.2) results in
\[
\begin{align*}
\frac{C_{\text{H}^+} C_{\text{OH}^-} + C_{\text{CT}^-}}{C} &= \frac{\bar{e}_{\text{H}^+} \bar{e}_{\text{OH}^-} + \bar{e}_{\text{CT}^-}}{\bar{e}}, \\
\frac{C_{\text{H}^+} + C_{\text{Na}^+} C_{\text{OH}^-} + C_{\text{CT}^-}}{C} &= \frac{\bar{e}_{\text{H}^+} + \bar{e}_{\text{Na}^+} \bar{e}_{\text{OH}^-} + \bar{e}_{\text{CT}^-}}{\bar{e}}.
\end{align*}
\] (B.3)

The electro-neutrality conditions for the gel and for the bath read
\[
C_{\text{OH}^-} + C_{\text{CT}^-} = C_{\text{H}^+} + C_{\text{Na}^+} - \alpha C_b, \\
\bar{e}_{\text{OH}^-} + \bar{e}_{\text{CT}^-} = \bar{e}_{\text{H}^+} + \bar{e}_{\text{Na}^+}.
\] (B.4)

Inserting equation (B.4) into equation (B.3), we find that
\[
X_i \left( X - \alpha \frac{C_b}{C} \right) = \frac{\bar{e}_{\text{H}^+} \bar{e}_{\text{H}^+} + \bar{e}_{\text{Na}^+}}{\bar{e}}, \\
X \left( X - \alpha \frac{C_b}{C} \right) = \left( \frac{\bar{e}_{\text{H}^+} + \bar{e}_{\text{Na}^+}}{\bar{e}} \right)^2,
\] (B.5)

where
\[
X_i = \frac{C_{\text{H}^+}}{C}, \\
X = \frac{C_{\text{H}^+} + C_{\text{Na}^+}}{C}.
\] (B.6)

Combination of equations (14) and (B.5) yields
\[
X_i \left( X - \alpha \frac{C_b}{C} \right) = \frac{1}{\kappa^3} (10^{-\phi H}(10^{-\phi H} + [\text{Na}^+])), \\
X \left( X - \alpha \frac{C_b}{C} \right) = \frac{1}{\kappa^3} (10^{-\phi H} + [\text{Na}^+])^2.
\] (B.7)

It follows from equation (B.7) that
\[
X_i = \frac{10^{-\phi H}}{10^{-\phi H} + [\text{Na}^+]}.X.
\] (B.8)

Substitution of equations (B.6) and (B.8) into equation (78) implies that
\[
\alpha = K_a \left( \frac{10^{-\phi H} + R[\text{Na}^+]}{10^{-\phi H} + [\text{Na}^+] X} \right)^{-1}.
\] (B.9)

Combination of equations (B.7) and (B.9) yields
\[
X \left[ X - K_a \frac{C_b}{C} \left( \frac{10^{-\phi H} + R[\text{Na}^+]}{10^{-\phi H} + [\text{Na}^+] X} \right)^{-1} \right] = \frac{1}{\kappa^3} (10^{-\phi H} + [\text{Na}^+])^2.
\] (B.10)

Chemical potential of water molecules in the gel is calculated by inserting equations (B.4) and (B.6) into equation (75),
\[
\mu = \mu^0 + k_b T \left[ \ln \frac{C_v}{1 + C_v} + \frac{1}{1 + C_v} + \frac{X}{(1 + C_v)^2} + \frac{\Pi_y}{k_b T} \right] \left( 2X - \alpha \frac{C_b}{C} \right).
\] (B.11)
Chemical potential of water molecules in the bath is given by equation (75) where the first four terms in the square brackets (which describe interaction between the polymer network and solvent) are disregarded

$$\bar{\mu} = \mu^0 - k_B T \bar{c} \bar{\bar{c}}_{HH} + \bar{c}_{Na}\bar{c} + \bar{c}_{OH} + \bar{c}_{CT}.$$ 

Combination of this expression with equations (14), (B.4) implies that

$$\bar{\mu} = \mu^0 - \frac{2k_B T}{\kappa} (10^{-pH} + [Na^+]).$$  \hspace{1cm} (B.12)

Substitution of equations (B.11) and (B.12) into equation (82) yields

$$\ln \frac{C_v}{1 + C_v} + \frac{1}{1 + C_v} \frac{\chi}{(1 + C_v)^2} + \frac{\Pi v}{k_B T} + \frac{\alpha C_b}{C} - 2 \left( X - \frac{1}{\kappa} (10^{-pH} + [Na^+]) \right) = 0.$$ \hspace{1cm} (B.13)

It follows from equation (B.7) that

$$\left( X - \frac{1}{\kappa} (10^{-pH} + [Na^+]) \right) \left( X + \frac{1}{\kappa} (10^{-pH} + [Na^+]) \right) = \frac{\alpha C_b}{C} X,$$

which implies that

$$\left( X - \frac{1}{\kappa} (10^{-pH} + [Na^+]) \right) = \frac{\alpha C_b}{C} \left( X + \frac{1}{\kappa} (10^{-pH} + [Na^+]) \right)^{-1}.$$ \hspace{1cm} (B.14)

Insertion of equation (B.14) into equation (B.13) results in

$$\ln \frac{C_v}{1 + C_v} + \frac{1}{1 + C_v} \frac{\chi}{(1 + C_v)^2} + \frac{\Pi v}{k_B T} - X \left( \frac{\alpha C_b}{C} \right)^2 \left( X + \frac{1}{\kappa} (10^{-pH} + [Na^+]) \right)^{-2} = 0.$$ \hspace{1cm} (B.15)

According to equation (B.7),

$$\left( \frac{\alpha C_b}{C} \right)^2 = \frac{1}{X^2} \left( X - \frac{1}{\kappa} (10^{-pH} + [Na^+]) \right)^2 \left( X + \frac{1}{\kappa} (10^{-pH} + [Na^+]) \right)^2.$$

Substitution of this expression into equation (B.15) implies that

$$\ln \frac{C_v}{1 + C_v} + \frac{1}{1 + C_v} \frac{\chi}{(1 + C_v)^2} + \frac{\Pi v}{k_B T} - \frac{1}{X} \left( X - \frac{1}{\kappa} (10^{-pH} + [Na^+]) \right)^2 = 0.$$ \hspace{1cm} (B.16)

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