

Hydrogel: pH Role on Polyelectrolyte Behaviour in Aqueous Media

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Polyelectrolytes are a class of polymer whose swelling depends on the external condition of pH. The dissociation of the ionizable groups is strongly depended on the concentration of the H⁺ ions in solution and this leads to different swelling behaviour changing the external pH. Since these materials are versatile and used in various fields, an in-depth knowledge of their behaviour becomes important to use them appropriately. The present work aims to offer an overview of the behaviour of these materials in solution through an experimental and a steady state modelling part. The results serve as a fundamental basis to understand the behaviour of these systems, including transient periods, leading to a comprehensive and predictable description.

1. Introduction

Hydrogels are polymers that can absorb large quantities of water and swell due to the presence of hydrophilic groups on their chain (Flory, 1953; Peppas & Khare, 1993). In this category there are the so-called “smart hydrogels” whose swelling is influenced by the different condition of the surrounding media, and, among them, there are polyelectrolytes (PEs) (Gao et al., 2013). PEs contain a percentage of ionizable groups, which, in polar solvent, can dissociate in a fixed part that remain on the chain and in a mobile part that goes into solution. The dissociation of the ionizable groups is strongly dependent on the pH of the external bath. Two types of PEs can be distinguished: the anionic hydrogels, whose swelling increases as the pH increases and the cationic hydrogels with the opposite behaviour. To fully understand all the phenomena involved, mathematical modelling has been widely used as an investigative tool during years. In this work, starting from the model studied for neutral hydrogels (Caccavo & Lamberti, 2017), the aim is to extend the treatment to an anionic polyelectrolyte, writing the equations that describe its steady state behaviour in a full range of pH. In addition, to tune and validate the model, a further aim is to obtain experimental data monitoring the swelling behaviour of a general anionic hydrogel in aqueous solution at different pH.

2. Materials and Methods

Acrylamide (CAS: 79-06-01), N,N'-MethylenBis (Acrylamide) (CAS: 110-26-9), Sodium Acrylate (7446-81-3), Ammonium Persulfate (CAS: 7727-54-0) and Sodium Metabisulfite (CAS: 7681-57-4) where purchased from Sigma Aldrich.

The anionic copolymer gel of acrylamide was prepared with this general recipe (Vasheghani-Farahani et al., 1990): a solution of acrylamide (632 mM), N,N'-MethylenBis (Acrylamide) (8.6 mM), sodium acrylate (71.2 mM) were dispersed in 50 mL of distilled water, then ammonium persulfate (1.75 mM) and sodium metabisulfite (2.1 mM) were added as initiator and accelerator respectively. The solution was transferred into cylinders moulds for 24 hours to obtain the chemical reticulation as shown in Figure 1 a). After 24h the gels were removed from the moulds and weighed to obtain the original mass M_0 of each sample Figure 1b). The sample of gel was soaked in different beaker containing 100mL of solution of known pH prepared by adding a proper quantity of HCl or NaOH Figure 1c). After equilibration for 48 h, the swollen gel was removed from the solution, and weighed Figure 1 d). The swelling ratio was defined as:

$$S_R = \frac{M}{M_D} = \frac{M}{M_0} \cdot \frac{M_0}{M_D} \quad (1)$$

Where M/M_0 is the ratio of swollen mass, M , to the original mass M_0 and M_0/M_D represents the swelling at the initial condition: it is the ratio of the original mass M_0 to the mass of dry polymer M_D , and it is roughly 24. Three different samples were prepared and weighed after equilibration for every pH values.

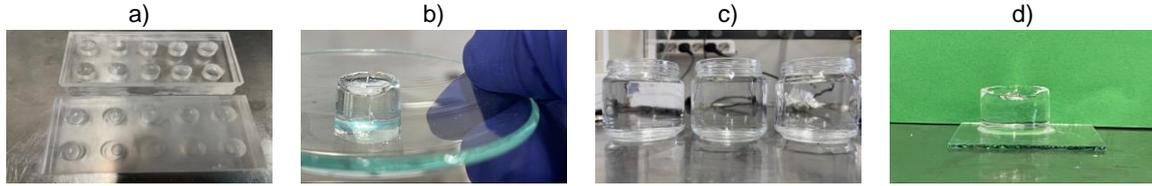


Figure 1 Experimental part: a) the solution was transferred into cylinder moulds; b) after 24h the gels were removed from the solution and weighed to obtain the initial mass M_0 ; c) the sample was soaked in different beaker containing 100mL of solution of known pH; d) after equilibration for 48h the swollen gel was removed from the solution and weighed.

3. Modelling

The model has been written for an anionic hydrogel whose swelling increases as the pH of the external bath increases. In addition, the hypothesis of “large hydrogel” has been done where with large is intended a gel with a dimension larger than the Debye length and in this way all the phenomena related to the interface could be neglected (Marcombe et al., 2010). For the anionic hydrogel the fixed part that remain on the chain is negatively charged, on the contrary the mobile part that goes in solution is positively charged. As shown in Figure 2 the species present in solution are: solvent (“s”), protons (“ H^+ ”), hydroxide ion (“ OH^- ”), undissociated acid groups (“ AH ”), dissociated acid groups (“ A^- ”), associated basic groups (“ ANa ”), cations (“ C^+ ”) and anions (“ C^- ”).

For pH lower than 7 the dissociation of the groups on the chain could be written as:



These three species are in equilibrium when their concentration satisfy the following equation:

$$\frac{[H^+][A^-]}{[AH]} = K_a \quad (3)$$

For pH higher than 7 another equation has been added which describe the association of the groups and could be written as:



In this way an equilibrium constant could be defined as:

$$\frac{[A^-][Na^+]}{[ANa]} = K_{Na} \quad (5)$$

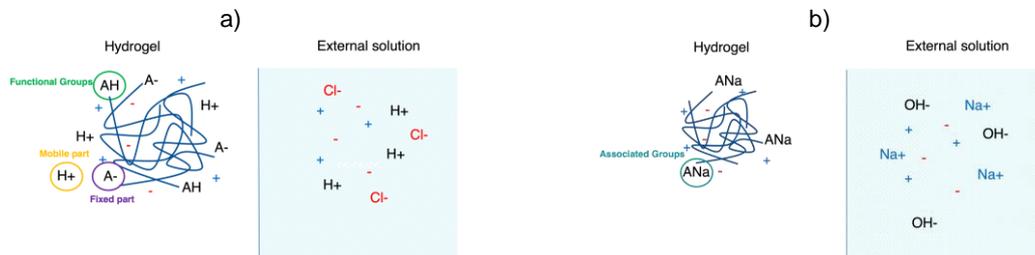


Figure 2 Schematic view of the hydrogel and the external solution for acid condition a) and basic condition b) of the external bath

The model has been developed through a monophasic approach (described as a single phase in which different components can coexist), which relies on a strong thermodynamic basis that is the dissipation inequality according to which for dissipative processes, “not all conventional power expended on a convecting spatial

region can be converted into changes in the net free and kinetic energy because a portion of that power must go into dissipation" (Gurtin et al., 2010) (the readers are directed to the Nomenclature section for definitions of the variables used):

$$\frac{dA}{dt} - \bar{P} : \dot{\bar{F}} - \sum_i \left(\mu_i \frac{dC_i}{dt} \right) + \sum_i (\bar{h}_i \cdot \bar{v} \mu_i) \leq 0 \quad (6)$$

Since the model describe the steady state behaviour, the first term of the equation vanishes. To calculate the constitutive equations is necessary to make explicit the Helmholtz free energy, in a similar way as it was done in (Caccavo & Lamberti, 2017), in this cases for the polyelectrolyte. In particular, the Helmholtz free energy for a polyelectrolyte can be seen a sum of four contributions: energy due to the deformation of the network, the free energy of mixing, energy of ionization and energy of dissociation and association of the charges.

$$A = A_{El} + A_{Mix} + A_{Ion} + A_{Diss/Ass} \quad (7)$$

The elastic contribution and the mixing contribution are written in according to the previous work, (Caccavo & Lamberti, 2017):

$$A_{El} = \frac{G}{2} [\bar{F} : \bar{F} - 3 - 2 \ln(\det \bar{F})] \quad (8)$$

$$A_{Mix} = RT \left[C_s \ln \left(\frac{C_s \Omega_s}{1 + C_s \Omega_s} \right) + \frac{\chi_{12} C_s}{1 + C_s \Omega_s} \right] \quad (9)$$

For polyelectrolyte hydrogel charge of ions causes ionic interactions that are ionization and polarization (the polarization rises only for dielectric material). Ionization phenomenon leads to a change in free energy, in term of entropy mixing, namely (Hong et al., 2010; Liu et al., 2015; Marcombe et al., 2010):

$$A_{ion} = RT \sum_{r \neq s} C_r \left[\log \left(\frac{C_r}{(1 + \Omega_s C_s) C_{rif}^r} \right) - 1 \right] \quad (10)$$

This equation must be written for all the species in the system, where C_{rif}^r is the reference concentrations of all the species in solution:

$$A_{ion} = RT \left\{ C^{H^+} \left[\log \left(\frac{C^{H^+}}{(1 + \Omega_s C_s) C_{rif}^{H^+}} \right) - 1 \right] + C^+ \left[\log \left(\frac{C^+}{(1 + \Omega_s C_s) C_{rif}^+} \right) - 1 \right] + C^- \left[\log \left(\frac{C^-}{(1 + \Omega_s C_s) C_{rif}^-} \right) - 1 \right] + C^{OH^-} \left[\log \left(\frac{C^{OH^-}}{(1 + \Omega_s C_s) C_{rif}^{OH^-}} \right) - 1 \right] \right\} \quad (11)$$

The contribution of the dissociation and the association of the acidic groups to the equation of the Helmholtz Free Energy is the following (Hong et al., 2010; Marcombe et al., 2010):

$$A_{Dis/Ass} = RT \left[C^{A^-} \log \left(\frac{C^{A^-}}{C^{A^-} + C^{Ass}} \right) + C^{Ass} \log \left(\frac{C^{Ass}}{C^{A^-} + C^{Ass}} \right) \right] + \gamma C^{A^-} \quad (12)$$

This equation is formed by a term representing the entropy of dissociation and a term that represent the enthalpy of dissociation. The term γ represents the enthalpy when a functional group on the chain is dissociated or associated. The total Helmholtz energy is the sum of these four contributions:

$$A_{TOT}(\bar{F}, C_s, C^{H^+}, C^+, C^-, C^{OH^-}) = A_{el}(\bar{F}) + A_{Mix}(C_s) + A_{Ion}(C^{H^+}, C^+, C^-, C^{OH^-}) + A_{Diss/Ass}(C^{H^+}, C^+, C^-, C^{OH^-}) \quad (13)$$

To relate the system deformation to the solvent concentration and vice-versa, a volumetric constraint with a Lagrange multiplier approach is used obtaining a "relaxed" version of the free energy density (Caccavo & Lamberti, 2017; Hong et al., 2008; Lucantonio et al., 2013):

$$A_R(\bar{F}, C_s, C^{H^+}, C^+, C^-, C^{OH^-}, p) = A_{TOT}(\bar{F}, C_s, C^{H^+}, C^+, C^-, C^{OH^-}) - p[J - (1 - \Omega_s C_s)] \quad (14)$$

The last term of the equation 3.3 is the volumetric constraint:

$$J - (1 + \Omega_s C_s) = 0 \quad (15)$$

The variables which describe the system are the following: $\lambda, p, C_s, C^{H^+}, C^{OH^-}, C^+, C^-, C^{A^-}, C^{Ass}$. The electroneutrality condition and the global balance of the functional groups on the system could be used to reduce the number of variables:

Electroneutrality:

$$C^{A^-} = C^+ - C^- + C^{H^+} + C^{OH^-} \quad (16)$$

Global balance of the functional groups:

$$C^{Ass} = C^{AH} + C^{ANa} = f/\Omega_m - C^{A^-} \quad (17)$$

At this point the field variables are: $\lambda, p, C_s, C^{H^+}, C^{OH^-}, C^+, C^-$. Once known the expression for the Helmholtz Free Energy and the variables, the constitutive equations can be obtained differentiating the relaxed version of the Helmholtz Free Energy to the respect of the variables:

$$\left\{ \begin{array}{l} \bar{p} = \frac{dA_R}{d\bar{F}} \\ \mu_s = \frac{dA_R}{dC_s} \\ \mu_- = \frac{dA_R}{dC^-} \\ \mu_+ = \frac{dA_R}{dC^+} \\ \mu_{H^+} = \frac{dA_R}{dC^{H^+}} \\ \mu_{OH^-} = \frac{dA_R}{dC^{OH^-}} \end{array} \right. \quad (18)$$

The system is formed by seven variables so seven equations are needed. Concentrations are calculated considering the thermodynamic criterion for the phase equilibrium:

$$(\mu_i)_{ext} = (\mu_i)_{int} \quad (19)$$

And $(\mu_i)_{ext}$ has the following expression and has to be written for all the species in solution:

$$(\mu_i)_{ext} = RT \log \left(\frac{c_{ext}^i}{c_{i,ref}^i} \right) \quad (20)$$

The stress and the pressure are calculated using the volumetric constraint and the linear momentum balance. In particular, the stretch is obtained considering a simple experiment that can be performed soaking the system of a dry polymeric network in water (a free swelling simulation). The dry network swells with isotropic stretches $\lambda_x = \lambda_y = \lambda_z$, that can be denoted as λ . The state of free swelling is characterized by the homogeneous deformation gradient:

$$\bar{F} = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & \lambda & 0 \\ 0 & 0 & \lambda \end{bmatrix} \quad (21)$$

In such situation, the first Piola–Kirchhoff stress tensor, obtained by solving the first equation of (18) is:

$$\bar{P} = \bar{I} \left(G \left(\lambda - \frac{1}{\lambda} \right) - p\lambda^2 \right) \quad (22)$$

The steady state in a free swelling experiment is a “stress free” state, where $\bar{P} = \bar{0}$. To obey to this condition, the following equation must hold:

$$G \left(\lambda - \frac{1}{\lambda} \right) - p\lambda^2 = 0 \quad (23)$$

In Table 1 are summarized the field variables and the equations used to fully characterize the anionic hydrogel behaviour subjected to a free swelling/deswelling test. A system of seven equations is formed, solving these equations gives the initial conditions of the various species in solution. The equation system is solved numerically through MATLAB.

Table 1 Field variables and equations used in the model

Field Variables	Equation
λ	$G \left(\lambda - \frac{1}{\lambda} \right) - p\lambda^2 = 0$ (24)
p	$J - (1 + \Omega_S C_S) = 0$ (15)
C_S	$(\mu_S)_{int} - (\mu_S)_{ext} = 0$ (25)
C^{H^+}	$(\mu_{H^+})_{int} - (\mu_{H^+})_{ext} = 0$ (26)
C^+	$(\mu_+)_{int} - (\mu_+)_{ext} = 0$ (27)
C^-	$(\mu_-)_{int} - (\mu_-)_{ext} = 0$ (28)
C^{OH^-}	$(\mu_{OH^-})_{int} - (\mu_{OH^-})_{ext} = 0$ (29)

4. Results and discussion

The experimental results are presented in Figure 3 along with the modeling results. It should be noted that the experimental definition of S_R is consistent with the volumetric deformation J as modeled. At very low pH the concentration of protons in solution is high and the functional groups on the chain do not need to dissociate to maintain the global electroneutrality, from the graph for these values of pH it can be observed a fully associated limit. The gel starts to swell when the pH is equal to the pKa (in this case at pH equal to 4 for the polyacrylic acid). Increasing the pH, the concentration of protons starts to decrease, and the functional groups starts to dissociate according to the equation (2). This behaviour takes place until pH 7 when all the functional groups on the chain are dissociate reaching a fully dissociated limit. The swelling reaches its maximum value also due to electrostatic repulsion between chain. At this point sodium hydroxide is added to the bath, the reaction of association described in the equation (4) takes place and this leads the hydrogel to shrink reaching the association limit at higher value of pH. As it can be seen from the Figure 3 the model is able to describe qualitatively the general behaviour of the polyelectrolyte hydrogel. The swelling curve has the same important focal point of the experimental part: the associated limit both for lower than for higher pH and a fully dissociated limit at pH equal to 7. The parameters used in the simulation are reported in Table 2.

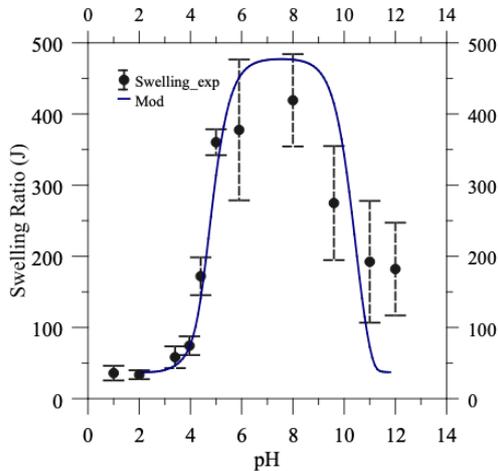


Figure 3 Steady state behaviour of a polyacrylic acid gel. Experimental S_R (black dots) and modelling volumetric deformation J (straight line) versus different values of pH.

Table 2 Parameters which describe the global behaviour of the hydrogel

Parameters	Value
c_{salt}	0.001M
pKa	4
χ_{12}	0.4
f	10%
G	40kPa
pKNa	2.5

5. Conclusions

Polyelectrolytes are polymeric material whose behavior changes due to different external condition of pH. Starting from a monophasic model that was used to describe neutral hydrogel, in this work was modeled the steady state behavior of polyelectrolyte hydrogel using the thermodynamic equilibrium between different phases. The swelling of the anionic hydrogel increases as the pH increases and this can be explained considering the movement of the solvent and the ions in solution coupled with the concentration of the H⁺ ions. The proposed model is able to describe the behavior of the hydrogel, and it could be considered an important instrument to understand the behavior of this kind of polymer. Furthermore a series of experimental results have been obtained and a comparison with modeling data has been done, obtaining a good result. This leads to the conclusion of realistic result generated from the model. In order to be more complete in the description of the behavior and with the aim to be predictable a transient model is going to be studied.

Nomenclature

S_R – Swelling Ratio, -	C_{rif}^r – reference concentrations, mol/m ³
M – Swollen mass, g	γ – Enthalpy, J/mol
M_0 – Initial mass, g	p – Pressure, Pa
M_D – Mass of the Dry Polymer, g	J – Volumetric deformation, -
A – Helmholtz Free Energy Density, J/m ³	λ – Stretch ratio, -
\bar{P} – First Piola Tensor, Pa	f – percentage of ionizable groups, -
\bar{F} – Deformation Gradient Tensor, -	K_a – Acidic Dissociation constant, mol/m ³
μ_i – Chemical potential of the i^{th} species, J/mol	K_{Na} – Association Constant, mol/m ³
C_i – Molar concentration of the i^{th} species, mol/m ³	
\bar{h}_i – Molar flux of the i^{th} species, mol/(s m ²)	
G – Elastic modulus, Pa	
R – Gas constant, J/ (mol K)	
T – Temperature, K	
χ_{12} – Flory-Huggins Interaction Parameter, -	
Ω_i – Molar volume, m ³ /mol	

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