

The Effects of the pH Value of the Swelling Medium on the Kinetics of the Swelling of a Poly(acrylic acid) Hydrogel

Jelena Jovanovic,¹ Borivoj Adnadjevic,¹ Aleksandar Kostic²

¹Faculty of Physical Chemistry, University of Belgrade, Studentski trg 16, 11000 Belgrade, Serbia

²Faculty of Agriculture, University of Belgrade, Nemanjina 6, 11080 Zemun, Belgrade, Serbia

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ABSTRACT: The isothermal kinetics curves of the swelling of a poly(acrylic acid) hydrogel in buffer solutions of different pH values (5, 7, and 9) at temperatures ranging from 30 to 40°C were determined. The possibilities of applying the Fick kinetics model and the Peppas equation were examined. It was found that the applicability of these models were limited. The kinetics model of a first-order chemical reaction was found to describe the swelling kinetics of the PAA hydrogel in all the investigated buffer solution at all the investigated temperatures. Swelling kinetics is deter-

mined by the rate of expansion of the network. The kinetic parameters (E_a , $\ln A$) of the swelling of the PAA hydrogel in buffer solutions of different pH values were determined. The activation energy and the pre-exponential factor of the swelling of the PAA hydrogel in buffer medium decreased with increasing pH value of the swelling medium. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1036–1043, 2010

Key words: kinetics; hydrogel; swelling; stimuli-sensitive polymer

INTRODUCTION

Hydrogels are an important class of materials which presents networks of hydrophilic polymers capable of absorbing significant amounts of water and biological liquids without dissolving or losing their structural integrity. Hydrogels have promising prospective as smart materials that show structural and physical changes to external signals. Environment stimuli factors include temperature, pH, electric field, light, and ion or certain chemical species.^{1,2} The application of hydrogels could be affected significantly by their swelling properties. The swelling kinetics and equilibrium degree of swelling are influenced by many factors, such as, the type of monomers, pH, ionic strength, network structure, hydrophilicity, degree of ionization of functional groups, crosslinking ratio, etc. The equilibrium degree of swelling is also a function of the properties of the swelling medium, including the pH and ionic strength.³ Ionizable, “environmentally sensitive” hydrogel networks are especially attractive because their properties can be controlled not only

by changing their molecular structure but also by adjusting the external conditions.³ Stimuli responsive hydrogels, especially those sensitive to temperature and pH, have received much attention because these factors are variables that change in typical physiological, biological, and chemical systems.⁴

Hydrogels of acrylic polymers and their copolymers were reported as having adjustable swelling kinetics that display special properties⁵ and the presence of polyacrylic segments in hydrogels significantly increases their water-uptake ability too.⁶ It is predictable that, due to the presence of carboxylic acid side groups, the swelling behavior of poly(acrylic acid) (PAA) hydrogel will be highly dependent on the pH of the surrounding medium.³ The swelling behavior of copolymeric acrylic hydrogels also depends on the pH value of the solution.^{7,8} PAA hydrogels swell significantly in a medium with a pH higher than 5 but they do not swell significantly in an environment with a pH below 4, which is the pH of the stomach. This enables one of the major applications of acrylic acid gels, that is, in sustained gastrointestinal drug delivery systems.^{3,9} A change in pH from 3 to 6 caused the ionization of hydrogels and an increase of the swelling degree of PAA-PVA IPNs.³

In the field of hydrogels, research on the kinetics of swelling is important and numerous papers have been published on this topic dealing with the swelling kinetics of various types of hydrogels. The kinetics of swelling of hydrogels are most frequently

Correspondence to: J. Jovanovic (jelenaj@ffh.bg.ac.rs or jelenajov2000@yahoo.com).

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formally described as first-order chemical reaction or as a diffusion controlled process.

The swelling behavior of PAA hydrogels in buffered media of pH 4 and pH 7 revealed that the swelling mechanism was dependent on the pH of the swelling medium. Based on the results of Jabbar et al., all possible mechanisms of transport of the solution into the gel were observed: Fickian diffusion, a combination of Fickian and anomalous diffusion, anomalous diffusion and diffusion between anomalous diffusion and Case II diffusion.¹⁰

Concerning the influence of temperature on swelling behavior, the swelling ratio of PAA gels increased with temperature, suggesting a UCST behavior.^{11,12} Positive swelling changes with temperature were observed in IPNs of PAA/PVA and PAA hydrogels during swelling at pH 7.⁴

In previous investigations, positive swelling changes of a PAA hydrogel with temperature were found within the temperature range from 20 to 45°C for swelling both in distilled water and physiological solution.^{13,14} In addition, an earlier investigation of PAA hydrogel swelling in buffer medium in the pH range from 4 to 10, at ambient temperature, reveal that the equilibrium degree of swelling and the initial swelling rate increased with the increasing pH value until pH 9. The maximum degree of swelling was achieved in buffer medium with pH = 9.¹⁵

Despite their both great fundamental and practical importance, to the best of our knowledge, there is not sufficient data concerning the systematic investigation of the kinetics of hydrogel swelling at different pH values at different temperatures.

In this work, the kinetics of isothermal swelling of a PAA hydrogel in buffer media with pH values 5, 7, and 9 were investigated in the temperature range from 30 to 40°C. The aim of this investigation was to compare the swelling kinetics of a PAA hydrogel at different pH values and to determine the kinetic parameters (activation energy and pre-exponential factor) for investigated swelling processes.

EXPERIMENTAL

Materials

Acrylic acid (99.5%) (AA) was supplied by Merck KGaA, Darmstadt, Germany. The free-radical polymerization initiator, 2,2'-azobis-[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) (99.8%) was supplied from Wako Pure Chemical Industries, Osaka, Japan. The crosslinker *N,N'*-methylene bisacrylamide (p.a) (MBA) was purchased from Aldrich Chemical Co., Milwaukee, USA. Sodium carbonate (Na₂CO₃) (p.a) and *n*-hexane (p.a) were obtained from Merck KGaA, Darmstadt, Germany. Buffer solutions were supplied by Zorka-Pharma, Šabac, Ser-

bia. The buffers of pH = 5 and 7 were potassium dihydrogenphosphate-disodium hydrogenphosphate and the buffer of pH = 9 was borax-hydrochloric acid solution.

Synthesis

The PAA hydrogel was synthesized using a one-pot process based on the radical polymerization of AA and crosslinking of the formed PAA in aqueous media using the following procedure.

A 20 wt % solution of AA was prepared and mixed with a 0.1 wt % solution of MBA. After stirring well to ensure homogeneity of the reaction mixture and nitrogen bubbling throughout the mixture for half an hour, the initiator solution (0.05 wt % of the monomer) was added and the reaction mixture was once again rapidly stirred and bubbled with nitrogen for a further 20 min. Immediately, the prepared reaction mixture was poured into glass molds (plates separated by a rubber gasket 2 mm thick) and placed in an oven at 80°C for 5 h. Then, the obtained gel-type product was transformed into the Na⁺ form (60%) by neutralization with a 3% solution of Na₂CO₃. The resulting hydrogel was stamped into approximately equally sized disks and immersed in excess distilled water. The water was changed every 2–3 h, except overnight, for 7 days to remove the sol fraction of polymer and unreacted monomer. Subsequently, the washed-out hydrogel was dried in an air oven in the temperature regime 80°C for 2 h, 90°C for 3 h, and finally at 105°C until constant mass was attained. The obtained product (xerogel) was stored in a vacuum exicator until use.

Structural characterization of the synthesized xerogel

The following structural properties of the synthesized PAA xerogel were determined and calculated: xerogel density (ρ_{xg}), average molar mass between the network crosslinks (M_c), degree of crosslinking (ρ_c), and the distance between the macromolecular chains (ξ).

The xerogel density of the synthesized sample was determined by the picnometer method, using the equation:

$$\rho_{xg} = \frac{m_{xg}\rho_T}{m_1 + m_{xg} - m_2} \quad (1)$$

where, m_{xg} is the weight of the xerogel sample, m_1 is the weight of the picnometer filled with toluene, used as the nonsolvent, m_2 is the weight of picnometer filled with toluene with the xerogel sample in it, and ρ_T is the density of toluene ($\rho_T = 0.87 \text{ g/cm}^3$).

The value of the M_c was determined by eq. (2), proposed by Flory and Rehner¹⁶:

$$M_c = \frac{-\rho_{xg} V_{H_2O} v_{2,s}^{1/3}}{\ln(1 - v_{2,s}) + v_{2,s} + \chi v_{2,s}^2} \quad (2)$$

where V_{H_2O} is the molar volume of H_2O , $v_{2,s}$ is the polymer volume fraction in the equilibrium swollen state and χ is the Flory-Huggins interaction parameter between a solvent (H_2O) and a polymer (PAA). The values of $v_{2,s}$ and χ were calculated using the following expressions:

$$v_{2,s} = \frac{1}{1 + \rho_{xg} SD_{eq}} \quad (3)$$

$$\chi = \frac{\ln(1 - v_{2,s}) + v_{2,s}}{v_{2,s}^2} \quad (4)$$

The degree of crosslinking was calculated as¹⁷:

$$\rho_c = \frac{M_0}{M_c} \quad (5)$$

where M_0 is the molar mass of the repeating unit.

The distance between the macromolecular chains was calculated as:

$$\xi = l v_{2,s}^{-1/3} \left(2C_n \frac{M_c}{M_0} \right)^{1/2} \quad (6)$$

where C_n is the Flory characteristic ratio ($C_n(AA) = 6.7$ and l is the carbon-carbon bond length (1.54 Å)).¹⁸

Swelling experiments

Dry hydrogel (xerogel) disks with an average weight of 0.10 g ($\pm 10\%$) were left to swell in a buffer solution (pH = 5, 7, or 9) at the temperatures 30, 35, or 40°C ($\pm 0.2^\circ\text{C}$). At the beginning of each experiment, the xerogel disks were weighed (m_0) and then entirely immersed in excess buffer solution. At pre-determined time intervals, the swollen hydrogels samples were taken out from the solution, wiped to remove excess surface solution, and weighed (m_t). This was done until the hydrogels attained constant mass, that is, until equilibrium was reached. The measurements were performed using the grid boat technique.

For each pH value and temperature, swelling measurements of at least three samples were performed and the mean values were used.

Determination of the swelling degree and the normalized swelling degree

The isothermal swelling degree (SD, %), defined as the difference between the weight of the swollen hydrogel sample at time t (m_t) and the weight of the

xerogel (dry hydrogel) (m_0) divided by the weight of the xerogel sample (m_0), was determined as a function of time at constant temperature and calculated using the equation:

$$SD = \frac{m_t - m_0}{m_0} \times 100 \quad (7)$$

The equilibrium swelling degree (SD_{eq}) is the swelling degree of the hydrogel at equilibrium, that is, when the hydrogel sample attained constant mass (m_{eq}).

The normalized swelling degree (α), defined as the ratio between the swelling degree at time (t) and the equilibrium swelling degree for certain temperature and pH values, was calculated as:

$$\alpha = \frac{SD}{SD_{eq}} \quad (8)$$

METHODS USED TO EVALUATE THE PARAMETERS OF THE SWELLING KINETICS

The Fick law of diffusion

When the kinetics of swelling is determined by the rate of penetration of molecules of the swelling medium, then the swelling is governed by the Fick law of diffusion according to eq. (9) and the swelling degree of the hydrogel is proportional to the square root of time^{19,20}:

$$SD = k\sqrt{t} \quad (9)$$

where the coefficient k is the diffusion constant and t is the swelling time.

Semi-empirical equation

The swelling kinetics of the PAA hydrogel was investigated by applying the well-known semi-empirical Peppas equation²¹:

$$\alpha = kt^n \quad (10)$$

where α is the normalized swelling degree, n is the swelling exponent which describes the mode of the transport mechanism of the penetrant, k is a constant of the hydrogel, and t is the swelling time. The parameters k and n were determined from the slopes and the intercepts of the straight lines of the plots $\ln \alpha$ versus $\ln t$.

Model-fitting method

According to the model-fitting method, the kinetic reaction models are classified into five groups depending on the reaction mechanism: (1) power law reaction, (2) phase controlled reaction, (3) reaction order, (4) reaction described by the Avrami equation, and (5) diffusion controlled reactions.²²

TABLE I
The Set of Kinetics Models Used to Determine the Kinetics Model of the Swelling of the PAA Hydrogel

Model	Reaction mechanism	General expression of the kinetics model $f(\alpha)$	Integral form of the kinetics model $g(\alpha)$
P1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
P2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
P3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
P4	Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
R1	Zero-order (Polany-Winger equation)	1	α
R2	Phase-boundary controlled reaction (contracting area, i.e., bidimensional shape)	$2(1 - \alpha)^{1/2}$	$[1 - (1 - \alpha)^{1/2}]$
R3	Phase-boundary controlled reaction (contracting volume, i.e., tridimensional shape)	$3(1 - \alpha)^{2/3}$	$[1 - (1 - \alpha)^{1/3}]$
F1	First-order (Mampel)	$(1 - \alpha)$	$-\ln(1 - \alpha)$
F2	Second-order	$(1 - \alpha)^2$	$(1 - \alpha)^{-1} - 1$
F3	Third-order	$(1 - \alpha)^3$	$0.5[(1 - \alpha)^{-2} - 1]$
A2	Avrami-Erofe'ev	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	$[- \ln(1 - \alpha)]^{1/2}$
A3	Avrami-Erofe'ev	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	$[- \ln(1 - \alpha)]^{1/3}$
A4	Avrami-Erofe'ev	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	$[- \ln(1 - \alpha)]^{1/4}$
D1	One-dimensional diffusion	$1/2\alpha$	α^2
D2	Two-dimensional diffusion (bidimensional particle shape)	$1/[- \ln(1 - \alpha)]$	$(1 - \alpha)\ln(1 - \alpha) + \alpha$
D3	Three-dimensional diffusion (tridimensional particle shape) Jander equation	$3(1 - \alpha)^{2/3}/2[1 - (1 - \alpha)^{1/3}]$	$[1 - (1 - \alpha)^{1/3}]^2$
D4	Three-dimensional diffusion (tridimensional particle shape) Ginstling-Brounshtein	$3/2[(1 - \alpha)^{-1/3} - 1]$	$(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$

The model-fitting method is based on the following. The experimentally determined conversion curve $\alpha_{\text{exp}} = f(t)_T$ has to be transformed into the so-called universal conversion curve $\alpha_{\text{exp}} = f(t_N)_T$, where t_N is the so-called normalized time. The normalized time, t_N , was introduced to normalize the time interval of the monitored process and was defined by the equation as follows:

$$t_N = \frac{t}{t_{0.9}} \quad (11)$$

where $t_{0.9}$ is the moment in time at which $\alpha = 0.9$. By applying the normalized time, it was possible to calculate the universal conversion curves for the different kinetics models.²³ The kinetics model of the investigated process was determined by comparing (graphically and analytically, using the sum of squares of the residuals) the experimentally determined curves with the theoretical curves. The chosen kinetics model is the one for which the sum of the squares of the residuals was minimal.

The set of the reaction kinetics models used to determine the model which best describes the kinetics of the MEPBA release process is shown in Table I.^{22,23}

RESULTS AND DISCUSSION

The basic structural properties of the PAA xerogel which was used in this investigation are presented in Table II.

Based on the obtained results for the determined basic structural properties, it may be concluded that the PAA xerogel used in this investigation was a medium crosslinked network ($\rho_c = 1.60 \times 10^{-4}$ mol/cm³) with a macroporous structure with pores of average diameter $\xi = 28.4$ nm.

The isothermal swelling kinetic curves of the PAA hydrogel in swelling media with different pH values at different temperatures are presented in Figure 1(A-C).

The results, as depicted in Figure 1, clearly revealed that the isothermal swelling kinetic curves were similar in shape for all the investigated temperatures for each of the pH values. Three characteristic regions of the changes of the swelling degree with swelling time can be distinguished in all of the swelling curves, a linear, nonlinear, and the saturation part or plateau. Increasing the temperature resulted in an increase of the slope of the linear part of the dependence of the swelling degree versus time and the equilibrium swelling degree for each pH value. The values of the equilibrium swelling degrees are presented in Table III.

TABLE II
The Basic Structural Properties of the Studied PAA Xerogel

ρ_{xg} (kg/m ³)	M_c (g/mol)	ρ_c ($\times 10^4$ mol/cm ³)	ξ (nm)
1140	7120	1.60	28.4

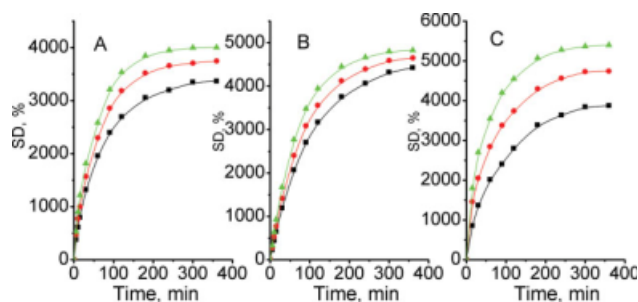


Figure 1 The swelling isotherms of the PAA hydrogel at different temperatures: (■) 30°C, (●) 35°C, (▲) 40°C; (A) pH = 5; (B) pH = 7; (C) pH = 9. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

To establish the kinetics model of the swelling process at different pH values, first the possibility of describing the swelling kinetics by the most common theoretical models, that is, the Fick law of diffusion and the well-known semi-empirical Peppas equation, was examined.

When the kinetics of swelling is determined by the rate of penetration of molecules of the swelling medium, then the swelling is governed by the Fick law of diffusion and the SD of a hydrogel obeying this law is proportional to the square root of time, that is, $SD = k\sqrt{t}$.

The plots of the SD as a function of \sqrt{t} for different temperatures at different pH values (5, 7, and 9) of the swelling medium are shown in Figure 2.

The plots of the SD as a function of \sqrt{t} significantly deviated from straight lines for all the investigated pH values of swelling medium and all the examined temperatures. These results may imply that the so-called Fickian type of solvent diffusion into the hydrogel had neither a dominant influence on the kinetics of the swelling of the hydrogel nor on the changes of the swelling kinetics with temperature for each of the investigated pH values within the investigated range of temperatures and pH values. For these reasons, it appears that the Fick law of diffusion is not suitable for describing the investigated swelling kinetics of the PAA hydrogel in buffered solutions.

In the case when the swelling kinetics of a hydrogel at different pH values can be described by the

TABLE III
The SD_{eq} for the PAA Hydrogel Swelling at Different pH Values and Temperatures

T (°C)	SD_{eq} (%)		
	pH 5	pH 7	pH 9
30	3370 ± 5	4420 ± 5	3870 ± 5
35	3750 ± 5	4650 ± 5	4740 ± 5
40	4000 ± 5	4830 ± 5	5420 ± 5

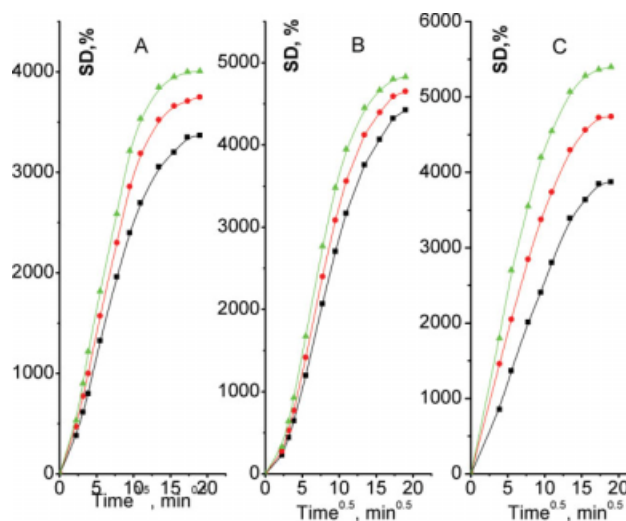


Figure 2 The plots of the SD versus \sqrt{t} for the swelling of the PAA hydrogel at different temperatures: (■) 30°C, (●) 35°C, (▲) 40°C; (A) pH = 5; (B) pH = 7; (C) pH = 9. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

semi-empirical Peppas equation, a plot of $\ln \alpha$ versus $\ln t$ would be linear. Plots of $\ln \alpha$ versus $\ln t$ for the swelling of the investigated PAA hydrogel at different temperatures in buffer solutions with different pH values are shown in Figure 3.

Based on the results presented in Figure 3, the plots of $\ln \alpha$ versus $\ln t$ gave straight lines in certain ranges of the swelling process, the so-called "range of applicability" (ΔL). Thus, it was possible to model the kinetic of swelling of the PAA hydrogel within the "range of applicability" with the aforementioned equation [eq. (11)] and to determine the values of the swelling kinetic parameters, n and k , from the slopes and the intercepts of these straight

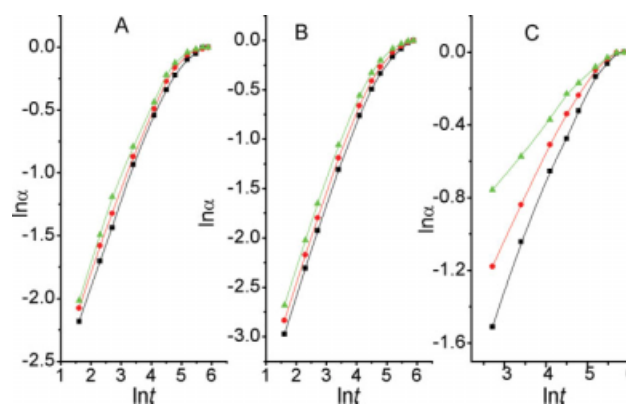


Figure 3 The plots of $\ln \alpha$ versus $\ln t$ for the swelling of the PAA hydrogel at different temperatures: (■) 30°C, (●) 35°C, (▲) 40°C; (A) pH = 5; (B) pH = 7; (C) pH = 9. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
The Peppas Swelling Kinetic Parameters and the “Range of Applicability” for the Swelling of the PAA Hydrogel in Buffer Solutions at Different pH Values and Temperatures ($R =$ Correlation Coefficient)

	T (°C)	k (min ⁻¹)	n	R	ΔL (%)
pH = 5	30	0.039 ± 0.05	0.67	0.9978	58
	35	0.046 ± 0.05	0.64	0.9966	61
	40	0.051 ± 0.05	0.63	0.9887	44
pH = 7	30	0.013 ± 0.05	0.89	0.9977	46
	35	0.015 ± 0.05	0.87	0.9970	51
	40	0.018 ± 0.05	0.85	0.9958	57
pH = 9	30	0.047 ± 0.05	0.56	0.9978	72
	35	0.090 ± 0.05	0.46	0.9966	78
	40	0.213 ± 0.05	0.39	0.9887	84

lines. The calculated values of the swelling kinetic parameters and the “range of applicability” for these parameters are given in Table IV.

It should be emphasized that the constant k for the hydrogel increased with increasing swelling temperature, for each of the pH values. The value of the Peppas’ swelling exponent was $n = 0.65$ for swelling at pH = 5 and $n = 0.87$ for swelling at pH = 7. These values were independent of the swelling temperature. In contrast, the swelling exponent n significantly decreased with increasing temperature for swelling at pH = 9.

As previously described by Alfrey and coworkers, there are three possible models which describe the penetration of a swelling medium into a polymer network. The first one is the so-called Fick diffusion model. This model is typical for systems in which the rate of solvent diffusion is lower than the rate of relaxation the chains of an elastic network. Characteristic for this model is that $n = 0.5$. In the case when the rate of solvent diffusion is equal to the rate of the relaxation the chains of an elastic network, the solvent penetration follows the so-called non-Fickian diffusion and the values of n are $0.5 < n < 1$. When the rate of solvent diffusion is higher than the rate of the relaxation the chains of an elastic network, the solvent penetration follows the so-called second diffusion law and is controlled by the relaxation of the chains of an elastic network. In this case, the value of n value is equal to or higher than 1 ($n \geq 1$).²⁴

Bearing this in mind, within the range of applicability of the Peppas equation, the established values of the swelling exponent imply that increasing the pH value led to changes in the mechanism of the swelling kinetics. The swelling kinetics at pH = 5 and 7 followed the so-called non-Fickian diffusion and with increasing pH value, the rate of the network expansion became dominant over the diffusion process. On the contrary, however, the results for swelling at pH = 9 revealed that the main process was the diffusion of the swelling medium.

To establish the model describing the kinetics of PAA hydrogel swelling in buffer media of varying pH, the “model-fitting” method was applied. For this reason, the experimentally determined swelling kinetics curves ($SD = f(t)$, i.e., $\alpha = f(t)$) were transformed into the so-called “universal conversion curve” $\alpha = f(t_N)$, which were then compared with the theoretical curves. All of the obtained curves were of the same shape. Based on the results obtained, by using the set of the kinetics models presented in Table I, it can be stated with great certainty that isothermal kinetics of PAA hydrogel swelling in buffer solution can be described by the so-called first-order chemical reaction rate model.

Considering the kinetics of a first-order reaction rate, the rate of swelling at any given time is directly proportional to the available swelling capacity before reaching the equilibrium swelling degree, SD_{eq} . The remaining swelling capacity is defined as $SD_{eq} - SD$, where SD is the swelling degree at a certain time. As the normalized swelling degree (α) is defined as the ratio between the swelling degrees at a certain time, the following expression is valid:

$$\frac{d\alpha}{dt} = k_M(SD_{eq} - SD), \quad (12)$$

which gives the following:

$$\ln\left(\frac{SD_{eq}}{SD_{eq} - SD}\right) = k_M t \quad (13)$$

$$\ln(1 - \alpha) = -k_M t. \quad (14)$$

This means that the following expression should be valid:

$$-\ln(1 - \alpha) = -k_M t \quad (15)$$

where k_M is the model constant.

The plots of $[-\ln(1 - \alpha)]$ versus time for the swelling of the PAA hydrogel at pH = 5, 7, and 9, at different temperatures, are shown in Figure 4.

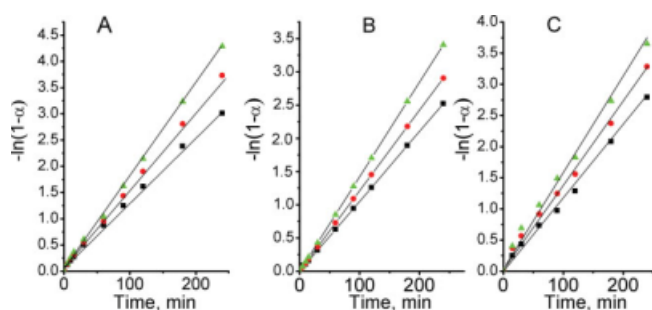


Figure 4 Plot of $\ln t$ versus $-\ln(1 - \alpha)$ for the swelling of the PAA hydrogel at different temperatures: (■) 30°C, (●) 35°C, (▲) 40°C; (A) pH = 5; (B) pH = 7; (C) pH = 9. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Bearing in mind the previously defined term “range of applicability” (L), as the range within which the experimental results are similar to those predicted by the theoretical model, the results presented in Figure 4 show that at all of the investigated pH values and temperatures, the dependences $-\ln(1 - \alpha)$ on time give straight lines over a very wide range of the swelling process ($\Delta L = 92\text{--}99\%$). The values of the rate constant k_M were determined from the slopes at these lines. The rate constant k_M for the predicted theoretical model of PAA hydrogel swelling in buffer media are given in Table V.

From the results presented in Table V, it can be observed that the rate constant exponentially increases with increasing temperature for each pH value. As the values of k_M increase exponentially with temperature, it was possible to determine the kinetics parameters: E_a and $\ln A$ for the applied model using the Arrhenius equation. As presented in Table VI, both the activation energy and the pre-exponential factor decrease with increasing pH of the swelling medium.

The established model of the kinetics, which is independent of the swelling degree, pH temperature and the calculated kinetic parameters E_a and $\ln A$, clearly revealed that the swelling kinetics is determined by the expansion of the polymer chains of the network.²⁵

The established decrease in the activation energy with increasing pH of swelling medium can be explained by the change in the ratio between the nonionized (COOH) and ionized (COO⁻) functional groups of the hydrogel. The increase in pH value of swelling medium leads to the increase in the degree of ionization of the functional -COOH groups of the hydrogel and to an increase in the ratio of these ionized groups. This, in turn, favored electrostatic repulsion between the ionized groups, which leads to an expansion of the polymer chains of the network and to an increase in the swelling degree and to a decrease in the activation energy.

TABLE V
The Model Constants and Their “Range of Applicability” for the Swelling of the PAA Hydrogel in Buffer Media at Different pH Values and Temperatures (R = Correlation Coefficient)

	T (°C)	k (min ⁻¹)	R	L (%)
pH = 5	30	0.0130	0.9978	95
	35	0.0157	0.9966	97.6
	40	0.0179	0.9887	98.6
pH = 7	30	0.0105	0.9998	92
	35	0.0121	0.9998	95
	40	0.0142	0.9998	98
pH = 9	30	0.0115	0.9978	95
	35	0.0136	0.9966	97.6
	40	0.0152	0.9887	98.6

TABLE VI
The Kinetic Parameters (E_a and $\ln A$) for the Swelling of the PAA Hydrogel in Buffer Media at Different pH Values

	pH = 5	pH = 7	pH = 9
E_a (kJ/mol)	25.24	23.8	20.9
$\ln A$ (min ⁻¹)	5.69	4.88	3.84

It was found that the observed decrease in the activation energy of the investigated swelling process with increasing pH is in a functional relation with the decrease in the pre-exponential factor, which means that a compensation effect exists which can be described by the expression:

$$\ln A = -4.90 + 0.416E_a \quad (16)$$

The appearance of the compensation effect with change in the pH of the swelling medium is, most probably, in connection with the so-called “screening effect” of the counter ions (K⁺) on the polyanion chain,²⁶ which leads to a decrease in the “active centers” per unit of network weight, which reflected in the decrease in $\ln A$. The presence of the compensation effect is reason for the maximal value of the swelling rate constant of the model at pH = 5 for all the investigated temperatures.

CONCLUSIONS

The swelling kinetics of PAA hydrogel in buffered solutions cannot be described by the Fick law of diffusion.

The semi-empirical Peppas equation can be applied over a limited range to describe the swelling kinetics in buffered solutions at pH = 5 and 7.

The isothermal kinetics of PAA hydrogel swelling at all of the investigated pH values is described by the first-order chemical reaction rate model, which means that it is controlled by the kinetics of the expansion of the network of polymer chains.

The decrease in the activation energy with increasing pH of the swelling medium is a consequence of the change in the ratio between the nonionized (COOH) and ionized (COO⁻) functional groups of the hydrogel.

The compensation effect and decrease in the $\ln A$ value are consequences of the screening effect of the counter ions.

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