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Comparison of the swelling kinetics of a partially neutralized poly(acrylic acid) hydrogel in distilled water and physiological solution

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Abstract: The isothermal kinetics curves of the swelling of a poly(acrylic acid) hydrogel in distilled water and physiological solution at temperatures ranging from 20 to 40 °C were determined. The possibility of applying both the Fick's kinetics model and kinetics model of the first order chemical reaction to the swelling kinetics of the PAA hydrogel in distilled water and physiological solution were examined. It was found that the possibilities of applying these models were limited. The new model of the kinetics of swelling in distilled water and physiological solution was established. The kinetic parameters (E_a , $\ln A$) for the swelling in distilled water and physiological solution were determined. The decrease of the equilibrium degree of swelling and the saturation swelling rate of the swelling of the PAA hydrogel in physiological solution compared to swelling in distilled water could be explained by the decreased differences in the ionic osmotic pressures between the hydrogel and the swelling medium. The increase of the initial swelling rate in the physiological solution might be caused by an increased density of charges at the network and by an increased affinity of the network towards the water molecules. The increase of the activation energy of the swelling of the PAA hydrogel in the physiological solution is a consequence of its additional "ionic crosslinking".

Keywords: swelling kinetics, kinetics parameters, model, poly(acrylic acid) hydrogel.

INTRODUCTION

Hydrogels are three-dimensional cross-linked polymeric structures which are able to swell in an aqueous environment. Due to their characteristic properties, such as swellability in water, hydrophilicity, biocompatibility, and lack of toxicity, hydrogels have been utilized in a wide range of biological, medical, pharmaceutical and environmental applications.^{1,2} In the biomedical field, hydrogels are

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used in diagnostics, therapeutics and implantable devices (catheters, biosensors, artificial skin, controlled release drug delivery systems and contact lenses). Environmental chemists are interested in utilizing these superabsorbent materials to purify waste water by removing heavy metal ions and organic pollutants.^{3,4}

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, cross-linking ratio, *etc.* The equilibrium degree of swelling is also a function of the properties of the swelling medium, including the pH and the ionic strength.⁵ 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 external conditions.⁵

Hydrogels of acrylic polymers and their copolymers have been reported as having adjustable swelling kinetics, which display special properties⁶ and that the presence of polyacrylic segments in the hydrogels significantly increases their ability to uptake water.⁷ It is predictable that, due to the presence of carboxylic acid side groups, the swelling behavior of a poly(acrylic acid) (PAA) hydrogel would be highly dependent on the pH of the surrounding medium.⁵ The swelling behavior of copolymeric acrylic hydrogels also depends on the pH value of the solution.^{8,9} It was shown that the swelling equilibria are primarily governed by an energy balance between the osmotic pressure within the polymer network and the elastic repulsive force of the network structure.⁸ It is known that PAA hydrogels swell significantly in a medium with a pH higher than 5 and that they do not swell significantly in an environment with pH below 4, which is the pH of the stomach. Thus one of the major applications of acrylic acid gels is in sustained gastro-intestinal drug delivery systems.^{5,10} A change in pH from 3–6 causes the ionization of the hydrogels and an increase of the degree of swelling.⁵

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 the swelling of hydrogels are most frequently formally described as first order chemical reaction or as a process controlled by diffusion.

The swelling behavior of hydrogels synthesized by γ -radiation cross-linking of poly(acrylic acid) was investigated by swelling the hydrogels in buffered media of pH 4 and 7. It was found that the swelling mechanism was dependent on the pH of the swelling medium and the concentration of PAA during irradiation. Based on the results of Jabbary *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.¹¹

Completely neutralized poly(acrylic acid) showed the highest degree of swelling in pure water compared to several salt solutions. In this case, free counter ions remain inside the gel to neutralize the fixed charges on the network chains. The driving force of the swelling process is the presence of mobile osmotically active counter ions. When salt is added to the system (1:1 salts; LiCl, NaCl, KCl and CsCl), ions diffuse from the solution into the network. The overall concentration of mobile ions in the gel is higher than before but the difference between ion concentrations inside and outside is reduced. Consequently, the driving force of swelling decreases gradually with increasing salt concentration.¹²

Bearing in mind the possible biomedical applications of PAA hydrogels, the kinetics of the isothermal swelling of a PAA hydrogel in bidistilled water and physiological solution in the temperature range of 20 to 40 °C were investigated. This investigation employed both usual and newly-established methods. The aim of this work was to compare the swelling kinetics of the PAA hydrogel in bidistilled water and a physiological solution and to determine the kinetic parameters (activation energy and pre-exponential factor) for the investigated swelling processes.

EXPERIMENTAL

Materials

Acrylic acid, in glacial form, was obtained from Merck, Darmstadt, Germany and was stored in a refrigerator before use. Sodium persulfate and sodium thiosulfate both p.a. purity, were also supplied by Merck and were used as a redox initiator pair with 30 % hydrogen peroxide, obtained from Zorka-Šabac, Serbia. *N,N'*-Methylenebisacrylamide (NMBA), purchased from Merck, Darmstadt, Germany, was used as the cross-linking agent. An activator, ethylenediaminetetraacetic acid (EDTA), p.a., was purchased from Merck, Darmstadt, Germany. Sodium carbonate (Na₂CO₃), p.a., Zorka-Šabac, Serbia, was used for neutralization. All chemicals were used as received. Bidistilled water was used in the polymerization and swelling experiments. Physiological solution was purchased from Hemofarm, Vršac, Serbia.

Synthesis of the partially neutralized poly(acrylic acid) hydrogel

The partially neutralized poly(acrylic acid) hydrogel used in this investigation was synthesized following a procedure based on the simultaneous radical polymerization of acrylic acid and cross-linking the formed poly(acrylic acid) according to the procedure described in a previous investigation,¹³ which is described below.

The hydrogel was synthesized under a nitrogen atmosphere in a polymerization reactor equipped with a magnetic stirrer, reflux condenser, nitrogen inlet and thermometer. The monomer solution was prepared from 80 ml of acrylic acid dissolved in 180 ml of distilled water and 0.8 g of NMBA and 0.08 g of EDTA, both dissolved in 60 ml of distilled water. This monomer solution was placed in the reactor, stirred and de-oxygenated with nitrogen gas bubbling through the solution for 60 min. Initiator stock solutions were: sodium persulfate and sodium thiosulfate (both 2.5 g dissolved in 22.5 ml bidistilled water) and hydrogen peroxide, 30 %. After completion of the de-oxygenation, the initiator solutions were added to the monomer solutions: 2.4 ml of sodium persulfate solution, 10 ml of hydrogen peroxide and 1.2 ml of sodium thiosulfate solution. Then, the reaction mixture was slightly warmed up to 50 °C until the temperature of the reaction mixture dramatically increased (gel point) and it was then left at 50 °C for a further 4 h. The obtained gel-type product was converted to the Na⁺ form (60 %) by neutralizing it with a 3 % solution of Na₂CO₃. Next, the

synthesized hydrogel was thoroughly washed with distilled water. The water was changed 7 times every 5 h or left over night and changed the following morning in order to remove the residual monomers and soluble fraction of the polymer. The hydrogel obtained in bulk was cut into small discs approximately the same size and then dried in an air oven in the temperature regime of 2 °C min⁻¹ up to 105 °C, to constant mass. The obtained product was stored in a vacuum desiccator before use.

Swelling experiments

To determine the swelling parameters, the samples of xerogels (with diameter of about 0.5 cm and thickness of 1 mm) of average weight of 0.1 g ($\pm 5\%$) were left to swell in distilled water and a physiological solution at temperatures ranging from 20 to 40 °C. At the beginning of each experiment, a piece of xerogel was weighed and immersed in an excess of the desired swelling medium to swell. At predetermined time intervals until a constant mass was attained, the swollen gel was removed from the swelling medium and weighed. Since the swollen gels appeared to be fragile, they were put on a grid boat with a mesh size of 1 mm. This technique allowed the polymer to be placed in water and to be weighed without it breaking. Each time the grid boat with the polymer was removed from the swelling medium, it was gently dried with a paper tissue in order to remove excess liquid.

Determination of the degree of swelling

The isothermal degree of swelling (*SD*), defined as the difference between the weight of the swollen hydrogel sample at time *t*, *m_t*, and the weight of the xerogel sample, *m₀*, divided by the xerogel weight, was calculated according to Eq. (1) and determined as a function of time:

$$SD[\%] = \frac{m_t - m_0}{m_0} \times 100 \quad (1)$$

The equilibrium degree of swelling, *SD_{eq}*, is the degree of swelling of the swollen hydrogel at equilibrium, *i.e.*, the hydrogel sample which had reached constant mass, *m_{eq}*. At least three swelling measurements were performed for each sample and the mean values are reported. The maximal error of the measurements was 0.5 %, *i.e.*, 10 % of the determined *SD*.

The normalized swelling degree, α , is defined as the ratio between the degree of swelling, *SD*, at time, *t*, and the equilibrium swelling degree, *SD_{eq}*:

$$\alpha = \frac{SD}{SD_{eq}} \quad (2)$$

Physico-chemical characterization of the xerogel

The xerogel was characterized by the following structural properties: density, ρ_{xg} , cross-link density, ρ_c , and the distance between the macromolecular chains, *d*, according to the methods proposed by Gudeman and Peppas.⁵

Xerogel density, ρ_{xg} , determination. The apparent density of the synthesized sample was determined by the picnometry method using *n*-hexane as the non-solvent.

The cross-link density, ρ_c , and the distance between the macromolecular chains were calculated using the following equations:

$$\rho_c = \frac{\rho_{xg}}{M_c} \quad (3)$$

$$d = 0.154v_2^{1/3}(0.19M_c)^{1/2} \quad (4)$$

where *M_c* is the molar mass between the network cross-links and is a nominal value estimated from the initial composition:

$$M_c = \frac{72}{2X} \quad (5)$$

where X is the nominal cross-link ratio (moles of NMBA/moles of acrylic acid in the reaction mixture) and v_2 is the volume fraction of the polymer gel in the equilibrium swollen state at 25 °C, which was determined as follows (Eq. 6):

$$v_2 = \frac{V_p}{V_{g,s}} \quad (6)$$

where V_p is the volume of the xerogel sample and $V_{g,s}$ is the volume of the gel sample after equilibrium swelling:

$$V_{g,s} = \frac{W_{a,s} - W_{h,s}}{\rho_h} \quad (7)$$

where $W_{a,s}$ is the weight of the polymer after swelling in air, $W_{h,s}$ is the weight of the polymer after swelling in *n*-hexane and ρ_h is the density of *n*-hexane.

RESULTS AND DISCUSSION

The determined basic structural properties of the synthesized PAA xerogel and the nominal cross-linking ratio, X , are given in Table I. Based on the results presented in Table I, it may be concluded that the synthesized xerogel was of a medium cross-linking density and macroporous (pores with average diameter ≥ 50 nm).

The swelling isotherms of the synthesized partially neutralized poly(acrylic acid) (PAA) xerogel in (a) distilled water and (b) physiological solution at temperatures from 20 to 40 °C are shown in Fig. 1.

TABLE I. The basic structural properties of the synthesized PAA xerogel sample and its nominal cross-linking ratio (X) in the reaction mixture

X	$\rho_{xg} / \text{kg m}^{-3}$	$M_c / \text{g mol}^{-1}$	$\rho_c \times 10^4 / \text{mol cm}^{-3}$	v_2	d / nm
0.005	994	7200	1.4	0.6	1.02

As can be seen from the results presented in Fig. 1, the swelling isotherm curves are similar in shape at all of the investigated temperatures, both in distilled water and in the physiological solution. Three characteristic regions of the degree of swelling changes with swelling time may be distinguished in all the swelling curves: a linear part, a non-linear part and a saturation range or plateau.

To analyze the influence of temperature on the kinetics curves of swelling, the following specific parameters were used: the initial swelling time, t_{in} , the initial swelling degree, SD_{in} , the initial swelling rate, v_{in} , the equilibrium swelling time, t_{eq} , the saturation swelling rate, v_{eq} , and the equilibrium swelling degree, SD_{eq} . These parameters are defined as follows: t_{in} is the time interval within which the degree of swelling increases linearly with swelling time (from the beginning of the process), SD_{in} is the degree of swelling at the end of this linear increase, v_{in} is the rate of swelling during the initial, linear region of swelling (Eq. (8)):

$$v_{in} = \frac{SD_{in}}{t_{in}} \quad (8)$$

t_{eq} represents the time when the equilibrium swelling degree is first attained, v_{eq} is the saturation swelling rate and is defined as the swelling rate when SD_{eq} is attained for the first time (Eq. 9):

$$v_{eq} = \frac{SD_{eq}}{t_{eq}} \quad (9)$$

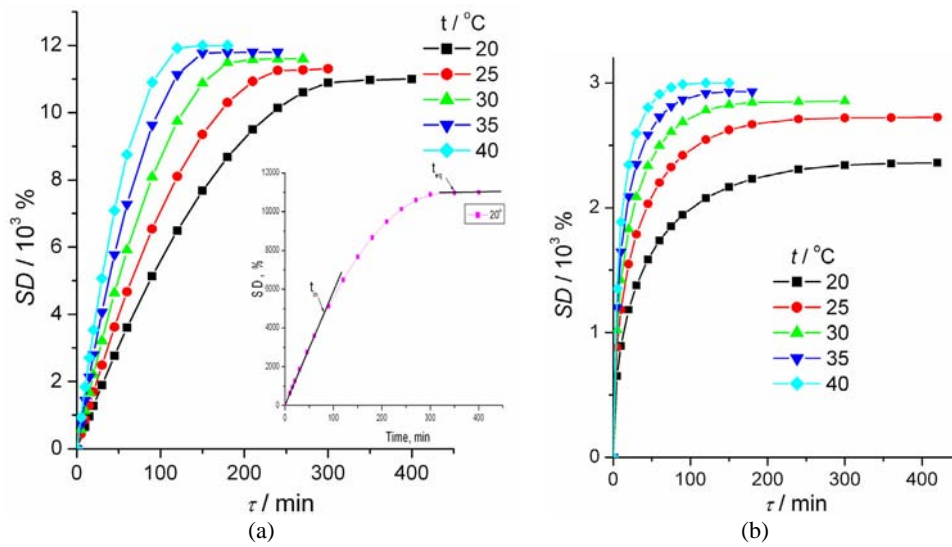


Fig. 1. Swelling isotherms of the PAA hydrogel at different temperatures in (a) distilled water and (b) physiological solution.

The changes of t_{in} , v_{in} , t_{eq} , v_{eq} and SD_{eq} with temperature for the swelling of the investigated hydrogel in water and the physiological solution are presented in Table II.

TABLE II. The influence of temperature on the specific parameters of the swelling kinetics curves: t_{in} , v_{in} , t_{eq} , v_{eq} and SD_{eq}

$t / ^\circ\text{C}$	Distilled water					Physiological solution				
	t_{in} min	v_{in} % min ⁻¹	t_{eq} min	v_{eq} % min ⁻¹	$SD_{eq} \times 10^{-3}$ %	t_{in} min	v_{in} % min ⁻¹	t_{eq} min	v_{eq} % min ⁻¹	$SD_{eq} \times 10^{-3}$ %
20	90	55.5	350	31.43	11.0	10.0	89.2	300	7.87	2.36
25	60	78.3	250	45.20	11.3	9.2	118.3	250	10.88	2.72
30	38	105.2	180	64.44	11.6	8.8	141.8	200	14.25	2.85
35	30	133.3	150	78.67	11.8	8.7	164.7	150	19.53	2.93
40	22	182.0	120	100.00	12.0	8.5	188.5	100	30.00	3.00

From the presented results, it is clear that as the temperature of the swelling increased, the initial swelling rate and the equilibrium degree of swelling increased in both investigated systems, while simultaneously, the values of t_{in} and t_{eq} decreased. The values of the initial swelling time and equilibrium degree swel-

ling, at the same swelling temperature, were significantly higher in water (2–9 times) than in the physiological solution. On the contrary however, the calculated values for the initial swelling rate were higher in the physiological solution than in distilled water.

When the kinetics of swelling are determined by the kinetics of penetration of molecules of the swelling medium, Fick's law of diffusion: $SD = kt^{1/2}$,^{14,15} could be used as a model for the kinetics of the isothermal swelling.

Plots of the degree of swelling as a function of the square root of time at different swelling temperatures in distilled water and in the physiological solution are presented in Fig. 2. These results deviate significantly from straight lines, both for distilled water and the physiological solution. In fact, it is possible to obtain straight lines only in certain period of swelling. For swelling in distilled water, the middle region of the swelling process gives a straight line for the dependence SD vs. $t^{1/2}$, while for swelling in the physiological solution, only the first stages give straight lines. Also, the shapes of the obtained curves of the process in water and in the physiological solution differ significantly from each other. These results imply that the so-called Fickian type of solvent diffusion into the hydrogel is not the dominant factor influencing the swelling kinetics of the hydrogel. They also imply that the swelling mechanisms in water and in the physiological solution are probably different.

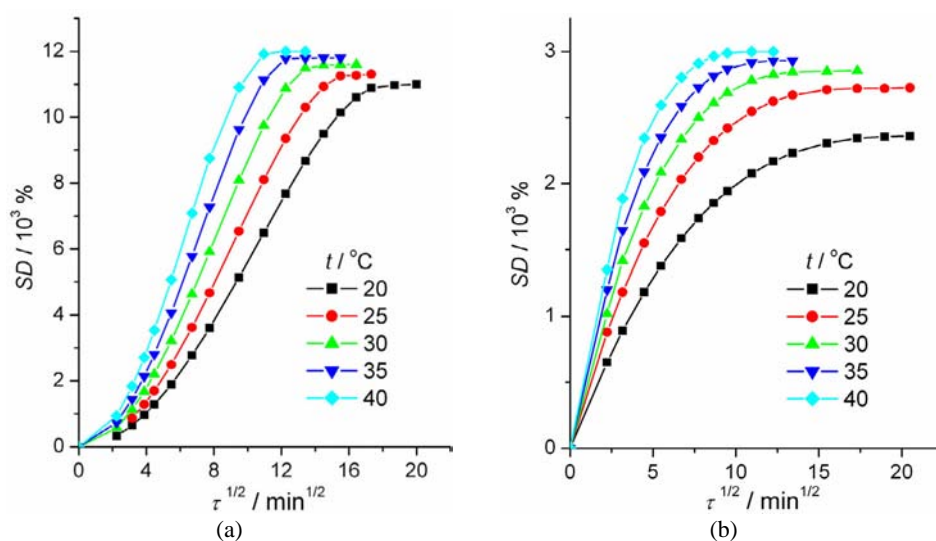


Fig. 2. Plots of the degree of swelling as a function of the square root of time in (a) distilled water and (b) physiological solution.

If the kinetics of swelling is determined by diffusion of the network, the isothermal swelling kinetics of the gel could be described by the Eq. (10):

$$\ln \frac{SD_{eq}}{SD_{eq} - SD} = kt \quad (10)$$

i.e., the plots of $\ln (SD_{eq}/(SD_{eq}-SD))$ vs. t give straight lines.

The dependences of $\ln (SD_{eq}/(SD_{eq}-SD))$ on time for the swelling of the investigated hydrogel at the investigated temperatures are presented in Fig. 3, from which it can be seen that the plots of $\ln (SD_{eq}/(SD_{eq}-SD))$ as a function of time give straight lines only in parts of both of the investigated swelling processes.

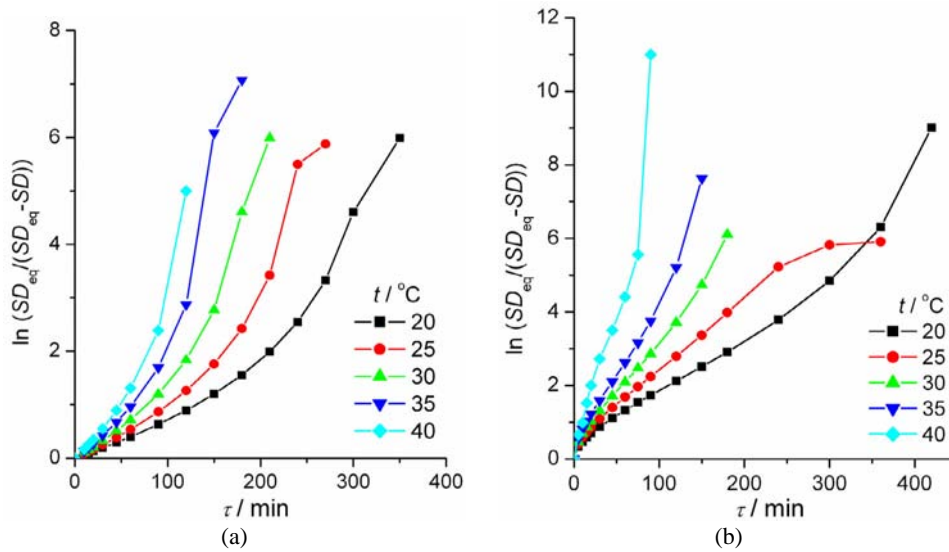


Fig. 3. Plot of $\ln (SD_{eq}/(SD_{eq}-SD))$ vs. time in (a) distilled water and (b) physiological solution.

Bearing in mind that the isothermal swelling kinetics, both in water and in the physiological solution may be described by the actually known models of swelling only over limited time intervals, an attempt was made to investigate the possible applicability of a new model for swelling kinetics. The choice of the new model is based on the so-called “model-fitting method” which is widely used to establish the reaction models for reactions occurring in the solid state.¹⁶

According to this procedure, the best choice of the approximate reaction model of the swelling process is achieved by comparing (both graphically and analytically) the shapes of the function: $\alpha_e = f(t_{e,red}^*)$ of the investigated systems to the shape of the function $\alpha = f(t_{red}^*)$ of common reaction kinetics models for heterogeneous processes, where, α is the normalized degree of swelling and t_{red}^* is the reduced time:

$$t_{red}^* = t_{\alpha}/t_{0.9} \quad (11)$$

where t_{α} is the swelling time which corresponds to the normalized degree of swelling α , while $t_{0.9}$ is the swelling time which corresponds to $SD = 0.9SD_{eq}$.

The sets of the common kinetics reaction models which were used to analyze the investigated swelling kinetics models are presented in Table III.^{17,18}

TABLE III. The set of kinetics models used for the determination of 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 (Polanyi–Winger equation)	1	α
R2	Phase-boundary controlled reaction (contracting area, <i>i.e.</i> , bidimensional shape)	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$
R3	Phase-boundary controlled reaction (contracting volume, <i>i.e.</i> , 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	$3/2[(1-\alpha)^{-1/3}-1]$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

Fig. 4 shows the plots $\alpha_e = f(t_{e,\text{red}}^*)$ for the theoretical reaction models presented in Table III (solid curves) and the experimental plots $\alpha_e = f(t_{e,\text{red}}^*)$ for the swelling of the employed partially neutralized poly(acrylic acid) hydrogel in distilled water and in physiological solution, 4a and b, respectively.

Based on the results presented in Fig. 4, it may be concluded that the isothermal swelling kinetics of PAA in distilled water could be described with the so-called kinetics model of “contracting area” which is characteristic for phase-boundary controlled reactions, of bidimensional shape.¹⁹ Furthermore, the isothermal swelling kinetics in the physiological solution could be described by the so-called kinetics model of tridimensional diffusion, which is characteristic for tridimensional shaped particles (Jander equation).²⁰ This means that the following expressions are, respectively, valid:

$$1-(1-\alpha)^{1/2} = k_m t \quad (12)$$

$$[1-(1-\alpha)^{1/3}]^2 = k_m t \quad (13)$$

where k_m is the model rate constant.

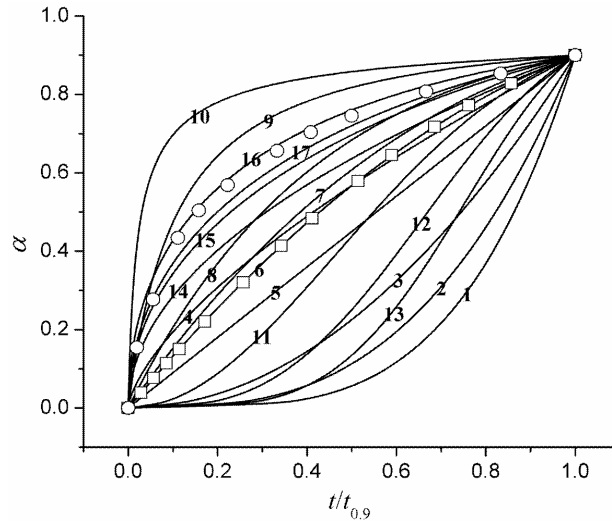


Fig. 4. Plot of $\alpha_e = f(t_{e,red}^*)$ for swelling in distilled water (\square) and in physiological solution (\circ) and the theoretical models (solid lines).

Fig. 5 presents the dependence of $1-(1-\alpha)^{1/2}$ on time for the swelling of PAA in distilled water at the investigated temperatures.

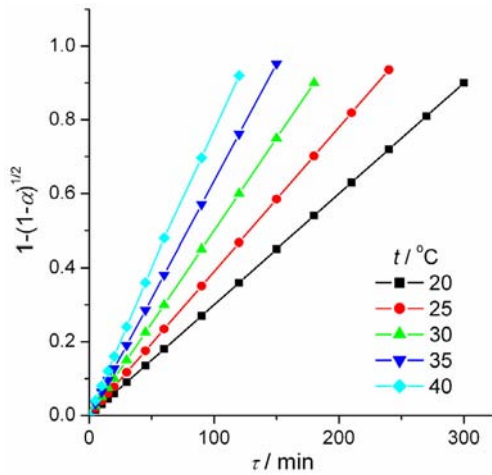


Fig 5. Plot of $1-(1-\alpha)^{1/2}$ vs. time for swelling in distilled water at the investigated temperatures.

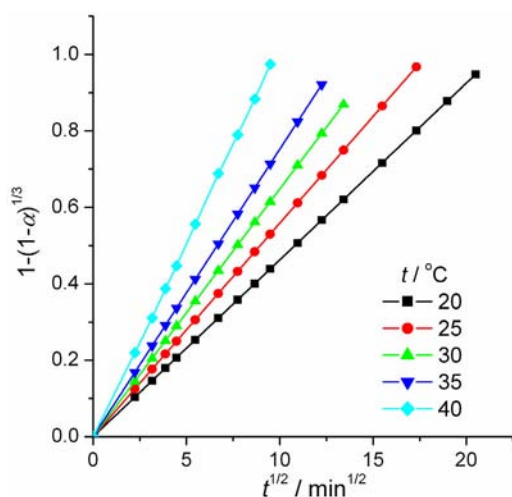
Over a very wide range of “periods of applicability” ($P \geq 90\%$) at all the investigated temperature in distilled water, the dependence $1-(1-\alpha)^{1/2}$ vs. time gives a straight line. The values of the model swelling rate constants (k_m) were determined from the slopes of the lines obtained according to Eq. (12), which are presented in Fig. 5. These values are shown in Table IV.

The dependences of $1-(1-\alpha)^{1/3}$ on the square root of time at the varying investigated temperatures are in Fig. 6 shown for the swelling process of PAA in the physiological solution.

TABLE IV. The temperature changes of model swelling rates constants (k_m) and their periods of applicability (P) for the swelling of the PAA hydrogel in distilled water and physiological solution

$t / ^\circ\text{C}$	Distilled water		Physiological solution	
	$P / \%$	$k_m / 10^{-3} \text{ min}^{-1}$	$P / \%$	$k_m / 10^{-3} \text{ min}^{-1}$
20	0–99	3.0	0–100	2.1
25	0–94	3.9	0–100	3.1
30	0–90	5.0	0–100	4.2
35	0–95	6.4	0–100	5.7
40	0–92	7.8	0–98	7.7

Over a very wide range of “periods of applicability” ($P \geq 90\%$), namely for the entire range at all of the investigated temperatures in the physiological solution, the dependence $1-(1-\alpha)^{1/3}$ on the square root of time gives a straight line. The swelling rate constants (k_m) of the model were determined based on the slopes of the lines obtained according to Eq. (13), which are presented in Fig. 6. These values are also shown in Table IV.

Fig 6. A plot of $1-(1-\alpha)^{1/3}$ versus the square root of time for swelling in the physiological solution at the investigated temperatures.

Based on the results presented in Table IV, it is easy to observe that as the temperature of swelling increases, the swelling rate constants (k_m) of the model also increases. As the swelling rate constants calculated for the determined “periods of applicability” (P) using the applied models exponentially increase with increasing temperature, it is possible to determine the kinetic parameters: activation energy (E_a) and pre-exponential factor ($\ln A$) for the applied kinetic models using the well-known Arrhenius equation.

The results of the determined values of the kinetic parameters (E_a and $\ln A$) determined for the reaction models and their corresponding “periods of applicability” (P) in distilled water and the physiological solution are summarized in Table V.

TABLE V. The values of the kinetics parameters obtained using the different kinetics models

Model	Distilled water			Physiological solution		
	$P / \%$	$E_a / \text{kJ mol}^{-1}$	$\ln(A / \text{min}^{-1})$	$P / \%$	$E_a / \text{kJ mol}^{-1}$	$\ln(A / \text{min}^{-1})$
Initial rate	0–(30–46)	44.36	22.24	0–(37.7–70)	27.9	16.01
Fickian diffusion	22–82	21.68	15.69	0–(37–62)	27.7	17.06
First order	0–(50–70)	32.07	8.38	0–(50–78)	49.6	16.14
Model	0–(9–95)	35.01	8.60	0–(99–100)	48.3	13.7

For all of the swelling kinetics models examined, the calculated kinetic parameters for the swelling of PAA hydrogels in the physiological solution are higher than the calculated values for the same process in distilled water.

The values of the kinetic parameters for both investigated processes, determined by the newly established models and those of the first order kinetics model, are mutually comparable and differ from one another by 5–10 %. The numerical values of the kinetics parameters determined using Fick's kinetics model are significantly lower. The established changes of the swelling kinetics model and the swelling kinetics parameters in physiological solution when compared to those obtained with distilled water imply that the swelling mechanism in the physiological solution when compared to distilled water is changed. Based on the obtained results, it may be proposed that the swelling kinetics of PAA hydrogel in distilled water are caused by the rate of two-dimensional movement of the reactive interface, which is formed during the interaction of the polymer network with the molecules of the swelling medium. On the contrary, the isothermal swelling kinetics in physiological solution can be described by the kinetics model of three-dimensional movement of the reactive phase boundary.²¹

According to Flory's theory,²² the degree of swelling of a gel in a specific medium is a function of its characteristic properties (cross-link density, affinity towards the molecules of the swelling medium, concentrations of the bonded charges, degree of ionization of the functional groups, *etc.*), as well as of the characteristics of the swelling medium (pH, ionic strength, valences of the opposite ions). This theory simply explains the established decrease of both the equilibrium degrees of swelling and the saturation swelling rate at all applied temperatures in the physiological solution when compared to those in distilled water. The penetration of the physiological solution into the gel, due to the higher content of cations, leads to an increase in the Na^+ concentration onto the gel, as well as to an increase of the osmotic pressure in the gel, *i.e.*, to a decrease in the difference in the osmotic pressure between the gel and the swelling medium,²³ which leads to decrease of SD_{eq} and v_{eq} .

The established increase of the rate of the initial swelling in the physiological solution compared to that in distilled water can be explained as a consequence of the increased concentration of the charges bonded to the network and

the affinity of the network to the molecules of the swelling medium compared to the molecules of distilled water. In the physiological solution (pH 6.4) the network's functional carboxylic groups of the network of the PAA hydrogel are completely ionized because the pK_a of PAA is 4.6. Thus, increasing the concentration of COO^- groups, *i.e.*, the fixed charges, leads to an increase of the affinity towards the molecules of the swelling medium, which in turn leads to electrostatic repulsion. This causes the initial swelling rate to increase in the physiological solution more than in distilled water (note: this comparison concerns two different time intervals. Approximately 10 min for the swelling in the physiological solution and about 80–100 min in distilled water). If the activation energy of the swelling process is equal to the energy necessary to cause elastic shrinkage of the hydrogel network, the established increase of the activation energy of the swelling process in the physiological solution compared to the one in distilled water, can be explained by the existence of so-called “ionic cross-linking”²³ in the physiological solution. That is, “ionic cross-linking” occurs due to the interaction of Na^+ ions with COO^- (of the network), which mainly occurs at the surfaces and makes them stronger, which additionally decreases the flexibility of the network.

The established changes of the swelling kinetics models in the physiological solution compared to that in distilled water, are in accordance with the theoretical and mathematical prediction of Wang and co-workers.²⁴ The hypothesis was postulated on the theory of gel swelling kinetics, which is based on the collective motions of both the network and swelling medium during the swelling process, *i.e.*, the diffusion motion of the “adsorption complex” formed from the network and diffusion of the swelling medium. According to their theory, the swelling medium moves together with the network, the swelling medium rate is the same as the network rate and the motion of the polymer network of a gel during the course of swelling is described by an equation called the “collective diffusion equation”.²⁴ When the rate of axial movement of the reactive interface is higher than the rate of radial movement of the reactive interface (as is the case for PAA hydrogels swelling in water) then for higher degrees of swelling, the reactive interface increases because the rate of network shrinkage is lower than the rate of penetration of the molecules of the swelling medium. On the contrary, when the rates of the axial and radial movement of the reactive interface are identical, as is the case for a PAA hydrogel swelling in the physiological solution, for higher degrees of swelling, the reactive interface and reactive boundary volume will be diminished and, hence, the rate of swelling of the hydrogel will be decreased.

CONCLUSIONS

The isothermal swelling kinetics of a poly(acrylic acid) hydrogel in distilled water and physiological solution were described by Fick's kinetics model and the kinetics model of first order chemical reaction only during limited stages of the process.

The isothermal swelling kinetics of the PAA hydrogel in distilled water could be described by the so-called kinetics model of “contracting area”, while the isothermal swelling kinetics in the physiological solution could be described by the so-called kinetics model of “tridimensional diffusion”.

The decrease of the equilibrium degree of swelling and the saturation swelling rate of the PAA hydrogel swelling in the physiological solution compared to the swelling in distilled water could be explained by the decreased differences in the ionic osmotic pressures between the hydrogel and the swelling medium.

The increase of the initial swelling rate in the physiological solution might be caused by an increased density of charges at the network and by the increased affinity of the network towards the water molecules.

The increase of the activation energy of the PAA hydrogel swelling in the physiological solution is explained as a consequence of the additional “ionic cross-linking”.

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ИЗВОД

ПОРЕЂЕЊЕ КИНЕТИКЕ БУБРЕЊА ХИДРОГЕЛА ДЕЛИМИЧНО НЕУТРАЛИСАНЕ ПОЛИ(АКРИЛНЕ) КИСЕЛИНЕ У ДЕСТИЛОВАНОЈ ВОДИ И ФИЗИОЛОШКОМ РАСТВОРУ

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У раду су испитиване изотермалне кинетичке криве бубрења хидрогела делимично неутралисане поли(акрилне) киселине у дестилованој води и физиолошком раствору у температурном опсегу од 20 до 40 °С. Испитивана је могућност примене Фиковог кинетичког модела као и кинетике и реда хемијских реакција на кинетику бубрења полиакрилног хидрогела. Утврђено је да су могућности за њихову примену врло ограничене. Из тих разлога примењен је нови модел кинетике бубрења. Одређени су кинетички параметри (E_a , $\ln A$) за процес бубрења у дестилованој води и физиолошком раствору. Смањење равнотежног степена бубрења и сатурационе брзине бубрења хидрогела делимично неутралисане поли(акрилне) киселине у физиолошком раствору у односу на дестиловану воду може се објаснити смањењем разлике у јонском осмотском притиску између хидрогела и медијума за бубрење. Повећање иницијалне брзине бубрења у физиолошком раствору у односу на дестиловану воду проузроковано је повећањем густине наелектрисања на полимерној мрежи и повећаним афинитетом према молекулима воде. Повећање енергије активације хидрогела делимично неутралисане поли(акрилне) киселине при бубрењу у физиолошком раствору се објашњава додатним “јонским умрежењем” хидрогела у физиолошком раствору.

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