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THE KINETICS OF ISOTHERMAL DEHYDRATION OF EQUILIBRIUM SWOLLEN HYDROGEL OF POLY(ACRYLIC-CO-METHACRYLIC ACID)*

The isothermal dehydration of equilibrium swollen hydrogel of poly(acrylic-co-methacrylic acid) (PAM) was investigated. Thermogravimetric dehydration curves of equilibrium swollen PAM hydrogel at temperatures 293, 303 and 313 K were recorded. Applying model-fitting method, it was established that kinetic of isothermal dehydration of equilibrium swollen PAM hydrogel was controlled with the rate of contracting area of hydrogel network. Based on the results of differential isoconversional method it was evaluated that the kinetic parameters of the dehydration process linearly decrease with the increase of dehydration degree. Both the kinetic complexity of the dehydration process and the change in the kinetic parameters with the change in the dehydration degree is explained by energetical distribution of the dehydration centers where there are two clearly distinguishable most probable distributions of the values of activation energies, E_a , of 60.4 and 64 kJ/mol.

Due to their specific properties like swelling ability, hydrophilicity, biocompatibility and non-toxicity, and to their abilities to respond to various changes of surrounding media such as pH, temperature, light, electrical and magnetic field, ionic strength and so on, hydrogels find significant application in medicine, pharmacy, hygienic devices, agrochemistry and ecology. Hydrogels can be used as carriers for controlled and target drug release, artificial muscles, regenerative tissues, as replacement for soft tissues, coating for burns, artificial cartilage, artificial glottis, contact lenses, biosensors, textile materials for special applications, superabsorbents for hygienic devices in agriculture and horticulture either as carriers for agrochemicals or reservoirs for water [1,2].

Synthesis of hydrogels based on acrylic acid, methacrylic acid and their co-polymers, as well as the influence of the temperature and the pH of the surrounding medium on the equilibrium swelling degree and the swelling kinetics, has been described in the literature [3–8].

The kinetics of isothermal dehydration of equilibrium swollen poly(acrylic acid) hydrogel (PAA) has been investigated [9,10]. Applying the model-fitting method the authors [9] established that the change in dehydration temperature caused a change in the dehydration kinetic model. Adnadjevic *et al.* [10] established that the isothermal dehydration of the PAA hydrogel can be mathematically described by Weibull distribution function (WDF) of reaction times.

The aim of this paper was to determine the kinetic model and the kinetic parameters, E_a and $\ln A$, of the isothermal dehydration of the PAM hydrogel and to establish the effect of methacrylic acid as co-monomer unit in

polymer network on the kinetic parameters, as well as on the model of kinetics of dehydration.

EXPERIMENTAL

Materials

Materials for hydrogel synthesis: Acrylic acid (99.5%) (AA) and methacrylic acid (MA) were supplied from Merck KGaA, Darmstadt, Germany. *N,N*-methylene bisacrylamide (p.a) (MBA) was purchased from Aldrich Chemical Co., Milwaukee, USA. The initiator, 2,2-azobis-[2-(2-imidazolin-2-yl)-propane dihydrochloride (VA044), (99.8%) was supplied from Wako Pure Chemicals Industries, Ltd, Osaka, Japan. Sodium carbonate (Na_2CO_3) (p.a) was obtained from Merck KGaA, Darmstadt, Germany.

Hydrogel synthesis

Poly(acrylic acid-co-methacrylic acid) hydrogel (PAM) was synthesized by a procedure based on radical polymerization of acrylic acid and methacrylic acid (1:1 mol ratio), and cross-linking of the polymers formed, using the previously described procedure [11].

Xerogel structural properties

Structural properties of the synthesized xerogel: the equilibrium swelling degree, SD_{eq} , the xerogel density, ρ_x , the molar mass between the networks cross-links, M_c , the cross-link density, ρ_c , and the distance between macromolecular chains, d , have been determined by the methods proposed by Gudman and Peppas [12].

The basic structural properties survey of the PAM xerogel which was used in this investigation are presented in Table 1.

Based on the obtained results for the determined basic structural properties, it may be concluded that the PAM xerogel used in this investigation was a low cross-linked network with a macro pores and with high equilibrium swelling degree. The structural properties of the

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Table 1. Structural properties of the PAM xerogel

Structural property	$SB_{eq} / \text{g g}^{-1}$	$\rho_x / \text{kg m}^{-3}$	$M_c / \text{g mol}^{-1}$	$\rho_c \times 10^6 / \text{mol dm}^{-3}$	d / nm
Value	197	1200	227000	5.3	6.4

investigated PAM hydrogel are different then the structural properties of the PAA xerogel investigated in previous papers [9,10].

Thermogravimetric measurements

The isothermal thermogravimetric curves were recorded by a TA Instruments-SDT simultaneous TGA–DSC thermal analyzer model 2960. The analyses were performed with 20 ± 2 mg samples of equilibrium swollen hydrogel in platinum pans under nitrogen atmosphere at a gas flow rate of 10 ml min^{-1} . Isothermal runs were performed at nominal temperatures of 293, 303 and 313 K . The samples were heated from the start to the selected dehydration temperature at the heating rate of 300 K min^{-1} and then held at that temperature for given reaction time. The degree of the dehydration is expressed as:

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \quad (1)$$

where m_0 , m and m_f refer to the initial, actual and final mass of the sample. The isothermal conversion curve represent the dependence of degree of conversion, α , on the reaction time, t , $\alpha = f(t)$, at constant value of experimental temperature, T .

Methods used to evaluate the kinetic model and kinetic parameters

The kinetic model and kinetic parameters were evaluated applying the following methods.

Model-fitting method

According to the model-fitting method the kinetic reaction model are classified in 5 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. The model-fitting method is based on the following: the experimentally determined conversion curve, $\alpha_{exp} = f(t)_T$, has to be transformed into the normalized conversion curve, $\alpha_{exp} = f(t_N)_T$, where t_N is the so-called normalized time, which was defined by the equation:

$$t_N = \frac{t}{t_{0.9}} \quad (2)$$

where $t_{0.9}$ is the moment in time at which $\alpha = 0.9$ [13]. The kinetic model of the investigated process was determined by analytically comparing the normalized conversion curves with the normalized model's conversion curves. The chosen kinetic model is the one for which the sum of squares of the residual is minimal.

A set of the reaction kinetics models used to determine the model which best describes the kinetics of the process of PAM isothermal dehydration is shown in Table 2 [13,14].

Determination of activation energy with the change in the dehydration degree

The activation energy of investigated dehydration for various dehydration degrees was established by the Friedman method [15].

The normalized distribution curve of the activation energy

Muira [16] established a simple method for determination the density distribution curve of the activation energy, $f(E)$. The basic principle of the method consists in accepting the fact that the investigated process can be described by the so-called distribution activation energy model (DAEM).

When the DAEM model is valid, the dehydration degree can be represented as:

$$\alpha = 1 - \int_{E_s}^{\infty} f(E) dt \quad (3)$$

where E_s is the activation energy of single reaction at given temperature.

Then, $f(E_s)$ is given by differentiating Eq. (3) by E_s as:

$$f(E_s) = \frac{d\alpha}{dE_s} \quad (4)$$

Actually, the density distribution function of activation energies could be directly obtained by differentiating the experimentally determined relationship α versus E ; i.e.:

$$f(E) = \frac{d\alpha}{dE}$$

RESULTS AND DISCUSSION

The experimentally obtained isothermal conversion curves (the dependence of α versus time) at different operating temperatures for the PAM hydrogel dehydration are given in Figure 1.

The conversion curves of PAM dehydration are of characteristic shape and exhibit three specific shapes of the changes in dehydration degree conversion on dehydration time. Actually, these shapes are a linear, non-linear and a saturation stage (plateau). With increasing dehydration temperature, the slope of the linear change in the

Table 2. The set of kinetic models used to determine the kinetic model of the dehydration of the PAM 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–Erofeev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
A3	Avrami–Erofeev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
A4	Avrami–Erofeev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
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	$3/2[(1-\alpha)^{-1/3}-1]$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

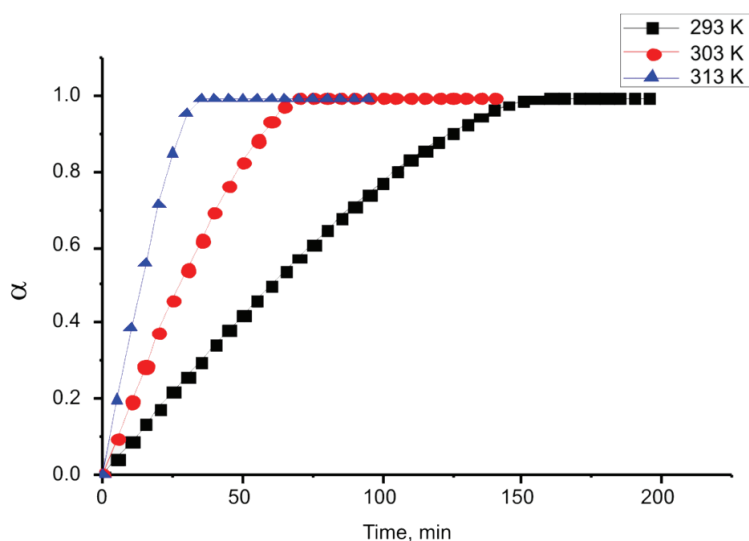


Figure 1. The isothermal conversion curves of the PAM hydrogel dehydration at different temperatures.

dehydration degree of PAM hydrogel versus time decreases while the duration of the both linear and non-linear changes decrease, for all dehydration temperatures.

With aim to establish the kinetic model of the PAM hydrogel dehydration, the normalized conversion curves were determined (α_c versus t_N). Figure 2 shows the normalized conversion curves of the PAM dehydration.

The normalized conversion curves of the PAM hydrogel dehydration at all of the investigated temperatures

are identical, which indicate the same kinetic model of dehydration independent on temperature within the investigated temperatures. By analytically comparing $\alpha_c = f(t_N)$ with the normalized models conversion curves $\alpha = f(t_N)$ for different solid state reaction models, it was found that the PAM hydrogel dehydration can be described by the phase-boundary controlled reaction model (contracting area) for which the following expression is valid:

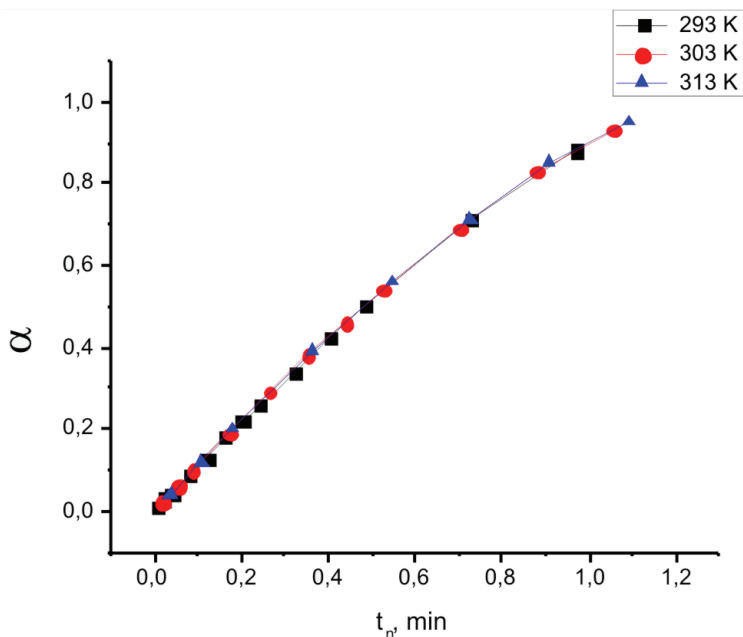


Figure 2. The normalized conversion curves of the PAM dehydration.

$$[1-(1-\alpha)^{1/2}] = k_M t \tag{5}$$

where k_M is model rate constant.

When the PAM hydrogel dehydration can be described by the Eq. (5), the dependences $[1-(1-\alpha)^{1/2}]$ on time should give straight lines whose slopes give the k_M values.

The dependence of $[1-(1-\alpha)^{1/2}]$ on time for the PAM dehydration at different temperatures is presented in Figure 3.

Since the plot of $[1-(1-\alpha)^{1/2}]$ versus time for the PAM dehydration gives a straight line at all of the investigated temperatures, it can be stated with great certainty that the kinetics of the PAM hydrogel dehydration is determined by Eq. (5). That means that the kinetics of dehydration are determined by the rate of the decrease in the area of the boundary phase.

The effects of temperature of isothermal dehydration on the k_M values and kinetic parameters of the PAM hydrogel dehydration isothermal process are given in Table 3.

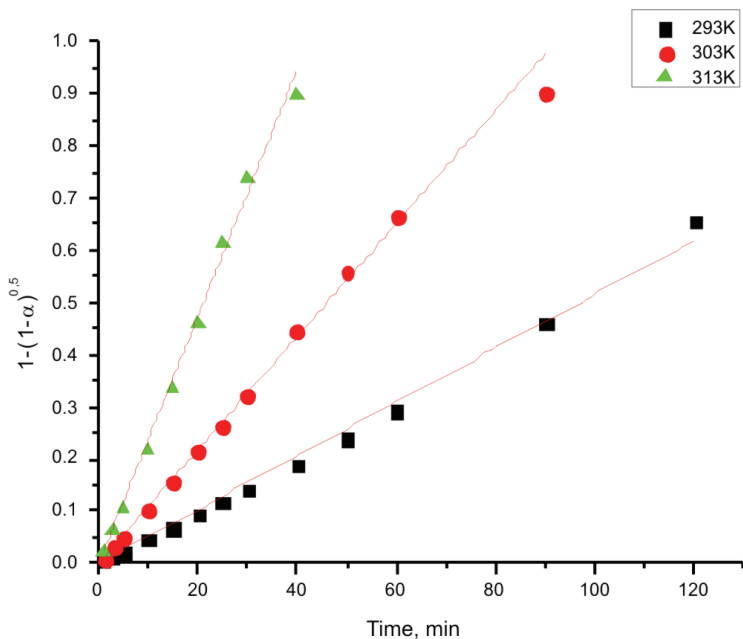


Figure 3. The plot of $[1-(1-\alpha)^{1/2}]$ versus time for the PAM dehydration at different temperatures.

Table 3. The effect of isothermal dehydration temperature on the k_M values and kinetic parameters of the PAM hydrogel dehydration isothermal process

T / K	k_M / min^{-1}	Range of applicability (% α)	Kinetic parameters
293	0.0052	99.8	$E_a = 54.5 \pm 0.5\%$ kJ/mol
303	0.0109	99	$\ln(A / \text{min}^{-1}) = 17.15 \pm 0.05\%$
313	0.0236	99	

Because the k_M values exponentially increase with temperature, it was possible to determine the kinetic parameters, namely, the activation energy, E_a , and pre-exponential factor, A , by using the Arrhenius equation, which are also presented in Table 3.

The different kinetic models of the PAM hydrogel isothermal dehydration process compared to the PAA hydrogel imply that an introduce of methacrylic acid into the polymer chain and polymer network unit as co-monomer unit, leads to the changes in the energy distribution of the networks boundary phase of the xerogel /hydrogel and the absorbed water. The presence of the methacrylic acid most probably leads to enhanced hydrophobicity and higher steric hindrance of the absorbed water. Because of that, dehydration of water from the inside of the hydrogel network is complex. The values of the kinetic parameters of dehydration are increased compared to the PAA hydrogel and the kinetic model of dehydration is changed.

The calculated kinetic parameters and the established kinetic model of the PAM hydrogel dehydration isothermal process enable us to propose a possible mechanism of that process.

If we assume that the equilibrium swollen PAM hydrogel can be considered as a sum of “ n ” cylindrical holes with the radius r_0 and the length H , and that these radii reduced during the dehydration process due to the shrinkage the hydrogel network in accordance with the Eq. (6):

$$r = r_0 - k_d t \quad (6)$$

where k_d is the rate dehydration constant. Then, the following expression can be obtained:

$$\alpha = \frac{n\rho H\pi r_0^2 - n\rho H\pi r^2}{n\rho H\pi r_0^2} \quad (7)$$

where ρ is the density of the absorbed water.

$$\alpha = \left(1 - \frac{r^2}{r_0^2}\right) \quad (8)$$

Changing the r in Eq. (8) with Eq. (6) we get the following expression:

$$\alpha = 1 - \left(\frac{r_0 - k_d t}{r_0}\right)^2 \quad (9)$$

If we denote k_D as:

$$k_D = \frac{k_d}{r_0}$$

the Eq. (5) transforms to:

$$1 - (1 - \alpha)^{1/2} = k_D t \quad (10)$$

The obtained form of Eq. (10) is equal to the previously determined kinetic model of isothermal dehydration of the PAM hydrogel.

In order to investigate possible effects of the dehydration degree on the investigated dehydration process, the kinetic parameters of PAM hydrogel dehydration were determined by applying the isoconversional method. Using that method, the kinetic parameters were determined for different dehydration degrees. The dependences of $\ln(da/dt)$ on $1/T$ are given in Figure 4, for different dehydration degrees.

Because the dependences of $\ln(da/dt)$ on $1/T$ for all of the dehydration degrees give straight lines, based on their slopes and intercepts, the kinetic parameters of PAM hydrogel dehydration, E_a and $\ln A$, were determined. Figure 5 presents the dependence of the E_a on the dehydration degree.

In the range of $\alpha \leq 0.8$ the increase in the dehydration degree leads to the decrease in the activation energy and then the $E_{a,\alpha} = 63.5$ kJ/mol decrease to the 60.6 kJ/mol. Further increase in the dehydration degree causes a significant decrease in the values of the $E_{a,\alpha}$. The changes in $\ln A$ with the dehydration degrees are in functional relationship with the variation in the values of the $E_{a,\alpha}$ (well known as a compensation effect), and can be described by the expression:

$$\ln A_\alpha = -13.50 + 0.48 E_{a,\alpha} \quad (11)$$

In agreement with the works of Dowdy [17] and Vyazovkin [18], this type of changes of E_a with the dehydration degree is characteristic either for a complex process which consists of two parallel independent first order reactions, or for a reaction system with a specific function of activation energies distribution.

In order to prove that hypothesis, by using the method of Muira the shape of distribution function of activation energies for the PAM hydrogel dehydration was determined and presented in Figure 6.

The density distribution function of activation energies E for PAM hydrogel has a characteristic shape with two well defined peaks at E_a values of 60.4 and 64 kJ/mol.

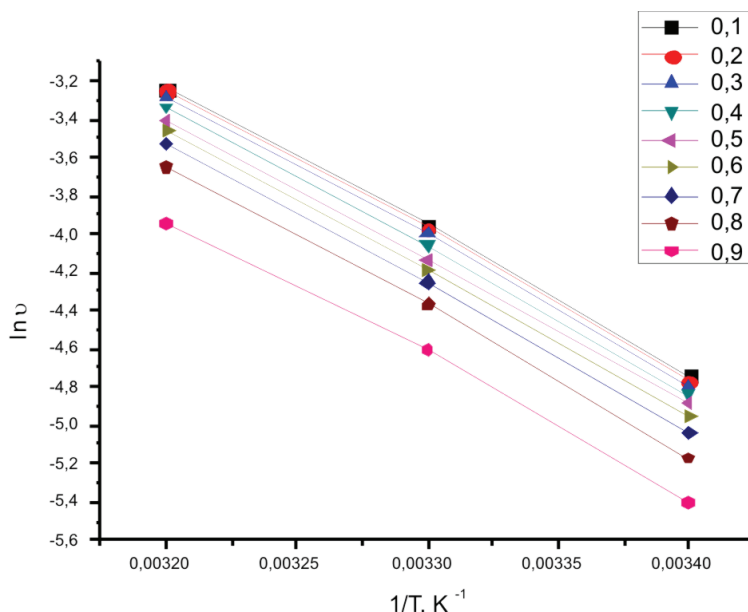


Figure 4. The dependences of $\ln v$ on $1/T$ for different dehydration degrees.

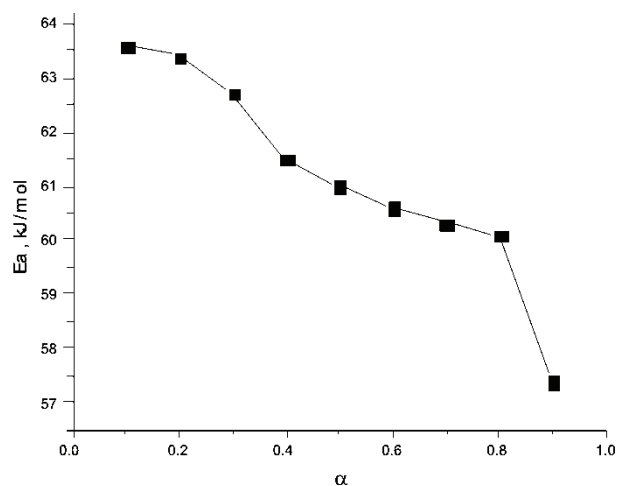


Figure 5. The dependence of E_a on the dehydration degree.

Because the peaks at the density distribution function of activation energies, E , correspond to the most probable value of activation energy it is clear that the kinetics of PAM hydrogel dehydration are of complex nature and that the dominant effect on the kinetics of the dehydration centers had the most probable values of activation energies values of 60.4 and 64 kJ/mol. The E_a and $\ln A$ values correspond to the minimal value of E_a at density distribution function of activation energies.

Bearing in mind that the E_a of dehydration of a hydrogel is practically equal to the heat of water absorption onto the xerogel, it may be assumed that an existence of the two characteristic values of E_a is in correlation with the two structurally different phases of water absorbed onto hydrogel [19]. The ratio of these different structures of water changes during the dehydration and their phase stage is different then the phase stage of ordinal water.

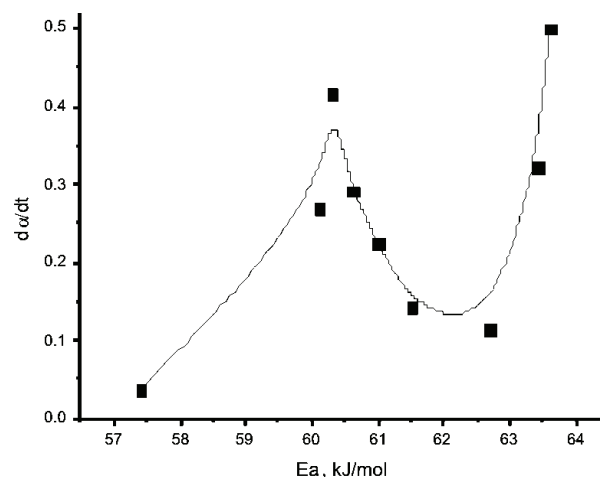


Figure 6. The density distribution function of activation energies, E_w , for the PAM hydrogel dehydration.

CONCLUSIONS

The isothermal dehydration of the equilibrium swollen PAM hydrogel is a complex process, kinetically controlled by the rate of contraction area of the polymer network. With increasing degree of dehydration the kinetic parameters of the PAM hydrogel dehydration decrease. The decrease in the kinetic parameters of dehydration with the increasing degree of dehydration is caused by the existence of energetical heterogeneity of the dehydration centers at the boundary phase. Density distribution function of activation energies of the dehydration process is specific in shape with two well distinguished peaks at $E_a = 60.3$ and 63.5 kJ/mol. An existence of energetical heterogeneity of the dehydration centers is a consequence of the presence of structurally different

phases of water in hydrogel, whose ratio is changed with the degree of dehydration.

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IZVOD

KINETIKA IZOTERMNE DEHIDRATACIJE RAVNOTEŽNO NABUBRELIH HIDROGELOVA POLI(AKRILNE-KO-METAKRILNE) KISELINE

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(Naučni rad)

Ispitana je izotermna dehidracija ravnotežno nabubrelog hidrogela poli(akrilne-ko-metakrilne kiseline) (PAM). Snimljene su termogravimetrijske dehidracione krive ravnotežno nabubrelog PAM hidrogela na temperaturama 293, 303 i 313 K. Primenom model-fiting metode utvrđeno je da je kinetika izotermne dehidracije ravnotežno nabubrelog PAM hidrogela kontrolisana brzinom skupljanja površine polimerne mreže. Na osnovu rezultata diferencijalne izokonverzije metode ustanovljeno je da vrednosti kinetičkih parametara procesa dehidracije linerano opadaju sa povećanjem stepena dehidracije. Utvrđena kinetička kompleksnost procesa dehidracije i promena vrednosti kinetičkih parametara sa stepenom dehidracije objašnjava se energetsom distribucijom dehidracionih centara na kojim se jasno uočavaju dve najverovatnije raspodele energije aktivacije sa vrednostima od 60,4 i 64,0 kJ/mol.

Ključne reči: Hidrogel • Poli(akrilna-ko-metakrilna kiselina) • Izotermna dehidracija • Model-fiting metod
Key words: Hydrogel • Poly(acrylic-co-methacrylic acid) • Isothermal dehydration • Model-fiting method