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# Kinetic of non-isothermal dehydration of equilibrium swollen poly(acrylic acid-co-methacrylic acid) hydrogel

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ABSTRACT

The kinetic of non-isothermal dehydration of equilibrium swollen poly(acrylic acid-co-methacrylic acid) hydrogel (PAM) has been investigated. Thermogravimetric and conversion dehydration curves were recorded at various heating rates 5–30 $\mathrm{K\,min^{-1}}$. The conversion dehydration curves at all investigated temperatures can be mathematically described using the logistic regression function in entire. It was found that activation energy complexly changes with the increasing dehydration degree. Physical meaning of the parameters of logistic function ($b$ and $w$) is given. It was established that, during the dehydration, changes in the fluctuating hydrogel structure occur, and that limiting step on the kinetics of hydrogel dehydration have rate of structural rearrangement of hydrogel (actual relaxation mechanism). A procedure for determining the dependence of effective activation energy on temperature and dehydration degree, based on logistic function, is exposed. Possible explanation for the existence of negative values of activation energy in the certain range of temperature, is given.

## 1. Introduction

Hydrogels are important class of materials which attract great attention in recent years. They are three-dimensional crosslinked polymeric structures that are able to absorb significant amount of water and biological liquids without dissolving and loosing their structural integrity. Because of their specific properties such as swellability in water, hydrophilicity, biocompatibility, low toxicity and to their abilities to respond to a variety of changes in the surrounding environment, hydrogels have been utilized in a wide range of biological, medical, pharmaceutical and environmental applications [1,2].

In the paper of Jankovic et al. [3] kinetics of non-isothermal dehydration of PAA has been investigated by applying different kinetic methods such as: Kissinger, Coats–Redfern, Van–Krevelen, Horowitz–Metzgen. By using model-fitting method Jankovic et al. [4] have shown that the change of heating rate leads to the change in kinetic model of non-isothermal dehydration of PAA hydrogel and confirmed that dependence of $E_a$ on $\alpha$ exists, as well as the compensation effect. Adnadjevic et al. [5] established that conversion curves of non-isothermal dehydration of PAA can be also mathematically described using the Weibull distribution function. Authors have elaborated a method for determining the density distribution function of activation energies and shown that there is a good correlation between the most probable $E_a$ value and experimentally obtained minimum $E_a$ value.

Having in mind the above said, the main goal of this paper was to establish the effect of introducing the methacrylic acid comonomer units into poly(acrylic acid) polymer network on the kinetics of dehydration of hydrogel: a kinetic model and the kinetic parameters.

## 2. Materials and methods

### 2.1. Materials

*Materials for hydrogel synthesis.* Materials for hydrogel synthesis: acrylic acid (99.5%) (AA) and methacrylic acid (MA) were supplied by Merck KGaA. Daramsatdt, 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-il)-propan dihydrochloride (VA044), (99.8%) was supplied by Wako Pure Chemicals Industries, Ltd., Osaka, Japan.

Here, the sodium salt form solution was used and $Na_2CO_3$ was used for neutralization.

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**Table 1**
Structural properties of the PAM and PAA xerogels.

| Xerogel | $SB_{eq}$ ($g\,g^{-1}$) | $\rho_x$ ($kg\,m^{-3}$) | $\chi$ | $M_c$ ($g\,mol^{-1}$) | $\rho_c$ ($10^6/mol\,dm^{-3}$) | $d$ (nm) |
|---|---|---|---|---|---|---|
| PAM | 197 | 1200 | −0.5 | 196000 | 6.12 | 240 |
| PAA | 113 | 1140 | −0.5 | 67300 | 16.9 | 87 |

### 2.2. 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 [6] which consists of the following. A solution of acrylic acid and methacrylic acid (1/1 (mol/mol)) in the form of 20 wt.% solution was prepared and mixed with solution of MBA (0.1 wt.%). After good stirring to assure homogeneity of reaction mixture and nitrogen bubbling through the mixture for half an hour, initiator solution (0.06 mol.% of the monomer) was added and reaction mixture was once again rapidly homogenized with stirring. The prepared solution was placed in Petridish and stored in a dry oven for 5 h at 80 °C. After the polymerization was completed, the obtained gel-type product was transformed into the $Na^+$ form (60%) by neutralization with a 3% solution of $Na_2CO_3$. The resulting hydrogel was cut to discs of same sizes and placed in excess of distilled water. The water was changed 7-times every 5 h (or 12 h during the night), in order to remove the unreacted monomers and the sol fraction of polymer. Then the obtained hydrogel was dried in an air oven at 80 °C for 2 h, 90 °C for 3 h and 105 °C until constant weight was reached. The obtained product was stored in a vacuum exicator before use. For this investigation, the obtained hydrogel was grounded and used in the form of powder.

### 2.3. Equilibrium swelling degree and xerogel structural properties

The equilibrium swelling degree ($SB_{eq}$) in distilled water at 298 K was determined by common gravimetric procedure [6].

Structural properties of the synthesized xerogel: the equilibrium swelling degree ($SB_{eq}$), the xerogel density ($\rho_x$), the Flory interaction parameter ($\chi$), the molar mass between the networks cross-links ($M_c$), the cross-link density ($\rho_c$), and the distance between macromolecular chains ($d$) have been determined by the methods proposed by Gudman and Peppas [7].

The structural properties survey of the synthesized xerogel is given in Table 1 together with the properties of PAA hydrogel with which was compared.

The introduction of methacrylic acid co-monomer units in poly(acrylic acid) polymer network leads to significant changes in structural properties of xerogel. The values of molar masses between the networks cross-links and the distance between macromolecular chains significantly increase while the cross-link density decrease and therefore the equilibrium swelling degree increase.

### 2.4. Thermogravimetric measurements

Thermogravimetric curves were recorded by a Du Pont thermogravimetric analyzer TGA model 9510. These analyses were performed with 25 ± 1 mg samples of equilibrium swollen hydrogel in platinum pans under nitrogen atmosphere at a gas flow rate of 10 mL $min^{-1}$. Experiments were performed at heating rates of 5, 10, 20 and 30 K $min^{-1}$, from ambient temperature to 623 K. The degree of the dehydration is expressed as:

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \tag{1}$$

where $m_0$, $m$, $m_f$ refer to the initial, actual and final mass of the sample.

### 2.5. Mathematical consideration

In order to fit obtained experimental data, two different models has been proposed. In the first model, it is assumed that a kinetic conversional curve can be fitted by Weibull distribution function:

$$\alpha(T) = 1 - e^{-((T-T_0)/\upsilon_h\eta)^{\beta}} \tag{2}$$

where $\alpha$ is the conversion degree, $T$ is the temperature ($T \geq T_0$, $T_0$ is the initial temperature of the process and acts as the location parameter of Weibull distribution function), the $\eta$ and the $\beta$ are the scale and shape parameters, respectively, and $\upsilon_h$ is the heating rate.

Linear form of Eq. (2) was used to estimate parameters $\beta$ and $\eta$ (Eq. (3)):

$$\ln[-\ln(1-\alpha(T))] = \beta \ln\left(\frac{1}{\eta}\right) + \beta \ln\left(\frac{T - T_0}{\upsilon_h}\right) \tag{3}$$

The values of $\beta$ and $\eta$ would be obtained from the slope and intercept of the plot of the dependence of $\ln[-\ln(1-\alpha(T)]$ on $\ln(T - T_0)$.

The second model that has been proposed, is the logistic regression model represented by the following expression:

$$\alpha(T) = 1 - \frac{w}{1 + e^{a+bT}} \tag{4}$$

where $w$ is indeterminate parameter, while $a$ and $b$ are parameters of the first degree polynomial that appears in this equation.

In order to fit the kinetic conversion data using a logistic regression model, some estimation of parameters in Eq. (4) was required. Regression model gives conservation degree values which can differ from experimental data:

$$\alpha_{e,i} = \alpha_{c,i} + \varepsilon_i; \quad i = 1, 2, \ldots, n \tag{4.1}$$

where $\alpha_{e,i}$ is the experimental value of the kinetic conversion degree in the data point $i$, $\alpha_{c,i}$ is value calculated from Eq. (4) in the corresponding point, $n$ is the number of data points, and $\varepsilon_i$ are the errors, assumed to have normal distribution with zero mean and constant variance. The parameters of the model have been estimated by Levenberg–Marquardt method, that minimizes $\sum_{i=1}^{n} \varepsilon_i^2$. Detailed information about this method can be found in the literature [8].

For performing the Levenberg–Marquardt method, Origin software developed by OriginLab Corporation has been employed.

### 2.6. Differential isoconversion method

The rate of the processes in condensed state is generally, at constant pressure, a function of temperature and conversion [9]:

$$\frac{d\alpha}{dt} = \Phi(T, \alpha) \tag{5}$$

where $d\alpha/dt$ is the reaction rate, $\alpha$ is the conversion degree, $T$ is the temperature and $\Phi$ is function of $\alpha$ and $T$.

The single-step approximation employs the assumption that the function $\Phi$ in Eq. (5) can be expressed as a product of two separable functions independent of each other, the first one $k(T)$ depending solely on temperature ($T$) and the other one, $f(\alpha)$, depending solely on the conversion of the process, $\alpha$:

$$\Phi(T,\alpha) = k(T)f(\alpha) \tag{6}$$

where $k(T)$ is the rate constant, $f(\alpha)$ is the reaction model which is considered to reflect the mechanism of the process.

Combining the Eqs. (5) and (6) we get the expression for the rate of single-step process in solid state:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{7}$$

If we accept that the dependence of the rate constant on temperature can be described by the Arrhenius law:

$$k(T) = A\exp\left(-\frac{E_a}{RT}\right) \tag{8}$$

where $E_a$ is the activation energy, $A$ is the pre-exponential factor and $R$ is the gas constant,

By substitution of expression for $k(T)$ in Eq. (7) with the expression for $k(T)$ in Eq. (8), we get the equation for the rate of single step reaction:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right)f(\alpha) \tag{9}$$

For non-isothermal conditions, when $d\alpha/dt$ in Eq. (9) is replaced with $\upsilon_{h,i}(d\alpha/dT)$, where $\upsilon_{h,i}$ is the heating rate, gives the following expression:

$$\upsilon_{h,i}\left(\frac{d\alpha}{dT}\right)_{\alpha,i} = A\exp\left(-\frac{E_a}{RT}\right)f(\alpha) \tag{10}$$

For non-isothermal experiments, the process rate at all times depends on both $f(\alpha)$ and $k(T)$, and the determination of kinetic triplet $f(\alpha)$, $A$ and $E_a$, is an interlinked problem [10]. In order to determinate this triplet, various methods are applied. These methods can, in general, be classified in two categories, the so called isoconversional and isokinetic methods. The isoconversional methods require the knowledge of temperatures $T_\alpha(\upsilon_{h,i})$ at which an equivalent stage of the process occurs for various heating rates. The equivalent stage of the process is defined as the stage with the same degree of conversion.

Linearization of Eq. (10) gives Eq. (11) which presents the basic of the differential isoconversion method of Friedman [11]:

$$\ln \upsilon_{h,i}\left(\frac{d\alpha}{dT}\right)_{\alpha,i} = \ln[A_\alpha f(\alpha)_i] - \frac{E_{a,\alpha}}{RT_{\alpha,i}} \tag{11}$$

where the subscript $\alpha$ designates values related to a given conversion and $i$ is an ordinal number at the experimental conducted at the heating rate $\upsilon_{h,i}$.

If we assume that the $f(\alpha)$ is independent on $\alpha$ for constant $\alpha$, plot of $\ln \upsilon_{h,i}(d\alpha/dT)_{\alpha,i}$ on the $(1/T_i)$ obtained from curves recorded at several heating rates should be a straight line whose slope gives the value of activation energy for different degrees of conversion.

## 3. Results and discussion

The experimentally obtained conversion curves (the dependence of $\alpha$ on $T$) at different heating rates for dehydration process of the PAM hydrogel are given in Fig. 1.

Conversion curves, at any heating rate, have sigmoid, asymmetric shape. The increase in heating rate causes the increase of asymmetry degree of the curve and shifts the inflection and the final temperatures on the conversion curve.

Bearing in mind the results obtained in the study of non-isothermal dehydration of poly(acrylic acid) hydrogel [5], the possibility of fitting the experimental conversion curves using Weibull distribution function (Eq. (2)) has been examined.

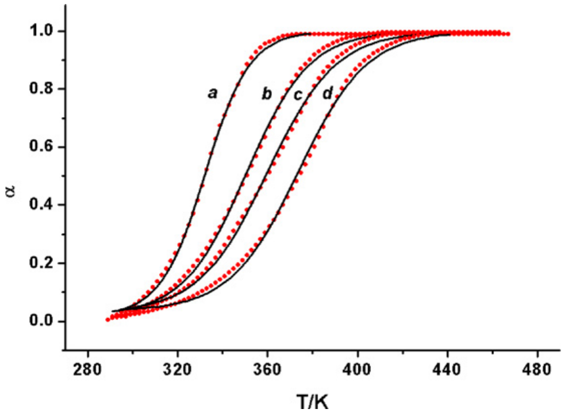

**Fig. 1.** Conversion curves of non-isothermal dehydration of PAM hydrogel at different heating rates (dots) and their mathematical fittings using logistic function (line): (a) $\upsilon_h = 5\,K\,min^{-1}$; (b) $\upsilon_h = 10\,K\,min^{-1}$; (c) $\upsilon_h = 20\,K\,min^{-1}$; (d) $\upsilon_h = 30\,K\,min^{-1}$.

Fig. 2 represents the plot of $\ln[-\ln(1-\alpha(T))]$ on $\ln(T-T_0)$ at different heating rates.

Since the dependence of $\ln[-\ln(1-\alpha(T))]$ on $\ln(T-T_0)$, at all examined heating rates of the system, shows severe deviation from linearity, it can be concluded, with great accuracy, that the Weibull distribution function cannot be used for mathematical description of non-isothermal dehydration of PAM hydrogel, opposite to dehydration of PAA hydrogel.

Bearing in mind sigmoid shape of the dehydration conversion curves and impossibility of their mathematical description using the distribution function of Weibull, in agreement with Brown et al, we investigated the possibility of using a logistic function (Eq. (4)) to describe dehydration conversion curves. [12].

Fig. 1 depicts a fitting of experimentally obtained conversion curves for dehydration of hydrogel at different heating rates, using logistic function. It is obvious from Fig. 1 that logistic function mathematically describes experimental conversion curves, at all examined heating rates, rather well. A change of values of logistic function parameters ($w$, $a$, $b$) with variation of heating rate $\upsilon_h$ and corresponding $R^2$ values (where $R$ is the correlation coefficient) are shown in Table 2.

The change of the parameters of logistic function with the change in heating rate is complex. The parameters $w$ and $b$ decreases with the increase in the heating rate. The parameter $a$ has a maximum value at $\upsilon_h = 20\,K\,min^{-1}$.

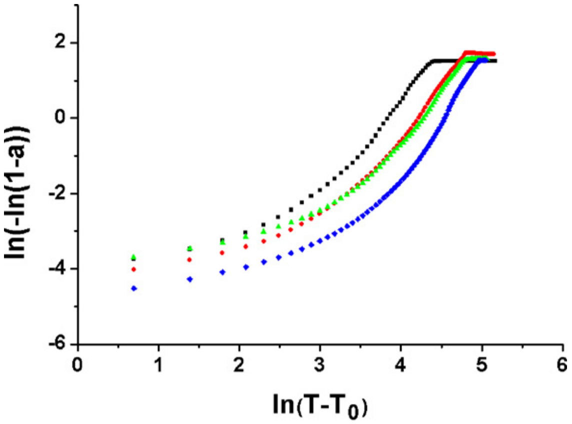

**Fig. 2.** Dependence of $\ln[-\ln(1-\alpha(T)]$ on $\ln(T-T_0)$ at different heating rates: (black) $\upsilon_h = 5\,K\,min^{-1}$; (red) $\upsilon_h = 10\,K\,min^{-1}$; (green) $\upsilon_h = 20\,K\,min^{-1}$; (blue) $\upsilon_h = 30\,K\,min^{-1}$ (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

**Table 2**
Influence of heating rate on logistic function parameter values and corresponding $R^2$ values between experimental data and the logistic regression model prediction.

| Heating rate (K min$^{-1}$) | $w$ | $a$ | $b$ (K$^{-1}$) | $R^2$ |
|---|---|---|---|---|
| 5 | 0.98088 | −33.58896 | 0.10111 | 0.99915 |
| 10 | 0.97944 | −25.08131 | 0.07156 | 0.99881 |
| 20 | 0.97028 | −23.69658 | 0.06583 | 0.99835 |
| 30 | 0.96448 | −24.62014 | 0.06586 | 0.99811 |

Logistic function is widely used for modeling processes of growth in various fields: ecology (population growth), medicine (growth of tumors, hemoglobin release), biology (growth of bacteria), physics (Fermi distribution), etc.

Naya et al. [13], Cao et al. [14], Barbadillo et al. [15], and Cai et al. [16], used logistic function for modeling non-isothermal kinetics of polymer degradation and pyrolysis of cellulose but without any explanation of its physical meaning in its application on modeling a non-isothermal kinetics.

By formal mathematical analyses of numerous expressions which describe kinetics of chemical reactions and physico-chemical processes in solid state, it is relatively easy to show that logistic function is most similar to Prout–Tompkins equation [17] which is developed to describe kinetics of isothermal decomposition of potassium permanganate.

By comparative analyses of expressions for reaction rate which can be described by Prout–Tompkins equation (Eq. (12)):

$$\frac{d\alpha}{dt} = \alpha(k_B - k_T\alpha) \tag{12}$$

and by logistic function:

$$\frac{d\alpha}{dt} = \upsilon_h b\alpha\left(1 - \frac{\alpha}{w}\right) \tag{13}$$

It is possible to make relationship between constants of Prout–Tompkins equation and parameters of logistic function ($b$ and $w$):

$$b = \frac{k_B}{\upsilon_h} \tag{14}$$

$$w = \frac{k_B}{k_T} \tag{15}$$

where $k_B$ is the rate constants of nucleus branching and $k_T$ is the rate constants of nucleus termination.

Table 3 presents effect of heating rate on the rate constants of nucleus branching and termination.

The increase in heating rate leads to the increase in the rate constants of both nucleus branching and termination. At same heating rate, rate constants of termination are higher than the constants for nucleus branching.

Eqs. (14) and (15) enable finding a physical meaning of the parameters of logistic function ($b$ and $w$). According to them parameter $b$ is proportional to the rate constant of nucleus branching and parameter $w$ is proportional to the ratio of rate constant of nucleus branching and rate constant of nucleus termination.

The established relationships between rate constants of Prout–Tompkins equation and parameters of logistic function, give one a possibility to assume kinetics model of a reaction, or a process, which can be formally described by the logistic function.

**Table 3**
Effect of heating rate on the rate constants of nucleus branching and termination.

| $\upsilon_h$ (K min$^{-1}$) | $k_B$ (min$^{-1}$) | $k_T$ (min$^{-1}$) |
|---|---|---|
| 5 | 0.505 | 0.515 |
| 10 | 0.716 | 0.731 |
| 20 | 1.316 | 1.356 |
| 30 | 1.974 | 2.047 |

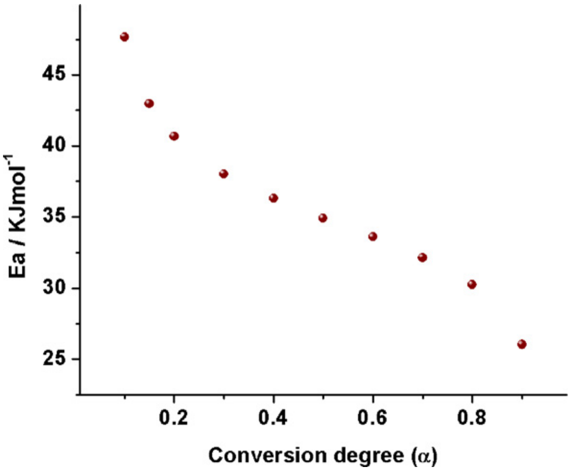

**Fig. 3.** Dependence of $E_{a,\alpha}$ on $\alpha$.

Therefore, logistic function can be used to describe process which consist of three elementary kinetics stages: nucleation, autocatalysis and termination.

During the stage of nucleation, clusters of products molecules with defined sizes are formed. After clusters formations reaction proceeds further. In autocatalytic stage, concentrations of cluster multiplies without growth of their sizes which is the reason for abrupt increasing of the process rate which achieve maximal value. In the termination stage, clusters concentrations decrease due to various processes which leads to slowing down of the process rate.

Keeping in mind that swollen hydrogel is fluctuating structure which is at the beginning of the dehydration in a viscoelastic state [18], based on the previously exposed kinetics model, it is possible to suggest the following mechanism of dehydration.

Dehydration of swollen hydrogel does not begin with the desorption of the absorbed molecules of water but by destroying ordered microblocks in the hydrogel structure. Due to that free hydrated segment of polymer chains are formed. The water absorbed on hydrated clusters is easily released in the form of water clusters. Dehydrated free segments interact with the residual microblocks in the hydrogel structure and form novel microblocks with less dimensions and less ordered. Due to that, concentration of the free hydrated segment rapidly increases and so the rate of dehydration abruptly increase. Complete destruction of the ordered and disordered microblocks in the hydrogels structure leads to the decreasing concentration of the free hydrated segments and so dehydration rate begins to decrease.

Because the formerly exposed kinetics model of dehydration of the PAM hydrogel implies on kinetics complexity of the investigated dehydration in conditions of continual heating, dependence of activation energy ($E_{a,\alpha}$) on the dehydration degree was established by application of isoconversional method.

In order to examine kinetic complexity of dehydration by isoconversion method [19], the change in activation energy with dehydration degree has been determined. Fig. 3 represents the established dependence of $E_{a,\alpha}$ on $\alpha$ for the dehydration of PAM hydrogel.

As can be seen from Fig. 3, activation energy of dehydration complexly changes with the increase in dehydration degree. In the range of $0 < \alpha \leq 0.25$ activation energy nonlinearly decrease from the value of $E_{a,\alpha} \sim 55$ kJ mol$^{-1}$ to 38.8 kJ mol$^{-1}$. In contrast to this, for $\alpha > 0.25$ $E_{a,\alpha}$ almost linearly decreases with the increase in dehydration degree from 38.8 to 25 kJ mol$^{-1}$.

The established changes in activation energy, with previously exposed model of dehydration kinetics in mind, can be explained as follows.

Keeping in mind the previously exposed model of the non-isothermal dehydration mechanism and due to the higher value of activation energy at the beginning of the process than the value of enthalpy of water evaporation and to the decreasing activation energy with the degree of dehydration, we can assume that the rate of structural rearrangement (structural relaxation) has dominant influence on the kinetics of dehydration. This assumption and the fact that the hydrogel is in viscoelasatic state at the beginning of the dehydration process, enable us to assume that for the low dehydration degrees ($0 \leq \alpha \leq 0.25$) dominant effect on the dehydration process has the so-called slow relaxation mechanisms (λ, φ and δ) [20,21]. Since, during the dehydration, decrease in the hydrogel's volume and the size of kinetic unit and activation energy of dehydration take place, it is logical to expect, for $\alpha > 0.25$, that relaxation mechanism changes and the dominant effect on the kinetics have the so called fast relaxation mechanisms (α and β) [22,23].

Because the mobility of various structural elements of hydrogel is defined by the different values of relaxation times, the relaxation times were calculated on the basis of the dimensions of kinetic unit (size of cooperatively rearranging region), denoted with $l$, and its effectively volume (volume of cooperatively rearranging region) of hydrogel in certain stage of dehydration, denoted with $\omega_u$, by using the equations:

$$\tau_o = \left(\frac{\omega_u \rho}{6kT}\right)^{1/2} \qquad (16)$$

$$\tau = \tau_o \exp\left(\frac{E_a}{RT}\right) \qquad (17)$$

where $k$ is Boltzman constant, $\rho$ is hydrogel density and $\tau_o$ is oscillation period of kinetic unit.

Therefore, for low dehydration degrees dominant effect on the kinetics of dehydration have the so called λ-relaxation mechanisms connected with changed mobility of the segments which are involved in the submolecular hydrogel structure.

Characteristic values of kinetics parameters of α-relaxation for the dehydration of the PAM hydrogel are: linear dimension of the kinetic unit $l$ = 25–50 nm, activation energy of dehydration $E_a$ = 55–50 kJ mol$^{-1}$ and the time of relaxation $\tau$ = 0.6–1.3 10$^2$ s.

When, $0.1 \leq \alpha \leq 0.25$ dominant effects on the kinetics of dehydration have the so called α-relaxation mechanisms connected with the changes in the mobility of the free segments of polymer chain in hydrogel network.

Characteristic values of kinetics parameters of α-relaxation for the dehydration of the PAM hydrogel are $l$ = 2–3 nm, $E_a$ = 50–41 kJ mol$^{-1}$ and $\tau$ = 1.3–1.6 10$^{-4}$ s.

The β-relaxation mechanisms connected with the changes in the mobility of the side-chain groups of polymer chain in hydrogel network has dominant effects on the kinetics of dehydration for the dehydration degrees of $\alpha > 0.25$.

Characteristic values of kinetics β-relaxation parameters for the dehydration of the PAM hydrogel are $l$ = 0.4 nm, $E_a$ = 39–25 kJ mol$^{-1}$ and the time of relaxation $\tau$ = 1–310$^{-7}$ s.

Determined possibility of almost complete mathematical description of non-isothermal conversion curves of PAM dehydration (Eq. (4)) enables a derivation of the equation which functionally describes the change of activation energy with the change in temperature.

By definition:

$$E(\alpha, T) = RT^2 \frac{d\alpha'/dT}{\alpha'} \qquad (18)$$

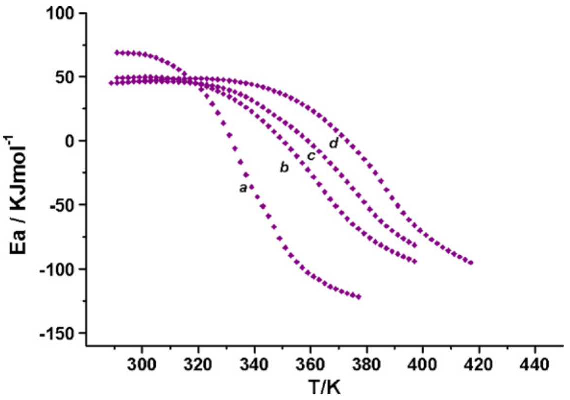

**Fig. 4.** Dependence of activation energy on temperature at various heating rates: (a) $\upsilon_h = 5\,\mathrm{K\,min^{-1}}$; (b) $\upsilon_h = 10\,\mathrm{K\,min^{-1}}$; (c) $\upsilon_h = 20\,\mathrm{K\,min^{-1}}$; (d) $\upsilon_h = 30\,\mathrm{K\,min^{-1}}$.

where $\alpha'$ is the rate of the process.Since:

$$\alpha' = \upsilon_h \frac{d\alpha}{dT} = \upsilon_h b\alpha\left(1 - \frac{\alpha}{w}\right) \qquad (19)$$

and

$$\alpha'' = b\alpha'\left(1 - \frac{2\alpha}{w}\right) \qquad (20)$$

it is easy to derive the functional dependence of activation energy on both, temperature and conversion degree (Eq. (21)).

$$E_a(\alpha, T)_{\upsilon_{h,i}} = RT^2 b\left(1 - \frac{2\alpha}{w}\right) \qquad (21)$$

Fig. 4 shows the change of activation energy with the change in temperature at all examined heating rates.

As seen from Fig. 4, the effective activation energy decreases with the increase in dehydration temperature. There are two distinctive temperature regions on the plot of activation energy versus temperature, for all heating rates, in which activation energy has positive or negative values. The two regions are separated by the temperature of the maximum dehydration rate ($T_{max}$) at which the value of $E_a$ approaches to zero. With the increase in heating rate the $T_{max}$ value shifts toward higher temperatures.

The established rapid, non-linear decrease in positive value of activation energy with the increase in temperature in one temperature region, and linear decrease of activation energy with the increase in temperature in the other temperature region, are in agreement with the Williams, Landel, Ferry theory [24] and confirm the existence of structural transformation of hydrogrel from viscoelastic to glassy state.

In the temperature region where the values of activation energy are negative, it is also easy to observe linear decrease of activation energy with the increase in temperature. The existence of temperature regions with negative values of activation energy is also found in works of Vyazovkin et al. [25–27]. Negative value of activation energy in certain temperature region, in the cases of non-isothermal crystallization of PET and PEN polymers is explained by Hoffman–Lauretzen theory. In contrast to that, the existence of negative value of activation energy in the case of gelatin gelation is explained by the decrease of free energy barrier of nucleation with the decrease in temperature. Negative values of activation energy for the PAM hydrogel dehydration in certain temperature region is a consequence of the decrease of dehydration rate with the increase in temperature, which is caused by the change in the relaxation mechanism of the hydrogel during the dehydration at that temperatures.

## 4. Conclusions

An introduction of methacrylic acid co-monomer into the poly(acrylic acid) polymer network leads to the significant changes in the non-isothermal dehydration of the hydrogel. Conversion curves of the non-isothermal dehydration of the PAM hydrogel, under the different heating rates, can be in entire mathematically described by logistic regression function. Parameter *b* of logistic function is proportional to the rate constant of multiplication of cluster products while the parameter *w* is proportional to the ratio of rate constant of cluster multiplication and rate constant of cluster termination. Kinetics of non-isothermal dehydration of the PAM hydrogel is a complex kinetic process which consists of three elementary stages, nucleation autocatalytic and termination. Dominant effect on dehydration rate for certain dehydration degree has rate of structural rearrangement. Negative value of activation energy, in certain temperature interval of hydrogel dehydration, is a consequence of negative temperature dependence of dehydration rate which is caused by the type of relaxation mechanism of structural recovery of the hydrogel.

## Acknowledgement

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