ELSEVIER

Chemical Engineering Journal 130 (2007) 11–17

Chemical Engineering Journal

www.elsevier.com/locate/cej

Normalized Weibull distribution function for modelling the kinetics of non-isothermal dehydration of equilibrium swollen poly(acrylic acid) hydrogel

B. Adnađević*, B. Janković, Lj. Kolar-Anić, D. Minić

Faculty of Physical Chemistry, University of Belgrade, Studentski Trg 12-16, P.O. Box 137, 11001 Belgrade, Serbia and Montenegro

Received 1 September 2006; received in revised form 6 November 2006; accepted 15 November 2006

Abstract

The possibility of applying the normalized Weibull distribution function of reaction times (WDt), for kinetic description of the non-isothermal dehydration of equilibrium swollen poly(acrylic acid) hydrogel, was investigated. It was found, that the dehydration conversion curves at different heating rates, may be successfully described by the Weibull distribution function of reaction times, in wide range of the degree of conversion ($\alpha = 0.12$–0.93). Also, it was found, that the increasing of heating rate leads to the exponentially increasing of Weibull distribution parameters (scalar (η) and shape (β) parameters). The procedure for kinetics parameters determination of hydrogel dehydration process and determination of the density distribution function of activation energies, based on the known normalized Weibull distribution of reaction times was exhibited. The obtained values of kinetics parameters calculated by the procedure mentioned above are in agreement with values of kinetics parameters, obtained using the stationary point (SP) and isoconversional methods.

Keywords: Weibull distribution function; Non-isothermal dehydration; Kinetics; Density distribution function; Poly(acrylic acid) hydrogel

1. Introduction

Hydrogels may be conveniently described as hydrophilic polymers that are swollen by, but not dissolved in water. They are three-dimensional cross-linked polymeric structures that are able to swell in the aqueous environment. Due to characteristic properties such as swellability in water, hydrophilicity, biocompatibility, and lack of toxicity, hydrogels have been utilized in a wide range of biological, medical and pharmaceutical applications [1].

The most important properties of hydrogels are their swelling capacity and swelling behavior, their mechanical properties and also dehydration behavior. These properties will be affected on usability of hydrogels in various applications. Although, the swelling behavior, swelling kinetics and mechanical properties of various types of hydrogels are extensively studied [2–12], but there are no available apparent investigations concerning on the kinetics and mechanism of hydrogel dehydration.

In the paper of Jovanović et al. [13], applying the non-isothermal Friedman isoconversional method (FR method) [14] to the poly(acrylic acid) hydrogel dehydration, it was established that the activation energy of the dehydration process depends on the degree of dehydration (α) and vary within the range from 98.2 to 11.2 kJ mol^{-1}. On the contrary to that, Janković et al. [15] determined the single value of the apparent activation energy (E_a) and pre-exponential factor (A), which depended only on the heating rate ($E_a = 38.6$–59.7 kJ mol^{-1} and $A = 4.55 \times 10^4$–7.47×10^7 min^{-1}), applying different kinetic methods such as Kissinger [16], Coats–Redfern [17], vanKrevelen et al. [18] and Horowitz–Metzger [19].

The possibility of applying the Weibull distribution function (WDf) for description of non-isothermal conversion curves, and determination of the kinetics parameters of dehydration process of poly(acrylic acid) hydrogel were investigated in this paper.

2. Experimental

2.1. Materials and methods

Super-absorbing cross-linked poly(acrylic acid) hydrogel, which has been applied for this investigation was synthesized

---

* Corresponding author. Tel.: +381 11 187 133; fax: +381 11 187 133.
E-mail address: bora@ffh.bg.ac.yu (B. Adnađević).

1385-8947/$ – see front matter
doi:10.1016/j.cej.2006.11.007

using the procedure based on the simultaneous radical polymerization of acrylic acid and cross-linking of the formed poly(acrylic acid), according to general procedure described in previous work [13]. For that process, acrylic acid monomer, initiators $Na_2S_2O_8$, $Na_2S_2O_5$, H_2O and cross-linking agent *N*,*N*′-methylenebisacrylamide (NMBA) were used. Equilibrium swelling degree (SD_{eq}) of the used hydrogel in distilled water at 25 °C was 8500%, determined by standard method based on weight difference of dry and swollen sample [2].

2.2. 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 $10\,\mathrm{ml\,min^{-1}}$. Experiments were performed at heating rates of 5, 10 and $20\,\mathrm{K\,min^{-1}}$, 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.

3. Methods for determination of kinetics parameters of the process

3.1. Stationary point (SP) method

In the heterogeneous chemical reaction kinetics, function $d\alpha/dt = f(T)$ (where $d\alpha/dt$ is the velocity of process and T is the absolute temperature), which have zero-initial velocity can be observed as functions with local maximum. This maximum appears in the so called stationary point: $S[(d\alpha/dt)_{max}, T_{max}]$ (T_{max} is the temperature at the maximal velocity of process $(d\alpha/dt)_{max}$), where $(d^2\alpha/dt^2) = 0$ [20]. Consequently, stationary point is defined as a point in which the reaction system, under given conditions, have maximal reaction velocity. In that case, the following equation is valid:

$$\left(\frac{d\alpha}{dt}\right)_{max} = k(T, p_j) f(\alpha_{max}), \tag{2}$$

where $(d\alpha/dt)_{max}$ is maximal velocity of considered reaction or process, $k(T, p_j)$ the temperature and partial pressure dependent rate constant, $f(\alpha_{max})$ a function of reaction mechanism at α_{max} value, α_{max} the degree of conversion at $T = T_{max}$, and p_j denotes the partial pressure of the gaseous products. For non-isothermal conditions, when the temperature varies with time with a constant heating rate $v_h = dT/dt$, Eq. (2) can be written in the form:

$$\left[v_h \left(\frac{d\alpha}{dT}\right)_{max}\right] = k(T, p_j) f(\alpha_{max}). \tag{3}$$

If Arrhenius dependence of $[k(T, p_j)]$ on temperature is supposed, Eq. (3) can be transformed in the following form:

$$\left[v_h \left(\frac{d\alpha}{dT}\right)_{max}\right] = A \exp\left(-\frac{E_a}{RT_{max}}\right) f(\alpha_{max}) \tag{4}$$

where E_a is the apparent activation energy of the overall process, whereas A and R are the pre-exponential factor and gas constant, respectively. Since the logarithmic form of Eq. (4) is

$$\ln\left[v_h \left(\frac{d\alpha}{dT}\right)_{max}\right] = \ln[A f(\alpha)_{max}] - \frac{E_a}{RT_{max}}, \tag{5}$$

and from the slope of the dependence between $\ln[v_h(d\alpha/dT)_{max}]$ and $1/T_{max}$, it is possible to determine the value of the apparent activation energy E_a of the investigated process. However, method of the stationary point does not enable directly calculation of the pre-exponential factor (A). The value of the pre-exponential factor (A) can be determined only in the case when the exact mathematical form of the function $f(\alpha_{max})$ is known [20]. Furthermore, by this method we obviously can obtain only one activation energy, the one that can be calculated comparing the $(d\alpha/dt)_{max}$ at different temperatures and which corresponds to α_{max} (the degree of conversion at $T = T_{max}$).

3.2. Friedman (FR) method

The differential isoconversional method suggested by Friedman [14] is based on the general kinetic equation in following form:

$$v_h \frac{d\alpha}{dT} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha). \tag{6}$$

where $d\alpha/dT$ is the rate of process at any α, and $f(\alpha)$ is the differential conversion function (reaction model). This method is based on Eq. (6) in logarithmic form and leads to:

$$\ln\left[v_{h,i} \left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = \ln[A_\alpha f(\alpha)_i] - \frac{E_{a,\alpha}}{RT_{\alpha,i}} \tag{7}$$

where subscripts i and α designates a given value of heating rate and the degree of conversion, respectively. For $\alpha = \text{const.}$, the plot $\ln\left[v_{h,i}(d\alpha/dT)_{\alpha,i}\right]$ versus $(1/T_{\alpha,i})$ should be a straight line whose slope can be used to evaluate the apparent activation energy. By this method, as well as by the previous one, the value of the pre-exponential factor (A) can be determined only in the case when the exact mathematical form of the function $f(\alpha)$ is known. However, here, on the contrary to the previous method, we can get different values of activation energies for a process depending on α.

4. Results and discussion

The experimentally obtained conversion curves at different heating rates for dehydration process of poly(acrylic acid) hydrogel are given in Fig. 1.

All the conversion (α–T) curves are asymmetric. Values of the initial temperature (T_i), the inflection temperature (T_p), the final temperature (T_f) and total mass loss (Δm_f or m_f) of the sample,

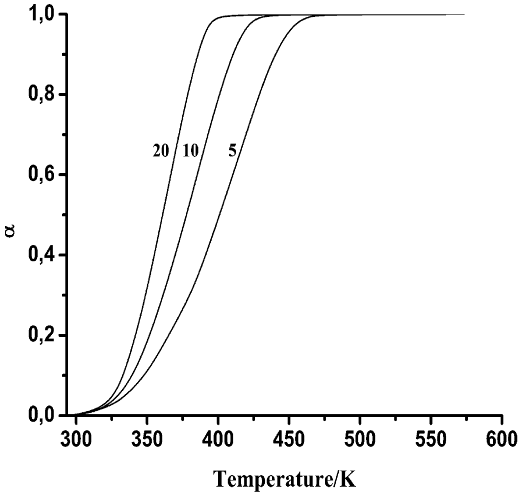

Fig. 1. The conversion (α–T) curves of non-isothermal dehydration of poly(acrylic acid) hydrogel at different heating rates (5, 10 and 20 K min^{-1}) (from right to left).

Table 1
Values of T_i, T_p, T_f and Δm_f for dehydration of equilibrated poly(acrylic acid) hydrogel determined by thermogravimetric analysis at different heating rates

υ_h (K min^{-1})	T_i (K)	T_p (K)	T_f (K)	Δm_f (%)
5	333	402	523	1.75
10	328	383	463	1.75
20	323	363	433	1.75

from conversion curves at various heating rates are presented in Table 1.

Increasing of heating rate leads to the decrease of all characteristic temperature values on the obtained conversion curves, but total mass loss of the samples is independent from the heating rates.

The differential conversion curves of hydrogel dehydration, obtained from the experimental α–T curves at different heating rates are shown in Fig. 2.

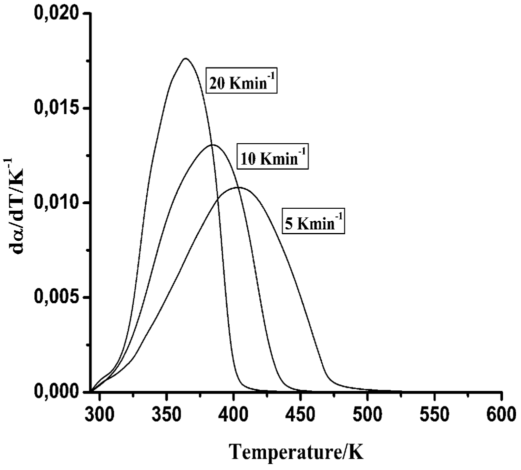

Fig. 2. The differential conversion ($d\alpha/dT - T$) curves of non-isothermal dehydration of poly(acrylic acid) hydrogel at different heating rates.

Table 2
Values of $T_{\max}$ (Fig. 2) and corresponding kinetics parameters obtained by stationary point (SP) method, at different heating rates for dehydration of poly(acrylic acid) hydrogel

υ_h (K min^{-1})	$T_{\max}$ (K)	E_a (kJ mol^{-1})	ln[$Af(\alpha_{\max})$], A (min^{-1})
5	402		
10	383	39.5	10.75
20	363		

The values of temperature $T_{\max}$, at which the velocity of dehydration has the maximal value $((d\alpha/dT)_{\max})$ (Fig. 2) and the values of kinetics parameters, E_a and ln[$Af(\alpha_{\max})$], obtained by stationary point (SP) method, are shown in Table 2.

Assuming that the reaction times of dehydration process are randomly distributed by the laws of Weibull distribution function, and assuming that the value of Weibull distribution function of reaction times is proportional to the degree of conversion (α), it can be written:

$$\alpha(t) = F = 1 - \exp\left[-\left(\frac{t-\gamma}{\eta}\right)^{\beta}\right], \tag{8}$$

where F is the cumulative Weibull distribution function, t the time, whereas β, η and γ are the shape, scalar and location parameters, respectively. The location parameter γ is often equal to zero. The fact that in such cases, time evolution of the process follows any probability function is ascribed to the nonuniform distribution of the free energies of active centers at the interface where considered reaction take place [21–24].

Moreover, in the thermogravimetry there is functional relation between the time (t) and temperature (T) defined by the selected form of the heating rate. If this relation is linear, as it is in the case considered here,

$$t = \frac{T - T_0}{\upsilon_h}, \tag{9}$$

where T_0 is the temperature of the system at the beginning of the process and υ_h is the heating rate, the time dependent degree of conversion, $\alpha(t)$, can be written as a function of temperature such that

$$\alpha(T) = 1 - \exp\left[-\left(\frac{T - T_0 - \upsilon_h\gamma}{\upsilon_h\eta}\right)^{\beta}\right]. \tag{10}$$

The last equation is applied for the analysis of the considered results, where $\alpha(t)$ is the degree of conversion of the studied hydrogel dehydration process at a given heating rate and the relation between time and temperature is linear. We found that the location parameter γ is equal to zero in all three cases. Using linear form of Eq. (10), given by the relation:

$$\ln[-\ln(1-\alpha(T))] = \beta\ \ln\left(\frac{1}{\eta}\right) + \beta\ \ln\left(\frac{T - T_0}{\upsilon_h}\right) \tag{11}$$

We obtained the results presented in Fig. 3 and in Table 3. The approximately linear relationship is satisfied in relative wide domain of the degree of conversion (in all three cases R^2 is higher than 0.9980).

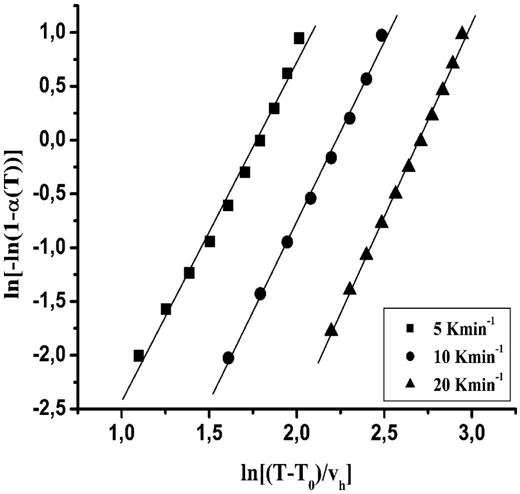

Fig. 3. The dependence of $\ln[-\ln(1-\alpha(T))]$ vs. $\ln[(T-T_0)/\upsilon_h]$ for dehydration of poly(acrylic acid) hydrogel at different heating rates: 5 K min^{-1} (■), 10 K min^{-1} (●) and 20 K min^{-1} (▲).

Obviously, the Weibull distribution function can be applied for the analysis of the considered conversion curves (Fig. 1) in the wide domain of the degree of conversion. The obtained values of the parameters β and η increase with increasing of the heating rate υ_h by the following empirical relations:

$$\beta = A + B\ e^{\upsilon_h/\theta} \tag{12}$$

$$\eta = C + D\ e^{\upsilon_h/\phi} \tag{13}$$

where A, B, C, D, θ and ϕ are corresponding fitting constants necessary to describe the relationships between mentioned parameters and heating rate. The constants A and B are dimensionless as it is the parameter β; C and D have dimensions of the parameter η, whereas θ and ϕ have dimensions of the heating rate (K min^{-1}). In the considered case: $A = 3.176$, $B = 0.133$, $\theta = 15.512$ K min^{-1}, $C = 32.610$ min, $D = 30.629$ min, $\phi = 36.622$ K min^{-1}.

If the temperature dependence of the degree of conversion is well described by Eq. (10) with $\gamma = 0$, then corresponding rate of dehydration can be given by first derivative of this function with respect to temperature. Thus, we can write

$$\frac{d\alpha}{dT} = \frac{\beta}{\upsilon_h \eta}\left(\frac{T-T_0}{\upsilon_h \eta}\right)^{\beta-1} \exp\left[-\left(\frac{T-T_0}{\upsilon_h \eta}\right)^{\beta}\right]. \tag{14}$$

Since time and temperature are directly correlated by Eq. (9), the kinetic Eq. (14) is used for description of the process of dehydration of poly(acrylic acid) hydrogel (Fig. 4).

Table 3
The linear domains of α ($\Delta\alpha$) and the parameters β and η of the Weibull distribution function with γ equal to zero, obtained for the dehydration of poly(acrylic acid) hydrogel at different heating rates with corresponding values of R^2

υ_h (K min^{-1})	$\Delta\alpha$	R^2	β	η (min)
5	0.15–0.93	0.9981	3.36	5.89
10	0.12–0.93	0.9987	3.43	9.30
20	0.13–0.92	0.9989	3.66	14.87

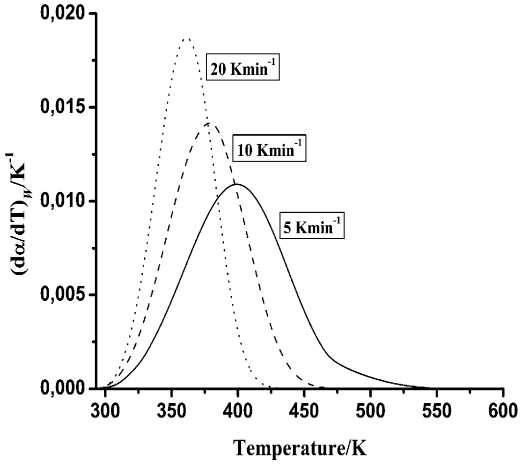

Fig. 4. The differential conversion ($(d\alpha/dT)_W - T$) curves of non-isothermal dehydration of poly(acrylic acid) hydrogel at different heating rates, based on the Weibull distribution function (WDf) with parameters in Table 3.

We can see that the maximum of the curve, $(d\alpha/dT)_{\max}$, depends of the heating rate, υ_h. The value of $T_{\max}$, obtained when the first derivative of Eq. (14) is equal to zero, is given by the relation

$$T_{\max} = \upsilon_h \eta \left[\frac{\beta-1}{\beta}\right]^{1/\beta} + T_0 \tag{15}$$

The corresponding value of $(d\alpha/dT)_{\max}$ is given by the expression

$$\left(\frac{d\alpha}{dT}\right)_{\max} = \frac{\beta}{\upsilon_h \eta}\left[\frac{\beta-1}{\beta}\right]^{\beta-1/\beta} \exp\left\{-\left[\frac{(\beta-1)}{\beta}\right]\right\} \tag{16}$$

The values for $T_{\max}$ and $(d\alpha/dT)_{\max}$ depend on heating rate since β and η are functions of them (Table 4).

It is obvious that the values for $T_{\max}$ are equal to the corresponding ones for temperatures of inflection points, T_p, given in Table 1, what would be if the experimental points are well fitted by the Weibull distribution function.

Since we have shown above that the experimentally obtained conversion curves are well fitted by the Weibull distribution function, we can also calculate the activation energies at different values for α, where α is taken from the mentioned function. For this purpose, we apply the Friedman's method (Eq. (7)). The isoconversion lines obtained by the Friedman's method at different values of the degree of conversion, α, where α is in the interval $0.05 \leq \alpha \leq 0.98$, are given in Fig. 5. Also, in the same figure, the symbols designate the values of corresponding magnitudes on the left-hand and right-hand sides of Friedman's equation (Eq. (7)), at three different heating rates.

Table 4
Values of $T_{\max}$ and $(d\alpha/dT)_{\max}$ obtained by using the Eqs. (15) and (16) for dehydration of poly(acrylic acid) hydrogel at different heating rates

υ_h (K min^{-1})	$T_{\max}$ (K)	$(d\alpha/dT)_{\max}$ (K^{-1})
5	402	0.0109
10	383	0.0141
20	363	0.0187

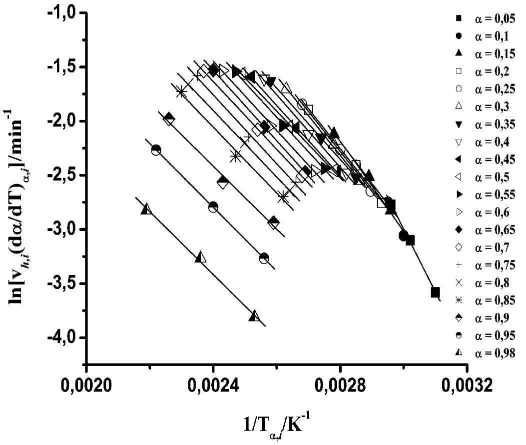

Fig. 5. The dependence of $\ln[\upsilon_{\mathrm{h},i}(\mathrm{d}\alpha/\mathrm{d}T)_{\alpha,i}]$ vs. $(1/T_{\alpha,i})$ at the different values of α, for dehydration of poly(acrylic acid) hydrogel (solid lines are linear fitting corresponding to different α).

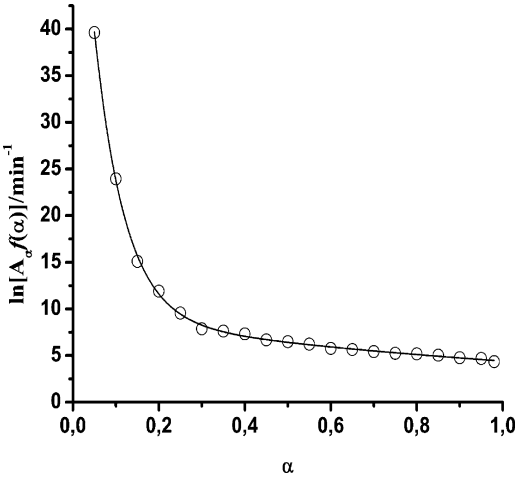

Fig. 7. Isoconversional logarithmic intercepts (Eq. (7)) plotted as a function of the degree of dehydration (α), for dehydration process of poly(acrylic acid) hydrogel (solid line represent the B-Spline curve which shows the trends of logarithmic intercept values (symbols) with progress of α, calculated by Friedman method).

Figs. 6 and 7 show the calculated changes of E_a and $\ln[A_\alpha f(\alpha)]$ values with the degree of conversion (α), for dehydration of poly(acrylic acid) hydrogel dehydration. Also, in the same figures, the symbols designate corresponding values of activation energies and intercepts, which were calculated from the Friedman's equation.

The analysis of curves E_a versus α and $\ln[A_\alpha f(\alpha)]$ versus α shows two regions of the characteristic changes of E_a and $\ln[A_\alpha f(\alpha)]$ with α. In the first region ($\alpha \leq 0.3$), Friedman's method shows a rapid drop in E_a and $\ln[A_\alpha f(\alpha)]$ values, but in the second region ($\alpha \geq 0.3$), the values of E_a and $\ln[A_\alpha f(\alpha)]$ were followed by a steady slow drop. Analyzing their mutual interdependence at the same degree of conversion, we have found the following linear relation, which is satisfied for every α:

$$\ln[A_\alpha f(\alpha)] = -4.141 + 0.383E_\alpha. \tag{17}$$

Using Eq. (9), we can now obtain the time dependent relation for activation energies (Fig. 8). The numerically fitted relation between activation energy and the time is given by the expression

$$E_a = \varphi \ \ln \frac{b}{t-a} \tag{18}$$

where a, b and φ are the fitting coefficients. The coefficients a and b must have the dimensions of time, whereas φ has the dimension of energy. The fitting coefficient φ corresponds to the threshold activation energy value for the investigated dehydration process (Table 5), until the coefficients a and b (in Eq. (18)) represents the "solid" constants and they do not have any physical meaning.

The influence of heating rate (υ_h) on the values of fitting coefficients a, b and φ is shown in Table 5.

The values of fitting coefficients, a and b, increase with the increasing of heating rate of the system. On the other hand, the value of fitting coefficients φ, decrease with increasing of heating rate.

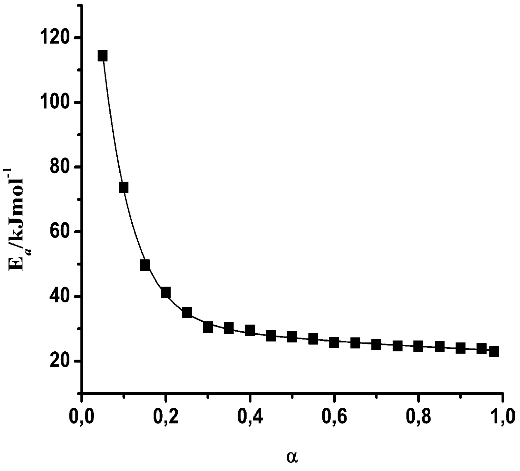

Fig. 6. The activation energy (E_a) plotted as a function of the degree of conversion (α), for dehydration process of poly(acrylic acid) hydrogel (solid line represent the B-Spline curve which shows the trends of activation energy values (symbols) with progress of α, calculated by Friedman method).

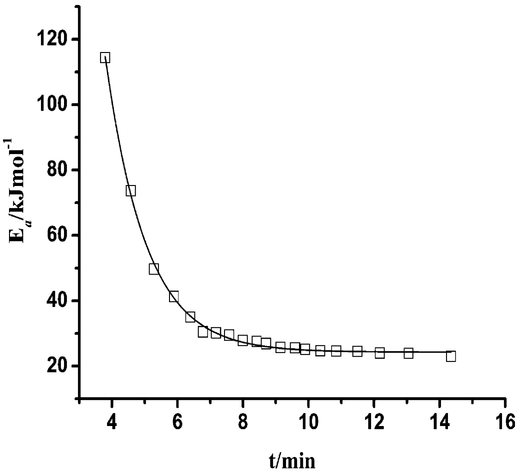

Fig. 8. Time dependent evolution of the effective activation energies (E_a) during the thermogravimetric analysis of the dehydration process of poly(acrylic acid) hydrogel (solid line represent the B-Spline curve which shows the trends of activation energy values (symbols) with progress of reaction times at different constant values of α).

Table 5
The influence of heating rate on the values of fitting coefficients a, b and φ, for dehydration process of poly(acrylic acid) hydrogel

υ_h (K min^{-1})	a (min)	b (min)	φ (kJ mol^{-1})
5	1.3201	23.1358	15.2388
10	3.0216	41.6306	13.0422
20	5.6272	65.0901	12.5823

The time dependence of activation energies can appear in very complex reaction systems or in a simple system where there is an energy distribution of active centers. In the last case we have the sum of the parallel reactions that differ only in activation energies and consequently in corresponding rate constants [25–32]. There effective value of α must depend on time or temperature (Eq. (9)) in a complex manner. Such dependence between α and temperature is already given by Eq. (14). Our next aim is to obtain $\mathrm{d}\alpha/\mathrm{d}E_\mathrm{a}$. Therefore, we need to write Eq. (14) in a function of time

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{\beta}{\eta}\left(\frac{t}{\eta}\right)^{\beta-1}\exp\left[-\left(\frac{t}{\eta}\right)^{\beta}\right], \tag{19}$$

and find $\mathrm{d}\alpha/\mathrm{d}E_\mathrm{a}$ using following relation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}E_\mathrm{a}}=\frac{\mathrm{d}\alpha}{\mathrm{d}t}\times\left|\frac{\mathrm{d}t}{\mathrm{d}E_\mathrm{a}}\right|. \tag{20}$$

From Eq. (18) we can easily obtain that

$$t=a+b\exp\left(-\frac{E_\mathrm{a}}{\varphi}\right), \tag{21}$$

and $|\mathrm{d}t/\mathrm{d}E_\mathrm{a}|$ equal to

$$\left|\frac{\mathrm{d}t}{\mathrm{d}E_\mathrm{a}}\right|=\frac{b}{\varphi}\exp\left(-\frac{E_\mathrm{a}}{\varphi}\right). \tag{22}$$

The distribution function $g(E_\mathrm{a})=\mathrm{d}\alpha/\mathrm{d}E_\mathrm{a}$ is now given in the form:

$$g(E_\mathrm{a})=\frac{b\beta}{\varphi\eta}\exp\left(-\frac{E_\mathrm{a}}{\varphi}\right)\left[\frac{a+b\exp(-E_\mathrm{a}/\varphi)}{\eta}\right]^{\beta-1}\times\exp\left\{-\left[\frac{a+b\exp(-E_\mathrm{a}/\varphi)}{\eta}\right]^{\beta}\right\}. \tag{23}$$

The influence of heating rate on the shape of density distribution function of activation energies is shown in Fig. 9.

The basic characteristics of the density distribution function of activation energies—$E_{\mathrm{a,max}}$: the value of activation energy at the maximal value of distribution function, $g(E_\mathrm{a})_{\mathrm{max}}$: the maximal value of density distribution function, $g(E_\mathrm{a})_{\mathrm{HW}}$: the value of density distribution function on the half-wide, SF: shape factor or factor of asymmetry, and HW: half-wide of the density distribution function, at different heating rates, are presented in Table 6.

From results in Table 6 and Fig. 9, the following facts existed: (a) the density distribution function of activation energies is independent from the heating rate of the system, and (b) because of that, this function is eigen characteristic of the investigated system.

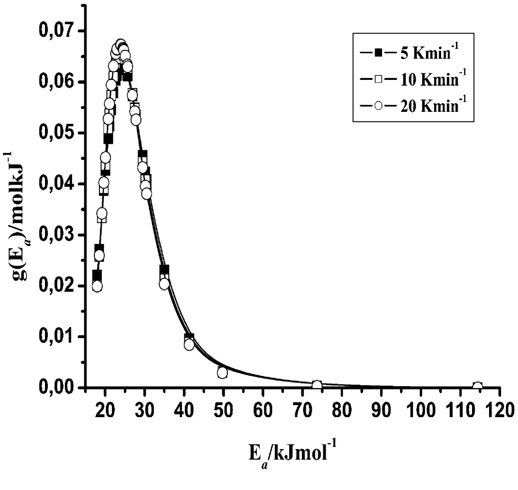

Fig. 9. The influence of heating rate on the shape of density distribution function of activation energies ($g(E_\mathrm{a})$ was calculated from Eq. (23)), for dehydration process of poly(acrylic acid) hydrogel.

Table 6
The influence of heating rate (υ_h) on the basic characteristics of the density distribution function of activation energies, $g(E_\mathrm{a})$, for dehydration process of poly(acrylic acid) hydrogel

υ_h (K min^{-1})	$E_{\mathrm{a,max}}$ (kJ mol^{-1})	$g(E_\mathrm{a})_{\mathrm{max}}$ (mol kJ^{-1})	$g(E_\mathrm{a})_{\mathrm{HW}}$ (mol kJ^{-1})	Shape factor, SF	Half-wide, HW (kJ mol^{-1})
5	23.9	0.0630	0.0425	0.7222	9.3
10	23.9	0.0659	0.0429	0.7222	9.3
20	23.9	0.0673	0.0435	0.7222	9.3

The dependence of the kinetics parameters from the degree of conversion (α) was a natural consequence of existing the distribution of activation energies, which leads to the accidental distribution of reaction times and characteristical kinetics of the investigated process.

The changes of T_{max}, $(\mathrm{d}\alpha/\mathrm{d}T)_{\mathrm{max}}$ and β, η, and φ parameters with heating rate, are consequences of different thermal activation of the considered system, which appeared because of the different heating rates.

5. Conclusions

The conversion curves of non-isothermal dehydration of poly(acrylic acid) hydrogel are fitted by the Weibull probability distribution function of reaction times (WDt), in wide range of the degree of conversion ($\alpha=0.12$–0.93).

The values of Weibull distribution parameters (β and η) increase exponentially with increasing of the heating rate of the system. Knowing the Weibull distribution function of reaction times, it is possible to determine the kinetics parameters of the investigated process and density distribution function of activation energies, $g(E_\mathrm{a})$.

The kinetical complexity of the non-isothermal dehydration of poly(acrylic acid) hydrogel is a consequence of energetical heterogenity of the desorption centers of the poly(acrylic acid) hydrogel.

Acknowledgement

The investigation was partially supported by the Ministry of Science and Environmental Protection of Serbia, under the Project 142025.

References

[1] N. Peppas, Hydrogels in Medicine and Pharmacy, vol. I: Fundamentals, CRC, Boca Raton, FL, 1986.
[2] E. Karadağ, D. Saraydin, Polym. Bull. 48 (2002) 299.
[3] D. Saraydin, Y. Caldiran, Polym. Bull. 46 (2001) 91.
[4] I. Katime, J.L. Velada, R. Novoa, E. Diaz de Apodaca, J. Puig, E. Mendizabal, Polym. Int. 40 (1996) 281.
[5] E. Karadağ, D. Saraydin, Turk. J. Chem. 26 (2002) 863.
[6] P.M. de la Torre, S. Torrado, S. Torrado, Biomaterials 24 (2003) 1459.
[7] N. Gundogan, D. Melekaslan, O. Okay, Macromolecules 35 (2002) 5616.
[8] O. Okay, S. Durmaz, Polymer 43 (2002) 1215.
[9] C. Sayil, O. Okay, Polymer 42 (2001) 7639.
[10] E.C. Muniz, G. Geuskens, Macromolecules 34 (2001) 4480.
[11] M. Ilavsky, G. Mamytbekov, Z. Sedlakova, L. Hanykova, K. Dusek, Polym. Bull. 46 (2001) 99.
[12] M. Rubinstein, R.H. Colby, A. Dobrynin, J.F. Joanny, Macromolecules 29 (1996) 398.
[13] J. Jovanović, B. Adnađević, S. Ostojić, M. Kićanović, Mater. Sci. Forum. 453–454 (2004) 543.
[14] H.L. Friedman, J. Polym. Sci. 6C (1963) 183.
[15] B. Janković, B. Adnađević, J. Jovanović, J. Therm. Anal. Calorim. 82 (2005) 7.
[16] H.E. Kissinger, Anal. Chem. 29 (1957) 1702.
[17] A.W. Coats, J.P. Redfern, Nature 201 (1964) 68.
[18] D.W. vanKrevelen, C. vanHerden, F.J. Huntjens, Fuel 30 (1951) 253.
[19] H.H. Horowitz, G. Metzger, Anal. Chem. 35 (1963) 1464.
[20] I. Klarić, U. Roje, T. Kovačić, J. Therm. Anal. Calorim. 45 (1995) 1373.
[21] Lj. Kolar-Anić, S. Veljković, S. Kapor, B. Dubljević, J. Chem. Phys. 63 (1975) 663.
[22] Lj. Kolar-Anić, S. Veljković, J. Chem. Phys. 63 (1975) 669.
[23] Lj. Kolar-Anić, V. Dondur, Z. Phys. Chem. 270 (1989) 737.
[24] P. Staszczuk, D. Sternik, V.V. Kutarov, J. Therm. Anal. Calorim. 69 (2002) 23.
[25] A.K. Burnham, R.L. Braun, Energy Fuels 13 (1999) 1.
[26] C.C. Lakshmanan, M.L. Bennett, N. White, Energy Fuels 5 (1991) 110.
[27] C.C. Lakshmanan, N. White, Energy Fuels 8 (1994) 1158.
[28] K. Miura, T. Maki, Energy Fuels 12 (1998) 864.
[29] M.J. McGuinness, E. Donskoi, D.L.S. McElwain, Appl. Math. Lett. 12 (1999) 27.
[30] C. Ulloa, A.L. Gordon, X. García, J. Anal. Appl. Pyrolysis 71 (2004) 465.
[31] A.K. Burnham, R.K. Weese, B.L. Weeks, J. Phys. Chem., B 108 (2004) 19432.
[32] A.K. Burnham, Chem. Eng. J. 108 (2005) 47.