ISOTHERMAL KINETICS OF DEHYDRATION OF EQUILIBRIUM SWOLLEN POLY(ACRYLIC ACID) HYDROGEL

B. Janković^{*}, B. Adnađević and J. Jovanović

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

An isothermal dehydration of equilibrium swollen poly(acrylic acid) hydrogel in the temperature range from 306 to 361 K was investigated. The specific parameters connected with shape of the conversion curves were defined. The activation parameters (E, lnA) of the isothermal dehydration of equilibrium swollen poly(acrylic acid) hydrogel were calculated, using Johnson–Mehl–Avrami (JMA), 'initial rate' and 'stationary point' methods. The reaction models for the investigated dehydration are determined using the 'model-fitting' method. It was established that both, the reaction model and activation parameters of the hydrogel dehydration were completely different for the isothermal process than for the non-isothermal one. It was found that the increase in dehydration temperature lead to the changes in isothermal kinetic model for the investigated hydrogel dehydration. It was established that the apparent activation energy (E) of hydrogel dehydration is similar to the value of the molar enthalpy of water evaporation.

Keywords: activation energy, dehydration, isothermal kinetics, poly(acrylic acid) hydrogel

Introduction

Hydrogels may be conveniently described as hydrophilic polymers that are swollen by, but not dissolve in water. They are three-dimensional crosslinked 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, pharmaceutical and environmental applications [1]. The most important properties of hydrogels are their swelling capacity and swelling behaviour, their mechanical properties and also dehydration behaviour. These properties will be effected hydrogel usability in various applications. Although, the swelling behaviour and swelling kinetics of various types of hydrogels are extensively studied [2-6], but there are much lesser information's concerning the kinetics of hydrogel dehydration.

Janković *et al.* [7] were investigated the non-isothermal kinetics of the dehydration of equilibrium swollen poly(acrylic acid) (PAA) hydrogel, where different kinetic methods such as Kissinger, Coats–Redfern, van-Krevelen and Horowitz–Metzger were applied and the activation parameters (E, lnA, n) of the hydrogel dehydration have been determined. Then, it was concluded that in the wide range of considered dehydration (degree of dehydration, α =0.15–0.99), the activation parameters of dehydration were independent on the degree of dehydration. The values of the activation parameters (E, lnA) which were determined under the same heating rate and using different methods are in good agreement one with each others. Also, it was found that independently from the applied method, the values of the activation parameters (E, $\ln A$) decreases with increase of the heating rate.

In addition, in our recent paper [8], the non-isothermal dehydration of equilibrium swollen poly(acrylic acid) hydrogel was analyzed by the model-free kinetic approach. It was concluded [8], that for $0 \le \alpha \le 0.50$, dehydration under considered conditions is complex, which probably involving a combination of several processes. The same authors were shown that one of this processes probably involve the diffusion of water molecules, which is submitted to the three-dimensional diffusion (Jander) mechanism (D3). In addition, it was concluded that the observed constant – E_a region of non-isothermal dehydration follows three-dimensional phase boundary (R3) kinetics. Also, the appearances of the compensation effect is explained by changes of energetic distribution of the active desorption centers [8].

Bearing in mind the above facts, in this paper the poly(acrylic acid) hydrogel isothermal dehydration kinetics was investigated, with purpose to determine the activation parameters and to compare the obtained results with those for the non-isothermal hydrogel dehydration.

Experimental

Materials and methods

Super-absorbing cross-linked poly(acrylic acid) hydrogel in Na⁺ form (60%), which was applied for

^{*} Author for correspondence: bojanjan@ffh.bg.ac.yu

this investigation, has been synthesized by the procedure based on the simultaneous radical polymerisation of acrylic acid and cross-linking of the formed poly(acrylic acid), according to general procedure described in previous works [7–9]. For that process, acrylic acid monomer, initiators Na₂S₂O₈, Na₂S₂O₅, H₂O₂ and crosslinking agent N,N -methylenebisacrylamide (NMBA) were used. Equilibrium swelling degree (SD_{eq}) of the used hydrogel in distilled water at 25°C was 85%, determined by standard method based on mass difference of dry and swollen sample.

Thermogravimetric measurements

The kinetics of dehydration was investigated by isothermal mass loss experiments carried out using a TA Instruments-SDT simultaneous TG-DSC thermal analyzer model 2960. These analyses were performed with $22-23\pm0.1$ 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 306, 324, 345 and 361 K. The samples was heated from the start to the selected dehydration temperature at the heating rate of 200 K min⁻¹ and then held at that temperature for given reaction time.

The conversion fraction α (degree of dehydration) is given by the expression:

$$\alpha = \frac{m_0 - m_{\rm t}}{m_0 - m_{\rm f}} \tag{1}$$

where m_0 , m_t and m_f are the initial, actual and final sample masses, respectively.

Methods for determination of activation parameters (E, lnA) of the isothermal dehydration

Johnson-Mehl-Avrami (JMA) method

Rather than fitting the data to one of a number of possible rate equations, and attempting to discern the rate controlling process by judging the goodness of fit between the data and each rate equation, it is possible to employ a general rate equation in which the function of reaction model ($f(\alpha)$), is expressed in some general manner with a variable parameter that reflects the rate controlling mechanism. Such rate equations are sometimes termed 'empirical rate equations'. One of these equations was developed by Johnson, Mehl and Avrami [10, 11].

In the simplest form, Johnson–Mehl–Avrami equation [10, 11], can be written as:

$$\alpha = 1 - \exp(-k_{a}t^{n}) \tag{2}$$

where t is the reaction time, k_a is the effective reaction rate constant and n is the controlling reaction parameter. Johnson–Mehl–Avrami equation [10, 11] in the logarithmic form, can be expressed as:

$$\ln[-\ln(1-\alpha)] = \ln k_a + n \ln t \tag{3}$$

The values of k_a and n can be calculated from the intercept and slope of a 'lnln' plot of the data by least-squares fitting method. The apparent activation energy (*E*) and pre-exponential factor (*A*) can be evaluated from the logarithmic form of Arrhenius equation (Eq. (4)):

$$k_{a} = A \exp(-E/RT) \tag{4}$$

where T is the absolute temperature and R is the gas constant.

Stationary point (SP) method

In the heterogeneous chemical reaction kinetics, functions $d\alpha/dt=f(t)$, which have zero-initial rate, can be observed as functions with local maximum. This maximum appears in the so called stationary point: $S[(d\alpha/dt)_{max}; t_{max}]$, where $(d^2\alpha/dt^2)=0$ [12]. According to that, stationary point is defined as a point in which the reaction system, in the given reaction conditions has a maximal reaction rate [12].

In that case, Eq. (5) is valid:

$$(d\alpha/dt)_{\max} = k(T, p_j) f(\alpha_{\max})$$
(5)

where $(d\alpha/dt)_{max}$ is the maximal rate of process, $f(\alpha_{max})$ is a function of reaction mechanism, α_{max} is the degree of conversion at $t=t_{max}$, p_j represent the partial pressure of the gaseous reactants.

If Arrhenius dependence of $(k(T,p_j))$ on temperature is supposed, than Eq. (5) can be transformed in the following form:

$$(d\alpha/dt)_{max} = Aexp(-E/RT)f(\alpha_{max})$$
 (6)

Making the logarithmic form of Eq. (6), from the slope of the straight line obtained from dependence $\ln(d\alpha/dt)_{max} = f(1/T)$, it is possible to determine the value of the apparent activation energy of the investigated process. 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 [12].

Results and discussion

Figure 1 represents the plots of the isothermal hydrogel mass change dependence on the dehydration time at different operating temperatures.

The isothermal dependences of the degree of dehydration (α) of the poly(acrylic acid) hydrogel on the



Fig. 1 Isothermal mass change curves for the isothermal dehydration of the equilibrium swollen poly(acrylic acid) hydrogel at the different operating temperatures



Fig. 2 The isothermal conversion $(\alpha - t)$ curves for the dehydration of the equilibrium swollen poly(acrylic acid) hydrogel at the different operating temperatures

dehydration time (*t*) (the conversion curves) at different operating temperatures are presented at Fig. 2.

At the presented conversion curves, three characteristic shapes of the time dependences of the degree of dehydration are clearly observable: a linear, non-linear and range of saturation.

With purpose to analyse the influence of reaction temperature on the shape of conversion curves the following, so called, shape parameters of conversion curves were defined: period of linearity (t_i) , initial dehydration rate (v_{in}) , saturation time (t_f) and the saturation dehydration rate (v_f) . Period of linearity of the conversion curve is defined as duration of the linear change of α with the dehydration time (t). Initial dehydration rate is the dehydration rate in the range of the linear changes of α with the dehydration time. The saturation time was defined as dehydration time at which α_{eq} is reachable.

Saturation dehydration rate (v_f) is calculated by Eq. (7):

$$v_{\rm f} = \frac{1}{t_{\rm f}} \tag{7}$$

Table 1 shows the changes of conversion shape parameters with operating temperature for dehydration of the equilibrium swollen poly(acrylic acid) hydrogel.

According with obtained results in Table 1, it can be concluded that with increasing of operating temperature, t_1 and t_f values decreases, while v_{in} and v_f values increases. Bearing in mind that changes of v_{in} and v_f with operating temperature have the exponential character, the following values: the apparent activation energy (*E*) and the pre-exponential factor (ln*A*) for both, the initial part (E_{in} , ln A_{in}) and saturation part (E_f , ln A_f) for the investigated process are calculated using Arrhenius equation (columns 2–5 in Table 1).

Figures 3a and b represents the dependences of the isothermal dehydration rate $(d\alpha/dt)$ on the dehydration time (*t*) for the poly(acrylic acid) hydrogel at four different operating temperatures.

Temperature changes of the maximal dehydration rate $(d\alpha/dt)_{max}$ for the poly(acrylic acid) hydrogel are presented in Table 2.

Because the increase of the maximal dehydration rate with operating temperature has an exponential form, using the Arrhenius equation and the method of the 'stationary point', the activation parameters $[E_{SP}, ln[Af(\alpha_{max})]_{SP}]$ for the dehydration of poly(acrylic acid)

 Table 1 The changes of conversion shape parameters with operating temperature for dehydration of the equilibrium swollen poly(acrylic acid) hydrogel

Temperature/K	t _l /min	$v_{\rm in}/{ m min}^{-1}$	t _f /min	$v_{ m f}/{ m min}^{-1}$
306	127.58	0.0075	135.78	0.0073
324	39.47	0.0241	43.22	0.0231
345	9.10	0.0714	16.74	0.0597
361	4.83	0.1139	9.16	0.1092
	$E_{\rm in}$ =51.6 kJ mol ⁻¹	$\ln A_{in} = 15.40 \text{ min}^{-1}$	$E_{\rm f}$ =44.8 kJ mol ⁻¹	$\ln A_{\rm f} = 12.78 \ {\rm min}^{-1}$



Fig. 3 Dependences $d\alpha/dt=f(t)$ for the dehydration of the equilibrium swollen poly(acrylic acid) hydrogel at a – 306 and 324 K; b – 345 and 361 K

Table 2	The changes of maximal dehydration rate $(d\alpha/dt)_{max}$
	with operating temperature for dehydration of the
	equilibrium swollen poly(acrylic acid) hydrogel

Temperature/K	$(d\alpha/dt)_{max}/min^{-1}$
306	0.0083
324	0.0252
345	0.0697
361	0.1764
$E_{\rm SP}$ =50.2 kJ mol ⁻¹	
$ln[A_{SP}f(\alpha_{max})]=14.95 min^{-1}$	



Fig. 4 The JMA plots of $\ln[-\ln(1-\alpha)]$ vs. $\ln t$ for the hydrogel dehydration at the different operating temperatures

hydrogel were calculated and the obtained values are given in Table 2 (column 1).

Figure 4 shows the plots of $\ln[-\ln(1-\alpha)] vs$. $\ln t$ at different operating temperatures for the equilibrium swollen poly(acrylic acid) hydrogel.

Table 3 The changes of values of the period of applicability
(PA), effective reaction rate constant (k_a) and reac-
tion parameter (n) for the Johnson-Mehl-Avrami
(JMA) equation with operating temperature (T), for
the poly(acrylic acid) hydrogel dehydration

Temperature/K	PA	$k_{\rm a}/{ m min}^{-1}$	п	r	
306	0.15-0.85	0.0131	1.24	0.9999	
324	0.15-0.85	0.0373	1.22	0.9999	
345	0.15-0.85	0.0913	1.11	0.9999	
361	0.15-0.85	0.1820	1.10	0.9998	
$E_{\rm JMA}$ =43.5 kJ mol ⁻¹					
$\ln A_{\rm JMA}$ =12.78 min ⁻¹					

The dependence of $\ln[-\ln(1-\alpha)]=f(\ln t)$ in the wide range of the degree of dehydration (α), i.e. in the given period of applicability (PA) for the Johnson-Mehl-Avrami equation (Eq. (3)) gives a straight line.

Table 3 shows the changes of values of the period of applicability (PA) and values of constants n and k_a with operating temperature for Johnson–Mehl–Avrami equation.

The plot of $\ln[-\ln(1-\alpha)]$ vs. $\ln t$ (JMA equation) in the relatively wide range of the degree of dehydration values (α =15-85%) gives a straight line. Coefficient of JMA equation, k_a , which is most frequently believed that represents an effective rate constant for the investigated process, exponentially increases with increasing of operating temperature. In the contrary with above fact, the change in operating temperature for the investigated dehydration process has more complex influence upon the values of the parameter *n*. At the temperatures lower than $T\leq324$ K, the value of parameter *n* is $n\sim1.22$, while at temperatures higher than $T\geq345$ K, the value of parameter *n* is $n\sim1.11$. The obtained values of parameter *n* and his complex changes with increase in operating temperature, im-

DEHYDRATION OF POLY(ACRYLIC ACID) HYDROGEL

Table 4 Algebraic expressions of	$f(\alpha)$ and $g(\alpha)$	for the reaction models	considered in the	present work
----------------------------------	-----------------------------	-------------------------	-------------------	--------------

Reaction mechanism	$f(\alpha)$	$g(\alpha)^{a}$
Zero-order (Polany–Winger equation)	1	α
Phase-boundary controlled reaction (contracting area, i.e., bidimensional shape)	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$
Phase-boundary controlled reaction (contracting volume, i.e., tridimensional shape)	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$
First-order (Mampel)	(1-α)	$-\ln(1-\alpha)$
Avrami–Erofe'ev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Avrami–Erofe'ev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
Avrami–Erofe'ev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
One-dimensional diffusion	1/2α	α^2
Two-dimensional diffusion (bidimensional particle shape)	$1/[-\ln(1-\alpha)]$	$(1-\alpha)\ln(1-\alpha)+\alpha$
Three-dimensional diffusion (tridimensional particle shape) Jander equation	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional diffusion (tridimensional particle shape) Ginstling–Brounshtein	$3/2[(1-\alpha)^{-1/3}-1]$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

^aIntegral form of the reaction model

plies that the investigated hydrogel dehydration represents one kinetically controlled reaction and dehydration mechanism was probably changed with increase in operating temperature [13].

Using the Arrhenius equation, the activation parameters (E_{JMA} and $\ln A_{\text{JMA}}$) for the investigated dehydration are calculated and shown in Table 3 (column 1).

The appropriate kinetic model for the investigated hydrogel dehydration was chosen using the model-fitting method. This method is widely used for founding the suitable shape of the reaction model function $f(\alpha)$, which is able that properly describe the examined process which took a place in the solid-state [14–19]. In accordance with this method, the selection of the reaction model for poly(acrylic acid) hydrogel dehydration is based on the comparison (graphical and analytical) of the experimentally determined function $\alpha_{exp} = f(t_{red,exp})$ with theoretical functions $\alpha_t = f(t_{red})$, for different reaction models (Table 4).

In this case, α_{exp} represents the experimentally determined values of the degree of dehydration, t_{red} represents the reduced time: $t_{red}=t/t_{0.9}$, while $t_{0.9}$ is the dehydration time which corresponds to $\alpha=0.9$ and $t_{red,exp}$ is the experimentally determined t_{red} .

Figures 5a and b, represents the theoretical reduced curves, for the used reaction models presented in Table 4 (denoted with full line and numbers) and the experimentally determined reduced curves, for hydrogel dehydration at operating temperatures: T=306, 324, 345 and 361 K (denoted with following symbols: \Box , \bigcirc , \blacksquare and \triangle , respectively).



Fig. 5 Comparison of the experimentally determined reduced curves with theoretical reduced curves (full line) for the poly(acrylic acid) hydrogel dehydration at operating temperatures a – *T*=306 and 324 K; b – *T*=345 and 361 K



Fig. 6 Functional relationship $g(\alpha)=f(t)$ for the poly(acrylic acid) hydrogel dehydration at the following operating temperatures: $\blacksquare - T=306$ K (model R1), $\bullet - T=324$ K (model R1), $\Box - T=345$ K (model R2) and $\circ - T=361$ K (model R2)

Based on the obtained results shown in Figs 5a and b, it can be concluded that dehydration of poly(acrylic acid) hydrogel at T=306 and 324 K could be modelled with reaction model R1 ($\alpha=k_rt$) [20], while for the same process at T=345 and 361 K, model R2 ($[1-(1-\alpha)^{1/2}]=k_rt$) [21] is more convenient.

Figure 6 represents the dependences $\alpha = k_r t$ (model R1) and $[1-(1-\alpha)^{1/2}] = k_r t$ (model R2), which were obtained by using the model-fitting method, for poly(acrylic acid) hydrogel dehydration at considered operating temperatures.

The presented dependences $g(\alpha)=f(t)$, for the reaction models R1 and R2 at considered operating temperatures in the wide range of the degree of dehydration (α) gives a straight line. Table 5 shows the values of the coefficients of the linear correlation for functional relationship $g(\alpha)=f(t)$ using the models R1 and R2, as well as the values of the corresponding rate constants, $k_{\rm r}$, for the investigated hydrogel dehydration.

Table 5 The values of rate constant k_r and corresponding values of the activation parameters $(E_r, \ln A_r)$ at the different operating temperatures for the poly(acrylic acid) hydrogel dehydration

Temperature/K	Reaction model	$k_{\rm r}/{ m min}^{-1}$	r	
306	R1	0.0075	0.9999	
324	R1	0.0243	0.9998	
345	R2	0.0537	0.9983	
361	R2 0.1019 0.9		0.9975	
$E_{\rm r}$ =42.7 kJ mol ⁻¹				
$\ln A_r = 11.98 \text{ min}^{-1}$				

Using the Arrhenius equation in logarithmic form, the activation parameters (E_r and $\ln A_r$) for the investigated process were calculated and presented in Table 5 (column 1).

The suggested reaction models as well as the kinetics of hydrogel dehydration at temperatures (T)within the operating temperature range for $T \leq 324$ K and $T \ge 345$ K are applicable, and therefore realistic in the wide range of the degree of dehydration $(\alpha=0-85\%)$. The limiting kinetic factor for the poly(acrylic acid) hydrogel dehydration at operating temperatures $T \leq 324$ K is the rate of the one-dimensional movement of the reaction boundary phase [22], which was formed by the water far-off from the hydrogel. Similar to the layers silicates [23], water from the hydrogel macromolecular chains release normally on the formed boundary phase. In the contrary, at higher operating temperatures, $T \ge 345$ K, the limiting kinetic factor is the two-dimensional shrinkage of the reaction boundary phase, i.e. the surface shrinkage only at the ends of the cylindrical boundary phase. The apparent activation energy values (E), which are determined by the different methods shows significantly differences. The values of apparent activation energy which were determined by 'saturation rate' method and JMA equation are very similar. Values of E which are calculated using the 'initial rate' method has the maximal value, while the value of Ecalculated using the suggested reaction models is the minimal one. The differences which were found for the calculated values of the apparent activation energy E can be explained as a consequence of the limitation of the concrete kinetic method, at the part or the parts of the examined hydrogel dehydration.

Furthermore, comparing the values of the activation parameters of the isothermal hydrogel dehydration with the values of the activation parameters for the same process conducted under the non-isothermal conditions, we can concluded that these values also differs one from the another. The values of activation parameters of the non-isothermal poly(acrylic acid) hydrogel dehydration process, which were determined by Coats–Redfern method at heating rate $v_h=10$ K min⁻¹ ($E_{CR}=43.5$ kJ mol⁻¹; $\ln A_{CR}=12.48$ min⁻¹) [7] are similar by magnitude to the values of the isothermal activation parameters, which were determined by using the 'stationary point' method and Johnson–Mehl–Avrami (JMA) equation.

The values of activation parameters, which were determined by suggested reaction models for the isothermal poly(acrylic acid) hydrogel dehydration are similar to the values of the non-isothermal activation parameters determined using van Krevelen method at heating rate $v_h=20$ K min⁻¹ ($E_{VK}=39.8$ kJ mol⁻¹; $\ln A_{VK}=11.22$ min⁻¹) [7], while the same values obtained by 'initial rate' method are similar to the values of the activation parameters calculated using Horowitz–Metzger method, at $v_h=10 \text{ Kmin}^{-1}$ ($E_{\text{HM}}=$ 50.7 kJ mol⁻¹; ln $A_{\text{HM}}=14.78 \text{ min}^{-1}$) [7].

The established values of activation parameters for the isothermal poly(acrylic acid) hydrogel dehydration and the suggested reaction model for the same process enable us to make preliminary hypothesis about state of water which is bonded to given hydrogel. The apparent activation energy (E), which is calculated from the suggested reaction models for the examined process, has the value similar to the enthalpy of water evaporation. In considered case, with great degree of certainty, it can be claimed that the primary mass of water bonded to the considered hydrogel has a structure close to the 'ordinary' water.

Conclusions

The reaction model and activation parameters of the isothermal poly(acrylic acid) hydrogel dehydration are different from the reaction model and activation parameters for the non-isothermal hydrogel dehydration. Changes in operating temperature lead to the changes in kinetics of the investigated poly(acrylic acid) hydrogel dehydration. At operating temperatures $T \leq 324$ K, dehydration kinetics is determined with the rate of one-dimensional movement of the reaction interface (normally to the bonded water layer) which was formed by the water removing from the hydrogel macromolecular chains. The higher operating temperatures ($T \ge 345$ K) leads to the changes in the kinetics of hydrogel dehydration, so. the limiting kinetic factor become the rate of two-dimensional cylindrical shrinkage of the reaction interface. The apparent activation energy for the investigated poly(acrylic acid) hydrogel dehydration, calculated by the suggested reaction models, has the value similar to the enthalpy of water evaporation. Structure of water bonded to the investigated hydrogel (more than 98%) is close to the 'ordinary' water.

Acknowledgements

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

References

- N. Peppas, Hydrogels in Medicine and Pharmacy, Vol. I: Fundamentals, CRC, Boca Raton, FL 1986.
- 2 E. Karadağ and D. Saraydin, Polym. Bull., 48 (2002) 299.
- 3 D. Saraydin and Y. Caldiran, Polym. Bull., 46 (2001) 91.
- 4 I. Katime, J.L. Velada, R. Novoa, E. Diaz de Apodaca,
- J. Puig and E. Mendizabal, Polym. Intern., 40 (1996) 281.
 5 E. Karadağ and D. Saraydin, Turk. J. Chem., 26 (2002) 863.
- 6 P. M. de la Torre, S. Torrado and S. Torrado, Biomaterials, 24 (2003) 1459.
- 7 B. Janković, B. Adnađević and J. Jovanović, J. Therm. Anal. Cal., 82 (2005) 7.
- 8 B. Janković, B. Adnađević and J. Jovanović, Thermochim. Acta, 452 (2007) 106.
- 9 J. Jovanović and B. Adnađević, XLI Consultation of Serbian Chemical Society, SSHD, Belgrade, 23–24 January, Book of Abstracts, HM13, 2003, p. 119.
- 10 W. A. Johnson and R. F. Mehl, Trans. Am. Inst. Miner. (Metall.) Eng., 135 (1939) 416.
- 11 M. Avrami, J. Chem. Phys., 7 (1939) 1103.
- 12 I. Klarić, U. Roje and T. Kovačić, J. Therm. Anal. Cal., 45 (1995) 1373.
- 13 J. D. Hancock and J. H. Sharp, J. Amer. Ceram. Soc., 55 (1972) 74.
- M. E. Brown, D. Dollimore and A. K. Galwey, Reactions in the Solid State in Comprehensive Chemical Kinetics, H. Bamford, C. F. H. Tipper, Eds, Elsevier, Amsterdam 1980, Vol. 22.
- 15 S. Vyazovkin and C. A. Wight, Thermochim. Acta, 340–341 (1999) 53.
- 16 S. Vyazovkin, J. S. Clawson and C. A. Wight, Chem. Mater., 13 (2001) 960.
- 17 S. Vyazovkin and C. A. Wight, Int. Rev. Phys. Chem., 17 (1998) 407.
- 18 F. Rodante, G. Catalani and S. Vecchio, J. Therm. Anal. Cal., 68 (2002) 689.
- 19 S. Vyazovkin and C. A. Wight, J. Phys. Chem. A, 101 (1997) 8279.
- 20 M. L. Franklin and T. B. Flanagan, J. Phys. Chem., 75 (1971) 1272.
- 21 S. F. Hilbert, J. Br. Ceram. Soc., 6 (1969) 11.
- 22 R. F. Walker, Trans. Faraday Soc., 65 (1969) 3324.
- 23 R. C. Eckhardt and T. B. Flanagan, Trans. Faraday Soc., 60 (1964) 1289.

Received: January 7, 2007 Accepted: January 4, 2008

DOI: 10.1007/s10973-007-7558-1