

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

B. Janković^{1*}, B. Adnađević¹ and J. Jovanović²

¹Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12–16, P.O. Box 137, YU–11001 Belgrade, Serbia and Montenegro

²Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Knez Mihajlova 35, YU–11000 Belgrade, Serbia and Montenegro

Kinetics of dehydration of equilibrium swollen poly(acrylic acid) hydrogel was investigated using methods of non-isothermal thermal analysis. Methods of Kissinger, Coats–Redfern, Van Krevelen and Horowitz–Metzger were applied for determination the kinetics parameters: activation energy (E), pre-exponent ($\ln A$) as well as the kinetics model $f(\alpha)$ for the process of hydrogel dehydration under different heating rates. An existence of good agreement between determined values of kinetic parameters (E and A), which were obtained applying different methods under the same heating rate. Functional relationship between changes of kinetic parameters of dehydration and changes of heating rate was established. An existence of compensation effect is accepted and explanation of compensation effect appearance during the hydrogel dehydration is suggested.

Keywords: activation energy, dehydration, non-isothermal kinetics, polyacrylic hydrogel, thermogravimetric analysis

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. Although many naturally occurring polymers may be used to produce this type of materials, the structural versatility available in synthetic hydrogels has given them distinctive properties, which in turn have enhanced their practical utility. 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 behavior and swelling kinetics of various types of hydrogels are extensively studied [2–6], there are much lesser information concerning hydrogel mechanical properties [7, 8] and according to our knowledge there are not available apparent investigations concerning the kinetics of hydrogel dehydration.

There are some recently published works concerning the dehydration of some other types of compounds, primarily crystallohydrates. For example, N. Deb, per-

formed thermal studies of cadmium(II)bis(oxalato)cobaltate(II)-pentahydrate. The kinetic parameters have been evaluated for the dehydration and decomposition steps using, non-mechanistic equations, such as, Freeman and Carroll, Coats and Redfern, Flynn and Wall, MacCallum and Tanner equations. Using mechanistic equations, the rate controlling processes of the dehydration and decomposition mechanism are also inferred. A tentative mechanism for the decomposition of that substance in air is proposed [9]. Thermal decomposition of nickel(II)sulfate(VI)hexahydrate in air and in helium atmosphere has been studied. Kinetic parameters of the Arrhenius equation were calculated applying the Coats–Redfern approximation [10]. The parameters of the Arrhenius equation were determined applying the third-law method to the results of kinetic studies reported in the literature and obtained by their own work for the dehydration kinetics of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The impact of self-cooling on the dehydration kinetics was investigated [11]. The kinetic of non-isothermal dehydration of Sn(II), Pb(II), Cd(II) and Hg(II) alginate ionotropic gels has been examined and it was found that dehydration of the investigated gel complexes occurred in one step process. The kinetic parameters were calculated by different models, such as Satava and Coats–Redfern [12].

The aim of this study was to investigate the kinetics of dehydration of poly(acrylic acid) hydrogel using non-isothermal methods.

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

Experimental

Materials and methods

Super-absorbing cross-linked poly(acrylic acid) hydrogel, which has been applied for this investigation was synthesized 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 previously work [13]. For that process, acrylic acid monomer, initiators $\text{Na}_2\text{S}_2\text{O}_8$, $\text{Na}_2\text{S}_2\text{O}_5$, H_2O_2 and crosslinking agent $\text{N,N}'$ -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].

Hydrogel synthesis

Hydrogel synthesis was performed in a polymerization reactor equipped with a magnetic stirrer, reflux condenser, nitrogen inlet and a thermometer, in a nitrogen atmosphere. Monomer solution was prepared from: 80 mL melted glacial acrylic acid dissolved in 180 mL distilled water, and 0.8 g $\text{N,N}'$ -methylenebisacrylamide (NMBA) and 0.08 g ethylenediaminetetraacetic acid (EDTA) both dissolved in 60 mL of distilled water. This monomer solution is placed into the reactor, stirred and deoxygenated with nitrogen gas bubbling through the solution for 60 min. Initiator stock solutions was prepared as follows: (A) 2.5 g sodium persulfate in 22.5 mL distilled water, (B) 2.5 g sodium metabisulfite in 22.5 mL distilled water, (C) hydrogen peroxide, 30%. When the requested deoxygenation time has passed, the following amounts of the initiator solutions was added to the monomer solutions using syringes, in the order listed with stirring: 2.4 mL of A, 10 mL of C and 1.2 mL of B. Then, reaction mixture was slightly warmed up to 50°C until happened dramatic growth of the reaction's mixture temperature (gel-point) and left following 4 (four) h at 50°C . The obtained gel-type product was converted into the Na^+ form (60%) by neutralization with a 3% solution of Na_2CO_3 . The obtained hydrogel in bulk was cut into smaller pieces, and dried in an air oven at 105°C to constant mass. The obtained products were stored in a vacuum exiccator before use.

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 and $20^\circ\text{C min}^{-1}$ from ambient temperature to 350°C .

The methods used to evaluate the kinetic parameters (E , A) of dehydration process

The kinetic parameters of the investigated dehydration process, the activation energy (E), and pre-exponential factor (A), were determined from the thermogravimetric curves using various methods: Kissinger [14], Coats–Redfern [15, 16], Van Krevelen [17, 18] and Horowitz–Metzger [19]. The existence of several methods for the calculation of the kinetic parameters from thermogravimetric measurements is a direct consequence of difficulties related with the integration procedure of the basic kinetic equation. Namely, if α is the degree of conversion defined as the ratio of actual mass loss to total mass loss, $d\alpha/dt$ is the reaction rate given in the form

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) (1-\alpha)^n \quad (1)$$

where, in analogy with homogeneous reactions A and n denotes some kind of pre-exponential factor and order of reaction, respectively, whereas E is the apparent activation energy, and R is the gas constant. If the heating rate v_h is given by the expression:

$$v_h = \frac{dT}{dt} \quad (2)$$

Equation (1) can be written in the form

$$\frac{d\alpha}{dT} = \frac{A}{v_h} \exp\left(-\frac{E}{RT}\right) (1-\alpha)^n \quad (3)$$

The integration of the last expression is a serious problem, which is done approximately in all methods.

Kissinger method

The method proposed by Kissinger [14] is based on the calculation of activation energy from a point of the maximal temperature, T_{max} , which is the temperature at the maximum of the heating derivative mass loss curve for different heating rates. The condition $T=T_{\text{max}}$ is satisfied when $d^2\alpha/dT^2=0$. At this point the following expression holds,

$$\frac{E}{RT_{\text{max}}^2} = \frac{A}{v_h} \exp\left(-\frac{E}{RT_{\text{max}}}\right) n(1-\alpha)_{\text{max}}^{n-1} \quad (4)$$

where v_h is the heating rate given by Eq. (2). Showing that product $n(1-\alpha)_{\text{max}}^{n-1} \approx 1$, Kissinger found the expression:

$$\ln \frac{v_h}{T_{\max}^2} = \ln \frac{AR}{E} - \frac{E}{R} \left(\frac{1}{T_{\max}} \right) \quad (5)$$

Using this expression (Eq. (5)) at several heating rates v_h , the activation energy (E) and the pre-exponential factor (A) can be determined.

Coats and Redfern method

Introducing several assumptions in the integration procedure, Coats and Redfern [15, 16] proposed the following expressions for $n \neq 1$ and for $n=1$, respectively,

$$\ln \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] = \ln \frac{AR}{v_h E} - \frac{E}{RT}, \quad n \neq 1 \quad (6)$$

$$\ln \left[-\frac{\ln(1-\alpha)}{T^2} \right] = \ln \frac{AR}{v_h E} - \frac{E}{RT}, \quad n=1 \quad (7)$$

In the case of $n=1$, the activation energy (E) and the pre-exponential factor (A) can be determined by plotting of dependence $\ln(-\ln(1-\alpha)/T^2)$ vs. $1/T$. If $n \neq 1$, it would also be done, but with correct selection of n .

Van-Krevelen method

For $n \neq 1$ and $n=1$, respectively, Van Krevelen [17, 18] obtained the following equations

$$\ln \left(\frac{1-(1-\alpha)^{1-n}}{1-n} \right) = \ln \left[\frac{A}{v_h} \left(\frac{E}{RT_{\max}} + 1 \right)^{-1} \left(\frac{0.368}{T_{\max}} \right)^{\frac{E}{RT_{\max}}} \right] + \left(\frac{E}{RT_{\max}} + 1 \right) \ln T \quad (8)$$

$n \neq 1$

$$\ln(-\ln(1-\alpha)) = \ln \left[\frac{A}{v_h} \left(\frac{E}{RT_{\max}} + 1 \right)^{-1} \left(\frac{0.368}{T_{\max}} \right)^{\frac{E}{RT_{\max}}} \right] + \left(\frac{E}{RT_{\max}} + 1 \right) \ln T \quad (9)$$

$n=1$

Obviously, as in the previous case, the activation energy (E) and the pre-exponential factor (A) can be calculated from these two equations. Thus, if $n=1$, a plot of $\ln(-\ln(1-\alpha))$ vs. $\ln T$ gives a straight line and the slope is related to the activation energy. The pre-exponential factor (A) can be calculated from the intersection of the y axis.

Horowitz and Metzger method

Horowitz and Metzger [19] introduced a characteristic temperature T_s and a parameter θ such that

$$\theta = T - T_s \quad (10)$$

In the case of $n=1$, T_s is defined as the temperature at which $(1-\alpha)_s = 1/e = 0.368$. If the reaction order is unknown, T_s is defined as the maximum heating rate. For $n \neq 1$ and $n=1$, respectively, they obtained the following equations as a function of the characteristic temperature T_s .

$$\ln \left[\frac{1-(1-\alpha)^{1-n}}{1-n} \right] = \ln \left(\frac{ART_s^2}{v_h E} \right) - \frac{E}{RT_s} + \frac{E\theta}{RT_s^2} \quad (11)$$

$$\ln(-\ln(1-\alpha)) = \ln \left(\frac{ART_s^2}{v_h E} \right) - \frac{E}{RT_s} + \frac{E\theta}{RT_s^2} \quad (12)$$

If n is properly selected, the activation energy and pre-exponential factor can be determined by plotting the functions (left hand sides of Eqs (11) and (12)) vs. θ .

In such a manner, if $n=1$, a plot of $\ln(-\ln(1-\alpha))$ vs. θ gives a straight line and the slope is related to the activation energy.

Results and discussion

The TG and DTG curves of the dehydration of equilibrated swollen SAP PAA samples obtained at different heating rates (5, 10, 20°C min⁻¹) are shown in Figs 1a and b.

All the thermogravimetric curves are asymmetric. Values of initial temperature (T_i), inflection temperature (T_p) and final temperature (T_f) from thermogravimetric curves at various heating rates are presented at Table 1.

Increasing of heating rate leads to increase of all of the characteristic temperature values on the obtained thermogravimetric curves. It is specific that the

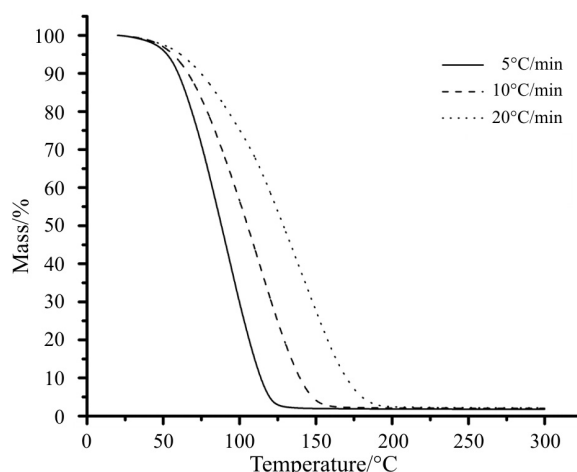


Fig. 1a Thermogravimetric curves of the dehydration of equilibrated swollen poly(acrylic-acid) hydrogel in nitrogen atmosphere at different heating rates

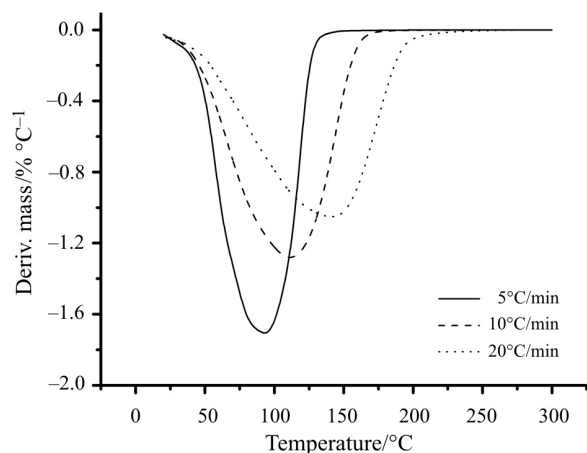


Fig. 1b The DTG curves of the dehydration of equilibrated swollen poly(acrylic-acid) hydrogel in nitrogen atmosphere at different heating rates

Table 1 Values of T_i , T_p and T_f for dehydration of equilibrated polyacrylic hydrogel determined by thermogravimetric analysis at different heating rates

$v_h/^\circ\text{C min}^{-1}$	T_i/K	T_p/K	T_f/K
5	331.2	361.1	391.8
10	344.0	376.5	421.7
20	348.8	396.1	476.2

degree of enhancement is the maximal for final temperature (T_f). On the DTG curves one well-defined peak can be distinguished. With heating rate increase, the maxima on DTG curves move to higher temperature and peaks become more widen.

The Kissinger plot obtained for dehydration of equilibrium swollen poly(acrylic-acid) hydrogel in nitrogen atmosphere is shown in Fig. 2.

The obtained values of the activation energy (E) and pre-exponential factor (A) are given in row 1 of Table 2. By this method, E and A , can be calculated only if there are several thermogravimetric curves obtained at different heating rates. Also, after assumptions

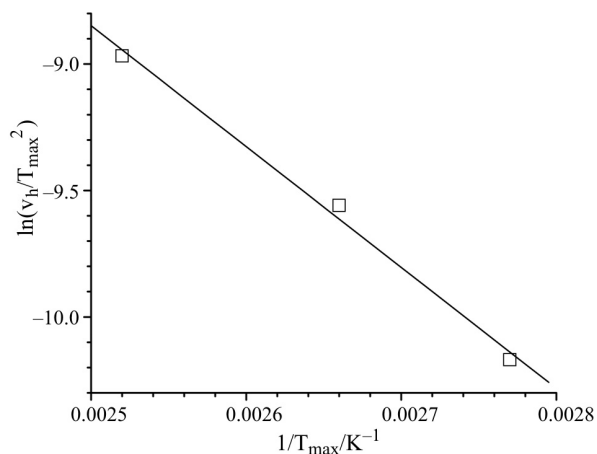


Fig. 2 Kissinger plot of $\ln(v_h/T_{\max}^2)$ vs. $1/T_{\max}/\text{K}^{-1}$ for the dehydration of equilibrated swollen poly(acrylic-acid) hydrogel in nitrogen atmosphere

that were performed during the evaluation of Eq. (5), this equation is not a function of the reaction order n . In the next three methods, Coats–Redfern, Van Krevelen and Horowitz–Metzger, activation energy (E) and pre-exponential factor (A), were calculated at every heating rate and they were sensitive to n . By systematic analysis, we found that $n=1$ in the considered process of dehydration in the region of $1 < \alpha < 0.99$ independently of the method used, and, therefore, only these results are given in the following section.

Figure 3 shows the relationship given by Eq. (7) of Coats–Redfern technique.

The obtained values of the activation energy (E) and pre-exponential factor (A) together with the range of α values for $n=1$, are given in rows 2, 3 and 4 of Table 2. The relationship given by Eq. (9) (Van Krevelen technique) is presented in Fig. 4.

The calculated values of the activation energy (E) and pre-exponential factor (A) together with the range of α values for $n=1$, are given in rows 5, 6 and 7 of Table 2. Figure 5 shows the relationship proposed by Horowitz and Metzger for dehydration of equilibrium

Table 2 Kinetic parameters of the dehydration of equilibrated swollen hydrogel determined by different methods

Method	$v_h/^\circ\text{C min}^{-1}$	n	α	A/min^{-1}	$\ln A/\text{min}^{-1}$	$E/\text{kJ mol}^{-1}$	Correlation coefficient
Kissinger	5–20	1	0.15–0.99	$1.06 \cdot 10^5$	11.57	39.7	0.997
	5	1	0.15–0.99	$8.14 \cdot 10^6$	15.91	53.1	0.999
Coats–Redfern	10	1	0.13–0.99	$2.63 \cdot 10^5$	12.48	43.5	0.999
	20	1	0.02–0.99	$4.55 \cdot 10^4$	10.72	38.6	0.998
Van Krevelen	5	1	0.16–0.99	$2.82 \cdot 10^7$	17.15	55.5	0.999
	10	1	0.13–0.99	$7.20 \cdot 10^5$	13.49	46.5	0.998
	20	1	0.12–0.99	$7.48 \cdot 10^4$	11.22	39.8	0.999
Horowitz–Metzger	5	1	0.16–0.99	$7.47 \cdot 10^7$	18.13	59.7	0.998
	10	1	0.13–0.99	$2.63 \cdot 10^6$	14.78	50.7	0.997
	20	1	0.13–0.99	$3.88 \cdot 10^5$	12.87	45.7	0.999

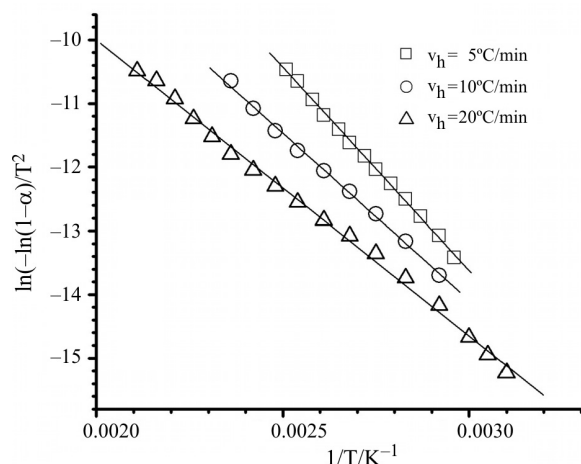


Fig. 3 Coats–Redfern plots of $\ln(-\ln(1-\alpha)/T^2)$ vs. $1/T$ for the dehydration of equilibrated swollen poly(acrylic-acid) hydrogel in nitrogen atmosphere

swollen poly(acrylic-acid) hydrogel in nitrogen atmosphere.

The obtained values of the activation energy and pre-exponential factors, together with the ranges of α values for $n=1$, are presented in Table 2, rows 8–10.

Analyzing of Table 2, we can see that the linear domains of the applied methods, when apparent reaction order is $n=1$, for the determination of the activation energies (E) and pre-exponential factors (A), are very long; the corresponding values of α are, at least, between 0.16 and 0.99.

The obtained values shown in the Table 2, enables us to conclude existence of a good agreement between value of energy of activation of the dehydration process obtained by use of different methods at the same heating rate of the investigated system.

Determined values for the apparent order, $n=1$, and activation energy higher than enthalpy of water evaporation, implies that process of hydrogel dehydration is a kinetically controlled one, and that their slowest stage is cleavage bond between adsorbed water and the adsorption center of the observed hydrogel.

Comparing one with each other, the values for E and $\ln A$ obtained using different methods, but at the same heating rate, we can conclude that Horowitz–Metzger methods gives the highest values of these parameters, while Coats–Redfern and Kissinger methods give lower values. Independently of the applied method, increase of the heating rate leads to decrease of the kinetic parameters.

Changes of the value of activation energy with heating rate, v_h , can be expressed by following Eq. (13)

$$E = E_1 + c \exp\left(-\frac{v_h}{d}\right) \quad (13)$$

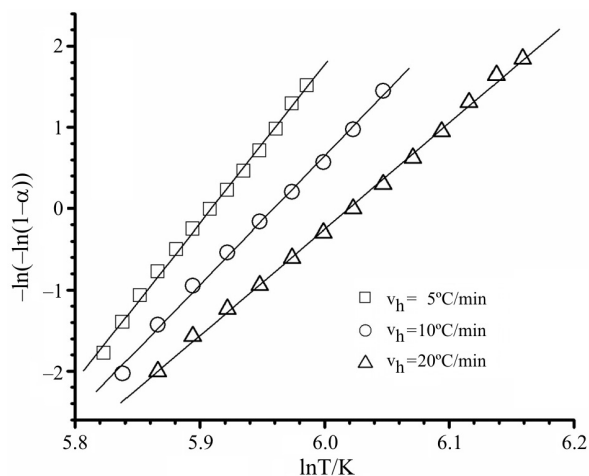


Fig. 4 Van–Krevelen plots of $\ln(-\ln(1-\alpha))$ vs. $\ln T$ for the dehydration of equilibrated swollen poly(acrylic-acid) hydrogel in nitrogen atmosphere

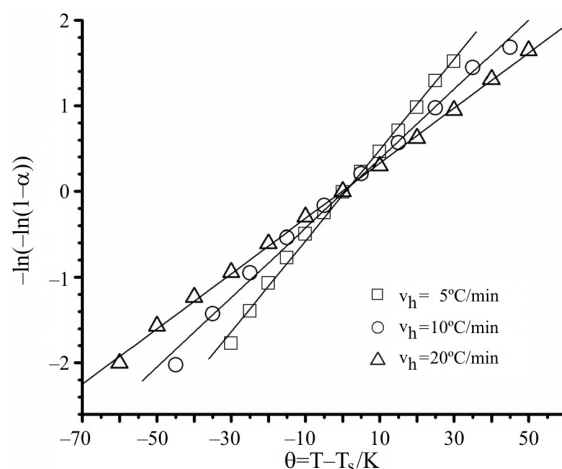


Fig. 5 Horowitz–Metzger plots of $\ln(-\ln(1-\alpha))$ vs. θ for the dehydration of equilibrated swollen poly(acrylic-acid) hydrogel in nitrogen atmosphere

Table 3 Values of constants of functional changing of activation energy with heating rate of the considered system

Method	$E_1 /$ kJ mol^{-1}	$c /$ kJ mol^{-1}	$d /$ $^{\circ}\text{C min}^{-1}$	$E_0 /$ kJ mol^{-1}
Coats–Redfern	37.81	41.09	5.06	78.9
Van Krevelen	37.60	36.00	7.15	73.6
Horowitz–Metzger	44.76	37.58	5.42	82.3

where E_1 , c and d , are constants. Table 3 presents values of constants E_1 , c and d , obtained by the used methods.

The column 5 of the Table 3, presented activation energy values of the investigated process, obtained by use of Eq. (13) for unlimited slow heating rate of the system ($v_h \rightarrow 0^{\circ}\text{C min}^{-1}$), E_0 . The obtained values for E_0 at unlimited slow heating of the considered system ($v_h \rightarrow 0^{\circ}\text{C min}^{-1}$), dependently on the ap-

plied method, are significantly higher (32–84%) than values of E obtained at non-isothermal conditions, which directly implies energetically redistribution of the desorption centers under different velocities of the thermal activation of the dehydration process of the investigated system.

By comparative analysis of the changes of the determined values for E and $\ln A$ with changes in the heating rate of the system, at all the methods, an existence of functional relationship the following type (14), i.e. compensation effect is established:

$$\ln A = a + bE \quad (14)$$

where a is a constant independent on temperature and is in relation to kinetic model of the process $f(\alpha)$, while b is:

$$b = \frac{1}{RT_{ic}} \quad (15)$$

where T_{ic} is the isokinetic temperature and R is the universal gas constant.

Table 4 Values of constants a and b of compensation effect and isokinetic temperatures T_{ic} obtained by different methods

Method	a	$b/\text{mol kJ}^{-1}$	T_{ic}/K
Coats–Redfern	−3.060	0.357	336.9
Van Krevelen	−3.976	0.379	346.8
Horowitz–Metzger	−2.591	0.355	339.0

Values of the constants a and b of the Eq. (14) are presented at Table 4.

Determined values of the isokinetic temperatures T_{ic} (Table 4) are in good agreement with the experimentally determined temperatures of the initial temperature (T_i) of the investigated dehydration process (Table 1, column 2).

In the Thomas's book [20], a detailed consideration of the compensation effect influence on the kinetics of the heterogeneous catalyzed reaction, where this problem have been postulated and explained for the first time. An appearance of the kinetic compensation effect is established in the many and various chemical reactions: thermal degradation of the substances in the solid state, reversible topochemical reactions, crystalhydrate dehydration, it is widely discussed and published in the references [21–25].

Existence of the compensation effect is established in the processes such as a curing of epoxy-resins [26], unsaturated polyester resins [27], curing of the diethylene glycol-bis(allylcarbonate) [28], thermal decomposition of thermotropic poly(oxybenzoate-co-oxynaphthoate) vectra copolyester [29].

In agreement with S. Vyazovkin [30], linear relationship can be generalized as follows (16)

$$\ln A_x = a + bE_s \quad (16)$$

where, x presents factor on the process which leads to the changes in Arrhenius parameters.

If, in Eq. (16) value of E would replace with value from Eq. (13), the following expression is obtained (17):

$$\ln A = a + b \left[E_1 + c \exp \left(-\frac{v_h}{d} \right) \right] \quad (17)$$

Equation (17) in entire gives description of the relationship of the kinetic parameters of the dehydration from the heating rate.

If we make an assumption, that factor x is the heating rate of the system, while the pre-exponential factor is proportional to the mass concentration of the desorption centers and activation energy is proportional to the energetically barrier of the observed process, it can be proposed that with the increase of the heating rate of the system comes to the energetic redistribution of the desorption centers. The increase of the heating rate, v_h , leads to the decrease of the number of active desorption centers per mass unit (decrease of $\ln A$) and to the decrease of the energy of the desorption centers (decrease of E), which has as a consequence changes of the kinetics parameters of the investigated process and appearance of the compensation effect.

Conclusions

Using different methods: Kissinger, Coats–Redfern, Van Krevelen and Horowitz–Metzger, kinetic parameters (E , $\ln A$, n) of the hydrogel dehydration are determined. In the wide range of dehydration, from 0.15 to 0.99%, kinetic parameters of dehydration are independent on dehydration degree. Values of kinetic parameters (E , $\ln A$, n) determined under same heating rate, applying different methods, are in good agreement one with each others. Independently on the applied method, values of the kinetic parameters (E and $\ln A$) decrease with increase of heating rate. An empirical equation, which describes changes of E and $\ln A$ from heating rate and existence of compensation effect, is specified. Values of the determined isoconversion temperatures are in good agreement with initial temperatures determined from thermogravimetric curves. The appearances of the compensation effect is explained by changes of energetic distribution of the desorption centers.

Acknowledgements

The investigation was partially supported by the Ministry of Science and Environmental Protection of Serbia, under the Project 1448.

References

- 1 N. Peppas, *Hydrogels in Medicine and Pharmacy*, Vol. I: Fundamentals, CRC, Boca Raton, FL, 1986.
- 2 E. Karadag 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. Int.*, 40 (1996) 281.
- 5 E. Karadag and D. Saraydin, *Turk. J. Chem.*, 26 (2002) 863.
- 6 Paloma M. de la Torre, Susana Torrado and S. Torrado, *Biomaterials*, 24 (2003) 1459.
- 7 C. M. A. Lopes and M. I. Felisberti, *Biomaterials*, 24 (2003) 1279.
- 8 J. Hao, Y. Liu, S. Zhou, Z. Li and X. Deng, *Biomaterials*, 24 (2003) 1531.
- 9 N. D. Deb, *J. Therm. Anal. Cal.*, 75 (2004) 837.
- 10 E. Tomaszewicz and M. Kotfica, *J. Therm. Anal. Cal.*, 77 (2004) 25.
- 11 B. V. L'vov and V. L. Ugolkov, *J. Therm. Anal. Cal.*, 74 (2003) 697.
- 12 K. S. Khairou, *J. Therm. Anal. Cal.*, 69 (2002) 583.
- 13 J. Jovanović and B. Adnadevič, XLI Consultation of Serbian Chemical Society, SSHD, Belgrade, 23–24 January, Book of Abstracts, HM13, 2003, p. 119.
- 14 H. E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
- 15 A. W. Coats and J. P. Redfern, *Nature*, 201 (1964) 68.
- 16 A. W. Coats and J. P. Redfern, *J. Polym. Sci. Polym. Lett. Ed.*, 3 (1965) 917.
- 17 D. W. Van Krevelen, C. Van Herden and F. J. Huntjens, *Fuel*, 30 (1951) 253.
- 18 D. W. Van Krevelen, P. J. Hoftyzen, *Properties of Polymers*, 2nd ed, Elsevier Scientific Publishing, Amsterdam 1980, p. 447.
- 19 H. H. Horowitz and G. Metzger, *Anal. Chem.*, 35 (1963) 1464.
- 20 J. M. Thomas and W. J. Thomas, *Introduction to the Principles of Heterogeneous Catalysis*, Acad. Press New York, London 1967, p. 263.
- 21 P. D. Garn, *J. Thermal Anal.*, 7 (1975) 475.
- 22 J. Zsako and M. Lungu, *J. Thermal Anal.*, 5 (1973) 77.
- 23 J. Zsako and M. Lungu, *J. Thermal Anal.*, 7 (1975) 33.
- 24 J. Zsako and H.E. Erz, *J. Thermal Anal.*, 6 (1974) 651.
- 25 P. Budrugaec and E. Segal, *Thermochim. Acta*, 260 (1995) 75.
- 26 S. Vyazovkin and N. Sbirrazzuoli, *Macromol. Chem. Phys.*, 200 (1999) 2294.
- 27 J. M. Salla, A. Cadenato, X. Ramis and J. M. Morancho, *J. Therm. Anal. Cal.*, 56 (1999) 771.
- 28 D. Klinar, J. Golob and M. Krajnc, *Chem. Biochem. Eng. Q.*, 18 (2004) 65.
- 29 X. G. Li and M. R. Huang, *Polym. Degrad. Stab.*, 64 (1999) 81.
- 30 S. Vyazovkin and W. Linert, *Int. Rev. Phys. Chem.*, 14 (1995) 355.

Received: February 07, 2005

In revised form: April 30, 2005

DOI: 10.1007/s10973-005-6839-9