

Kinetics of isothermal dehydration of equilibrium swollen PAAG hydrogel under the microwave heating conditions

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Received: 26 October 2015 / Accepted: 1 April 2016 / Published online: 15 April 2016
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Abstract The isothermal dehydration kinetics under microwave heating (MWH) of the equilibrium swollen poly(acrylic acid)-*g*-gelatin hydrogel (PAAG) was investigated. Dehydration kinetics curves have been measured for this recently synthesized and structurally defined hydrogel using a microwave thermogravimetric analyzer, within the temperature range from 323 to 353 K. It was found that the isothermal dehydration of the PAAG hydrogel was 15–17 times faster under the MWH than under the conventional heating (CH). We have established that the investigated dehydration is an elementary kinetics process. By applying the model-fitting method, it was found that the kinetics of isothermal dehydration under the microwave heating is mathematically best described by the Polanyi–Winger’s equation. The model rate constant values of the PAAG hydrogel isothermal microwave dehydration have been calculated. In accordance with the Arrhenius equation, the values of kinetics parameters have been obtained: $E_a = 52.0 \text{ kJ mol}^{-1}$ and $\ln(A/\text{min}^{-1}) = 12.1$. The higher values of dehydration rate under MWH, than under CH, are a consequence of the increase in the preexponential factor value caused by the change in the activated-state entropy of water molecules.

Keywords Microwave heating · Poly(acrylic acid)-*g*-gelatin hydrogel · Kinetics · Dehydration · Nucleation model

Introduction

Hydrogels are three-dimensional cross-linked polymeric structures that have the capability to swell in aqueous environments [1]. Hydrogels are considered of great significance in various fields like medicine, pharmacy, hygienic devices, agrochemistry and ecology. The widest practical application of hydrogels, particularly in agrochemistry and ecology, is based on their ability to reversibly absorb (swelling) and release (dehydrate) water [2, 3]. In order to optimize their applications, the characterization of the mechanism and kinetics of both hydrogel swelling and deswelling is important. The swelling behavior and swelling kinetics of various types of hydrogels have been extensively studied [4, 5]. However, there has been a focus on swelling in the literature, and the mechanism and kinetics of hydrogel’s dehydration have not been sufficiently investigated.

Hawladar et al. [6] used a one-dimensional diffusion model to describe the heat and the mass transfer, from the wet to the dry region of the hydrogel, during its drying process. The water diffusion kinetics, during the drying of polyacrylamide hydrogel, was examined by Roquez et al. [7]. Kemp et al. [8] have examined the applicability of a variety of mathematical models to fit the hydrogel’s kinetics in the process of drying. The mechanism of drying for polyacrylamide hydrogel, based on the changes in fluorescent spectra during drying, was presented in the research of Evinger et al. [9].

The normalized Weibull function of the dehydration time probability distribution was used for modeling the kinetics of both the isothermal and the non-isothermal dehydrations (under CH conditions) of equilibrium swollen poly(acrylic acid) hydrogel in the work of Adnadjevic et al. [10]. The isothermal dehydration kinetics of the

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equilibrium swollen poly(acrylic-co-methacrylic acid) hydrogel (PAM), under the conventional conditions, was explained by the energetic distribution of dehydration centers [11, 12]. In the work of Adnadjevic et al. [13], it was shown that the isothermal dehydration kinetics of PAM hydrogel is kinetically limited by the rate of the changes in the fluctuation structure of the hydrogel during the dehydration. The dominant effect on the dehydration kinetics of PAM hydrogel, in the range of dehydration degree (α) of $0.1 \leq \alpha \leq 0.8$, is referred to the so-called “ λ -relaxation process” (associated with mobility of sub-molecular structure), whereas, in the range of $\alpha \geq 0.8$, it is referred to the “ α -relaxation process” (associated with the “freezing” of segment mobility).

Siourousaz et al. [14] have investigated the isothermal dehydration kinetics of the polyvinyl alcohol nanocomposite hydrogel containing Na-montmorillonite nanoclay and found that the kinetics can be best described by the power-law equation and that the dehydration mechanism changes with temperature. At the temperature of 293 K, the dehydration kinetics can be described as a non-Fickian diffusion. However, at temperatures higher than 310 K, it proceeds as Fickian diffusion.

Recently, Potkonjak et al. [15] performed a comparative analysis on isothermal kinetics of water evaporation and poly(acrylic acid)-*g*-gelatin (PAAG) hydrogel dehydration under the conventional conditions. It was shown that the hydrogel dehydration kinetics can be mathematically described by a novel dehydration nucleation model.

Non-isothermal hydrogel dehydration was also investigated by different authors. Kinetic of non-isothermal dehydration of a polyacrylic hydrogel was investigated in the works of Jankovic [16] and Adnadjevic [17]. Bellich et al. [18] investigated non-isothermal dehydration of alginate gel microparticles, whereas Sovizi et al. [19] performed a kinetic study of non-isothermal dehydration of a silver nanocomposite hydrogel.

Microwave heating (MWH) significantly accelerates the rate of chemical reactions, gives higher yields of the products, and improves the properties of the products, which is the reason why the use of microwaves is attracting more and more attention [20]. The effect of microwave irradiation on the kinetics of chemical reactions is usually explained by thermal effects, such as overheating, hot-spots, selective heating, or as the consequence of specific microwave effects [20, 21]. There has been extensive research on biomaterials microwave drying, examining a broad spectrum of fruits and vegetables [22–24]. Jaya et al. [25] investigated the microwave power effects on vacuum drying kinetics of alginate–starch gel. In spite of that, to the best of our knowledge, there is no existing data on the kinetics of isothermal dehydration of the PAAG hydrogel or other hydrogels under the microwave heating.

With a motivation to address the gap in the literature regarding the effects of microwave heating on dehydration of hydrogels—particularly the dehydration kinetics—the major objectives of this work were to: (a) comprehensively study the kinetics of isothermal dehydration of synthesized PAAG hydrogel in the conditions of microwave heating, (b) compare MWH dehydration with the CH dehydration and (c) suggest the mechanism of the microwave heating effects on the hydrogel dehydration kinetics.

Materials and methods

Materials

The monomer acrylic acid (99.5 %) (AA) was purchased from Merck KGaA, Darmstadt Germany, stored in refrigerator and melted at room temperature before use. Gelatin (70–100 Blooma, puriss) was obtained from Kemika d.d, Zagreb, Croatia. The cross-linker *N,N'*-methylene bisacrylamide (p.a.) (MBA) was supplied by Aldrich Chemical Co., Milwaukee, USA. The initiator 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (99.8 %), (VA-044), was supplied by Wako Pure Chemical Industries, Osaka, Japan. Potassium hydroxide (p.a. 85.8 %) purchased from Centrohem, R. Serbia, was used as neutralization agent. Distilled water was used in all experiments.

Synthesis of poly(acrylic acid)-*g*-gelatin hydrogels

The poly(acrylic acid)-*g*-gelatin hydrogels were synthesized via cross-linking free-radical graft polymerization of AA and gelatin in aqueous media [15, 26]. The synthesized product was immersed in excess distilled water. The water was changed every 2–3 h for 7 days except overnight to remove the sol fraction of polymer and unreacted monomer. Subsequently, the washed-out hydrogel was dried in air oven at 333 K until constant mass was attained. The obtained products, PAAG xerogels, were stored in a vacuum exicator until use. For this investigation, the obtained hydrogel was grounded and allowed to swell to the equilibrium state in distilled water at room temperature.

Equilibrium swelling degree and structural properties of the synthesized xerogel

The equilibrium swelling degree (SD_{eq}) in distilled water at 298 K was determined by gravimetric procedure [15, 27]. The structural properties of the synthesized xerogel: xerogel density (ρ_{xg}), average molar mass between the network cross-links (M_c), cross-linking degree (ρ_c) and the distance between the macromolecular chains (d) have been determined and calculated by the methods proposed by

Gudeman and Peppas [28]. The structural property survey of the synthesized xerogel is given in Table 1.

As it can be seen, investigated hydrogel may be classified as a highly swellable, lightly cross-linked and macroporous.

Dehydration under microwave heating

The isothermal dehydration of the PAAG hydrogel under microwave heating (MWH) was investigated by using microwave thermogravimetric analyzer, a new device which is constructed in our laboratory. The samples of the equilibrium swollen hydrogel with average mass of 500 ± 10 mg were placed into a pan made out of Teflon. The pan with the sample was attached for Teflon filament and connected with the analytical balance to measure the changes in the sample mass with ± 0.1 mg accuracy. The analytical balance was connected through an interface to the PC processor in order to perform continuous measurements of the sample mass during the dehydration at defined temperature. The Balint software was used for this purpose. The Teflon filament, along with the pan, was placed in the central part of a commercially available monomode microwave unit (Discover, CEM Corporation, Matthews, North Carolina, USA). The machine consists of a continuously focused microwave power delivery system with an operator selectable power output from 0 to 300 W. All the dehydration processes were done in a microwave field of 2.45 GHz. The microwave unit was modified with a device to keep the temperature under isothermal MW measurements. The used microwave unit automatically maintains the required temperature in the reaction system by rapid variation (every few seconds) in input power and/or in N_2 flow change. When the sensor of the instrument detects a decrease in the temperature of the reacting system in comparison with the required temperature, the input power of the microwave field automatically increases and N_2 flow decreases; and opposite, when an increase in temperature in the reacting system is detected, the input power of the microwave field is automatically decreased, and N_2 flow is increased in order to achieve the desired temperature.

The PAAG hydrogel isothermal dehydration was performed at the temperatures of 293, 303, 313, 323 and 333 K. The temperature of the hydrogel was monitored by using a calibrated fiber-optic probe inserted into the device.

The temperature was measured with the accuracy of ± 1 K. The temperature, pressure and profiles were monitored using commercially available software provided by the microwave reactor manufacturer.

The degree of the dehydration was calculated as [17]:

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

where m_0 , m and m_f refer to the initial, actual and final mass of the sample, respectively. The isothermal conversion curve represents the dependence of the dehydration degree (α) on the reaction time (t) at constant experimental temperature (T).

Methods used to evaluate the kinetics model and kinetics parameters

The kinetics model of dehydration and the values of the kinetics parameters were evaluated with the application of the following methods:

Model-fitting method

According to the model-fitting method, reaction models of solid-state kinetics are, depending on the reaction mechanism, classified into five groups: (1) power law reactions, (2) phase-boundary-controlled reactions, (3) reaction orders, (4) reactions explained with the Avrami equation and (5) diffusion-controlled reactions. The model-fitting method is based on the following. The experimentally determined conversion curve $\alpha_{\text{exp}} = f(t)_T$ must be transformed into the experimentally normalized conversion curve $\alpha_{\text{exp}} = f(t_N)_T$, which is function of normalized time, t_N , defined by the equation:

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

where $t_{0.9}$ is the moment in time at $\alpha = 0.9$ [11, 29]. The kinetic model of the investigated process was determined by analytical comparing the experimental normalized conversion curves with the model normalized conversion curves. As a criterion of a variation between the experimental normalized conversion curves and the normalized conversion curves of the model, sum of squared residuals was used. Kinetic model of the exchange was determined

Table 1 Structural properties of the synthesized PAAG xerogel [15]

Property	$SD_{\text{eq}}/\text{g g}^{-1}$	$\rho_x/\text{kg m}^{-3}$	$M_c/\text{g mol}^{-1}$	$\rho_c/\text{mol dm}^{-3}$	d/nm
Value	340	1465	8.23×10^5	1.78×10^{-3}	310

as the one for which sum of squared residuals has minimal value.

A set of the reaction kinetic models used to determine the model which best describes the kinetics of the process of PAAG isothermal dehydration is shown in Table 2.

Differential isoconversion method

The dehydration activation energy for various dehydration degrees was established using the Friedman's method [42] which is based on the following. The rate of the process in condensed state is, in general, a function of temperature and degree of conversion, and in case of the isothermal dehydration of the PAAG hydrogel, it is function of temperature and dehydration degree:

$$\frac{d\alpha}{dt} = \Phi(T, \alpha) \quad (3)$$

that is,

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (4)$$

where $d\alpha/dt$ is the reaction rate, the function of α and T , α is the dehydration degree, $k(T)$ is the rate constant, t is the

time, T is the temperature and $f(\alpha)$ is the reaction model associated with a certain reaction mechanism.

The dependence of the rate constant on the temperature is ordinarily described by the Arrhenius law:

$$k(T) = A \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

where E_a is the activation energy, A is the preexponential factor and R is the gas constant.

By substituting Eq. (5) in Eq. (4), the following equation arises:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha) \quad (6)$$

Considering that the reaction rate constant is only a function of the temperature, which is known as the isoconversional principle of Friedman, Eq. (6) is easily transformed into:

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = \ln[A \cdot f(\alpha)] - \frac{E_{a,\alpha}}{RT} \quad (7)$$

That allows the evaluation of the activation energy for the particular degree of dehydration.

Table 2 Set of kinetics models used to determine the kinetics model of dehydration

Model	Reaction mechanism	General expression of the kinetics model, $f(\alpha)$	Integral form of the kinetics model, $g(\alpha)$	References
P1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$	[30]
P2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$	[30]
P3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$	[31]
P4	Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$	[32]
R1	Zero-order (Polanyi–Winger equation)	1	α	[32]
R2	Phase-boundary-controlled reaction (contracting area, i.e., bidimensional shape)	$2(1 - \alpha)^{1/2}$	$[1 - (1 - \alpha)^{1/2}]$	[33]
R3	Phase-boundary-controlled reaction (contracting volume, i.e., tridimensional shape)	$3(1 - \alpha)^{2/3}$	$[1 - (1 - \alpha)^{1/3}]$	[33]
F1	First-order (Mampel)	$(1 - \alpha)$	$-\ln(1 - \alpha)$	[34]
F2	Second-order	$(1 - \alpha)^2$	$(1 - \alpha)^{-1} - 1$	[35]
F3	Third-order	$(1 - \alpha)^3$	$0.5[(1 - \alpha)^{-2} - 1]$	[35]
A2	Avrami–Erofe'ev	$2(1 - \alpha)[-\ln(1 - \alpha)]^{1/2}$	$[-\ln(1 - \alpha)]^{1/2}$	[36, 37]
A3	Avrami–Erofe'ev	$3(1 - \alpha)[-\ln(1 - \alpha)]^{2/3}$	$[-\ln(1 - \alpha)]^{1/3}$	[36, 37]
A4	Avrami–Erofe'ev	$4(1 - \alpha)[-\ln(1 - \alpha)]^{3/4}$	$[-\ln(1 - \alpha)]^{1/4}$	[36, 37]
D1	One-dimensional diffusion	$\alpha/2$	α^2	[38]
D2	Two-dimensional diffusion (bidimensional particle shape)	$1[-\ln(1 - \alpha)]$	$(1 - \alpha)\ln(1 - \alpha) + \alpha$	[39]
D3	Three-dimensional diffusion (tridimensional particle shape) Jander equation	$3(1 - \alpha)^{2/3}/2[1 - (1 - \alpha)^{1/3}]$	$[1 - (1 - \alpha)^{1/3}]^2$	[40]
D4	Three-dimensional diffusion (tridimensional particle shape) Ginstling–Brounshtein	$3/2[(1 - \alpha)^{-1/3} - 1]$	$(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$	[41]

Results and discussion

Figure 1 shows isothermal thermogravimetric curves (dependence of the sample residual mass on time) of the equilibrium swollen PAAG hydrogel dehydration under microwave heating (MWH) for different temperatures.

As seen in Fig. 1, the isothermal thermogravimetric curves (TG) of hydrogel dehydration under MWH are linear, i.e., with the increase in the dehydration time, the residual mass of hydrogel decreases monotonically. The linear decrease points out that the rate of dehydration does not change with the changes in the dehydration degree. The temperature increases lead to the decrease in the dehydration time which is necessary to complete dehydration process (denoted as t_f in Fig. 1). Consequently, with the increase in the dehydration temperature, the slopes of the TG curves increase which indicate the increase in the rates of dehydration.

With aim to evaluate the kinetic complexity of the PAAG hydrogel dehydration process, the shape of the dependence of the activation energies ($E_{a,\alpha}$) on the degree of dehydration (α) was determined by the Friedman's method. Figure 2 shows dependence of $E_{a,\alpha}$ versus α .

Based on the results presented in Fig. 2, it may be seen that the value of $E_{a,\alpha}$ for the dehydration process of PAAG hydrogel is independent on the dehydration degree. Therefore, in accordance with the Vyazovkin's criterion [43], one can conclude that the investigated dehydration process under MWH is a kinetically elementary process which takes place in one step.

By applying model-fitting method, it had been established that the dehydration of PAAG hydrogel can be modeled by Polanyi–Winger's equation, $\alpha = k_m t$ [32].

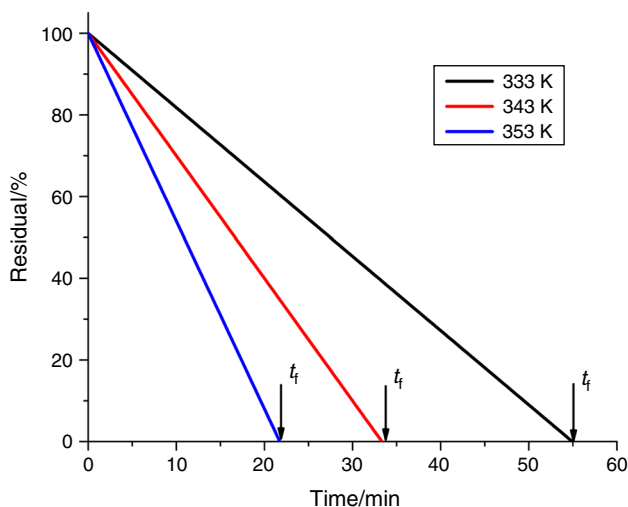


Fig. 1 Isothermal TG curves of PAAG hydrogel under MWH for different temperatures

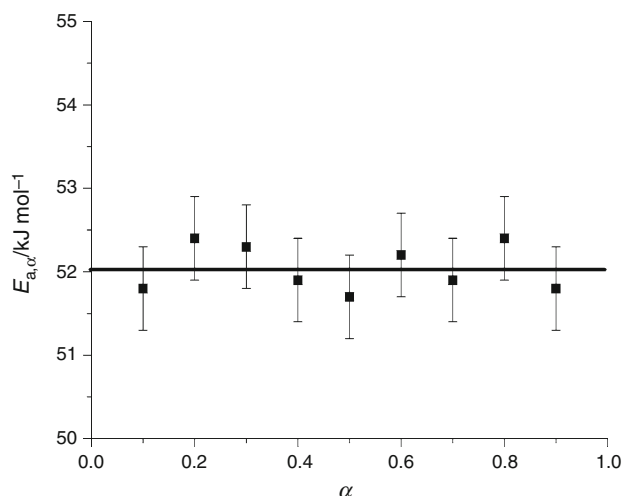


Fig. 2 Dependence of $E_{a,\alpha}$ versus α

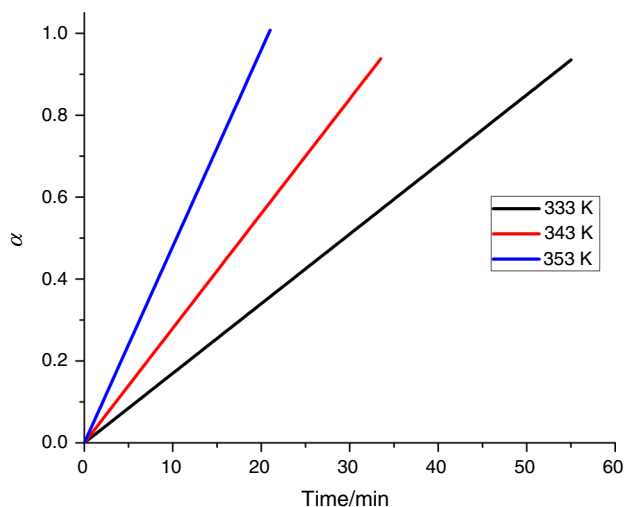


Fig. 3 Dependence of α versus time

Figure 3 shows dependence of the α versus dehydration time.

The dependence of α on dehydration time gives straight line for all of the investigated temperatures. Based on the slopes of those linear dependencies, the model constant rates (k_m) are calculated. The effect of temperature on the values of k_m for PAAG hydrogel dehydration under the MWH is presented in Table 3. The values of k_m of dehydration under MWH increase with the increase in the temperature in accordance with the Arrhenius equation. Therefore, the values of model kinetic parameters ($E_{a,m}$ and $\ln A_m$) were calculated based on the obtained k_m and presented in Table 3.

In the work of Potkonjak et al. [15], the isothermal kinetics of equilibrium swollen PAAG dehydration under the conventional heating conditions was performed and the

Table 3 Effects of temperature on the k_m and kinetic parameters of PAAG hydrogel dehydration under MWH

T/K	k_m/min^{-1}	Kinetic parameters
333	0.017	$E_{a,m} = 52 \pm 2 \text{ kJ mol}^{-1}$
343	0.028	$\ln[A_m/\text{min}^{-1}] = 12 \pm 2$
353	0.0048	$*R^2 = 0.99$

* R^2 is square of linear correlation coefficient

authors established that hydrogel dehydration is a kinetically complex process whose kinetics can be mathematically described by a linear combination of the two logistic functions and which proceeds through the nucleation mechanism. If we compare those results obtained for the CH dehydration with the results obtained herein for the dehydration under MWH (and for the same hydrogel), one can conclude that the MWH leads to the changes in the kinetic complexity of the dehydration process and kinetics model, and to increase in the kinetics parameters.

Having in mind kinetic complexity of the PAAG hydrogel dehydration under the conventional heating and different kinetics model in comparison with the conditions of microwave heating and with the aim to postulate an independent criterion that can be used to describe the influence of MWH on the PAAG hydrogel dehydration, we define the so-called average rate of dehydration (v_{avg}), given with the following expression:

$$v_{\text{avg}} = \frac{dm_t}{t_f} \quad (8)$$

where dm_t is total mass loss during the dehydration and the t_f is the time required to achieve the complete dehydration. Table 4 shows the effect of temperature on the values of v_{avg} for the PAAG hydrogel dehydration under the conditions of CH and MWH.

Value of v_{avg} increases with temperature in accordance with Arrhenius equation. Therefore, values of kinetics parameters calculated from v_{avg} ($E_{a,\text{avg}}$ and $\ln A_{\text{avg}}$) were obtained on the bases of dependence of $\ln v_{\text{avg}}$ on $1/T$ (Table 4). The v_{avg} of the isothermal dehydration of PAAG

hydrogel under the MWH conditions is 13–17 times higher for a given temperature, than under the conventional conditions. The value of $E_{a,\text{avg}}$ obtained for MWH is 66 % higher than $E_{a,\text{avg}}$ for the CH, whereas the value of pre-exponential factor (A_{avg}) is as much as 77,000 times higher. If we compare values of kinetics parameters for MWH, it can be seen that $E_{a,\text{avg}}$ is lower than $E_{a,m}$, whereas the values of the preexponential factors are within the error of determination.

In accordance with the general theoretical assumptions about the kinetics of chemical reactions and processes, the increase in the value of activation energy for the dehydration should lead to the decrease in the rate of dehydration. However, on the other hand, the increase in the value of preexponential factor should lead to the increase in the rate of dehydration. Therefore, one can conclude that the increase in the rate of the PAAG hydrogel isothermal dehydration under the MWH is caused by the increase in the value of the preexponential factor. Since the preexponential factor is in relationship with the change in entropy of activation (ΔS^*) by the following expression [44]:

$$\Delta S^* = R \left(\ln A - \ln k_B \cdot T/h \right) \quad (9)$$

where k_B is Boltzmann's constant and h Planck's constant, the values of ΔS^* were calculated for both MWH and CH conditions at all investigated temperatures. Table 5 shows the effects of temperature on the values of ΔS^* for MWH and CH conditions

Since the values of ΔS^* , at all of the investigated temperatures, both under the MWH and CH conditions, are negative by sign, one can conclude that the initial-state entropy values of water molecules are higher than the values of transition (activated)-state entropy. Therefore, formation of activation complex in a PAAG dehydration process is connected with decrease in entropy, i.e., activated complex is more organized than water cluster in initial state. The lower activated-state entropy values of water molecules in activated complex is in accordance with the nucleation mechanism of hydrogel dehydration by which activation of water molecules takes place through

Table 4 Effect of temperature on the values of v_{avg} for the PAAG hydrogel dehydration under the CH and MWH conditions

T/K	MWH		CH	
	$v_{\text{avg}}/\text{g min}^{-1}$	Kinetics parameters	$v_{\text{avg}}/\text{g min}^{-1} \times 10^4$	Kinetics parameters
313	–	$E_{a,\text{avg}} = 45 \pm 2 \text{ kJ mol}^{-1}$	4.3	$E_{a,\text{avg}} = 27 \pm 1 \text{ kJ mol}^{-1}$
323	–	$\ln[A_{\text{avg}}/\text{min}^{-1}] = 11 \pm 2$	5.8	$\ln[A_{\text{avg}}/\text{min}^{-1}] = 3 \pm 1$
333	0.009		–	
343	0.015		11.4	
353	0.023		13.6	

Table 5 Effects of temperature on the values of ΔS^* for MWH and CH conditions

<i>T</i> /K	MWH $\Delta S^*/J \text{ mol}^{-1} \text{ K}^{-1}$	CH $\Delta S^*/J \text{ mol}^{-1} \text{ K}^{-1}$
313	–	–188
323	–	–188
333	–114	–189
343	–114	–189
353	–114	–189

Table 6 Effects of dehydration temperature on the ΔG^* under the MWH and CH conditions

<i>T</i> /K	MWH		CH	
	$\Delta H^*/\text{kJ mol}^{-1}$	$\Delta G^*/\text{kJ mol}^{-1}$	$\Delta H^*/\text{kJ mol}^{-1}$	$\Delta G^*/\text{kJ mol}^{-1}$
333	43	81	25	88
343	42	80	25	89
353	42	80	24	91

forming structurally arranged nucleuses. The higher ΔS^* value for water molecules under the MWH condition than under the CH condition indicates that activation complex formation entropy is higher than initial-state formation entropy. Higher value of activation complex formation entropy is a consequence of microwave energy absorption (i.e., nonthermal absorption) by water molecules. Due to that, the oscillation frequency of the water molecules in the absorbed phase clusters increases and the reaction pathway is reduced, which leads to the increase in the preexponential factor value. Furthermore, this entails the increase in the number of the dehydration potential nucleation centers, which in accordance with the model of nucleation changes kinetics model of dehydration process from kinetic complex to kinetic elementary Polanyi–Winger model [15].

The obtained values of E_a and ΔS^* enable one to calculate the values of the changes of activated enthalpy (ΔH^*) and Gibbs free energy for dehydration (ΔG^*) under the MWH and CH conditions, using the following expressions, respectively [44]:

$$\Delta H^* = E_a - RT \quad (10)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (11)$$

Table 6 presents the effects of temperature of dehydration on the values of ΔH^* and ΔG^* under the MWH and CH conditions.

At the all temperatures, values of ΔH^* are significantly higher for MWH than for CH, and under both MWH and CH, temperature increase does not considerably change value of ΔH^* . Also, at the all temperatures and under the

both conditions, the values of ΔG^* are positive by sign, which further proves that PAAG dehydration is a non-spontaneous (i.e., endothermic) process and that is related with thermic activation mode. Lower ΔG^* values obtained for MWH than for CH clarify experimentally found higher dehydration rates under MWH conditions.

Conclusions

The isothermal dehydration of the PAAG hydrogel is as much as 15–17 times faster under the MWH than in the CH conditions. The isothermal MWH dehydration is a kinetically elementary process. Kinetics of MWH dehydration can be described with the Polanyi–Winger equation. The kinetics parameters of the dehydration under the MWH are higher than the ones under the CH. The increase in the rate of dehydration under the MWH is a consequence of the increase in the entropy of the activated dehydration state which is formed due to the nonthermal absorption of MW energy from the absorbed water molecules.

Acknowledgements This research was supported by the Ministry of Science and Technical Development of the Republic of Serbia, through Project No. 172015-OI.

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