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The Effect of Microwave Heating on the Isothermal Kinetics of Chemicals Reaction and Physicochemical Processes

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1. Introduction

Microwave heating is a widely accepted, non-conventional energy source which is now applied in numerous fields. In many of the examples published in the literature, microwave heating has been shown to lead to dramatically reduce reaction times, increased product yields and enhanced product purities by reducing unwanted side reactions compared to the conventional method of heating.

Several reviews have been published on the application of microwaves in organic synthesis (Kingston & Haswall, 1997; Loupy, 2002), polymer synthesis (Bogdal & Prociak, 2007), material science (Perelaer et al., 2006), nanotechnology (Tsuji et. al., 2005), homogeneous and heterogeneous catalyses (Larhed et. al., 2002; Will, et. al., 2004), medicinal chemistry (Shipe et. al., 2005), drug delivery (Kappe & Dallinger, 2006), biochemical processes (Collins & Leadbeather, 2007), synthesis of radioisotopes (Elander et. al., 2000), combination chemistry (Kimini et. al., 2000), green chemistry (Nüchter et. al., 2004), sintering (Saberli et. al., 2009), ceramics (Vanderach, 2002), extraction (Luchesi, et. al., 2004), nucleation and crystallization (Sung et. al., 2007; Cundy 1998), annealing (Bhaskar, et. al., 2007), solid-state reactions (Li et. al., 2007), adsorption (Turner, 2000) and combustion (Y-Pee, et. al., 2005).

The region of microwave radiation in the electromagnetic spectrum is located between infrared radiation and radio waves. Microwaves have wavelengths of 1 mm to 1 m, corresponding to frequencies between 0.3 and 300 GHz. In industrial and household microwave equipment, a frequency of 2.45 GHz with a wave number 12.2 cm is used.

The process by which matter absorbs microwave energy is known as dielectric heating. Three mechanism of dielectric heating of materials under the influence of microwave irradiation are recognized: the dipolar polarization mechanism, the conduction mechanism and the interphase polarization mechanism (Gabriel, et. al., 1998). Microwave heating of materials which occurs due to the dipolar polarization mechanism is provoked by the molecular friction caused by the re-orientation of the dipole moments of the material under the influence of a microwave field, *i.e.*, by the breaking and reforming of intermolecular bonds, due to which irreversible dissipation of the kinetic energy and thermal energy of the sample occurs. In the case when a substance contains mobile ions, the solvated ion due to attending the change in the oscillation of electrical component of the microwave field, increase the energy of collision and provokes the breakage and re-establishment of

intermolecular bonds. This means that the substance will be heated in the same manner as in the case of the dipolar polarization mechanism, *i.e.*, by the conduction mechanism. When metals are used, the third mechanism, of heating materials under the influence of microwave field, interphase polarization, is possible.

The coupling of microwave energy in the medium depends on the dielectric properties of the substance to be heated, *i.e.*, it depends on the quantity of microwave radiation that fails to penetrate the substance. The dielectric constant or relative permittivity (ϵ) is a property which describes the ability of a substance to store charge irrespective of the dimensions of the sample.

In an electromagnetic field, ϵ_r is defined by the equation:

$$\epsilon_r = \epsilon' + i\epsilon'' \quad (1)$$

where ϵ' is the real part of the dielectric constant and ϵ'' is the dielectric loss factor (dynamic dielectric coefficient) and i is imaginary number. The dielectric loss factor is obtained by comparing the irradiated microwave energy to the energy that has coupled with the sample. The degree of energy coupling in a reaction system depends on both parameters ϵ' and ϵ'' and is called the dissipation factor D :

$$D = \frac{\epsilon''}{\epsilon'} \quad (2)$$

The dissipation factor defines the ability of a medium at a given frequency and temperature to convert electromagnetic energy into heat. The efficiency on conversion of microwave energy into thermal energy depends on both the dielectric and thermal properties of a material. The fundamental relationship is:

$$P = \sigma |E|^2 = (\omega \epsilon_0 \epsilon'') |E|^2 = (\omega \epsilon_0 \epsilon' D) |E|^2 \quad (3)$$

where ϵ_0 is permittivity of free space, P is the power dissipation per unit volume, σ is the conductivity of the material, E is the strength of the electric field in the sample and ω is the angular frequency.

Assuming negligible heat loss and diffusion, the rate of heating or temperature rise (ΔT) in a time interval can be expressed as:

$$\frac{\Delta T}{t} = \frac{\sigma |E|^2}{\rho \cdot c} \quad (4)$$

where ρ is the density and c is the specific heat capacity.

The effect of microwave irradiation in chemical reactions and physico-chemical processes is a combination of thermal effects (overheating (Baghurst & Mingos, 1992), hot-spots (Zhang et. al., 1999) and selected heating (Raner et. al., 1993), as well as specific microwave effects (Hoz et. al., 2005). The thermal effects are connected with the different characteristics of microwave dielectric heating and conventional heating. Table 1 presents basic characteristics of microwave and conventional heating.

Microwave heating is based on the ability of some components of a material to transform electromagnetic energy into heat, whereby the magnitude of the heating depends on the

MICROWAVE HEATING	CONVENTIONAL HEATING
Energetic coupling	Conduction/ convection
Coupling at the molecular level	Superficial heating
Rapid	Slow
Volumetric	Superficial
Selective	Non-selective
Dependant on the properties of the materials	Less dependant on the properties of the materials

Table 1. The basic characteristics of microwave and conventional heating

dielectric properties of the molecules. Energy transmission is produced by dielectric losses, which is in contrast to conduction and convection processes observed in conventional heating. Microwave heating is rapid and volumetric, with the whole material being heated simultaneously. In contrast, conventional heating is slow and is introduced into the sample from the surface.

The thermal effects observed under microwave heating are a consequence of the inverted heat transfer, the inhomogeneties of the microwave field within the sample and the selective absorption of the radiation by polar compounds. These effects can be used efficiently to improve processes, modify selectivities or even to perform reactions that do not occur under conventional heating.

The issue of specific microwave effects is still a controversial matter. Several theories have been postulated and also some predicted models have been published.

Berlan et al., 1998, observed the acceleration of a cycloaddition reaction under isothermal microwave reaction conditions and explained the change in entropy of the reaction systems. Microwave enhanced the imidization reaction of a sulfone and ketone group-containing polyamic acid, which Lewis et al., 1992, elucidated with a mechanism based on "excess dipole energy", in which it was proposed that the localized energy (temperature) of the dipole groups was higher compared to the non-polar bonds within these systems.

Rybakov and Semenov, 1994, explained the effect of microwave reaction conditions on the kinetics of reactions in the solid state with the formation of a ponderomotive force, which influences the time-average motion of charged particles and enhances ionic transport in the solid state.

The ability of microwave radiation to excite rotational transitions and thus enhance the internal energy of a system was used by Strauss and Trainor, 1995, to explain the effects of microwave fields on the kinetics of chemical reactions. Binner et al., 1995, investigating the effect of a microwave field on the kinetics of titanium carbide formation, concluded that in the presence of a microwave field, the molecular mobility increases which leads to the increasing value of Arrhenius pre-exponential factor which further causes an acceleration of the synthesis of titanium carbide. Stuerga and Gaillard, 1996, explained the acceleration of the reaction rate in condensed states under microwave reaction conditions in comparison to conventional reacting conditions by the enhanced rate of collisions in condensed phases, which induces transfer between rotational and vibrational energy levels and reaction acceleration. Booske et al., 1997, used the existence of non-thermal energy distributions to explain microwave-enhanced solid-state transport.

Based on the experimentally confirmed decrease in the values of the activation energy of sodium bicarbonate decomposition under microwave reaction conditions, Shibata et al., 1996, concluded that the effect of a microwave field on dielectric materials is to induce rapid

rotation of the polarized dipoles in the molecules. This generates heat due to friction while simultaneously increasing the probability of contact between the molecules, thus enhancing the reaction rate and reducing the activation energy.

Perreux and Loupy, 2000, studied and classified the nature of the microwave effects considering the reaction medium and reaction mechanism, *i.e.*, the polarity of the transition state and the position of the transition state along with the reaction coordinate. Blanco and Auerbach, 2003, theoretically proved that the energy of a microwave field is initially transferred to select molecular modes (transition, vibration and/or rotation) and used this information to explain the inverse desorption of benzene and methanol from zeolite, compared to thermal desorption.

Conner and Tumpsett, 2008, explained specific microwave effects with the capability of microwaves to change the relative energies of rotation of intermediates in a given sequences. Bearing the preceding discussion in mind, this Chapter provides results of investigations of the kinetics of a) chemical reactions: isothermal PAA hydrogel formation, fullerole formation, and sucrose hydrolyses and b) physicochemical process: ethanol adsorption and PAM hydrogel dehydration; under conventional and microwave conditions with the aim to present the effects of microwave reaction conditions on kinetics model, values of kinetic parameters, the complexity of the kinetics of the investigated processes and to explain the effects of a microwave field on the kinetics of chemical reaction and physico-chemical processes.

2. Results

2.1 Isothermal kinetics of acrylic acid polymerization and crosslinking

Due to their extraordinary properties, such as swellability in water, hydrophilicity, biocompatibility, low toxicity and to their abilities to respond to a variety of changes in the surrounding environment, superabsorbing hydrogels of crosslinked poly(acrylic acid) (PAA) and their copolymers have been utilized in a wide range of biological, medical and pharmaceutical applications. Despite the importance of PAA hydrogels and the numerous publications concerning investigations of the absorptive properties of PAA hydrogels, information regarding the kinetics of polymerization is sparse.

Presently, crosslinked PAA hydrogels are usually synthesized following a procedure based on the radical polymerization of acrylic acid and crosslinking of the formed PAA, which could be realized either by a solution polymerization technique (Zhou et al. 1997a; Zhou et al. 1997b; Takeda, 1985) or by inverse suspension polymerization (Mayoux et.al., 2000; Chen & Zhao, 1999).

In a previous paper, the kinetics of the overall process of poly(acrylic acid) hydrogel formation, in both the case of conventional and microwave reacting conditions, were investigated (Jovanovic & Adnadjevic, 2010). It was found that the reaction rate was accelerated by about 50 times under isothermal microwave reaction conditions (MWIRC) when compared to conventional isothermal reaction conditions (CIRC), while the kinetics model is the same for both processes. Herein, a comparison of the kinetics of PAA hydrogel synthesis by aqueous solution polymerization and crosslinking will be presented. The procedure of PAA hydrogel formation, which occurred through the polymerization of acrylic acid and the crosslinking of the formed poly(acrylic acid), is thoroughly described in previous papers (Adnadjevic & Jovanovic, 2008; Jovanovic & Adnadjevic, 2010). The microwave-assisted reactions were conducted using a commercially available monomode microwave unit. (Discover, CEM Corporation, Matthews, North Carolina, USA) presented in Figure 1.

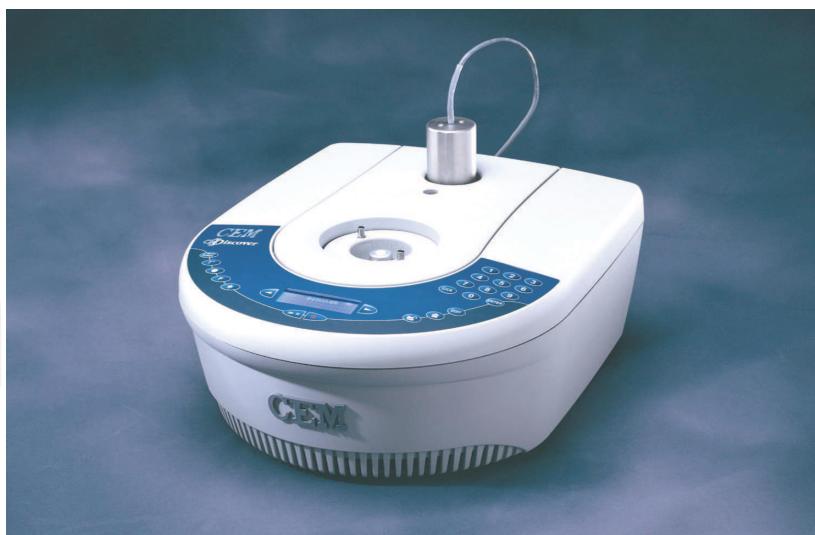


Fig. 1. Microwave unit

The machine consists of a continuously focused microwave power delivery system with an operator selectable power output from 0–300 W. All the reactions were realized in a microwave field of 2.45 GHz. The reactions were performed in glass-tubes (working volume 10 mL) which were supplied by the manufacturer of the microwave reactor. The temperature of the content of the reactor was monitoring using a calibrated fiber-optic probe inserted into the reactor. The temperature, pressure, and profiles were monitored using commercially available software provided by the manufacturer of the microwave reactor.

The temperature of the reaction mixture was controlled by the simultaneously varying of the input power of the microwave field and cooling of the reaction mixture by dry nitrogen. The temperature ranged from 303 to 323 K (± 1 K) during 0.5 min to 5 min, which was sufficient to approximately reach 100 % yield of the PAA hydrogel.

The yield (%) of the obtained cross-linked PAA product was determined gravimetrically by measuring the weight of the washed-out hydrogel, dried to constant weight (W_t). The yield, Y , was calculated as the ratio of W_t and the weight of the monomers (monomer and crosslinker) in the reaction mixture (W_o) (Eq. 5):

$$Y = \frac{W_t}{W_o} \quad (5)$$

The degree of PAA hydrogel formation (α) was calculated using Eq. 6:

$$\alpha = \frac{Y}{Y_{\max}} \quad (6)$$

where Y is the yield of the obtained PAA hydrogel at time t , and Y_{\max} is the maximum value of the hydrogel yield obtained at a certain temperature. Figure 2 shows the isothermal kinetics of PAA hydrogel formation under conventional conditions (a) and under microwave conditions (b) at different temperatures.

All the conversion curves for the formation of PAA hydrogels for both CIRC and MWIRC, are similar in shape. For all the curves, three specific shape of change of PAA hydrogel formation with time can be clearly observed: a linear, non-linear and a saturation stage.

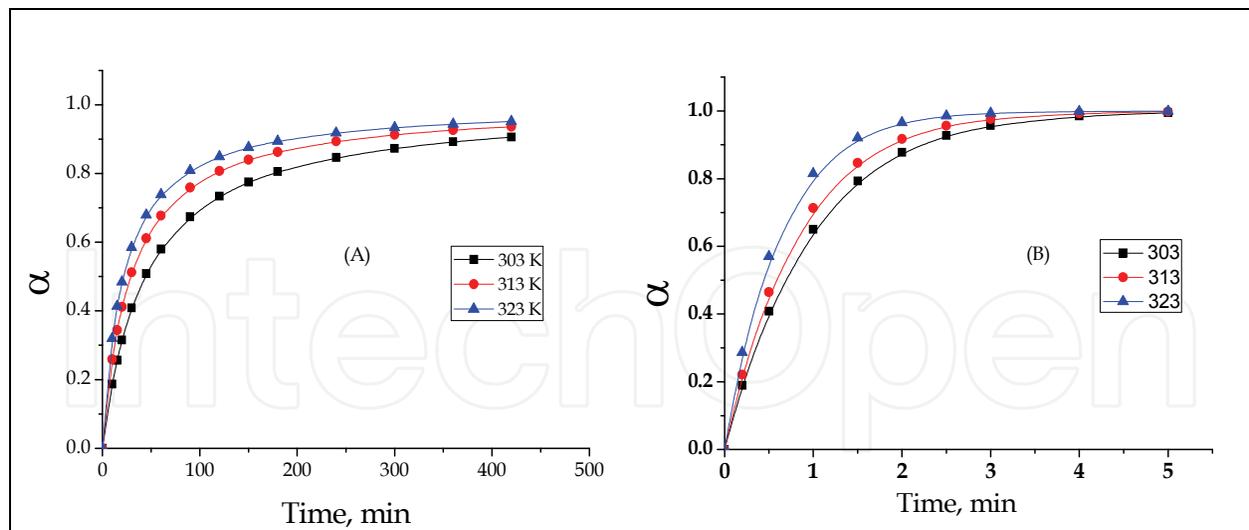


Fig. 2. Conversion curves for the formation of PAA hydrogel under the (A) CIRC conditions and (B) MWIRC conditions

With increasing temperature, for both conventional and microwave heating, the duration of the linear change in the degree of PAA hydrogel formation and the time required to achieve the saturation stage decreased.

With the intention of initially finding a kinetic model of the formation of PAA hydrogel formation both under conventional and microwave conditions, in agreement with the method of Khawan, 2006, the dependence of da/dt on the degree of PAA hydrogel formation (a) was analyzed (presented in Figure 3 for conventional conditions and under microwave conditions).

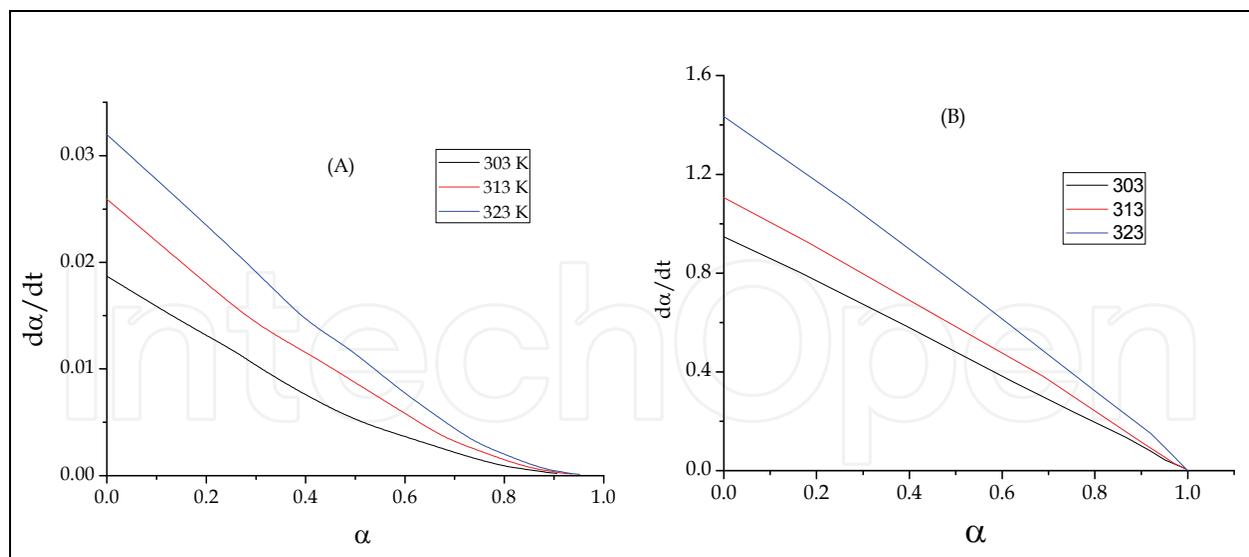


Fig. 3. Dependence of da/dt on the degree of PAA hydrogel formation under (A) conventional conditions and (B) microwave conditions

As depicted, for the both CIRC and MWIRC, the maximal rate was achieved at the beginning of the process and it decreased with increasing degree of PAA hydrogel formation but in a different manner. Under microwave conditions, the rate of PAA hydrogel formation decreased linearly with increasing degree of PAA hydrogel formation, while

under conventional conditions, the decrease was concave shaped. The established maximal values of the rate of PAA hydrogel formation and the changes in the dependence of da/dt on a imply different kinetic models of PAA hydrogel formation under conventional and microwave conditions. In order to prove this hypothesis, the values of kinetic parameters, activation energy and pre-exponential factor were determined by application of the “stationary point” method of Klaric, 1995, and the “model fitting” method (Brown et al., 1980; Adnadjevic et al., 2008) was used with the aim of determining the kinetic model of PAA hydrogel formation. The changes of $(da/dt)_{max}$ of PAA hydrogel formation and the kinetic parameters for both processes are presented in Table 2.

T, K	Conventional process		Microwave process	
	$(da/dt)_{max}$ [min ⁻¹]	Kinetic parameters	$(da/dt)_{max}$ [min ⁻¹]	Kinetic parameters
303	0.019	$E_a=22\pm0.2$ kJ/mol $\ln A = 5\pm0.1$	0.947	$E_a=17\pm0.3$ kJ/mol $\ln A=7\pm0.1$
313	0.023		1.105	
323	0.032		1.433	

Table 2. The changes of maximal reaction rate with temperature and kinetic parameters for PAA hydrogel formation for the conventional and the microwave process

The isothermal maximal rates for PAA hydrogel formation are approximately 50 times higher for the microwave heated process than for the conventionally heated process. With increasing temperature, the values of maximal rates for both processes exponentially increased, which enabled the kinetic parameters of PAA hydrogel formation (E_a and $\ln A$) to be determined using the Arrhenius Equation (given in Table 1). The activation energy for PAA hydrogel formation under MWIRC was $E_a=17$ kJ/mol, which is 1.3 times lower than the E_a of the process under CIRC, while the value of the pre-exponential factor for microwave conditions is 7.4 times higher than the value for the conventional conditions. By application of the “model fitting method”, it can be proved that the isothermal kinetics curves of PAA hydrogel formation during the conventional and microwave conditions can be described by equations (7) and (8), respectively:

$$\alpha = \frac{k_M \cdot t}{1 + k_M \cdot t} \tag{7}$$

$$\alpha = 1 - \exp(-k_M \cdot t) \tag{8}$$

which are characteristic for the so-called kinetic model of a second-order chemical reaction and a first-order chemical reaction, respectively. If Equations (7) and (8) describe the isothermal kinetics of PAA hydrogel formation, this means that the dependences of $\left[\frac{1}{1-\alpha} - 1\right]$ and of $[-\ln(1-a)]$ on reaction time should give straight lines for the conventional and microwave conditions, respectively, based on the slopes of which, the isothermal model constants of PAA hydrogel formation could be determined. Isothermal plots of $\left[\frac{1}{1-\alpha} - 1\right]$ and $[-\ln(1-a)]$ versus reaction time at different temperatures are shown in Figure 4 for the conventional and microwave conditions, respectively.

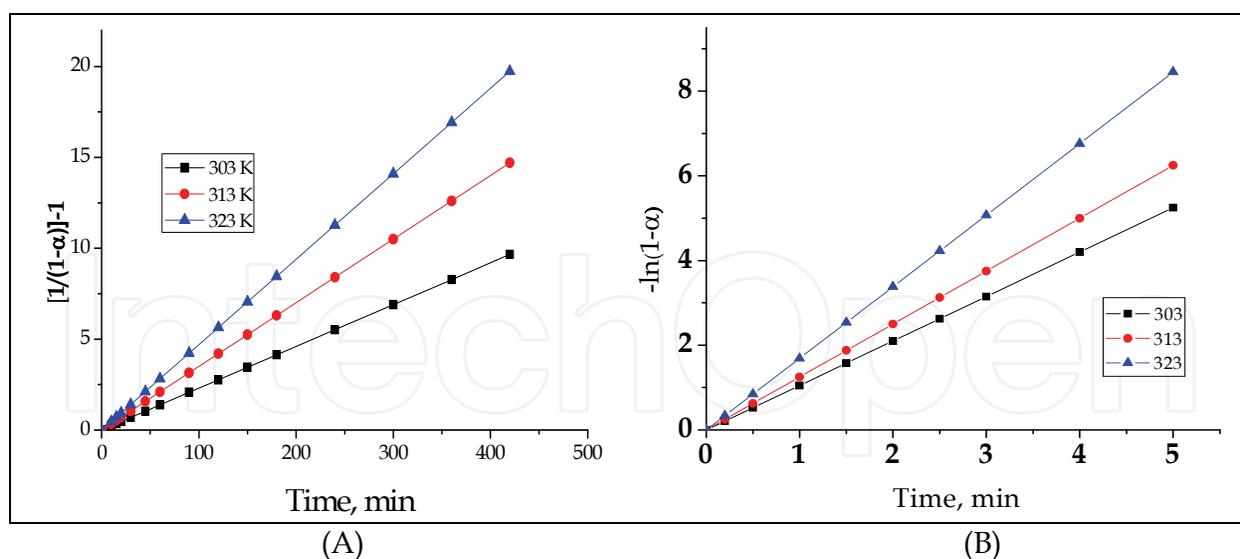


Fig. 4. A. Isothermal dependence of $[1/(1-\alpha)]-1$ on reaction time for PAA hydrogel formation under the conventional conditions; B. Isothermal dependence of $[-\ln(1-\alpha)]$ on reaction time for PAA hydrogel formation under microwave conditions.

As depicted in Figure 4 A and B, both the dependence of $\left[\frac{1}{1-\alpha}-1\right]$ and $[-\ln(1-\alpha)]$ on reaction time gave straight lines, which confirms the postulated kinetic model and enabled to calculate the model's constant of PAA hydrogel formation to be calculated, the values of which are given in Table 3 together with the kinetic parameters determined using the Arrhenius Equation.

T, K	Conventional process		Microwave process	
	$k_M^{\text{conv}}, \text{min}^{-1}$	Kinetic parameters	$k_M^{\text{mw}}, \text{min}^{-1}$	Kinetic parameters
303	0.023	$E_{a,M}=21\pm 1 \text{ kJ/mol}$	1.008	$E_{a,M}=17\pm 1 \text{ kJ/mol}$
313	0.035	$\ln(A_M/\text{min}^{-1})=$	1.180	$\ln(A_M/\text{min}^{-1})=8.6\pm 0.2$
323	0.047	9.4±0.2	1.590	

Table 3. The model's rate constants and kinetic parameters for PAA hydrogel formation for the conventional and the microwave process

The values of the rate constant of the model for the microwave process are temperature dependant and 34 to 44 times higher than the constants for the conventional process at the same temperature.

As the values of k_M exponentially increase with increasing temperature for both the conventional and the microwave process, the kinetic parameters of PAA hydrogel formation (E_a and $\ln A$) were determined using the Arrhenius Equation and the obtained values are presented in Table 2.

The energy of activation of PAA hydrogel formation under MWIRC is $E_a=17\text{kJ/mol}$, which is 1.2 times lower than the energy of activation under CIRC, while the $\ln A$ value is 10 % lower for the microwave process. The values of the kinetic parameters calculated using the rate constants of the model agree well with those based on the stationary point method.

The increase in the rate of some chemical reactions and physico-chemical processes are most frequently explained by the existence of local overheating, *i.e.*, by the presence of "hot-spot" points (Baghurst, 1992; Zhang, 1999; Raner, 1993; Hoz, 2005).

The established values of the rate constants of the model and their changes with temperature under conventional and microwave reaction conditions enabled the effects of so-called “hot-spots” on the kinetics of the investigated process to be objectively evaluated. In fact, if it is assumed that the values of the activation energy and the pre-exponential factor obtained for microwave reaction conditions are identical to the values for conventional reaction conditions, then, based on the experimentally determined values of the rate constants of the model under the microwave reacting conditions (k_M^{mw}), it is possible to calculate the temperature of the reacting system under microwave reacting conditions – the calculated microwave temperature (T^*) using the following equation:

$$T^* = \frac{E_{a,M}^c}{R(\ln A_M^c - \ln k_{mw}^T)} \quad (9)$$

where $E_{a,M}^c$ is the activation energy under conventional conditions, R is the universal gas constant, $\ln A_M^c$ is the pre-exponential factor for CIRC and k_{mw}^T is the reaction rate constant for MWIRC at a defined temperature. Table 4 presents values of the calculated microwave temperature T^* .

T, K	303	313	323
T^* , K	269	274	283

Table 4. Values of calculated microwave temperature

As the calculated values of the temperatures of the reaction system are significantly lower than the real macroscopic values, it can be stated that the acceleration of PAA hydrogel formation under microwave condition is not the consequence of the existence of “hot spots” in the reaction system.

Bearing in mind the established changes of the kinetic model of PAA hydrogel formation under microwave reaction conditions compared to conventional conditions, the Vyazovkin method was applied to examine the complexity of the kinetics of this process (Vyazovkin & Lesnikovich, 1990). In order to apply the Vyazovkin method, the dependences of $E_{a,\alpha}$ on the degree of conversion were established by the Friedman differential isoconversional method (Friedman, 1964) for the investigated process under conventional and microwave conditions and the results are presented in Figure 5.

The results shown in Figure 5 enabled it to be said with great certainty that the E_a of PAA hydrogel formation is independent of the degree of formation in both the conventional and microwave-heated process. This confirms that the investigated processes occurred through the elementary, overall single-stage formation the PAA hydrogel in both processes.

The established decrease in the values of the kinetic parameters of PAA hydrogel formation under microwave isothermal reaction conditions in comparison to conventional isothermal reacting conditions permit the possibility of an entirely new explanation of the action of a microwave field on the kinetics of chemical reactions and physico-chemical processes. The essence of this novel approach is the existence of a functional relationship between the values of the kinetic parameters of PAA hydrogel formation under the conventional and microwave reacting conditions, which is expressed as:

$$\ln A_F = 5.23 + 0.195 E_{a,F} \quad (10)$$

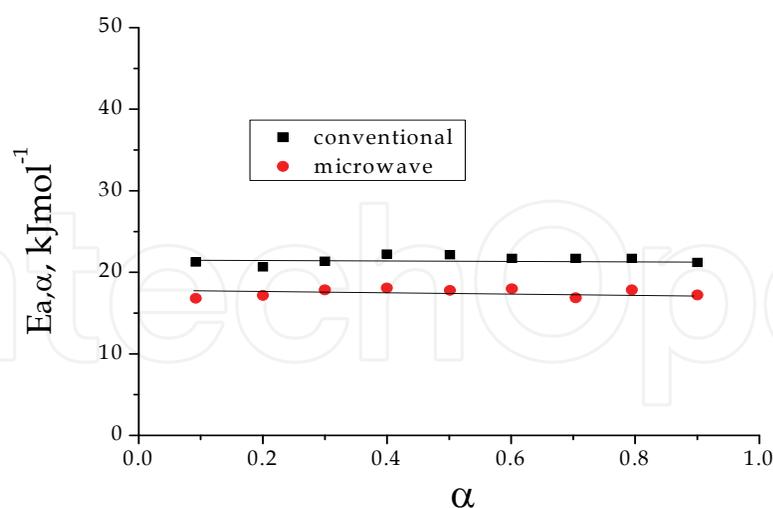


Fig. 5. The dependence of the $E_{a,\alpha}$ on the degree of conversion for PAA hydrogel formation where $E_{a,\alpha}$ and $\ln A_F$ are the activation energy and pre-exponential factor in a defined physical field (thermal or microwave). The form of equation (10) is recognized as the equation of the compensation effect, which is in relation to distinct changes in the conditions of a reaction or process (Vyazovkin & Wight, 1997). According to the Larsson Model of selective energy transfer during the interaction of a catalyst with reacting molecules, the existence of a compensation effect and the formation of an "active complex" (Larson, 1989) is explained as the consequence of transfer of the necessary amount of vibrational energy from an energetic reservoir onto the reacting molecule, which is aimed at "active complex" formation. The established changes in the kinetics parameters (decrease) can be explained with the decrease in: required amount of vibration energy necessary for "active complex" formation and in resonance frequency of the energetic transfer the between the oscillators under MWIRC in comparison to CIRC.

It can be assumed that a reacting molecule can be modeled as a sum of normal oscillators and that that molecule convert into an "active complex" anytime when it accepts the necessary amount of energy (energy of activation) and that during the formation of such an "active complex", vibrational changes occur which are in relation with changes connected with the localization of the energy on a defined bond (normal oscillator). Then, in accordance with the Larsson Model (Larsson, 1989) the wave number of the resonant oscillation (ν) and the energy of activation (E_a) of the reaction can be calculated. The wave number of the resonant oscillation is given by the Equation (11):

$$\nu = 0.715 / R \cdot b \quad (11)$$

where b is the energetic parameter: slope of the compensation effect equation, while the values of the activation energy is quantized and given as:

$$E_a = (n\nu + n^2 \nu x) + RT \quad (12)$$

where n is the number of quantum of vibrational energy transferred from one to another oscillator or from an energy reservoir („heat bath”) to the resonant oscillator, which are necessary to overcome the energetic barrier (activation energy) and x is the anharmonicity

constant of the oscillator. The calculated values for ν , n , x for the formation of a PAA hydrogel are presented in Table 5.

Variable	CIRC	MWIRC
ν (cm ⁻¹)	429	429
n	4	3
x	-0.022	-0.0017

Table 5. The values of ν , n and x under CIRC and MWIRC

During the formation of the “active complex” in the process of PAA hydrogel formation, resonance between the oscillator of the energetic reservoir and a molecules of acrylic acid under both CIRC and MWIRC is achieved at the same frequency of $\nu = 429 \text{ m}^{-1}$. That frequency corresponds to the so-called C-C-C skeleton bending vibration along the acrylic acid (Rufino & Monteiro, 2003) and therefore the formation of the “active complex” commences with the focusing and increasing of the energy of this oscillator. The number of quanta of vibrational energy that must be transferred from the energetic reservoir to the activated oscillator of a molecule of acrylic acid in order to overcome the energetic barrier for active complex formation under CIRC is higher than under MWIRC. Therefore, the established decrease in activation energy of the reaction under the MWIRC is a consequence of the increased ground vibration energetic level of the activated oscillator due to energy absorption from the microwave field. In addition, the recognized decrease in the pre-exponential factor of a reaction is a result of the decreasing number of energetic transfers per time unit (frequency of transfer), which is caused by an increase in the energy of an oscillator and by an increase in anharmonic oscillators.

2.2 Isothermal kinetics of fullerol formation under conventional and microwave reacting conditions

Water-soluble C₆₀ fullerols are one of the most interesting fullerene derivatives extensively investigated nowadays. They have potential applications in aqueous solution chemistry, electrochemistry, material chemistry and biochemistry. Fullerols have been used as preparatory material for syntheses of dendritic star-shaped polymers (Dai, 1997) and hypercrosslinked networks, as probes for investigating the surface properties of biomaterials (Zhao et al., 2004) and as coatings for solid-phase micro extraction (Lu et al., 2004). They exhibited excellent free-radical scavenging abilities against reactive oxygen species and radicals under physiological conditions (Lai et al., 2000; Dugan et al., 1996). Also, they show, *in vivo* and *in vitro*, potentially high biological activity in many important biological processes such as inhibition of HIV protease, lipid peroxidation and neuronal degeneration in Alzheimer’s disease, antiviral and antioxidant effects, specific cleavage of DNA (Bosi et al., 2003).

Different methods have been developed to synthesize water-soluble C₆₀. C₆₀ - fullerols can be obtained either directly from C₆₀ (Li et al., 1993) or from their derivatives (Taylor, 1995). Some of the most published methods involve the hydrolysis of a fullerene intermediate made by nitronium chemistry (Chiang et al., 1992a), aqueous acid chemistry (Chiang et al., 1993), mechanochemical synthesis (Chen et al., 1992b), nitrogen dioxide radicals (Chiang et al., 1996), hydroboration (Schneier et al., 1994) or by hydrolysis of polycyclosulfated precursors (Chiang et al., 1994). A much simpler method of polyhydroxylation involves the reaction of an aqueous NaOH solution in contact with a toluene or benzene solution of C₆₀

in the presence of a phase transfer catalyst. Phase transfer is usually accomplished with tetrabutyl-ammonium hydroxide (Li et al., 1993), cetyl trimethyl ammonium bromide (CTAB) (Lu et al., 2004) or polyethylene-glycol (Alves et al., 2006).

Fullerol was synthesized by the procedure described in detail previously (Adnadjevic et al., 2008). The degree of transformation of C_{60} to $C_{60}(OH)_{24}$ (α) at time (t) was calculated using Equation (13):

$$\alpha = \frac{C_0 - C_i}{C_0} \quad (13)$$

where C_0 is the starting concentration of C_{60} in the benzene solution and C_i is the concentration of C_{60} in the organic layer of the reaction mixture at time (t). The concentration of C_{60} was determined by measuring the absorption at $\lambda = 538$ nm and using Beer's law. The VIS spectra of both the C_{60} solution in benzene and the organic layer of the reaction mixture were obtained using a UV-Visible Spectrophotometer Cintra 10e, UK. The C_{60} benzene solution was deep violet in color and had two characteristic absorption maxima at $\lambda_1 = 538$ nm and $\lambda_2 = 592$ nm. During the reaction of fullerol formation, the intense color of the C_{60} benzene solution decreased, due to the decrease of fullerene concentration in the reaction mixture.

Figure 6 shows the isothermal changes of the degrees of transformation of fullerene (C_{60}) to fullerol ($C_{60}(OH)_{24}$) with reaction time (conversion curves) at different temperatures for conventional and microwave reacting conditions.

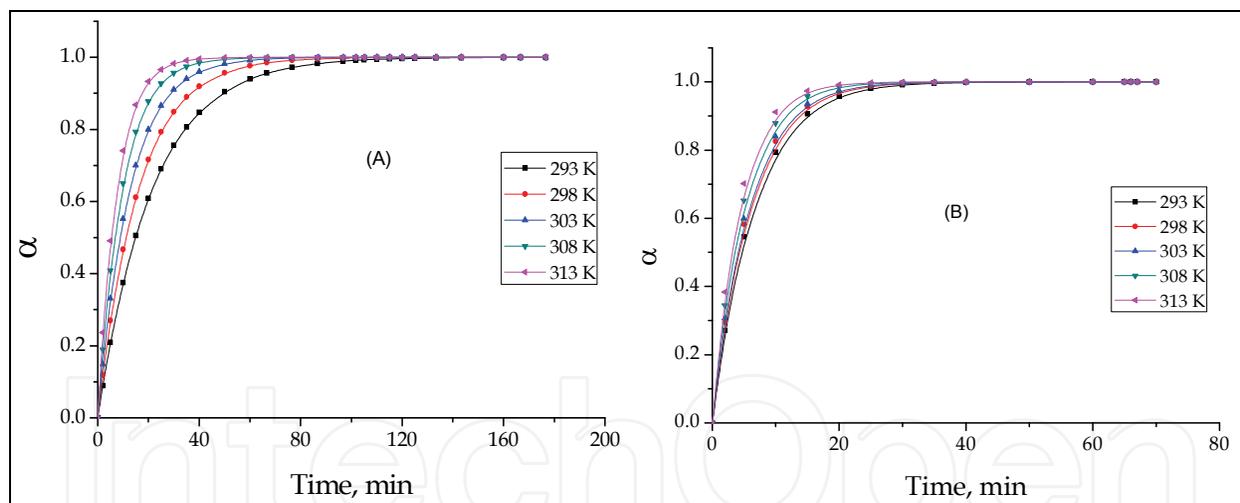


Fig. 6. The isothermal conversion curves for fullerol formation under (A) conventional reacting conditions and (B) microwave reacting conditions

Conversion curves of fullerol formation both for conventional and microwave reacting conditions are of same shape which points out to independence of kinetic model of fullerol formation on reacting conditions. By applying the "model-fitting method" it is easy to conclude that the kinetic's model for the formation of fullerol both under the conventional and microwave reacting conditions can be described with the Equation which is characteristic for first-order chemical reactions:

$$\alpha = 1 - \exp(-k_M \cdot t) \quad (14)$$

where k_M is a model constant for the first-order chemical reaction rate. The dependences of $[-\ln(1-a)]$ on reaction time for fullerol formation at different temperatures, for the microwave and conventional reacting conditions are shown in Figure 7.

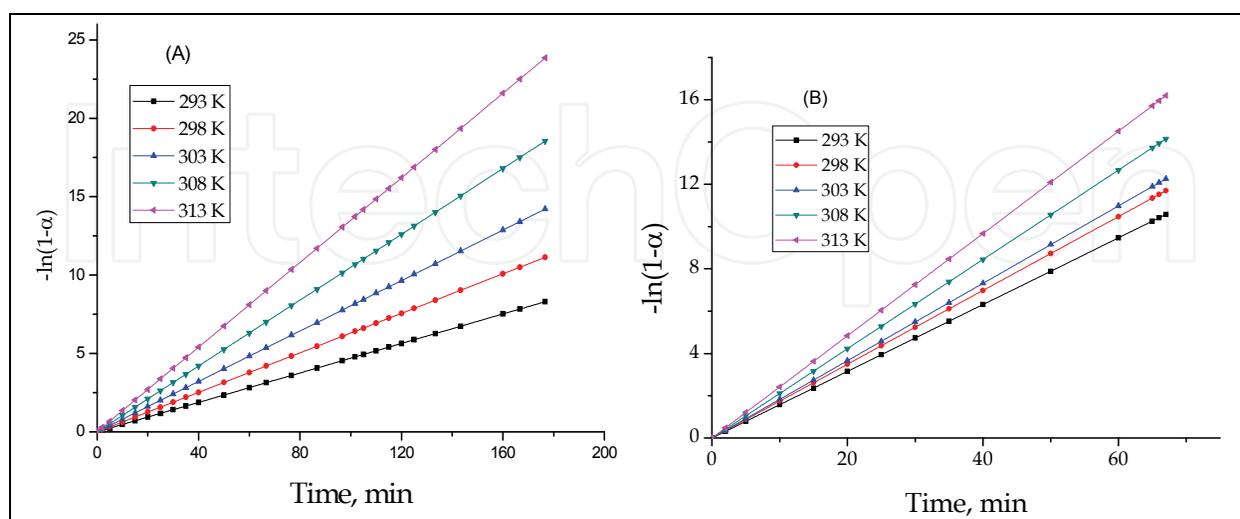


Fig. 7. The dependence of $[-\ln(1-a)]$ on reaction time for fullerol formation for (A) conventional reacting conditions and (B) microwave reacting conditions

The dependences of $[-\ln(1-a)]$ on time give straight lines for both conventional and microwave processes, which implies on properly selected kinetic's model and make possible to calculate the model's reaction rate constants from the slopes of these linear dependences. The calculated values of the k_M for the microwave and conventional reacting conditions at investigated temperatures are shown in Table 6.

T, K	Conventional process		Microwave process	
	$k_M^{conv}, \text{min}^{-1}$	Kinetics parameters	$k_M^{mw}, \text{min}^{-1}$	Kinetics parameters
293	0.047	$E_{a,M}=38\pm 2 \text{ kJ/mol}$ $\ln(A_M / \text{min}^{-1})=12.6\pm 0.5$	0.101	$E_{a,M}=10.5\pm 0.5 \text{ kJ/mol}$ $\ln(A_M / \text{min}^{-1})=2.44\pm 0.04$
298	0.066		0.175	
303	0.080		0.186	
308	0.106		0.192	
313	0.135		0.211	

Table 6. The temperature influence on the model's reaction rate constants and the kinetics parameters for fullerol formation, for the conventional and the microwave reacting conditions

The k_M values for microwave reacting conditions are 3.4 to 1.5 times higher in comparison to the values at same temperatures for conventional reacting conditions. As reaction temperature increase the k_M values increase exponentially for the each reacting conditions. By applying the Arrhenius equation, the kinetic parameters of fullerol formation, activation energy and pre-exponential factor, were calculated and are also given in Table 6.

The activation energy for the fullerol formation process under the microwave reacting conditions is about 4 times lower than the activation energy for the conventionally reacting conditions and the pre-exponential factor for the microwave process is 25000 times lower than the pre-exponential factor for the conventional process.

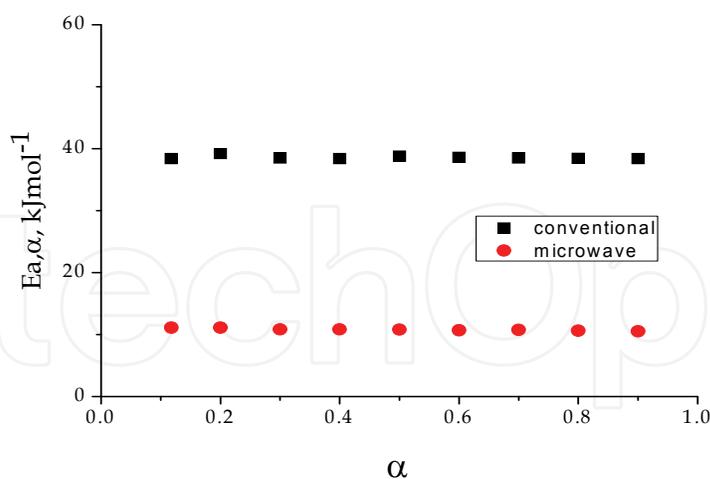


Fig. 8. The dependence of the $E_{a,\alpha}$ on the degree of fullerol formation

The dependence of $E_{a,\alpha}$ as a function of the degree of fullerol formation, for microwave and conventional reacting conditions is presented in Figure 8.

The values of $E_{a,\alpha}$ for each of the reacting conditions are independent on the degree of fullerol formation, which verify elementary character of the formerly presented kinetic model of fullerol formation. As in previously given examples, the values of kinetic parameters of fullerol formation for conventional and microwave reacting conditions are in mutually relationship by the compensation effect equation:

$$\ln A_F = -1.440 + 0.368E_{a,F} \quad (15)$$

Based on the compensation effect's parameters, values of the wave number of the resonant oscillator, the number of quantum of vibrational energy and the anharmonicity constant, under the CIRC and MWIRC were calculated and given in Table 7.

Parameter	CIRC	MWIRC
ν (cm ⁻¹)	233	233
n	14	3
x	-0.004	-0.0013

Table 7. The values of the ν , n and, x under the CIRC and MWIRC

The microwave reacting conditions do not lead to the change in the value of wave number of resonant vibrator. That, once again proves that reaction of fullerole formation is kinetically elementary process. The wave number of resonant oscillations corresponds to the so called H_g normal C-C vibrations in molecule of fullarene (Schettino et al., 2001). Therefore, activation of fullerene molecule for reaction of fullerol formation starts with the intensification of the so called H_g normal C-C vibrations and with new bond formations. Due to enhanced ground vibration level of the fullerene's molecule resonant oscillator, the number of vibrational quanta which are necessary for „active complex “ formation is significantly lower for MWIRC then for the CIRC. As, with the increasing energy of vibrational level frequency of energy transport from energetically reservoir on resonant oscillator decreases as well as the $\ln A$ value while the x value increases under the microwave reacting conditions when compared to the conventional reacting conditions.

2.3 Isothermal kinetics of acid catalysed sucrose hydrolyses under the conventional and microwave conditions

Recently, biomass attracts much attention as a renewable feed stock due to its CO₂ neutral impact on the environment. Sugars are key intermediates from biomass to chemicals and conversion of sugar also requires a green process. However, the present enzyme-catalyzed process for hydrolyses of starch to glucose need two steps with several drawbacks such as generation of waste, low thermal stability of enzymes and difficulty in separations of products and enzymes (Reilly,1999). Heterogeneous catalysts may find an opportunity for replacing the enzyme catalyst if glucose is obtained in one-step reaction with high catalytic activity and selectivity.

Kinetics of acid catalyzed sucrose hydrolyze on ion-exchange resins is widely investigated in the papers of (Gilliland, 1971; Siggers & Martinola, 1985; Dhepe et al., 2005). Plaze presented results for sucrose hydrolyses, under the conventional and microwave conditions in stirred tank reactor (Plaze et al., 1995).

Herein, strongly acid cation-exchanged resin, IRA-120 (Amberlit), was used as catalyst for hydrolyses of sucrose (pro analysis, Merck, Germany) to glucose and fructose. Water solution of sucrose at the initial concentration $C_s=57$ g/L and 15 g acid cation-exchange was used in all experiments. During the conventional reacting conditions (CRC) reactor ($V=100$ mL) was placed in thermostated controlled water bath. The contents were agitated at a stirring rate of 400 rpm to suspend the solid catalysts, to eliminate the mass transport resistance and to assure a thermally homogeneous suspension. The temperature was maintained within ± 0.5 K and monitored with a thermometer. Microwave reactions were conducted using a commercially available monomode microwave unit (CEM Discover) as it is thoroughly described in previous parts of this Chapter. Reactions were performed in 100mL glass reactor. In all cases, the contents of reactors were stirred by means of rotating magnetic plate located below the floor of the microwave cavity and a Teflon-coated magnetic stirrer bar in the reactor.

Glucose concentration in a reaction mixture was determined by spectrophotometry method (Miller, 1959). Degree of sucrose conversion was determined by the Eq 16:

$$\alpha = \frac{C_i}{C_{\max}} \quad (16)$$

where C_i is glucose concentration in reacting time and a C_{\max} is theoretically maximal value of glucose in reacting system. Figure 9 presents conversion curves of acid catalyzed sucrose hydrolyses, under the conventional and microwave conditions.

Conversion curves of sucrose hydrolyses are of same shape which point out on identical kinetic's model for both reacting conditions, conventional and microwave.

By applying the "model fitting method" it was revealed that kinetics of acid catalyzed sucrose hydrolyses under each reacting conditions can be modelled with the equation characteristic for kinetics of first order chemical reaction:

$$\alpha = 1 - \exp(-k_M \cdot t) \quad (17)$$

where the k_M is a model constant for the first-order chemical reaction rate. If kinetic of hydrolyses occurs in agreement with equation (17), then the dependences of $[-\ln(1-\alpha)]$ on reaction time should give straight line. Figure 10 (A and B) show the dependences of $[-\ln(1-$

a)] on reaction time for sucrose hydrolyses at different temperatures, for microwave and conventional reacting conditions, respectively.

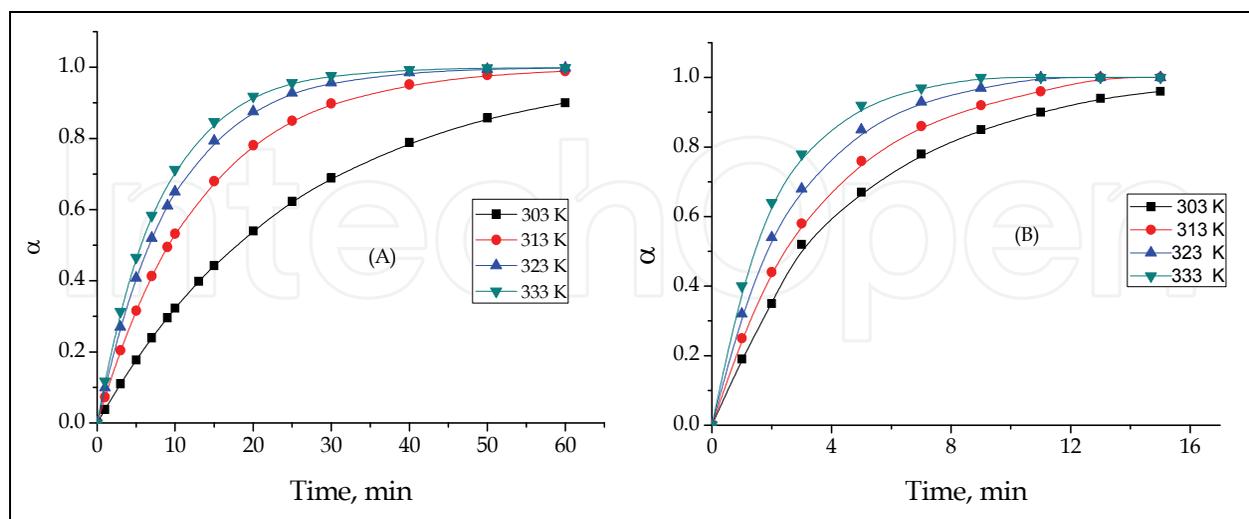


Fig. 9. The isothermal conversion curves for sucrose hydrolyses under (A) conventional and (B) microwave reacting conditions

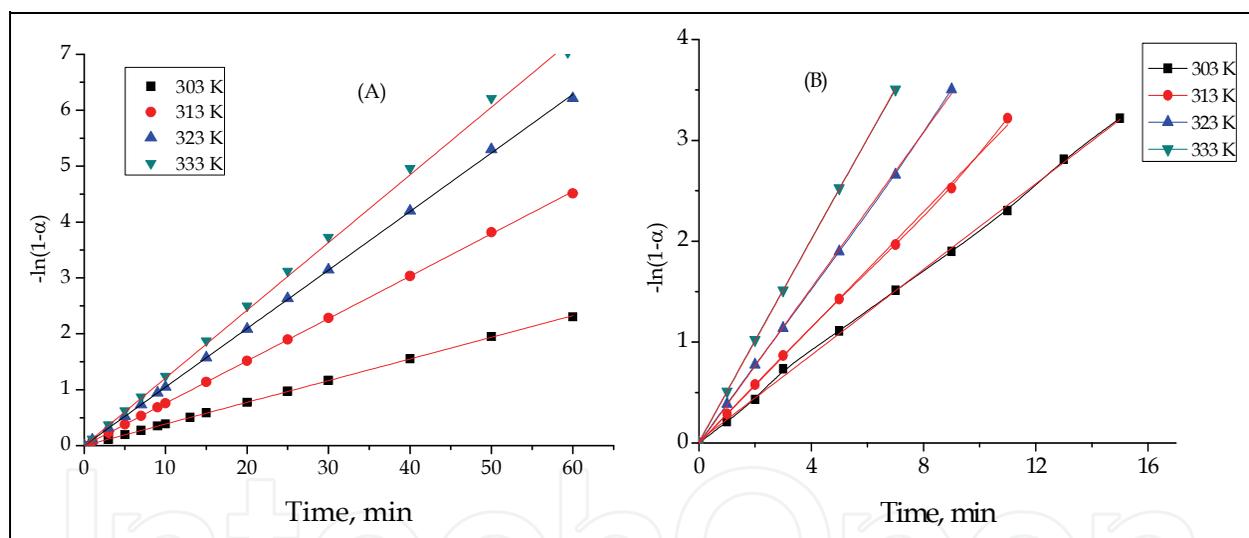


Fig. 10. Dependence of $[-\ln(1-a)]$ on reaction time for (A) conventional and (B) microwave reacting conditions of sucrose hydrolyses

The dependences of $[-\ln(1-a)]$ on time give straight lines for both conventional and microwave sucrose hydrolyses, which enables to calculate the reaction rate constants of the model. Table 8 presents dependence of the calculated values for k_M on temperature for both microwave and conventional reacting conditions.

The k_M values for microwave reacting conditions are ~ 5 to 10 times higher than the comparable values for conventional reacting conditions. The increasing reaction temperature leads to the exponentially increase of the k_M values for the both reacting conditions. The kinetic parameters of sucrose hydrolyses, activation energy and pre-exponential factor, were calculated by applying the Arrhenius Equation and they are shown in Table 8.

T, K	Conventional process		Microwave process	
	$k_M^{conv}, \text{min}^{-1}$	Kinetics parameters	$k_M^{mw}, \text{min}^{-1}$	Kinetics parameters
303	0.024	$E_{a,M}=32\pm 2 \text{ kJ/mol}$ $\ln(A_M/\text{min}^{-1})= 9\pm 1$	0.204	$E_{a,M}=25.15\pm 1 \text{ kJ/mol}$ $\ln(A_M/\text{min}^{-1})=8.4\pm 0.1$
313	0.039		0.287	
323	0.076		0.386	
333	0.105		0.510	

Table 8. The temperature influence on the k_M and the kinetic parameters for sucrose hydrolyses under the conventional and the microwave reacting conditions

The activation energy of sucrose hydrolyses under the conventionally reacting conditions is ~1.3 times higher than the value of E_a for the microwave reacting conditions, while the value of the pre-exponential factor for the conventional hydrolyses process is for ~7 % higher than the corresponding value for the microwave process.

The dependence of $E_{a,\alpha}$ as a function of the degree of sucrose hydrolyses, for microwave and conventional reacting conditions is presented in Figure 11.

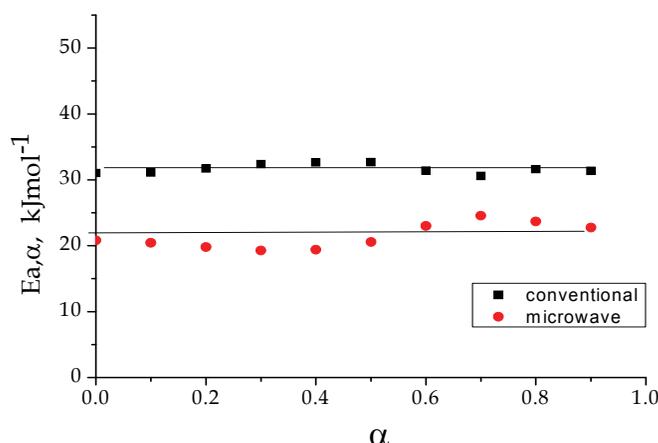


Fig. 11. The dependence of activation energy on the degree of sucrose hydrolyses

As in previously given examples of PAA hydrogel formation and fullerol formation, the values of $E_{a,\alpha}$ are independent on the degree of sucrose hydrolyses, for conventional and microwave reacting conditions. Therefore, acid catalyzed sucrose hydrolyses on ion-exchange resin, presents an elementary chemical reaction with unique kinetic model and mechanism, both under the conventional and microwave reacting conditions. The kinetic's parameters of sucrose hydrolyses, for conventional and microwave reacting conditions are interconnected by the compensation effect Equation as in former examples:

$$\ln A_F = 5.407 + 0.119E_{a,F} \tag{18}$$

Based on the parameters of the compensation effect, the values of the ν, n, x for microwave and conventional reacting conditions were calculated and presented in Table 9.

During the formation of the "activated complex" for the reaction of sucrose hydrolyses, for conventional and microwave reacting conditions, resonance between the oscillators of energetically reservoir takes place at the same frequency. As wave number of resonant frequency corresponds to the so called C-H out of plane deformation vibration (Ring, 2010)

Variable	CIRC	MWIRC
ν (cm ⁻¹)	723	723
n	4	3
x	-0.035	-0.042

Table 9. The values of the ν, n, x for sucrose hydrolyses, under the CIRC and MWIRC

of sucrose molecule, it may be concluded that activation of sucrose molecule for hydrolyses begins with the intensification of that vibration, which is in the following stage accompanied with the breaking of glycoside bond. The presence of microwave field leads to the decreasing number of vibrational quanta which should be accepted from the sucrose molecule in order to form "activated complex". That decreases, as in previously given examples, is a consequence of the increased energy of the ground vibration level of resonant oscillator due to the absorption of microwave energy. The decreased value of the pre-exponential factor and the enhanced values of anharmonicity factor under the microwave reacting conditions in comparison to the conventional conditions, is caused with the decreasing frequency of energy transfer from one to another oscillators which is provoked with the increase in vibrational energetically level of oscillators.

2.4 Isothermal kinetics of ethanol adsorption from aqueous solutions onto carbon molecular sieve under the conventional and microwave conditions

The bioethanol which is produced from renewable resources (waste lignocelluloses materials, algae, is now main alternatively source for promising economic production of novel fuels and chemicals (Kosaric et al, 2001). Selective ethanol adsorption from low concentrated aqueous solutions, which are usually formed after fermentation process, on hydrophobic materials of the zeolite type presents an effective technological process for development of profitable production of bioethanol (Adnadjevic et. al., 2007).

Kinetics adsorption curves of ethanol from aqueous ethanol solution onto carbon molecular sieve (CMS-3A) were performed by batch adsorption experiments. A measured quantity (5 g) of thermally activated CMS-3A granules was added to a predetermined quantity (50 g) of 10 wt.% aqueous ethanol solution thermostated at the required temperature (± 0.2 °C). The adsorption system was stirred at a rotation rate of 500 rpm at the given temperature. In the case of microwave conditions, the adsorption system was placed in a focused microwave reactor (Discover, CEM). Samples were taken from the adsorption system at regular time intervals. After their centrifugation, the zeolite was removed from solution and the ethanol concentration remaining in the solution was determined by measuring the refraction index of the solution using a Reichart-Jung Auto Abbe refractometer at 298K.

The amount of adsorbed ethanol (x) at a certain reaction time of the adsorption process can be calculated from Eq. 19:

$$x = \frac{C_0 - C}{m} \cdot m_s \quad (19)$$

where: C_0 is ethanol concentration in solution before adsorption (wt.%); C is ethanol concentration after a definite adsorption time (wt.%); m_s is the mass of solution (g) and m is mass of the zeolite (g). The degree of ethanol adsorption (α) was calculated from Eq. 20:

$$\alpha = \frac{x}{x_{\max}} \quad (20)$$

where: x_{max} is the experimentally determined maximal value of specific CMS-3A adsorption capacity at a given temperature. The isothermal dependences of the amount of adsorbed ethanol *versus* adsorption time at different temperatures under conventional and microwave conditions are shown in Figure 12.

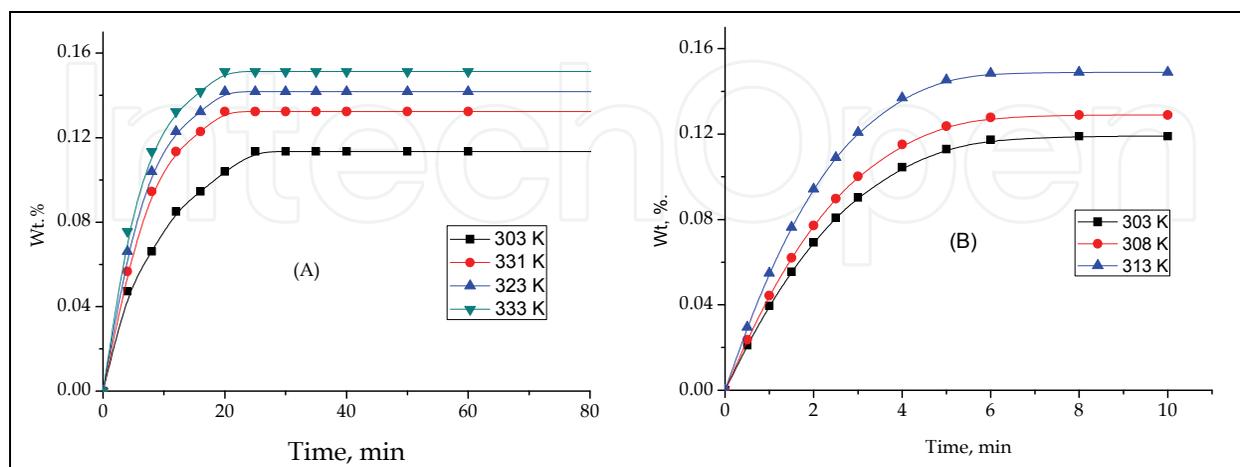


Fig. 12. The kinetic curves of ethanol adsorption on CMS-3A for (A) conventional and (B) microwave conditions

The kinetic curves of ethanol adsorption on CMS-3A for both conventional and microwave conditions have same shape at all the investigated temperatures. Three specific shapes of change of the degree of ethanol adsorption with time can be clearly seen at all kinetic curves, a linear, nonlinear and saturation region. With increasing temperature for both conventional and microwave conditions the period of linear change of the adsorption capacity with time became shorter, while the maximal value of adsorption capacity increased.

In order to preliminary find kinetic model of the isothermal adsorption of ethanol on CMS-3, for both conventional and microwave conditions, the dependence of da/dt on the degree of adsorption of ethanol was analyzed and presented in Figure 13.

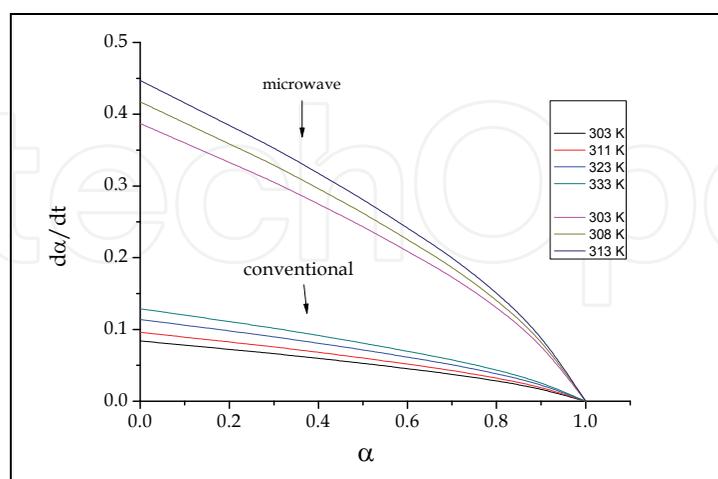


Fig. 13. Dependence of da/dt on the degree of ethanol adsorption

The changes in the (da/dt) on the degree of adsorption of ethanol are of identical shape; the so called concavely decreasing shape, for both conventional and microwave reacting conditions. The identical shapes of the changes in the (da/dt) on the degree of ethanol

adsorption, imply on unique kinetic model of adsorption of ethanol on CMS under the conventional and microwave conditions. For the each reacting conditions the maximal rate is achieved at the beginning of the process. Table 10 presents the temperature influence on the $(da/dt)_{max}$ for the adsorption of ethanol and kinetic parameters, for the conventional and microwave reacting conditions.

The maximal rates of the isothermal adsorption of ethanol on CMS-3A are approximately 4.6 times higher for the microwave process then for the conventional process. With the increasing temperature of adsorption system the values of maximal rates exponentially increase for both conventional and microwave conditions. Based on that, by using the Arrhenius Equation the kinetic parameters of adsorption of ethanol (E_a and $\ln A$) were determined by applying the method of stationary point and are given in Table 10.

Conventional process			Microwave process		
T, K	$(da/dt)_{max}$ [min ⁻¹]	Kinetics parameters	T, K	$(da/dt)_{ma}$ [min ⁻¹]	Kinetics parameters
303	0.084	$E_a=11.9\pm 0.2$ kJ/mol $\ln A = 2.2\pm 0.1$	303	0.387	$E_a=10.9\pm 0.2$ kJ/mol $\ln A=2.6\pm 0.1$
311	0.094		308	0.417	
323	0.114		313	0.447	
333	0.129				

Table 10. Temperature influence on $(da/dt)_{max}$ for adsorption of ethanol and kinetic parameters, for the CIRC and MWIRC processes

The activation energy for adsorption of ethanol under the microwave reacting conditions is lower for 8.4 % than under the conventional conditions. The value of the pre-exponential factor for microwave conditions is higher, for 3 times than the value for the conventional process.

By application of the "model fitting method", it was established that isothermal kinetics of adsorption of ethanol can be described by the Equation (21) both for the conventionally and microwave conditions. The Equation (21) is characteristic for the phase-boundary controlled reaction (tridimensional contracting volume):

$$\alpha = 1 - (1 - k_M \cdot t)^3 \quad (21)$$

where k_M is a model constant of the adsorption rate. The isothermal dependences of $[1-(1-\alpha)^{1/3}]$ on adsorption time for the conventionally and microwave conditions are shown in Figure 14.

The dependences $[1-(1-a)^{1/3}]$ on time, over the whole range of the adsorptions degrees and at all investigated temperatures for both CIRC and MWIRC are linear, which confirms that the correct model of kinetic was selected for describing ethanol adsorption on CMS-3A and it enable to calculate the model's constant of the adsorption rate. The changes of the model's constant with temperature for conventional and microwave conditions are given in Table 11.

The values of the k_M for the microwave conditions are approximately 4.5 times higher than the k_M values for the conventional conditions at the same temperatures. As the temperature increases, the values of the model constant of the ethanol adsorption rate exponentially increase, so the model parameters ($E_{a,M}$ and $\ln A_M$) of ethanol adsorption can be determined by applying the Arrhenius Equation. The obtained results are given in Table 11.

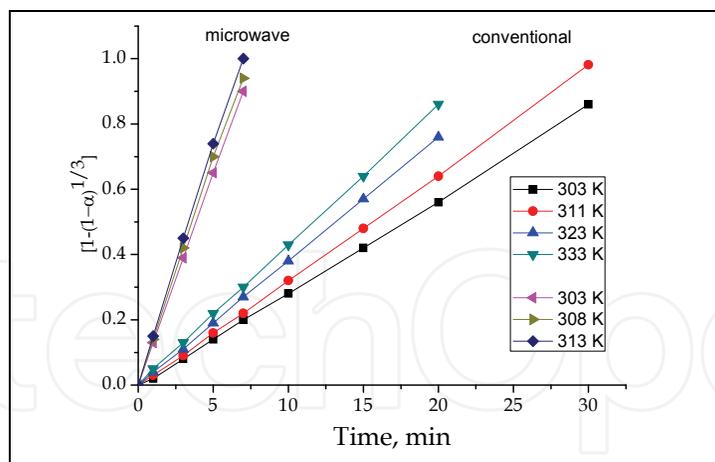


Fig. 14. Dependence of $[1-(1-a)^{1/3}]$ on adsorption time for the (A) conventional and (B) microwave conditions

Conventional process			Microwave process		
T, K	k_M^{conv} [min ⁻¹]	Kinetics parameters	T, K	k_M^{mw} [min ⁻¹]	Kinetics parameters
303	0.028	$E_a=12\pm 0.5$ kJ/mol $\ln A = 1.15\pm 0.05$	303	0.129	$E_a=11.2\pm 0.5$ kJ/mol $\ln A=2.4\pm 0.1$
311	0.032		308	0.139	
323	0.038		313	0.149	
333	0.043				

Table 11. The influence of temperature on model’s kinetic constants of the ethanol adsorption rate and kinetic parameters, for the CIRC and MWIRC processes

The activation energy for the adsorption of ethanol under the MWIRC is lower (~6%) while the pre-exponential factor is 3.5 times higher than for the CIRC.

The dependence of the activation energy on the degree of adsorption for conventional and microwave heating are presented in Figure 15.

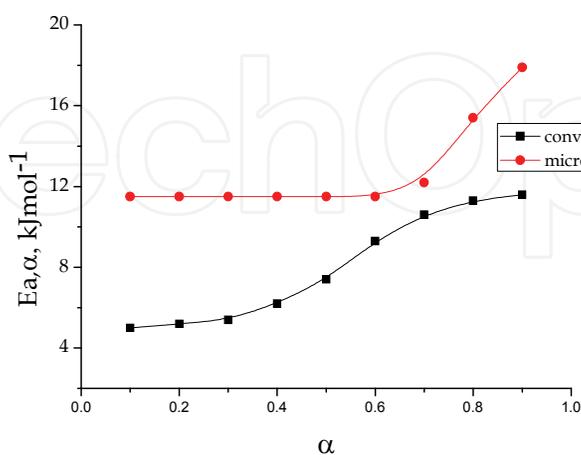


Fig. 15. The dependence of the $E_{a,\alpha}$ on the degree of conversion

As can be seen in Figure 15, the change in activation energy with degree of adsorption using conventional heating is completely different from the same change applying microwave

heating. This difference indicates a different mechanism (such as the order of the elemental steps) of adsorption using microwave heating in comparison to conventional heating. With conventional heating, three specific regions of change of the activation energy with degree of adsorption can be easily seen. At $\alpha \leq 0.3$, the value of activation energy does not change with increasing degree of adsorption, which indicates the dominant influence of an elemental step with $E_{a,\alpha} \approx 5$ kJ/mol on the mechanism and kinetics of adsorption. Likewise, at $\alpha \geq 0.8$, an increase of value of the degree of adsorption does not lead to a change in the activation energy. Therefore, another elemental step with $E_{a,\alpha} \approx 11$ kJ/mol has a dominant influence on the adsorption. At values $0.3 \leq \alpha \leq 0.8$, with increasing degree of adsorption, the value of the activation energy rapidly increased, indicating an increase in the influence of other elemental steps on the adsorption.

Contrary to this, with microwave heating, only two specific regions of change in the activation energy with degree of adsorption can be seen. In the region $\alpha \leq 0.8$, the value of the activation energy is independent of changes in the degree of adsorption, *i.e.*, an elemental step with $E_{a,\alpha} \approx 11.5$ kJ/mol has a dominant influence on the adsorption kinetics. At $\alpha \geq 0.8$, activation energy value increase rapidly with increasing degree of adsorption.

The established changes in the activation energy with degree of adsorption by applying microwave and conventional heating indicate that microwave heating leads, in comparison to conventional heating, to changes in the complexity of the reaction mechanism of the adsorption process.

The change of $\ln A_a$ for both conventional and microwave process of adsorption of ethanol are in functional relationship with the change in $E_{a,\alpha}$ (Eqs 22 and 23) and confirms the existence of a compensation effects against the degree of adsorption:

$$\ln A_a^{conv} = -1.907 + 0.295E_{a,\alpha} \quad (22)$$

$$\ln A_a^{mw} = -1.937 + 0.223E_{a,\alpha} \quad (23)$$

In accordance with the previously exposed model of influence of microwave field on the kinetic of the process, the values of the wave number of the resonant oscillator, the number of quantum of vibrational energy and the anharmonicity constant, under the CIRC and MWIRC were calculated and given in Table 12.

Variable	CIRC	MWIRC
ν (cm ⁻¹)	292	386
n	3	2
x	-0.025	-0.0016

Table 12. The values of the ν , n and x under the CIRC and MWIRC of ethanol adsorption process

The wave number of resonant frequency is higher for the MWIRC then the value for the CIRC of ethanol adsorption process. The wave number of resonant oscillations corresponds to the OH twisting vibrations in molecule of ethanol (Plyler, 1952) while the wave number of resonant frequency under the CIRC corresponds to the first overtone of rotation of ethanol molecule. Thus, in the presence of microwave field, molecules of ethanol absorb microwave energy and distribute to the rotation and vibration levels. Consequently, ground vibrational level of resonant oscillator increases and also the wave number of resonant frequency. As in

the case of all previous examples, number of transferred vibrational quanta is lower for MWIRC than for the CIRC. The decreased numbers of transferred quanta is a result of the increased energy of the ground level of vibrational level of the resonant oscillator which is formed due to the absorption of microwave energy. Also, established decreases of the pre-exponential factor and increases of value of anharmonicity factor is consequence of the increasing energy of the ground rotational level of the resonant oscillator.

2.5 Isothermal dehydration of poly(acrylic -co-methacrylic acid) hydrogels

Despite the enormous practical importance of the dehydration of hydrogels, especially concerning their possible application in agrochemistry and ecology, and the evaluation of the kinetics of dehydration process of hydrogels, which could lead to significant advancement in the theoretical consideration of the molecular mechanisms of the dehydration process, which is furthermore interconnected with the state of water in hydrogels, investigations of the dehydration of hydrogels are sparse.

The kinetics of isothermal dehydration under the conventional conditions of equilibrium swollen poly(acrylic acid) hydrogels (PAA) was investigated (Jankovic et al., 2008; Adnadjevic et al., 2009). Applying the model-fitting method, Jankovic et al., 2008, established that a change in the dehydration temperature caused a change in the dehydration kinetic model. Adnadjevic et al., 2009, established that the isothermal dehydration of a PAA hydrogel under conventional conditions could be mathematically described by a Weibull distribution function (WDF) of reaction times.

The poly(acrylic acid-co-methacrylic acid) hydrogel (PAM) was synthesized by a procedure based on the radical polymerization of acrylic acid and methacrylic acid (1:1 mol ratio) and cross-linking of the formed polymers, using a previously described procedure (Adnadjevic & Jovanovic, 2009).

Dehydration under the conventional isothermal process conditions (CIPC) was performed by the usual thermogravimetric measurements. The isothermal thermogravimetric curves were recorded on a simultaneous DSC-TGA thermal analyzer, Model 2960, TA Instruments, USA. The analyses were performed with $(20 \pm 2 \text{ mg})$ samples of equilibrium swollen hydrogel in platinum pans under a nitrogen atmosphere at a gas flow rate of 10 ml min^{-1} . Isothermal runs were performed at nominal temperatures of 293, 313, and 333 K. The samples were heated from the ambient to the selected dehydration temperature at a heating rate of 300 K min^{-1} and then held at that temperature for a given reaction time.

Dehydration under the microwave isothermal process conditions (MWIPC) was performed in a focused microwave reactor, as described in a former subchapter. At the beginning of each experiment, the equilibrium swollen hydrogel was placed in a glass device specially designed for these experiments. The analyses were performed with $(500 \pm 10 \text{ mg})$ samples of equilibrium swollen hydrogel at temperatures of 313 K, 323 K and 333 K.

The degree of dehydration under both conventional and microwave conditions was calculated as:

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \quad (24)$$

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

The experimentally obtained isothermal conversion curves of dehydration at different operating temperatures for the dehydration of the PAM hydrogel under the conventional and microwave conditions are shown in Figure 16.

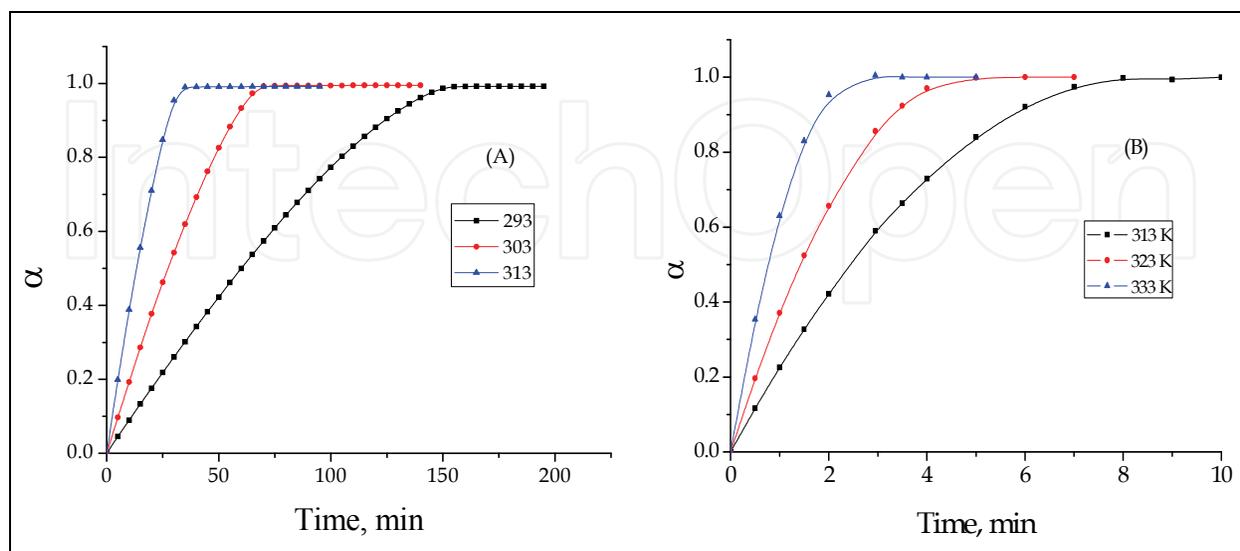


Fig. 16. The conversion curves for (A) conventional and (B) microwave dehydration process of the hydrogel

The conversion curves of PAM dehydration are of characteristic shape and exhibit three specific shapes of changes of the degree dehydration on dehydration time (linear, non-linear and plateau).

By means of the “model fitting method”, it was established that the kinetics of isothermal PAM hydrogel dehydration, for both conventional and microwave conditions, can be modeled by an equation which is specific for a phase-boundary controlled reaction model (contracting area), as follows:

$$\left[1 - (1 - \alpha)^{1/2}\right] = k_M \cdot t \quad (25)$$

where k_M is the model rate constant for the dehydration the PAM hydrogel. The dependence of $[1 - (1 - \alpha)^{1/2}]$ on time for the dehydration of PAM at different temperatures is presented in Figure 17 for conventional and microwave conditions.

Since, the dependence of $[1 - (1 - \alpha)^{1/2}]$ on time for the dehydration of PAM gives a straight line over the entire range of degrees of dehydration at all of the investigated temperatures for both the processes, the validity of the selected kinetics model was confirmed, enabled the calculation of the rate constant of the dehydration model. The effects of temperature of isothermal dehydration on the k_M values and the kinetic parameters of the process of isothermal dehydration the PAM hydrogel are given in Table 13.

Similar to the process of ethanol adsorption (described formerly), the values of the model rate constant for PAM hydrogel dehydration are approximately 5.0 times higher under microwave conditions than for the conventional heating process. As the k_M values for both processes exponentially increase with the increasing temperature, it is possible to determine the kinetic parameters of PAM hydrogel dehydration (E_a and $\ln A$) by means of the Arrhenius Equation. The obtained results are also presented in Table 13.

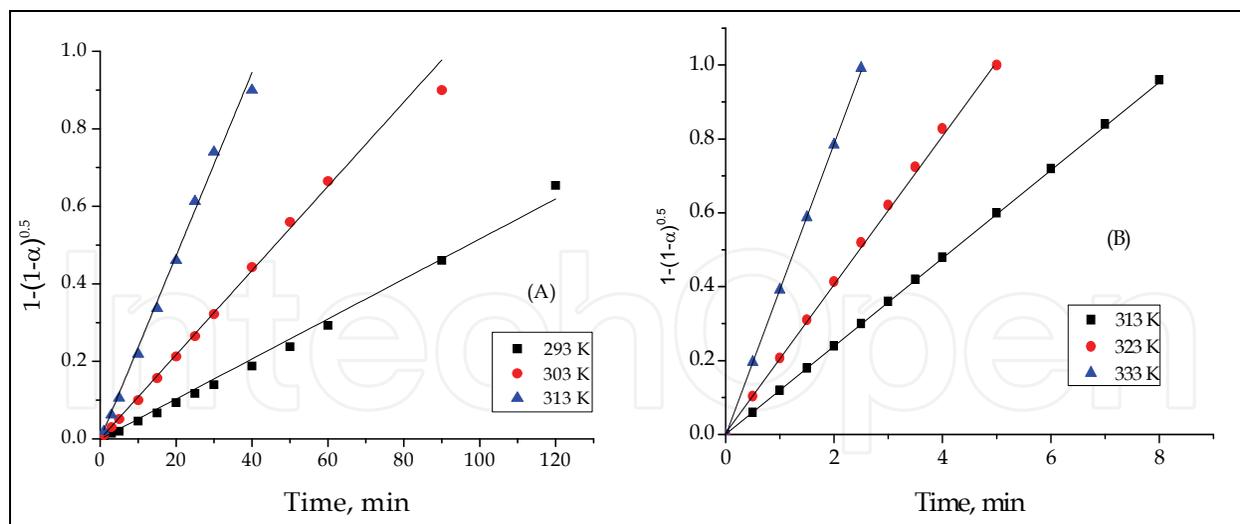


Fig. 17. The dependence of $[1 - (1 - \alpha)^{1/2}]$ on time for (A) conventional and (B) microwave dehydration process of the hydrogel

T, K	Conventional process		T, K	Microwave process	
	k_M [min ⁻¹]	Kinetics parameters		k_M [min ⁻¹]	Kinetics parameters
293	0.0052	$E_a=58.5\pm 0.5$ kJ/mol $\ln A = 18.5\pm 0.2$	313	0.120	$E_a=51.6\pm 0.5$ kJ/mol $\ln A=17.7\pm 0.2$
303	0.0109		323	0.207	
313	0.0236		333	0.393	

Table 13. The effect of temperature on the k_M values and kinetic parameters of the isothermal dehydration of the PAM hydrogel by the conventional and the microwave process

The activation energy for PAA hydrogel dehydration under microwave conditions is $E_a=51.6\pm 0.5$ kJ/mol, which is 12 % lower than the value of activation energy for the conventional process. The value of the pre-exponential factor for the microwave process is also lower than for the conventional process.

The plots of $E_{a,\alpha}$ versus the degree of PAA hydrogel dehydration for the investigated processes under conventional and microwave conditions are presented in Figure 18.

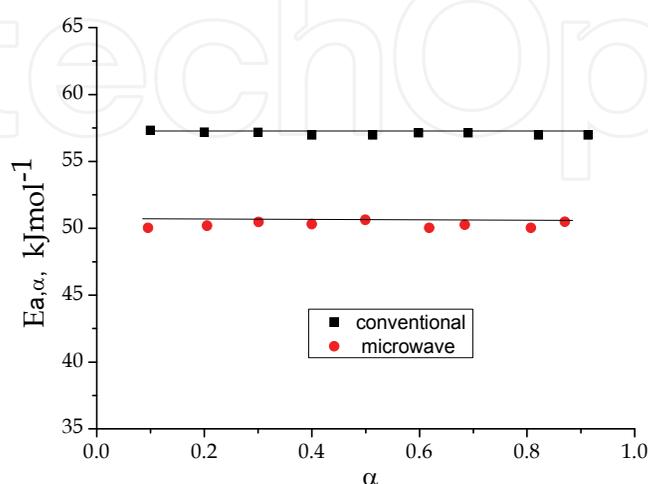


Fig. 18. The dependence of the $E_{a,\alpha}$ on the dehydration degree of the hydrogel

In the whole range of degrees of dehydration $0.1 \leq a \leq 0.9$, the activation energy is practically independent of the degree of dehydration, for both the investigated dehydration processes. As the independence of $E_{a,\alpha}$ on the degree of dehydration is distinctive for an elementary (single-stage) processes, it may conclude that the investigated process of dehydration is an elementary one and that the microwave field does not lead to changes in the mechanism of the process. A functional relationship exists between the values of the kinetic parameters for conventional and microwave process, which is defined by the compensation effect in relation to an interactive field, which can be presented as:

$$\ln A_F = 11.71 + 0.116 \cdot E_{a,F} \quad (26)$$

where $\ln A_F$ and $E_{a,F}$ are the values of the pre-exponential factor and the activation energy, respectively, in a specific field. The existence of a compensation effect against the interactive field, thermal or microwave, enables to calculate the values of the wave number of the vibrational energy of the vibrators which are in resonant interaction (ν), the vibrational quantum number (n) and the anharmonicity constant (χ) under conventional and microwave conditions, as shown in Table 14.

Variable	CIPC	MWIPC
ν	726	830
n	7	6
χ	-0.011	-0.015

Table 14. The values of ν , n , and χ under conventional and microwave conditions

Microwave reacting conditions does not lead to the change in wave number of resonant oscillation, which proves that dehydration process is an elementary kinetic process, both under the conventional and microwave conditions. Wave number of the resonant vibrations corresponds to the bond of intermolecular oscillations of molecules of water in cluster (Eisenberg, 1975). Therefore, activation of the absorbed water molecules for dehydration begins with the intensification of intermolecular oscillation of absorbed water in the clusters and with the breakage the certain intermolecular bonds. In the presence of microwave field, due to absorption of energy, energy of the ground vibrational level increases. For that reason, number of vibrational quanta required to overcome potential barrier under the microwave reacting conditions decreases compared to the conventional conditions. Due to increases in the vibrational energy of resonant oscillator in the molecules of absorbed water decreases energy transfer and for that reason pre-exponential factor has lower value for the microwave reacting conditions while the anharmonicity constant has higher value than the corresponding values for conventional conditions.

3. Conclusions

Under the influence of microwave reacting conditions, depending on dielectric properties of the reacting material, kinetics model and kinetics complexity of chemical reaction and/ or physical-chemical process could be altered or not altered.

Constant of chemical reaction or physical-chemical process are always higher for process under the influence of microwave field than when compared to their values obtained for the chemical reaction or process performed under the conventional reacting conditions.

The increase in the temperature of reaction and/or process leads to the changes in the values of rate constant of the reaction /process in accordance with the Arrhenius dependence.

The increase in the rate of reaction/ process under the microwave reacting /process conditions is a consequence of the decreased values of activation energy and pre-exponential factor of the investigated reacting /process.

The values of kinetics parameters of the reaction / process under the microwave reacting and conventionally reacting conditions are mutually interconnected with the Equation of compensation effect.

The decrease in the value of activation energy of the reaction/ process under the microwave reacting and conventionally reacting conditions is consequence of the increased energy of the ground level of the resonant oscillator which happened due to the absorption and distribution of microwave energy.

The decreased value of pre-exponential factor and the increased value of the anharmonicity under the influence of microwave reacting conditions is caused with the decreased value of energy transfer frequency and with the change in oscillator due to the change in energetically state.

In the investigated reaction of PAA hydrogel formation through acrylic acid polymerization and crosslinking, microwave reacting condition leads to change in the kinetics model of reaction when compared to the same process under the conventionally reacting conditions.

Activation energy of chemical reaction is quantized value which is predetermined with the number of transferred quant of resonant oscillator from energetically reservoir onto the active oscillator of reactants.

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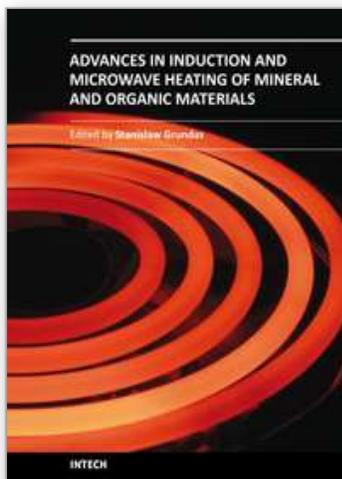
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