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Comparative analyses on isothermal kinetics of water evaporation and PAAG hydrogel dehydration under the microwave heating conditions

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ABSTRACT

The isothermal kinetic of water evaporation and poly(acrylic-*g*-gelatin) hydrogel (PAAG) dehydration in temperature range from 333 K to 363 K was investigated under microwave heating conditions (MWH). The isothermal kinetic curves of water evaporation and hydrogel dehydration could be entirely mathematically described by the Polanyi–Winger equation. The values of the rate constant for water evaporation and hydrogel dehydration and their kinetics parameters were calculated. Both the value of activation energy (E_a) and pre-exponential factor (lnA) for hydrogel dehydration under MWH is higher than those for water evaporation. The existence of a linear correlation relationship — compensation effect was established between the values of kinetics parameters for water evaporation and hydrogel dehydration. The values of thermodynamic parameters of activated complex formation for water evaporation and hydrogel dehydration (standard enthalpy of activation (ΔH^*), standard entropy activation (ΔS^*), and standard free Gibbs energy of activation (ΔG^*)) were calculated. The mechanism of water molecules activation, both for evaporation and dehydration, by the resonant transfer of certain energy amount from the reaction system to the libration vibration of molecules of water is suggested.

1. Introduction

Microwave heating significantly accelerates the rate of chemical reactions (de la Hoz et al., 2005) and physicochemical processes (Adnadjevic and Jovanovic, 2011), gives higher yields of the products and improves the properties of the products. That is a reason why the use of microwaves attracts more and more attention and accordingly microwave heating grows into broadly accepted non-conventional energy source for organic and polymer synthesis (Kappe et al., 2009; Bogdal and Prociak 2007) as well as different physicochemical processes such as adsorption (Liu et al., 2010), extraction (Rahim et al., 2014), etc.

Evaporation, as a physicochemical process, is of extreme importance for sustainable life at the earth planet. Evaporation plays significant role in a wide range of technologies in different industries. Kinetics of evaporation of water at free surfaces has been the subject of investigations by various researchers owing to its wide technical applications (Adamson, 1982; Badam et al., 2007), The earliest classical theory of water evaporation based on the kinetic theory of gases was developed by Hertz–Knudsen–Langmuir (Hertz, 1913). Based on the experimentally found significant temperature difference between the liquid and the vapour phase, Ward and Fang used the statistical rate theory and derived a non-linear expression for the evaporation rate as a function of entropy change (Ward and Fang, 1999). Bedeaux and Kjelstrup derived expression for evaporation rate using the non-equilibrium thermodynamics methods (Bedeaux and Kjelstrup, 1991). Until know, to the best of our knowledge there are not presented literature reports which deals with the kinetics of water evaporation under the conditions of microwave heating with controlled cooling with aim to maintain constant temperature within the investigated sample — isothermal microwave heating (MWH).

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Hydrogels are unique materials that are able to absorb huge amounts of water or water–liquids and usually consist of more than 99% water in their swollen state (Ganji et al., 2010) . Actually, the widest practical applications of hydrogels are based on their ability to reversibly absorb (swelling) and release (dehydrate) water. In spite the both practical and theoretical prospective significance, dehydration of hydrogels is not sufficiently studied.

Hawlader et al. 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 dehydration (Hawlader et al., 1991). The water diffusion kinetics, during the polyacrylamide hydrogel dehydration, was examined by Roques et al. (Roques et al., 1994). Kemp et al. examined the applicability of a variety of mathematical models to fit the kinetics of hydrogel dehydration (Kemp et al., 2001). The mechanism of polyacrylamide hydrogel dehydration, based on the changes in fluorescent spectra, was presented in the research of Evinger et al. (Evinger et al., 2009). Siorousazar et al. 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 changed with temperature. At the temperature of 293 K the dehydration kinetic was described as a non-Fickian diffusion, whereas at temperatures higher than 310 K the Fickian diffusion was found (Siorousazar et al., 2011). Adnadjevic et al. used normalized Weibull function of the dehydration time probability distribution to describe the kinetics of both the isothermal and the non-isothermal dehydration of poly(acrylic acid) hydrogel under conventional heating (CH) (Adnadjevic et al., 2009). The isothermal dehydration kinetics of poly (acrylic-co-methacrylic acid) hydrogel (PAM) under CH was explained by the energetic distribution of dehydration centres (Adnadjevic and Jovanovic, 2010).

Recently, Jovanovic et al. comprehensively investigated the kinetics of isothermal dehydration of the PAM hydrogel under MWH and compared the kinetics data of isothermal dehydration in the conditions of CH to those in MWH. It was concluded that the dehydration of the PAM hydrogel under MWH was kinetically elemental process and that its kinetics can be described by the kinetics model of the phase-boundary controlled process (contracting area). The established influence of MWH on the kinetics of dehydration was explained with a specific activation mechanism of water molecules for dehydration due to the absorption of microwave energy (Jovanovic et al., 2016).

Potkonjak et al. performed a comparative analysis on isothermal kinetics of water evaporation and equilibrium swollen poly(acrylic acid)-*g*-gelatin (PAAG) hydrogel dehydration under the CH. Based on the obtained results, they found that water evaporation was kinetically elemental process which could be mathematically described by the Polanyi–Winger equation whereas hydrogel dehydration was kinetically complex process which could be successfully described by a linear combination of logistic functions. The logistic function can be described as a function which can be presented in general form:

$$\alpha = \frac{w \exp(\alpha + k \cdot t)}{C + \exp(\alpha + k \cdot t)} \tag{1}$$

where α is the degree of conversion, w represent the limiting value of α, a is parameter, k is rate constant and C is constant. With aim to find unique model for both water evaporation and hydrogel dehydration the authors suggest a novel, so called nucleation model, which was appropriate to explain the obtained results (Potkonjak et al., 2015).

The kinetics of water evaporation has dominant importance on water circulation in nature and therefore can effect on clime change. In regard to that, grows the importance of knowing mathematical models to describe the kinetics and thermodynamics of the evaporation, since their awareness enable developing the systems for management the clime change. The knowing mathematical models present base for designing and construction of new devices and plants that would use microwave heating for the evaporation of water and for the development of novel technological systems for land irrigation using hydrogel. In regard to this, to be able to give and develop adequate kinetics model for the evaporation and dehydration using microwave heating it is necessary to know the degree of kinetics complexity, kinetics model and the values of the kinetics parameters of the processes. In this framework, in this manuscript the kinetics of water evaporation and hydrogel dehydration using MWH was thoroughly evaluated, which requires to determine the degree of kinetics complexity, kinetics model and the values of the kinetics parameters of the investigated evaporation and dehydration processes.

2. Experimental

2.1. 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 crosslinker *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 the all experiments.

2.2. Synthesis of poly(acrylic acid)-g-gelatin hydrogels

The poly(acrylic acid)-*g*-gelatin hydrogels hydrogel was synthesized via crosslinking free-radical graft polymerization of AA and gelatin in aqueous media (Adnadjevic et al., 2013). A part of 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 353 K until constant mass was attained. The obtained product, PAAG xerogel, was stored in a vacuum exicator until use. For this investigation, the obtained xerogel was grounded and allowed to swell to the equilibrium state in distilled water at room temperature.

2.3. Equilibrium swelling degree and structural characterization of the synthesized xerogel

The equilibrium swelling degree (SD_{eq}) in distilled water at 298 K was determined by common gravimetric procedure (Jovanovic and Adnadjevic, 2013) using the technique with a grid boat with a mesh size of 1 mm which consist in the following. Dry hydrogel (xerogel) samples were weighted (m_0) (average weight of 0.100 g ± 10%) and then immersed entirely in excess distilled water (100 mL) at 298 K ± 0.2 K. The swollen hydrogels samples were periodically taken out from the water, wiped to remove excess surface water and weighted (m_t). The measurements were continued until the hydrogels reached equilibrium and attained constant mass (m_{eq}). The equilibrium swelling degree is defined as the difference between the weights of the swollen hydrogel sample at the equilibrium (m_{eq}) and the weight of xerogel (m_0) divided by the weight of the xerogel sample (m_0), and calculated using Eq. (2):

$$SD = \frac{m_{eq} - m_0}{m_0} \tag{2}$$

The three swelling measurements were performed and the mean value was used.