Comparative analyses on isothermal kinetics of water evaporation and hydrogel dehydration by a novel nucleation kinetics model

B. Potkonjak[a], J. Jovanović[b], B. Stanković[b], S. Ostojić[c], B. Adnadjević[b,*]

[a] ACT Cosmetics Canada Inc., Unit #1, 11 Canadian Road, Toronto, ON, Canada
[b] Faculty of Physical Chemistry, University of Belgrade, Studentski Trg 12-16, Belgrade 11050, Serbia
[c] Institute of General and Physical Chemistry, Studentski Trg 12-16, Belgrade 11050, Serbia

ABSTRACT

A comparative analysis of the isothermal kinetics of water evaporation and equilibrium swollen poly(acrylic-g-gelatin) hydrogel (PAAG) dehydration was performed. The isothermal thermogravimetric (TG) curves of water evaporation and PAAG hydrogel dehydration were obtained in temperature range from 313 K to 353 K, at the same conditions. We found that the kinetics of water evaporation could be mathematically described by the model of zero order chemical reaction. The values of the kinetic parameters: $E_{e,a} = 29$ kJ/mol and $\ln(A_e/\min = 12.1)$ for water evaporation were calculated. By the application of the isoconversional method it was found that water evaporation was a kinetically complex process. It was shown that the kinetics of hydrogel dehydration could be described by a linear combination of logistic functions. A novel model, called the nucleation model, able to describe the kinetics of hydrogel dehydration and water evaporation was presented. The rate constants values for nucleation and the multiplication of the nuclei centers (bubbles) at different temperatures were calculated. The values of activation energy of the multiplication of the nuclei centers were calculated. The difference found between the kinetics of water evaporation and hydrogel dehydration was explained by different values for the constant rates of nucleation and multiplication of the nuclei centers during the water evaporation and hydrogel dehydration.

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1. Introduction

Evaporation processes are of great importance for a wide range of physico-chemical technologies, methodological and environmental application. Evaporation of water at free surfaces has been the subject of investigations by various researchers in the past decades owing to its wide technical applications (Adamson, 1982), Classical theory of water evaporation based on the kinetic theory of gases was developed by Hertz–Knudsen–Langmuir (Hertz, 1913). Based on this theory the rate of water evaporation (dm/dt), the net mass evaporation per unit time and unit area, under isothermal conditions is given by the following equation:

$$\frac{dm}{dt} = e(P_L - P_V)\left(\frac{M}{2\pi RT}\right) \tag{1}$$

where e is the evaporation coefficient, represents the ratio between the measured and calculated evaporation rates, M is the molar mass, R is the gas constant, P_L is the pressure in the liquid, P_V is the pressure in vapor and T is the temperature.

Based on the experimentally found significant temperature difference between the liquid and the vapor phase (Fang and Ward, 1999; Ward and Fang, 1999) used the statistical rate theory and derived a non-linear expression for the evaporation rate as a function of entropy change:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = 2K_e \sinh\left(\frac{M}{R} - \Delta S_{LV}\right) \tag{2}$$

where K_e is the equilibrium molecular exchange rate between liquid and vapor, ΔS_{LV} is the entropy change associated with the transfer of molecules between liquid and vapor continuous phases, sinh is sinus hyperbolic. By means of methods of non-equilibrium thermodynamics Bedeaux and Kjelstrup (1991) derived expression for evaporation rate:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -l_{ww}^S \frac{RT_L}{M} \ln\left(\frac{P_V}{P_{sat}(T_L)}\right) - l_{wq}^S \frac{T_V - T_L}{T_V} \tag{3}$$

where l_{ww}^S and l_{wq}^S are the component of the Onsager transfer coefficient matrix, T_L is the temperature of the liquid and T_V is the temperature of the vapor.

Hydrogels as an important class of smart materials can be described as hydrophilic polymers that are swollen by, but not dissolve in water. They are three-dimensional cross-linked polymeric structures that are able to swell in the aqueous environment (Peppas et al., 2012). The widest practical applications of the hydrogels are based on their ability to reversibly absorb (swelling) and release (dehydrate) water. That is why to optimize their actions, it is very important to know the mechanism and kinetics of the hydrogel swelling and dehydration. Although, the swelling behavior and swelling kinetics of various types of hydrogels are extensively studied (Li et al., 2005; Ganji et al., 2010; Jovanovic and Adnadjevic, 2013) in spite of this, the mechanism and kinetics of dehydration of hydrogels is not known enough or is not well explained.

Hawlader et al. (1991) used the one-dimensional diffusion model to describe the heat and mass transfer from wet to dry region of the hydrogel during its drying. Diffusion of water during the drying polyacrylamide hydrogel was investigated by the Roques et al. (1994). By obtaining results, a mathematical model was appointed with independent parameters to describe the diffusion of water during the drying of the hydrogel. Kemp et al. (2001) have examined the applicability of a variety of kinetic models to fit the drying kinetics of hydrogels. The mechanism of drying polyacrylamide hydrogel based on the changes in fluorescent spectra during drying is presented in the investigation of Pekcan and Yilmaz (Pekcan and Yilmaz, 1996; Evinger et al., 2009; Tari and Pekcan, 2008).

Jankovic et al. (2005) used different kinetic methods such as Kissinger, Coats–Redfern, van-Krevelen and Horowitz–Metzger with the aim to evaluate the kinetics parameters of non-isothermal dehydration of equilibrium swollen poly(acrylic acid) hydrogel Good agreement was established between the values of kinetics parameters (E_a, $\ln A$) that were calculated by using different kinetic methods and their dependence on the degree of dehydration.

The normalized Weibull distribution function of dehydration times was used for modeling the kinetics of non-isothermal dehydration of equilibrium swollen poly(acrylic acid) hydrogel in the work of Adnadjevic et al. (2007). The shape of distribution function of the probability of activation energies was determined and the procedure for describing the kinetics of dehydration by the model of dispersive

kinetics was presented. The possibility of mathematical describing the isothermal dehydration of equilibrium swollen poly(acrylic acid) hydrogel was confirmed in the papers of Adnadjevic et al. (2009), Jankovic et al. (2011). Adnadjevic et al. investigated the possibility of mathematically describing the non-isothermal dehydration of the equilibrium swollen poly(acrylic-co-methacrylic acid) hydrogel by using the logistic function. The parameters values of the logistic function were calculated and their physical meaning was given. Based on the suggested kinetics model it was established that limiting kinetics step of dehydration have a rate of structural rearrangement of hydrogel (actual relaxation mechanism) (Adnadjevic et al., 2011).

In regard to previously exposed, the main goals of this investigation were: (a) to asses under identical conditions the kinetics of water evaporation and hydrogel dehydration; (b) to found kinetics model, kinetics complexity and the values of kinetic parameters for water evaporation and hydrogel dehydration and (c) develop unique kinetics model applicable for water evaporation and hydrogel dehydration.

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 all experiments.

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

The poly(acrylic acid)-g-gelatin hydrogels (PAAG) hydrogels were 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 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.

2.2.1. 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). The structural properties of the synthesized xerogel: xerogel density (ρ_{xg}), average molar mass between the network crosslinks (M_c), crosslinking degree (ρ_c) and the distance between the macromolecular chains (d), have been determined and calculated by the methods proposed by Gudman and Peppas (1995).