



Nucleation model for mesopore-confined water freezing kinetics

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ABSTRACT

Cyclic freezing of water is the main reason of microstructure damages in porous materials exploited in cold climate. It is usually assumed that water freezes much faster than temperature changes, therefore the kinetic effects are neglected. Nevertheless, in the reality such assumption might be often violated. In this paper the kinetics of water freezing in mesopores of two silica gels with dominant pore diameter equal 11 and 36 nm has been investigated. To obtain the freezing rate functions the differential scanning calorimetry test with multiple cooling rate program has been performed. The activation energy is calculated using both, differential and local integral methods. It is found that the activation energy is proportional to the reciprocal temperature. The most suitable kinetic model has been selected by means of two methods: the classical procedure recommended by ICTAC KC and the linear model-fitting method. The former method indicates that two models are appropriate: the empirical Šesták–Berggren model and physical Johnson–Mehl–Avrami model. The SB model demonstrates high accordance with the experimental data, whereas the JMA model allows to approximate the experimental data with high accuracy only if the activation energy is calculated using differential approach. The application range of linear model-fitting method has been extended with the fractional numbers for JMA model parameter. The best correlation between experimental data and theoretical model is obtained for the non-integer values of JMA parameter. It indicates that nucleation and nuclei growth for both silica gels are of fractional dimensions.

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1. Introduction

The freezing of water is one of the most fundamental subject of interest in many fields of science and engineering such as civil engineering, atmospheric science, and food science. The vast majority of materials occurring in nature and manufactured by mankind is porous. Their structure usually covers wide range of pores, including micro-, meso- and macropores. The pores are frequently saturated with water containing various contaminations. The depression of temperature for liquid/solid phase transition in the confined geometries is observed. It is related to the pore size by the Gibbs–Thomson equation, which assumes the cylindrical shape of pores, as follows [1–3]:

$$\Delta T_m = \frac{2T_0\gamma_{cl} \cos \theta}{\rho_l \Delta H_f r_p - \delta} \quad (1)$$

where T_0 is the melting temperature of the bulk state, γ_{cl} is solid/liquid surface tension, ρ_l is the liquid density, r_p is the radius of the pore, δ is the thickness of the unfrozen water film and θ is the

contact angle. A non-freezable liquid layer of thickness between 0.5 and 2.0 nm along the pore walls was observed by many researchers [3,4].

Cyclic freezing of water is recognized as the main reason of jeopardizing durability of materials exploited in cold climate [5–9]. It is usually assumed that water freezes much faster than temperature changes, therefore the kinetic effects are neglected. However, in the reality such assumption might be often violated, i.e. during sudden weather changes, and fire in cold climate.

The dynamic non-equilibrium water freezing and ice melting in porous materials was profoundly analysed by Setzer [10,11]. Employing the Dedoner's concept of the second law of thermodynamics he investigated the affinity of the in pore water-ice system as the main thermodynamic force which pushes the system towards equilibrium. Bronfenbrener and co-workers [12,13] observed the kinetic effects of water phase transition and formulated rather simple, based on the characteristic time, mathematical model of mass and energy transport in porous system. They assumed that the characteristic time is the constant value independent of the pore microstructure. The latest study [14,15] proved that the freezing of water in mesopores is the thermally activated process. It was showed that the empirical Šesták–Berggren model fits best with the experimental data for water freezing in pores

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smaller than ap. 10 nm. This time we analyse much wider range of pore diameters. There is a lot of research concerning the kinetics of homogenous nucleation of water [16,17]. Moreover in vast majority of studies conducted by now, the researchers analysed the kinetics of water freezing with regard to droplets, which can be identified with bulk water. The presented study concerns the freezing of water confined in mesopores, which diameters equal a few nm. Moreover, in previous study [14,15] it was assumed that the activation energy is constant. During further research we observe that this assumption can no longer be justified. Therefore, the activation energy is determined as inversely proportional to the temperature, what resembles the results presented in [18,19]. The similar relation is also applied to calculate the Gibbs free energy for homogenous freezing of water [20]. Additionally our purpose is to identify the most appropriate model describing analysed phenomenon. As mentioned above the results contained in the previous papers indicate that Šesták–Berggren (SB) model describes the experiment in the best way. The SB equation is frequently applied to the analysis of both isothermal and non-isothermal processes, though it does not provide a deeper insight into mechanism of described phenomena. In the presented research we extend the previous study with the investigation of the physical process behind the in pore water freezing kinetics using differential scanning calorimetry. We apply four cooling rates (2.5 °C/min, 5.0 °C/min, 7.5 °C/min and 10.0 °C/min). Due to purely empirical character of Šesták–Berggren equation, which has been previously identified as the best approximation for water freezing kinetics, we make no assumption on the physical mechanism. We investigate the following kinetic mechanisms: nucleation and nuclei growth model, geometrical contraction model, diffusion model, order-based model. We analyse two silica gels with one dominant pore diameter, which is equal to 11 nm and 36 nm. To determine the physical mechanism we firstly apply the Málek's method [21,22], recommended by ICTAC [23] to recognize the kinetic equation. The two kinds of isoconversional methods, i.e. Friedman's and Vyazovkin's, are used to determine the activation energy for the process. Pérez-Maqueda et al. [24,25] observed that the Šesták–Berggren equation can be associated with one of the basic physical models. They introduced the linear model-fitting method. In the presented research we show that this approach is the effective way to obtain the most suitable physical mechanism related to the freezing kinetics of pore-confined water. The influence of cyclic water freezing on the microstructure of porous materials has been reported [26]. The possible alteration of silica gel microstructure due to cyclic water freezing would influence on the kinetic model and its parameters and consequently preclude the reliable identification of the mechanism. Therefore, we perform the nitrogen adsorption/desorption test of the materials under investigation before and after 10 water freezing cycles.

2. Experimental and theoretical methods

The measurements of heat effects associated with the freezing of the in pore water are conducted by means of Perkin Elmer DSC 4000 Calorimeter equipped with a cooling device. The nitrogen is supplied by Linde Gas in 99.999% quality.

2.1. Material properties

We investigate the freezing kinetics of water confined in pores with diameter 11 nm and 36 nm. A silicon dioxide, commonly known as silica gel, is selected as the material under investigation. It is highly hygroscopic, granular, porous substance obtained synthetically from a sodium silicate. Silica gels are mainly used as desiccants, active phase supports in heterogeneous catalysis

and stationary phases in chromatography. Two types of silica gel provided by Sigma-Aldrich Co. and Carl Roth Co. are used in the research. The textural properties provided by the producer are as follows:

SG1 (Sigma Aldrich Co., No. 236845)

- Average pore diameter: 15 nm,
- Particle size: 250–500 µm,
- Pore volume: 1.15 cm³/g,
- Surface area: 300 m²/g.

SG2 (Carl Roth Co., No. 5407)

- Average pore diameter: 50 nm,
- Particle size: 35–70 µm,
- Pore volume: ≥0.75 cm³/g,
- Surface area: 70–90 m²/g.

Additionally the textural properties are determined using Micromeritics ASAP 2020 equipment. The specific surface area (SSA) analysis is based on BET model of N₂ low temperature adsorption and assumption that nitrogen molecules cover 0.162 nm² of adsorbent surface. The Barret-Joyner-Halenda (BJH) model applied to the adsorption branch of the isotherm is used to obtain the mesopore size distribution. Samples are placed in measurement ampoule and degassed for 4 h at 60 °C. Then, the ampoule is attached to the instrument and the adsorption process is carried out at –195 °C. We study the properties of the silica gels before the water freezing experiment as well as after ten water freezing cycles. These tests should indicate the possible influence of cyclic in pore water freezing on the microstructure of silica gels under investigation. Results are presented in Table 1 and Figs. 1 and 2. The obtained data of textural parameters for virgin samples is in a good agreement with that declared by the producers.

The isotherms show characteristic S-like shapes and belong to the IV type according to IUPAC classification. For SG2 we can detect some attributes of the II type isotherms which are accompanied by the small volume of macropores. Nevertheless, we confirm that each silica gel under investigation has one dominant pore diameter. Characteristic features of the isotherms are hysteresis loop, associated with capillary condensation in mesopores and the limiting uptake at high relative pressure (p/p^0), where p and p^0 are the equilibrium absolute pressure of adsorbate and the saturation vapor pressure of nitrogen relatively. The isotherms have both a capillary condensation and an evaporation steps. The former implies a nitrogen capillary condensation while the latter corresponds to a nitrogen evaporation from pores. That fact confirms regular microstructure of the sample, which framework consists of pores with similar diameters. Both the course of isotherms and the textural data of the materials after water freezing are very close, in fact almost identical to those of virgin materials. It proves that the influence of the in pore water freezing on the silica gel microstructure can be neglected. As a consequence, one can assume, that the results of kinetic analysis are not affected by the alteration of material microstructure.

We assume the following properties of distilled water: heat of fusion is given by the equation [27,28]:

$$\Delta H_f = 334.1 + 2.119(T - T_0) - 0.00783(T - T_0)^2, \quad \text{J/g} \quad (2)$$

water and ice densities are described by the following empirical equations [27,28]:

$$\rho_l = -7.1114 + 0.0882T - 3.1959 \cdot 10^{-4}T^2 + 3.8649 \cdot 10^{-7}T^3, \quad [\text{g/cm}^3] \quad (3)$$

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