

The general mechanism of water sorption on foodstuffs – Importance of the multitemperature fitting of data and the hierarchy of models

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Abstract

This paper points out the importance of the multitemperature fitting procedure in description of water sorption on foodstuffs. The data tabulated in literature (water sorption at different temperatures on: chickpea seeds, lentil seeds, potato and on green peppers) were described applying the BET, GAB and recently proposed GDW models. Our results explain total failure of the first model in description of multitemperature data and the similarities between the GAB and GDW are shown. Finally the general mechanism of water sorption on foodstuffs is proposed. This mechanism can be of the GAB or GDW type, depending on the arrangement and features of the primary water sorption sites. If the geometrical constraints for creation of the BET – like type clusters do not occur on surface, and if each from primarily sorbed water molecules convert only into one secondary surface site, one can say that the mechanism follows the GAB scenario (as for example in the case of lentil seeds). Contrary, in the case of rough or porous surfaces, where there are the geometric constraints for creation of secondary sites (for example sorption on chickpea seeds), and/or where one primary site produces more than one secondary site (potato and green peppers), the mechanism of water sorption is of the GDW type.

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1. Introduction and the aim of the study

It is well known that sorption isotherms of foodstuffs are very important for design, modelling and optimization of many processes. Different authors (for example Czepirski, Komorowska-Czepirska, & Szymońska, 2002, 2005; Hossain, Bala, Hossain, & Mondol, 2001; Lewicki, 1997, 2000) pointed out the importance of those data in drying, aeration, predicting of stability and quality during packaging and storage of food. Therefore, different more or less advanced adsorption models have been used (with greater or smaller success) in the field of food engineering science for description water sorption data. Here very important question arises about the purpose of application of those models. Analyzing different results presented in many

papers from the area of interest one can conclude that in the most of cases authors apply a model since they have (or try) to do something with experimental data (i.e. describe them applying mathematics). In many cases they do not analyze the fundamental assumptions of the applied theory, its physical validity for the studied case and so on. Moreover, often the model applied to describe of a set of experimental data says anything about the mechanism of the adsorption process and, what is more important, the data obtained from the fitting of different models lead authors only to the conclusion that a model, say, A is better than model B. In our opinion the major features of a chosen model should be the reality and simplicity, while the major purpose of its usage is something that one can call “the predictive ability”. Therefore, the evaluated (by fitting to experimental data) parameters of the model can be applied to predict different sets of data, for example the sorption results measured for different temperature(s). The measurements of temperature dependence of water sorption on foodstuffs is

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Nomenclature

C	the kinetic constant related to the sorption in the first layer	m	monolayer capacity (BET/GAB model) and/or the concentration of primary active surface sites (GDW model), % (dry basis)
C_0	the pre-exponential entropic factor related to C constant	m^*	the constants in Eqs. (19) and (20), % (dry basis)
C^*	the constants in Eqs. (17)–(20)	N	the number of temperatures for which the experimental data were measured
DC	the global determination coefficient value	p_s	saturated vapour pressure, Pa
DC_T	the value of DC calculated for the data measured at the considered temperature	Q	the enthalpy values related to the primary sorption sites, kJ mol^{-1}
h_r	relative humidity	q	the enthalpy values related to the secondary sorption sites, kJ mol^{-1}
K	the kinetic constant related to multilayer sorption (GAB model), the kinetic constants related to the sorption on primary sorption sites (GDW model)	q_C	the value of the enthalpy related to C constant, kJ mol^{-1}
K_0	the pre-exponential entropic factor related to K constant	q_K	the value of the enthalpy related to K constant (GAB model), kJ mol^{-1}
k	the kinetic constants related to sorption on secondary sorption sites	q^{st}	isosteric enthalpy of sorption, kJ mol^{-1}
k_0	the pre-exponential entropic factor related to k constant	q_X	the value of the enthalpy related to X constant, kJ mol^{-1}
L	the enthalpy of condensation of water, $43.96 \text{ kJ mol}^{-1}$	R	the universal gas constant, $0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1}$
M_e	equilibrium moisture content, % (dry basis)	T	temperature, K
$M_{e,i}^o$	observed moisture content for i th experimental point, % (dry basis)	w	the parameter determining what part of water molecules adsorbed on primary sites convert into the secondary adsorption sites
$M_{e,i}^t$	theoretical value of the moisture content, % (dry basis)	X	the kinetic constants
\bar{M}_e^o	the average value of the observed moisture content, % (dry basis)	X_0	the pre-exponential entropic factor related to X constant

very important task in the field of food science (Myhara, Sablani, Al-Alawi, & Taylor, 1998) however, the attempts of description of those data (i.e. determined at different temperatures) are rarely met in the literature and they mainly deal with the GAB model. It is obvious that the temperature dependence of the parameters of each model should be clearly defined. Moreover, since in the correctly derived models the meaning of the parameters is well known, the *whole* set of sorption data determined for the same material at different temperatures should be fitted by *one* sorption isotherm equation. What is also important, the application of this procedure is equivalent to the simultaneous description of the enthalpy of sorption, since the isosteric sorption enthalpy is strictly related to the branch of isotherms determined at different temperatures by the Clausius – Clepeyron formula. This procedure reduces the number of variables and increases the reality of the applied model. This is the fundamental (and known for many years in the field of adsorption science) difference between the multitemperature fitting of the data and the separate fitting of each isotherm (from the branch determined at different temperatures) by a chosen model (Steele, 1974).

In previous study the application of Generalised D'Arcy and Watt (GDW) model to the description of

water vapour sorption on different foodstuffs was proposed (Furmaniak, Terzyk, Gauden, & Rychlicki, 2007). The applicability of this model for description of the data on macaroni, sardine and pistachio nut paste was shown. The GDW is capable of describing a set of data on pineapple measured at different temperatures. The major aim of this paper is to check the applicability of the GDW and two additional widely applied models to description of multitemperature (determined at different temperatures) water sorption data on foodstuffs. As it will be shown below, this can lead to the proposition of the general mechanism of water sorption, and makes it possible to arrange the models according to the complicity of water sorption mechanism they postulate.

2. Models and the temperature dependence of parameters

In this study the considerations will be limited only to the models having theoretical basis, since for those cases the temperature dependence of the parameters is clearly defined. Thus the most widely used models were chosen: BET, GAB and the one mentioned above the GDW (Furmaniak, Gauden, Terzyk, Wesolowski, & Rychlicki, 2005b; Furmaniak et al., 2007). They can be written in the following forms:

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