

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

Sylwester Furmaniak, Artur P. Terzyk *, Piotr A. Gauden

N. Copernicus University, Department of Chemistry, Physicochemistry of Carbon Materials Research Group, Gagarin St. 7, 87-100 Torun, Poland

Received 9 November 2006; received in revised form 5 January 2007; accepted 5 March 2007

Available online 19 March 2007

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.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Enthalpy of sorption; Equilibrium moisture content; Isotherm model; Water sorption mechanism; GAB; GDW

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

* Corresponding author. Tel.: +48 056 611 43 71; fax: +48 056 654 24 77.

E-mail address: aterzyk@chem.uni.torun.pl (A.P. Terzyk).

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, Wesołowski, & Rychlicki, 2005b; Furmaniak et al., 2007). They can be written in the following forms:

BET:

$$M_e = \frac{mCh_r}{(1-h_r)(1+(C-1)h_r)} \quad (1)$$

GAB:

$$M_e = \frac{mCKh_r}{(1-Kh_r)(1-Kh_r+CKh_r)} \quad (2)$$

GDW:

$$M_e = \frac{mKh_r}{1+Kh_r} \cdot \frac{1-k(1-w)h_r}{1-kh_r} \quad (3)$$

where M_e is the equilibrium moisture content, h_r is the relative humidity, m is the monolayer capacity (BET/GAB) and/or the concentration of primary active surface sites (GDW), C is the kinetic constant related to the sorption in the first layer, K (GAB) is the kinetic constant related to multilayer sorption, and in the case of the GDW K and k are the kinetic constants related to the sorption on primary and secondary sorption sites, respectively. The coefficient w determines the ratio of water molecules sorbed on the primary sites which is converted into the secondary sorption sites.

The physical meaning of the parameters m and w leads to the conclusion about their temperature independence

$$m \neq f(T) \quad (4)$$

$$w \neq f(T) \quad (5)$$

On the other hand, for all kinetic constants (X) physical chemistry formulates the following temperature dependence equation:

$$X = X_0 \exp\left(\frac{q_X}{RT}\right) \quad (6)$$

where X_0 is almost independent on temperature pre-exponential entropic factor, q_X is the value of the enthalpy related to a given constant (in the case of equations where the relative humidity occurs the enthalpy q_X should be diminished by the value of the enthalpy of condensation), R is the gas constant and T is the absolute temperature. Therefore, for the parameters of Eqs. (1)–(3) the relation (6) for the BET and GAB can be written as

$$C = C_0 \exp\left(\frac{q_C}{RT}\right) \quad (7)$$

$$K = K_0 \exp\left(\frac{q_K}{RT}\right) \quad (8)$$

while for the GDW

$$K = K_0 \exp\left(\frac{Q}{RT}\right) \quad (9)$$

$$k = k_0 \exp\left(\frac{q}{RT}\right) \quad (10)$$

3. Experimental data

In this study four sets of tabulated water sorption data measured at different temperatures on the same foodstuff

were chosen, namely: on chickpea seeds (Menkov, 2000a), on lentil seeds (Menkov, 2000b), on potato (McMinn & Magee, 2003) and on green peppers (Kaymak-Ertekin & Sultanoglu, 2001). Those data were applied as the raw data for the fitting using the procedure described below.

4. Data description

The simultaneous fitting procedure of theoretical equations to the whole set of data (determined at different temperatures) was used, applying the genetic algorithm (differential evolution (DE)) constructed by Storn and Price (1996, 1997) and applied successfully (Furmaniak, Terzyk, Gauden, & Rychlicki, 2006; Furmaniak et al., 2006; Furmaniak et al., 2005a; Furmaniak, Terzyk, Gauden, & Rychlicki, 2005; Gauden, 2005; Terzyk, Rychlicki, Ćwiertnia, Gauden, & Kowalczyk, 2005) also in the field of food science (Furmaniak et al., 2007). The value of the determination coefficient (DC_T) for the data measured in the whole temperature range was calculated

$$DC_T = 1 - \frac{\sum_i (M_{e,i}^o - M_{e,i}^t)^2}{\sum_i (M_{e,i}^o - \bar{M}_e^o)^2} \quad (11)$$

where $M_{e,i}^o$ is the observed moisture content for i th experimental point, $M_{e,i}^t$ is the theoretical value of the moisture content calculated from Eq. (3), and \bar{M}_e^o is the average observed moisture content. The global fitness parameter is the mean square root of DC determined for the particular temperatures

$$DC = \sqrt{\frac{\sum_T DC_T^2}{N}} \quad (12)$$

where N is the number of temperatures.

The best fit parameters are: m , C_0 , q_C (for the BET), m , C_0 , K_0 , q_C , q_K (for the GAB), and m , K_0 , k_0 , Q , q , w (for the GDW model). Since (theoretically) the entropic terms can change in the range even of few orders of magnitude they were applied during the fitting in the logarithmic form. The program fitting is simply the maximization of the value of DC (Eq. (12)).

5. Results and discussion

The BET model did not provide satisfactory fitting to experimental data, that is why the results for this equation are not presented. The reasons of such behaviour is the small temperature dependence of the BET curve, and the most pronounced temperature dependence is visible only at the initial ranges of the relative humidity (in the case of sorption on foodstuffs, due to experimental procedure, there is usually small number of points in this range). The consequence of this property leading to the failure of the BET model, is that when one tried to use the multitem-

Table 1

The best fit parameters for the GAB model (the values of DC_T are given according to the rise in T)

Product	m (% (db))	C_0	K_0	q_C (kJ mol ⁻¹)	q_K (kJ mol ⁻¹)	DC_T	DC
Chickpea seeds	5.266	1.971×10^{-5}	0.5003	36.09	1.449	0.9932; 0.9806; 0.9966; 0.9919	0.9906
Lentil seeds	7.093	1.009×10^{-3}	0.3390	24.01	2.017	0.9880; 0.9681; 0.9958; 0.9822	0.9836
Potato	5.282	1.925×10^{-13}	4.499×10^{-2}	83.43	7.637	0.9911; 0.9843; 0.9797	0.9851
Green peppers	6.706	6.497×10^{-9}	0.7351	52.19	0.5063	0.9912; 0.9914; 0.9917	0.9914

Table 2

The best fit parameters for the GDW model

Product	m (% (db))	K_0	k_0	Q (kJ mol ⁻¹)	q (kJ mol ⁻¹)	w	DC_T	DC
Chickpea seeds	6.157	2.811×10^{-4}	0.6790	27.97	0.7852	0.7557	0.9953; 0.9876; 0.9975; 0.9930	0.9934
Lentil seeds	7.307	5.055×10^{-4}	0.5046	25.27	1.096	0.9915	0.9898; 0.9753; 0.9967; 0.9877	0.9874
Potato	4.066	2.918×10^{-17}	5.790×10^{-2}	108.3	6.853	1.748	0.9960; 0.9922; 0.9910	0.9931
Green peppers	4.230	3.852×10^{-9}	0.8801	55.89	~0	2.001	0.9917; 0.9935; 0.9924	0.9925

perature fitting it was noticed relatively good fit in one of the temperatures studied, while completely bad fit for the other ones. Contrary, GAB and GDW lead to very good fits and consequently to large values of the DCs (0.99 and more). It can be mentioned here that the GDW model leads to the better fits for all studied isotherms (Tables 1 and 2, Figs. 1 and 2).

For all cases, as well as for the both models (GAB and GDW) one can notice the following regularities: the kinetic

constants related in the GDW model to sorption on primary sites (or in the GAB to adsorption in the first layer) are associated with large enthalpy values, and therefore they strongly decrease with the rise in the temperature. On the other hand, the constants associated with the covering of the secondary adsorption sites in the GDW model (or related to polymolecular sorption in the GAB) are of the magnitude of enthalpy of water condensation and are dependent on temperature in small extent.

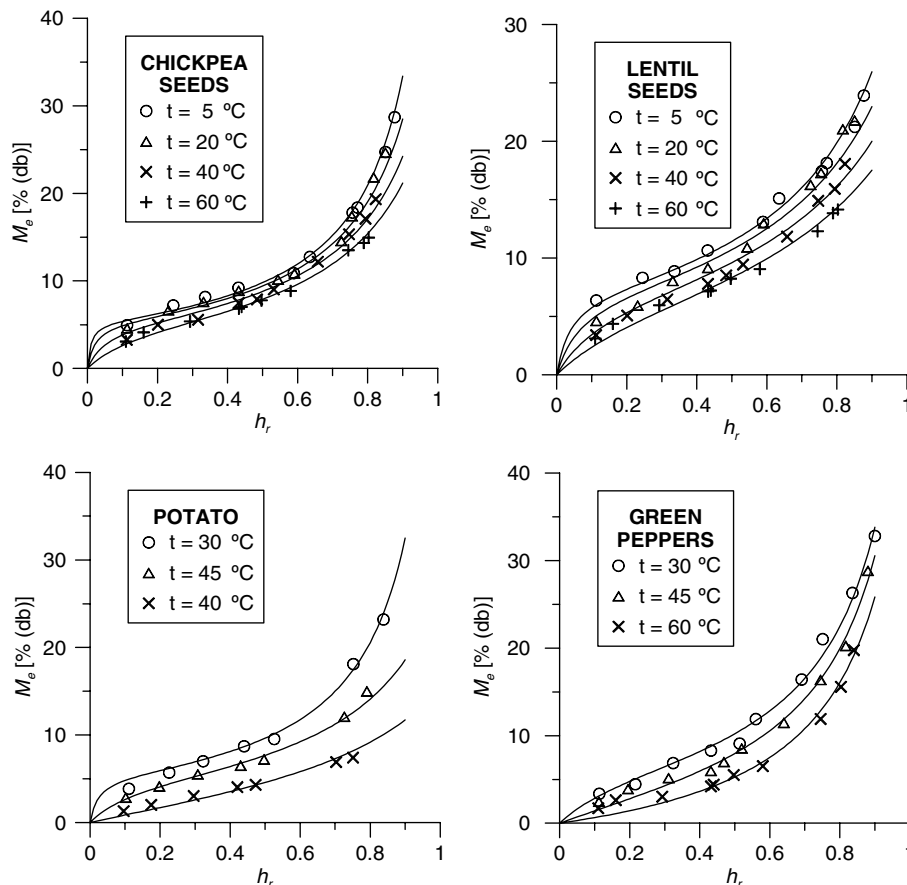


Fig. 1. The results of the multitemperature fitting of studied experimental data by the GAB model (points – experimental data, lines – theory).

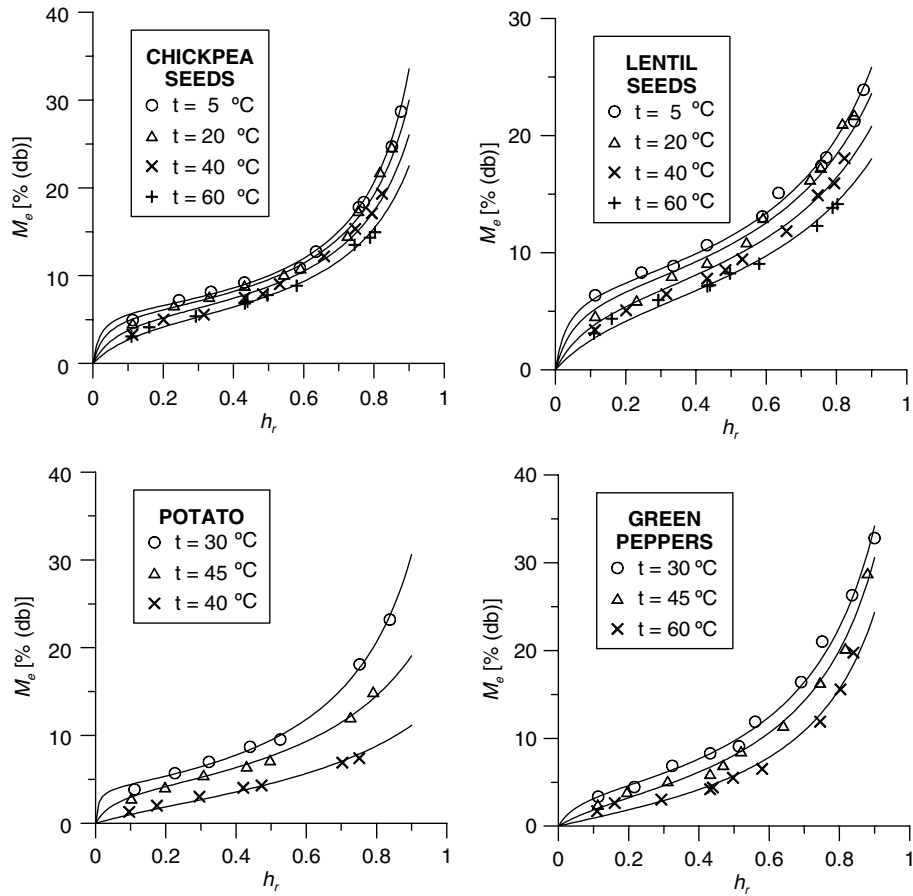


Fig. 2. The same as in Fig. 1 but for the GDW model.

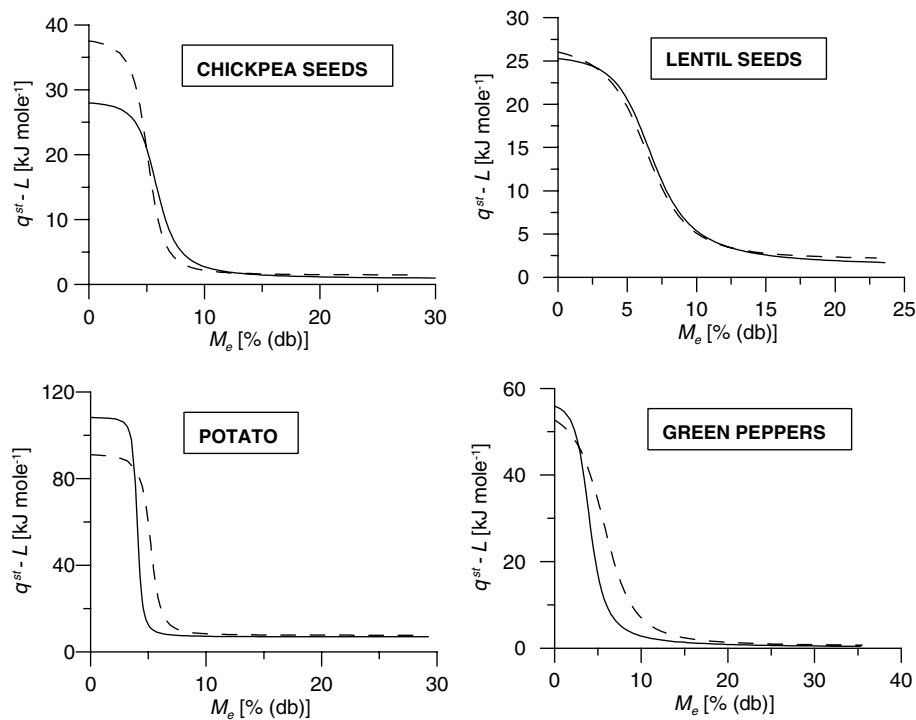


Fig. 3. The plots of the enthalpy of water sorption generated from Eqs. (14) and (15) applying the data from Tables 1 and 2. GAB – dashed lines, GDW – solid lines (for chickpea seeds and lentil seeds $t = 20^\circ\text{C}$, while for potato and green peppers $t = 30^\circ\text{C}$).

6. Isotheric enthalpy of sorption

An additional advantage of the multitemperature fitting applied in this study is the possibility of generating the isosteric enthalpy (q^{st}) of water sorption on foodstuffs. The formula applied for this purpose is

$$q^{st} - L = RT^2 \left(\frac{\partial \ln h_r}{\partial T} \right)_{M_c} \quad (13)$$

where L is the enthalpy of water condensation. The analytical equation describing the enthalpy of sorption related to the GDW model was derived previously (Furmaniak et al., 2005b, 2007)

$$q^{st} - L = \frac{\frac{K}{(1+Kh_r)^2} \cdot \left(1 + \frac{wkh_r}{1-kh_r}\right) \cdot Q + \frac{Kh_r}{1+Kh_r} \cdot \frac{wk}{(1-kh_r)^2} \cdot q}{\frac{K}{(1+Kh_r)^2} \cdot \left(1 + \frac{wkh_r}{1-kh_r}\right) + \frac{Kh_r}{1+Kh_r} \cdot \frac{wk}{(1-kh_r)^2}} \quad (14)$$

Applying Eq. (13) and the same method (Furmaniak et al., 2005) to the GAB model one obtains

$$q^{st} - L = \frac{(1 - Kh_r)^2 q_C + q_K + (C - 1)K^2 h_r^2 q_K}{1 + (C - 1)K^2 h_r^2} \quad (15)$$

Fig. 3 shows the sorption enthalpy plots related to the both studied models. As one can see similar plots are observed, moreover for some cases very close enthalpy values can be seen.

7. The GAB equation as the special case of the BET, and the GDW as the most general model. The mechanism of water sorption on foodstuffs

The similarity in the DC values obtained for the GAB and GDW (Tables 1 and 2) as well as similar shapes of sorption enthalpy plots (Fig. 3) suggest similarity between the both models. To consider this one can start from the BET model (Eq. (1)) and compare it with the GAB equation (Eq. (2)). One can see that assuming in Eq. (2) $K = 1$, the GAB model simplifies to the BET one. Therefore the GAB is more complicated version of the BET where the original BET assumption ($K = 1/p_s$) is treated as invalid. This leads to the large improvement of the fit of GAB model (comparing to the BET) to multitemperature data of sorption on foodstuffs.

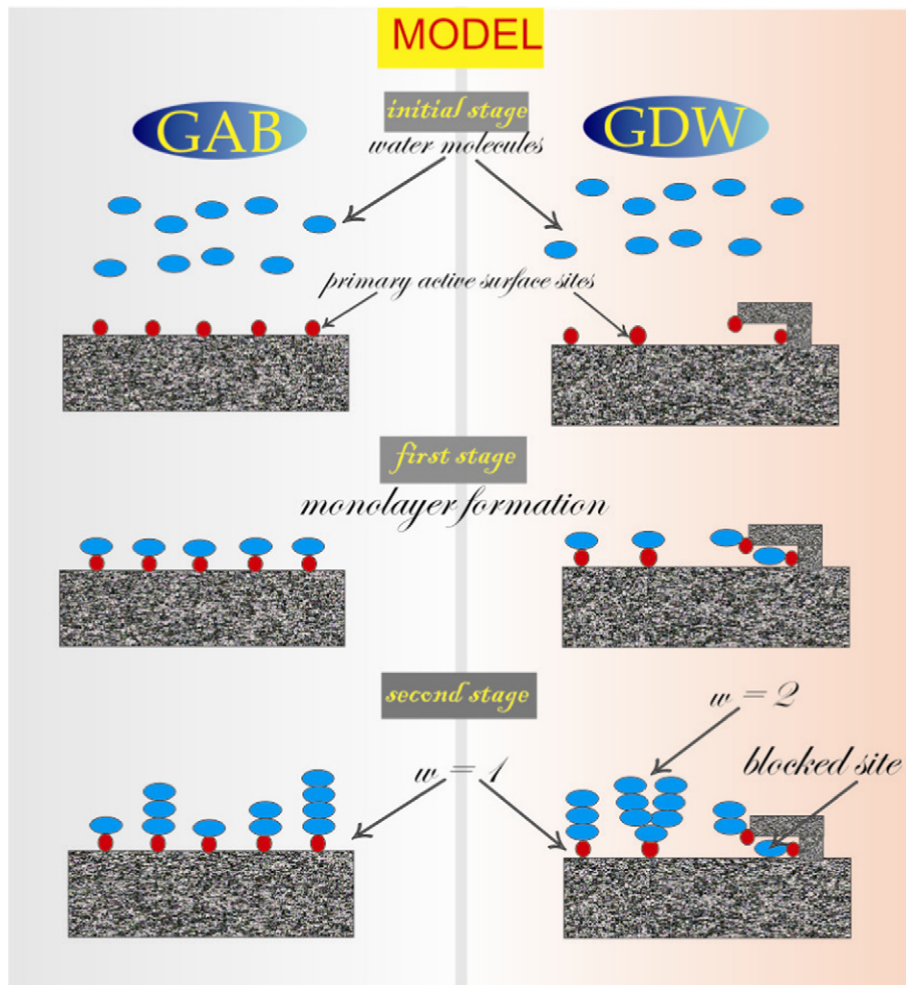


Fig. 4. The schematic representation of the general mechanism of water sorption on foodstuffs according to the GAB and GDW models.

Next one can analyze the GDW model but for the special case, i.e. assuming $w = 1$. This means that each primary adsorption site converts exactly into one secondary site. In this case Eq. (3) can be rewritten as

$$M_e = \frac{mKh_r}{(1 + Kh_r)(1 - kh_r)} \quad (16)$$

One can define a new constant C^* related to constants K and k by

$$K = (C^* - 1)k \quad (17)$$

and now re-write Eq. (16) as

$$M_e = \frac{m(C^* - 1)kh_r}{(1 - kh_r)(1 + (C^* - 1)kh_r)} \quad (18)$$

Finally denoting

$$m^* = m \frac{C^* - 1}{C^*} \quad (19)$$

Eq. (18) can be written in the same form as the GAB Eq. (2)

$$M_e = \frac{m^* C^* kh_r}{(1 - kh_r)(1 + (C^* - 1)kh_r)} \quad (20)$$

For large values of the parameter C^* in numerator of Eq. (19) one can neglect unity, and in this situation m from Eq. (16) equals m^* from Eq. (20).

Therefore it can be stated that the differences in the fits of the GAB and GDW to experimental data are mainly caused by the assumption of possibility of w parameter to be different than unity. Therefore summing up this part of the study hierarchy of the models arranging them from the most general to the simplest one can be created as: GDW > GAB > BET.

The analysis of the results obtained in previous study, as well as shown in the current paper leads to the conclusion about the general mechanism of water sorption on foodstuffs, showing in Fig. 4. This mechanism can be of the GAB or GDW type, depending on the arrangement 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 (see for example 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 (chickpea seeds case), 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.

8. Conclusions

The failure of the BET model in description of multi-temperature water sorption data on foodstuffs is caused by small changes of the isotherm generated from this model

with temperature. Such a situation is rarely observed in the case of experimental data on foodstuffs.

The hierarchy and the applicability of the models, arranged from the most sophisticated to the simplest one, is as follows: GDW > GAB > BET.

Water sorption mechanism on foodstuffs consists of two steps: high energetically sorption on primary active surface centres, and the forming of water clusters. In the latter case the energy of formation is close to the value of enthalpy of water condensation.

GAB and GDW models differ by the assumption of the number of secondary sites created from the primary ones. Experimental data of sorption on foodstuffs show that the scenario assumed in the both models is possible.

9. Program availability

The listing of the program fitting the GDW and GAB models to experimental sorption data is available upon request.

Acknowledgement

A.P.T. and S.F. gratefully acknowledge the financial support from UMK Grant No. 350-Ch.

References

- Czepirski, L., Komorowska-Czepirska, E., & Szymońska, J. (2002). Fitting of different models for water vapour sorption on potato starch granules. *Applied Surface Science*, *196*, 150–153.
- Czepirski, L., Komorowska-Czepirska, E., & Szymońska, J. (2005). Adsorptive properties of biobased adsorbents. *Adsorption*, *11*, 757–761.
- Furmaniak, S., Gauden, P. A., Terzyk, A. P., Rychlicki, G., Wesolowski, R. P., & Kowalczyk, P. (2005a). Heterogeneous Do and Do model of water adsorption on carbons. *Journal of Colloid Interface Science*, *290*, 1–13.
- Furmaniak, S., Gauden, P. A., Terzyk, A. P., Wesolowski, R. P., & Rychlicki, G. (2005b). Improving fundamental ideas of Dubinin, Serpinsky and Barton – Further insights into theoretical description of water adsorption on carbons. *Annales (Sectio AA, Chemia, UMCS Lublin – Polonia)*, *60*, 151–182.
- Furmaniak, S., Terzyk, A. P., Gauden, P. A., & Rychlicki, G. (2005). Parameterization of the Corrected Dubinin–Serpinsky adsorption isotherm equation. *Journal of Colloid Interface Science*, *291*, 600–605.
- Furmaniak, S., Terzyk, A. P., Gauden, P. A., & Rychlicki, G. (2006). Simple model of adsorption in nanotubes. *Journal of Colloid and Interface Science*, *295*, 310–317.
- Furmaniak, S., Terzyk, A. P., Gauden, P. A., & Rychlicki, G. (2007). Applicability of the generalised D'Arcy and Watt model to description of water sorption on pineapple and other foodstuffs. *Journal of Food Engineering*, *79*, 718–723.
- Furmaniak, S., Terzyk, A. P., Szymański, G. S., Gauden, P. A., Motak, M., Kowalczyk, P., & Rychlicki, G. (2006). Thermodynamics of the CMMS Approach and Carbon Surface Chemistry in SO₂ Adsorption. *Langmuir*, *22*, 6887–6892.
- Gauden, P. A. (2005). Does the Dubinin–Serpinsky Theory Adequately Describe Water Adsorption on Adsorbents with High-Energy Centers? *Journal of Colloid Interface Science*, *282*, 249–260.
- Hossain, M. D., Bala, B. K., Hossain, M. A., & Mondol, M. R. A. (2001). Sorption Isotherms and Heat of Sorption of Pineapple. *Journal of Food Engineering*, *48*, 103–107.

- Kaymak-Ertekin, F., & Sultanoglu, M. (2001). Moisture Sorption Isotherm Characteristics of Peppers. *Journal of Food Engineering*, 47, 225–231.
- Lewicki, P. P. (1997). Water Sorption Isotherms and Their Estimation in Food Model Mechanical Mixtures. *Journal of Food Engineering*, 32, 47–68.
- Lewicki, P. P. (2000). Raoult's Law Based Food Water Sorption Isotherm. *Journal of Food Engineering*, 43, 31–40.
- McMinn, W. A. M., & Magee, T. R. A. (2003). Thermodynamic Properties of Moisture Sorption of Potato. *Journal of Food Engineering*, 60, 157–165.
- Menkov, N. D. (2000a). Moisture Sorption Isotherms of Chickpea Seeds at Several Temperatures. *Journal of Food Engineering*, 45, 189–194.
- Menkov, N. D. (2000b). Moisture Sorption Isotherms of Lentil Seeds at Several Temperatures. *Journal of Food Engineering*, 44, 211–505.
- Myhara, R. M., Sablani, S. S., Al-Alawi, S. M., & Taylor, M. S. (1998). Water Sorption Isotherms of Dates: Modeling Using GAB Equation and Artificial Neural Network Approaches. *Lebensmittel-Wissenschaft und Technologie*, 31, 699–706.
- Steele, W. A. (1974). *The Interaction of Gases with Solid Surfaces*. Oxford: Pergamon Press.
- Storn, R., & Price, K. (1996). Minimizing the Real Functions of the ICEC'96 Contest by Differential Evolution. In Proceedings of 1996 IEEE International Conference on Evolutionary Computation (ICEC '96), Nagoya University, 842–844.
- Storn, R., & Price, K. (1997). Differential Evolution—a Simple and Efficient Heuristic for Global Optimization Over Continuous Spaces. *Journal of Global Optimization*, 11, 341–359.
- Terzyk, A. P., Rychlicki, G., Cwiertnia, M., Gauden, P. A., & Kowalczyk, P. (2005). The Chemical Composition of Carbon Surface Layer and Benzene Adsorption from Vapour and from Dilute Aqueous Solutions. *Langmuir*, 21, 12257–12267.