

Focus on Food Engineering Research and Developments



Vivian N. Pletney

Editor

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**FOCUS ON FOOD ENGINEERING
RESEARCH AND DEVELOPMENTS**

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VIVIAN N. PLETNEY
EDITOR

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Chapter 11

WATER SORPTION ON FOODSTUFFS - ALTERNATIVE MODELS

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ABSTRACT

It is well known that sorption isotherms of foodstuffs are very important for design, modeling and optimization of important processes for example drying, aeration, predicting of stability and quality during packaging and storage of food. Many literature reviews conclude that the BET (and its modifications) and the GAB sorption isotherm equations are the most popular and applicable for description of isotherms of foodstuffs. We showed recently the applicability of the GDW model for description of water sorption on different foodstuffs. Moreover, it was also shown that the GAB model (also widely applied in food science) is the special case of the GDW equation. In this review we present the current state of art and also an attempt of application of different models of water sorption, namely CMMS, DD and modified CDS for description of water sorption data on different starch samples and other foodstuffs.

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1. INTRODUCTION

It is well known that sorption isotherms of foodstuffs are very important for design, modeling and optimization of important processes for example drying, aeration, predicting of stability and quality during packaging and storage of food [1-3]. Many literature reviews conclude that the BET (and its modifications) and the GAB sorption isotherm equations are the most popular and applicable for description of isotherms of foodstuffs [1,4-6]. It was shown recently the applicability of the GDW model for description of water sorption on different foodstuffs (pineapple, macaroni, sardine, pistachio nut paste, chickpea seeds, lentil seeds, potato and on green peppers) [7,8]. Moreover, it was also shown that the GAB model (also widely applied in food science) is the special case of the GDW equation [8]. Obtained results explained the total failure of the BET model in description of multitemperature data and the similarities between the GAB and GDW. Finally the general mechanism of water sorption on foodstuffs was also proposed [8]. 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 sorption site, one can say that the mechanism follows the GAB scenario. Contrary, in the case of rough or porous surfaces, where there are the geometric constraints for creation of secondary sites, and/or where one primary site produces more than one secondary site, the mechanism of water sorption is of the GDW type.

All models discussed above originate from adsorption science, therefore it is interesting to check the validity of different (i.e. alternative) approaches to describe water sorption data on foodstuffs. In this review we also present the current state of art and an attempt of application of GAB, GDW, CMMS, simplified DD and modified CDS models for description of water sorption data on different starch granules and other foodstuffs.

2. MODELS

First studied model is the Generalized D'Arcy and Watt (GDW) one proposed previously for description of adsorption of water on carbonaceous adsorbents [9], and next applied successfully for description of water sorption on many foodstuffs [7,8]. It was applied in the form:

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

where M_e is the moisture equilibrium content, h_r – relative humidity, m – the maximum adsorption value on the primary sorption centers. K and k are the kinetic constants related to sorption on primary and secondary centres, and w is the parameter determining what part of water molecules sorbed on primary sorption sites convert into the secondary sorption sites.

Next studied model is proposed in 2000 (to description of adsorption of alcohols on polymers) by Malakhov and Volkov [10] and widely propagated by Rutherford et al. (to description of water sorption on different adsorbents) [11-13] and others [14,15]. This new equation of cooperative the multimolecular sorption (called the CMMS) assumes that the sorption process follows the scenario of cooperative filling of channels (interrelated nanovoids) of the sorbent, and this process is combined with the growth of associates of sorbed molecules within the sorbent bulk. The final sorption equation, which can be reduced to the Henry's, Langmuir, Ising and/or BET models, can be written as:

$$M_e = \frac{mK_0h_r}{(1 - K_{as}h_r)(K_0h_r + \omega^2(1 - K_{as}h_r))} \quad (2)$$

where:

$$\omega = \frac{1}{2} \left(1 - \frac{K_I h_r}{1 - K_{as} h_r} + \sqrt{\left(1 - \frac{K_I h_r}{1 - K_{as} h_r} \right)^2 + \frac{4K_0 h_r}{1 - K_{as} h_r}} \right) \quad (3)$$

and m is the maximum sorption on primary sites, K_0 is the equilibrium constant for sorption of the central unit on the primary sites, K_I – the equilibrium constant for sorption of the side unit on the primary side, K_{as} – the equilibrium constant for sorption of the site associate.

As the reference model we used the GAB one [1,4-6]. This model, widely accepted as valid and the most popular in the field of food engineering, is applied in the form:

$$M_e = \frac{mCKh_r}{(1 - Kh_r)(1 - Kh_r + CKh_r)} \quad (4)$$

where m is the monolayer capacity, C is the kinetic constant related to the sorption in the first layer, K is the kinetic constant related to multilayer sorption.

Finally, since the mentioned above concepts are more or less applicable to description of water sorption on foodstuffs (see below), we wish to mention unsuccessful attempt of application of two models. The Corrected Dubinin - Serpinsky (CDS) concept, recently derived (from some empirical observation) for description of water sorption on carbons containing high energetic sites [15-17] as well as its modifications are inapplicable to description of water sorption data on foodstuffs. Similarly the Do - Do model [18], with modifications [19] and simplifications (i.e. the neglecting of the term related to the micropore filling, or the assumption of the existence of one type of sorption centres). The model led to good fit however, some numerical problems occurred with the irreproducible results (irreproducibility of the parameter N (the maximum number of water molecules adsorbed on the secondary surface sites) values). This is caused by the mathematical form of this equation namely, for the smaller than unity values of the constant describing sorption of subsequent water molecules on the secondary sorption sites, the rise in the value of the parameter N does not change the results in the meaningful way.

3. TEMPERATURE DEPENDENCE OF THE PARAMETERS OF SORPTION ISOTHERMS

As it was shown recently [7,8] in the case of the data determined at different temperatures the simultaneous description of the whole branch of adsorption isotherms leads to many different advantages. However, before the application of this procedure the exact definition of the temperature dependence of the parameters is necessary. On the other hand, it is well known from fundamental physical chemistry, that for all kinetic and or equilibrium constants (X) parameters one can write:

$$X = X_0 \exp\left(\frac{q_X}{RT}\right) \quad (5)$$

where X_0 is the almost temperature independent entropic term, q_X is the enthalpy related to this parameter, T is the temperature, and R is the gas constant. Below we show the forms of the Eq. (5) for the models presented in the previous paragraph.

GDW:

$$K = K_0 \exp\left(\frac{Q}{RT}\right) \quad (6)$$

$$k = k_0 \exp\left(\frac{q}{RT}\right) \quad (7)$$

CMMS:

$$K_0 = K_0^0 \exp\left(\frac{q_0}{RT}\right) \quad (8)$$

$$K_1 = K_1^0 \exp\left(\frac{q_1}{RT}\right) \quad (9)$$

$$K_{as} = K_{as}^0 \exp\left(\frac{q_{as}}{RT}\right) \quad (10)$$

GAB:

$$C = C_0 \exp\left(\frac{q_C}{RT}\right) \quad (11)$$

$$K = K_0 \exp\left(\frac{q_K}{RT}\right) \quad (12)$$

4. THE EQUATIONS FOR ISOSTERIC ENTHALPY OF SORPTION FROM THE STUDIED MODELS

The simultaneous multitemperature fitting of the data of water sorption makes it possible to generate the plot of the theoretical isosteric enthalpy of this process (q^{st}) calculated from the model (and the comparison of this plot with this determined experimentally). For the GDW model the equation defining the isosteric enthalpy of sorption was derived recently [7-9] and has the form:

$$q^{st} - L = \frac{\frac{K}{(1 + Kh_r)^2} \cdot \left(1 + \frac{wkh_r}{1 - kh_r}\right) \cdot Q + \frac{Kh_r}{1 + Kh_r} \cdot \frac{wk}{(1 - kh_r)^2} \cdot q}{\frac{K}{(1 + Kh_r)^2} \cdot \left(1 + \frac{wkh_r}{1 - kh_r}\right) + \frac{Kh_r}{1 + Kh_r} \cdot \frac{wk}{(1 - kh_r)^2}} \quad (13)$$

For the CMMS model [14,15] this equation can be written as:

$$q^{st} - L = \frac{q_0 m K_0 + q_{as} M_e K_{as} (K_0 h_r + \omega^2 (1 - K_{as} h_r)) + M_e (1 - K_{as} h_r) (-q_0 K_0 + \omega B_2 (1 - K_{as} h_r) + q_{as} \omega^2 K_{as})}{m K_0 + M_e K_{as} (K_0 h_r + \omega^2 (1 - K_{as} h_r)) + M_e (1 - K_{as} h_r) (-K_0 - \omega B_1 (1 - K_{as} h_r) + \omega^2 K_{as})} \quad (14)$$

where:

$$B_1 = -\frac{I}{(1 - K_{as} h_r)^2} \left(K_1 + \frac{K_1 \left(1 - \frac{K_1 h_r}{1 - K_{as} h_r}\right) - 2K_0}{\sqrt{\left(1 - \frac{K_1 h_r}{1 - K_{as} h_r}\right)^2 + \frac{4K_0 h_r}{1 - K_{as} h_r}}} \right) \quad (15)$$

$$B_2 = \frac{I}{(1 - K_{as} h_r)^2} \left(K_1 (q_1 + (q_{as} - q_1) K_{as} h_r) + \frac{K_1 \left(1 - \frac{K_1 h_r}{1 - K_{as} h_r}\right) (q_1 + (q_{as} - q_1) K_{as} h_r) - 2K_0 (q_0 + (q_{as} - q_0) K_{as} h_r)}{\sqrt{\left(1 - \frac{K_1 h_r}{1 - K_{as} h_r}\right)^2 + \frac{4K_0 h_r}{1 - K_{as} h_r}}} \right) \quad (16)$$

Finally, for the GAB model [8]:

$$q^{st} - L = \frac{(1 - Kh_r)^2 q_C + q_K + (C - 1) K^2 h_r^2 q_K}{1 + (C - 1) K^2 h_r^2} \quad (17)$$

where L is the enthalpy of water condensation.

5. THE DESCRIPTION OF EXPERIMENTAL DATA

Theoretical models were fitted to experimental data by applying the minimization procedure using the differential evolution (DE) algorithm proposed by Price and Storn [20,21]. The DE algorithm is a very simple heuristic approach for minimizing non-linear and non-differentiable continuous space functions. Moreover, it was successfully used in different fields [14-17,19,22], and also in the field of food engineering [7,8] for verification of different theoretical models. In the other words, to optimize the objective function with DE the following settings for the input file are taken into account: DE/best/2/bin method is chosen (this time, the new vector to be perturbed is the best performing vector of the current generation); the number of parents (i.e. number of population members), NP is 10 times greater than the number of parameters of the objective function, D; weighting factor, F is equal to 0.8 and crossover probability constant CR=0.5; the value to reach, VTR is equal to $1 \cdot 10^{-25}$ (the procedure stops when ofunc < VTR, if either the maximum number of iterations (generations) "itermax" is reached, or the best parameter vector "bestmem" has found a value $f(\text{bestmem}) \leq \text{VTR}$). The algorithm seems to work well only if $[XV_{\min}, XV_{\max}]$ covers the region where the global minimum is expected. Therefore, we taken into account the very wide ranges of XV. Moreover, the calculations are repeated at least five times.

To describe the goodness of the fit of theoretical models to experimental data the value of the determination coefficient can be chosen. This parameter for the description of the single temperature data is defined as:

$$DC_T = 1 - \eta_T \quad (18)$$

where:

$$\eta_T = \frac{\sum_i (M_{e,i}^o - M_{e,i}^t)^2}{\sum_i (M_{e,i}^o - \overline{M}_e^o)^2} \quad (19)$$

and $M_{e,i}^o$ is the observed moisture content for i -th experimental point, $M_{e,i}^t$ is the theoretical value of the moisture content calculated from theory, and \overline{M}_e^o is the average observed moisture content.

For the simultaneous fitting of the data determined at different temperatures the global DC value is calculated from deviations (η_T) determined for the data at individual temperatures:

$$DC = 1 - \sqrt{\frac{\sum_T \eta_T^2}{N}} \quad (20)$$

where N is the number of considered temperatures. Table 1 collects the best - fit parameters for all considered in this study models.

Table 1. The best-fit parameters of the considered models

Model	Best fit parameters	
	Single temperature fit	Multitemperature fit ^{*)}
GDW	m, K, k, w	m, K ₀ (log K ₀), k ₀ (log k ₀), Q, q, w
CMMS	m, K ₀ , K ₁ , K _{as}	m, K ₀ ⁰ (log K ₀ ⁰), K ₁ ⁰ (log K ₁ ⁰), K _{as} ⁰ (log K _{as} ⁰), q ₀ , q ₁ , q _{as}
GAB	m, C, K	m, C ₀ (log C ₀), K ₀ (log K ₀), q _C , q _K

^{*)} – in the case of entropic terms, due to the large range of values the logarithms were used in minimization.

6. EXPERIMENTAL DATA AND RESULTS

The samples of corn starch (National Starch and Chemical Co., USA), rye starch (Kröner Stärke, GmbH and Co., Ibbenburen, Germany), oat starch (Alko Ltd., Ramajaki, Finland) and sago starch (Wah Chang Int. Group Co., Singapore) were used either in the air-dried state (as native starch) or after fourfold freezing/thawing in liquid nitrogen according to the procedure described by Szymońska and coworkers [23,24]. After such preparation following by equilibration to the room temperature starch was stored in closed vessels for adsorption investigations.

Water vapour sorption isotherms were measured volumetrically at $t = 25$ °C using a device for simultaneous determination of isotherms and kinetic of sorption [25]. Before the experiment samples were outgassed at 70 °C to residual pressure about 10^{-4} mmHg. The values of the best fit parameters are put together in tables 2-4, and some selected results are shown in figure 1.

The second set of experimental data contains the series of isotherms measured for chosen foodstuffs however, at different temperatures. Here we applied the method of simultaneous fitting of all sorption isotherms described previously [8]). In this group we analyzed the data measured on: quinoa grains [26] (at $t = 20, 30$ and 40 °C), chickpea flour [27] (at $t = 10, 20, 30$ and 40 °C), fufu [28] (at $t = 25, 32$ and 45 °C), vetch seeds [29] (at $t = 5, 20, 40$ and 60 °C) and on potatoes [30] (at $t = 30, 45$ and 60 °C). Tables 5-7 show the values of the best – fit parameters, and figures 2-6 the results for all considered products.

Figure 7 shows the plots of the isosteric sorption enthalpy generated for considered models (Eqs.(13-17)) basing on the best fit parameters collected in tables 5-7.

Table 2. The values of the best-fit parameters obtained from the fitting of experimental data by the GDW model (Eq. (1))

Starch sample	m [mmol g ⁻¹]	K	k	w	DC _T
Corn native	8.072	5.107	0.6588	0.5436	0.9992
Corn frozen	10.87	2.646	0.9012	0.1300	0.9997
Oats native	4.680	11.34	0.5856	1.270	0.9997
Oats frozen	4.652	8.214	0.5367	1.657	0.9996
Sago native	4.471	12.81	0.6718	1.079	0.9996
Sago frozen	6.038	8.197	0.6588	0.6523	0.9974
Rye native	6.260	7.353	0.8585	0.3699	0.9978
Rye frozen	10.44	2.832	1.021	0.05009	0.9937

Table 3. The values of the best-fit parameters obtained from the fitting of experimental data by the CMMS model (Eqs.(2) and(3))

Starch sample	m [mmol g ⁻¹]	K ₀	K ₁	K _{as}	DC _T
Corn native	5.784	5.782	8.478	0.5930	0.9995
Corn frozen	5.200	4.990	7.422	0.6436	0.9986
Oats native	4.970	12.02	9.489	0.6077	0.9998
Oats frozen	5.380	7.454	5.951	0.5936	0.9995
Sago native	4.458	14.11	12.09	0.6747	0.9997
Sago frozen	5.478	13.14	9.367	0.5695	0.9977
Rye native	4.344	13.06	13.44	0.7229	0.9969
Rye frozen	4.426	18.26	14.09	0.7027	0.9897

Table 4. The values of the best-fit parameters obtained from the fitting of experimental data by the GAB model (Eq.(4))

Starch sample	m [mmol g ⁻¹]	C	K	DC _T
Corn native	6.612	12.14	0.5342	0.9991
Corn frozen	5.742	10.18	0.6110	0.9981
Oats native	4.687	17.29	0.6286	0.9997
Oats frozen	4.942	11.62	0.6204	0.9995
Sago native	4.336	18.95	0.6834	0.9996
Sago frozen	5.097	18.10	0.5922	0.9974
Rye native	4.359	18.53	0.7219	0.9969
Rye frozen	4.291	20.33	0.7120	0.9895

Table 5. The values of the best-fit parameters obtained from the fitting of experimental data by the GDW model (Eqs.(1),(6), and (7))

Foodstuff	m [% (db)]	K ₀	k ₀	Q	q	w	DC _T ^{*)}	DC
				[kJ mol ⁻¹]				
Quinoa grains	9.476	2.605 10 ⁻⁹	0.8263	54.64	~ 0	0.6180	0.9822, 0.9908, 0.9845	0.9854
Chickpea flour	8.812	3.679 10 ⁻⁶	0.6186	37.99	0.8411	0.6202	0.9913, 0.9905, 0.9890, 0.9928	0.9908
Fufu	4.933	1.041 10 ⁻¹¹	0.1936	72.26	3.194	0.9927	0.9906, 0.9877, 0.9962	0.9908
Vetch seeds	8.248	1.424 10 ⁻³	0.6563	22.41	0.7592	0.5842	0.9892, 0.9825, 0.9905, 0.9880	0.9872
Potatoes	4.765	7.688 10 ⁻⁴	0.1852	26.19	3.939	1.843	0.9974, 0.9931, 0.9891	0.9924

^{*)} – the values arranged according to the rise in temperature.

Table 6. The values of the best-fit parameters obtained from the fitting of experimental data by the CMMS model (Eqs.(2),(3), and (8)-(10))

Foodstuff	m [% (db)]	K ₀ ⁰	K ₁ ⁰	K _{as} ⁰	q ₀	q ₁	q _{as}	DC _T ^{*)}	DC
					[kJ mol ⁻¹]				
Quinoa grains	18.55	4.681 10 ⁻¹³	1.317 10 ⁻⁴	0.6951	75.15	14.87	~ 0	0.9787, 0.9920, 0.9856	0.9845
Chickpea flour	14.95	6.841 10 ⁻¹³	5.731 10 ⁻¹⁷	0.7868	78.46	89.78	~ 0	0.9896, 0.9866, 0.9926, 0.9963	0.9906
Fufu	9.258	2.299 10 ⁻¹⁶	1.069 10 ⁻¹⁴	0.4504	100.4	82.43	0.8895	0.9917, 0.9882, 0.9964	0.9914
Vetch seeds	13.56	1.271 10 ⁻⁶	1.037 10 ⁻¹⁵	0.4901	41.71	- 0.5999	1.276	0.9891, 0.9768, 0.9904, 0.9897	0.9854
Potatoes	11.23	0.02053	2.010 10 ⁻³	0.2140	14.83	17.12	3.507	0.9973, 0.9933, 0.9890	0.9924

^{*)} – the values arranged according to the rise in temperature.

Table 7. The values of the best-fit parameters obtained from the fitting of experimental data by the GAB model (Eqs.(4),(11), and (12))

Foodstuff	m [% (db)]	C ₀	K ₀	q _c	q _k	DC _T ^{*)}	DC
				[kJ mol ⁻¹]			
Quinoa grains	8.007	5.270 10 ⁻¹²	0.3540	71.34	1.779	0.9802, 0.9934, 0.9836	0.9847
Chickpea flour	7.343	2.776 10 ⁻⁹	0.3594	57.76	1.965	0.9871, 0.9870, 0.9903, 0.9926	0.9890
Fufu	4.807	5.440 10 ⁻¹²	0.1060	74.99	4.700	0.9896, 0.9865, 0.9947	0.9897
Vetch seeds	6.400	1.412 10 ⁻⁴	0.3873	30.26	1.855	0.9866, 0.9751, 0.9873, 0.9841	0.9826
Potatoes	6.431	6.798 10 ⁻³	0.2114	18.74	3.718	0.9948, 0.9914, 0.9889	0.9914

^{*)} – the values arranged according to the rise in temperature.

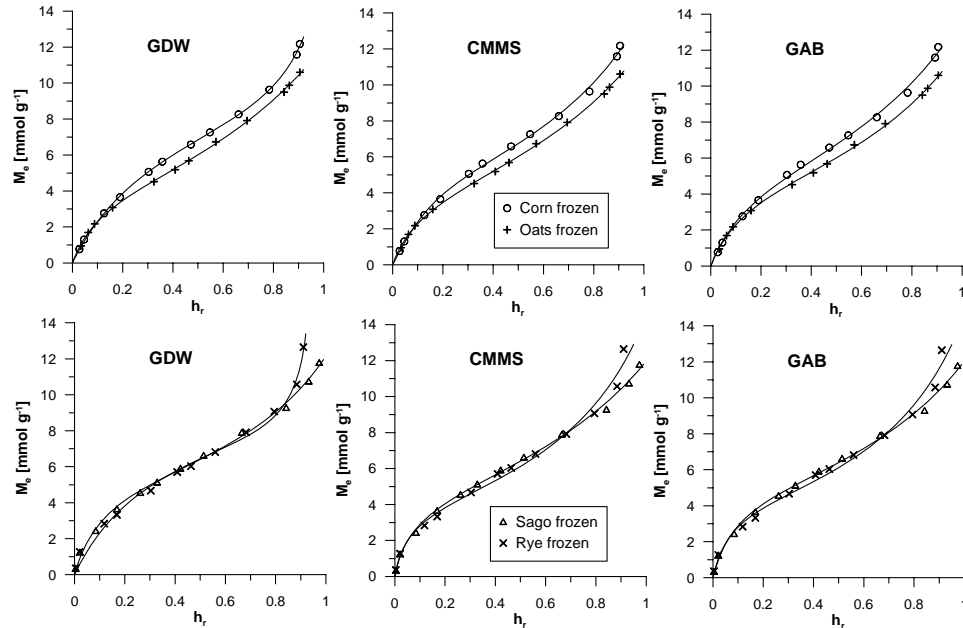


Figure 1. The results of fitting the sorption data on starch, points – experimental data, lines – fitting.

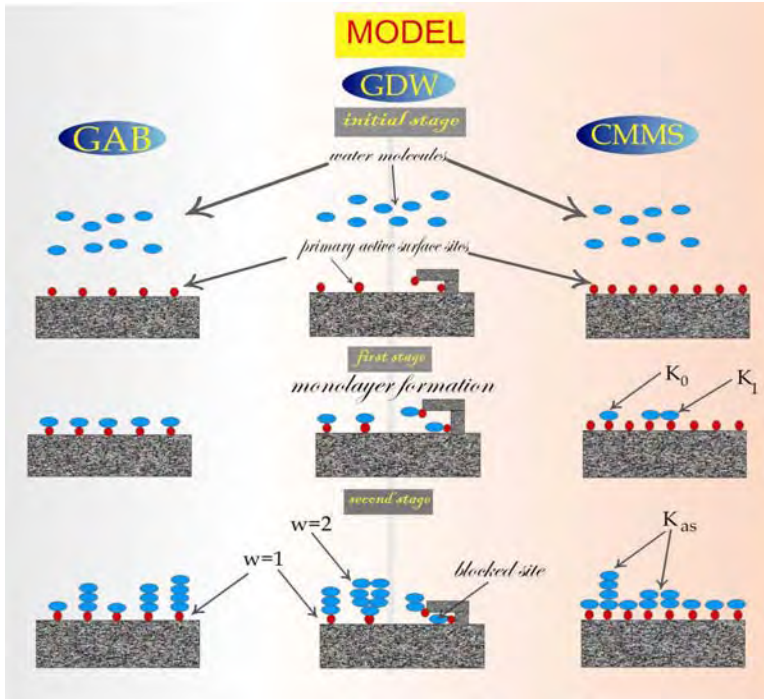
6.1. Fitting the Single Temperature Data

From tables 2 - 4 and from figure 1 it can be seen that all three models describe very well the data on starch. If one considers the arithmetic average values of DC_T the models can be arranged in the sequence GDW (0.9983), CMMS (0.9977), and GAB (0.9975). The strongly marked predominance of the GDW approach is visible for the data measured on rye frozen (figure 1) especially, in the range of large h_r values. Interesting is the comparison of the values of the parameter m i.e. the concentration of primarily sorption centres. This concentration is similar for all approaches. The parameter w of the GDW model shows that the process of conversion of primarily sorption sites into the secondary ones is for some cases strongly restricted (this is the most pronounced for the case of rye frozen), for some cases one primarily sorption site practically converts into one secondary centre (sago native), and sometimes from one primarily site arise more than one secondary centre (most pronounced for oats frozen).

6.2. Fitting the Multitemperature Data

From the results shown in tables 5 - 7 and from figures 2 - 6 it can be concluded that the GAB model leads to the poorest fit. This model poses the smallest number of the best fit parameters, moreover it assumes the simplest mechanism of sorption, and as it was shown previously it is in fact the simplified form of the GDW model [8]. It is surprising that the seven best fit parameter CMMS leads to worse fit than the GDW model (having six best fit parameters). This is caused by differences in the mechanisms assumed in the both models. In the CMMS model there is only one parameter (K_{as}) responsible for the shape of isotherm at larger h_r values, contrary in the GDW there are two such parameters (k and w). In the CMMS model the constants K_0 and K_1 have the most visible influence for small h_r values i.e. in the range where there is small number of experimental points. Scheme 1 shows the comparison of the mechanisms of all three models. One can see the similarities between GAB and GDW model however the latter assumes the possibility of the incomplete conversion of primarily centres into the secondary ones and/or the creation of more than one secondary centre from the primarily site. In the CMMS model the basic differences (comparing to the GAB and GDW) are caused by the behaviour of water molecules sorbed on two adjacent sites. In this model the mechanism of sorption at larger h_r values is similar to this assumed in the GAB model.

From figure 7 one can see the similarities in the behaviour of the plots of generated isosteric enthalpy values. At low M_e values all models generate relatively large enthalpy, usually the largest for the CMMS model and the smallest for the GDW one. At larger M_e values all enthalpy plots converge and are similar. The reason of the differences at small M_e 's is relatively small number of experimental points in this range, leading to the enthalpy values that are in fact approximated by the considered models. Neglecting the quantitative differences in enthalpy one can see that foodstuffs contain two types of sorption sites i.e. high - energetically (primarily sites - responsible for sorption at low h_r values) and low - energetically ones (secondary centers) - where the enthalpy of sorption is close to the enthalpy of water condensation.



Scheme 1. The comparison of the mechanisms proposed in the considered models.

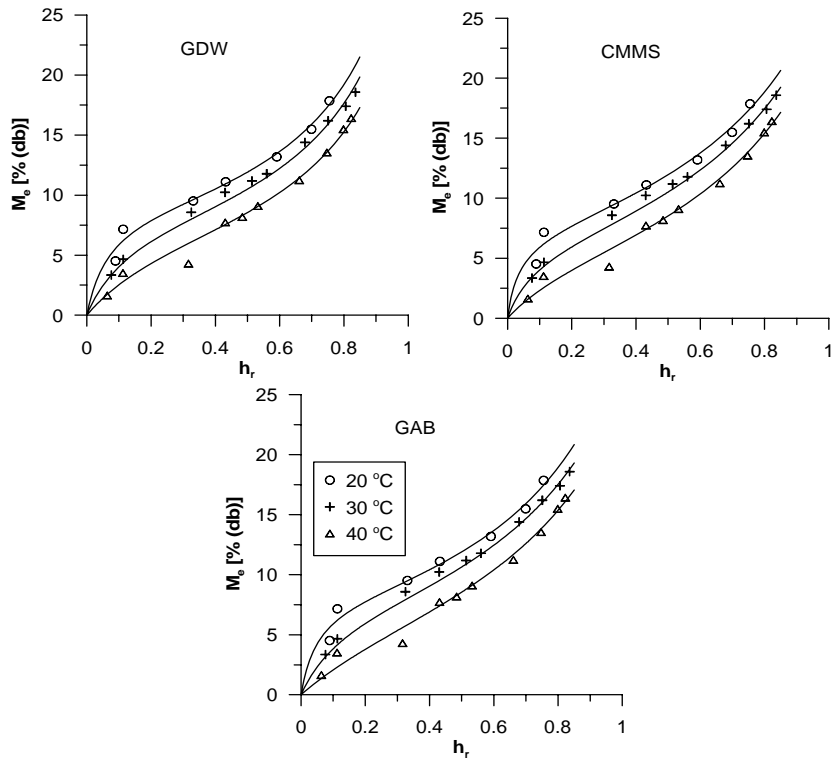


Figure 2. The results of fitting the sorption data on quinoa grains, points – experimental data, lines – fitting.

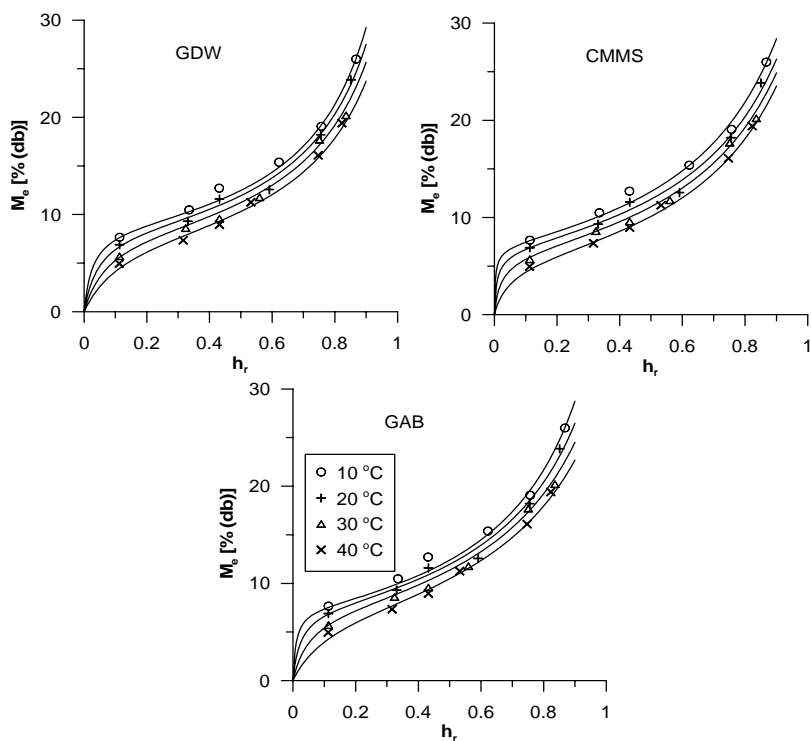


Figure 3. The results of fitting the sorption data on chickpea flour, points – experimental data, lines – fitting.

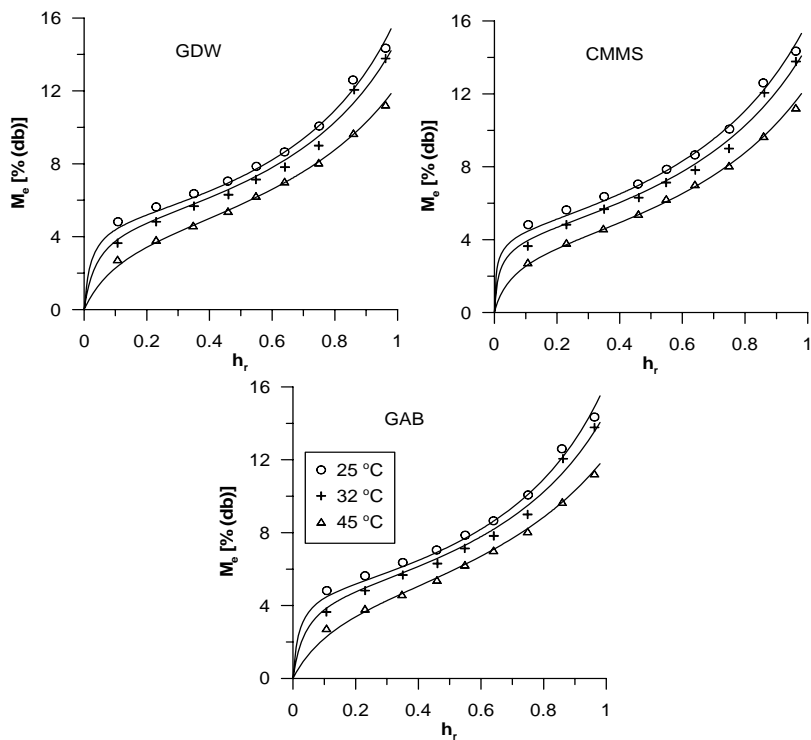


Figure 4. The results of fitting the sorption data on fufu, points – experimental data, lines – fitting.

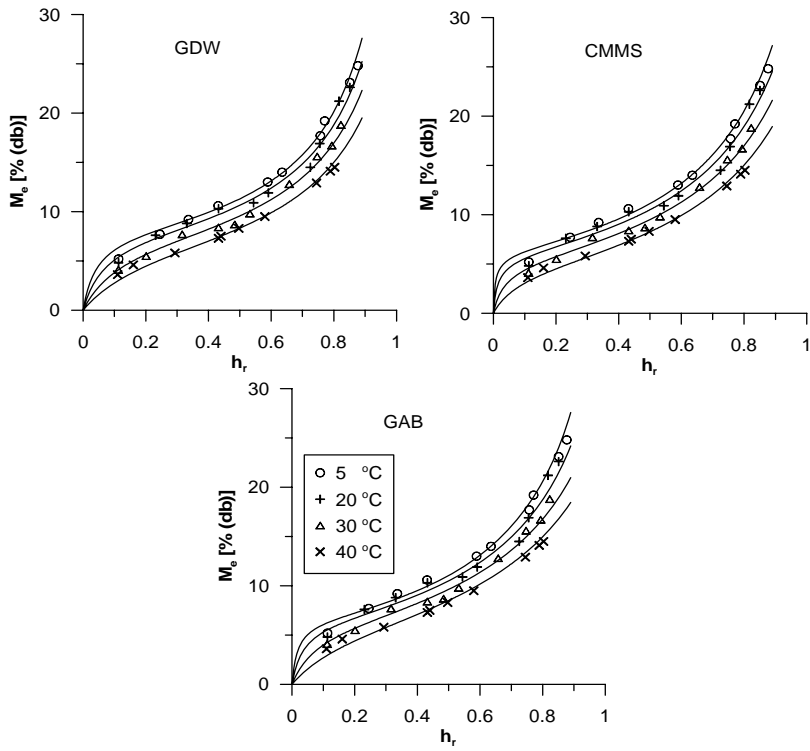


Figure 5. The results of fitting the sorption data on vetch seeds, points – experimental data, lines – fitting.

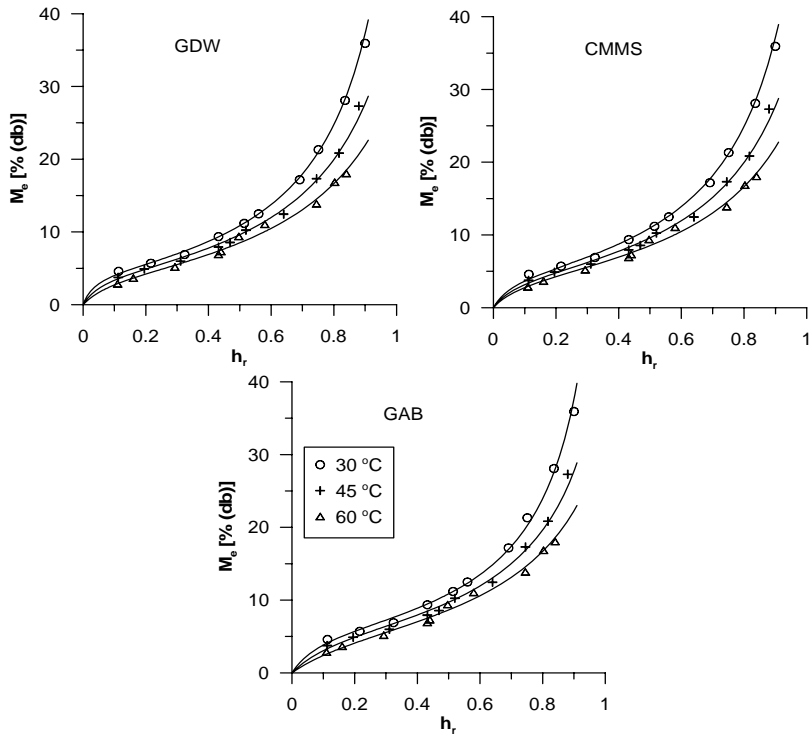


Figure 6. The results of fitting the sorption data on potatoes, points – experimental data, lines – fitting.

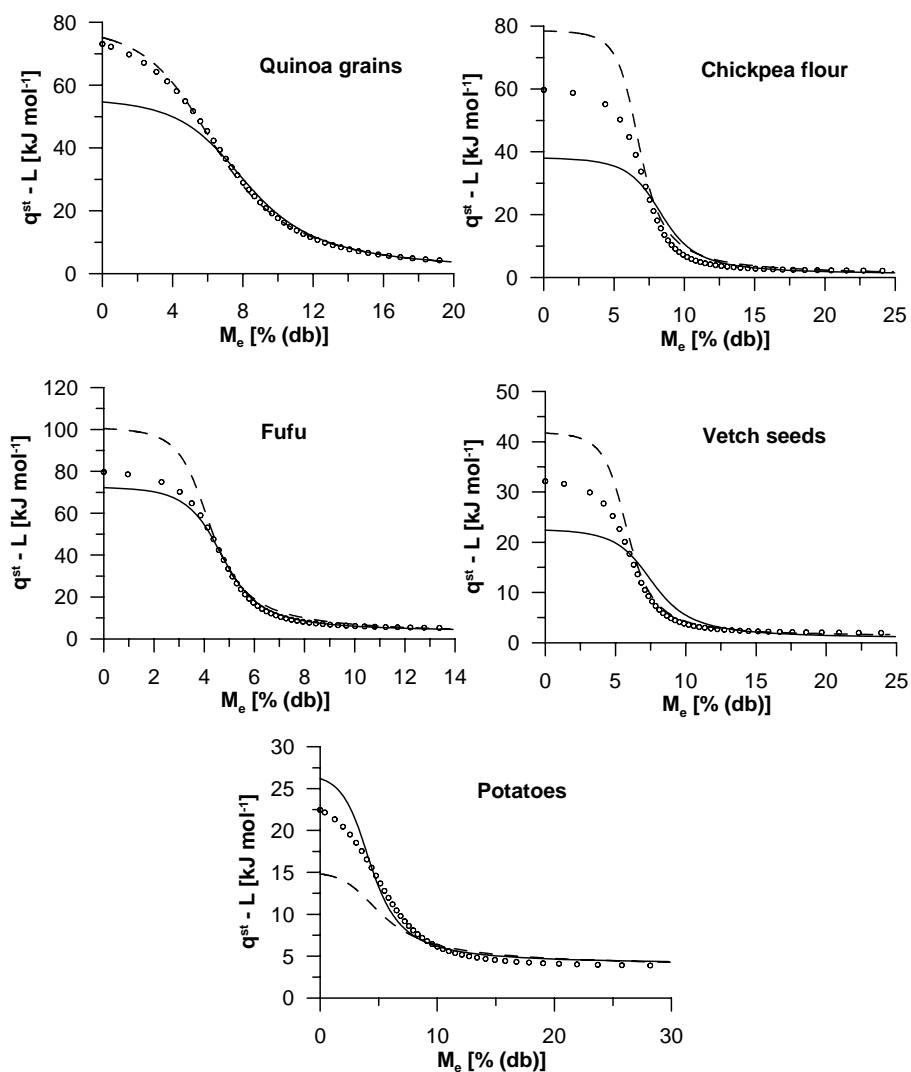


Figure 7. Theoretical enthalpy of sorption plots generated from considered models (Eqs.(13-17), parameters from Tabs. 5 – 7). solid line – GDW, dashed line – CMMS, circles – GAB. The curves were generated for the following temperatures: quinoa grains: 30 °C, chickpea flour: 20 °C, fufu: 32 °C, vetch seeds: 20 °C, potatoes: 45 °C).

7. CONCLUSION

Our results confirm, mentioned previously, large applicability of the GDW model to description of water sorption data (determined at single as well as at different temperatures) on foodstuffs. Moreover, the CMMS model shows good applicability in this field. We point out that the both models lead to better results than the GAB approach, which is the reference model in the food science engineering. Although the CMMS as well as the GDW contain more best - fit parameters than the GAB approach, they lead to better and more realistic description of sorption process. In the age of the progress in computer science and the development of new numerical algorithms fitting of many - parameter equations is relatively

easy. Moreover the GDW points out the importance of the effect of conversion of primarily sorption sites into the secondary ones.

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NOMENCLATURE

B_1, B_2	the constants defined in Eqs.(14 and 15)
C	the kinetic constant related to the sorption in the first layer
C_0	the pre-exponential entropic factor related to C constant
DC	the global determination coefficient value
DC_T	the value of DC calculated for the data measured at the considered temperature
h_r	relative humidity
K	the kinetic constant related to multilayer sorption (GAB model), the kinetic constants related to the sorption on primary sorption sites (GDW model)
K_0	the equilibrium constant for sorption on the central unit on the primary side (CMMS model) and/or the pre-exponential entropic factor related to K constant (GDW and GAB model)
K_0^0	the pre-exponential entropic factor related to K_0 constant (CMMS model)
K_1	the equilibrium constant for sorption of the side unit on the primary side
K_1^0	the pre-exponential entropic factor related to K_1 constant
K_{as}	the equilibrium constant for sorption of the site associate
K_{as}^0	the pre-exponential entropic factor related to K_{as} constant
k	the kinetic constants related to sorption on secondary sorption sites
k_0	the pre-exponential entropic factor related to k constant
L	the enthalpy of condensation of water, $43.96 \text{ kJ mol}^{-1}$
M_e	equilibrium moisture content, % (dry basis)
$M_{e,i}^o$	observed moisture content for i -th experimental point, % (dry basis)
$M_{e,i}^t$	theoretical value of the moisture content, % (dry basis)
\overline{M}_e^o	the average value of the observed moisture content, % (dry basis)
m	monolayer capacity (GAB model) and/or the concentration of primary active surface sites (GDW model) and/or maximum sorption on primary sites (CMMS model), % (dry basis), mmol g^{-1}
N	the number of temperatures for which the experimental data were measured
Q	the enthalpy values related to the primary sorption sites, kJ mol^{-1}
q	the enthalpy values related to the secondary sorption sites, kJ mol^{-1}
q_0	the value of the enthalpy related to K_0 constant, kJ mol^{-1}
q_1	the value of the enthalpy related to K_1 constant, kJ mol^{-1}
q_{as}	the value of the enthalpy related to K_{as} constant, kJ mol^{-1}
q_C	the value of the enthalpy related to C constant, kJ mol^{-1}
q_K	the value of the enthalpy related to K constant (GAB model), kJ mol^{-1}
q^{st}	isosteric enthalpy of sorption, kJ mol^{-1}
q_X	the value of the enthalpy related to X constant, kJ mol^{-1}
R	the universal gas constant, $0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1}$
T	absolute temperature, K

t	temperature, °C
w	the parameter determining what part of water molecules adsorbed on primary sites convert into the secondary adsorption sites
X	kinetic constants
X ₀	the pre-exponential entropic factor related to X constant
η _T	the sum (normalized) of the squares of deviations between theoretical and experimental data at considered temperature
ω	the parameter defined by Eq.(3)