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Searching the most optimal model of water sorption on foodstuffs in the whole range of relative humidity

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ABSTRACT

Water sorption on foodstuffs is very important in different areas of food science engineering. However, usually measured range of relative humidity covers only two of three stages of water sorption mechanism i.e. polymolecular sorption and capillary condensation. Since in this range different water sorption models can fit the experimental data well it is hard to decide which model is the most correct. In this study the results of water sorption isotherms measured from low humidity levels on marjoram, dill, granulated garlic, semolina, skim milk powder and ground coffee are reported. They are fitted by the most popular models applied in food science (i.e. proposed by: Halsey, Lewicki, Henderson, Chung and Pfost, Ferro Fontan et al. and Guggenheim, Anderson and de Boer (GAB)). We also extend the study to the newest models successfully applied in food engineering, i.e. the generalized D'Arcy and Watt model (GDW) and the approach of the cooperative multimolecular sorption (CMMS). Finally, we discuss the limits of the models at low humidity levels, the possibility of reduction to Henry's law and we show the advantages and disadvantages of all approaches. It is concluded that among studied models the GDW equation seems to be the best for description of data in the whole range of relative humidity.

1. Introduction

It is well known that sorption isotherms of foodstuffs are very important for design, modeling and optimization of many processes. Different authors (for example (Gabas, Telis, Sobral, & Telis-Romero, 2007; Ghodake, Goswami, & Chakraverty, 2007; Jensen & Risbo, 2007; Landfeld et al., 2008; Mestdagh, De Meulenaer, Cucu, & Van Peteghem, 2006; Oyelade, Tunde-Akitunde, Igbeka, Oke, & Raji, 2008; Toğrul & Arslan, 2007; Venturi et al., 2007; Włodarczyk-Stasiak & Jamroz, 2008; Yan, Sousa-Gallagher, & Oliveira, 2008; Zhou & Labuza, 2007; Zhou, Liu, & Labuza, 2008)) 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 sorption models have been used (with greater or smaller success) in the field of food engineering science for description water sorption data. Those data are usually measured via the static-desiccator's method (Bell & Labuza, 2000) in the range of relative humidity shown in Fig. 1. Therefore, as it is shown schematically in this figure, the typical data measured by this method cover only two of three stages of the mechanism of sorption (i.e. polymolecular sorption and capillary condensation) while the range of monolayer sorption is rarely measured and discussed. On the other hand, in this figure we also show (for a set of representative data – see captions) that different models (sometimes basing on contrary assumptions) describe relatively well mentioned above two stages (this situation occurs quiet often in adsorption on different adsorbents, i.e. carbons, silica and so on). Therefore, one can ask how to find the most realistic model? In this study we try to find the answer to this question basing on the series of data measured in our laboratory on different foodstuffs. Using the data measured *for all three stages* (*ranges*) of the sorption mechanism shown in Fig. 1, and using the fitting procedure supported by mathematical analysis of the most popular approaches applied in the field of food science, we show that the behavior of sorption models in the monolayer range is crucial.

There are many water sorption models in food (and generally in adsorption) science but in this study we apply only those having strong theoretical basis and position in food science i.e. proposed by: Halsey, Lewicki, Henderson, Chung and Pfost, Ferro Fontan et al. and Guggenheim, Anderson and De Boer (GAB). We also extend the study to the newest models successfully applied in food engineering, i.e. the generalized D'Arcy and Watt model (GDW) and the approach of the cooperative multimolecular sorption (CMMS). All studied models, if it is has not been done before, were converted into the form moisture content (M_e, the ratio of the mass of sorbed water to the mass of dry sample, %) vs. water activity

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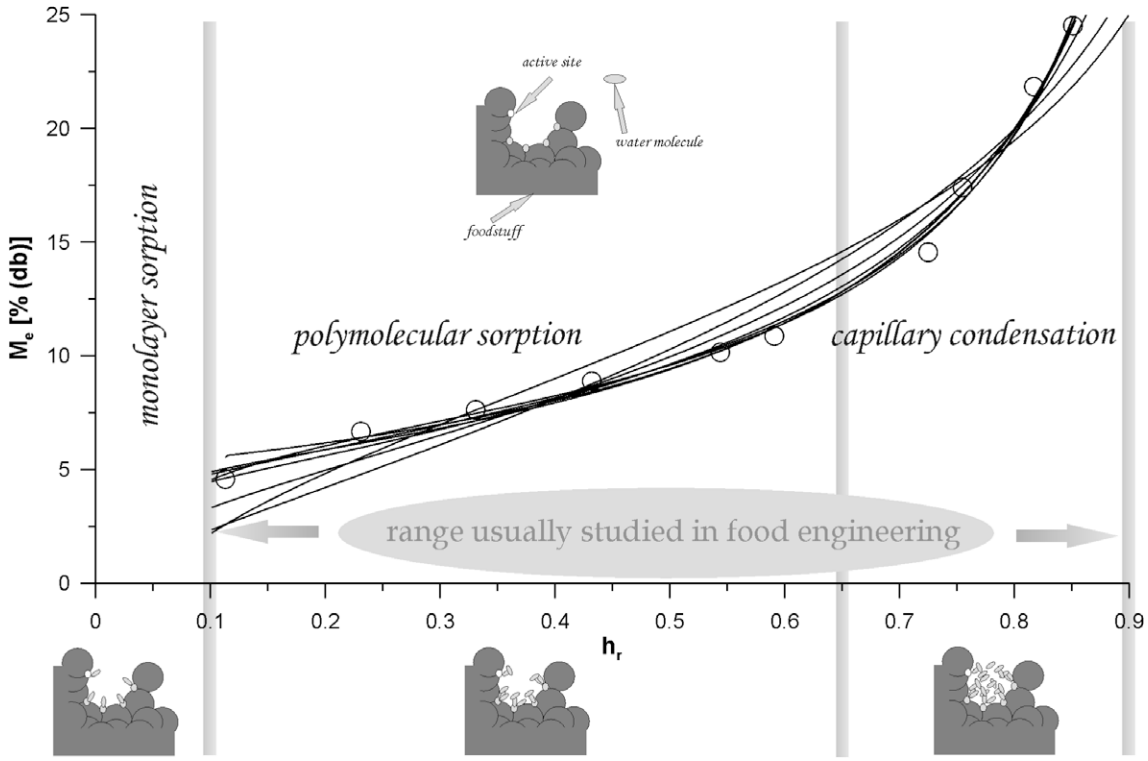

Fig. 1. Schematic representation of three stages of water sorption mechanism on foodstuffs with the typical range studied in food science. Symbols – the data of water sorption on chickpea seeds at 293 K (from (Menkov, 2000)), solid lines – the description of the data by models discussed in the text (h_r is the relative humidity).

(a_w, the ratio of the equilibrium vapour pressure to the saturated vapour pressure at given temperature).

As mentioned above the empirical approaches (proposed for example by Lewicki (1998), Peleg (1993), or Iglesias and Chirife (1978)) are not considered.

2. Studied models

2.1. Halsey model

Halsey (1948) proposed as the alternative to the BET equation (Brunauer, Emmett, & Teller, 1938) the model of polymolecular sorption. In this model he assumed that the energy of bonding of the sorbate is the power function of sorption:

$$a_w = \exp\left\{-\frac{a}{RT}\left(\frac{M_e}{M_0}\right)^{-r}\right\} \tag{1}$$

where a and r are constants; M_0 is the monolayer capacity. His model has been widely applied in the food science to description of water sorption data (Basu, Shivhare, & Mujumdar, 2006; García-Pérez, Cárcel, Clemente, & Mulet, 2008; Goula, Karapantsios, Achilias, & Adamopoulos, 2008; Sinija & Mishra, 2008; Tirawanichakul, Tirawanichakul, & Sniso, 2008). Eq. (1) can be converted into the following form:

$$M_e = A_1(-\ln a_w)^{A_2} \tag{2}$$

where:

$$A_1 = M_0\left(\frac{RT}{a}\right)^{-\frac{1}{r}} \tag{3}$$

$$A_2 = -\frac{1}{r} \tag{4}$$

2.2. Lewicki model (Oswin equation)

Another equation widely used to description of water sorption data on foodstuffs was proposed by Oswin (1946). The form of this equation permits generating of sigmoid plot of sorption isotherm:

$$M_e = A_1\left(\frac{a_w}{1-a_w}\right)^{A_2} \tag{5}$$

where A_1 and A_2 are empirical parameters. Few years ago Lewicki (2000) basing on Raoult's law derived the model of water sorption having the same mathematical form as Oswin equation, and in this way the physical meaning of the parameters of Eq. (5) was provided. Although Eq. (5) was proposed sixty years ago it is still widely used (Basu et al., 2006; De Temmerman, Verboven, Delcour, Nicolaï, & Ramon, 2008; Goula et al., 2008; Iguedjtal, Louka, & Allaf, 2008; Sinija & Mishra, 2008).

2.3. Henderson model

Among widely applied models one should mention the proposition of Henderson (1952):

$$a_w = 1 - \exp[-aTM_e^b] \tag{6}$$

where a and b are the best fit parameters. Eq. (6) can be converted to the form:

$$M_e = A_1[-\ln(1-h_r)]^{A_2} \tag{7}$$

where:

$$A_1 = (aT)^{-\frac{1}{b}} \tag{8}$$

$$A_2 = \frac{1}{b} \tag{9}$$

The applicability of Henderson model is still confirmed in different reports (see for example: (Barrozo, Silva, & Oliveira, 2008; Cervenka, Rezkova, & Kralovsky, 2008; García-Pérez et al., 2008; Peng, Chen, Wu, & Jiang, 2007; Sinija & Mishra, 2008)).

2.4. Chung and Pfost model

Chung and Pfost (1967a, 1967b) developed their model of water sorption on foodstuffs considering the changes in the value of the free energy during sorption with the moisture content. As the result they obtained:

$$a_w = \exp\left\{-\frac{a}{RT}\exp(-bM_e)\right\} \tag{10}$$

where a and b are the best fit parameters. Eq. (10) can be converted to:

$$M_e = A_1 \ln(A_2 \ln a_w) \tag{11}$$

where:

$$A_1 = -\frac{1}{b} \tag{12}$$

$$A_2 = -\frac{RT}{a} \tag{13}$$

Basic faults of Eqs. (10) and (11) can be proven analysing the properties at low values of a_w and M_e. Namely, at the limit:

$$\lim_{M_e \to 0} a_w = \exp\left(-\frac{a}{RT}\right) \tag{14}$$

$$\lim_{a_w \to 0} M_e = -\infty \tag{15}$$

those models cannot predict zero moisture content (at zero water activity limit). Despite this the Chung and Pfost model has found applicability for description of many experimental data (Barrozo et al., 2008; Basu et al., 2006; Iguaz & Vírseda, 2007; Samapundo et al., 2007; Tirawanichakul et al., 2008).

2.5. Ferro Fontan et al. model

Ferro Fontan, Chirife, Sancho, and Iglesias (1982) developing their model starting from the differential Clausius–Claypeyron equation and the empirical relation between the isosteric enthalpy of sorption and moisture content. From integration they obtained:

$$\ln\frac{\gamma}{a_w} = \frac{\overline{Q}}{RT}\left(\frac{M_e}{\overline{M}_e}\right)^{-r} \tag{16}$$

where γ is connected with the integration constant and $\overline{Q}$ is the value of the isosteric enthalpy of sorption for $\overline{M}_e$. Iglesias and Chirife (1995) suggested that γ is the parameter which accounts for the "structure" of sorbed water. Eq. (16) can be converted to:

$$M_e = A_1\left(-\ln\frac{a_w}{\gamma}\right)^{A_2} \tag{17}$$

where:

$$A_1 = \overline{M}_e\left(\frac{RT}{\overline{Q}}\right)^{-\frac{1}{r}} \tag{18}$$

$$A_2 = -\frac{1}{r} \tag{19}$$

It can be easily noticed (as it was mentioned by Ferro Fontan et al. (1982)) that for $\gamma = 1$ Eqs. (16) and (17) reduce to Halsey model (Eqs. (1) and (2)). Iglesias and Chirife (1995) checked the applicability of Ferro Fontan et al. model, and this model is still widely applied (Basu et al., 2006; De Temmerman et al., 2008; Pochat-Bohatier, Sanchez, & Gontard, 2006; Roca, Broyart, Guillard, Guilbert, & Gontard, 2008; Rougier, Bonazzi, & Daudin, 2007).

2.6. GAB model

The GAB model (Anderson, 1946; de Boer, 1953; Guggenheim, 1966) is still one of the most popular models applied for the description of water sorption in food science engineering (see for example (Basu et al., 2006; Di Scala & Crapiste, 2008; García-Pérez et al., 2008; Goula et al., 2008; Iguedjtal et al., 2008)). Therefore, this model has been widely analysed in many studies (for example (Lewicki, 1997; Timmermann, 2003; Timmermann, Chirife, & Iglesias, 2001)). The mathematical form of this model is (Furmaniak, Terzyk, & Gauden, 2007; Furmaniak, Terzyk, Czepirski et al., 2007):

$$M_e = \frac{mCKa_w}{(1-Ka_w)(1-Ka_w+CKa_w)} \tag{20}$$

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.

2.7. Simplifications of the GAB model and equivalent approaches

It can be easily shown that assuming in Eq. (20) $K = 1$, this equation simplifies to the Brunauer–Emmett–Teller (BET) model (Brunauer et al., 1938):

$$M_e = \frac{mCa_w}{(1-a_w)(1+(C-1)a_w)} \tag{21}$$

However, the applicability of this model in the food engineering is limited for the range of water activity not exceeding c.a. 0.5 (see for example (Basu et al., 2006; Timmermann et al., 2001)).

Vazquez, Chenlo, Moreira, and Carballo (1999) showed that the GAB model is equivalent to Hailwood and Horrobin (1946) model and the latter is rarely used to description of water sorption data on foodstuffs (see for example: (Boente, González, Martínez, Pollio, & Resnik, 1996; Delgado & Sun, 2002; Filho, Romanelli, Barboza, Gabas, & Telis-Romero, 2002)). This equivalence can be proved in the easiest way re-writing the Hailwood and Horrobin equation not in the open form:

$$M_e = M_0\left(\frac{\alpha\beta a_w}{1+\alpha\beta a_w} + \frac{\alpha a_w}{1-\alpha a_w}\right) \tag{22}$$

(where: M_0 is the starting constant (equal in the original derivation to the ratio of the molar mass of water and sorbing polymer, multiplied by 100%), and α and β have the same meaning as in the original derivation (Hailwood & Horrobin, 1946)), but in the quadratic form (being widely used and proposed by authors themselves (Hailwood & Horrobin, 1946)):

$$\frac{a_w}{M_e} = A_1 + A_2 a_w + A_3 a_w^2 \tag{23}$$

Then between the parameters of the given above equation and those of the GAB model the following relations occur (Vazquez et al., 1999):

$$A_1 = \frac{1}{mCK} \tag{24}$$

$$A_2 = \frac{C-2}{mC} \tag{25}$$

$$A_3 = \frac{(C-1)K}{mC} \tag{26}$$

2.8. GDW model

GDW model was proposed in our group to description of water sorption on carbons (Furmaniak, Gauden, Terzyk, & Rychlicki, 2008; Furmaniak, Gauden, Terzyk, Wesołowski, & Rychlicki, 2005), and next it was successfully applied to description of water

sorption on foodstuffs (Furmaniak, Terzyk, Gauden, & Rychlicki, 2007; Furmaniak, Terzyk, & Gauden, 2007; Furmaniak, Terzyk, Czepirski et al., 2007). The model assumes the existence of the primarily sorption centers where the mechanism of Langmuir sorption occurs. Water molecules bounded to those centers convert into the secondary centers where the mechanism follows the Dubinin and Serpinsky (1981) scenario. The form of this equation is (Furmaniak, Terzyk, Gauden, & Rychlicki, 2007; Furmaniak, Terzyk, & Gauden, 2007; Furmaniak, Terzyk, Czepirski et al., 2007):

$$M_e = \frac{mKa_w}{1+Ka_w}\cdot\frac{1-k(1-w)a_w}{1-ka_w} \tag{27}$$

where m is the maximum sorption value on primarily centers, K and k are the kinetic constants connected with sorption on primary and secondary centers, and w is the parameter determining the ratio of molecules bonded to primary centers and converted into the secondary ones.

As it was shown earlier (Furmaniak, Terzyk, & Gauden, 2007) the GDW model can be simplified to the GAB equation (Eq. (21)). To do this one can assume $w = 1$, and this is equivalent to the assumption that each water molecule bounded to the primary center becomes the secondary site. Assuming this simplification the following relations between parameters of Eq. (27) (subscripted GDW) and Eq. (21) (subscripted GAB) (Furmaniak, Terzyk, & Gauden, 2007):

$$m_{GAB} = m_{GDW}\frac{K_{GDW}}{K_{GDW}+k_{GDW}} \tag{28}$$

$$C_{GAB} = 1+\frac{K_{GDW}}{k_{GDW}} \tag{29}$$

$$K_{GAB} = k_{GDW} \tag{30}$$

2.9. CMMS model

Malakhov and Volkov (2000) proposed (to description of adsorption of alcohols on polymers) the model of cooperative multimolecular sorption (called the CMMS). It 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. This model was widely propagated by Rutherford (2003, 2006) and Rutherford and Coons (2004) who applied it to description of water sorption on different adsorbents, and also was also used by others (Furmaniak, Terzyk, Szymański et al., 2006; Furmaniak et al., 2008). This model was previously applied (Furmaniak, Terzyk, Czepirski et al., 2007) to description of water sorption on foodstuffs. The major equations can be written as (Furmaniak, Terzyk, Czepirski et al., 2007):

$$M_e = \frac{mK_0a_w}{(1-K_{as}a_w)(K_0a_w+\omega^2(1-K_{as}a_w))} \tag{31}$$

where:

$$\omega = \frac{1}{2}\left(1-\frac{K_1a_w}{1-K_{as}a_w}+\sqrt{\left(1-\frac{K_1a_w}{1-K_{as}a_w}\right)^2+\frac{4K_0a_w}{1-K_{as}a_w}}\right) \tag{32}$$

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_1 – the equilibrium constant for sorption of the side unit on the primary side, K_{as} – the equilibrium constant for sorption of the site associate.

3. Materials and methods

In this study we applied the samples of the following products: marjoram (Kamis–Przyprawy S.A., Poland), dill (P.P.H. Prymat Sp. z o.o., Poland), granulated garlic (Cykoria S.A., Poland), semolina (P.P.H. „Alta", Poland), skim milk powder (Spółdzielnia Mleczarska Gostyń, Poland) and ground coffee (Tchibo Warszawa Sp. z o.o., Poland). All samples of products were bought at supermarket. Following the specifications of the producers the spices do not contain food additives. Semolina contains 8.65% of protein, 77.30% of carbohydrates and 1.36% of fat. Skin milk powder contains 35.7% of protein, 51.2% of carbohydrates and 0.8% of fat.

The measurements (at $T = 298$ K) were performed in a thermostated (with accuracy of ±0.1 K) vacuum apparatus constructed for gravimetric measurement of sorption isotherms, and shown schematically in Fig. 2. The equilibrium pressure (as well as the water saturated vapour pressure) was measured using the baratron transducers (MKS Instruments Germany, working in three ranges i.e. up to 200 Pa, up to 1000 Pa and up to 1.33×10^4 Pa). The construction of this apparatus makes it possible to perform the measurement of four sorption isotherms simultaneously. The samples were desorbed under vacuum at 343 K for 10 h. Next samples were hold in apparatus (and desorbed) until the pressure lower than 10^{-2} Pa was attained. Next the proper measurement was performed. The measurement is performed following the procedure of adding (by the valve Z_A) a portion of water vapour and next waiting until the equilibrium is reached (i.e. there are not changes in the mass of sample with sorbed water). According to the Hook's law the change of the length of quartz spiral, S (measured using cathetometer) is equivalent to the change in the mass of the sample. The total change in the spiral length is the measure of water sorption, and this makes possible to calculate the equilibrium moisture content. Equilibrium water pressure (making possible to calculate water activity from dividing by the saturated water vapour pressure at given temperature) is measured directly using

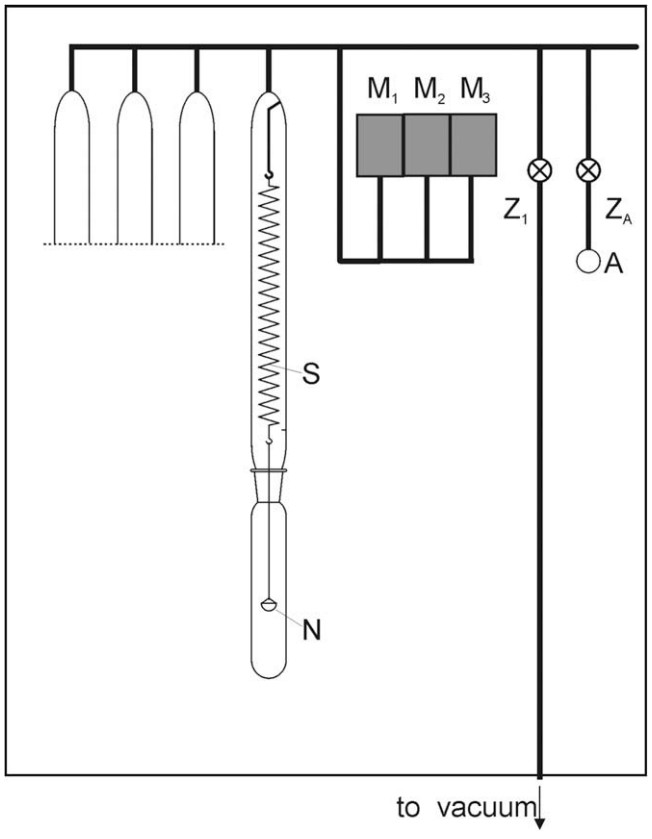

Fig. 2. The scheme of the sorption apparatus. A – ampoule with a sorbate, Z_A and Z_1 – valves, M_1, M_2, M_3 – pressure gauges, S – Mc Bain balance (quartz spiral), N – the vessel with sample).

baratron transducers. After the measurement for a given adsorption point is finished the next portion of water vapour is added to the system to measure the subsequent point on the isotherm. The final results obtained using this procedure are collected in Table 1 (the results are new and have not been reported yet). Obtained sorption isotherms are almost or exactly the same as obtained for analogous products by other authors (Cepeda, Ortiz de Latierro, San José, & Olazar, 1999; Jouppila & Roos, 1994; Ocieczek, 2007; Pezzutti & Crapiste, 1997; Soysal & Öztekin, 1999; Vélez-Ruiz, Lima Carrera, & Macedo y Ramírez, 2004).

4. Description of the data

As the measure of the goodness of the fit the theoretical curves to experimental data we assumed the value of determination coefficient (*DC*) defined as:

$$DC = 1 - \frac{\sum_{i=1}^{N}\left(M_{e,i}^{o} - M_{e,i}^{t}\right)^2}{\sum_{i=1}^{N}\left(M_{e,i}^{o} - \overline{M}_{e}^{o}\right)^2} \tag{33}$$

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 models, and $\overline{M}_{e}^{o}$ is the average observed moisture content. The value equal to 1 shows the ideal fit, the lower *DC* value the worse fit is observed.

Experimental data were fitted using the genetic algorithm (DE) proposed by Storn and Price (1996, 1997) and used successfully to description of many systems (Furmaniak, Gauden, Terzyk, Rychlicki, 2005; Furmaniak, Terzyk, Gauden, & Rychlicki, 2005; Furmaniak, Terzyk, Gauden, & Rychlicki, 2006; Furmaniak, Terzyk, Szymański et al., 2006; Furmaniak et al., 2008; Gauden, 2005; Terzyk et al., 2007; Terzyk, Wiśniewski, Gauden, Rychlicki, & Furmaniak, 2008), also in the field of food science engineering (Furmaniak, Terzyk, Gauden, & Rychlicki, 2007; Furmaniak, Terzyk, & Gauden, 2007; Furmaniak, Terzyk, Czepirski et al., 2007).

The DE algorithm is a very simple heuristic approach for minimizing non-linear and non-differentiable continuous space functions. In the other words, to optimize the objective function (ofunc: (1-*DC*)) 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 1×10^{-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(bestmem) ⩽ 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 were repeated at least five times in order to check the reproducibility.

5. Results and discussion

The results from Table 1 reveal small values of standard deviations and it can be stated that the measurements were performed with high precision. The results of the fitting of data from Table 1 using the models mentioned above are collected in Tables 2–4 and in Figs. 3–10. Below they are discussed for all studied approaches.

5.1. Halsey model

For this approach the average *DC* value for all studied systems is equal to 0.9784, with the best fit for marjoram and coffee, and the worst fit for semolina. From Fig. 3 one can notice that except the results for semolina, this model describes the data well in the range of medium and large a_w values. In the initial range of sorption isotherms poor fit is usually observed, especially for dill, milk powder, garlic and semolina.

5.2. Lewicki model

For this model the average *DC* value is equal to 0.9915. The best fit is observed for milk powder, the worst for garlic (Fig. 4). Contrary to Halsey model this approach describes well the ranges of medium and large a_w values for all systems. As for the Halsey approach the problems occur with the description of the data for low a_w values, however for milk and garlic relatively good fit is observed.

5.3. Henderson model

The average *DC* value for all studied systems is equal to 0.9854. This model works well for dill and semolina, but for marjoram the worse fit is recorded (Fig. 5). With the exception of the data for semolina (where the fit is satisfactory for all studied a_w ranges) for the remaining systems the fit is satisfactory only at large water activity levels.

Table 1
Collected experimental data (in the case of marjoram, dill, garlic and coffee this is the average for three measurements, in the case of semolina and milk powder this is the average for four measurements). The values of the standard deviations of the average (*SD*) for each point are also shown. M_e and *SD* are in % (dry basis).

Marjoram			Dill			Granulated garlic			Semolina			Skim milk powder			Ground coffee		
a_w	M_e	*SD*	a_w	M_e	*SD*	a_w	M_e	*SD*	a_w	M_e	*SD*	a_w	M_e	*SD*	a_w	M_e	*SD*
0.0051	0.50	0.09	0.0047	0.29	0.06	0.0047	0.10	0.05	0.0047	0.12	0.04	0.0047	0.09	0.04	0.0047	0.03	0.02
0.0141	1.20	0.14	0.0095	0.61	0.03	0.0095	0.24	0.11	0.0096	0.51	0.12	0.0095	0.24	0.10	0.0095	0.23	0.07
0.0253	1.65	0.02	0.0253	1.15	0.12	0.0189	0.65	0.11	0.0253	1.11	0.16	0.0189	0.35	0.11	0.0189	0.54	0.04
0.0505	2.38	0.10	0.0505	1.89	0.08	0.0379	1.23	0.09	0.0505	2.59	0.15	0.0379	0.99	0.08	0.0379	1.19	0.10
0.0695	2.58	0.07	0.1010	2.41	0.08	0.0884	2.06	0.11	0.1010	4.29	0.11	0.0884	1.55	0.11	0.0884	1.89	0.08
0.0947	2.87	0.10	0.2021	3.84	0.04	0.1326	3.24	0.08	0.2021	6.60	0.09	0.1326	2.25	0.05	0.1326	2.39	0.07
0.1831	4.26	0.17	0.3157	5.20	0.07	0.2052	4.57	0.04	0.3157	8.69	0.13	0.2052	3.05	0.15	0.2052	2.98	0.06
0.2560	4.77	0.09	0.3789	6.91	0.11	0.2684	5.00	0.15	0.3789	9.74	0.09	0.2684	4.46	0.12	0.2684	3.73	0.06
0.3267	5.53	0.18	0.4841	9.55	0.08	0.3252	6.60	0.11	0.4630	11.48	0.08	0.3368	5.53	0.07	0.3368	4.18	0.04
0.4012	7.24	0.14	0.5893	13.18	0.12	0.3789	7.08	0.14	0.5472	13.34	0.15	0.4209	7.33	0.18	0.4209	4.70	0.05
0.5056	9.02	0.14	0.6946	19.80	0.19	0.4841	9.60	0.07	0.6314	14.50	0.14	0.5262	9.41	0.10	0.5262	6.00	0.12
0.5923	11.18	0.26	0.7577	26.70	0.22	0.5893	13.30	0.13	0.7156	16.18	0.15	0.6314	11.25	0.09	0.6314	7.96	0.17
0.6975	13.76	0.26	0.8419	43.61	0.47	0.6946	19.84	0.22	0.7998	19.23	0.18	0.7156	14.24	0.08	0.7156	11.57	0.07
0.7615	19.28	0.16	0.9076	63.03	2.04	0.7577	25.95	0.17	0.8419	21.22	0.16	0.7998	18.94	0.15	0.7998	16.45	0.10
0.8419	28.80	0.35				0.8419	46.69	1.27	0.9050	26.13	0.11	0.8419	23.04	0.20	0.8419	20.03	0.20
0.9059	44.87	0.85				0.9050	54.21	0.59				0.9050	33.39	0.34	0.9050	30.13	0.62

Table 2
The values of the best fit parameters for Halsey (Eq. (2)), Lewicki (Eq. (5)), Henderson (Eq. (7)) and Chung and Pfost (Eq. (11)) models.

Product	Halsey model			Lewicki model			Henderson model			Chung and Pfost model		
	A_1 [% (db)]	A_2	DC	A_1 [% (db)]	A_2	DC	A_1 [% (db)]	A_2	DC	A_1 [% (db)]	A_2	DC
Marjoram	6.231	−0.8561	0.9980	8.760	0.7134	0.9933	13.09	1.368	0.9716	−9.094	−0.3173	0.8253
Dill	7.781	−0.9137	0.9898	10.90	0.7784	0.9956	16.56	1.536	0.9944	−13.31	−0.3532	0.8081
Garlic	8.214	−0.8579	0.9647	11.70	0.7105	0.9774	17.82	1.341	0.9818	−12.59	−0.3500	0.8343
Semolina	8.394	−0.5280	0.9355	11.24	0.3874	0.9877	14.93	0.6023	0.9952	−6.455	−0.2166	0.9948
Milk powder	5.719	−0.7791	0.9871	8.141	0.6240	0.9987	12.16	1.105	0.9882	−7.417	−0.3143	0.9020
Coffee	4.359	−0.8489	0.9951	6.156	0.7023	0.9963	9.211	1.328	0.9810	−6.336	−0.3214	0.8498

Table 3
The same as in Table 2 but for Ferro Fontan et al. (Eq. (17)) and GAB (Eq. (20)) models.

Product	Ferro Fontan et al. model				GAB model			
	A_1 [%(db)]	A_2	γ	DC	m [% (db)]	C	K	DC
Marjoram	6.194	−0.8993	1.012	0.9982	4.797	13.18	0.9875	0.9985
Dill	7.493	−1.461	1.144	0.9989	10.48	1.177	0.9429	0.9973
Garlic	9.723	−1.732	1.301	0.9876	19.48	0.6084	0.8485	0.9852
Semolina	30.14	−1.721	2.812	0.9855	8.291	11.47	0.7571	0.9962
Milk Powder	5.940	−1.067	1.107	0.9939	5.123	5.512	0.9394	0.9984
Coffee	4.299	−1.021	1.050	0.9976	3.619	7.573	0.9756	0.9982

Table 4
The same as in Table 2 but for GDW (Eq. (27)) and CMMS (Eqs. (31) and (32)) models.

Product	GDW model					CMMS model				
	m [% (db)]	K	k	w	DC	m [% (db)]	K_0	K_1	K_{as}	DC
Marjoram	3.818	25.99	0.9769	1.466	0.9989	5.146	28.05	11.56	0.9807	0.9989
Dill	1.028	182.1	0.9450	10.18	0.9983	14.03	1.102	0.5941	0.9279	0.9979
Garlic	0.8620	104.4	0.9010	14.77	0.9856	21.08	0.5976	0.3853	0.8608	0.9856
Semolina	16.69	3.091	0.9266	0.2160	0.9992	7.641	5.489	10.03	0.7797	0.9975
Milk powder	24.23	0.7461	0.9837	0.2988	0.9995	4.816	2.366	5.162	0.9470	0.9989
Coffee	2.446	20.64	0.9607	1.805	0.9990	5.548	9.465	1.863	0.9456	0.9991

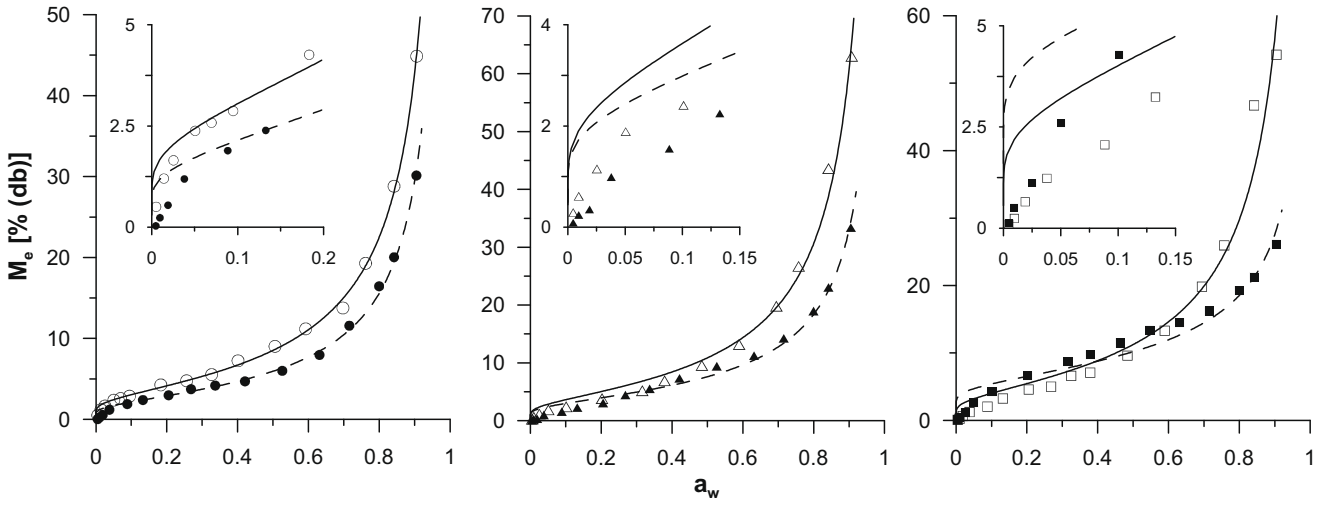

Fig. 3. The results of the fitting of experimental data using the Halsey model (Eq. (2)). Symbols: open circles – marjoram, closed circles – ground coffee, open triangles – dill, closed triangles – skim milk powder, open squares – granulated garlic, closed squares – semolina; solid lines – fit of the model to data marked by open symbols, dashed line – fit of the model to data marked by closed symbols.

5.4. Chung and Pfost model

This model, excepting semolina, gives unacceptable fit for all systems. Therefore in Fig. 6 the fit of the data is shown only for water sorption on semolina. For this system, with exception of extremely low water activity levels, the fit is good. As we mentioned above (Eqs. (14) and (15)) this model is able to generate the zero value of M_e for a_w different than zero, and for smaller values of a_w the values of M_e become negative (this is not shown in Fig. 6).

5.5. Ferro Fontan et al. model

The average DC value for all studied systems is equal to 0.9936. The best fit is observed for marjoram while the worse for semo-

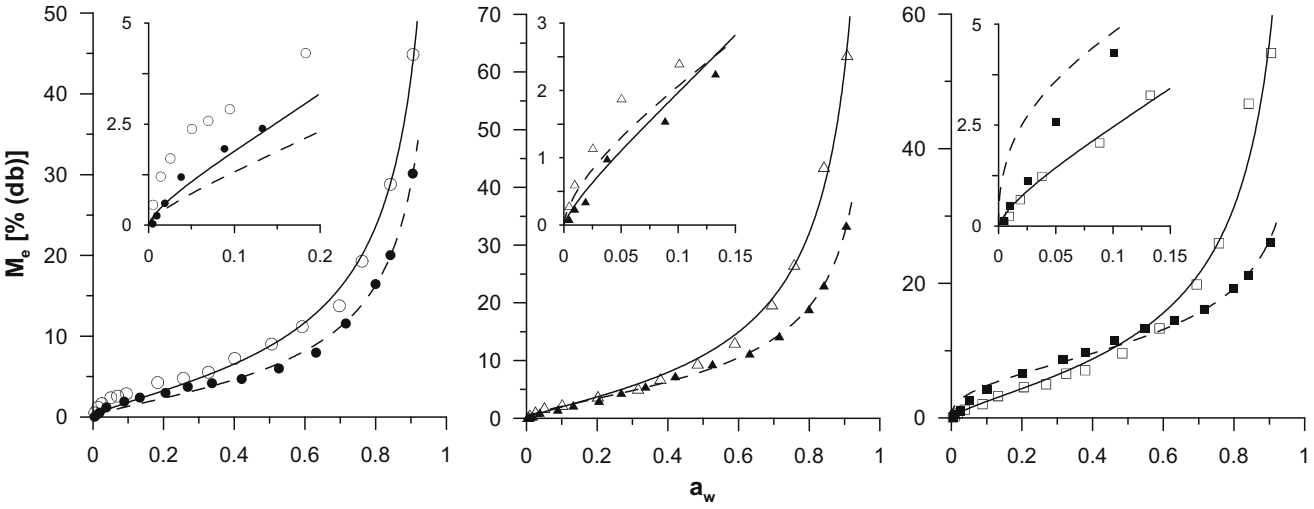

Fig. 4. The results of the fitting of experimental data using Lewicki model (Eq. (5)). Symbols as in Fig. 3.

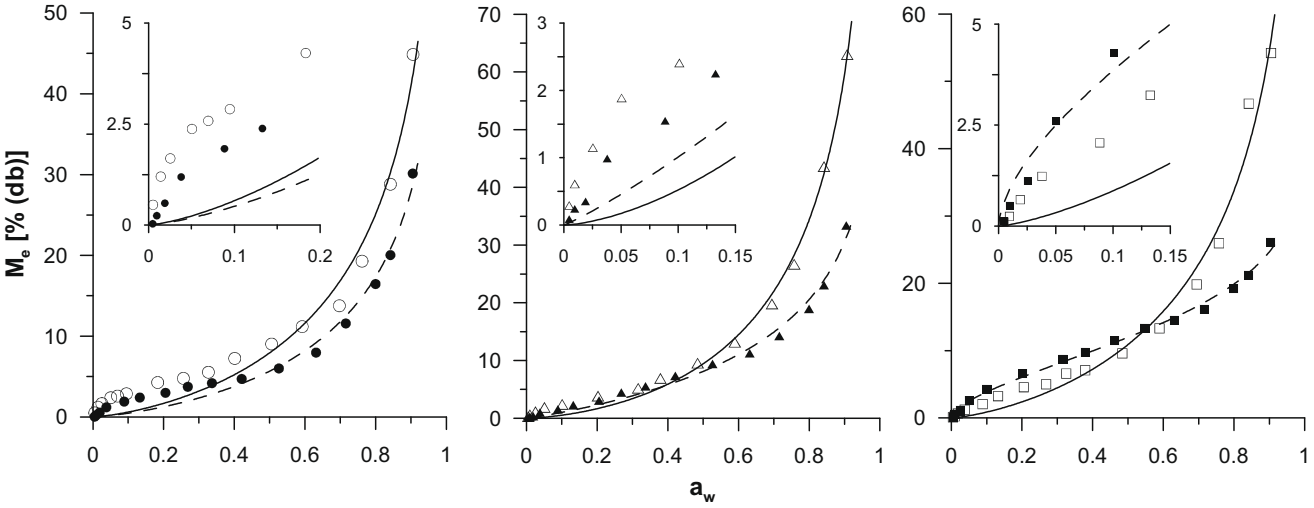

Fig. 5. The results of the fitting of experimental data using Henderson model (Eq. (7)). Symbols as in Fig. 3.

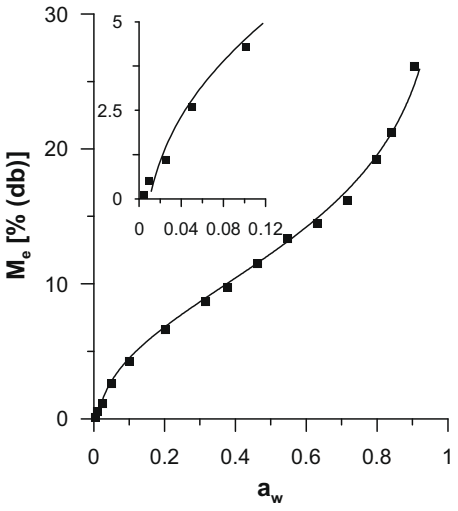

Fig. 6. The results of the fitting of experimental data for semolina using Chung and Pfost model (Eq. (11)).

lina. From Fig. 7 it can be observe that this model leads to the satisfactory fit almost in the whole range of a_w with exception a few initial points. Excepting semolina, the value of the parameter γ is close to unity. As mentioned above Iglesias and Chirife (1995) suggested that γ is the parameter which accounts for the "structure" of sorbed water. Therefore, the "structure" of water sorbed in all studied products, with exception of semolina, is close to liquid.

5.6. GAB model

This model gives the average *DC* value equal to 0.9956. From Fig. 8 it can be see that excepting dill and garlic (where the model has problems with fitting the low range of a_w) the model gives good fit in the whole studied range. This model provides reliable values of the monolayer capacity form c.a. 3.6 up to 20. However taking into account the results of the mathematic analysis of the GAB model performed by Lewicki (1997), the *C* values for dill and garlic seem to be slightly underestimated. This effect explains too large values of monolayer capacities for the both systems, and the worse fit for those systems in the low range of a_w.

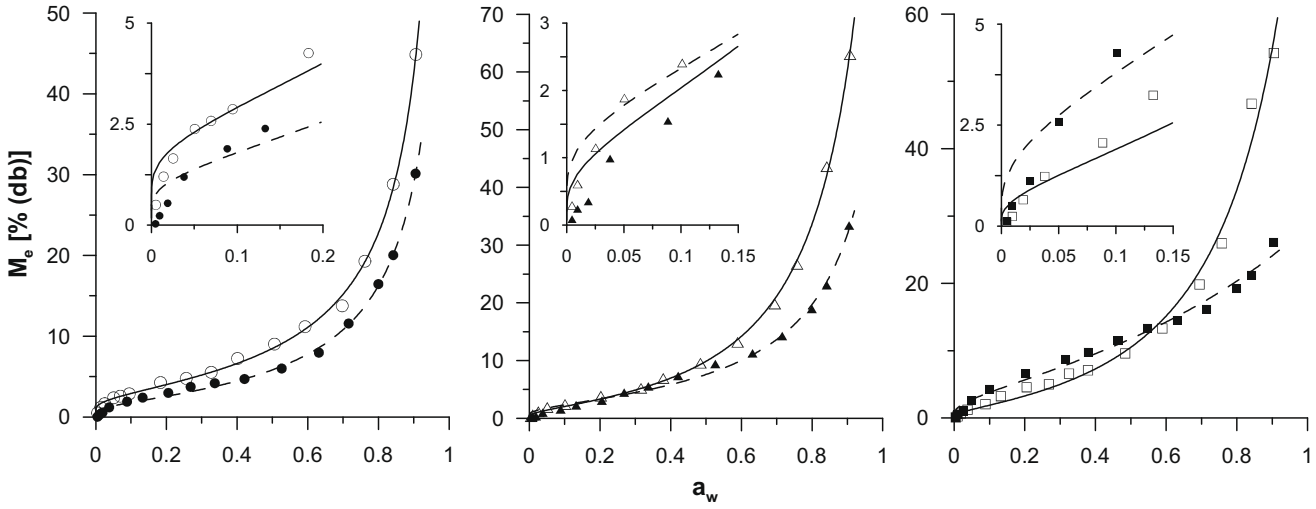

Fig. 7. The results of the fitting of experimental data using Ferro Fontan et al. model (Eq. (17)). Symbols as in Fig. 3.

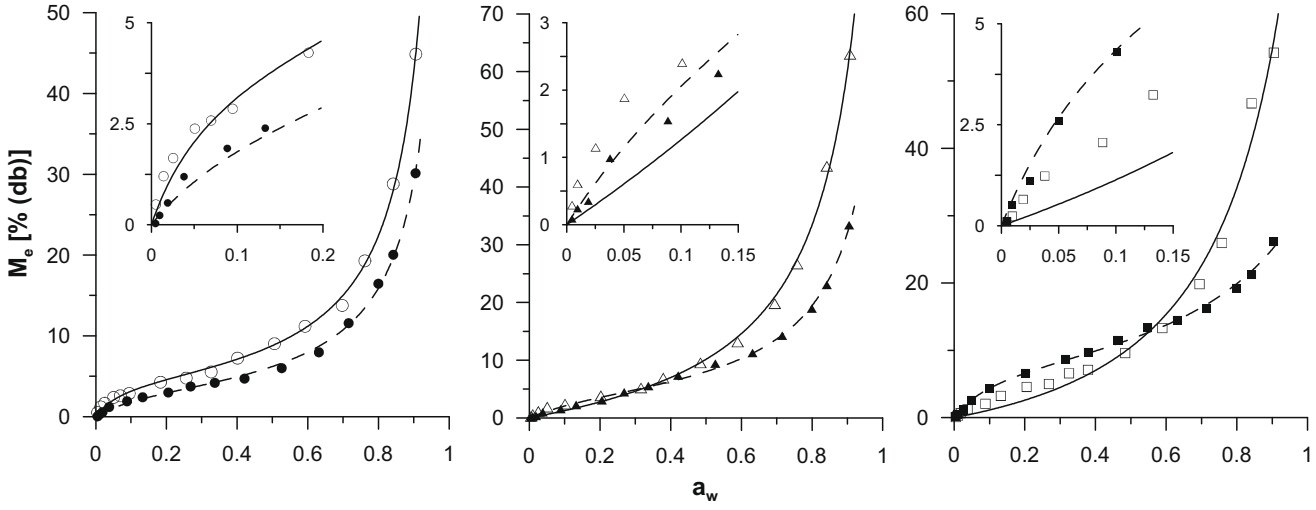

Fig. 8. The results of the fitting of experimental data using the GAB model (Eq. (20)). Symbols as in Fig. 3.

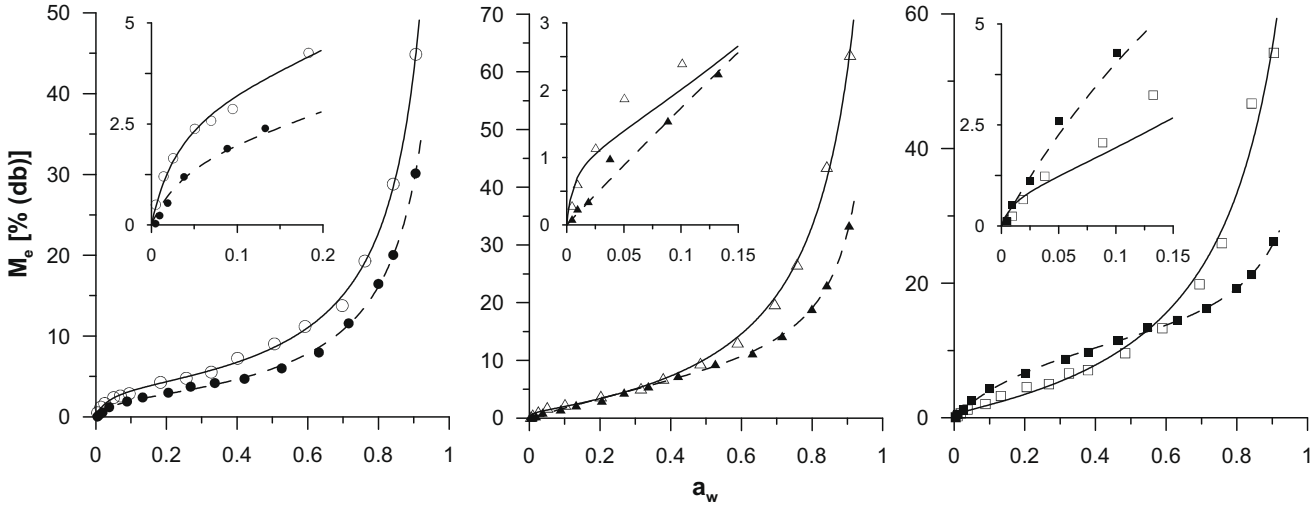

Fig. 9. The results of the fitting of experimental data using the GDW model (Eq. (27)). Symbols as in Fig. 3.

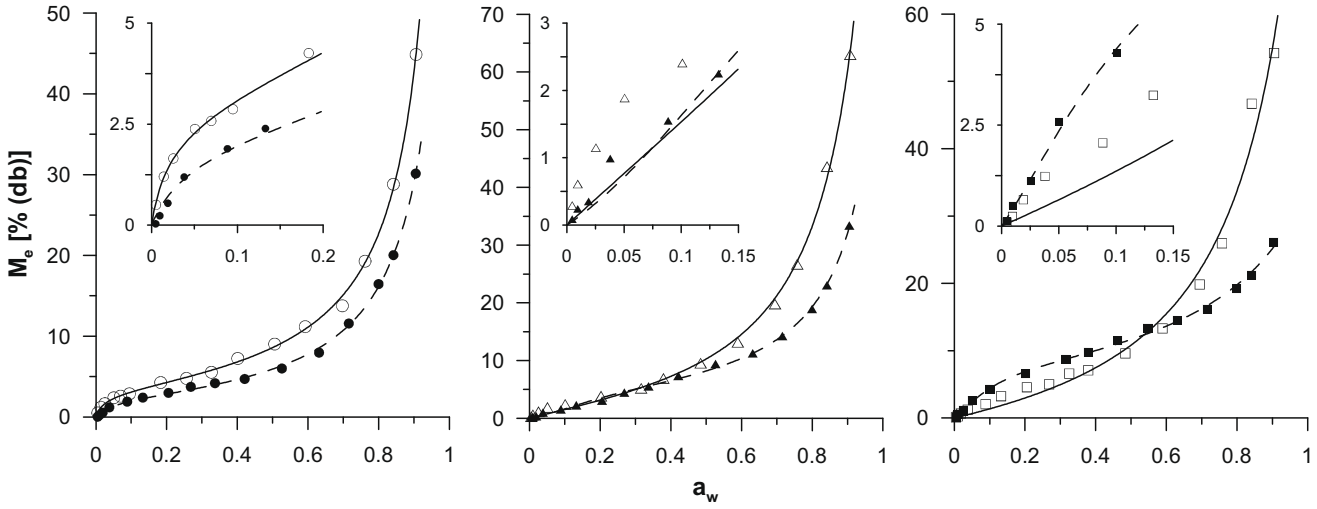

Fig. 10. The results of the fitting of experimental data using the CMMS model (Eqs. (31) and (32)). Symbols as in Fig. 3.

5.7. GDW model

This model provides the largest value of the average *DC* (0.9968). The best fit is recorded for milk powder, the worse for garlic. From Fig. 9 one can observe that a good fit is recorded in the whole studied range of a_w. For two studied systems (semolina and milk powder) the value of w is considerably smaller than unity, therefore only small amount of water molecules sorbed on primary sites converts into the secondary centers. For marjoram and coffee w is in the range between 1 and 2 therefore one water molecule bounded to primary sorption site creates more than one secondary site. In the case dill and garlic w is larger than 10 and this can be explained by the location of primarily sites. As we mentioned before (Furmaniak, Terzyk, & Gauden, 2007; Furmaniak, Terzyk, Czepirski et al., 2007), for such a case there are no geometrical restrictions for growing up of water clusters on surface.

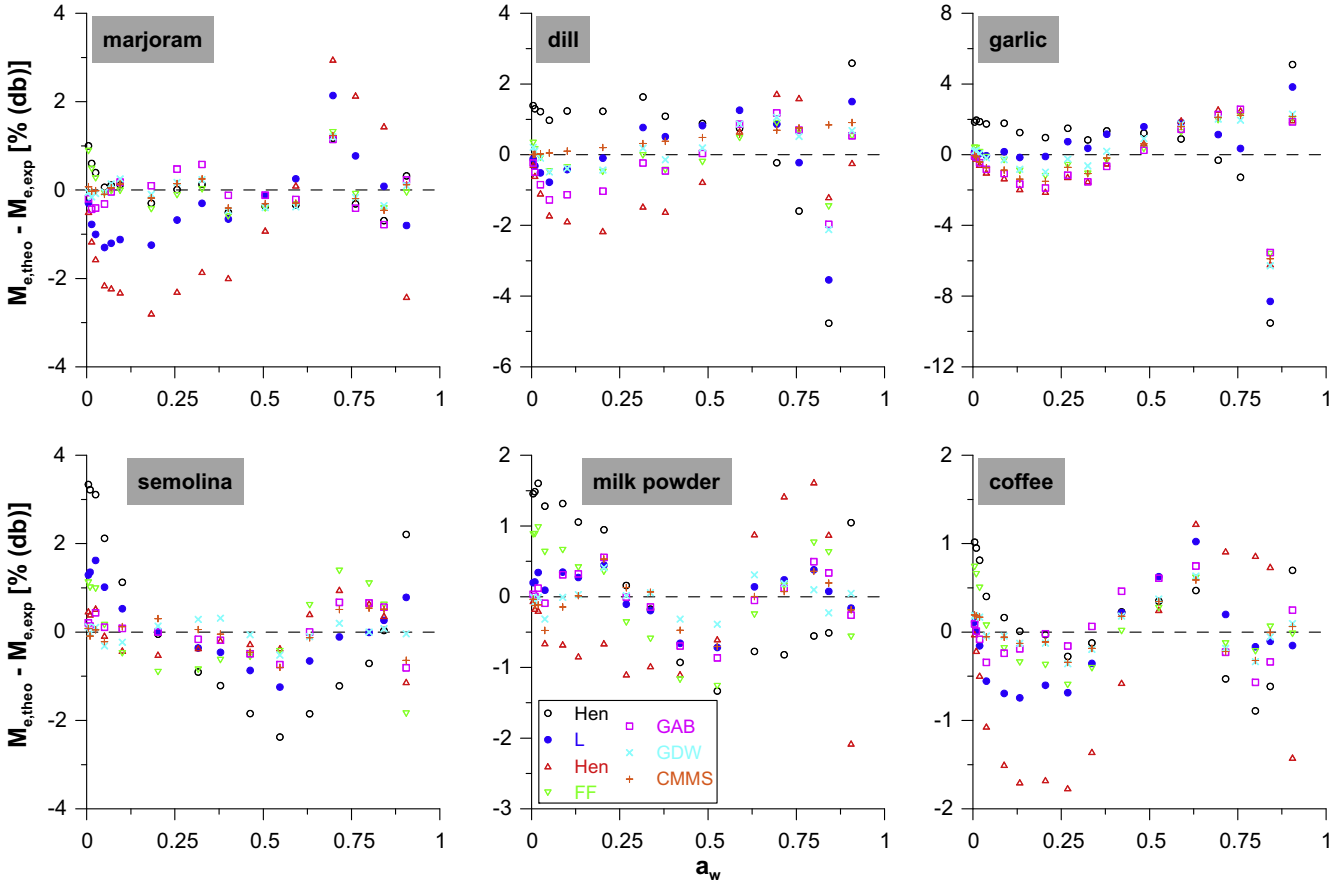

Fig. 11. The difference between equilibrium moisture sorption values predicted by the studied models ($M_{e,theo}$) and measured experimentally ($M_{e,exp}$) for particular experimental points and products (abbreviations: Hal – Halsey model, Hen – Henderson model, L – Lewicki model, FF – Ferro Fontan et al. model).

5.8. CMMS model

The average *DC* value equal 0.9963. The best fit is observed for coffee and the worse for garlic. Similarly to the GAB model, for dill and garlic the CMMS leads to poor fit in the low range of a_w (Fig. 10). For those systems, similarly as in the case of the GAB model, one can observe too large values of the monolayer capacities.

5.9. Summary

In Fig. 11 we present the comparison of the deviation of theoretical points from the experimental ones for all studied products and models. Those results confirm the observations given above.

Summing up one can see that for two studied systems (i.e. dill and garlic) the Ferro Fontan et al. model leads to the largest *DC* values (here those values for CMMS, GDW and GAB are only slightly smaller). In the case of other systems the best working model is the GDW (in the case of coffee and marjoram the CMMS has almost the same *DC*'s), GAB works slightly worse than the GDW (since the latter is more general and can be simplified to the GAB) but better than the Ferro Fontan et al. model.

Fig. 12 shows that there exists the relation between the average *DC* value and the number of the best fit parameters. Four-parameter models (CMMS, GDW) work the best. Three parameter GAB model works slightly worse than four-parameter models, and better than (also three parameter) Ferro Fontan et al. approach. For two parameter models the worse fit is observed and here Lewicki approach works better than Henderson and Halsey, and here the average *DC* for Halsey model is reduced by poor fit for semolina.

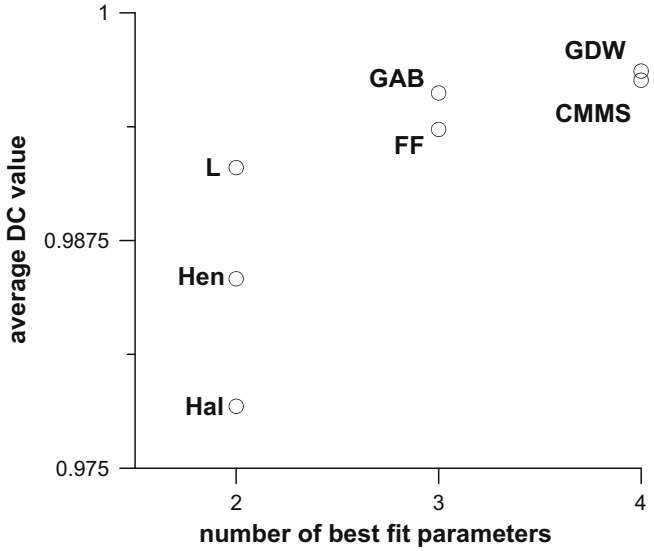

Fig. 12. The comparison of the average determination coefficients (*DC*) and the number of the best fit parameters for studied models (abbreviations as in Fig. 11).

It is well known from adsorption science that each correct isotherm model should be reduced to the so called Henry's law limit (for small a_w values) and this is manifested by the linear range of the isotherm (Rudziński & Everett, 1992). Mathematical analysis leads to the conclusion that this is possible if the derivative of the moisture content with respect to the water activity in the limit of a_w approaching to zero has non-zero finite value. In Table 5 we collected the equations describing this derivative and the value of the limit for all studied models (with exception of the Chung and Pfost model where the generated isotherm does not reach the 0, 0 point). Only three models, namely GAB, GDW and CMMS models show the correct behavior, i.e. show the correct Henry's limit. This explains the poor fit of remaining models during the fitting of low a_w limit data.

It is worth to pay attention to relatively high values of the parameter m (maximum sorption on primary centers) obtained for some products (especially for those having isotherms of the III type) from description of experimental data by GAB, GDW and/or CMMS models. Those values seem to be overestimated (as we mentioned in the paragraph 5.6) in comparison to expected from the shapes of isotherms however, they should be interpreted in the context of considered models. Those high values of monolayer capacities are connected to low values of kinetic parameters describing sorption on primary centers and this can be interpreted as the consequence of low energy of interaction of water molecules with those centers. As the consequence the theoretical plots of isotherms on primary centers are practically linear and sometimes possessing small deviations downward (at higher values of water activity) and the primarily centers are not fully saturated.

6. Conclusions

Excepting the GAB model all the most popular models applied in food science describe the data worse than more sophisticated models considered in this study. Moreover, the analysis of the properties of the most popular models applied in food science (excepting GAB) during description of experimental data, and the mathematical analysis of the properties of those models in the range of small values of a_w show the incorrect behavior.

Among studied models the GDW model seems to be the best for description of data in the whole range of a_w. This model has four best fit parameters however, the development of the current methods of optimization makes this problem easy to solve. CMMS and GAB models also show good fit and behavior in the whole range of a_w. In the case of GDW and GAB this is obvious, since the first

Table 5
The equations describing the derivative of M_e with respect to a_w and the values of the limits at a_w tending to zero.

Model	Eq. number	$\frac{dM_e}{da_w}$	$\lim_{h_r \to 0} \frac{dM_e}{da_w}$ [a]
Halsey	(2)	$-\frac{A_1 A_2 (-\ln a_w)^{A_2-1}}{a_w}$	$+\infty$ ($A_2 < 0$)
Lewicki	(5)	$A_1 A_2 \left(\frac{a_w}{1-a_w}\right)^{A_2-1} \frac{1}{(1-a_w)^2}$	$+\infty$ ($0 < A_2 < 1$)
Henderson	(7)	$\frac{A_1 A_2 [-\ln(1-a_w)]^{A_2-1}}{1-a_w}$	$+\infty$($0 < A_2 < 1$) or 0 ($A_2 > 1$)
Ferro Fontan et al.	(17)	$-\frac{A_1 A_2 \left(-\ln\frac{a_w}{\gamma}\right)^{A_2-1}}{a_w}$	$+\infty$ ($A_2 < 0$)
GAB	(20)	$m\left(\frac{K}{(1-Ka_w)^2} + \frac{(C-1)K}{(1+(C-1)Ka_w)^2}\right)$	$m\ C\ K$
GDW	(27)	$m\left(\frac{K}{(1+Ka_w)^2} \cdot \frac{1-k(1-w)a_w}{1-ka_w} + \frac{mKa_w}{1+Ka_w} \cdot \frac{wk}{(1-ka_w)^2}\right)$	$m\ K$
CMMS	(31) and (32)	– [b]	$m\ K_0$

[a] In brackets the values of the parameters (generating sensible shape of isotherm) leading to shown values of limits.
[b] Due to complicated mathematical form the formula is omitted.

can be easily reduced to the second (i.e. GAB is simplified form of the GDW). In the case of the CMMS model slightly worse average fit than this for the GDW is caused by the form of this formula. Among three kinetic constants present (K_0, K_1 and K_{as}) only one (namely K_{as}) is responsible for the shape of isotherm in the range of medium and high a_w values. In the case of the GDW model there are two parameters influence the shape in this range (k and w). In other words, in the case of CMMS model each molecule bounded to primary site converts into one secondary site. But in the case of GDW model this situation is different; due to the parameter w showing what part of molecules bounded to primarily centers becomes the secondary sites. Of course it is possible that $w = 1$ however, the results of the current study as well as the results published previously show that this situation is rarely met during water sorption on foodstuffs.

Summing up, we can postulate that the GDW model, due to its strong thermodynamic and kinetic basis, gives the most realistic description of all three ranges of water sorption mechanism considered in Fig. 1. This model in comparison with the GAB one (having strong position in the food science and which can be developed by the simplification of the GDW) offers new insights into the mechanism of water sorption on foodstuffs. This is caused by the modification of the basic assumption of the GAB model namely that each water molecule attracted to primary center is converted into the secondary one. The GDW model by the introduction of the parameter w offers the possibility of taking into account the situations where water molecules sorbed on primary centers do not convert completely into the secondary centers ($w < 1$), convert completely (the situation adequate to the GAB model) ($w = 1$), as well as the situation following the scenario of creation of more than one secondary centers from the primary ones ($w > 1$). As it was shown in the current study as well as in our previous studies (Furmaniak, Terzyk, Gauden, & Rychlicki, 2007; Furmaniak, Terzyk, & Gauden, 2007; Furmaniak, Terzyk, Czepirski et al., 2007) all three cases can be observed during water sorption on foodstuffs. Excepting the case where $w = 1$ the GDW model leads to the better description of experimental data comparing to the GAB model. Following this, in our opinion, the application of the GDW model to description of water sorption on foodstuffs makes it possible not only better description of experimental data but also makes deeper insight into the mechanism of water sorption on those products.

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