

Modeling of Sorption of Water on Potato and on Potato Starch

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ABSTRACT

It is well known that sorption isotherms of water vapour on foodstuffs are very important for design, modelling and optimization of important processes for example drying, aeration, predicting of stability and quality during packaging and storage of food. In this study we present water sorption data on potato and on potato starch measured for a few temperatures. Our results are described using the most applicable and advanced models of water sorption applied in the field of food engineering. The procedure of simultaneous description of multitemperature data provides the insights into the mechanism and energetics of water sorption on studied products.

Keywords: enthalpy of sorption, isotherms, sorption mechanism, sorption model

INTRODUCTION

Water plays an essential role in almost every aspect of food science, including the processing response of raw materials, food stability, organoleptic properties and microbial safety (Bell and Labuza 2000; Lewicki 2000; Stencl 2004; Basu *et al.* 2006; Furmaniak *et al.* 2007c). The most fundamental manner of demonstrating the relationship between water vapor and a solid is the water sorption isotherm, which describes the relationship between the equilibrium moisture content and the water activity at constant temperature.

The thermodynamic properties of foodstuffs relate the concentration of water in the food to its partial pressure, which is also crucial in analysis of the heat and mass transport phenomena. The thermodynamic functions are readily calculated from sorption isotherms, which enable interpretation of experimental results in accordance with the statement of the theory (see for example: Ferro Fontan *et al.* 1982; Chen 2006; Furmaniak *et al.* 2007a, 2007b, 2007c).

For food materials information about the sorption mechanism and the interaction of food biopolymers with water are extremely important in modelling the drying process, in design and optimisation of drying equipment, in predicting shelf-life stability, in calculating moisture changes, which may occur during storage, and in selecting appropriate packaging material. Therefore, searching the most valuable models describing water sorption on foodstuffs including potato is still in demand, and this is the subject of the present study.

APPLIED THEORETICAL MODELS

In the current study we limit our considerations only to those models having a strong thermodynamic and kinetic basis, since this makes the application of the procedure of fitting of multitemperature sorption data possible (Furmaniak *et al.* 2007a, 2007b, 2007c). This procedure also enables insight into the energetics of the sorption process, and more importantly, into the mechanism of water sorption on foodstuffs.

The first studied model, proposed by Guggenheim (1995), Anderson (1946) and de Boer (1995) (called **GAB**), has a strong position in the field of food science engineering (Lewicki 1997; Timmermann *et al.* 2001; Basu *et al.*

2006). It is usually presented in the form (Furmaniak *et al.* 2007b, 2007c):

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

where M_e [mmol g⁻¹] is the equilibrium moisture content, m [mmol g⁻¹] 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, and h_r is the relative humidity.

The next studied model is called the Generalised D'Arcy and Watt (GDW), developed for description of water sorption on activated carbons (Furmaniak *et al.* 2005, 2008), and next successfully applied to description of water sorption on different foodstuffs (Furmaniak *et al.* 2007a, 2007b, 2007c). It can be written as (Furmaniak *et al.* 2007a, 2007b, 2007c):

$$M_e = \frac{mKh_r}{1 + Kh_r} \cdot \frac{1 - k(1 - w)h_r}{1 - kh_r} \quad (2)$$

where m [mmol g⁻¹] is the maximum sorption value on the primary sorption centres. 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.

The next studied model was proposed (to describe the adsorption of alcohols on polymers) by Malakhov and Volkov (2000) and was widely propagated by Rutherford *et al.* (2003, 2004, 2006) (to describe water sorption on different adsorbents) and by others (Furmaniak *et al.* 2006, 2008). This equation of cooperative multimolecular sorption (or CMMS) assumes that the sorption process follows the scenario of cooperative filling of channels (interrelated nanovoids) of the sorbent, and that this process is combined with the growth of associates of sorbed molecules within the sorbent bulk. This model was applied with success in the field of food science (Furmaniak *et al.* 2007c), and its final form is:

$$M_e = \frac{mK_0h_r}{(1 - K_{as}h_r)(K_0h_r + \omega^2(1 - K_{as}h_r))} \quad (3)$$

where:

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

and m [mmol g⁻¹] 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.

To perform a simultaneous description of multitemperature sorption data it is necessary to apply the relations taking into account the temperature dependence of parameters of the studied models. Therefore, we assumed (as previously) that m and w are temperature independent ($m, w \neq f(T)$) (Furmaniak *et al.* 2007a, 2007b, 2007c). In contrast, the remaining kinetic/equilibrium constants (C and K (GAB model); K and k (GDW model); K_0 , K_I and K_{as} (CMMS model)) depend on temperature according to the general relation (Furmaniak *et al.* 2007a, 2007b, 2007c):

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

where X is the considered constant, X_0 is the almost temperature independent entropic term, q_X [kJ mol⁻¹] is the enthalpy related to this parameter, T [K] is the temperature, and R is the gas constant. For the constants occurring in Eqs. (1) - (4) the following notation is applied in Eq. (5) for the GAB model:

$$C = C_0 \exp\left(\frac{q_C}{RT}\right) \quad (6)$$

$$K = K_0 \exp\left(\frac{q_K}{RT}\right) \quad (7)$$

for the GDW:

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

$$k = k_0 \exp\left(\frac{q}{RT}\right) \quad (9)$$

and for the CMMS:

$$K_0 = K_0^0 \exp\left(\frac{q_0}{RT}\right) \quad (10)$$

$$K_I = K_I^0 \exp\left(\frac{q_I}{RT}\right) \quad (11)$$

$$K_{as} = K_{as}^0 \exp\left(\frac{q_{as}}{RT}\right) \quad (12)$$

ISOSTERIC ENTHALPY OF SORPTION

For the models having strong thermodynamic basis the application of Clausius–Clapeyron relation (Furmaniak *et al.* 2005, 2008) makes it possible to derive the equation describing the isosteric sorption enthalpy (q^{st}):

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

where L [kJ mol⁻¹] is the enthalpy of water condensation.

For all considered equations the related enthalpy of sorption relations were developed previously, and they have the following forms:

for the GAB model (Furmaniak *et al.* 2007b, 2007c):

$$q^{st} - L = \frac{(1 - Kh_r)^2 q_C + q_K + (C - 1) K^2 h_r^2 q_K}{1 + (C - 1) K^2 h_r^2} \quad (14)$$

for the GDW model (Furmaniak *et al.* 2005, 2007a, 2007b, 2007c, 2008):

$$q^{st} - L = \frac{\frac{K}{(1 + Kh_r)^2} \cdot \left(1 + \frac{wkh_r}{1 - kh_r} \right) \cdot Q + \frac{Kh_r}{1 + Kh_r} \cdot \frac{wk}{(1 - kh_r)^2} \cdot q}{\frac{K}{(1 + Kh_r)^2} \cdot \left(1 + \frac{wkh_r}{1 - kh_r} \right) + \frac{Kh_r}{1 + Kh_r} \cdot \frac{wk}{(1 - kh_r)^2}} \quad (15)$$

and for the CMMS model (Furmaniak *et al.* 2006, 2007c, 2008):

$$\text{See Appendix} \quad (16)$$

where:

$$B_I = -\frac{I}{(I - K_{as} h_r)^2} \left(K_I + \frac{K_I \left(I - \frac{K_I h_r}{I - K_{as} h_r} \right) - 2K_0}{\sqrt{\left(I - \frac{K_I h_r}{I - K_{as} h_r} \right)^2 + \frac{4K_0 h_r}{I - K_{as} h_r}}} \right) \quad (17)$$

$$\text{See Appendix} \quad (18)$$

MATERIALS AND METHODS

The samples of granular potato starch isolated in Nowamyl (Łobez, Poland) according to Polish Standard PN-A-74710 were used either in the air-dried state (as ambient native starch – 13% (w/w) moisture content) or after freezing/thawing in liquid nitrogen according to the procedure described by Szymońska and coworkers (Szymońska *et al.* 2000, 2003). Moreover, dehydrated potato products, obtained from raw potato, such as dried potato cubics and dried potato granules were investigated. The products were supplied by the vegetable and fruit drying plant in Kamionka (Piasieczno, Poland). Water vapour sorption isotherms were measured using a volumetric type apparatus with adsorption microburettes described previously (Ciembroniewicz *et al.* 1986) at 298.15, 308.15 and 318.15 K. Its operating parameters enable to work up to an equilibrium pressure of *ca.* 4000 Pa, which corresponds to a whole range of relative humidity (h_r) at 298.15 K, $h_r < 0.7$ at 308.15 K and $h_r < 0.4$ at 318.15 K. Before the experiment samples were outgassed at 343 K to residual pressure of about $1.3 \cdot 10^{-2}$ Pa. The data are new and have not been published yet. As one can see in **Figs. 1-4** obtained adsorption isotherms for both samples of potato starch (native and frozen) belong to type II of the BET isotherms. On the other hand, in the case of the dried potato granules and cubics we observe the isotherm of type III.

DESCRIPTION OF EXPERIMENTAL DATA

Theoretical models were fitted to experimental data by applying the minimization procedure using the differential evolution (DE) algorithm proposed by Storn and Price (1996, 1997). This procedure was successfully applied for description of multitemperature water sorption data in the field of food engineering science (Furmaniak *et al.* 2007a, 2007b, 2007c). The details can be found elsewhere (Furmaniak *et al.* 2007c).

In particular the measure of the fit of theoretical models to experimental data can be measured by the value of the determination coefficient:

$$DC_T = 1 - \eta_T \quad (19)$$

where:

$$\eta_T = \frac{\sum_i (M_{e,i}^o - M_{e,i}^t)^2}{\sum_i (M_{e,i}^o - \bar{M}_e^o)^2} \quad (20)$$

and $M_{e,i}^o$ is the observed moisture content for the 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.

The global parameter describing the goodness of the fit of theory to the set of experimental data determined for different temperatures is defined by:

$$DC = 1 - \sqrt{\frac{\sum \eta_T^2}{N}} \quad (21)$$

where: DC_T is the value of the determination coefficient calculated for individual temperatures, and N is the number of considered temperatures.

RESULTS AND DISCUSSION

The values of the best-fit parameters obtained from description of the experimental data by all studied models are collected in **Tables 1-3**, and the graphical representation of the fits is shown in **Figs. 1-4**. To show the differences between obtained isotherms they are not plotted as the function of relative humidity (as usually), but as functions of the equilibrium water pressure (p) (relative humidity values can be easily obtained by dividing the values of p by the values of saturated vapour pressure (p_s) i.e. $T = 298.15$ K, $p_s = 3167.2$ Pa; $T = 308.15$ K, $p_s = 5622.9$ Pa and $T = 318.15$ K, $p_s = 9583.2$ Pa).

One can observe that all studied models describe the experimental data well. However, the best fit is recorded for the GDW equation (average $DC = 0.9980$), and slightly worse for CMMS (average $DC = 0.9963$) and GAB models (average $DC = 0.9940$). Similar situation was observed in our previous study where the models were applied to description of water sorption on different foodstuffs (Furmaniak *et al.* 2007c). The predominance of GDW and CMMS models in comparison to GAB is not surprising, since the last has one best fit parameter less. Moreover, as it was previously proved (Furmaniak *et al.* 2007b), the GAB model can be considered as a simplification of GDW, therefore the GDW equation is more general. The differences between GDW and CMMS (as we pointed out previously, Furmaniak *et al.* 2007c) can be explained by the form of the GDW equation, having two parameters (k and w) responsible for the shape of isotherm in the range of medium and large

levels of relative humidity, while the CMMS has only one such a parameter (namely K_{as}).

The detailed analysis of the values of the parameter w of the GDW model (**Table 2**) makes it possible to discuss some differences in the mechanisms of water sorption on studied samples. In the case of the samples of potato starch the value of this parameter (9.100 and 28.47, respectively) shows that the molecules bonded to primarily sorption sites can be easily converted into the secondary sites. On the other hand, in the case of potato a different situation is observed ($w = 1.040$ for granules and 0.4347 for cubics). One can see that the conversion of sorbed water molecules into the secondary centres is hindered due to, for example, steric effects. In the case of granules one water molecule bound to the primarily sorption site is converted into c.a. one sorption centre. Therefore here the sorption mechanism follows the GAB scenario (Furmaniak *et al.* 2007b) explaining the similarity between the values of the DC for the GDW and GAB models (**Tables 1, 2**). In the case of cubics only c.a. half of water molecules sorbed on primarily centres were converted into secondary sites. It is interesting that a similar situation was observed previously (Furmaniak *et al.* 2007c) during the application of the GDW model for description of water sorption data on potato published by Kaymak-Ertekin and Gedik (2004). In that case one water molecule sorbed on the primary site was converted only into c.a. 2 secondary sites.

The values of the enthalpy related to the respective parameters of the studied models (and collected in **Tables 1-3**) show that in the case of dried potato granules and cubics they are almost equal or close to zero. This is caused by almost the same plots of the sorption isotherms determined for different temperatures (after plotting in the function of the relative humidity). Therefore, plotting the enthalpy of water sorption for those sorbents is not possible. A different situation is observed for native and frozen potato starch, where the values of the sorption enthalpy related to the parameters showing influence at low values of relative humidity (i.e. during the creation of a monolayer) are markedly different than zero (they even reach as large values as c.a. 20 kJ mol⁻¹). Similar enthalpy values were obtained by Kaymak-Ertekin and Gedik (2004). Therefore for those systems it is possible to draw up the plots of the isosteric sorption enthalpy basing on Eqs. (14)-(18). They are collected in **Fig. 5**, showing – with the exception of the CMMS model applied to description of the data for frozen potato starch –

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

Sample	m [mmol g ⁻¹]	C_0	K_0	q_c	q_k	DC_T^*	DC
				[kJ mol ⁻¹]			
potato starch native	6.648	4.347 10 ⁻²	0.6333	13.94	~ 0	0.9972; 0.9943; 0.9967	0.9959
potato starch frozen	6.210	6.761 10 ⁻²	0.6995	12.99	~ 0	0.9894; 0.9827; 0.9831	0.9848
dried potato granules	8.993	1.926	0.5163	~ 0	~ 0	0.9969; 0.9981; 0.9962	0.9969
dried potato cubics	7.086	0.7527	0.5931	2.628	~ 0	0.9984; 0.9995; 0.9977	0.9984

* Values arranged according to the rise in temperature.

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

Sample	m [mmol g ⁻¹]	K_0	k_0	Q	q	w	DC_T^*	DC
				[kJ mol ⁻¹]				
potato starch native	3.697	7.049 10 ⁻³	0.2423	19.93	0.3523	9.100	0.9983; 0.9983; 0.9985	0.9984
potato starch frozen	2.155	8.883 10 ⁻²	0.1015	16.63	1.678	28.47	0.9984; 0.9978; 0.9986	0.9982
dried potato granules	17.23	0.5207	0.5201	~ 0	~ 0	1.040	0.9970; 0.9981; 0.9961	0.9969
dried potato cubics	35.71	0.1276	0.6722	1.648	~ 0	0.4347	0.9983; 0.9996; 0.9977	0.9984

* Values arranged according to the rise in temperature.

Table 3 The values of the best-fit parameters obtained from the fitting of experimental data by the CMMS model (Eqs. (3) and (4)).

Sample	m [mmol g ⁻¹]	K_0^o	K_1^o	K_{as}^o	q_0	q_1	q_{as}	DC_T^*	DC
					[kJ mol ⁻¹]				
potato starch native	9.252	5.041 10 ⁻³	3.833 10 ⁻²	0.5463	17.98	11.19	~ 0	0.9983; 0.9969; 0.9983	0.9977
potato starch frozen	8.428	1.100	4.370 10 ⁻²	0.6112	4.680	11.39	~ 0	0.9943; 0.9892; 0.9923	0.9917
dried potato granules	29.04	0.3084	~ 0	0.4717	~ 0	-	~ 0	0.9967; 0.9981; 0.9961	0.9969
dried potato cubics	5.766	5.704 10 ⁻³	1.656	0.5673	14.47	~ 0	0.3693	0.9995; 0.9994; 0.9985	0.9990

* Values arranged according to the rise in temperature.

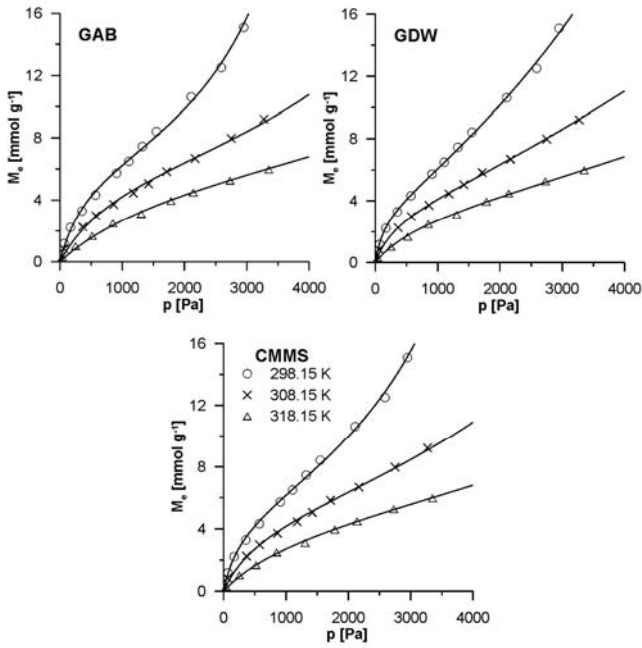


Fig. 1 Results of fitting the sorption data on potato starch native. Points: experimental data; lines: fitting.

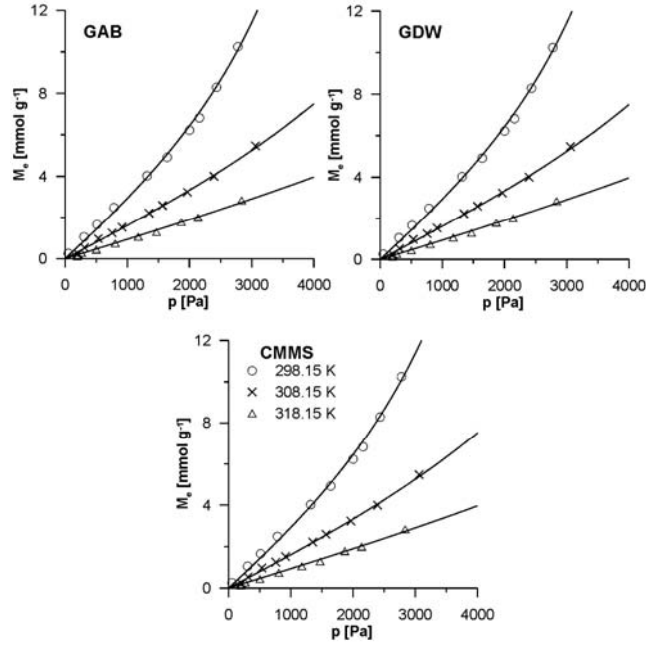


Fig. 3 Results of fitting the sorption data on potato granules. Points: experimental data; lines: fitting.

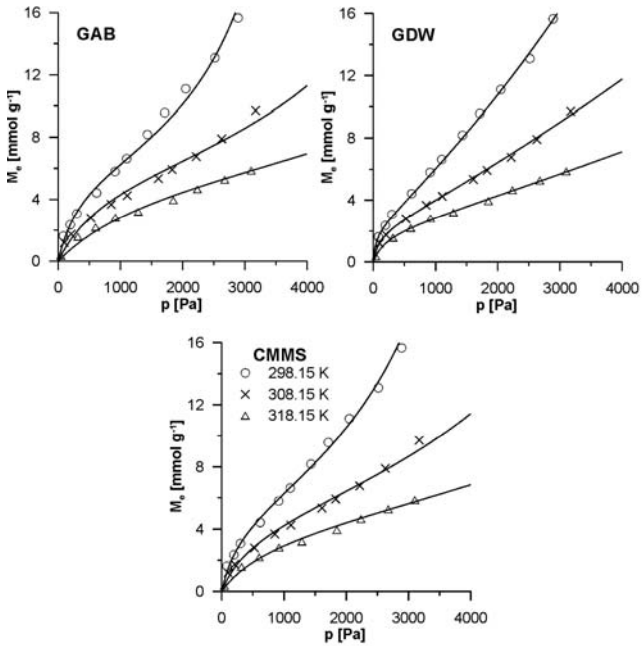


Fig. 2 Results of fitting the sorption data on potato starch frozen. Points: experimental data; lines: fitting.

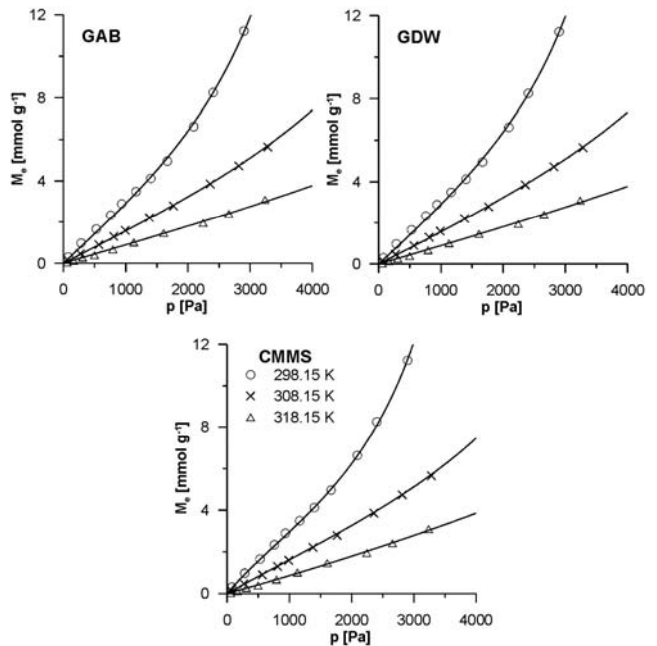


Fig. 4 Results of fitting the sorption data on potato cubics. Points: experimental data; lines: fitting.

qualitatively similar plots, i.e. they start at relatively large values of enthalpy (for small equilibrium moisture content values), and next they decrease finally reaching the value of enthalpy of water condensation at large M_e limits (i.e. in the range of polymolecular sorption and capillary condensation). The different shape of the plot for the data measured on potato starch frozen and described by the CMMS model can be explained by small number of experimental points in the range of low h_r values.

CONCLUDING REMARKS

Presented procedure of fitting of multitemperature water sorption data on potato and potato starch is successfully applied to description of experimental data. Moreover, using this procedure the isosteric enthalpy of water sorption can be easily calculated, if the recorded at different temperatures isotherms show different plots. The plot of the en-

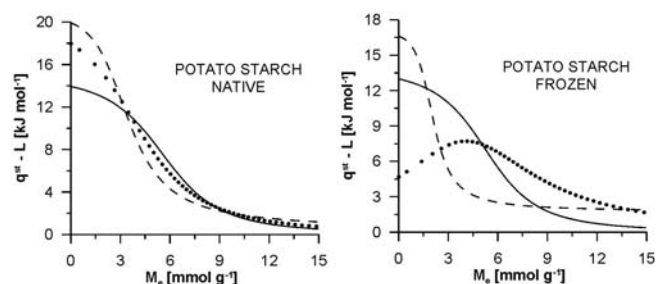


Fig. 5 Plots of the isosteric enthalpy of water sorption for potato starch native and frozen ($T = 298.15\text{ K}$). Solid line, GAB model (Eq. (14)); dashed line, GDW model (Eq. (15)); points, CMMS (Eqs (16)-(18)).

thalpy shows that there are three major stages of the mechanism of water sorption on studied materials. At low relative

humidity levels there is a strong bonding of water molecules to primarily centres, next the multilayer sorption on those primarily sites occurs, and finally we observe the condensation of water molecules.

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Appendix (Due to column size restrictions, the following two equations are represented below)

$$q^{st} - L = \frac{q_0 m K_0 + q_{as} M_e K_{as} (K_0 h_r + \omega^2 (1 - K_{as} h_r)) + M_e (1 - K_{as} h_r) (-q_0 K_0 + \omega B_2 (1 - K_{as} h_r) + q_{as} \omega^2 K_{as})}{m K_0 + M_e K_{as} (K_0 h_r + \omega^2 (1 - K_{as} h_r)) + M_e (1 - K_{as} h_r) (-K_0 - \omega B_1 (1 - K_{as} h_r) + \omega^2 K_{as})} \quad (16)$$

$$B_2 = \frac{1}{(1 - K_{as} h_r)^2} \left(K_1 (q_1 + (q_{as} - q_1) K_{as} h_r) + \frac{K_1 \left(1 - \frac{K_1 h_r}{1 - K_{as} h_r} \right) (q_1 + (q_{as} - q_1) K_{as} h_r) - 2 K_0 (q_0 + (q_{as} - q_0) K_{as} h_r)}{\sqrt{\left(1 - \frac{K_1 h_r}{1 - K_{as} h_r} \right)^2 + \frac{4 K_0 h_r}{1 - K_{as} h_r}}} \right) \quad (18)$$