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Sorption isotherms, GAB parameters and isosteric heat of sorption

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Abstract: The diffusion–sorption drying model has been developed as a physics-based way to model the decreasing drying rate at low moisture contents. This new model is founded on the existence of different classes of water: free and bound water. The transition between these classes and the corresponding thermodynamics form distinct components of the drying model. This paper shows that the characteristics of the different classes of water and of the transition between them can be deduced from the GAB sorption isotherm. The parameters in the GAB sorption isotherm support the theory of localised sorption, establishing the existence of different classes of water. Moreover, the sorption mechanism retrieved from the GAB parameters is in accordance with the sorption mechanism, which is obtained from the moisture dependence of the net isosteric heat of sorption. This holds for experimental sorption data of corn and starch as well as for literature data on five vegetables and four fortified cassava products. An extremum in the net isosteric heat of sorption coincides with the transition between bound and free water, and the partition moisture content corresponds with the monolayer value derived from the GAB equation. This confirms that the GAB monolayer value can be chosen as model boundary between bound and free water. Moreover, it reveals that this method can be developed into a technique to estimate the bound water content in foods.

Keywords: sorption isotherm; isosteric heat; physical background; bound and free water; diffusion–sorption drying model; GAB parameters

NOMENCLATURE

a_w	Water activity of material	[—]
C_g	Guggenheim constant in GAB sorption equation	[—]
C_{g0}	Arrhenius type constant to express temperature dependence of C_g	[—]
dm	Dry matter	[kg]
H_1	Molar enthalpy of sorption of molecules sorbed in the first layer	$[\mathrm{J\,mol^{-1}}]$
H_ℓ	Molar enthalpy for condensation of bulk liquid	$[\mathrm{J\,mol^{-1}}]$
H_m	Molar enthalpy of sorption of molecules sorbed in the multilayer	$[\mathrm{J\,mol^{-1}}]$
K	Constant in GAB sorption equation, factor correcting properties of the multilayer molecules relative to the bulk liquid	[—]
K_0	Arrhenius type constant to express temperature dependence of K	[—]
Q_{st}	Total heat of sorption	$[\mathrm{J\,mol^{-1}}]$
q_1	Partition function of molecule in monolayer	[—]
q_ℓ	Partition function of molecule in bulk liquid	[—]
q_m	Partition function of molecule in multilayer	[—]
$\Re$	Gas constant	$[\mathrm{J\,mol^{-1}\,K^{-1}}]$
T	Temperature	[K]
X	Moisture content	$[\mathrm{kg\,kg^{-1}}_{\mathrm{dm}}]$
X_m	Number of molecules in monolayer or monolayer moisture content	$[\mathrm{kg\,kg^{-1}}_{\mathrm{dm}}]$
X_{m0}	Constant to express temperature dependence of X_m	$[\mathrm{kg\,kg^{-1}}_{\mathrm{dm}}]$
ΔH_{Cg}	Difference in enthalpy between monolayer and multilayer $= H_1 - H_m$	$[\mathrm{J\,mol^{-1}}]$
ΔH_{is}	Isosteric enthalpy of sorption	$[\mathrm{J\,mol^{-1}}]$

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ΔH_K	Difference in enthalpy between bulk liquid and multilayer $= H_\ell - H_m$	[J mol^{-1}]
ΔH_v	Evaporation enthalpy of water	[J mol^{-1}]
ΔH_X	Constant to express temperature dependence of X_m	[J mol^{-1}]

INTRODUCTION

Biological materials have a decreasing drying rate at low moisture contents. In most drying models this behaviour is captured by making the diffusion coefficient dependent on moisture content. During drying, the effective diffusion coefficient is constant with moisture down to a critical moisture content. Below this critical value, the diffusion coefficient shows a sharp decrease with decreasing water concentration.[1–3] It can be assumed that the observed decrease of the drying rate is mainly caused by the decreasing availability of free water molecules.[1,4] This assumption is based on the existence of two classes of water: the bound and free water. The bound moisture corresponds to water molecules connected strongly to the material molecules. The free moisture corresponds to the water molecules connected loosely to the material molecules.[1,4] The portion of free moisture content is initially very large. As drying reaches its last stages, the bound moisture molecules form the majority of the water molecules, and then the conversion between the bound and free water controls the overall mass transfer phenomenon.[1,4] This forms the basis of the newly developed diffusion–sorption drying model, which is presented by Quirijns *et al.*[5] In this model, the moisture transfer during the drying process is described by three basic transfer phenomena: free water diffusion, conversion between bound and free water inside the material, and external convection at the boundary of the material. The model for the conversion between bound and free water makes the diffusion–sorption model original. The conversion is physically described as a sorption process. The interaction between water and the material is then modelled through the adsorption of free water to become bound water and, in reverse, the desorption of bound water to become free water. The thermodynamic variables for sorption required in the model are derived from the sorption isotherm.

The sorption isotherm relates the water activity to the water content of the mixture of water and material at a certain temperature and pressure. The water activity is defined as the ratio of the partial vapour pressure in equilibrium with the water in the food material and the vapour pressure in equilibrium with pure water at the same temperature.[3] Therefore, it characterises the state of the water in foods. This means that the sorption isotherm gives an impression how strong and in which way water is bound by the material constituents.[3,6,7] The diffusion–sorption drying model uses this information for three purposes. First, it describes the existence of two different classes of moisture in the material: bound and free moisture. Second, it determines the boundary between bound and free water. Since the distinction between the different classes is not sharp,[3] the term boundary is mainly an operational term, required for the model.[5] Third, the thermodynamics corresponding to this boundary are derived from the sorption isotherm. Both the boundary and the corresponding thermodynamics are used to model the conversion between bound and free water.[8]

In this paper, we investigate whether this physicochemical background is supported by experimental sorption isotherms at different temperatures. To this end, the experimental sorption isotherms need to:

(a) give an accurate prediction of sorption at low moisture contents, since the conversion between bound and free water takes place at low moisture contents;
(b) describe the localised sorption behaviour, in order to derive the characteristics of the different classes of water and the transition between them.

More specifically, it is the goal of the present paper to investigate whether the characteristics of the different classes of water and of the transition between them can be deduced from the experimental GAB (Guggenheim, Anderson and de Boer) sorption isotherm. This endeavour is successful when:

1. the theoretical sorption behaviour is supported by the experimentally derived sorption behaviour from the GAB parameters and from the net isosteric heat of sorption;
2. from the experimental isosteric heat of sorption a model of the boundary between bound and free water is obtained and subsequently is related to the GAB parameters.

THEORY

Theoretical background of the GAB sorption isotherm

The GAB sorption isotherm represents a refined extension of the Langmuir and BET theories. The theoretical basis for the GAB sorption isotherm is the assumption of localised physical adsorption in multilayers with no lateral interactions. The first shell of water evenly covers the sorbent surface and is very tightly bound in a monolayer. Subsequent layers of water have less interaction with the sorbent surface. The molecules in this so called multilayer (layers 2–9) have interactions with the sorbent which range in energy levels somewhere between those of the monolayer molecules and the bulk liquid. Succeeding layers of water molecules exhibit more and more bulk liquid properties.[3,6,9–12]

The GAB model thus discriminates between multilayer and condensate properties of molecules sorbed on top of the first molecule at a site. For the derivation of the GAB equation three assumptions are made: the sorption system consists of identical active sites (distinguishable and independent), it is isothermal and it is open to the sorbing vapour. Statistical thermodynamics then lead to the GAB sorption isotherm, expressing $X = \mathrm{f}(a_w)$:[3,9]

$$\frac{X}{X_m} = \frac{C_g \cdot K \cdot a_w}{(1 - K \cdot a_w) \cdot (1 - K \cdot a_w + C_g \cdot K \cdot a_w)} \quad (1)$$

where the three GAB parameters, C_g, K and X_m have a physical meaning:

C_g is defined as the ratio of the partition function of the first molecule sorbed on a site (q_1) and the partition function of molecules sorbed beyond the first molecule in the multilayer (q_m).[3] C_g is almost enthalpic in nature.[3] It is a measure of the strength of binding of water to the primary binding sites. The larger C_g, the stronger water is bound in the monolayer and the larger the difference in enthalpy between the monolayer molecules and multilayer molecules. Since the water molecules are still localised in the multilayer, the entropic contributions to C_g are less in comparison with the enthalpic.[3]

K is defined as the ratio of the partition function of molecules in bulk liquid (q_ℓ) and the partition function of molecules sorbed in the multilayer (q_m).[3] Next to an enthalpic part, K contains an important entropic part. The enthalpic contribution to K is less compared with C_g, due to the considerably lower interaction enthalpy of the multilayer molecules with the sorbent. The higher entropic content of K can be explained by the strongly increased number of configurations and mobility of molecules in the bulk liquid compared with the molecules in the multilayer.[3,13] K is called a correction factor, since it corrects the properties of the multilayer molecules relative to the bulk liquid.[14–16] When K approaches one, there is almost no distinction between multilayer molecules and liquid molecules. In that case the water molecules beyond the monolayer are not structured in a multilayer, but have the same characteristics as the molecules in the bulk liquid. The GAB equation is then reduced to the BET equation for sorption. The more the sorbed molecules are structured in a multilayer, the lower the value for K.

The theoretical interpretation of the GAB parameters makes it possible to derive the sorption behaviour of moisture in materials from the combination of the values of C_g and K, as is elucidated in Table 1.

X_m is called the monolayer value. It is a measure of the availability of active sites for water sorption by the material.[3,6,9,17]

Table 1. The combination of the magnitude of GAB parameters C_g and K and the corresponding mechanism of sorption, where mono stands for monolayer, multi for multilayer and liquid for the bulk liquid

Mono ≈ multi ≈liquid	Mono ≈ multi ≠liquid	Mono ≠ multi ≠ liquid	Mono ≠ multi ≈liquid
$C_g \approx 1$ $K \approx 1$	$C_g \approx 1$ $K << 1$	$C_g >> 1$ $K << 1$	$C_g >> 1$ $K \approx 1$

The influence of temperature on sorption isotherms

Sorption isotherms are temperature dependent. A higher temperature will decrease the binding energy between molecules. Because of an increased state of excitation of the molecules, their mutual distances increase and the attractive forces between them decrease. They become less stable and break away from the water binding site of the food materials. Consequently, an increase in temperature induces a reduction in the equilibrium moisture content at a specific water activity. This is consistent with the thermodynamics of sorption.[18–20] It is also established in other fields of food research, for example in a study to dielectric properties of foods, where the increased mobility of the water molecules as well as the reduced amount of hydrated water with increasing temperature are demonstrated.[21]

The character of the sorption process will become less strongly localised, due to the increasingly shorter residence time for the sorbed molecules in the first layer.[3]

Owing to their thermodynamic character, the temperature dependence of sorption can be incorporated in the parameters C_g and K:[3]

$$C_g = \frac{q_1}{q_m} = C_{g0} \cdot \exp\left(\frac{\Delta H_{C_g}}{\Re \cdot T}\right) \quad (2)$$

$$K = \frac{q_\ell}{q_m} = K_0 \cdot \exp\left(\frac{\Delta H_K}{\Re \cdot T}\right) \quad (3)$$

in which:

$\Delta H_{Cg} = H_1 - H_m$ = difference in enthalpy between monolayer and multilayer sorption. This value is expected to be positive, due to the exothermic interaction of water with primary sorption sites.

$\Delta H_K = H_\ell - H_m$ = difference between the heat of condensation of water and the heat of sorption of a multimolecular layer. This value will be negative and smaller, since the multilayer molecules are less firmly bound. Sometimes a positive value can be found because of the endothermic dissolution of fruit sugars, as in Maroulis *et al*[22] and Gabas *et al*.[23]

C_{g0} and K_0 are entropic in nature. They are defined as the ratio of reduced partition functions or accommodation functions between the first and multilayer, and between the bulk liquid and the multilayer, respectively.[3] C_{g0} is expected to be smaller than 1, since the molecules prefer to be in the multilayer above the monolayer from entropic point of view. Similarly, K_0 will be larger than 1, due to the high entropy of the molecules in the bulk liquid.

In the majority of cases in literature, X_m is considered to be constant with temperature. Yet independent fits elucidate that the parameter decreases with temperature.[6,22,24] The decrease in the monolayer with temperature may be due to a reduction in the total number of active sites for water binding as a result of physical or chemical changes induced by temperature.[13,14,25,26] Hence, a dependence of the X_m

on temperature has to be considered, which can be expressed in an exponential relationship:

$$X_m = X_{m0} \cdot \exp\left(\frac{\Delta H_X}{\Re \cdot T}\right) \tag{4}$$

The heat of sorption derived from sorption isotherm

Thermodynamic parameters can be derived from sorption isotherms at different temperatures.[3,12,23,27,28] An important thermodynamic parameter is the net isosteric heat of sorption, which measures the binding energy of the forces between the water vapour molecules and the solid. It yields information for the understanding of the sorption mechanism. Moreover, it can help to detect the type of water binding that is occurring at a given moisture content.[18,20,27,29,30]

The difference between the amount of energy required to remove water from the material (Q_{st}) and the amount of energy required for normal water vaporisation (ΔH_v) is defined as the net isosteric heat of sorption (ΔH_{is}): $\Delta H_{is} = Q_{st} - \Delta H_v$.

The molar net isosteric heat of sorption, can be derived from sorption isotherms at several temperatures using the Clausius–Clapeyron equation:[3,26,31,32]

$$\Delta H_{\text{is}} = -\Re \cdot \left(\frac{\partial \ln a_w}{\partial T^{-1}}\right)_X \tag{5}$$

The values obtained from this equation are adequate only for qualitative considerations of thermodynamic properties for two reasons. First, these values can include considerable error, arising from various graphical manipulations as well as the experimental error in the isotherm data.[33,34] Second, the Clausius–Clapeyron equation is based on the assumption that ΔH_{is} is invariant with temperature.[17,20,29,32] This assumption can be met for pure systems at low temperatures.[14] However, irreversible changes in the binding properties at increased temperatures cause ΔH_{is} to depend on temperature for almost all foods.[35] Nevertheless, temperature invariance of ΔH_{is} is assumed, because it allows analysis of more sorption isotherms at different temperatures, resulting in more accurate fits of the Clausius–Clapeyron equation. Therefore, the resulting net isosteric heat of sorption is considered as the average value for the temperature range under consideration.

Hysteresis effects may complicate thermodynamic data derived from sorption isotherms.[12,27,36] In this research hysteresis is avoided since only desorption characteristics are considered.[8] This is justified as drying is the practical application. An additional advantage is that equilibria during desorption give the best representation.[3]

MATERIAL AND METHODS

Materials

Corn was purchased in cans (Dutch supermarket C1000). The average initial moisture content was 2.6 [kg kg$^{-1}{}_{\text{dm}}$].

Starch cylinders with immobilised catalase were prepared, by manually mixing native potato starch (Perfectamyl D6, AVEBE, Veendam, The Netherlands) with 0.05 M phosphate buffer (pH = 7) containing catalase (EC 1.11.1.6, Sigma, Zwijndrecht, The Netherlands, C-40) in a mass ratio 1.5:1 to a homogeneous paste. The paste was extruded into cylinders of diameter 3 mm and length >30 mm. During preparation the starch cylinders were kept on ice, and then stored in a sealed glass container in a refrigerator (4 °C) until use. The average initial moisture content was 0.97 [kg kg$^{-1}{}_{\text{dm}}$].

Experimental GAB sorption isotherm

The experimental sorption data for corn and starch cylinders at four different temperatures were taken from Quirijns *et al.*[8] The sorption isotherms were always related to desorption. The major difference of these experiments with respect to standard sorption isotherm determinations were the measurement at very low water activity ($a_w < 0.11$) and the long equilibration time of several weeks. Moreover, an improved regression methodology, based on the weighed sum of squares, was applied. This yielded accurate, consistent and physically relevant GAB parameters. The corresponding GAB parameters are presented in Table 2 at each temperature. In Table 3 the temperature dependence of the parameters is given.

Experimental determination of heat of sorption

It follows from eqn (5) that the isosteric heat can be obtained from the slope of the plot representing $\ln(a_w)$ versus $1/T$, at constant value for X. In order to construct this plot, a_w values at different temperatures are required at constant moisture content. However, the sorption data were not determined at constant moisture content. Therefore, the following procedure was applied. The experimental sorption data were used as much as possible, starting from the lowest experimental data point. Since at one moisture content

Table 2. GAB parameters and confidence intervals for desorption isotherms of corn at 30, 45, 60 and 70 °C ($0.11 \leqslant a_w \leqslant 0.9$) and starch cylinders at 4, 30, 45 and 60 °C ($0.05 \leqslant a_w \leqslant 0.9$) (regression method: weighed least squares)

		GAB parameters		
Material	Temp (°C)	C_g	K	X_m (kg kg^{-1})
Corn	30	9 × 10^{3a}	0.89 (±7%)	0.072 (±16%)
	45	9 × 10^{3a}	0.97 (±2%)	0.059 (±3%)
	60	16 (±59%)	0.97 (±3%)	0.048 (±10%)
	70	19 (±36%)	1.03 (±3%)	0.046 (±9%)
Starch cylinders	4	24 (±15%)	0.67 (±5%)	0.16 (±5%)
	30	11 (±9%)	0.54 (±7%)	0.16 (±6%)
	45	21 (±10%)	0.73 (±3%)	0.10 (±4%)
	60	18 (±17%)	0.72 (±3%)	0.088 (±5%)

[a]: confidence interval larger than 100%.

data points were mostly available at only one or two temperatures, the data points at other temperatures were obtained by applying the GAB parameters of Table 2 in the transformed GAB equation form $a_w = \mathrm{f}(X)$:[37]

$$a_w = \frac{\left[\begin{array}{c} 2 + \left(\frac{X_m}{X} - 1\right) \cdot C_g \\ - \left\{ \left(2 + \left(\frac{X_m}{X} - 1\right) \cdot C_g\right)^2 - 4 \cdot (1 - C_g) \right\}^{\frac{1}{2}} \end{array}\right]}{[2 \cdot K \cdot (1 - C_g)]} \tag{6}$$

When the predicted sorption isotherms began to deviate considerably from the experimental ones, these predictions were not applied any more ($a_w > 0.85$). A least-squares analysis was performed to acquire the slope of the plot of $\ln(a_w)$ versus $1/T$.

Literature data

Experimental desorption data at 30, 45 and 60 °C were taken from Kiranoudis *et al*[17] for several vegetables: potato, carrot, green pepper, onion and tomato. These data were obtained using the standard experimental set-up ($a_w > 0.11$). The GAB parameters presented by Kiranoudis *et al*[17] could not be used in present paper since X_m was considered to be constant with temperature, giving wrong values for C_g and K. To obtain the GAB parameters at each temperature, the data were analysed again according to the regression methodology presented by Quirijns *et al*.[8] Since the parameters are only used for comparison in sorption behaviour of the vegetables, the average of the resulting parameters is presented in Table 4. The isosteric heat of sorption was determined from the experimental sorption data with the presented method.

GAB parameters for fortified cassava products were taken from Sanni *et al*[38] for fufu and tapioca and from Sanni and Kuye[19] for soylafun and soyfufu. These data were obtained applying standard experimental ($a_w > 0.11$) and regression methodology. The average parameters are presented in Table 5 together with the isosteric heat of sorption.

RESULTS AND DISCUSSION

Sorption behaviour derived from experimental GAB sorption isotherms

For corn a (very) high value for C_g is accompanied by a value for K, approaching 1 (Table 2). This means that the multilayer molecules have properties comparable with those of bulk liquid molecules. The sorption of water by corn is apparently characterised by a monolayer of molecules, which are strongly bound to the material (high C_g). The subsequent molecules are not or slightly structured in a multilayer, but have characteristics comparable with the molecules in the bulk liquid.

In the case of the starch cylinders, a lower value of C_g is accompanied by a value of K smaller than 1. Those values of the GAB parameters indicate that the water molecules are organised in a monolayer with water molecules strongly bound with the material and a multilayer, in which the water molecules do differ considerably from bulk liquid molecules. Since C_g is smaller for starch cylinders compared with corn, the water molecules are less strongly bound to the material. These two combinations of C_g and K values demonstrate the way in which water molecules are organised in layers (localised sorption). The existence of different classes of water molecules in the materials is established.

In the literature, the combination of GAB parameter values has never been related before to the sorption mechanism of water molecules to the material. Nevertheless, in the majority of the reported data and parameters, a mechanism of sorption can be deduced from the combination of C_g and K values. The GAB parameters for potato[17] ($C_g = 19$, $K = 0.82$, $X_m = 0.068$) in Table 4 illustrate the presence of a monolayer, with strongly bound water molecules and a multilayer, which has characteristics comparable with bulk liquid. Carrot,[17] in contrast ($C_g = 6.4$, $K = 0.76$, $X_m = 0.15$) has a less strong monolayer and a more structured multilayer, where the water molecules are different from bulk liquid molecules. The GAB parameters of the fortified cassava products (Table 5) illustrate that soylafun has the strongest monolayer, followed by fufu, soyfufu and tapioca. The water sorbed by tapioca is the least tightly bound. The water in the multilayer, however, has comparable properties for tapioca, soyfufu and soylafun, while the multilayer is less structured for fufu. Much more examples can be found in comprehensive overviews of sorption data.[11,39–42]

The GAB parameters reported in literature do not always support the theory of localised sorption. For example, a low value for C_g accompanied with K approaching 1 would mean that the monolayer

Table 3. Temperature dependence and confidence intervals of GAB parameters for sorption isotherms of corn ($0.11 < a_w < 0.9$) and starch cylinders ($0.02 < a_w < 0.9$) obtained after direct regression based on weighed least squares

Material	GAB parameters					
	C_{g0}	ΔH_{Cg} (J mol^{-1})	K_0	ΔH_K (J mol^{-1})	X_{m0} (kg kg^{-1})	ΔH_X (J mol^{-1})
Corn	4×10^{-5}[a]	4×10^4 (±94%)	3.6 (±41%)	-3.6×10^3 (±31%)	8×10^{-4} (±98%)	1.2×10^4 (±23%)
Starch cylinders	1×10^{3}[a]	-1.1×10^4 (±36%)	3.5 (±60%)	-4.3×10^3 (±36%)	9.5×10^{-4} (±68%)	1.3×10^4 (±14%)

[a]: confidence interval larger than 100%.

Table 4. Average GAB parameters for desorption isotherms of several vegetables[17] at 30, 45 and 60 °C ($0.11 \leqslant a_w \leqslant 0.9$) and characteristics of the moisture dependence of the net isosteric heat of sorption $\Delta H_{is,max}$ and moisture content where $\Delta H_{is} = 0\,\text{kJ mol}^{-1}$

	Product				
Parameter	Potato	Carrot	Green pepper	Onion	Tomato
GAB parameters (average of 30, 45 and 60 °C)					
C_g	18.70	6.38	10.86	9.38	18.48
K	0.820	0.764	0.790	0.750	0.777
X_m (kg kg^{-1})	0.068	0.150	0.146	0.155	0.149
Isosteric heat of sorption					
$\Delta H_{is,max}$ (kJ mol^{-1})	52	23	31	28	33
$X_{\Delta His=0}$	0.35	0.8	0.6	0.8	0.6

Table 5. Average GAB parameters for adsorption isotherms of fortified cassava products at 25, 32 and 45 °C ($0.11 \leqslant a_w \leqslant 0.9$)[19,27] and characteristics of the moisture dependence of the net isosteric heat of sorption $\Delta H_{is,max}$ and moisture content where $\Delta H_{is} = 0\,\text{kJ mol}^{-1}$

	Product			
Parameter	Fufu	Tapioca	Soyfufu	Soylafun
GAB parameters (average of 25, 32 and 45 °C)				
C_g	61.76	14.72	52.24	72.36
K	0.688	0.566	0.579	0.594
X_m (kg kg^{-1})	0.046	0.057	0.059	0.06
Isosteric heat of sorption				
$\Delta H_{is,max}$ (kJ mol^{-1})	78	52	72	82
$X_{\Delta His=0}$	0.1	>>0.10	0.11	0.11

and multilayer molecules do not differ very much and that the multilayer molecules behave like liquid molecules at the same time. Consequently, all three classes behave similarly. No localised sorption can be illustrated by the parameters. Examples of this are the parameters for grapefruit ($C_g = 0.54$, $K = 0.83$, $X_m = 0.275$) and pineapple ($C_g = 0.87$, $K = 0.82$, $X_m = 0.21$) in Lomauro *et al*,[11] and for grapes ($C_g = 0.701$, $K = 0.929$, $X_m = 0.119$) in Vazquez *et al*.[43] It is possible that the experimental sorption data do illustrate a gradual increase of moisture content, indicating that the water is not sorbed in a localised way, which is in accordance with the GAB parameters.[44,45] However, it is also possible that those parameters are a consequence of limitations of the applied experimental or regression methodology as explained in Quirijns *et al*.[8]

Sorption behaviour derived from isosteric heat of sorption

The isosteric heat of sorption of corn and the starch cylinders are presented in Fig 1 as function of the moisture content of the material. The isosteric heat is given as a positive quantity, illustrating the endothermic character of desorption. For both materials, the isosteric heat of sorption decreases with increasing moisture content after a maximum has been reached. This is indicative of intermolecular attraction forces between sorptive sites and water vapour.[30,34] At moisture contents in the monolayer region, the water is tightly bound to the material, corresponding with high interaction energy. At increasing moisture content, the most active sites become occupied and sorption occurs on the less active sites giving lower heats of sorption.[26,29] The net isosteric heat of sorption ultimately approaches zero, indicating that the total heat of sorption is equal to the heat of vaporisation. The water molecules behave as the molecules in the liquid state. From a drying point of view, the higher the moisture content, the less energy is required to remove water molecules from the material. Desorption will initially occur at the least active sites, requiring low interactive energies in addition to the latent heat of vaporisation of pure water. As drying continues sorption will occur at active sites requiring higher interactive energies.[20] Consequently, the existence of different classes of water is demonstrated by the isosteric heat of sorption: three classes with a continuous transition from the tightly bound water to the free water molecules. The classes correspond with the classification of Van den Berg[3] and Vertucci and Leopold.[12]

The maximum net isosteric heat for corn ($\Delta H_{is} \approx 47\,\text{kJ mol}^{-1}$) is achieved at $X = 0.065\,\text{kg kg}^{-1}$. At $X \approx 0.27\,\text{kg kg}^{-1}$, ΔH_{is} becomes zero. For starch cylinders the maximum net isosteric heat is approximately $17\,\text{kJ mol}^{-1}$ at $X = 0.090{-}0.110\,\text{kg kg}^{-1}$. ΔH_{is} reaches zero at $X \approx 0.60\,\text{kg kg}^{-1}$. The net isosteric heat of both materials shows an increase at very low moisture contents (Fig 1). An initial increase of the net isosteric heat of sorption has been found for adsorption.[13,27,46] Only once, has this increase also

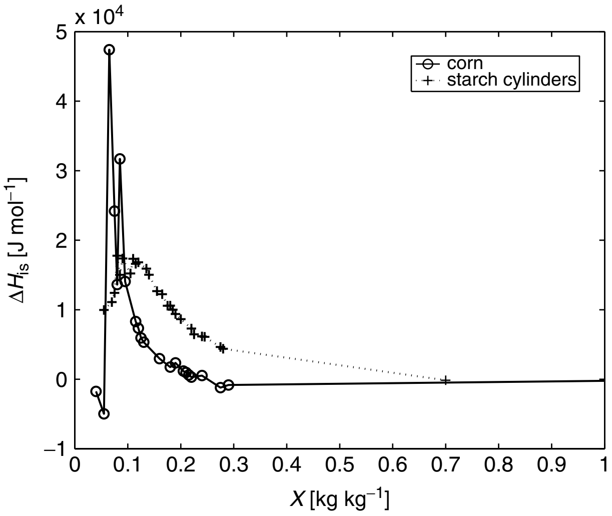

Figure 1. Average net isosteric heat of sorption as function of moisture content derived from experimental sorption data for corn and starch cylinders.

found for desorption.[46] The increase at low moisture contents has been explained by considering that the sorption of water by the dry matrix leads to swelling of the material, resulting in the exposure of sorption sites of higher binding energies, which were previously not available.[13,27,46] However, this explanation is not convincing in the case of desorption. It is more likely that, during desorption at moisture contents near the monolayer value, the attraction between adjacent sorbed water molecules plays a cooperative role. The binding force of the water molecules on the material surface is strengthened by attractive forces between the water molecules. This means that the energy needed to remove water molecule **a** in Fig 2 from the material will be larger than for molecule **b**. When desorption proceeds, the attractive forces between water molecules will vanish, leading to the decrease in net isosteric heat of sorption at lower moisture contents.

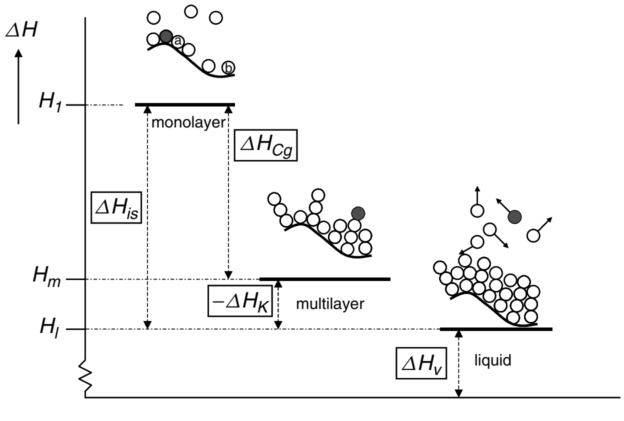

Figure 2. Illustration of localised sorption and the corresponding enthalpy levels of the shaded water molecules to derive the relation between the net isosteric heat of sorption, ΔH_{is} and GAB parameters ΔH_{Cg} and ΔH_K.

Comparison of the experimentally derived sorption behaviours

To be able to deduce the characteristics of the different classes of water and of the transition between them from the experimental GAB sorption isotherm, the sorption behaviour derived from the GAB parameters needs to match with the sorption behaviour derived from the isosteric heat of sorption. Figure 1 shows that the maximum net isosteric heat of sorption is much higher for corn than for starch cylinders. Moreover, after reaching the maximum the net isosteric heat reduces much faster to zero for corn, indicating that, after the monolayer, the molecules are less structured and behave like water in the liquid state at lower moisture content. This corresponds with the sorption behaviour for corn and starch cylinders derived from the physical interpretation of the GAB parameters C_g and K. For corn C_g was higher, illustrating the stronger binding of the monolayer compared with the multilayer molecules, which in turn corresponds with a higher net isosteric sorption heat. However, K was smaller for the starch cylinders. The water molecules in the multilayer deviate considerably in behaviour from the molecules in the liquid state. Therefore, the net isosteric heat of the starch cylinders will approach zero at higher moisture contents. It is clear that the mechanism of sorption derived from the independent knowledge of the heat of sorption is in accordance with the one deduced from the physical relevance of the GAB parameters.

This relationship between the GAB parameters, C_g and K, and the moisture dependence of the isosteric heat of sorption is schematically illustrated by Fig 3. A stronger monolayer corresponds with a higher value of C_g and of the isosteric heat of sorption. When the water molecules are subsequently less structured in a multilayer, K increases and the isosteric heat of sorption reaches zero at lower moisture contents. The literature examples of both desorption and adsorption (Tables 4 and 5) confirm the pattern in this figure. The maximum isosteric heat of sorption has the highest value for potato, followed by those for tomato, green pepper, onion and carrot. This corresponds with the sequence in magnitude of C_g (Table 4). The isosteric heat of sorption reaches zero at the lowest moisture content for potato, that also has the highest value for K. Green pepper and tomato have comparable values for K and the net isosteric heat of sorption reaches zero at higher moisture content. The net isosteric heat of sorption reaches zero at the highest moisture content for onion and carrot, corresponding with the lowest value for K. The GAB parameters for adsorption of fortified cassava products describe a sorption behaviour that supports the moisture dependence of the heat of sorption presented in the corresponding papers:[19,38] soylafun has the highest heat of sorption followed by fufu, soyfufu and tapioca. The heat of sorption of fufu reaches zero at the lowest moisture content (highest K), while the other products reach zero at comparable higher moisture contents.

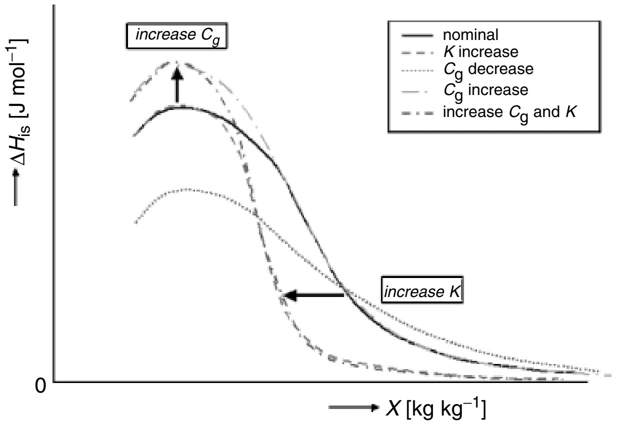

Figure 3. The relationship between the moisture dependence of the net isosteric heat of sorption and the ratio of the GAB parameters, C_g and K.

Theoretically it is also possible to derive the maximum net isosteric heat of sorption from the parameters expressing the temperature dependence of the GAB equation, ΔH_{Cg} and ΔH_K. This is demonstrated in Fig 2, referring to the enthalpy levels of the shaded molecules: $\Delta H_{is} = \Delta H_{Cg} + (-\Delta H_K)$. Since these values have very large confidence intervals (Table 3), it is questionable to use ΔH_{Cg} independently from C_{g0} or ΔH_K independently from K_0. Moreover, this analysis is only allowed when the magnitude of the parameters is corresponding with the theoretical expectation. In Quirijns *et al*,[8] it was argued that the physical relevance of those parameters (ΔH_{Cg} and ΔH_K) could get lost during direct regression methods. With the discussion about the physical relevance of the parameters kept in mind, the analysis is only illustrated for corn. The parameters presented in Table 3 are applied in the analysis, leading to a value of 41 kJ mol^{-1}, which is very close to the value of $\Delta H_{is} \approx 47$ kJ mol^{-1}. Because of the high correlation between the parameters expressing the temperature dependence of the GAB parameters and their large confidence intervals, this is only a rough indication of the net isosteric heat of sorption. Tsami *et al*[32] and Vazquez *et al*[43] also try to derive ΔH_{is} from the GAB parameters. However, they equate the value for ΔH_{Cg} with ΔH_{is}, which is not according to the theory outlined in Fig 2.

Model boundary between bound and free water

The main reason for deriving the heat of sorption from experimental data is to obtain a model boundary between bound and free water. This model boundary plays a crucial role in the diffusion–sorption model.[5] The moisture content at which the heat of sorption approaches the heat of vaporisation of water (ie $\Delta H_{is} \approx 0$ J mol^{-1}) is generally taken as indicative of the amount of bound water existing in the material.[17,20,27,29,34] In view of the localised sorption theory, this point corresponds with the level of moisture content where the multilayer molecules behave like liquid water molecules. Related studies on thermodynamic properties show that the maximum enthalpy is reached at the same moisture content as the extremum in entropy.[3,12,13,28,36] Since at this moisture content the water behaves quite differently from free or bulk water, it is presumed to be the transition between bound and free water. For corn, this boundary corresponds with $X_{part} = 0.065$ kg kg^{-1}, for starch cylinders with $X_{part} = 0.110$ kg kg^{-1}. From Table 2, it appears that this boundary is comparable with the average of the monolayer values X_m. This confirms the statement that, due to the assumed invariance of ΔH_{is} with temperature, only average conditions can be considered. Moreover, it shows that the GAB monolayer value X_m can be considered as a suitable model boundary between bound and free water.

The correspondence between the GAB parameter X_m and the maximum isosteric heat of sorption for corn and starch cylinders demonstrates that the presented method can be used as a technique to estimate the amount of tightly bound water in the material. The maximum in isosteric heat of sorption clearly indicates a different behaviour between the tightly bound and the less bound water molecules. This method will also be useful to make a distinction between BET and GAB monolayer values, which always differ in magnitude.[20,42] To establish the technique, the demonstrated correspondence needs to be illustrated for more materials. Moreover, to attain the possibility to retrieve accurate values for the bound water as function of temperature, the sorption isotherms need to be determined for more temperatures, otherwise the sensitivity of the Clausius–Clapeyron equation to experimental and graphical errors would cause unacceptable large inaccuracy of the results. The experimental and regression methodology of Quirijns *et al*[8] is recommended for the determination of the sorption isotherm, in order to obtain data at low water activity as well as accurate, consistent and physically relevant GAB parameters. Although not the purpose of this paper, it is illustrated that the comparison of the moisture dependence of the isosteric heat of sorption with the GAB parameters can be used as a technique for estimating the tightly bound water content in foods.

CONCLUSION

The diffusion–sorption drying model uses a sorption process to describe the conversion between bound and free water at low moisture content. The drying model is founded on the existence of different classes of water, ie the bound and free water, caused by localised sorption. The transition between the bound and free water and the corresponding thermodynamics form distinct components of the drying model. In this paper, we show that the characteristics of the different classes of water as well as the transition between them can be deduced from the GAB sorption isotherm.

The ratio of the estimated GAB parameters, C_g and K, elucidate the mechanism of sorption in layers, establishing the existence of different classes of water. Not two, but three classes of water can be distinguished: the monolayer, the multilayer and the free water. The multilayer forms a continuous transition from the tightly bound water to the free water molecules. Knowledge of the net isosteric heat of sorption derived from experimental sorption data is confirming this mechanism of sorption. This correspondence in the mechanism of sorption is found for our own measurements as well as for results reported in literature.

The extremum in the net isosteric heat of sorption as function of the moisture content reveals the transition between tightly bound and free water, which corresponds with the monolayer value X_m obtained from the GAB sorption isotherm. Hence, X_m can be used as a suitable independent parameter in the diffusion–sorption model.

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