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Sorption of Water by Bidisperse Mixtures of Carbohydrates in Glassy and Rubbery States

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Water sorption by bidisperse carbohydrate mixtures consisting of varying ratios of a narrow-molecular-weight distribution maltopolymer and the disaccharide maltose is investigated to establish a quantitative relation between the composition of the carbohydrate system and the water sorption isotherm. The sorption of water is approached from two limiting cases: the glassy state at low water content and the dilute aqueous carbohydrate solution. In the glassy state, the water content at a given water activity decreases with increasing maltose content of the matrix, whereas in the rubbery state it increases with increasing maltose content. The water sorption behavior in the glassy state is quantified using a variety of models, including the often-utilized but physically poorly founded Guggenheim−Anderson−de Boer model, several variants of the free-volume theory of sorption by glassy polymers, and a two-state sorption model introduced in the present paper. It is demonstrated that both the free-volume models and the two-state sorption model, which all encompass the Flory−Huggins theory for the rubbery-state sorption but which differ in their modeling of the glassy-state sorption, provide a physically consistent foundation for the analysis of water sorption by the carbohydrate matrixes.

Introduction

The isotherm for the sorption of water on matrixes of amorphous biopolymers, in particular amorphous carbohydrates, is of fundamental importance in understanding and predicting the properties of foods and pharmaceutics, and a very significant body of experimental data exists on equilibrium water sorption by biopolymer-based systems and amorphous carbohydrates (refs 1 and 2 and references therein) as well as the effect of water on the properties of, for example, foods.[3] The sorption models most widely used to analyze and fit such sorption data in the food and pharmaceutical fields are based on the multilayer adsorption model originally due to Brunauer, Emmett, and Teller (BET).[4] The BET model, which has been derived for adsorption of low-molecular-weight compounds on the surfaces of materials, combines a Langmuir isotherm model for the formation of a monolayer of molecules adsorbed on a regular lattice of energetically uniform sites, followed by a multilayer condensation of the adsorbate (Figure 1a). For the surface adsorption of low-molecular-weight compounds, it is generally accepted that BET-type models provide a picture that, although simplified, is essentially correct in its physical description. It is clear, however, that such models are descriptive rather than mechanistic when applied to the sorption of water by amorphous carbohydrates (ref 5 and references therein).

Several approaches for the sorption of low-molecular-weight penetrants by polymer matrixes that include explicit molecular models for the sorption in the glassy and rubbery states have been forwarded. Whereas virtually all models that account for the rubbery-state sorption are based on the Flory−Huggins theory of polymer solutions (Figures 1b−d),[6] a number of different models exist for the sorption in the glassy state. Most established are the approaches that are based on the so-called free-volume theory of the amorphous state.[7−10] The general assumption behind the free-volume theory in its application to penetrant sorption is that the molecular structure of the glassy polymer matrix is different at each penetrant concentration. Because of the quenched nature of the polymer matrix below the glass transition temperature (T_g), swelling and deswelling of the polymer matrix upon changes in penetrant concentration are constrained, which leads to both anomalous volumetric behavior[8] and a plateau formation at low partial pressures of the sorbent molecules (Figures 1b−d).[9,10] By analyzing the sizes of the free-volume holes, we recently have confirmed that, in the glassy state, the carbohydrate molecular-weight distribution and the water content indeed determine the molecular structure and packing[11,12] by a mechanism that involves both hole filling by the low-molecular-weight carbohydrates and by water at low water activities and hole expansion by water at higher water activities.[13] Similar behavior of water is observed also for other polar polymers, such as polyamide.[14]

Three different free-volume models proposed for the sorption of low-molecular-weight penetrants by glassy polymer matrixes are readily applicable to the water sorption by amorphous carbohydrates. The first model that we consider was derived by Tomka and co-workers[15,16] to account for the sorption of water by biopolymer matrixes. In their work, they distinguish between two fractions of absorbed water: one fraction associated with the glassy polymer, for which they use Freundlich isotherm model,[17] and one fraction dispersed in the rubbery fraction of the biopolymer matrix, for which a Flory−Huggins model is used (Figure 1b).[6]

A second class of models that we will consider in this paper are the free-volume sorption models by Vrentas and Vrentas[9] and by Leibler and Sekimoto.[10] Their models are based on certain assumptions on the volumetric behavior and thermal expansion of the polymer matrix in the glassy and rubbery states and directly include data on the glass transition of the polymer−penetrant mixture. A special feature of these models is that over the whole concentration regime from pure polymer to pure penetrant the mixing entropy according to the Flory−Huggins model is assumed to remain valid. In effect, in these models it

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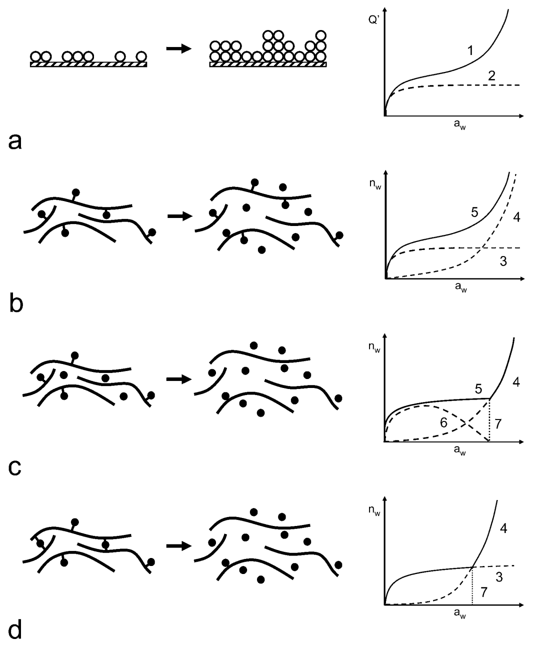

Figure 1. Various models for the sorption of water by carbohydrate matrixes and their related sorption isotherms. (a) Surface adsorption followed by condensation of water according to the BET and GAB models. (b) Water binding by the glassy fraction of the polymer matrix and simultaneous formation of a Flory–Huggins solution of the polymer–water complex in water.[15,16] (c) Isotherm following the free-volume models,[9,10] where the fraction of water absorbed in the glassy state vanishes at the water activity corresponding to T_g, with Flory–Huggins absorption occurring in both the rubbery and the glassy states. (d) Water absorption in the glassy matrix followed by the formation of a Flory–Huggins solution of polymer in water above the glass transition temperature. (1) BET or GAB isotherm; (2) formation of a Langmuir monolayer in a BET or GAB isotherm; (3) Freundlich isotherm; (4) Flory–Huggins isotherm; (5) combined isotherm; (6) water absorbed in the glassy fraction of the polymer matrix according to the free-volume theories; (7) critical a_w at the glass transition.

is assumed that freezing out the polymer conformations in the glassy state does not influence the overall entropy of the system. When applied to the sorption of water by pharmaceutical excipients, the free-volume model by Vrentas and Vrentas[9] was found to satisfactorily fit the experimental data.[5,18,19]

A third and last model that we will use in the analysis of the sorption of water by amorphous carbohydrate matrixes is a modification of the model proposed by Tomka and co-workers.[15,16] As in their model, we will assume that the glassy-state sorption may be accounted for using a Freundlich isotherm and the rubbery-state sorption by the Flory–Huggins theory. However, in contrast to the approaches in the previous models, we will assume that in the glassy state, there is no entropic contribution due to residual degrees of freedom of the polymer. Our model is thus effectively a two-state model, with distinct mechanisms of sorption in the glassy and rubbery states (Figure 1d).

Both Tomka and co-workers and Zhang and Zografi find that the various isotherm models provide a satisfactory fit of the experimental data on thermoplastic starch,[16] on ethyl cellulose,[15] and on amorphous mixtures of poly(vinyl pyrrolidone) with various disaccharides.[5,19] Several important aspects are not yet resolved, however. First, there is no analysis of the effects of the molecular-weight distribution and consequently the molecular packing and entropy of the carbohydrates on the sorption behavior. Second, the studies are fairly restricted in the water-activity regime and therefore do not include the theoretically important limiting regime of a dilute solution of polymer in water. The analysis of Zhang and Zografi in principle contains useful information on the sorption of water by bidisperse mixtures of a polymer and a disaccharide, but important information on the relation between density and water content is lacking.[5,19] The study by Beck and Tomka[15] on ethyl cellulose and the papers by Benczédi et al.[16,21] on thermoplastic starch contain such density information but are unfortunately restricted to one carbohydrate molecular-weight distribution. Third, we infer that the model of Tomka and co-workers[15,16] is thermodynamically inconsistent toward high water content as a continuous coexistence is assumed between glassy-state and rubbery-state sorption modes over the whole water-activity domain from $a_w = 0$ (fully dehydrated state) to $a_w = 1$ (fully hydrated state) (Figure 1b). In addition, in their model, the Flory–Huggins interaction parameter varies with concentration, which is unusual, and as we shall see, unnecessary. Fourth, as stated, in the free-volume models by Vrentas and Vrentas[9] and by Leibler and Sekimoto,[10] the Flory–Huggins mixing entropy is assumed to contribute to the sorption properties even in the glassy state. It is not clear if this assumption is justified, as the polymer conformations are frozen out even though water remains mobile.

In an attempt to resolve these issues, we approach the sorption of water by amorphous carbohydrate matrixes from two limiting cases: the glassy state at low water content and the dilute solution of carbohydrates in water. To enable a quantitative study of the effects of density, water content, carbohydrate molecular weight, and glass transition on the water sorption, we study the water sorption of a systematic series of bidisperse carbohydrate mixtures. These mixtures consist of various fractions of a fractionated intermediate-molecular-weight maltopolymer of fairly narrow-molecular-weight distribution ($M_w/M_n \approx 2$, where M_w and M_n are the weight-average and number-average molecular weights, respectively) and the disaccharide maltose. The water sorption experiments are complemented by density measurements to investigate the effect of molecular packing and by calorimetric measurements to assess the role of the glass transition on the water sorption characteristics. In a forthcoming paper, we relate the water sorption of the carbohydrate matrixes to molecular packing by positron annihilation lifetime spectroscopy to formulate a detailed structural model for amorphous carbohydrate–water systems.[13]

Materials and Methods

Preparation of Matrixes and Solutions. Dense carbohydrate matrixes were prepared from mixtures of a fractionated maltopolymer and maltose with weight fractions 100% and 0%, 95% and 5%, 90% and 10%, 80% and 20%, 60% and 40%, 40% and 60%, 30% and 70%, 20% and 80%, and 0% and 100% of the maltopolymer and maltose. The maltopolymer LAB 2490 (lot no. 337301E, Roquette Frères, Lestrem, France) is a chromatographically fractionated starch hydrolysate of intermediate molecular weight ($M_w = 1.2 \times 10^4$ Da) and a polydispersity that is relatively narrow for such materials ($M_w/M_n = 2.2$). LAB2490 is further characterized by a limited degree (6.8%) of α-(1 → 6) branching. The disaccharide maltose (4-*O*-α-D-glucopyranosyl-D-glucose; $M_w = 342$ Da) was obtained from Fluka (Buchs, Switzerland). Both samples were used without further purification. Matrixes were prepared by solvent casting and controlled evaporation as previously described.[11] The cast samples were ground and further dried until a final water activity of about 0.1 was reached. The ground samples were sieved into size fractions; the size fractions between 100 and 300 μm were used for water-activity equilibration and all further experiments. High-water-activity samples where prepared by dissolution

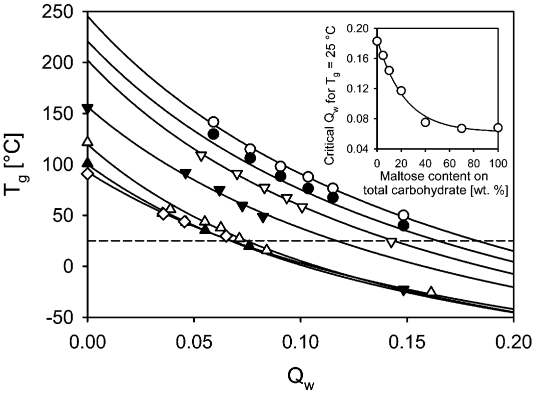

Figure 2. Glass transition temperature T_g of maltopolymer−maltose matrixes as a function of the weight fraction of water. The solid lines represent the fit of the experimental data using the Gordon−Taylor equation (eq 1). The fitting parameters are collected in Table 1. The inset shows the dependence of the weight fraction of water Q_w at which the glass transition temperature of the maltopolymer−maltose matrixes equals the temperature of the sorption experiments (25 °C).

of a known quantity of carbohydrate in water, taking into account the initial water content of the carbohydrate powders. From these solutions, sorption data were obtained by direct measurement of the water activity.

Determination of Water Content. The water content of the samples after preparation was determined using a home-built extraction unit as described previously.[11] The extraction of water was followed as a function of time by monitoring the decrease of the water peak at $\lambda = 1940$ nm in near-infrared reflectance spectroscopy (Multi-Purpose Analyzer, Bruker, Germany). The variation between duplicates was <0.1% w/w on initial weight.

Water-Activity Equilibration. Samples were equilibrated at 25 ± 1 °C at various water activities in desiccators containing saturated salt solutions of known relative humidities ($a_w = 0.11$ (LiCl); $a_w = 0.22$ (CH_3COOK); $a_w = 0.33$ ($MgCl_2$); $a_w = 0.43$ (K_2CO_3); $a_w = 0.54$ ($Mg(NO_3)_2$); $a_w = 0.75$ (NaCl)).[22] The sorption of water was followed gravimetrically until equilibrium was achieved.

Water-Activity Determination. The water activity of the samples was determined with one of two different techniques, depending on the anticipated water activity. For the water-activity regime $0 \leq a_w \leq 0.75$, the water activity was determined using a humidity sensor (Hygroscop DT, Rotronic AG, Switzerland) kept at 25.0 ± 0.1 °C and calibrated with saturated salt solutions of known relative humidities (see above). The signal was recorded for at least 1 h to ensure that equilibrium between sample and headspace was established. For the water-activity regime $0.75 < a_w \leq 1$, the water activity was determined at 25 ± 1 °C using an automated dew-point technique (Aqualab CX-2, Decagon Devices Inc., USA). All analyses were carried out in duplicate; the variation between the duplicates was <0.005.

Analysis of Glass Transition by Differential Scanning Calorimetry (DSC). Calorimetric measurements were carried out using a Seiko 220C differential scanning calorimeter (Seiko, Japan) as described previously.[11] The T_g was determined from the onset of the change in heat flow observed at the second heating ramp.

Determination of Density. The specific volume of the samples was determined using an Accupyc 1330 pycnometer (100 mL cell with 10 mL insert) (Micromeritics, USA). Helium was used as displacement gas at an equilibration rate of 0.1 kPa/min. Ten sample runs were found to be sufficient for values of the specific volume significant up to the third decimal place.

Results and Discussion

As we anticipate that the glass transition will have a significant effect on the sorption of water by the carbohydrate−water systems, we start by analyzing the effect of water on the glass transition of the carbohydrate systems. In Figure 2, the glass transition of the various maltopolymer−maltose matrixes is plotted as a function of the weight fraction of water Q_w. As expected the glass transition temperature decreases strongly with an increasing weight fraction of water, in particular at relatively low-molecular-weight fractions. At higher-molecular-weight fractions, the rate of decrease of T_g with an increasing weight fraction of water levels off and approaches the glass transition temperature of water (−134 °C) at a weight fraction of water close to one.

We fit the glass transition data using the Gordon−Taylor equation[3,23]

$$T_g = \frac{Q_c T_{g,c} + k_{GT} Q_w T_{g,w}}{Q_c + k_{GT} Q_w} \tag{1}$$

where $Q_c = 1 - Q_w$ is the carbohydrate weight fraction, $T_{g,c}$ is the glass transition temperature of the anhydrous carbohydrate matrix, $T_{g,w}$ is the glass transition temperature of water, and k_{GT} is the Gordon−Taylor coefficient. In modeling the experimental data, both $T_{g,c}$ and k_{GT} are considered as fitting parameters. Furthermore, in eq 1, we assume that in the evaluation of the plasticizing effect of water the two carbohydrate components can be taken together, $Q_c = Q_p + Q_m$, where Q_p is the maltopolymer weight fraction and Q_m is the maltose weight fraction. Q_w is related to the mole fractions of water n_w by $Q_w = \{n_w M_{w,w}\}/\{(n_w M_{w,w} + n_c M_{w,c})\}$. $M_{w,w}$ is the molar weight of water, and the carbohydrate concentrations are expressed in mole fractions of glucose monomers n_c (as water is eliminated in the carbohydrate polymerization, $M_{w,c} = 180$ Da for a single glucose molecule or for the first glucose ring in a glucose oligomer or polymer, and $M_{w,c} = 162$ Da for the following anhydroglucose units in a chain).

In Figure 2, it is observed that the glass transition of the carbohydrate−water mixtures is well fitted using the Gordon−Taylor equation, as is generally the case for carbohydrate−water systems.[2] The fitting data are collected in Table 1. The values of the fitting coefficients fall well within the range reported for carbohydrate−water systems.[2] In addition, the values for the T_g of the anhydrous maltopolymer and for pure maltose agree well with literature data.[11,24] We note that the Gordon−Taylor equation has been derived based on assumptions concerning the ideality of mixing of copolymers, which are not necessarily fulfilled for carbohydrate−water systems.[23] However, the Gordon−Taylor equation is only used here as an empirical fit in this paper to obtain the critical weight fraction of water at which the T_g of the maltopolymer−maltose systems is 25 °C as a function of the maltose content (inset in Figure 2).

We observe that this critical weight fraction of water initially decreases rapidly with increasing maltose content from about 18 wt % for the pure maltopolymer and levels off at a water content of about 6−7 wt % for maltose contents on total carbohydrate higher than about 70 wt % (Table 1). For the various carbohydrate compositions, the critical weight fraction of water at which the glass transition temperature is 25 °C corresponds to a critical water activity included in Table 1. With increasing maltose composition, this critical water activity decreases from 0.91 for the pure maltopolymer matrix to 0.31 for the pure maltose matrix.

In Figure 3a, the water sorption isotherms of the various maltopolymer−maltose matrixes in the water activity range between 0 and 0.75 (25 °C) are shown. As is customary,[1] the water content is expressed as the ratio of sorbate to sorbent, in our case for water denoted by $Q' = Q_w/(1 - Q_w)$. Q' is also

Table 1. Carbohydrate Composition of the Matrixes, Glass Transition Temperature of the Dehydrated Systems, Gordon−Taylor Parameter, Weight Fraction of Water at Which the Glass Transition Temperature Is 25 °C, and Anhydrous Specific Volume

maltopolymer content[a] (wt %)	maltose content[a] (wt %)	T_g(dry)[b] (°C)	k_{GT}	Q_w (T_g = 25 °C)	Q' (T_g = 25 °C)	a_w^* (T_g = 25 °C)	V_{sp} (cm^3 g^{-1})[c]
100	0	246	6.20	0.183	0.224	0.91	0.6704
95	5	221	6.27	0.164	0.197	0.86	0.6685
90	10	202	6.64	0.144	0.168	0.76	0.6681
80	20	157	6.24	0.117	0.132	0.63	0.6643
60	40	120	7.39	0.075	0.081	0.44	0.6619
30	70	100	6.56	0.067	0.072	0.38	0.6575
0	100	92.6	5.86	0.068	0.073	0.31	0.6545

[a] Carbohydrate composition is expressed on the basis of the total carbohydrate content. [b] Glass transition temperature of the anhydrous carbohydrate matrix following the fit of the data to the Gordon−Taylor equation (eq 1). [c] Anhydrous specific volume.

known as the water content on a dry basis. The sorption isotherms show the familiar sigmoidal shape commonly observed for the sorption of water in biopolymer matrixes: Upon the sorption of the first water molecules, the water activity increases only very slowly. At a water activity of around 0.1−0.2 (corresponding to a water content on a dry basis between 3.5 and 9 wt %), the rate of increase in water content with increasing water activity slowly decreases but does not level off completely. At intermediate water activities ($a_w \approx 0.35-0.55$), the water sorption isotherms turn upward again, and the water content increases very rapidly with increasing water activity at high water activities.

Several common isotherm models for the multilayer sorption of small molecules onto solid surfaces are routinely used to fit the sorption of water by food and pharmaceutical products. These multilayer sorption models combine two modes of sorption (Figure 1a). The first sorption mode comprises the formation of a monolayer of sorbate molecules on the surface of the sorbent. The second sorption mode is the multilayer condensation of the sorbate onto the sorbate monolayer, whereby the properties approach those of the pure liquid. The best known example of such multilayer sorption isotherm models is the BET equation in which the multilayer condensation is combined with the Langmuir sorption model for the formation of the monolayer[4]

$$\frac{Q'}{Q_{mono}} = \frac{Ca_w}{(1 - a_w)[1 - (1 - C)a_w]} \tag{2a}$$

where C and Q_{mono} are model parameters.

Whereas the physical interpretation of surface sorption on rigid adsorbents following the BET equation is rather clear,[4,17] the interpretation of the sorption of water by biopolymer matrixes is much less evident, as for these systems the surface adsorption of water is much smaller than the absorption of water by the bulk of the material, even at low water contents. In addition, the BET equation fails to take into account the glass transition of the matrix and the molecular mixing of carbohydrate and water in the rubbery state.

Experience has shown that the BET equation does in fact poorly fit the water sorption by biopolymer matrixes at higher water activities. For this reason, the so-called Guggenheim−Anderson−de Boer (GAB) isotherm equation is often used in analyzing the water sorption by biopolymer matrixes.[2,27] The GAB equation is obtained from the BET equation by transformation of the water-activity axis[27]

$$a_w \rightarrow Ka_w' \tag{2b}$$

Figure 3a shows that the sorption of water by the maltopolymer−maltose matrixes is well fitted using the GAB equation in the water-activity regime between 0 and 0.75. However, it should be noticed that the physical significance of the GAB equation for the sorption of water by biopolymer matrixes is even more limited than the BET equation because of its unphysical divergence at water-activity values below unity for values of K larger than 1: Whereas the BET equation diverges as $(1 - a_w)^{-1}$ for $a_w \rightarrow 1$, the GAB equation diverges at a critical water activity $a_w^* = K^{-1}$. This unphysical divergence is observed for the GAB fit of all maltopolymer−maltose samples with a maltose content on total carbohydrate of 40 wt % and higher (Table 2; Figure 4c).

The sorption behavior of the maltopolymer−maltose matrixes changes as a function of the maltose content below and above the glass transition. Whereas in the rubbery state, the amount of water absorbed in the carbohydrate matrixes increases rapidly with increasing maltose content at constant water activity, in the glassy state the opposite trend is seen. This is even better observed if we replot the water sorption data at a constant water activity as a function of the fraction of maltose in the carbohydrate mixture (Figure 3b). For the various water activities we observe that the amount of water absorbed first decreases with increasing maltose content, but at water activities above the critical water activity for the glass transition at 25 °C, the amount of absorbed water increases with increasing maltose content.

In a first attempt to quantitatively understand the sorption of water by amorphous carbohydrates, it is of interest to investigate the relation between the three coefficients Q_{mono}, C, and K from the GAB isotherm model on the one hand and the composition and the physical state of the maltopolymer−maltose matrixes on the other, where we proceed in a manner somewhat similar to Zhang and Zografi in their study of the applicability of the BET equation to the moisture sorption by pharmaceutical solids.[5] Q_{mono} is usually interpreted as the water content at which full monolayer coverage is reached, and in the relevant limit of $C \gg 1$, C determines the steepness of the initial rise to the monolayer plateau and is thus related to the free energy of sorption at low partial pressures.[4] Therefore, we anticipate that both parameters are related to the glassy-state properties of the carbohydrate matrixes. In contrast, K should be related to either the rubbery-state properties or to the glass transition of the matrixes, as K^{-1} equals the water activity at which the GAB equation diverges. Interestingly, Q_{mono} turns out to decrease with increasing maltose content (Figure 4a). In fact, Q_{mono} is linearly related to the anhydrous specific volume of the carbohydrate matrixes (Figure 4b; Table 1). This hints at the importance of molecular packing for the sorption of water by carbohydrate glasses. A useful interpretation of Q_{mono} is therefore that it signifies the amount of water needed to saturate either the accessible interstitial spaces or the sites available for hydrogen

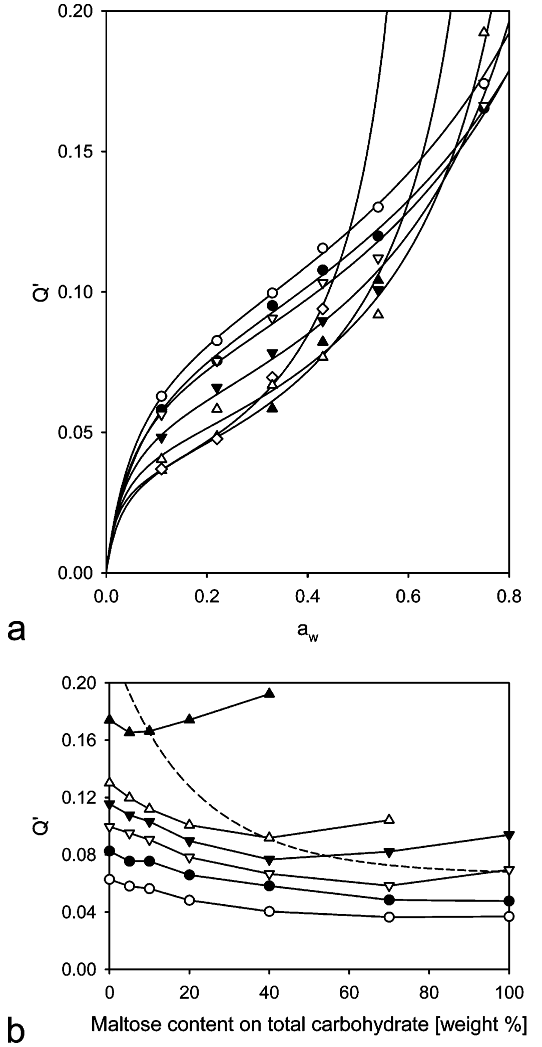

Figure 3. (a) Water sorption isotherms at 25 °C of the maltopolymer−maltose matrixes in the regime $0 < a_w < 0.75$. Solid lines, fit of the water sorption by the GAB equation (eq 2). The water sorption data are expressed the weight ratio of water to carbohydrate. The symbols represent the various maltopolymer−maltose compositions (all in wt % based on total carbohydrate content). Open circles, 100−0 (pure maltopolymer); filled circles, 95−5; open triangles down, 90−10; filled triangles down, 80−20; open triangles up, 60−40; filled triangles up, 30−70; open diamonds, 0−100 (pure maltose). (b) Dependence of the water sorption data at 25 °C on the maltose content of the maltopolymer−maltose matrixes for various water activities. The dashed line is derived from the inset in Figure 2 and denotes the relation between carbohydrate composition and the weight fraction of water at which the glass transition temperature is 25 °C; below this line, the samples are in the glassy state, and above this line the samples are in the rubbery state. Open circles, $a_w = 0.11$; filled circles, $a_w = 0.22$; open triangles down, $a_w = 0.33$; filled triangles down, $a_w = 0.43$; open triangles up, $a_w = 0.54$; filled triangles up, $a_w = 0.75$.

Table 2. Fitting Coefficients of the GAB Isotherm Model for the Water Sorption by Bidisperse Carbohydrate Matrixes in the Water-Activity Regime between 0 and 0.75 ($T = 25$ °C)

maltopolymer content[a] (wt %)	maltose content[a] (wt %)	K	C	Q_{mono}
100	0	0.682	23.1	0.0887
95	5	0.695	22.3	0.0821
90	10	0.739	25.9	0.0750
80	20	0.884	29.5	0.0584
60	40	1.011	34.4	0.0458
30	70	1.174	27.1	0.0396
0	100	1.480	35.4	0.0352

[a] Carbohydrate composition is expressed on the basis of the total carbohydrate content.

Table 3. Fitting Coefficients of the Flory−Huggins Theory for the Water Sorption by Bidisperse Carbohydrate Matrixes in the Rubbery State ($T = 25$ °C)

maltopolymer content[a] (wt %)	maltose content[a] (wt %)	r[b]	χ
100	0	0	−0.72
95	5	0.0526	−0.63
90	10	0.111	−0.57
80	20	0.250	−0.69
60	40	0.667	−0.64
30	70	2.33	−0.30
0	100	∞	0.15

[a] Carbohydrate composition is expressed on the basis of the total carbohydrate content. [b] Calculated as the weight ratio of maltose to maltopolymer.

bonding within the carbohydrate matrixes and not a surface monolayer of water as such. The parameter C turns out to be essentially independent of both the matrix composition and specific volume (Table 2). This is in contrast to the study by Zhang and Zografi,[5] who find that C increases with increasing molecular weight of their polymers. The parameter K^{-1} relates to the critical water activity a_w^* at which the glass transition temperature of the carbohydrate matrixes are equal to the experimental temperature (25 °C) (Figure 4c). This correlation is an artifact of the fitting procedure, which excludes the sorption data beyond a water activity of 0.75. If we include dilute solution data, as for the isotherm models discussed below, then K will approach unity and the GAB equation reverts to the BET equation with an overall poor fit of the sorption data.

Even though several parameters of the GAB model are well correlated with several physical properties of the carbohydrate matrixes, the model is not physically well-founded for the sorption of water by amorphous carbohydrates. Therefore, to develop a quantitative understanding of the mechanism of water sorption, we will proceed by analyzing the water sorption by the bidisperse carbohydrate mixtures using sorption models that are based on physical models of the molecular behavior in the rubbery and glassy states.

The sorption of water in the rubbery state is best approached starting at high dilution, as in the limit of infinite dilution the solution properties should become ideal. For ideal solutions of consisting of a solute in water, the entropy of mixing is written as[6,29]

$$-\frac{\Delta S}{k_B} = n_w \ln X_w + n_s \ln X_s \tag{3}$$

where X_i denotes the mole fraction of the component i, k_B is Boltzmann's constant, and the subscripts "w" and "s" indicate water and the solute, respectively. If the solute is a polymeric compound, then the entropy of mixing becomes the classical Flory−Huggins expression[6]

$$-\frac{\Delta S}{k_B} = n_w \ln \phi_w + n_p \ln \phi_p \tag{4}$$

where ϕ_w and ϕ_p are the lattice volume fractions of water and the polymer (Appendix 1). In Appendix 1, we derive the analogous expression for the mixing entropy of a three-component system with two low-molecular-weight species and one polymeric one, representative for solutions of maltopolymer, maltose, and water.

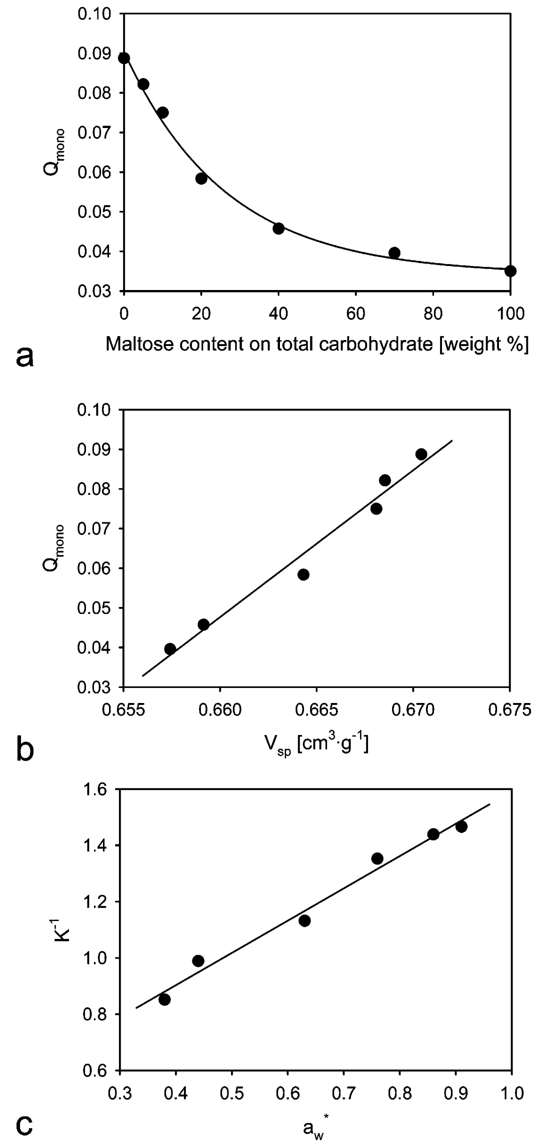

Figure 4. (a) Dependence of the of the monolayer weight fraction of water Q_{mono} from the GAB isotherm model (eq 2) on the maltose content of the carbohydrate matrixes. The solid line is the exponential regression of the data; $R^2 = 0.99$. (b) Dependence of the of the monolayer weight fraction of water Q_{mono} from the GAB isotherm model on the specific volume of the anhydrous maltopolymer–maltose compositions. The solid line is the linear regression of the data; $R^2 = 0.99$. (c) Dependence of the inverse of the a_w-rescaling parameter K from the GAB isotherm model on the critical water activity a_w^* at which T_g of the maltopolymer–maltose system equals the experimental temperature of 25 °C. The solid line is the linear regression of the experimental data; $R^2 = 0.98$.

Within the Flory–Huggins theory, the enthalpy of interaction between the various molecular units is taken into account following[29]

$$\frac{\Delta H}{k_B T} = \chi n_w \phi_p \tag{5}$$

where T is the absolute temperature.

From the total free energy of mixing $\Delta G = \Delta H - T\Delta S$ the water activity of the polymer–water is obtained

$$a_w = \phi_w \exp[(1 - \phi_w) + \chi(1 - \phi_w)^2] \tag{6}$$

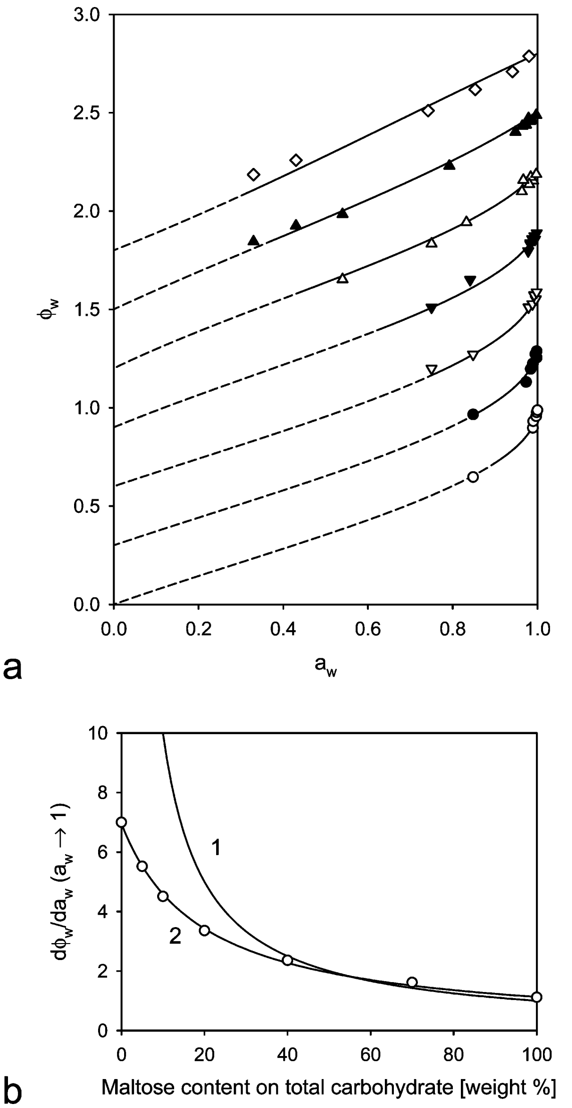

Figure 5. (a) Fit of the rubbery-state and solution data using the Flory–Huggins equation for a ternary mixture (eqs A.5 and A.6). Solid lines, Flory–Huggins fit of the rubbery state and solutions; dashed lines, extrapolation of the Flory–Huggins fit into the glassy state. The values of the Flory–Huggins parameter are collected in Table 3. The symbols represent the various maltopolymer–maltose compositions (all in wt % based on total carbohydrate content): open circles, 100–0 (pure maltopolymer); filled circles, 95–5; open triangles down, 90–10; filled triangles down, 80–20; open triangles up, 60–40; filled triangles up, 30–70; open diamonds, 0–100 (pure maltose). The curves are shifted along the vertical axis by 0.3 units (95–5), 0.6 units (90–10), 0.9 units (80–20), 1.2 units (60–40), 1.5 units (30–70), and 1.8 units (0–100). The critical water activity at which the glass transition temperature equals the experimental temperature is calculated from the Gordon–Taylor fit of the DSC data and the GAB fit of the sorption isotherms. (b) Slope of the isotherm at infinite dilution. The curve denoted by "1" is the Flory–Huggins prediction for $x_m = 1$ and $x_p = \infty$; the curve denoted by "2" is the optimal fit with $x_m = 1.13$ and $x_p = 6.96$.

In Appendix 1, the equivalent expression for the ternary system of carbohydrate polymer, maltose, and water is listed (eq A.5) as well as the expression for a solution of maltose in water (eq A.6b).

An important aspect of lattice models such as the Flory–Huggins theory is the choice of the lattice units and the definition of the lattice volume fractions. Whereas for polymers in solutions of chemically similar monomeric compounds this choice is not so difficult, as molecular sizes of the effective units are very close, it becomes more problematic for mixtures involving chemically highly disparate units, such as carbohydrates and water. Within the framework of the Flory−Huggins theory this issue cannot be fully solved, and various choices remain possible. For instance, in previous work on the sorption of water in thermoplastic starch[16] and in mixtures of disaccharides and poly(vinyl pyrrolidone),[5,19] the lattice volume fraction of water is equated with the volume fraction of water in the system, which may be calculated from the dependence of the specific volume on the weight fraction of water. This approach, however, underestimates the mixing entropy of water with respect to carbohydrates, as the actual volume fraction of water is much lower than the number fraction of water molecules because of the large differences in molecular weight between water ($M_{w,w}$ = 18 Da) on the one hand and glucose ($M_{w,c}$ = 180 Da) or maltose ($M_{w,c}$ = 342 Da) on the other hand. Therefore, we will analyze the sorption behavior assuming that water and maltose behave like single monomeric units and that the polymer consists of a large number of such units. Our approach is approximate as well as it neglects the contribution of internal degrees of freedom to the mixing entropy. However, toward high dilutions our approach is thermodynamically more consistent and is also more in line with the original formulation by Flory.[6]

In Figure 6, the rubbery-state sorption data of the maltopolymer−maltose matrixes is shown for various weight ratios of maltose to the maltopolymer. It turns out that the fit of the rubbery-state sorption data using the three-component Flory−Huggins equation (eq A.5) and the two limiting cases for binary systems (eqs A.6a and A.6b) is rather good. This is in agreement with previous studies on water sorption by carbohydrates and water-soluble polymers,[18] although our value for χ is somewhat lower. This is because we plot our data on lattice volume fractions whereas in ref 5 volume fractions are used. Our values for χ indicate that water is a good solution for the carbohydrates, as anticipated. For maltose, the sorption regime in which the Flory−Huggins equation is applicable is very wide ($0.35 < a_w \leq 1$), because of the low critical water activity for the glass transition. Conversely, for the maltopolymer, this water-activity window is small ($0.9 < a_w \leq 1$), reflecting its high glass transition temperature.

Additional conformation of the validity of the Flory−Huggins theory for the water sorption by rubbery carbohydrates is the limiting behavior at infinite dilution. At infinite dilution, the derivative of the lattice volume fraction of water with respect to the water activity becomes independent of the interaction parameter and is dependent only on the weight ratio of maltose to maltopolymer

$$\left.\frac{d\phi_w}{da_w}\right|_{a_w=1} = 1 + \frac{1}{r} \tag{7}$$

where r is defined as the ratio of the lattice volume fractions of maltose to maltopolymer (Appendix 1), which for all practical purposes equals the ratio of the weight fraction of maltose to maltopolymer. In Figure 5b, the initial slope at vanishing carbohydrate concentrations as calculated from eq 8 using the weight fractions of maltose and maltopolymer is seen to decrease with increasing maltose concentrations but less rapidly than predicted based on an infinite degree of polymerization for the maltopolymer (curve 1). If the sorption data at infinite dilution are fitted with free parameters x_m and x_p (curve 2), then we obtain x_m = 1.13, which is very close to our assumed value of 1, and x_p = 6.96, which is lower than the value of about 40 that we expect based on the molecular-weight characterization (see the Materials and Methods section). This could be caused by the branching of the maltopolymer, which would influence the entropy of the chain and thereby could limit its effective degree of polymerization. Interestingly, maltose−water mixtures behave as ideal solutions in the rubbery state, as is witnessed by the slope $d\phi_w/da_w$, which is close to unity over the whole concentration range. This is confirmed by published data on maltose−water solutions,[30] when replotted on molar basis.

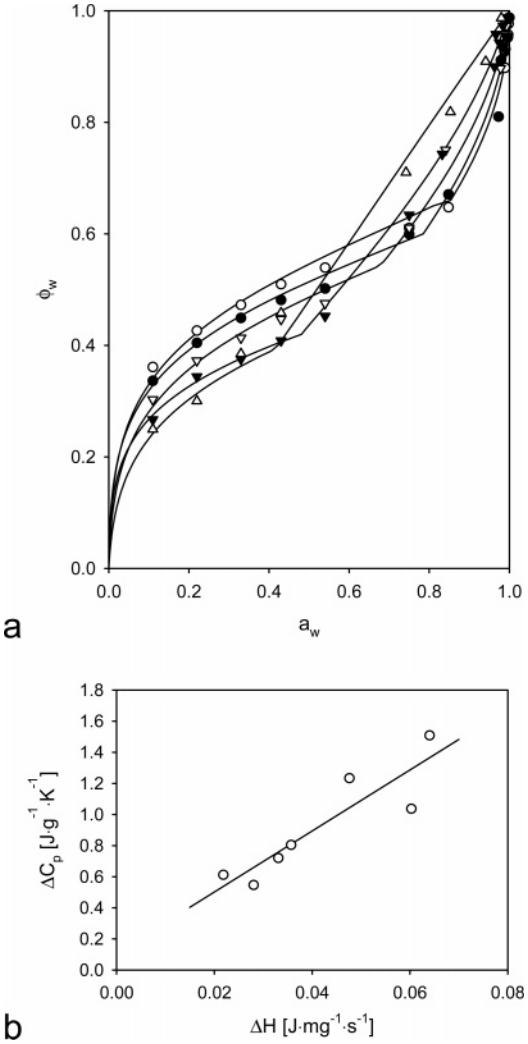

Figure 6. (a) Fit of the water sorption data expressed on a molar basis using the free-volume model by Vrentas and Vrentas.[9] Fitting parameters are given in Table 4: open circles, 100% maltopolymer system; filled circles, 90−10; open triangles down, 80−20; filled triangles down, 60−40; open triangles up, 100% maltose system. (b) Correlation between the difference in heat capacity between the glassy and rubbery states from the fit of the sorption isotherm and the change in heat flow in the vicinity of T_g. The heat flow data are from the samples equilibrated at a_w = 0.43 (a_w = 0.33 for the 100% maltose sample; T = 25 °C). The solid line is the linear regression of the data; R^2 = 0.81.

If water is removed from the dilute solution state, then the Flory−Huggins model will initially remain valid. However, if enough water is removed, then the carbohydrate−water system will pass through the glass transition. In the glassy state, the sorption mechanism will become dependent on the carbohydrate molecular packing and the history of the glassy state. Consequently, in the vicinity of the glass transition, the sorption mechanism changes from one dominated by the mixing entropy of carbohydrates and water to one dependent on the properties of a single, quenched conformation of the carbohydrates.

Various theoretical approaches have been forwarded for the sorption of low-molecular-weight diluents by glassy polymer matrixes, the principal of which are the free-volume models discussed in the Introduction. The isotherm equations resulting for glassy-state sorption from the free-volume models have the general form[9,10]

$$a_w = \phi_w \exp[(1 - \phi_w) + \chi(1 - \phi_w)^2 + F(\phi_w)] \qquad (8)$$

where $F(\phi_w)$ is a function that is dependent on the volume fraction of water or polymer and that vanishes at the volume fraction of water ϕ_{w,T_g} at which the glass transition temperature equals the experimental temperature.

Specifically, in the free-volume theory by Vrentas and Vrentas, the function F takes on the following form[9]

$$F(\phi_w) = \frac{1}{RT} M_{w,w} Q_c(\phi_w)^2 \Delta\bar{C}_p \left(\frac{dT_g(\phi_w)}{dQ_w(\phi_w)}\right)\left(\frac{T - T_g(\phi_w)}{T_g(\phi_w)}\right) \qquad (9)$$

where R is the gas constant and $\Delta\bar{C}_p$ is the difference in heat capacity between the polymer matrix in the rubbery and glassy states.

Within the framework of their free-volume theory incorporating the osmotic elasticity of the polymer glass, Leibler and Sekimoto derive the following expression for F[10]

$$F(\phi_w) = -\bar{v}_m K_g \log\left(\frac{1 - \phi_w}{1 - \phi_{w,T_g}}\right) \qquad (10)$$

where $\bar{v}_m$ is the partial molar volume of the penetrant and K_g is the contribution to the bulk modulus resulting from the softening of the matrix at T_g.

An issue with isotherm models of the form of eq 8 is that they assume ideal mixing of polymer chains and water in the glassy state. Whereas the mobility of water remains relatively high in the glassy state, the overall conformations of the polymer chains are effectively frozen out, and only some minor local rearrangements are possible. We thus expect that the mixing entropy of water and polymer in the glassy state is overstated by the Flory−Huggins theory.

An alternative approach to sorption in the glassy state is by assuming that within the glassy carbohydrate matrix water binds to essentially discrete sites, which, because of the quenched nature of the glassy state, may structurally and energetically be heterogeneous. As argued by Benczédi et al.,[16] such localized binding of water on a heterogeneous distribution of sites in the carbohydrate glass may be modeled by a Freundlich type equation.[17] Following our previously published work on maltodextrin−water systems, we will use the Freundlich equation in the following form[11,12]

$$\phi_w = K_{Fr} {a_w}^{1/c} \qquad (11)$$

where ϕ_w is the lattice volume fraction of water (Appendix 1) and K_{Fr} and c are fitting coefficients. It has been shown that within the Freundlich model the sorption is taking place on a system characterized by a distribution of sorption sites of which the sorption energy varies logarithmically with the degree of sorption.[17,25,26] Even though based on a physical model, the Freundlich model is generally not considered to be a truly predictive sorption model as its parameters are difficult to estimate from independent experiments. These parameters include molecular distribution of sorption sites and the heat of sorption of these sites.[16]

Table 4. Fitting Coefficients of the Free-Volume Model by Vrentas and Vrentas[9] for the Water Sorption by Bidisperse Carbohydrate Matrixes in the Glassy State ($T = 25$ °C)[a]

maltopolymer content[b] (wt %)	maltose content[b] (wt %)	ΔC_p (J g^{-1} K^{-1})
100	0	0.547
95	5	0.612
90	10	0.720
80	20	0.804
60	40	1.23
30	70	1.04
0	100	1.51

[a] The Flory−Huggins parameters are as in Table 3. [b] Carbohydrate composition is expressed on the basis of the total carbohydrate content.

The modeling of the glassy-state water sorption by the Freundlich equation and the rubbery-state sorption by the Flory−Huggins theory implies a two-state model. In the glassy state, the entropy of the carbohydrate molecules is assumed to be zero, but water can still diffuse and occupy sites within the carbohydrate structure. In the rubbery state, the sorption mechanism is largely determined by the mixing entropy of the carbohydrate and water molecules. To be thermodynamically consistent, we assume that, at the glass−rubber transition, the carbohydrates and water, which are completely or almost completely in the glassy state, are converted to a mobile phase allowing free mixing. In this case, the conditions for coexistence between the glassy and the rubbery states become

$$\phi_{w,G}(a_w^*) = \phi_{w,R}(a_w^*) = \phi_w(a_w^*) \qquad (12)$$

where a_w^* indicates the critical value of the water activity at which the glass transition temperature equals the experimental temperature (25 °C) and the subscripts "G" and "R" denote the glassy and rubbery states.

We start by analyzing the glassy-state sorption of the bidisperse carbohydrate matrixes using the two free-volume models. In Figure 6a, the sorption isotherms following the optimal fit to the model by Vrentas and Vrentas[9] are shown, where it should be noted that the rubbery-state data are fitted using the Flory−Huggins theory. As the Gordon−Taylor fit of the T_g data can be used as an input to eq 9, the only fitting parameter that is left is the heat capacity of the carbohydrate matrix (Table 4). Data on ΔC_p of the maltopolymer−maltose matrixes are not available; however, we note that the fitted values are of the proper order of magnitude and fairly close to a value judged to be reasonable for poly(vinyl pyrrolidone) in water.[18] In addition, ΔC_p is proportional with a fair degree of accuracy to the step in heat flow observed around the glass transition temperature (Figure 6b). As the overall fit of the sorption data by the model by Vrentas and Vrentas is satisfactory, we conclude that, within the symplifying assumptions of the theory, their free-volume model is physically robust and rather well adapted to fit the water sorption by the amorphous carbohydrate systems.

The alternative free-volume model, based on the theory of the osmotic elasticity of the polymer glass,[10] may also be used to fit the sorption data (Figure 7a). Again, we observe a rather good fit of the sorption data, but we require that the two fitting parameters, K_g and Q_w^*, have physically realistic values (Table 5). The values obtained for the elasticity coefficient K_g are of the proper order of magnitude[10] and, in addition, agree rather well with the difference in the value of the bulk modulus of maltodextrin matrixes between the glassy and the rubbery

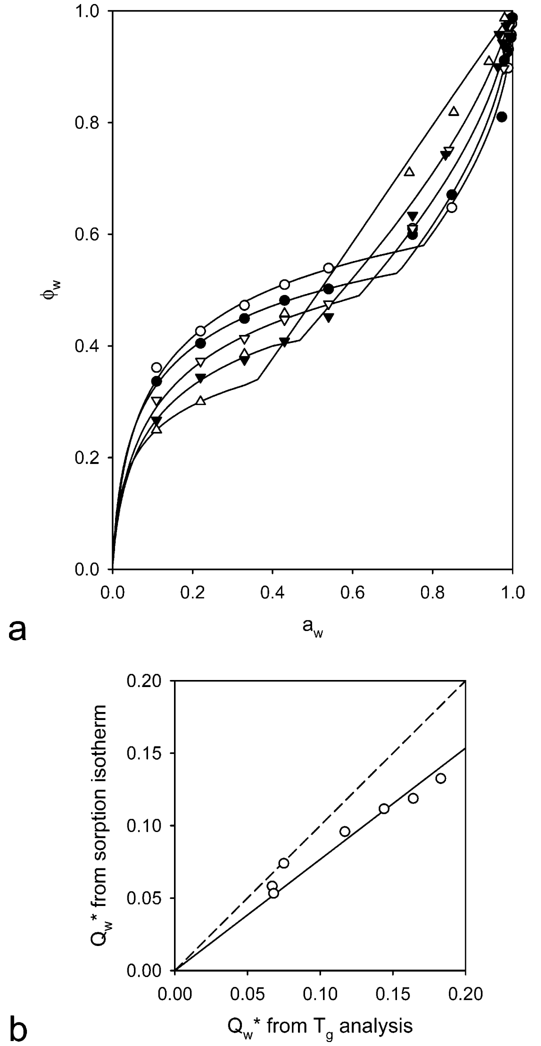

Figure 7. (a) Fit of the water sorption data expressed on a molar basis using the free-volume model by Leibler and Sekimoto.[10] Fitting parameters are given in Table 5: open circles, 100% maltopolymer system; filled circles, 90−10; open triangles down, 80−20; filled triangles down, 60−40; open triangles up, 100% maltose system. (b) Correlation between the critical weight fraction of water at which the glassy- and rubbery-state branches of the sorption isotherms according to the model by Leibler and Sekimoto intersect and the critical weight fraction of water at which T_g as determined by DSC equals the experimental temperature (25 °C). The dashed line has a slope of 1, and the solid line represents the linear regression of the data; $R^2 = 0.92$.

states.[12] K_g has been obtained from the fit of the sorption data using the partial molar volume of water in the carbohydrate matrixes (Table 5), which in the glassy state turns out to be virtually independent of the water content but which, interestingly, depends on the maltose content of the blends.[13] The second fitting parameter is the weight fraction of water Q_w* at which the glass transition of the maltopolymer−maltose matrixes equals the experimental temperature of 25 °C. Consequently, if the model by Leibler and Sekimoto[10] is physically correct, then Q_w^* as determined from the sorption isotherm should equal Q_w^* from the DSC analysis. Figure 7b indeed shows a linear relation between the two parameters but with values of Q_w^* from the sorption analysis that are generally somewhat too low. However, we note that deviation is not large enough to invalidate the physical assumptions behind the free-volume model by Leibler and Sekimoto, and it provides an interesting viewpoint complementary to the theory by Vrentas and Vrentas[9] for the sorption of water by the glassy-state carbohydrate matrixes.

Table 5. Fitting Coefficients of the Free-Volume Model by Leibler and Sekimoto[10] for the Water Sorption by Bidisperse Carbohydrate Matrixes in the Glassy State ($T = 25$ °C)[a]

maltopolymer content[b] (wt %)	maltose content[b] (wt %)	$\bar{v}_m$ [c] (cm^3 g^{-1})	$K_g \times 10^9$ (Pa)	Q_w^* [d]
100	0	9.68	1.93	0.132
95	5	9.50	2.22	0.117
90	10	9.69	2.39	0.112
80	20	10.60	1.96	0.0958
60	40	11.93	2.05	0.0739
30	70	12.74	2.31	0.0582
0	100	12.69	3.33	0.0532

[a] The Flory−Huggins parameters are as in Table 3. [b] Carbohydrate composition is expressed on the basis of the total carbohydrate content. [c] The partial molar volume in the glassy state is found to be independent of the water content.[13] [d] Weight fraction of water at which the glassy-state sorption vanishes.

The fit of the water sorption of the glassy maltopolymer−maltose matrixes by the Freundlich equation is best observed from a log−log plot of the sorption data

$$\ln \phi_w = \ln K_{Fr} + \frac{1}{c} \ln a_w \tag{13}$$

Figure 8a shows that for all maltopolymer−maltose compositions the fit of the glassy-state sorption by eq 13 is very good. The coefficients of the fit of the Freundlich equation are collected in Table 6.

The coefficients from the Freundlich model are directly related to the specific volume of the anhydrous carbohydrate matrixes. To a high degree of precision, K_{Fr} is linearly related to the specific volume of the anhydrous carbohydrate matrixes (Figure 8b). This linear variation of the water sorption with the specific volume in the anhydrous state strongly hints at the role of interstitial spaces or free volume in the sorption of water. In addition, it could well be that because of the denser and more optimal packing of the carbohydrates in matrixes containing higher amounts of the low-molecular-weight maltose the degree of hydrogen bonding between the carbohydrate molecules becomes significantly higher with increasing maltose content,[11,28] which reduces the number of sites available for the binding of water.

If the Freundlich isotherm for the glassy state and the Flory−Huggins isotherm for the rubbery-state sorption are combined following eq 12, then we obtain an excellent fit of the sorption data (Figure 9a). An important test for the validity of the two-state model is the correlation between the critical water activity a_w^* at which T_g is 25 °C from the calorimetric analysis and from the two-state model, which we observe to be excellent (Figure 9b).

In our combination of the Freundlich and Flory−Huggins models, we have assumed a discrete transition between the glassy-state and the rubbery-state sorption at T_g (eq 12). Tomka and co-workers, however, have argued that over the range $0 \leq a_w \leq 1$, the solid phase, modeled by the Freundlich isotherm, and the fluid phase, modeled by the Flory−Huggins isotherm, are in coexistence[6,16]

$$\phi_c + \phi_w = \phi_c + \phi_{w,G} + \phi_{w,R} \tag{14}$$

where the subscripts “G” and “R” denote the glassy and rubbery states. In this representation, the volume fraction of water absorbed in the solid phase is essentially immobile (bound to the carbohydrate). The equilibrium sorption isotherm is then obtained by fitting the combined Freundlich and Flory−Huggins

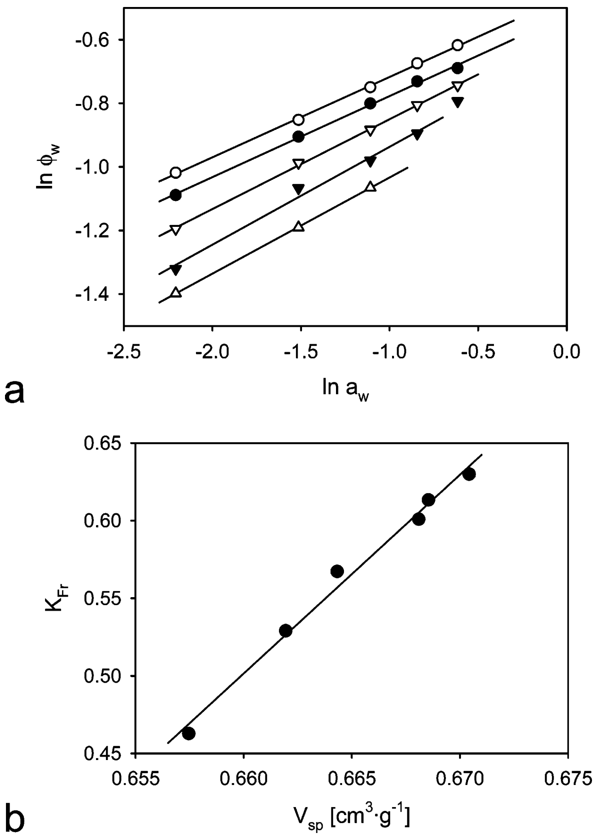

Figure 8. (a) Fit of the glassy-state sorption data to the Freundlich equation (eq 8). The symbols represent the various maltopolymer−maltose compositions (all in wt % based on total carbohydrate content): open circles, 100−0 (pure maltopolymer); filled circles, 90−10; open triangles down, 80−20; filled triangles down, 60−40; open triangles up, 30−70. The fitting coefficients are collected in Table 6. The regression coefficients of the fits to the data are $R^2 \geq 0.99$ for all maltopolymer−maltose compositions (including the 95−5 and the 0−100 compositions which are not shown). (b) Relation between the Freundlich isotherm model coefficient K_{Fr} and the specific volume of the anhydrous maltopolymer−maltose compositions at $T = 25$ °C. Regression coefficient of the linear fit to the data; $R^2 = 0.99$.

Table 6. Fitting Coefficients of the Freundlich Model for the Water Sorption by Bidisperse Carbohydrate Matrixes in the Glassy State ($T = 25$ °C)[a]

maltopolymer content[b] (wt %)	maltose content[b] (wt %)	K_{Fr}	c	a_w^* [c]
100	0	0.630	3.928	0.79
95	5	0.613	3.769	0.76
90	10	0.601	3.813	0.74
80	20	0.567	3.539	0.63
60	40	0.529	3.311	0.43
30	70	0.463	3.623	0.38
0	100	0.450	3.740	0.35

[a] The Flory−Huggins parameters used to calculate a_w^* are as in Table 3. [b] Carbohydrate composition is expressed on the basis of the total carbohydrate content. [c] Critical water activity at which the Freundlich fit to the glassy-state data and the Flory−Huggins fit to the rubbery-state data intersect.

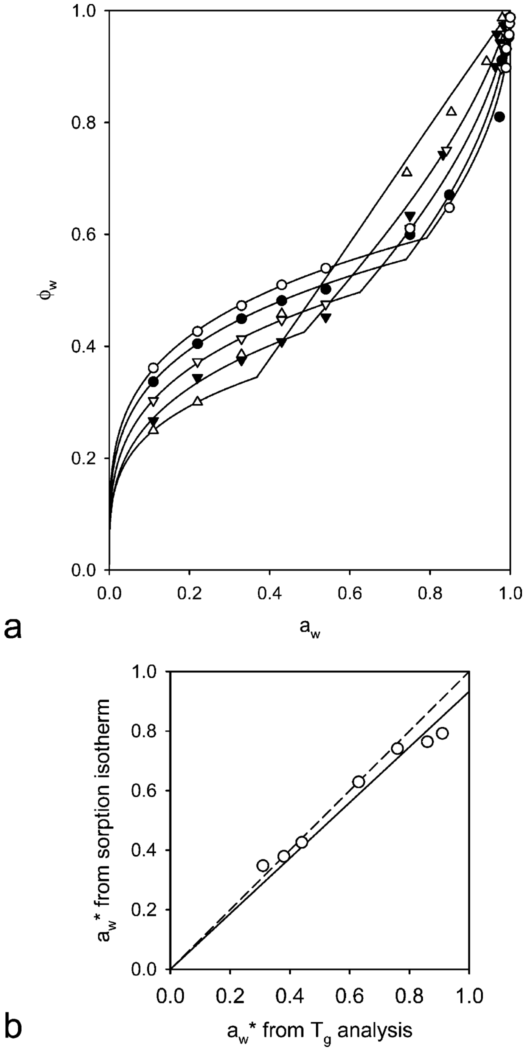

Figure 9. (a) Fit of the water sorption data expressed on a molar basis using the Freundlich model for sorption in the glassy state and Flory−Huggins sorption for the rubbery state. Fitting parameters are given in Table 6: open circles, 100% maltopolymer system; filled circles, 90−10; open triangles down, 80−20; filled triangles down, 60−40; open triangles up, 100% maltose system. (b) Correlation between the critical water activity at which the glassy- and rubbery-state branches of the sorption isotherms of Figure 7 intersect and the critical water activity at which the T_g as determined by DSC equals the experimental temperature (25 °C). The dashed line has a slope of 1, and the solid line represents the linear regression of the data; $R^2 = 0.95$.

isotherms to the experimental data with a variable set of parameters for each individual data point,[16] which we feel is incorrect. One other feature of the approach taken by Benczédi et al.[16] is that the fraction of water bound by the carbohydrate remains high even in the rubbery state. Whereas for thermoplastic starch, this could be an acceptable assumption, as such starch matrixes do not readily dissolve but rather swell when exposed to liquid water, for carbohydrate matrixes in general this assumption is not justified. In any case, the fraction of water bound to the polymer should vanish in the limit of infinite dilution. This theoretically important limit is however not included in ref 16.

Both the free-volume models and the two-state sorption model combining a Freundlich model for the glassy-state model and a Flory−Huggins model for the rubbery-state sorption are consistent with all physical data presented in our paper (specific volume, glass transition, and molecular-weight dependence of the rubbery-state sorption data). However, we emphasize that the consistency of such correlations is a necessary but not a sufficient condition to unequivocally prove the applicability of the physical mechanism underlying a specific model. We suggest further studies to enable a clear choice between the two approaches toward the modeling of the moisture sorption by carbohydrate matrixes in the glassy state. Such studies could encompass temperature-dependent sorption isotherms, Fourier transform infrared (FTIR) spectroscopy and NMR studies of hydrogen bonding between water and carbohydrates in the glassy state, and computer simulations.

Both the GAB model and the model by Tomka and coworkers[16] can be eliminated as being physically appropriate to model the sorption of water by amorphous carbohydrates. For GAB model, one of the parameters is shown to correlate with the specific volume, but the correlations with the glass transition and the molecular-weight dependence of the rubbery-state sorption data are inconsistent. As discussed above, the model by Benczédi et al.[16] contains an interesting point of view for the glassy-state sorption but is in its present formulation thermodynamically not fully consistent.

Concluding Remarks

The sorption of water by carbohydrate systems is strongly dependent on the carbohydrate composition but in different ways in the glassy and rubbery states. This is demonstrated by approaching the sorption of water from two limiting cases: the glassy state at low water content and the dilute solution of the carbohydrates. In the glassy state, a principal factor determining the sorption of water is the molecular packing of the carbohydrates. The carbohydrate molecules pack more densely when the molecular weight is decreased, giving rise to a reduced interstitial volume and most likely a higher degree of hydrogen bonding between the carbohydrates. Both factors lead to a reduced water uptake at constant water activity by the carbohydrate glass containing a higher amount of low-molecular-weight carbohydrates. Conversely, in the rubbery state, the carbohydrate system with the lowest molecular weight will have the highest water uptake at a constant water activity because at a constant number of carbohydrate units the mixing entropy increases with decreasing molecular weight.

Of the various theoretical approaches forwarded to explain the sorption of low-molecular-weight penetrants by glassy polymer matrixes, the free-volume models and the two-state sorption model are consistent with all available experimental data. Both free-volume models analyzed in the context of the present paper provide physically realistic values for the model parameters, and both models are thus essentially predictive. As good agreement is also obtained for the two-state sorption model, the issue of the glassy-state entropy remains open for the moment. We suggest temperature-dependent sorption experiments, eventually combined with FTIR and NMR measurements and computer simulations to probe the impact of hydrogen bonding on the state of absorbed water, to resolve this issue. We anticipate that the quantitative, mechanistic understanding of the sorption of water in carbohydrate matrixes will enable a rational control of processing and storage conditions of carbohydrate-based systems. In addition, the use of concepts such as mixing entropy and molecular packing provides a basis to analyze functional properties of carbohydrates, such as barrier properties and swelling.

Appendix 1: Flory−Huggins Theory for Ternary Systems Consisting of Maltopolymer, Maltose, and Water

We consider a ternary system consisting of water (component 1), maltose (component 2), and a maltopolymer (component 3). In the rubbery state, a major contribution to the sorption isotherm is the mixing entropy of carbohydrate molecules and water.

In the Flory−Huggins approximation, the system is considered as a lattice fluid with sites of uniform size. These sites may each contain one effective unit of water, maltose, or the maltopolymer. If we assume that the number of units in water and maltose is equal to one and that there are x units in the maltopolymer, then we can express the concentrations of each component in terms of the volume fraction of lattice sites[6]

$$\phi_{\mathrm{w}} = \frac{n_{\mathrm{w}}}{n_{\mathrm{w}} + x_{\mathrm{m}}n_{\mathrm{m}} + x_{\mathrm{p}}n_{\mathrm{p}}}$$

$$\phi_{\mathrm{m}} = \frac{x_{\mathrm{m}}n_{\mathrm{m}}}{n_{\mathrm{w}} + x_{\mathrm{m}}n_{\mathrm{m}} + x_{\mathrm{p}}n_{\mathrm{p}}}$$

$$\phi_{\mathrm{p}} = \frac{x_{\mathrm{p}}n_{\mathrm{p}}}{n_{\mathrm{w}} + x_{\mathrm{m}}n_{\mathrm{m}} + x_{\mathrm{p}}n_{\mathrm{p}}} \tag{A.1}$$

where n_{w} and n_{m} denote the number of water and maltose molecules, respectively, and n_{p} is the number of maltopolymer molecules. The factors x_{m} and x_{p} are not necessarily equivalent to the degree of polymerization but rather reflect the number of effective units, which, however, should be reasonably close to the degree of polymerization, which is 2 for maltose and about 40 for the maltopolymer.

The entropy of mixing of the three components is then given by

$$-\frac{\Delta S}{k_{\mathrm{B}}} = n_{\mathrm{w}} \ln \phi_{\mathrm{w}} + n_{\mathrm{m}} \ln \phi_{\mathrm{m}} + n_{\mathrm{p}} \ln \phi_{\mathrm{p}} \tag{A.2}$$

where k_{B} is Boltzmann's constant.

As usual in the Flory−Huggins theory, we use a Scatchard type relation for the enthalpy of mixing of the three components[6]

$$\frac{\Delta H}{k_{\mathrm{B}}T} = \chi_{\mathrm{wm}} \frac{n_{\mathrm{w}}x_{\mathrm{m}}n_{\mathrm{m}}}{n_{\mathrm{w}} + x_{\mathrm{m}}n_{\mathrm{m}} + x_{\mathrm{p}}n_{\mathrm{p}}} + \chi_{\mathrm{wp}} \frac{n_{\mathrm{w}}x_{\mathrm{p}}n_{\mathrm{p}}}{n_{\mathrm{w}} + x_{\mathrm{m}}n_{\mathrm{m}} + x_{\mathrm{p}}n_{\mathrm{p}}} + \chi_{\mathrm{mp}} \frac{x_{\mathrm{m}}n_{\mathrm{m}}x_{\mathrm{p}}n_{\mathrm{p}}}{n_{\mathrm{w}} + x_{\mathrm{m}}n_{\mathrm{m}} + x_{\mathrm{p}}n_{\mathrm{p}}} \approx \chi n_{\mathrm{w}}(\phi_{\mathrm{m}} + \phi_{\mathrm{p}}) \tag{A.3}$$

where T is the absolute temperature. For simplicity, we assume that $\chi_{\mathrm{wm}} = \chi_{\mathrm{wp}} \equiv \chi$ and $\chi_{\mathrm{mp}} = 0$.

From the total free energy of mixing $\Delta G = \Delta H - T\Delta S$ the activity coefficient of water is calculated by partial differentiation

$$a_{\mathrm{w}} = \exp\left(\frac{\mu_1 - \mu_1^{\circ}}{RT}\right) = \exp\left(\frac{1}{RT}\left(\frac{\partial \Delta G}{\partial n_{\mathrm{w}}}\bigg|_{T,p,n_{\mathrm{m}},n_{\mathrm{p}}} - \mu_1^{\circ}\right)\right) = \phi_{\mathrm{w}} \exp\left((1 - \phi_{\mathrm{w}}) - \frac{\phi_{\mathrm{m}}}{x_{\mathrm{m}}} - \frac{\phi_{\mathrm{p}}}{x_{\mathrm{p}}} + \chi(1 - \phi_{\mathrm{w}})^2\right) \tag{A.4}$$

Assuming that $x_{\mathrm{p}} \gg 1$ and $x_{\mathrm{m}} = 1$ and realizing that in the sorption experiments the ratio of maltose to maltopolymer is constant, we may write

$$a_{\mathrm{w}} = \phi_{\mathrm{w}} \exp\left[(1 - \phi_{\mathrm{w}})\frac{1}{1 + r} + \chi(1 - \phi_{\mathrm{w}})^2\right] \tag{A.5}$$

where $r = \phi_{\mathrm{m}}/\phi_{\mathrm{p}}$. In the limits of vanishing maltose concentration and vanishing maltopolymer concentration, eq A.5 simplifies to

$$a_{\mathrm{w}} = \phi_{\mathrm{w}} \exp[(1 - \phi_{\mathrm{w}}) + \chi(1 - \phi_{\mathrm{w}})^2] \quad r \rightarrow 0 \tag{A.6a}$$

$$a_{\mathrm{w}} = \phi_{\mathrm{w}} \exp[\chi(1 - \phi_{\mathrm{w}})^2] \quad r \rightarrow \infty \tag{A.6b}$$

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