WATER ADSORPTION ISOTHERMS OF SOME MALTODEXTRIN SAMPLES

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Abstract

The water sorption isotherms of some maltodextrins with dextrose equivalent values ranging from 5 to 25 were determined using an isopiestic method in the range of water activity between 0.1 to 0.98 and at a temperature of 298 K. The Guggenheim - Anderson - de Boer model (GAB), the Brunauer - Emmett - Teller model (BET) and the Caurie model were tested to fit the experimental data. Equations of the GAB type and Caurie model fit the experimental data well between a_w = 0.1 to 0.9, while the BET equation fits only up to a_w = 0.6. The water content adsorbed in the monomolecular layers was evaluated. The constants related to the heat of sorption for the first and subsequent layers of molecules and to the heat of condensation of pure water were estimated. On the basis of the Caurie model the number of monolayers of water adsorbed and the area of one gram of adsorbent which contains only water molecules in the monolayer were calculated.

Introduction

A knowledge and understanding of the water sorption isotherms of foods or food ingredients is of greatest importance in food science and technology for many reasons, such as the design and optimisation of processing or shelf life stability predictions.

Many empirical relations describing the sorption characteristics of food or food ingredients have been proposed in the literature. Some workers[1] collected and classified more than 70 such equations. In the past, the well-kown Brunauer - Emmett - Teller (BET) sorption isotherm was the model with the greatest application to water sorption by foods and foodstuffs,[2,3] although it was known to hold only for a limited range of water activity. In more recent years, among the sorption models, the Gugenheim-Anderson de Boer (GAB) equation has been applied most successfully to various foods.[4,5] Adequately representing the experimental data in the range of water activity of most practical interest in foods, the GAB model has been recommended by the European Project Group COST 90 on the Physical Properties of Foods as the fundamental equation for the characterisation of the water sorption of food materials.[6]

The objectives of this research were to determine the water sorbtion isotherms at 298K for some maltodextrin samples of different dextrose equivalent values by an isopiestic method; to establish a sorption model capable of fitting the data in order to predict the moisture sorption isotherms at the temperature studied; to calculate the monolayer moisture content; to estimate the constants related to the heat of sorption for the first and subsequent layers of molecules and to the heat of condensation of pure water; and to calculate the number of monomolecular layers of water adsorbed and the area of one gram adsorbent which contains only water molecules in the monolayer.

Experimental

The samples of investigated maltodextrins were first dried under vacuum at room temperature over P_2O_5 to constant weight. The origin and quality of the maltodextrin samples is given in Table 1.

To determine the moisture sorption isotherms the isopiestic method was used.[7] Maltodextrin samples (approximately 0.3g) were weighed into gold-plated silver containers and placed inside a vacuum desiccator containing a saturated salt solution of known water activity.[8] The range of a_w from 0.1105 to 0.9800 was studied. The desiccators with the samples were kept in a temperature controlled environment at 298±0.1K. After four days equilibrium was considered to be reached and the amount of water adsorbed on the maltodextrin sample was determined by re-weighing the containers and the contents. The uncertainty in the determination of water adsorbed on the sample was ±0.001g.

Results and discussion

The experimental data of the eqilibrium water content of maltodextrin samples at each water activity at 298 K are given in Table 2. The eqilibrium water content at each a_w represents the mean value of two replictes. The standard deviation of each experimental value ranged from 0.0002 to 0.0080.

Table 1: The origin and the dextrose equivalent, DE, of investigated maltodextrin samples.

Sample No.	Origin	DE
1	KMS-X, Helios	5-10
2	KMS-X-50, Helios	10-15
3	KMS-X-70, Helios	15-20
4	Ipok	5-25
5	Cerestar	17-20
6	Maldex150, Helios	15

Table 2: Thermodynamic water activity, a_w, and water content expressed on a dry weight basis, w (g/g), for maltodextrin samples at a temperature of 298 K.

a_w	w (g/g)					
	Sample No.					
	1	2	3	4	5	6
0.1105	0.0361	0.0363	0.0455	0.0266	0.0298	0.0368
0.2245	0.0556	0.0528	0.0611	0.0390	0.0421	0.0533
0.3300	0.0641	0.0624	0.0723	0.0497	0.0527	0.0598
0.4276	0.0821	0.0813	0.0860	0.0710	0.0676	0.0730
0.4997	0.0898	0.0905	0.1007	0.0847	0.0853	0.0888
0.6183	0.1136	0.1144	0.1204	0.1142	0.1107	0.1150
0.7528	0.1629	0.1574	0.1524	0.1794	0.1719	0.1631
0.8640	0.1980	0.1996	0.1966	0.2478	0.2538	0.2458
0.9248	0.3165	0.3296	0.2349	0.4322	0.3962	0.4139
0.9730	0.5397	0.6057	0.4059	0.9932	0.8815	0.8609
0.9800	0.5162	0.5507	0.3839	1.1499	1.0416	1.0068

The data for water adsorption were correlated by the GAB equation[9] given as:

$$\frac{a_w}{w} = \frac{1 - 2ka_w + Cka_w + k^2 a_w^2 - Ck^2 a_w^2}{Ckw_m} \quad (1)$$

where a_w denotes the water activity, w is the water content adsorbed on 1 g of sample, w_m is the water content adsorbed in the monolayer, and C and k are the sorption constants. After introducing the parameters $\alpha = (k/w_m)[(1/C)-1]$, $\beta = (1/w_m)[1- (2/C)]$, and $\chi = 1/(w_mCk)$, the GAB equation takes the form:

$$\frac{a_w}{w} = \alpha . a_w^2 + \beta . a_w + \chi \qquad (2)$$

The values of parameters α, β, χ obtained by non-linear regression analysis of the experimental data in the a_w range 0.1105 - 0.9800 are given in Table 3. In Figure 1, where the dependence of w on water activity for sample No.6. is presented, we can see that through the whole range of a_w the experimental data for w agree very well with the theoretical values obtained by the GAB equation.

Table 3: Values of parameters of equation (2), α, β, χ and the standard deviation of regression analysis, s_d, for maltodextrin samples at a temperature of 298 K.

Sample No.	α	β	χ	s_d
1	-16.4 ± 1.3	17.0 ± 1.5	1.23 ± 0.36	0.28
2	-17.0 ± 1.3	17.3 ± 1.4	1.26 ± 0.35	0.27
3	-17.1 ± 1.1	17.4 ± 1.3	1.24 ± 0.33	0.26
4	-17.3 ± 1.3	14.8 ± 1.5	3.06 ± 0.39	0.30
5	-18.9 ± 1.0	17.2 ± 1.2	2.29 ± 0.30	0.23
6	-19.9 ± 0.7	19.6 ± 0.8	1.01 ± 0.21	0.16

The temperature dependent sorption constant C from Eq. (1) is given through the following relation:

$$C(T) = C^{'} \exp(\Delta H_1 - \Delta H_m)RT \qquad (3)$$

where ΔH_1 means the total heat of sorption of water molecules on the first layer on primary sites and ΔH_m means the total heat of sorption of the multilayer, while C' is the proportionality constant. The constant k in Eq.(1) is given as:

$$k(T) = k^{'} \exp(\Delta H_L - \Delta H_m)RT \qquad (4)$$

where ΔH_L is the heat of condensation of pure water and k' is the proportionality constant.

From the parameters α, β, χ the values of w_m, C and k were calculated through the following realtions:

$$w_m = \frac{1}{\sqrt{\beta^2 - 4\alpha\chi}} \quad (5)$$

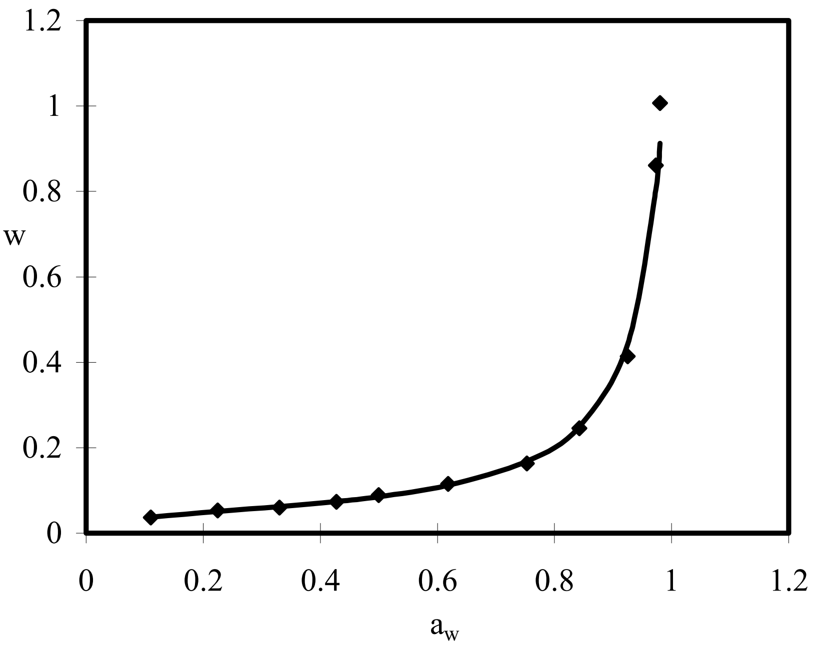
$$C = \frac{2 \pm \sqrt{\beta^2 - 4\alpha\chi}}{-\beta + \sqrt{\beta^2 - 4\alpha\chi}} \quad (6)$$

$$k = \frac{\beta \pm \sqrt{\beta^2 - 4\alpha\chi}}{2\chi} \quad (7)$$

The values of constants k and C are given in Table 4.

Table 4: Values of parameters w_m, k and C for maltodextrin samples at a temperature of 298 K.

Sample No.	w_m	k	C
1	0.0522	0.91	17.11
2	0.0510	0.92	16.91
3	0.0507	0.92	17.27
4	0.0482	0.97	6.96
5	0.0463	0.97	9.71
6	0.0464	0.97	22.09



Graph 1: The dependence of w against a_w for maltodextrin sample No. 6 at 298 K (◆, experimental values; –, GAB adsorption isotherm).

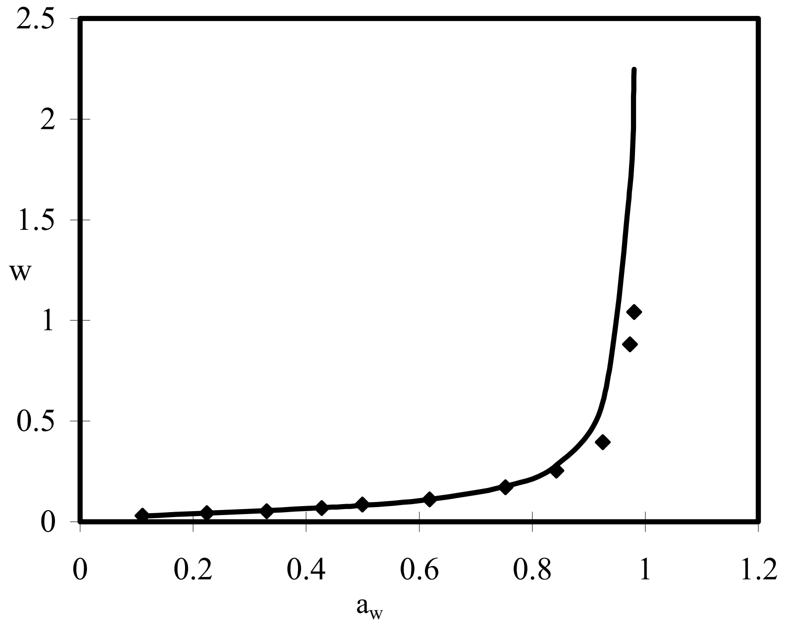
The experimental data were also fitted to the BET adsorption isotherm equation[10] given in linearised form:

$$\frac{a_w}{(1-a_w)w} = \frac{1}{w_m C} + \frac{a_w(C-1)}{w_m C} \tag{8}$$

The values of parameters $1/(w_m.C)$ and $(C-1)/(w_m.C)$ obtained by linear regression analysis and the values of w_m and constant C are given in Table 5. The range of a_w where the data were fitted was 0.1105-0.6183. It was observed by many workers[2,3,11] that BET plots are linear plot only at low water activities, $a_w < 0.5$. For $a_w > 0.5$ deviation from linearity is observed with the upswing of the BET plot indicating that at higher water activities less water is adsorbed than that predicted by the BET equation. The same was observed in our investigation, as could be seen in Figure 2 where for maltodextrin sample No. 5 the sorption isotherm obtained through the BET equation is plotted.

Table 5: The values of parameters of equation (3), $1/(w_mC)$, $(C-1)/(w_mC)$, w_m, C and the standard deviation of regression analysis, s_d, for maltodextrin samples at a temperature of 298 K.

Sample No.	$\frac{C-1}{w_m C}$	$\frac{1}{w_m C}$	sd	w_m	C
1	21.1 ± 1.1	0.68 ± 0.46	0.47	0.0458	31.65
2	20.6 ± 1.0	0.91 ± 0.39	0.40	0.0463	23.70
3	20.5 ± 1.0	0.15 ± 0.43	0.44	0.0483	129.60
4	17.8 ± 1.3	3.18 ± 0.53	0.54	0.0476	6.59
5	19.9 ± 1.0	2.29 ± 0.40	0.41	0.0450	9.67
6	21.1 ± 0.6	0.97 ± 0.27	0.27	0.0452	22.58

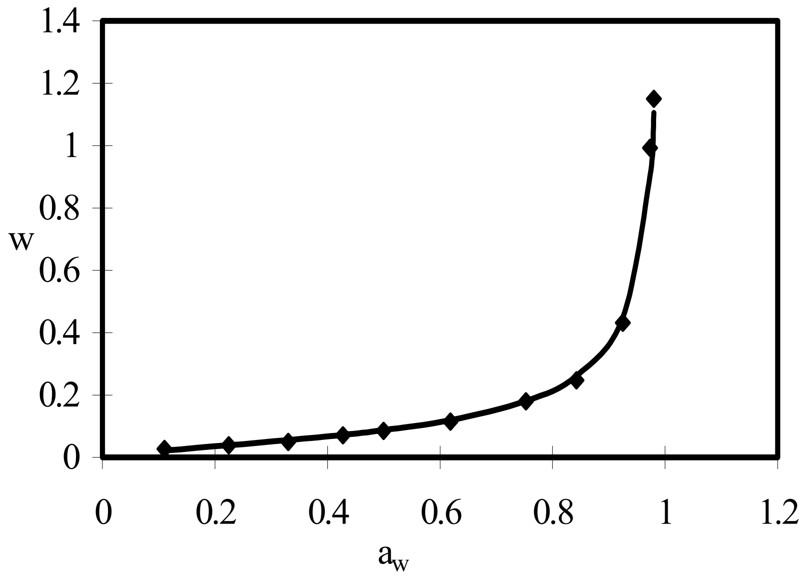


Graph 2: The dependence of w against a_w for maltodextrin sample No. 5 at 298 K (◆, experimental values; –, BET adsorption isotherm).

To test the experimental results the Caurie adsorption isotherm equation[12] was also used:

$$\ln\left(\frac{1}{m}\right) = -\ln(c.m_0) + \frac{2c}{m_0}\ln\left(\frac{1-a_w}{a_w}\right) \tag{9}$$

where m is the water content adsorbed on 100g of sample, m_0 is the water content in the monolayer adsorbed on 100 g of sample and c is a constant proportional to the heat of adsorption in the monolayer. The values of parameters $\ln(c.m_0)$ and $2c/m_0$ were obtained by linear regression analysis of the experimental data in the range of a_w of 0.1105 - 0.9800. The values of parameters $\ln(c.m_0)$ and $2c/m_0$ and the values of m_0 and constant c are given in Table 6. In Figure 3 the sorption isotherm obtained on the basis of the Caurie equation is plotted.



Graph 3: The dependence of w against a_w for maltodextrin sample No. 4 at 298 K (◆, experimental values; –, Caurie adsorption isotherm).

A parameter closely related to the phenomena of adsorption is the area of one gram of adsorbent which contains only water molecules in the monolayer, A and the number of monolayers of water adsorbed, N. Assuming that the magnitude of c in Eq.(9) equals the density of adsorbed water in the monolayer, A was calculated as:

$$A = \frac{m_0}{cd10^8} \tag{10}$$

where d is the diameter of a water molecule ($d = 3.673.10^{-10}$m)[12]. N was calculated as:

$$N = \frac{m_0}{c} \tag{11}$$

The values of N and A are given in Table 6.

Table 6: Values of parameters of Eqation (4), $\ln(cm_0)$, $2c/m_0$, c, m_0, N, A and the standard deviation of regression analysis, s_d, for maltodextrin samples at a temperature of 298 K.

Sample No.	$\ln(cm_0)$	$2c/m_0$	s_d	c g/cm^3	m_0 g/100g	N	A m^2/g
1	2.241 ± 0.015	0.475 ± 0.009	0.045	1.495	6.289	4.206	114.51
2	2.237 ± 0.020	0.495 ± 0.011	0.061	1.523	6.152	4.039	109.98
3	2.288 ± 0.015	0.383 ± 0.008	0.045	1.374	7.175	5.221	142.15
4	2.169 ± 0.026	0.651 ± 0.013	0.080	1.688	5.183	3.069	83.56
5	2.183 ± 0.030	0.617 ± 0.015	0.092	1.655	5.361	3.238	88.17
6	2.274 ± 0.042	0.576 ± 0.020	0.127	1.673	5.809	3.471	94.50

It should be noted from Tables 3, 5 and 6 that the values for water content adsorbed in the monolayer, expressed as the mass of water adsorbed on one gram of sample, obtained by the GAB equation were higher than those obtained by the BET model, but the highest values were those calculated through the Caurie equation. This is in agreement with results obtained by some other authors.[13, 14] On the other had, it has been observed by many workers[2,15] that the energy constant obtained by the BET model is larger than the GAB value. That is also the case in our investigation.

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Povzetek

Nekaterim vzorcem maltodekstrina z dekstroznim ekvivalentom od 5 do 25 smo z izopiestično metodo določili sorpcijske izoterme v območju aktivnosti vode, a_w od 0,1 do 0,98 pri temperaturi 298 K. Eksperimentalne podatke smo obravnavali z Guggenheim - Anderson - de Boerovim modelom (GAB), Brunauer - Emmett - Tellerjevim model (BET) in Caurijevim modelom. Ugotovili smo, da GAB model in Caurijeva relacija dobro opišeta eksperimentalne podatke v celotnem a_w območju, medtem ko BET model zadovoljivo opiše eksperimentalne podatke samo do vrednosti a_w = 0.6. Izračunali smo količino vode, ki se adsorbira v monomolekulski plasti. Izračunali smo tudi konstante povezane s toploto sorpcije vode v prvem in višjih slojih ter s toploto kondenzacije vode. S Caurijevim modelom smo izračunali število monomolekulskih plasti in površino enega grama adsorbenta, ki je zasedena z molekulami vode v monomolekulski plasti.