Water activity of freeze dried mushrooms and berries

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Khalloufi, S., Giasson, J. and Ratti, C. 2000. **Water activity of freeze dried mushrooms and berries**. Can. Agric. Eng. **42**:051-056. Sorption isotherms at 4, 13, and 27°C were obtained for two types of berries (strawberries and blueberries) and three types of commercial and wild mushrooms (Shiitake *Lentinus edodes*, Enoki *Flammulina velutipes* and Morel *Morchella esculenta*). The products had been freeze-dried for 72 h and equilibrated over saturated salt solutions in a range of relative humidity from 11 to 87%. The equilibrium moisture content was obtained when there was no appreciable change in sample weight. The sorption of powdered and whole pieces of mushrooms was studied in order to evaluate possible effects of particle size on sorption characteristics. Two equilibrium models, GAB and one previously developed by one of the authors, were tested against the experimental data in order to determine the most appropriate mathematical representation. The constants required for each model were determined by non-linear regression analysis. **Keywords**: water activity, freeze-dried products, sorption isotherms, modelling.

Des isothermes de sorption ont été obtenues pour deux variétés des petits fruits (fraises et bleuets) et pour trois types de champignons comestibles (Shiitake *Lentinus edodes*, Enoki *Flammulina velutipes* et Morille *Morchella esculenta*). Les expériences se sont déroulées à 4, 13 et 27°C. Après avoir été lyophilisés durant 72 h, les échantillons sont mis en équilibre avec des solutions saturées entre 11 et 87% d'humidité relative. L'équilibre était observé lorsqu'il n'y avait plus de changement appréciable dans le poids de l'échantillon. Le comportement des champignons en poudre et des champignons en entier a été étudié afin de voir l'effet de la taille de particule sur les caractéristiques d'adsorption. Deux modèles, celui de GAB et un autre développé par un des auteurs, ont été testés afin de trouver la représentation mathématique la plus appropriée pour les résultats expérimentaux. Les constantes intervenantes dans chaque modèle ont été déterminées par l'analyse de la régression non-linéaire.

INTRODUCTION

Water activity (a_w) is defined as the ratio of the equilibrium water vapour pressure of a foodstuff (p_w, kPa) to the saturated vapour pressure (p_{wo}, kPa) at the same temperature. It is an important concept in the food industry since it is related to microbiological stability and physico-chemical deterioration reactions. Indeed, water is often the main component of a foodstuff, which also contains carbohydrates, proteins, fats, and mineral salts. At particular conditions of temperature and moisture, the interactions between these constituents can cause browning and lipid oxidation, among other reactions, and can provide the appropriate conditions for microbiological growth. Sorption isotherms, which describe water activity at a given temperature at different moisture contents, are therefore of special interest in the design of food preservation processes such as drying, freeze-drying, mixing, packaging, storage, etc., since they are required for the prediction of food stability, shelf life, and glass transitions, for estimating drying times, etc.

The sorption behaviour of various types of foods and the influence of temperature on equilibrium moisture content have been studied and modelled extensively during the past 50 years (Iglesias and Chirife 1976; Van den Berg 1984; Pioter 1997a, 1997b). The numerous mathematical expressions reported in the literature may be classified as theoretical, semi-empirical, or empirical models. Each of these models had relative success in reproducing equilibrium moisture content, depending on the water activity range or the type of foodstuff. Some of the better known correlations of water activity as a function of moisture content and temperature are the Thompson (1972) modification of the Henderson (1952) correlation, the Pfost et al. (1976) modification of Chung and Pfost's (1967) equation, and the Iglesias and Chirife (1976) modification of Halsey's (1948) equation. However, none of these are applicable to both high and low moisture products. A very popular general correlation, which is recommended by the European project COST90 on physical properties of foods (Van den Berg 1984; Maroulis et al. 1988), is the Guggenheim-Anderson-de Boer (GAB) equation. Other semi-empirical correlations based on thermodynamic considerations are those of Crapiste and Rotstein (1986) and Ratti et al. (1989). Several criteria to evaluate the applicability of different equilibrium correlations were tested on both latter expressions giving good results for a number of high and low moisture foodstuffs (Ratti et al. 1989).

Another interesting aspect that may be present in some mathematical models is water binding energy. The heat of sorption gives information on interaction forces between the water vapour molecules and the adsorbent surface (binding energy). This important thermodynamic parameter can also be determined from water sorption isotherms. The level of moisture content at which the heat of sorption approaches the heat of vaporisation of water is often taken as indicative of the amount of bound water existing in food (Medeni and Fahrettin 1997).

Table I shows information on highly perishable products of importance to Canada, such as berries and mushrooms. The market availability of these Canadian grown products is narrow, which in addition to their short shelf life due to high respiration rates, makes their preservation a crucial task. Freezing can increase their shelf life up to a year; however the thawed products usually exhibit structural collapse and lack of flavour. Drying, modified atmosphere storage, or freeze drying are preservation alternatives that may result in better quality in

Table I. Information on perishable products.

Product	Market availability	Respiration rate[1] at 5°C ($mg\ CO_2\ kg^{-1}\ h^{-1}$)		Shelf life[1] Cold store 4°C	Shelf life[1] Freezer -18°C	Market price (Can$)	
Berries (500 ml)						Season	Imported
Blueberries	July - September	moderate	10 - 20	2 d	1 y	1.69	3.59[3]
Strawberries	June - September	very high	40 - 60	2 d	1 y	0.69	3.19[3]
Raspberries	July - August	high	20 - 40	2 d	1 y	4.48	9.48[3]
Mushrooms (113 g)							
White	All year around			5 d	1 y	1.39 (fresh)	
Chanterelles	July			2 d	—	4.50 (fresh)	
Morels	May - June	very high	>60	2 d	—	30.00 (dried)	
Enoki	All year around			5 d	1 y	1.99 (fresh)	
Shiitake	All year around			5 d	1y	2.99 (fresh)	

1 - Khader (1992)

2 - MAPAQ (1997)

3 - Daily Fruit & Vegetable Wholesale Market Prices Service (1997)

the short or long term, the choice of process depending on the end use of the product and its market price (see Table I). Since differences in variety, maturity, storage, processing temperature, etc. can greatly affect the water activity of a product, there is a continuing need for reliable data on sorption of perishable commodities.

The objectives of this work are: (i) to determine the water activity of wild and commercial mushrooms (Shiitake, Enoki, and Morel) and berries (strawberries and blueberries) as a function of water content and temperature; (ii) to evaluate two sorption models, GAB and Ratti et al. (1989), and to compare their goodness of fit in the description of experimental data; and (iii) to determine the heat of sorption of foodstuffs.

Table II. Relative humidity over different saturated solutions.

Temperature (°C)	Salt	RH (%)
5	LiCl	11.3
	$MgCl_2•6H_20$	33.6
	NaBr	65.3
	NaCl	75.7
	KCl	87.7
15	LiCl	11.3
	$MgCl_2•6H_20$	33.3
	NaBr	63.0
	NaCl	75.7
	KCl	85.9
25	LiCl	11.3
	$MgCl_2•6H_20$	32.8
	NaBr	57.6
	NaCl	75.3
	KCl	84.3

MATERIALS and METHODS

Materials and preparation of samples

Sorption experiments were conducted for three types of edible mushrooms and two types of berries. Commercial mushrooms Shiitake *Lentinus edodes* and Enoki *Flammulina velutipes* (grown in greenhouses in Québec) were bought from the local market while the wild mushroom Morel *Morchella esculenta* was collected near lake Pohénégamook, Québec. The required quantities of strawberries (c.v. Seascape) and blueberries (wild lowbush from the region of Lake Saint-Jean, Québec) were bought from a local wholesale dealer. The berries and mushrooms were frozen at -30°C for 5 days. The materials were then freeze dried in a Freeze Mobile (25L EL, Virtis, New York, NY) for 72 h with a tray temperature of 25°C, under vacuum (13 Pa of total pressure) and a condenser temperature of -90°C. After freeze-drying, the samples were put in a vacuum oven for 48 hours at 50°C in the presence of P_2O_5 (powerful desiccant) in order to obtain anhydrous products. Freeze-dried berries were then powdered. Some of the dried Shiitake mushrooms were powdered manually with a pestle and mortar and the rest were cut into small pieces (about 5 mm long) in order to see the effect of particle size on sorption characteristics. Morel mushrooms were only powdered due to the small quantity available for the experiments while Enoki mushrooms were cut into small pieces since their very fibrous structure made it impossible to powder the samples.

Saturated salt solutions

Saturated salt solutions were prepared according to the method described by Labuza (1984). The relative humidities of the solutions were verified at different temperatures with a Humidiat IC II (Novasina, Zürich, Switzerland) and the results are presented in Table II.

Sorption isotherms

Water sorption isotherms were determined gravimetrically by

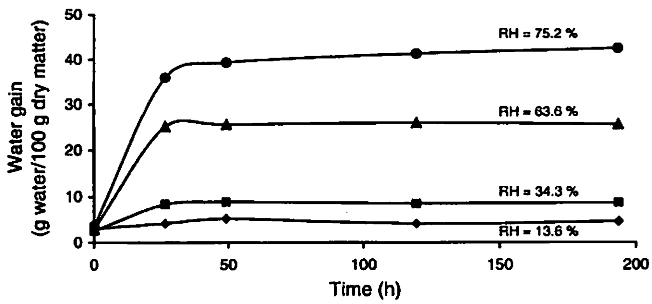

Fig. 1. Sorption curve for Enoki mushrooms at 4°C and various relative humidities.

exposing mushroom and berry samples at 4, 13, or 27°C in the presence of different salt solutions (in the approximate range of 10 to 85%). An approximate 500 mg mass of freeze-dried sample was spread on aluminium cups and put into desiccators containing the saturated salt solutions. The desiccators were already placed inside temperature controlled chambers. The mass of each sample was measured daily using an analytical balance (AE 200, Mettler, Greifensee, Switzerland). The experiment was completed when less than 1% weight change was found after two measurements. The dry matter of the solids was determined at 60°C in a vacuum oven using P_2O_5 as desiccant (De Jong et al. 1996; Pääkkönen and Kurdela 1986). Sorption experiments were done in triplicate for berries and in duplicate for mushrooms.

Mathematical modelling

The GAB and Ratti et al. (1989) models of sorption equilibrium were tested against the experimental data. The GAB equation is usually presented in the form:

$$\frac{X}{X_m} = \frac{CKa_w}{(1-Ka_w)(1-Ka_w+CKa_w)} \tag{1}$$

Table III. Water activity of different mushroom species at various temperatures.

Temperature (°C)	a_w	Water content (g water/100 g dry matter)			
		Shiitake (pieces)	Shiitake (powder)	Enoki (pieces)	Morels (powder)
4	0.136	3.02	2.87	4.40	4.60
	0.343	5.09	5.70	8.19	4.94
	0.636	13.98	13.58	24.53	10.11
	0.752	22.94	22.73	43.17	15.52
13	0.121	2.36	2.69	2.26	—
	0.340	4.45	5.09	8.04	—
	0.605	12.56	11.52	21.99	7.57
	0.743	21.40	20.58	37.98	12.84
27	0.120	0.45	0.50	1.80	2.51
	0.339	2.18	2.28	6.27	2.95
	0.570	8.25	8.25	16.94	5.95
	0.739	19.57	19.57	36.52	13.31

where:
- X = water content (dry basis, kg water/kg dry solids),
- a_w = water activity,
- X_m = monolayer water content, a constant of the GAB equation, and
- C,K = constants related to temperature (defined by Eqs. 2 and 3).

$$C = C_o \exp\left(\frac{\Delta H_1}{RT}\right) \tag{2}$$

$$K = K_o \exp\left(\frac{\Delta H_2}{RT}\right) \tag{3}$$

where C_o, K_o, ΔH_1, ΔH_2 = fitting constants, which can be obtained through non-linear regression.

The mathematical model developed by Ratti et al. (1989) is an equilibrium equation based on thermodynamic concepts:

$$\ln a_w = M(X) + N(X)\ln p_{wo} \tag{4}$$

where the effect of temperature is included in the vapour pressure of pure water, p_{wo}. For high moisture foods, such as fruits, mushrooms, and vegetables, the parameters M(X) and N(X) are functions of water content, expressed as:

$$M(X) = -k_1 X^{k_2} \tag{5}$$

$$N(X) = k_3 \exp(-k_4 X) X^{k_5} \tag{6}$$

The parameters k_1, k_2, k_3, k_4, and k_5 of Eqs. 5 and 6 can be obtained from experimental data through non-linear regression.

Parameter optimisation

When fitting the models to the experimental data, constants were obtained using the Levenberg-Marquardt procedure for non-linear least squares problems as implemented in SigmaPlot (1992). In this method, the stopping criterion that determines when the least squares minimum has been attained is based on the tolerance, which is set to 0.0001 by default. The parameter *Norm*, used by the method, represents the closeness of the most recent iteration. Numerically, it is the square root of the sum of the residuals (SigmaPlot 1992):

$$Norm = \sqrt{\sum_{i=1}^{n}(yp_i - y_i)^2} \tag{7}$$

where yp_i, y_i = predicted and experimental values, respectively.

The comparison to find the best correlation to represent the experimental data was based on the percentage standard error, E, of experimental versus predicted water activity:

$$E = 100\sqrt{\sum_{i=1}^{n}(yp_i - y_i)^2 / n} \tag{8}$$

where n = number of observations.

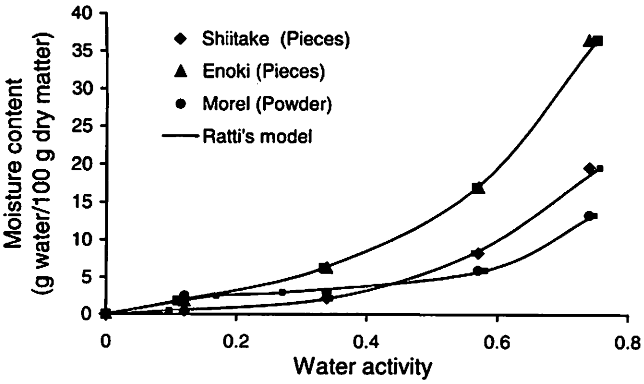

Fig. 2. Water activity of different mushrooms at 27°C. Continuous line represents Ratti et al. (1989) model.

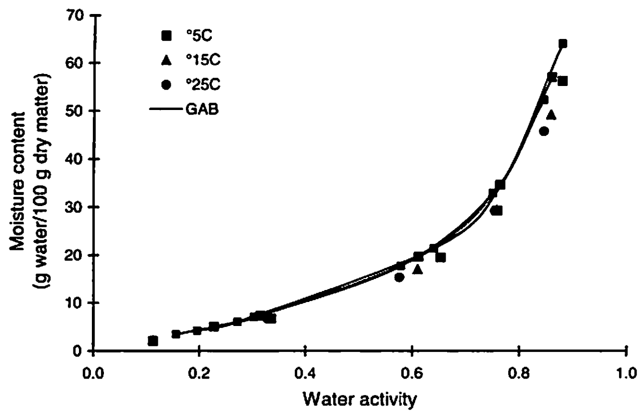

Fig. 4. Water activity of blueberries at various temperatures. Continuous line represents GAB model.

RESULTS and DISCUSSION

Figure 1 shows the water gain over time for Enoki mushrooms at different relative humidities. For this type of mushrooms, as well as for the other two species explored in this work, equilibrium was attained after approximately 50 h. Nevertheless, when no microbiological or physico-chemical deterioration was visually observed in the samples, the equilibrium measurement was taken about 200 h from the beginning of the experiment.

Table III shows the results of the equilibrium moisture content as a function of water activity and temperature for all mushroom species. In the case of Shiitake mushrooms, it was found that the sorption phenomena did not depend on particle size (powdered or pieces), based on student t-test of the means (0.05 level). This may be attributed to the high porosity of freeze-dried samples, as has been previously reported for coffee (Apostolopoulos and Gilbert 1988) and soybean curd (Kim et al. 1980).

The sorption data for Shiitake, Enoki, and Morel mushrooms at 27 °C are shown in Fig. 2. Enoki is clearly the most hygroscopic species, and similar differences were also noted at 13 and 4°C. For example, at 4°C and 0.75 water activity, this variety has 43.17 g water /100 g dry matter, which is double the corresponding quantity of Shiitake (see Table III). The water content for Morel mushrooms at the same conditions is approximately 64% lower than that of Enoki.

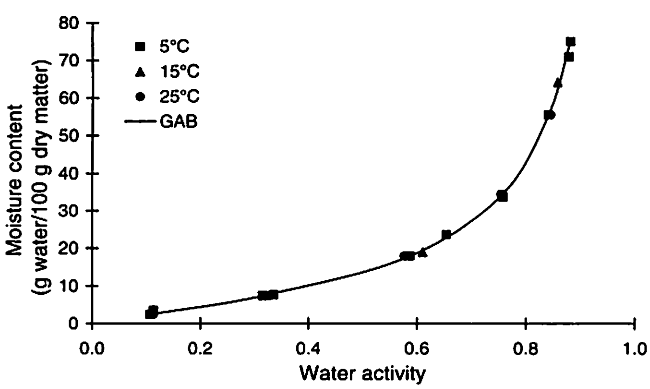

Fig. 3. Water activity of starwberries as various temperatures. Continuous line represents GAB model.

An increase in temperature will usually result in a decreased water activity. The effect of temperature on the water activity of Shiitake and Morel mushrooms (Table III) was significant. Nevertheless, the effect of temperature on water activity for Enoki mushrooms was less marked (Table III). A t-test for Enoki sorption data at 4 and 13°C, as well as at 13 and 27°C showed that the means of the samples were not different at the 5% level. However, the same test applied to 4 and 27°C data gave significant differences between both means at the same level.

Figures 3 and 4 show the sorption results for strawberries and blueberries, respectively. The shape of the curves is common for materials with high sugar content (Vidales et al. 1995). For low water activities, the water sorption is not marked, but the increase of water content is quite noticeable as of $a_w = 0.6$. As can be clearly seen, the effect of temperature (in the range 5 to 25°C) was negligible for both types of berries as confirmed by an ANOVA test (α = 5 %). Pääkönen and Mattila (1991) drew similar conclusions about the effect of this variable on the water adsorption curves of freeze-dried strawberries in the 20-60 °C range.

Sorption modelling

The GAB model (Eqs. 1 to 3) and the Ratti et al. (1989) model (Eqs. 4 to 6) were fitted to the experimental sorption data of berries and mushrooms, through non-linear regression analysis. The fitted parameters are shown in Table IV, together with the parameter *Norm* (Eq. 7) and the standard error E (Eq. 8). For the GAB model, the estimated constants W_m, K, and C, are comparable to those cited by Van den Berg (1984). For most of the products, the GAB equation gave a better representation of the experimental data, as can be observed from the lower standard error values for this equation (Table IV). Nevertheless, the standard errors obtained with the model of Ratti et al. (1989) were also reasonable except in the case of Morel mushrooms. The GAB predictions using fitted coefficients (Table IV) are plotted with the experimental sorption data in Figs. 3 and 4. The fit of the Ratti et al. (1989) model is given in Fig. 2. The agreement between experimental and predicted values is good for both models.

Heat of sorption

The model by Ratti et al. (1989) was developed on the basis of thermodynamic considerations (the Clapeyron -Clausius equation,

Table IV. Constants for GAB and Ratti et al. (1989) models.

Model	Constants	Shiitake (pieces)	Enoki	Morels	Strawberry	Blueberry
GAB	W_m	0.120	0.451	0.043	0.093	0.1065
	C_o	4.99x10^{-5}	0.001	3.96x10^{-7}	0.384	5.374
	ΔH_1	2817	1816	4709	566.2	-272.6
	K_o	1.570	1.817	0.0516	1.099	0.983
	ΔH_2	-171.3	-268.1	186.1	-26.49	-4.608
	Norm	*0.028*	*0.056*	*0.029*	*0.036*	*0.043*
	E (%)	6.35	3.50	3.13	1.62	4.26
Ratti et al. (1989)	k_1	0.096	0.163	0.045	0.112	0.095
	k_2	-0.810	-0.782	-1.058	-0.884	-0.949
	k_3	0.0081	0.0011	10.45	-37.79	-54.29
	k_4	-0.575	-6.074	26.63	266.8	16.28
	k_5	-1.103	-1.686	0.740	41.83	2.395
	Norm	*0.081*	*0.137*	*0.159*	*0.075*	*0.129*
	E (%)	2.34	3.97	26.71	1.93	3.35

Van Wylen and Sonntag 1978). The heat of sorption can therefore be obtained from:

$$\frac{\Delta H_s}{\Delta H_w} = k_3 \exp(-k_4 X) X^{k_5} - 1 \qquad (9)$$

where ΔH_w = vaporisation heat of pure water.

Figure 5 presents the results of heat of sorption for the three types of mushrooms, as predicted from Eq. 9 and using fitted parameters from Table IV. The energy for desorption is inversely proportional to water content. This observation confirms the difficulty in removing remaining water from the product during the last stage of drying. As can be seen in Fig. 5, Morel mushrooms have the highest heat of sorption at low water content, followed by Shiitake and Enoki. This means that the energy required for drying mushrooms to a safe water activity (less than 0.1) will be higher for Morel than for Shiitake and Enoki mushrooms. The low ΔH_s for Enoki species is in accord with the insignificant temperature effect found on its sorption properties.

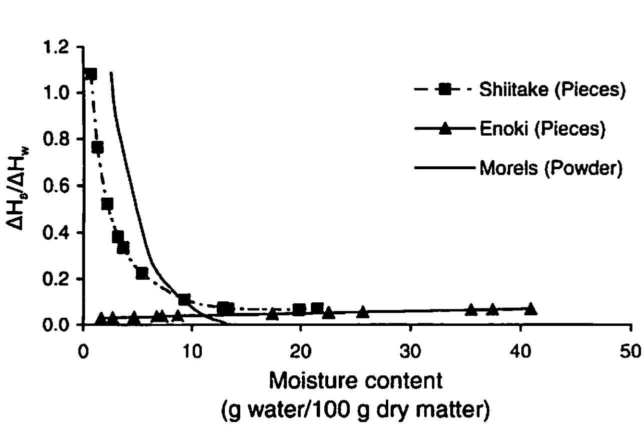

Fig. 5. Heat of sorption of different mushrooms from Eq. 10.

CONCLUSIONS

Sorption isotherms were determined for different freeze-dried berries and mushroom species. For berries, there was no significant effect of temperature on the equilibrium sorption in the range of temperatures studied. However, the effect of temperature on equilibrium moisture content was significant for mushrooms.

In general, the GAB model provided a better fit to the experimental data than the Ratti et al. (1989). Nevertheless, the latter model fit the data reasonably well except in the case of Morel mushrooms.

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