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Water Vapor Sorption Behavior of Some Agricultural Products Produced in Korea

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一部 韓国産 農産物의 等温吸湿曲線에 関한 研究

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Abstract

The water vapor sorption isotherms for a great variety of agricultural products were determined by using the standard salt solution technique at the temperatures of 25°, 35° and 45°C.

The B.E.T. monomolecular layer moisture contents were evaluated from experimental data on the sorption isotherms, and an analysis was made of the thermodynamic functions for water vapor sorption behaviors with respect to the storage stability of dehydrated foods. It may be concluded that the variation of entropy with moisture content of some agricultural products and seaweeds investigated would be a guide for the elucidation of the storage stability of dehydrated foods.

Introduction

It is well recognized that the water vapor sorption isoltherms is an important property in drying, packaging and storage of foods. And there is a well established relationship between water activity and stability characteristics of dried products, since water activity provides valuable informations on the chemical and physical properties of dried foods.[1, 2]

It is also recognized that the determination of B.E.T. monomolecular layer derived from the sorption isotherm is an effective method for predicting the storage stability of dried products. In spite of over-simplified theory, the B.E.T. monomolecular layer is practically used as a guide for storage of dehydrated foods. Therefore, the B.E.T. monomolecular layer moisture content has been extensively studied in connection with enzyme activity,[3, 4] lipid oxidation,[5] non-enzymatic browning reaction,[6] aroma retention[7] and textural characteristics of dried foods.[8]

Thermodynamic functions calculated from the water vapor sorption isotherm allow also for the theoretical interpretation of the physico-chemical conditions of the water sorbed.[9] For instance, the change in an integral free energy required for the transference of a water molecule from the vapor state to the solid state is a quantitative measurement of dried food/water affinity, and the variation of entropy might be related to the order/disorder concept, which is applied to the interpretation of such phenomena as dissolution, swelling and crystalization.[1, 9] The variation of total drying enthalpy also indicates up to which level the interaction between water and substrate is greater than the interaction of water molecules themselves.

This study has aimed firstly at determining the water vapor sorption isoltherms for some agricultural products and seaweeds, which is not yet thoroughly investigated. Secondly, this research is to present the relationship between the B.E.T.-monomolecular layer and the thermodynamic functions such as enthalpy, free energy, and entropy with respect to the storage stability.

Materials and Methods

Materials

Samples used in the experiment includes; sorghum (Sorghum nervosum, BESS. et Schult), corn(Zea mays, L.), italinian millet (Setaria italica, BEAUVOIS), ginkgo nut (Ginkgo biloba, L.), pine nut(Pinus koraiensis, S. et Z.), egg plant (Solanum melongena, L.), burdock(Arcticum lappa, L.), bamboo shoot(Phyllostachys pubescens, MAZEL), garlic(Allium sativum, L.), welsh onion (Ailium fistulosum, L.) pumpkin (Cucurbita maxima), Champignon(Mushroom;Agaricus campestris), Pyogoo(Shiitake), Fungus(Pleurotus estreatus), bracken (Pteridium aquilinum var. lactinsulum(DESV.), UNDERW), mung bean(Phaseolus aureus, L.), peas (Pisum sativum, L.), laver and brownseaweeds (Tangle; Undaria pinnatifida).

The sample was dried at 40°C in a forced convection dryer and then ground to pass 40 mesh screen. Finally each sample was dried at 10^{-2} mmHg pressure until reaching a constant dry weight.

Methods

Measurement of water vapor sorption

The water vapor sorption isotherm of foodstuffs was experimentally determined by the equilibration method (gravimetric method at 3 temperatures: 25°, 30° and 45°C) in the range between 11% and 79% R.H. About 2 g of sample was sieved through 40 mesh screen and then placed in each equilibration chamber. The desired relative humidity in the chamber was controlled with the saturated salt solution.[10, 11]

The equilibrium moisture content of samples were calculated in the following manner.[12]

$$\text{x\% Moisture} = \left(\frac{\text{Wt. of sample x\% original } H_2O}{100}\right) \pm \frac{(+\text{Wt. gain or} - \text{Wt. loss})}{\text{Wt. of sample} \pm (\text{Wt. gain or Wt. loss})} \times 100$$

Determination of B.E.T. monomolecular layer

For the B.E.T. analysis the authors used sorption data at the water activites of about 0.11 to 0.40 in accordance with the suggestion of Brunauer, Emmet and Teller.[13]

Least squares analysis was used to obtain the B.E.T. monolayers of each samples tested.

Results and Discussion

The results obtained from the investigation on the water vapor sorption isotherms of some agricultural products and seaweeds produced in Korea are presented in Fig. 1-1, Fig. 1-2 and Fig. 1-3.

As shown in Fig. 1-1, the different water vapor sorption isotherms of dried foods investigated presented different hyproscopicity. With a few exception, vegetables were generally more hygroscopic than other products.

It is clearly evident from the water vapor sorption isotherms for foodstuffs tested that a decrease in temperature has considerably increased the equilibrium

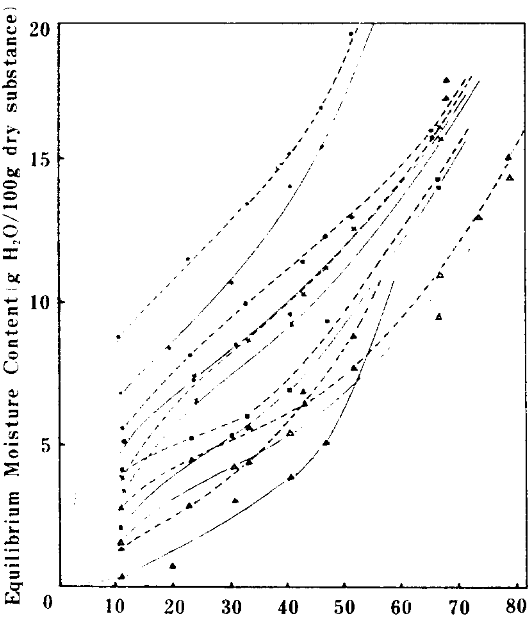

Fig. 1—1. Water vapor adsorption isotherms for pumpkin, bracken, burdock, garlic, corn and welsh onion at 25℃ and 45℃.

●	Pumpkin at 25℃	□	Garlic at 25℃		
-●-	〃 at 45℃	-□-	〃 at 45℃		
··o··	Bracken at 25℃	△	Corn at 25℃		
o	〃 at 45℃	-△-	〃 at 45℃		
·	Burdock at 25℃	▲	Welsh onion at 25℃		
·	〃 at 45℃	▲	〃 at 45℃		

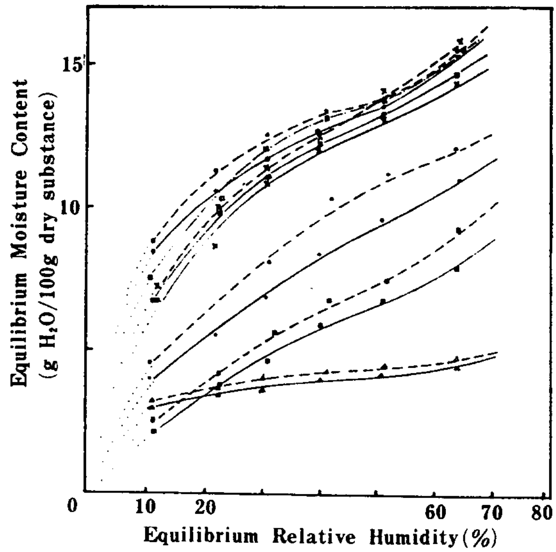

Fig. 1—2. Water vapor adsorption isothemrs for ginko nut, millet, laver, Shiitake, Fungus and pine nut at 35℃ and 45℃.

··○··	Ginko nut at 30℃	··×··	Laver	at 35℃
—○—	〃 at 45℃	—×—	〃	at 45℃
··□··	Millet at 35℃	··●··	Shiitake	at 35℃
—□—	〃 at 45℃	—●—	〃	at 45℃

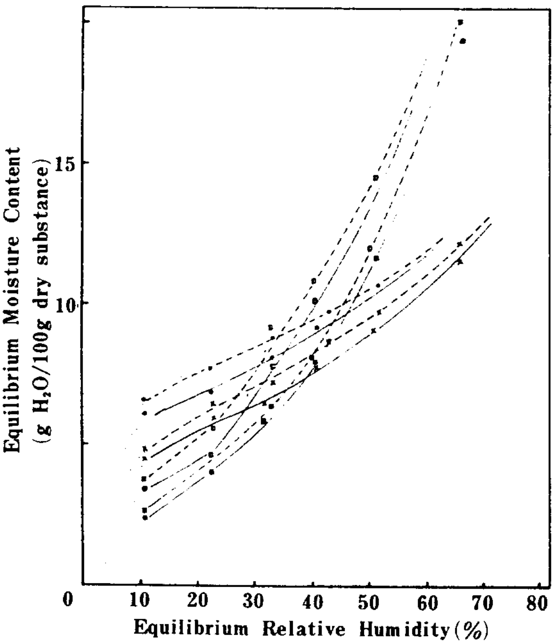

Fig. 1—3. Water vapor adsorption isotherms for egg plant, champignon mung bean and peas at 25℃ and 35℃.

··□··	Egg plant at 25℃	··○··	Mung bean	at 25℃
—□—	〃 at 35℃	—○—	〃	at 35℃
··■··	Champignon at 25℃	··×··	Peas	at 25℃
—■—	〃 at 35℃	··×··	〃	at 35℃

moisture content. That is, at each relative humidity, the water vapor sorption was inversely related to the temperature, because a change in an ambient temperature lead to a change in a vapor pressure and, therefore, a change in ERH. This indicates that the agricultural products investigated are much more hygroscopic at room temperature than at 45°C. Among all the products tested, the pine nut was least hygroscopic, whereas the egg plant and the pumpkin were most hygroscopic.

It is well recognized that the B.E.T. monomolecular concept is reasonable correct guide with respect to the storage stability of dried foods.[14] As described by Labuza[2], B.E.T. monomolecular layer moisture contents were calculated from the experimental data on water vapor sorption isotherms investigated. The results are shown in Table 1 together with the corresponding correlation coefficients. It was also found that the monomolecular layer values decrease considerably with increasing temperature. The observed effect is presumably due to a reduction in the number of active sites as a result of physical and chemical changes induced by temperature.[14, 15]

Since the B.E.T. analysis is based on oversimplified assumption, sorption heat values at various moisture content were computed by applying the Clausius-Clapeyron's equation.

The differential sorption heat estimated here is subjected to the following equation:

$$\text{In p} = \lambda \frac{\Delta H_s}{R_D T} + C_1 \qquad (1)$$

$$\text{In po} = \frac{\Delta H_L}{R_D T} + C_2 \qquad (2)$$

Subtracting the equation (2) from the equation(1):

$$\text{Inp}/p_0 = -\Delta H/R_D T$$

Provided that the amount sorbed, x%(D.B.), held constant:

$$\left[\frac{\text{InAw}}{1/T}\right]_x \text{x=constant} = \left[\frac{-\Delta H_B}{R_D}\right] \qquad (3)$$

By politting the sorption isostere as In Aw versus 1/T and determining the slop, In AW1T, the isoteric heat of dried foodstuffs tested may be estimated from the equation (3).

Table 1. The determination of B.E.T. - layers of some agricultural products and seaweeds

Products	Temp.(°C)	Xm	r
Sorghum	30	7.59	0.9971
	45	7.45	0.9972
Corn	25	4.73	0.9939
	45	4.11	0.9905
Millet	30	8.10	0.9941
	45	7.69	0.9961
Ginkgo nut	30	7.81	0.9920
	45	7.80	0.9955
Pine nut	30	2.39	0.9904
	45	2.34	0.9973
Egg plant	25	7.63	0.9476
Bamboo shoot	25	8.13	0.9778
Welsh onion	25	6.38	0.9149
Pumpkin	25	9.41	0.9999
	45	9.12	0.9716
Champignon	25	5.77	0.9990
	35	6.34	0.9788
Shiitake	30	6.91	0.9543
	45	5.54	0.9984
Fungus	30	4.71	0.9922
	45	4.33	0.9951
Bracken	25	7.03	0.9968
	45	5.76	0.9973
Mung bean	25	5.73	0.9941
	35	5.68	0.9997
Peas	25	5.03	0.9986
	35	4.72	0.9986
Laver	30	8.27	0.9416
	45	7.58	0.9912
Brownseaweeds	30	6.96	0.9982
	45	6.75	0.9981

where Xm: the percent monomolecular layer moisture content (g H_2O/100 g dry matter)
r: correlation coefficient

Similarly, Iglesias and Chirife[16] have calculated the isosteic heat from the intergrated from of equation 4 applied to sorption isotherms measured at two temperatures,

$$H_S = R_D(T_1T_2/T_2\text{-}T_1)\ \text{In}\ (A_{W2}/A_{W1}) \qquad (4)$$

where, p/p_0 = Aw
H_S = drying enthalpy in KJ/Kg($H_S = H_B + H_L$)
H_L = latent heat of vaporization in KJ/Kg
H_B = sorption heat of bound water in KJ/Kg
R_D = gas constant

and the free energy and the entropy of dehydrated foodstuffs were calculated in the following manner: $\Delta H = \Delta G - T\Delta S$, $\Delta G = RT\ \text{In}\ Aw$

As a first approximation, the sorption heat and other thermodynamic parameters for sorption data on welsh onion were evaluated. As shown in Table 2, it appeared that the heat of sorption for welsh onion became greater with reduced equilibrium moisture content. The similar behavior was observed with the variation of free energy. That is, the free energy decreased as the equilibrium moisture content increased. The entropy change decreased gradually with the increase of moisture content. And, as it has been stated by Iglesias and Chirife[16] the value of $-\Delta S$ did not rapidly decrease in the range of equilibrium moisture content between 4.0(D.B.) and 7.0(D.B). It is worth noticing that the B.E.T. monomolecular layer of welsh onion lies in this range of equilibrium moisture content.

Since the free energy and the variation of entropy might be related either to the dried food/water affinity or to the order/disorder concept, the water vapor sorption isotherms for other foodstuffs determined experimentally were also evaluated. Fig. 2-1 and Fig. 2-2 show the en-

Table 2. Sorption heat and intergral entropy for water vapor adsorption isotherm on welsh onion

x (D.B.)*	Aw		$-\Delta H_S$	ΔH_B	$-\Delta S$	$-\Delta G$
	25°	45°	(KJ/Kg)	(KJ/Kg)	(KJ/KgK)	(KJ/Kg)
2.0	0.15	0.32	3,986	1,568	12.9	246
3.0	0.24	0.37	3,313	895	10.5	185
4.0	0.30	0.42	3,114	696	9.9	156
5.0	0.35	0.47	3,028	610	9.7	136
7.0	0.43	0.50	2,932	514	9.4	122
8.0	0.48	0.53	2,623	205	8.4	95

* x(D.B.): g H_2/100 g dry matter.

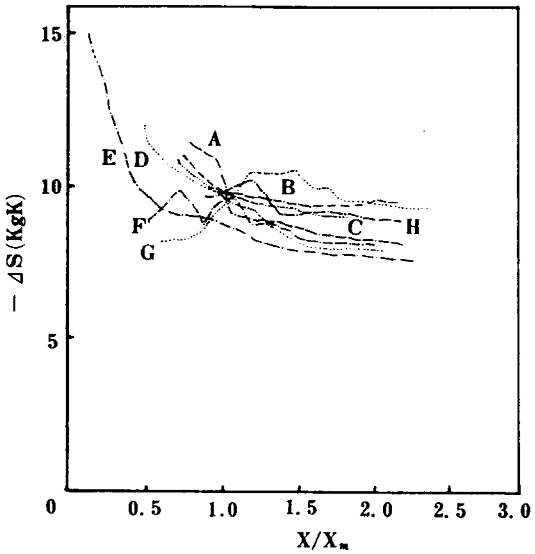

Fig. 2—1. Variation of the intergral entropy with coverage of BET—monolayer (X/X_m : number of monolayers).

A : Pumpkin E : Welsh onion
B : Mung bean F : Champignon
C : Egg plant G : Bamboo shoot
D : Corn H : Peas

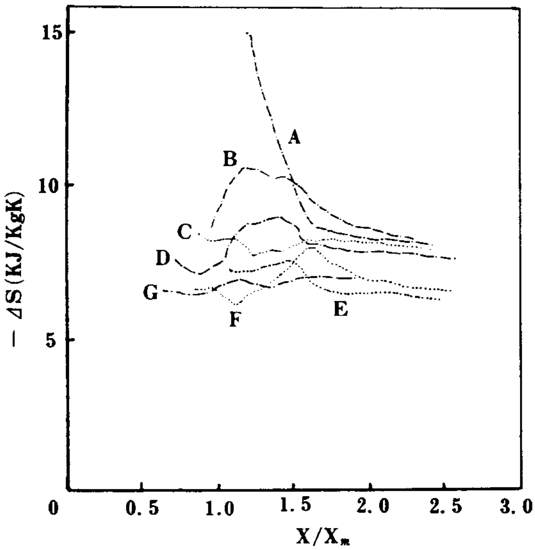

Fig. 2—2. Variation of the intergral entropy with coverage of BET—monolayer (X/X_m : number of monolayers).).

A : Pine nut E : Sorghum
B : Laver F : Millet
C : Brown seaweed G : Fungus
D : Shiitake

tropy change plotted as a function of number of BET-monomolecular layer. It is seen that the variation of intergral entropy for most foodstuffs tested was observed near the BET-monomolecular layer region (X/Xm:0.5-1.5), Once the BET-monomolecular layer was formed, the variation of entropy was practically negligible. This allow us to assume that the variation of entropy as a function of equilibrium moisture content will be an indicative for the storage stability of dehydrated foods.

要 約

本 硏究에서는 国内에서 아직 調査되지 않은 16개 品目의 農産物에 対한 等温吸湿曲線을 測定温度, 25℃, 30°, 및 45℃에서 決定하였다.

温度範圍 25°~45℃ 사이에서는 温度의 增加에 따라 平衡水分含量이 減少하는 경향을 보였다. 또한 等温吸湿曲線의 測定値로 부터 BET單分子膜水分含量을 分析, 決定하였다.

等温吸湿機作의 熱力学的 함수인 엔트로피의 変化는 乾燥食品의 安全貯藏 水分含量영역인 BET單分子膜水分含量과 밀접한 関係에 놓인 것으로 사료되고 있다.

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