Note

Water Sorption Analysis in Vegetables Using a Modified Dubinin-Astakhov Equation

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Water sorption isotherms at 298 K for six kinds of fresh vegetables (carrot, daikon (Japanese radish), eggplant, potato, pumpkin and sweet-potato) were measured using a static equilibration method over saturated salt solutions in the relative humidity range from 11.3 to 97.3%. The equilibrium moisture content data were fitted to a modified Dubinin-Astakhov (DA) equation that assumes a Weibull probability density function to the desorption probability under the adsorption potential change. The modified DA equation was confirmed to be very accurate in predicting the water sorption isotherms of the vegetables. In addition, the test vegetables could be classified into two groups by the n (one of the DA parameters) values, which denote the porous degree of the adsorbent. One group consisted of carrot, eggplant and pumpkin. Daikon, potato and sweet potato belonged to the other group.

Keywords: vegetable, water sorption, isotherm, modified Dubinin-Astakhov equation, adsorption potential

The equilibrium moisture content of foods is a very important parameter to relate the moisture transfer with the heat transfer during the operations such as drying, storage and freezing. Agricultural products such as vegetables have complicated chemical and geometrical structure, and their metabolisms occur even after harvest. Therefore, it is necessary to consider the state of water in the primary and secondary metabolic processes. Moreover, vegetables as well as their components show significant differences in their water-binding properties.

The state of water in vegetables changes varies from single layer adsorption to capillary condensation, and this shows that cooperative sorption takes place. The Guggenheim, Anderson, de Boer (GAB) equation is usually applied to describe the moisture sorption of foods, but the GAB equation is not applicable in the water activity region higher than 0.9 (Bizot, 1983; De Jong *et al.*, 1996; Iglesias & Chirife, 1995; Lim *et al.*, 1995). The Dubinin-Astakhov (DA) equation (Dubinin & Astakhov, 1971) is well proven to predict the equilibrium moisture content in all sorption regions. However, the influence of temperature on the interrelation between the adsorbate and water cannot be neglected (Iglesias & Chirife, 1982). Therefore, Kameoka *et al.* (1994a, 1995) proposed a modified DA equation by assuming a Weibull probability density function to the desorption probability under the adsorption potential change.

In this paper, we report the water desorption isotherms of fresh vegetables, which were measured by a static equilibration method over saturated salt solutions for a wide relative humidity range, and the experiments reported in this paper were carried out not with frozen dried ones but with fresh ones because of the following reasons. Though the metabolism in fresh vegetable occurs even after harvest, the mass of water taking part in the metabolism could be neglected, and

the difference between the states of water in the fresh vegetable and in the dried one should be significant. Moisture sorption characteristics in the fresh vegetables are generally more important than those in the dried ones for operations such as drying, storage and freezing. Furthermore, by focusing our attention on the parameters obtained by fitting the equilibrium moisture content data to the modified DA equation, the equilibrium moisture content differences among the vegetables can be discussed.

Materials and Methods

As the test vegetables, carrot, daikon (Japanese radish), eggplant, potato pumpkin and sweet potato were properly prepared. Saturated salt solutions with an excess of the salts were used to control the humidity at 298 K. The relative humidity values for the various salts at that temperature were from 11.3 to 97.3% (Table 1), which were obtained from published data (Japanese Industrial Standards, 1981; Winston & Bates, 1960).

For the arrangement of the moisture sorption, the saturated salt solutions were introduced into air-tight polyvinyl chambers. Nine humidity-controlled chambers were placed in a constant temperature room (Hitachi, CR-14) which was controlled to an accuracy of 0.5 K. About 15 g of each fresh vegetable cut into about 5 mm cubes with a knife was put into a petri dish made of aluminum, and then the sample container was placed in the humidity-controlled chamber. The weight change was measured each day using an electric balance until the change in weight was less than $1 \text{ mg} \cdot \text{d}^{-1}$; it took about 10 to 20 days to reach this stage. The moisture content, which was obtained by drying for 48 h at 358 K, of the sample at that stage was considered to be an equilibrium value.

Table 1. Relative humidities provided by saturated solutions at 298 K.

Salt	Relative Humidity [%]
LiCl	11.3
CH ₃ COOK	22.5
MgCl ₂	32.8
Mg(NO ₃) ₂	52.9
NaNO ₂	64.0
NaCl	75.3
KCl	84.3
KNO ₃	93.6
K ₂ SO ₄	97.3

Results and Discussion

Application of modified DA equation The equilibrium moisture content, M_e [kg-H₂O/kg-dry material], was expressed by the modified DA equation (Eq. (1)).

$$M_e = M_0 \exp\{-(A/A_e)^n\} \quad (1)$$

where M_0 [kg-H₂O/kg-dry material] is the limit of the moisture content of the adsorption space represented by n [—], which is the distribution order of the Weibull probability density function and is a positive real number less than unity. A_e [J·mol⁻¹] is a characteristic energy, and the adsorption potential, A [J·mol⁻¹], can be calculated as a decrease in the Gibbs's free energy.

$$A = -RT \ln(p/p_0) \quad (2)$$

p [Pa] and p_0 [Pa] are the equilibrium partial vapor pressure and its saturated value at the temperature, T [K], respectively.

Taking the natural logarithm of both sides of Eq. (1), it is rewritten as follows:

$$\ln M_e = \ln M_0 - (A/A_e)^n \quad (3)$$

The plot of $\ln M_e$ versus A^n should be linear for the most suitable n . A linear regression using the least squares method was applied for different n values, and the n value giving the best correlation coefficient was adopted. Figure 1 illustrates the results, and the ordinate and abscissa are, respectively, the natural logarithm expression of M_e and A^n . The DA parameters obtained by the above procedure and the correlation coefficient are listed in Table 2. The various n values were obtained, as the correlation coefficient with these n values for all series of data were above 0.97. The n values, which mean the porous degree, in Table 2 were less than those for rice ($n=0.65$; Kameoka & Horibe, 1994a) and for nonporous foods such as amorphous sugars ($n=0.3-0.5$; Kameoka & Horibe, 1994b). In addition, the test vegetables could be classified into two groups based on the obtained n

Fig. 1. DA plots of water in vegetables. The n value giving the best correlation coefficient was adopted. **Fig. 2.** Equilibrium moisture content curves of water in the vegetables. Points show the observed data, and the lines were calculated using the modified DA equation with the parameters in Table 2.

values. One group consisted of carrot, eggplant and pumpkin. Daikon, potato and sweet potato belonged to the other group. Therefore, these results suggested that the n values in Table 2 could be used to measure the chemical and geometrical structure interrelated with water.

Moisture sorption isotherms The equilibrium moisture content curves are represented in Fig. 2. The points show the observed data, and the lines were calculated using the modified DA equation with the parameters listed in Table 2. The modified DA equation accurately represented the sorption isotherms of all vegetables in the range of relative humidities less than 100%. Hence, the modified DA equation can be used to predict the equilibrium moisture content of the vegetables in all sorption regions: single layer adsorption,

Table 2. Parameters of the modified DA equation^{a)} and correlation coefficient.

	Carrot	Daikon	Eggplant	Potato	Pumpkin	Sweet-potato
n [—]	0.235	0.074	0.192	0.049	0.222	0.048
M_0 [kg-H ₂ O/kg-dry material]	5.77×10^0	6.31×10^3	1.86×10^1	3.19×10^4	2.64×10^0	1.09×10^4
A_e [J/mol]	1.08×10^1	4.09×10^{-11}	7.50×10^{-1}	8.14×10^{-20}	1.30×10^1	1.41×10^{-19}
$r^{b)}$ [—]	0.975	0.979	0.997	0.999	0.990	0.999

^{a)}The modified DA equation is expressed in Eq. (1). ^{b)} r is the correlation coefficient used to fit the equilibrium moisture content data to the modified DA equation.

multilayer adsorption and capillary condensed water. Moreover, each curve had a similar shape, indicating that each material is roughly a similar sorption medium because cellulose and starch are the major components of the test vegetables.

By the way, the obtained M_0 values (Table 2) of daikon, potato and sweet potato were much greater than those calculated under the assumption that their voids were filled with water (data not shown). This experimentally suggested that the modified DA equation is theoretically unfounded for the less porous foods, for which the n values were small, in the water activity range close to unity.

In conclusion, the modified DA equation can very accurately predict the water sorption isotherms for all test vegetable in the wide relative humidity range less than 100%. Moreover, it is possible that the influence of temperature on the DA parameters (n , M_0 , A_e) for various vegetables should be analyzed in order to interrelate the vegetable structure with water. In addition, the modified DA equation needs to be theoretically combined with the equilibrium moisture content equation in the water activity range close to unity.

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