

Moisture Sorption and Thermodynamic Properties of Vacuum-Dried *Capsosiphon fulvescens* Powder

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ABSTRACT: The moisture sorption isotherms of vacuum-dried edible green alga (*Capsosiphon fulvescens*) powders were determined at 25, 35, and 45°C and water activity (a_w) in the range of 0.11 ~ 0.94. An inversion effect of temperature was found at high water activity (>0.75). Various mathematical models were fitted to the experimental data, and Brunauer, Emmett, and Teller model was found to be the most suitable model describing the relationship between equilibrium moisture content and water activity (<0.45). Henderson model could also provide excellent agreement between the experimental and predicted values despite of the intersection point. Net isosteric heat of adsorption decreased from 15.77 to 9.08 kJ/mol with an increase in equilibrium moisture content from 0.055 to 0.090 kg H₂O/kg solids. The isokinetic temperature (T_β) was 434.79 K, at which all the adsorption reactions took place at the same rate. The enthalpy-entropy compensation suggested that the mechanism of the adsorption process was shown to be enthalpy-driven.

Keywords: *Capsosiphon fulvescens*, moisture sorption, thermodynamic properties, vacuum-dried

INTRODUCTION

Capsosiphon fulvescens (CF) is a green alga, which is high in protein, low in fat, and contains essential minerals and vitamins. This green alga has been widely used in the food industries, as well as in cosmetics and pharmaceutical industries due to its beneficial effects on the human immune system and various health-enhancing properties (1,2). Recently, CF has attracted attention due to its potential use in foods, cosmetics, and pharmaceuticals, and its powder has been successfully used in the processing of sponge cakes (3), white pan breads (4), to-fu (5), rice noodles (6), and cookies (7).

The drying conditions of the alga play an important role in the application of the alga as a raw material. The dried CF powder has a prolonged shelf life and can be easily used for the production of value-add products in various industrial fields. Information on moisture adsorption isotherms, which describes the inherent relationship between water activity and moisture content of food materials, is essential for drying, storage, packaging, assessing the energy requirements for drying, and shelf life prediction (8,9). Moreover, proper modeling for predicting the relationship between equilibrium moisture, water activity, and temperature helps to determine

the optimum moisture conditions with good storage stability, especially for dehydrated foods.

Many mathematical models have been applied to describe moisture sorption isotherms and several theoretical, semi-theoretical, and empirical models to fit the equilibrium moisture content data have been proposed. The GAB (Guggenheim, Anderson, and De Boer) model is one of the most widely used to fit sorption isotherms of many food materials (10), and other commonly applied equations include: BET (Brunauer, Emmett, and Teller), Oswin, Halsey, Henderson, and Kuhn models (11,12).

A thermodynamic approach can be used to study the behavior of water and the energy requirement of heat and mass transfer in biological systems (13). Thermodynamic functions such as heat of vaporization (differential heat of sorption), net isosteric heat of sorption, and differential entropy are readily calculated from moisture sorption isotherms. The endpoint to which food must be dehydrated for a stable product with optimal moisture content, and the theoretical minimum amount of energy needed to remove water to a certain level of moisture content from the food can be determined from this information (14).

Therefore, understanding the sorption isotherm of CF

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powder is of critical importance to determine the process and storage conditions, and to select appropriate packaging materials for the final products. Nevertheless, no attempt has been made to determine the sorption isotherms of CF powder. The objectives of the present study were to establish the relationship between equilibrium moisture content and water activity of CF powder at three different temperatures (25, 35, and 45°C), to determine the best moisture sorption isotherm equation to fit the experimental adsorption data, and to determine the thermodynamic properties.

MATERIALS AND METHODS

Materials and sample preparation

CF was dried using a vacuum oven (EYELA vacuum oven, VOS-301SD, Tokyo Rikakikai Co., Ltd., Tokyo, Japan) at 60°C and then milled into powder. Triplicate samples, about 1.0 g each, were taken and placed in an aluminum dish (Disposable Al Dish D57, Korea Ace Scientific Co. Ltd., Seoul, Korea) in desiccators with nine different saturated salt solutions of known relative humidities (15). The saturated salt solutions included LiCl, K_2CO_3 , $MgCl_2$, K_2CO_3 , $Mg(NO_3)_2$, KI, NaCl, KCl, and KNO_3 , with a water activity range of 0.11 to 0.94. The desiccators were kept in three incubators maintained at 25, 35, and 45°C, respectively. Samples were weighed until they reached the equilibrium condition (when three consecutive weight measurements had the same reading). All the analyses were conducted in triplicates and expressed as dry weight basis, kg H_2O /kg solids.

Sorption isotherm modeling

Selected sorption isotherm equations, including BET, GAB, Oswin, Halsey, Henderson, and Kuhn, which are widely used for food materials were used (11,12). The coefficients of sorption equations were determined by nonlinear regression within the water activity range of 0.11 to 0.94, whereas, the BET equation was fitted to water activity up to 0.45. The goodness of fit of these equations was evaluated using coefficients such as R-square (R^2), mean relative error (MRE), and root mean square error (RMSE) values (16).

MRE (%) value is defined as

$$\text{MRE (\%)} = \frac{100}{N} \sum_{i=1}^N \frac{|M_{\text{exp}} - M_{\text{pre}}|}{M_{\text{exp}}} \quad (\text{Eq. 1})$$

RMSE is defined as

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (M_{\text{pre}} - M_{\text{exp}})^2}{df}} \quad (\text{Eq. 2})$$

where M_{exp} and M_{pre} are experimental and predicted moisture content values, respectively; df is the degrees of freedom (the number of experimental data minus the number of coefficients of the model). A model is considered acceptable if the MRE values are less than 10% (17-19).

Isosteric heat of sorption

The net isosteric heat of sorption (q_{st}) is the difference between the total heat of sorption in the food and the vaporization heat of pure water (ΔH_{vap}), which can be determined based on the moisture sorption data using the Clausius-Clapeyron equation at a given temperature (19-21):

$$q_{\text{st}} = Q_{\text{st}} - \Delta H_{\text{vap}} = -R \left[\frac{\partial \ln a_w}{\partial (1/T)} \right]_m \quad (\text{Eq. 3})$$

where a_w is the water activity, q_{st} is the net isosteric heat of sorption (kJ/mol), Q_{st} is the isosteric heat of sorption (kJ/mol), ΔH_{vap} is the heat of vaporization (kJ/mol), R is the universal gas constant (8.314 J/mol·K), and T is the absolute temperature (K). By re-plotting the sorption isotherm in the form of $-\ln a_w$ versus $1/T$ (Eq. 3), net isosteric heat of sorption (q_{st}) can be determined based on the slope (q_{st}/R) of the regression line at specific moisture contents. Under this assumption, q_{st} is dependent on temperature, so it requires more than two temperatures in the sorption isotherms study (22,23).

The net isosteric heat (q_{st}) can also be expressed as the function of moisture content as follows (24):

$$q_{\text{st}} = a \exp(-bM_e) \quad (\text{Eq. 4})$$

where a and b are constants and M_e is the equilibrium moisture content, kg H_2O /kg solids.

The relationship between the isosteric heat (ΔH_d) and differential entropy (ΔS_d) can be determined as (25):

$$-\ln(a_w)|_m = \frac{\Delta H_d}{RT} - \frac{\Delta S_d}{R} \quad (\text{Eq. 5})$$

Similar to the net isosteric heat of sorption (q_{st}), the isosteric heat (ΔH_d) can be determined based on the slope of plotting $-\ln a_w$ versus $1/T$, and ΔS_d can be determined from the intercept ($-\frac{\Delta S_d}{R}$).

RESULTS AND DISCUSSION

Water sorption isotherms

Fig. 1 represents a comparison of sorption curves of experimental and predicted (Henderson model) equilibrium moisture content vs. water activity values at three different temperatures. At a constant temperature, the equilibrium moisture content increased with water activity, and an intersection point was clearly observed at a water activity of 0.75. This behavior is manifested in the form of a J-shaped curve, which belongs to type III isotherms. Below the intersection point, the equilibrium moisture content decreased with temperature at the same water activity, while above the intersection point, the equilibrium moisture content began to increase with temperature at the same water activity. Despite the value around the intersection point, the predicted equilibrium moisture content values agreed with the experimental data.

Only food materials with high-protein or high-sugar contents show similar trends because the sugar can sorb more water and overcome the negative effects of temperature at higher hydration levels (21,26,27). The sorption isotherm curves obtained agreed well with those of high-protein or high-sugar content materials since CF contains significant amounts of essential proteins, polysaccharides, and glycoproteins (1). On the contrary, food materials with low sugar content (hulls, dried tomato pulp, and tea) or high starch content (rice and corn starch) do not display an intersection point with an increase in water activity or temperature (24,28-32).

The sorption isotherm curves of CF powder are described as the equilibrium moisture content (EMC) against water activities at different temperatures. Six mathematical models were used to fit the curves using nonlinear regression analysis, and the estimated coefficients are shown in Table 1. In general, all the mod-

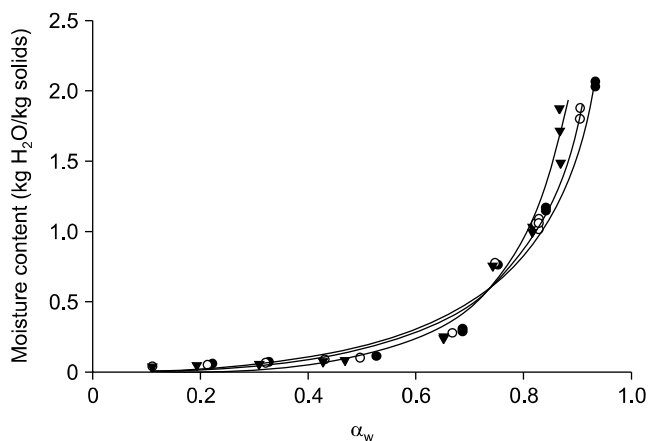


Fig. 1. Moisture adsorption isotherms for *Capsosiphon fulvescens* at selected temperature (25°C, 35°C, 45°C, —Henderson model).

els used for sorption isotherms presented R^2 values above 0.87, whereas the MRE values were over 10% except for the BET equation; therefore, the BET equation had the best fit for the experimental sorption data of vacuum-dried CF powder with the highest R^2 (0.96~0.99), lowest MRE ($\leq 4.8\%$), and lowest RMSE values (0.002~0.004) (Table 1), but it covers only low water activities (≤ 0.45). The statistics analysis also suggested that the Henderson model was in second order to appropriately fit the sorption isotherm data. The solid line in Fig. 1 showed the simulated EMC vs. water activity within the temperature range of 25 to 45°C using the Henderson model.

The monolayer values decreased with the increase in temperature because the movement of water molecules increased and the total number of active water binding

Table 1. Estimated coefficients obtained from modeling analysis

Model ¹⁾	Coefficient ²⁾	Temperature (°C)		
		25	35	45
BET	m_{0B}	0.059	0.051	0.047
	C_B	16.28	33.06	18.85
	R^2	0.994	0.961	0.990
	MRE (%)	1.966	4.715	2.189
	RMSE	0.002	0.004	0.002
GAB	m_{0G}	0.081	0.079	0.074
	C_G	1.269×10^8	0.532×10^8	0.109×10^8
	k_G	1.027	1.055	1.101
	R^2	0.873	0.886	0.912
	MRE (%)	49.041	50.927	61.605
Oswin	RMSE	0.246	0.21	0.175
	A	0.247	0.214	0.162
	B	0.802	0.949	1.239
	R^2	0.963	0.974	0.977
	MRE (%)	50.971	41.328	32.37
Halsey	RMSE	0.129	0.099	0.088
	A	0.154	0.174	0.204
	B	1.114	0.928	0.704
	R^2	0.953	0.966	0.974
	MRE (%)	76.526	56.061	30.913
Henderson	RMSE	0.148	0.113	0.093
	A	1.801	1.741	1.648
	B	0.572	0.512	0.412
	R^2	0.982	0.984	0.980
	MRE (%)	37.879	35.861	36.123
Kuhn	RMSE	0.092	0.076	0.083
	A	-0.144	-0.192	-0.252
	B	0.007	-0.081	-0.178
	R^2	0.945	0.972	0.969
	MRE (%)	53.527	40.44	75.642
	RMSE	0.158	0.101	0.103

¹⁾BET, Brunauer, Emmett, and Teller model; GAB, Guggenheim, Anderson, and De Boer model.

²⁾Coefficients A and B are constant for each model equation and have no theoretical meaning except for those in the GAB and BET models. The constants (C_G and k_G) in the GAB model are related to the heat of adsorption while m_{0B} and m_{0G} in both GAB and BET models represent the monolayer value.

sites were reduced at higher temperature. Theoretically, the monolayer values could be estimated from the BET and GAB models. In the present study, the monolayer values of CF powder ranged from 0.074 to 0.081 kg H₂O/kg solids based on the GAB model, while it ranged from 0.047 to 0.059 kg H₂O/kg solids based on the BET model, which are comparable to those obtained from red alga reported by Lemus et al. (26).

Heat of adsorption

A linear relationship was observed between $-\ln a_w$ and $1/T$ as shown in Fig. 2, and the slope was used to obtain the net isosteric heat of adsorption (q_{st}). The net isosteric heat of adsorption for CF decreased from 15.77 to 9.08 kJ/mol with an increase in EMC from 0.055 to 0.090 kg H₂O/kg solids. An exponential decrease in q_{st} with an increase in M_e was observed in Fig. 3, and thus, an exponential decay model was used to indicate the relationship between q_{st} and M_e with a high R^2 value as follows:

$$q_{st}=38.707e^{-15.932M_e} \quad R^2=0.997 \quad (\text{Eq. 6})$$

where q_{st} is the net isosteric heat of adsorption, kJ/mol.

Enthalpy-entropy compensation

Fig. 4 shows the net differential entropy for vacuum-dried CF powder vs. M_e . A typical exponential decrease in entropy was also observed with increasing M_e . The relationship between ΔS_d and M_e was obtained as follows:

$$\Delta S_d=87.333e^{-14.569M_e} \quad R^2=0.989 \quad (\text{Eq. 7})$$

where ΔS_d is the net differential entropy, kJ/mol.

A linear relationship was observed between differential enthalpy (ΔH_d) and differential entropy (ΔS_d) as shown in Fig. 5, which shows the existence of enthalpy-entropy compensation.

$$\Delta H_d=0.434\Delta S_d-0.959 \quad R^2=0.995 \quad (\text{Eq. 8})$$

The slope of Eq. 8 gives the isokinetic temperature ($T_\beta=434.79$ K), at which all adsorption reactions take place at the same rate (32,33). The intercept of Eq. 8 is the free energy change ΔG , which represents the sorb-

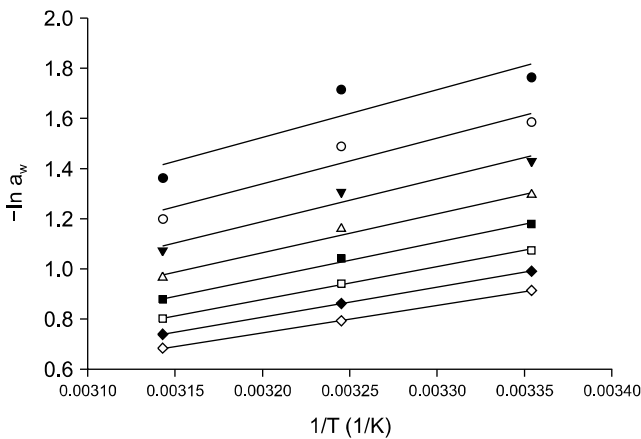


Fig. 2. Plots of $\ln a_w$ versus $1/T$ for calculating the net isosteric heat of sorption ($M_c=0.055$, $M_c=0.060$, $M_c=0.065$, $M_c=0.070$, $M_c=0.075$, $M_c=0.080$, $M_c=0.085$, $M_c=0.090$).

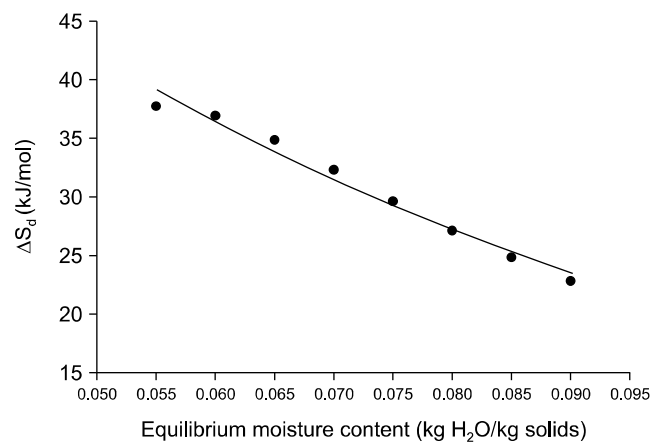


Fig. 4. Effect of moisture content on the net differential entropy.

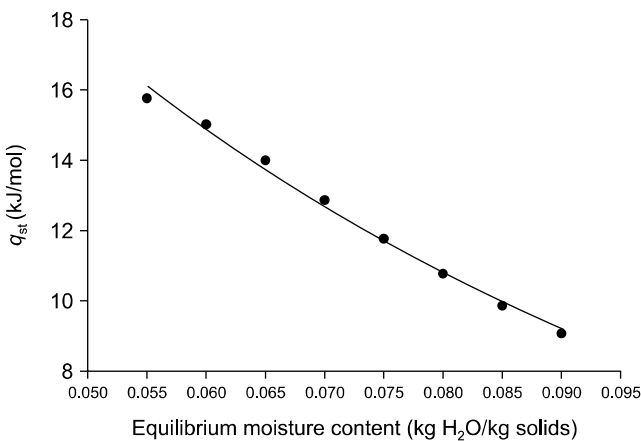


Fig. 3. Effect of moisture content on the net isosteric heat of adsorption values.

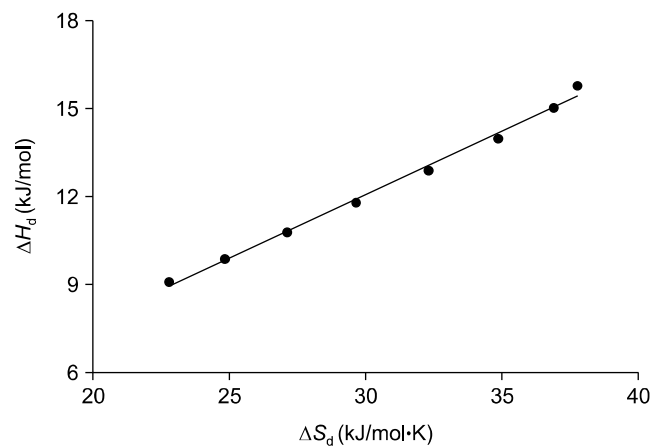


Fig. 5. Heat of adsorption/differential entropy relationship.

ent water affinity. In addition, a negative ΔG (-0.959 kJ/kg) indicates a spontaneous process (32). The harmonic mean temperature (T_{hm}) was calculated as 307.93 K by using Eq. 9:

$$T_{\text{hm}} = \frac{n}{\sum_{i=1}^n (1/T)} \quad (\text{Eq. 9})$$

where n is the number of isotherms.

The linearity of the enthalpy-entropy compensation plot indicates that the adsorption phenomenon in CF follows one mechanism in the entire range of the moisture contents investigated. The isokinetic temperature, T_{β} (434.79 K), is significantly higher than the harmonic mean temperature, T_{hm} (307.93 K), which confirms the suitability of the isokinetic theory for water adsorption of vacuum-dried CF powder, and the mechanism is enthalpy-controlled in the range of moisture contents studied rather than entropy-driven (34).

CONCLUSIONS

The moisture adsorption of CF powder at different temperatures and water activities were determined using the standard gravimetric method. The moisture adsorption showed a J-shaped curve with an intersection point around a_w of 0.75. Below the intersection point, the equilibrium moisture content decreased with increases in temperature; however, it became more hygroscopic above the intersection point. Among the sorption models, the BET equation describes the sorption data well over the range of temperatures and water activities up to 0.45. The sorption data were also well expressed by the Henderson model in the wide range of water activities. The net isosteric heat of sorption can be calculated using the Clausius-Clapeyron equation. Both q_{st} and ΔS_{d} exponentially decreased with increases in moisture content. The isotherm study of vacuum-dried CF is essential for quality control of CF during processing and storage.

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AUTHOR DISCLOSURE STATEMENT

The authors declare no conflict of interest.

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