

Heats of Moisture Adsorption for Sunflower Nutmeat Products

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Abstract

Heats of moisture adsorption of the sunflower nutmeat products (ground nutmeat, meal, protein concentrate and protein isolate) were determined from their isosteres at temperatures 10, 20 and 30°C. The changes in the heat of adsorption with moisture level were analyzed by Hunter equation. The Hunter equation was valid for representing the relationship between the heat of adsorption and the moisture content for the sunflower nutmeat products, and the accuracy-of-fit increased as protein content of the materials increased. The heat of adsorption decreased as moisture content increased, but increased as protein content increased. The heats of adsorption were 11.8-10.6 kcal/mole for the ground nutmeat at 4-12% moisture (d.b.) and 12.4-11.0 kcal/mole for the protein isolate at 6-20% moisture (d.b.).

Key words : sunflower nutmeat products, ground nutmeat, meal, protein concentrate, protein isolate, isostere, heat of adsorption

Introduction

Hygroscopy of food materials affects their storage, handling and processing. The hygroscopicity of food material is directly related to the water binding capacity and usually determined by the moisture sorption isotherms. Moisture sorption isotherms are also useful in indicating product quality after drying and the potential storage stability of food materials. In addition to the moisture sorption isotherms, the thermodynamics involved in sorption process is also of great interest from the standpoint of economy and efficiency of the processing operations.

Sunflower seed has become a popular oil source because of its high oil content (42-50%) and high level of unsaturated fatty acids (68-71% linoleic acid, 16-20% oleic acid).^(1,2) The high levels of unsaturated fatty acids in sunflower seed oil has been shown to decrease serum cholesterol levels.⁽³⁾ Sunflower meal that remains after solvent extraction of the oil is a good source of edible protein showing 90% digestibility and no antinutritional factor.⁽⁴⁾ Sunflower protein also has a great potential for incorporation into human food products as an ingredient showing favorable functional properties such as emulsion capacity and stability and foam capacity and stability.^(2,5-9) The meal can be processed into protein concentrate or

protein isolate to enhance nutritional quality and functional properties.

The objectives of this study were to determine the heats of adsorption of sunflower nutmeat products at various moisture contents and to find appropriate isostere equations for the establishment of their thermodynamic data of moisture adsorption.

Material and Methods

Material

Sunflower hybrid (847A) nutmeats obtained from Sigco Inc. (Breckenridge, MN, U.S.A.) were used for this study.

Preparation of samples

Sunflower nutmeats were ground in a coffee mill for 20 sec and the meal, the protein concentrate (PC) and the protein isolate (PI) were prepared from the ground nutmeat by the method of Mok and Hettiarachchy.⁽¹⁰⁾ The protein contents of the prepared samples were determined by the Kjeldahl method⁽¹¹⁾ using the protein factor of 6.25.

Moisture adsorption

The samples were dried under vacuum (25.4 mmHg) at 37°C for 48 hr before the adsorption study. The adsorption study of duplicate predried samples was done by the method of Mok⁽¹²⁾ at 10, 20°C and 30°C using various concentrations of sulfuric acid. The equilibrium moisture contents were determined

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by the method of Chung and Pfost.⁽¹³⁾ The acquired moisture adsorption isotherms were analyzed by the Chen-Clayton equation⁽¹⁴⁾ since it had been found to be the best-fit equation for the sunflower products as reported in previous paper.⁽¹⁰⁾ The corresponding A_w at different moisture content and temperature was calculated by introducing the estimated values of the parameters into the Chen-Clayton equation. A graph representing the relationship between A_w and temperature at a given moisture content was prepared as described by Pixton and Warburton.⁽¹⁵⁾

Model of heat of adsorption

The equilibrium vapor pressure is related to saturation vapor pressure by the following⁽¹⁶⁾

$$\frac{1}{h_s} \frac{dP}{P} = \frac{1}{h_v} - \frac{dP_s}{P_s} \quad (1)$$

where h_s and h_v are the heats of adsorption of adsorbed water and free water, respectively, P is the vapor pressure of the adsorbed water, and P_s is the saturated vapor pressure of free water.

Water activity (A_w) is defined by

$$P = A_w P_s \quad (2)$$

From Eq (1) and (2)

$$\frac{d(A_w)}{A_w} = \left[\frac{h_s}{h_v} - 1 \right] \frac{dP_s}{P_s} \quad (3)$$

Integrating Eq (3) assuming that h_s/h_v is temperature independent results in

$$\ln(A_w) = \left[\frac{h_s}{h_v} - 1 \right] \ln \left[\frac{P_s}{P_0} \right] \quad (4)$$

where P_0 is the intercept pressure. Therefore,

$$A_w = \left[\frac{P_s}{P_0} \right]^{(h_s/h_v - 1)} \quad (5)$$

$(h_s/h_v - 1)$ is a function of moisture content (l.c.).

Hunter⁽¹⁷⁾ assumed that the P_0 were independent of moisture content to simplify the Eq (5) and found that if $(h_s/h_v - 1)$ were plotted against $\ln(w)$ for low and high moisture contents, straight line asymptotes resulted, with a transition region between. Based upon this finding, he developed an empirical equation (6) for the entire moisture range.

$$\frac{h_s}{h_v} - 1 = \frac{a \ln(bw) - \left[\frac{w}{w_0} \right]^n c \ln(dw)}{1 - \left[\frac{w}{w_0} \right]^n} \quad (6)$$

where a , b , c , d and n are the constant, w is the moisture content (d.b.) and w_0 is the transitional moisture content (d. b.). The values of a and b can be evaluated by a least square method for small w , and those of c and d for large w . w_0 indicates the transition region and is the value of w at which the logarithms are equal. Therefore,

$$w_0 = \left[\frac{b^a}{d^c} \right]^{1/(c-a)} \quad (7)$$

Heat of adsorption

The heat of adsorption (h_s) was calculated by plotting the sorption isostere as $\ln(A_w)$ vs. $1/T$ and determining the slope which is equal to $-h_s/R$ as described by Rodriguez-Arias *et al.*⁽¹⁸⁾ The $(h_s/h_v - 1)$ versus $\ln(w)$ data were analyzed by a least square method and the values of the parameters a and b were calculated for small w and those of c and d for large w as described by Hunter.⁽¹⁷⁾ From these values, the transition moisture content (w_0) was calculated by Eq (7). The value of n was then calculated from Eq (6) using Gauss-Newton method on IBM 3081D computer.

Results and Discussion

Isosteres are curves or functions relating equilibrium pressure of an adsorbed component to temperature, when the amount adsorbed is held constant.⁽¹⁹⁾ An isostere equation therefore represents the variation of water activity with temperature for a fixed moisture content. The isosteres of the sunflower nutmeat, the meal, the pretein concentrate and the protein isolate as shown in Figs 1, 2, 3 and 4, respectively. These plots are also useful to determine the condensation temperature of the water in the equilibrated sample which has been stored under specific temperature and humidity condition⁽¹⁵⁾. To relate the moisture content of the product at a given temperature to A_w is straightforward, merely drawing a horizontal line from the point where the moisture line cuts the vertical temperature line to the A_w axis. The diagonal lines refer to the vapor pressure of the atmosphere in equilibrium with the product.

The dew-point data are important for a safe storage since deterioration may occur even if the products are initially at a safe and uniform moisture con-

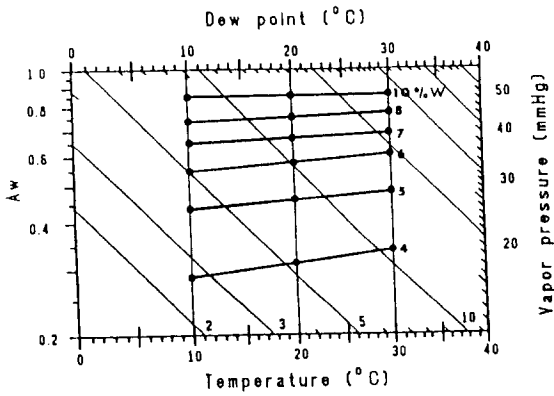


Fig. 1. Water activity of sunflower nutmeat for a given moisture content (w, % d.b.) at varying temperatures

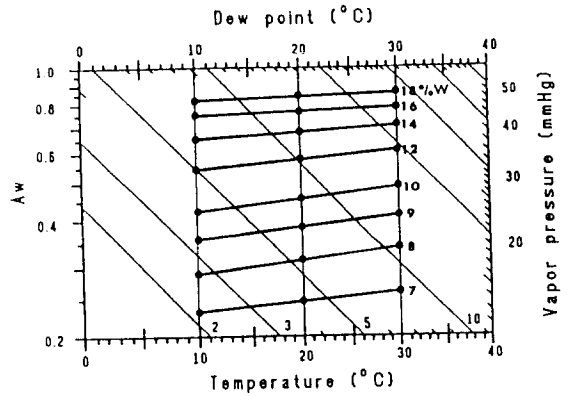


Fig. 3. Water activity of sunflower protein concentrate for a given moisture content (w, % d.b.) at varying temperatures

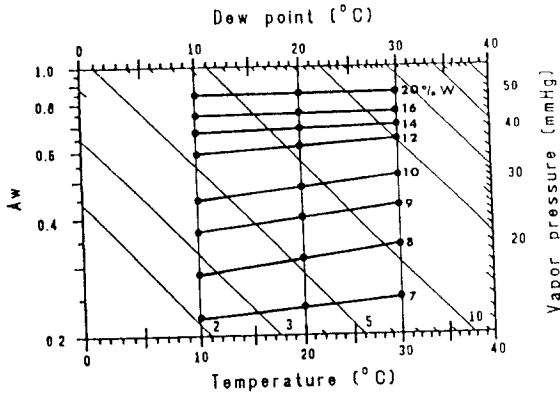


Fig. 2. Water activity of sunflower meal for a given moisture content (w, % d.b.) at varying temperatures

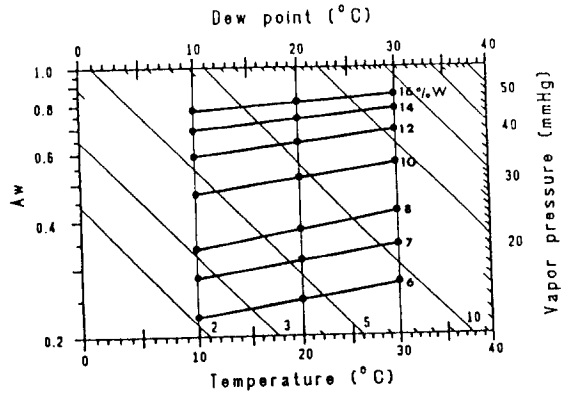


Fig. 4. Water activity of sunflower protein isolate for a given moisture content (w, % d.b.) at varying temperatures

tent if there are marked difference in temperature in the bulk. Moisture will move along any temperature gradients from warm to cooler regions where the equilibrium relative humidity may consequently exceed the safe level. The intergranular air is dynamic and may condense out onto the wall of the storage bin, or onto the surface of the product if it is cooled below the dew point.

To obtain the temperature required for condensation to form in an atmosphere in equilibrium with each product at a given temperature, a line is drawn parallel to the vapor pressure line from the point where the moisture content line cuts the temperature line to the dew-point temperature scale in Fig. 1-4.

Fig. 5 shows the changes in the heat of adsorption with the moisture content of the material studied. The validity of the Hunter equation (Eq. (6)) was ob-

served and the heat of adsorption decreased with increasing moisture content. The protein content and the values of the parameters of the Hunter equation for each sample are listed in Table 1. The percent root mean square of error (%RMS) was used to measure the goodness-of-fit.

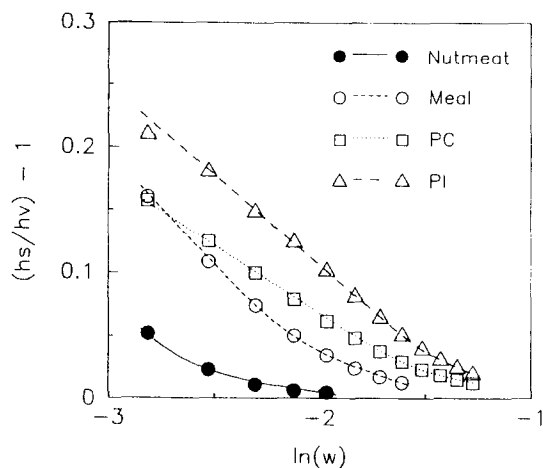
$$\%RMS = \sqrt{\frac{\sum \left[\frac{X_{obs} - X_{est}}{X_{obs}} \right]^2}{N}} \times 100 \quad (8)$$

where X_{est} is the estimated value and X_{obs} is the observed value, and N is the number of observations.

The %RMS were 10.5% for the ground nutmeat and less than 3% for the meal, the PC and the PI. The %RMS decreased with protein content indicating that the Hunter equation fitted better for proteinous materials than for non-proteinous materials.

Table 1. Values of parameters of the Hunter equation and percent root mean square of error (% RMS) for sunflower nutmeat products

Sample	Protein content (% d.b.)	a	b	c	d	w ₀	n	% RMS
Nutmeat	33.1	-0.2200	14.2250	-0.0239	6.1466	0.0635	9.7146	10.50
Meal	63.7	-0.1814	6.8139	-0.0556	4.0377	0.1165	11.9850	2.90
PC	72.5	-0.1077	3.9555	-0.0344	2.5058	0.2041	17.0668	1.90
PI	99.4	-0.1440	3.5539	-0.0683	2.6945	0.2192	24.5206	1.55

**Fig. 5. Observed and estimated ratios of latent heats as calculated by the Hunter equation for sunflower nutmeat products of varying moisture contents (symbols: observed, lines: estimated)**

As the protein content increased, the values of the parameters n and the transitional moisture content (w_0) increased, while those of the parameters b and d generally decreased.

When the curve is extrapolated toward high moisture content to the horizontal axis where the heat of adsorption of the adsorbed moisture becomes equal to that of the free liquid water, the corresponding moisture may represent theoretically the finite moisture content which would be reached when the sample is immersed in liquid water⁽¹⁷⁾. The moisture content at which this occurs is given by the reciprocal of the parameter d given in Table 1. The finite moisture content increased in the order of nutmeat < meal < PI < PC.

It should be noted that the heat of adsorption at a given moisture content increased as the protein content increased as shown in Fig. 5. This implies that the protein has higher heat of adsorption than other components of sunflower. The sunflower nutmeat showed the lowest heat of adsorption among the ma-

terials studied at constant moisture content. It seemed to be because the lesser numbers of active site for moisture adsorption were available due to its high oil content (49.7% d.b.).

The heat of adsorption of the ground sunflower nutmeat were 11.8-10.6 kcal/mole at moisture contents between 4 and 12% (d.b.) showing comparable values to those of peanut kernel⁽²⁰⁾. The heats of adsorption were 11.7-10.7 kcal/mole and 11.8-10.8 kcal/mole for the meal and the PC, respectively, at moisture contents 8-18% (d.b.). The heats of adsorption of the PI were 12.4-11.0 kcal/mole for moisture contents of 6-20% (d.b.), which were slightly lower than those of corn gluten, 15.3-10.6 kcal/mole at moisture content 4-20% (d.b.)⁽¹³⁾ and were similar to those of wheat gluten.⁽²¹⁾

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해바라기 종실제품의 수분흡착열

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해바라기종실제품(종실, 착유박, 농축단백, 분리단백)의 수분흡착열을 10, 20, 30°C에서 측정한 등습곡선(isostere)으로부터 구하였고, 수분함량에 따른 흡착열의 변화를 Hunter 방정식에 의거하여 해석하였다. Hunter 방정식에 의한 예측치는 실측결과와 잘 일치하였으며 단백질함량이 증가할수록 정확도가 높았다. 흡착열은 수분함량이 높을수록 감소하였으며, 단백질함량이 높을수록 증가하였다. 해바라기종실의 흡착열은 건물기준 수분함량 4-12%에서 11.8-10.6 kcal/mole이었으며 분리단백의 경우 수분함량 6-20%에서 12.4-11.0 kcal/mole 이었다.