

農產品平衡相對濕度的觀念與模式

The Concepts of Equilibrium Relative Humidity and Its Models

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摘 要

平衡相對濕度的觀念是研究農產品貯運，乾操作業的一種重要物性因素。更由於此物性可用以預測食品穩定性質的變化，因此亦可應用於食品混合與包裝作業。

此研究之目的在於介紹平衡相對濕度的基本概念和十三種常用以描述平衡相對濕度與農產品含水率關係的數學模式。有些方程式是導源自基本原理，某些方程式經修正後增加溫度項。這些方程式對於農產品平衡相對濕度與含水率關係的適稱性都需要深入的研究。此評論對於需要應用平衡相對濕度模式的研究者都能夠提供有用的資料。

ABSTRACT

The concept of equilibrium relative humidity is a very important factor in the study of handling, storing, and drying process on foods. It is also a valuable tool to predict the change of food stability, so it can be applied on packaging and mixing operation.

The objectives of this study is to introduce the basic principle of equilibrium relative humidity and to present a review of literature on thirteen equations for fitting sorption isotherms of foods. Some of these equations are original, some are modified by incorporating the temperature term. The evaluative method and criterion for the fitting-agreement of these models on isotherm data need to be further studied. This review may provide a useful guide for those researchers interested in the mathematical description of the sorption isotherms of foods.

1. The Concept of EMC (ERH)

The concept of equilibrium moisture content (EMC) and equilibrium relative humidity

(ERH) are important factors in the study of handling, storing, and drying processes.

When a biological material is exposed to a

particular environment (temperature and relative humidity) for an infinitely long period, it reaches a final moisture content which is in equilibrium with the environmental condition. This moisture content is called the equilibrium moisture content.

When a biological material is enclosed in a container or storage, the interstitial air reaches a relative humidity which is in equilibrium with the material at the particular moisture content and temperature. This relative humidity is called the equilibrium relative humidity. The equilibrium relative humidity is usually called water activity, or A_w , by food scientists and food engineers. A_w and ERH/100 have the same meaning.

If a biological material is exposed to wet environment, it will adsorb moisture to reach the final state. This process is called adsorption. When a biological material is exposed to a drying environment, it will lose moisture. This is a desorption process.

Plotting the EMC value of cereal grains versus relative humidity at a constant temperature results in a sigmoid type curve. The S-shaped curve is called the moisture equilibrium isotherm. A hysteresis usually exists between the adsorption isotherm and desorption isotherm.

Temperature and relative humidity have a significant effect on the EMC value. An increase of temperature at a constant relative humidity decreases the EMC value. Increasing the relative humidity at a constant temperature increases the EMC value.

Water takes various forms in biological materials. These complicated phenomena deserve a brief introduction.

From the study of Young and Nelson (1967), there are three mechanisms by which water is held in biological materials.

First, a unimolecular layer of water molecules may be bound to the cell surface. The bound moisture is held within the material by surface force. The heat of adsorption of this moisture is the force that binds it to the surface of the materials.

Second, multimolecular layers of water molecules may be stacked on the top of the first layer. the water may be present as normally

condensed moisture, or "free" water.

Finally, moisture may exist in the cells. The energy at this state has not been specified.

Moisture held in the first two forms may be called adsorbed moisture. The adsorption phenomenon is considered to take place on the surface of cells rather than on the exterior surface of the material.

When a dry, biological material is exposed to a wet environment, moisture first adheres to the surface of the cells in a unimolecular layer. As the unimolecular layer builds up on the surface, the diffusional force tends to cause moisture transfer to the cells. But the surface molecules of the cell will prevent the moisture from moving inward. As moisture condenses and stacks at the unimolecular layer, second and higher layers are formed. When more molecules adhere to the surface, the diffusional force exceeds the binding force and some moisture penetrates the cell surface.

When the material is exposed to a drying environment, the reduction of the vapor pressure allows moisture removal from the surface. When all the moisture has been removed from the surface, the concentration gradient causes the adsorbed moisture to move out of the cell.

From the state of water present, the isotherm curve can be mainly divided into three regions—the adsorption of a monomolecular film of water, the adsorption of additional layers over this monolayer, and the condensation of water in the pores of the material (Labuza 1968). Unfortunately, no definite relative humidity can be stated for the cross-over from one region to the next.

Recently, the concept of sorption region has been modified. Labuza (1984) concluded that three major factors (colligative effect, capillary effect, and surface interaction effect) occur over the entire moisture range for food, and these factors result in the characteristic moisture sorption isotherm. The colligative effect (Raoult effect) is not only significant at high moisture contents but also in the low RH range. For the capillary effect (Kelvin effect), the capillaries of small diameter are the last to empty on drying, therefore, this effect occurs over the entire isotherm. Due to surface interaction, water

molecules which interact with other chemical groups, require extra energy to be transferred from liquid into the vapor state and this restricts the flow of liquid to the vapor phase. This effect also happens over the entire isotherm.

Many isotherm equations have been derived from the concepts of water in biological materials (Van den Berg and Bruin, 1981). Because of the overlap of these sorption regions, no mathematical model developed from sorption theory can describe the entire isotherm.

II. RH Equations

A number of theoretical, semi-theoretical, and empirical isotherm equations have been developed to model the relationship between EMC, or ERH (A_w), and temperature.

Seventy-seven isotherm equations have been reviewed by Van den Berg and Bruin (1918). Some of the equations are based on the sorption model such as the BET equation. Some of them are simply empirical equations with two or three fitting parameters. Some of the different isotherm equations were found to have the same form after rearrangement (Chirife and Iglesias, 1978).

Empirical equations have been found to be more accurate and convenient than theoretical and semi-theoretical relationships. Isotherm equations used most frequently are presented and discussed in the following section. In these equations, A_w denotes water activity, RH reative humidity, M moisture content on dry basis, and T temperature.

1. The BET equation

One of the oldest and most widely known theories of adsorption is described by the Langmuir equation. The model describes the adsorption of a monolayer of vapor on the surface of biological materials. Due to the simplifying assumptions, this model only fits well in the low range of relative humidity.

Brunauer, Emmett, and Teller (1938) assumed multimolecular adsorption where the rate of condensation was equal to the rate of evaporation in each adsorbed layer. They also assumed all layers after the first were condensed with a regular heat of condensation.

Their derived equation becomes:

$$\frac{RH}{(1-RH)*M} = \frac{1 + RH*(C-1)}{Mo*C} \quad (1)$$

Where M_o is the monolayer value, C is a constant.

The equation usually holds only below the range of 45% RH. However, the concept of the monolayer value has been found to be very useful for food scientists. In the study of chemical reactions in foods, it has been found that there is a moisture content below which the rates of quality loss are negligible. The BET M_o value can thus be viewed as a critical moisture content (Labuza, 1984). In a drying process, the value could serve as an index for the lowest moisture content that the dried materials could attain (Aguerre et al., 1984).

2. The Smith equation

Smith (1947) assumed that absorbed water is bound on the inner or outer surface of the solid adsorbent and is condensed with the adsorbent. He considered that the amount of moisture bound by excessive forces would reach the maximum at a vapor pressure less than that of saturation.

The equation is:

$$M = M_b - M_a * \ln(1-RH) \quad (2)$$

Where M_b = Bound moisutre

M_a = Moisture in a unimolecular layer

This equation fits the data reasonably well in the high relative humidity range, where bound moisture can be realized completely. Chirife et al. (1979) found that this equation described EMC values very well for 47 isotherms in the RH range of 50-92 %.

3. The Henderson equation

The most widely used and best known model for the sorption isotherm of biological materials is this semi-empirical equation derived from Gibbs adsorption theory.

Henderson (1952) presented this equation:

$$1 - RH = \text{Exp}(-K^*T^*M^N) \quad (3)$$

K and N are constants, thus the equation cannot predict the correct shift of the isotherm as the temperature changes (Iglesias and Chirife, 1976a).

4. The Modified-Henderson equation

To study the simulation of corn drying, Thompson et al. (1978) modified the Henderson equation by adding another constant into the temperature term. The practical effect of the modification is to move the temperature of absolute zero to a higher temperature.

The modified equation becomes:

$$1 - RH = \text{Exp}(-A^*(T+c)^*M^b) \quad (4)$$

Where A, B, and C are constants.

Kumar et al. (1978) defined K, and N as linear functions of temperature resulting in a four-parameter equation.

A different modification of the Henderson equation was presented by Zuritz et al. (1979) to describe the desorption isotherms of rough rice from 10 to 40°C.

5. The Chung-Pfost equation

Based directly upon an assumption that the way the free energy changes for sorption is related to moisture content Chung and Pfost (1967, Part II) presented a model of the form:

$$RH = \text{Exp}\left(\frac{A}{RT}\right) \text{Exp}(-B^*M) \quad (5)$$

Where R is the universal gas constant, and A and B are constants.

As with the Henderson equation, this equation cannot be used to predict the effect of temperature since the use of the T term does not eliminate the temperature dependence of parameters A and B.

In order to obtain a better fit, Pfost et al. (1976) added a new parameter to the temperature term and combined that R value in the constant term.

The new equation is:

$$RH = \text{Exp}\left(\frac{-A}{T+C}\right) \text{Exp}(-B^*M) \quad (6)$$

Where A, B and C are constants.

The equation and the Modified-Henderson equation was adopted as the ASAE standards (ASAE Data D245.4).

6. The Halsey equation

Halsey (1948) developed an equation to describe the condensation of multilayers at a large distance from the surface.

The equation is:

$$RH = \text{Exp}\left(\frac{A}{RT}\right) * M^{-c} \quad (7)$$

Because the use of the RT term does not eliminate the temperature dependence of constants A and C, Iglesias and Chirife (1976b) simplified it to the form:

$$RH = \text{Exp}(-A^*M^{-c}) \quad (8)$$

They found this equation could be used to describe the sorption behaviour of 69 food materials reasonably well.

7. The Modified-Halsey equation

In studying the effect of temperature on water sorption isotherms, Iglesias and Chirife (1976a) analyzed the parameter A of the Halsey equation (Eq. 8) and found that it could be related to temperature by an empirical exponential function. A new Modified-Halsey equation was proposed:

$$RH = \text{Exp}(-\text{Exp}(A+B^*T)^*M^{-c}) \quad (9)$$

Where A, B, and C are constants.

8. The Day-Nelson equation

Because the T term in the Henderson equation does not eliminate the temperature dependence of constants K and N, Day and Nelson (1965) omitted the T term and replaced the constants with an empirical power function of temperature.

The new four-parameter equation is:

$$1 - RH = \text{Exp}(-a \cdot T^b \cdot M^c \cdot T^d) \quad (10)$$

Where a, b, c, and d are constants.

9. The Chen-Clayton equation

In order to predict the temperature dependence of the isotherm, Chen and Clayton (1971) proposed a four-parameter equation to describe the relation of moisture, temperature, and relative humidity. The model is:

$$RH = \text{Exp}(-a \cdot T^b \cdot \text{Exp}(-c \cdot T^d \cdot M)) \quad (11)$$

Where a, b, c, and d are constants.

The equation is a modification of the Chung-Pfost equation (Eq. 5) with the constants A and B represented as empirical power functions of temperature.

10. The Oswin equation

Oswin (1946) presented an equation primarily to solve a packaging problem. The equation is a mathematical series expansion for a sigmoid shaped curve and can be written as follows:

$$M = K \cdot \left(\frac{RH}{1 - RH} \right)^N \quad (12)$$

K and N are constants.

Since it is purely empirical, it received relatively little attention in the literature. Labuza et al. (1972) applied the equation to correlate EMC data in non-fat dry milk and freeze dried soluble tea. Andrien et al. (1985) found that sorption data of Durum wheat pasta could be fit by the Oswin equation with good precision.

Parameters K and N do not account for the temperature dependence. The Oswin equation has been modified by expressing K as a function of temperature (Chen, 1988).

The new modified nonlinear equation with three parameters can be expressed as:

$$M = (A + BT) \left(\frac{RH}{1 - RH} \right)^N \quad (13)$$

11. The Iglesias-Chirife equation

Iglesias and Chirife (1976b) found that high-

sugar foods like most fruits, have sorption isotherms which resemble a Type III isotherm. They expressed this isotherms as the arc-sinh function, which may be expressed as $\text{Ln}(X + \sqrt{X^2 + 1})$. A empirical equation was proposed:

$$\text{Ln}(M + \sqrt{M^2 + M_{0.5}}) = a \cdot RH + b \quad (14)$$

Where $M_{0.5}$ is the moisture content at $RH=50\%$ and a and b are constants. They found that this equation described adequately EMC values for seventeen isotherms comprising nine high-sugar foods.

12. Special equation

To find a equation to fit some uncommon water sorption isotherms that having an intermediate shape between BET type II and III, Iglesias and Chirife (1981) proposed an empirically developed equation.

$$M = A \left(\frac{RH}{1 - RH} \right) + B \quad (15)$$

The concluded that this simple equation could represent twenty-eight sorption isotherms very well.

13. The GAB equation

This equation, derived independently by Guggenheim, Anderson, and de Boer from a physical adsorption model related to the BET theory, has been adopted widely among food scientists recently (Van den Berg, 1984; 1985).

The GAB equation has the following form:

$$M = \frac{M_o C K A_w}{(1 - K A_w)(1 - K A_w + C K A_w)} \quad (16)$$

Where

$$C = C_l \cdot \text{Exp}((H_m - H_n)/RT) \quad (17)$$

$$K = K_l \cdot \text{Exp}((H_l - H_n)/RT) \quad (18)$$

A_w = Water activity

M_o = Molecular value

Hm = Molar sorption enthalpy of the monolayer

Hn = Molar sorption enthalpy of the multilayers on the top of the monolayer

Hl = Molar sorption enthalpy of the bulk liquid, Cl and Kl are constants.

The GAB model describes the moisture contact as a function of temperature and water activity. If water activity is chosen as a function of moisture content and temperature, this equation transforms to a form given by,

$$A_w = \frac{2 + (M_m/M - 1) \cdot C - ((2 + (M_m/M - 1) \cdot C)^2)}{2 \cdot K \cdot (1 - C)} \cdot \frac{-4 \cdot (1 - C)^{0.5}}{C} \quad (19)$$

The major advantages of GAB model, according to Van den Berg (1984), are:

1. It has a theoretical background that is refined from the BET theory.
2. It describes sorption behavior of nearly all foods from zero to 0.9 A_w .
3. It has a relatively simply mathematical form with only three parameters.
4. Its parameters have a physical meaning in terms of the sorption process.
5. It is able to describe some temperature effects of isotherms by Arrhenius-type equations.

After transformation, the GAB equation has an equivalent form to the Hailwood and Horrobin equation (1946).

$$\frac{A_w}{M} = a_1 + a_2 \cdot A_w + a_3 \cdot A_w^2 \quad (20)$$

The equivalent of parameters for GAB equation are:

$$K = \frac{\sqrt{a_2^2 - 4a_1 \cdot a_3} - a_2}{2a_1} \quad (21)$$

$$C = \frac{a_2}{a_1 \cdot k} + 2 \quad (22)$$

$$M_o = \frac{1}{a_1 \cdot k \cdot c} \quad (23)$$

With this simple algebraic form, the parameters of the nonlinear GAB equation can be calculated easily by linear multiple regression analysis. This method was used by Bizot (1984) to construct sorption isotherms and by Wesier (1985) to find the parameters for four food materials. Schar (1985) compared the method of obtaining the parameters and found that the values depended on the type of regression procedure used.

After using the GAB model to construct sorption isotherms, Bizot (1984) proposed that the equation with physically meaningful coefficients could fit data very well up to 0.9 A_w in many cases. However, he also emphasized the GAB model had some limitations. The model did not apply to all shapes of isotherms. As the temperature changed, the fit might be less satisfactory. The model did not fit the more crystalline forms of starch at A_w range 0.6-0.7.

Iglesias and Chirife (1984) represented the monolayer value as an Arrhenius relation with temperature.

$$M_o = M_l \cdot \text{Exp}(-M_2/T) \quad (24)$$

Using this equation to express the temperature dependence of M_o , Weisser (1985) showed that the GAB equation with temperature coefficients is suitable for describing the influence of temperature on the sorption behavior of four food components in the range of 25-80°C. The same method was applied to ground roasted coffee for five temperatures (Weisser, 1986). Conversely, Gencturk et al. (1986) studied the sorption isotherms of wild rice and found that the three parameters were not a function of temperature.

Conclusions

Thirteen isotherm equations that have been widely used are reviewed in this research. Some of these equations are theoretical, some are

widely used are reviewed in this research. Some of these equations are theoretical, some are modified by these equations and others are obtained by curve fitting of the experimented data.

This review suggests that the evaluation of these equations is needed to obtain the fitting-agreement of the adequate model on isotherm data. The evaluative procedure and criteria of statistical methods need to be further studied.

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