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A General Model for Sorption Hysteresis in Food Materials

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ABSTRACT

A hypothesis is proposed in this study to account for the origin of sorption hysteresis. The hypothesis is based on the published research evidence that during a sorption process phase change within a material causes temperature gradients which induces heat transfer. The rate of heat transfer in turn greatly influences phase changes and mass transfer leading to the redistribution of the sorbate during a sorption process. Hysteresis is a result of the sorbate mass redistribution. It is shown thermodynamically that sorbate mass redistribution, or rather hysteresis, is an inherent process in order for a material to protect itself from distortion under the extremity of local temperature alteration. Based on the proposed hypothesis, a general mathematical model is developed to quantify the hysteresis loop. The model agrees with the published hysteresis data for food materials. © 1997 Elsevier Science Limited. All rights reserved

NOTATION

a_w	Water activity
A	A model constant
A'	A model constant
B	A model constant
c	Specific heat
C	A model constant

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E	Enthalpy
ΔE	Enthalpy due to sorbate–sorbent interactions
g	Magnitude of the energy of a spherical source
GF	Green's function
h	Amount of redistributed sorbate in either adsorption or desorption
H	Overall hysteresis either inside or outside the spherical source (with subscript); total hysteresis in the entire material (without subscript)
k	Thermal conductivity
L	Latent heat of vaporization or condensation; enthalpy due to phase change
m	Mass of sorbate
N	Molar number
P	Pressure of the system
p	Vapor pressure of water
p_0	Vapor pressure of water at saturation
r	Radius in spherical polar coordinates
r_0	Radius of a continuously distributed spherical energy source
R	Universal gas constant
t	Time
t_0	Time at which the energy of spherical energy source pulses
T	Temperature
V	Molar volume of the sorbate
α	Thermal diffusivity
β	Coefficient between 0 and 1
θ	Angle of contact
ρ	Density
σ	Surface tension
μ	Chemical potential
δ	Dirac delta function
ϕ	Surface potential or spreading pressure
Γ	An intermediate temperature

Subscripts

a	Pure sorbent; adsorption
b	Sorbate in sorbent
ave	Average
b, c	Pertinent to boundary condition
c	Mean
d	Desorption
i	Pertinent to initial condition; within spherical source
g	Pertinent to internal generation
p	Point source
pa	Sorbent containing sorbed water
s	The whole material (sorbent plus sorbate); sorbate vapor
T	Pertinent to a temperature T
w	Sorbate in liquid state
0	Outside spherical source
Γ	At an intermediate temperature Γ

0	Initial; equilibrium; pertinent to spherical source; saturation
1	Local; altered; pertinent to temperature T_1; sorbed water

INTRODUCTION

Sorption hysteresis refers to the difference in the sorbate content of a sorbent between adsorption and desorption process at the same relative vapor pressure. Although the phenomenon has been well observed in most substances for more than a century, the origin of its occurrence remains poorly understood. A great deal of work has so far been published on the theories, hypotheses and interpretations to account for the origin of sorption hysteresis. Kapsalis (1981, 1987) did an extensive review on earlier works. Rizvi and Benado (1984) discussed the hysteresis behavior of dehydrated foods from a thermodynamic perspective where the effect of hysteresis was focally addressed. There has been no generalized model hitherto available that describes the phenomenon quantitatively. Because of this deficiency, the difficulty as how to deal with hysteresis in the thermodynamics of sorption processes remains untangled (Rizvi & Benado, 1984).

It has long been established that sorption hysteresis is affected by temperature, the properties of sorbates and sorbents, equilibration methods, and the history of materials. Sorption hysteresis is also time dependent (Benson & Richardson, 1955; Kapsalis, 1987). The existing theories are unable to address these factors quantitatively as to how much they contribute to the magnitude of hysteresis.

Like many other spontaneous processes, sorption is governed by chemical potential law. A material starts with its initial equilibrium state, goes through a series of heat and mass transfer processes, and ends up with a new equilibrium state. The existing theories, based mostly on equilibrium thermodynamics, are inclined to lay emphasis on the equilibrium states of a material at the beginning and at the end of sorption. They circumvent the process that occurs between the initial and final equilibrium states. The process that connects these two states plays an important role in the occurrence of sorption hysteresis and it should not have been overlooked.

It is well known that sorption is either exothermic or endothermic. The amount of heat involved as a result of the interaction between a sorbate and a sorbent must be transferred via the material itself. One example is the immersion calorimetry. During the measurement, the material being mixed with water releases heat to the water surrounding it. This causes water temperature to rise. The heat evolved must first be transferred through the matrix of the material before it reaches water. Many recent research works (Pierce & Benner, 1986; Tao *et al.*, 1992a,b; Simonson *et al.*, 1993) have demonstrated that phase change mass transfer is coupled with heat transfer during a sorption process, while the resultant heat transfer can alter the local temperature significantly. The change in temperature at a point or in the whole system would in turn induce mass transfer inside the material.

An attempt was made in this study to account for the causes for sorption hysteresis through a proposed hypothesis that considered the correlated heat and mass transfer in a material during a sorption process. Based on this hypothesis, a heat and mass transfer model was developed to quantify the hysteresis loop. The objective of this paper is to present this hypothesis, derive a general mathematical model, and verify the model with published sorption hysteresis data. This model was used to explain the sorption hysteresis commonly presented in the literature.

THE HYPOTHESIS

The motivation for this hypothesis was the behavior of sorption isotherms as affected by temperature changes. It has been well established that both the adsorption and desorption isotherms are shifted downward in response to temperature increase. Because of this shift, it can, sometimes, be observed that an adsorption isotherm overlaps with a desorption isotherm at a higher temperature. This observation suggests that the temperature at which an adsorption occurred is somehow equivalent to that of a desorption proceeding at a higher temperature than the counterpart desorption of this very adsorption process. In other words, an adsorption process may actually take place at a higher temperature than its counterpart desorption process at the same environment temperature. This might be because of the exothermic or endothermic nature of a sorption process.

To present the hypothesis, moisture sorption is taken as an example. To reach an equilibrium between the sorbed water within a material and water vapor in the environment during an isothermal process of moisture sorption (either adsorption or desorption), moisture is transferred from environment to sorbent or vice versa, as governed by the chemical potential law. In adsorption, the interaction of water molecules with a hydrophilic surface accompanies a release of thermal energy. In desorption, when water molecules in the material changes into the vapor phase (or environment), heat is absorbed to initiate phase change. The enthalpy components for a system consisting of the sorbent, the sorbate contained in the sorbent, and the sorbate vapor in the environment before and after sorbate vapor phase change during an adsorption are as follows:

Before phase change
Enthalpy of sorbent (E_a)
Enthalpy of sorbate in sorbent (E_b)
Enthalpy of sorbate vapor (E_s+L)

After phase change
Enthalpy of sorbent (E_a)
Enthalpy of sorbate in sorbent (E_b+E_s)
Enthalpy of sorbate vapor (0)
Enthalpy due to phase change (L)
Enthalpy due to sorbate–sorbent interactions (ΔE)

where E_s is the enthalpy of saturated sorbate and L the latent heat of vaporization. The enthalpy of both sorbent (E_a) and the sorbate in the sorbent (E_b) is assumed to change little during the process. The net enthalpy change in the process before and after phase change is ΔE as shown above. ΔE is positive in adsorption. Similarly, a negative ΔE results during desorption. Excessive heat generated in adsorption must dissipate in the material. Likewise, the excessive heat required in desorption must transfer through the material itself before it would reach desorption sites.

It is hypothesized that the excessive heat involved could not move out of the material to reach the environment instantly in adsorption, nor could the required energy be supplied from the environment and reach the sorption sites instantly in desorption, as a result of heat resistance of the material. In other words, heat had to be transferred through the matrix of the material before it would reach the environment or sorption sites, thus creating a temperature gradient within the material following the onset of the energy release. Here, 'heat accumulation' and 'heat evacuation' are used to characterize the changes in sensible heat of the material during adsorption and desorption, respectively. This hypothesis is readily supported by the experimental results observed by Pierce and Benner (1986), Tao *et al.* (1992a,b), and Simonson *et al.* (1993). For example, Simonson *et al.* (1993) investigated moisture sorption in a fibrous insulation with conditioned air and found that the temperature of the air leaving the insulation was much higher than the inlet temperature in adsorption and vice versa in desorption, especially within first 10 min.

Therefore, adsorption would proceed at raised local temperatures and desorption at lowered local temperatures. It is further hypothesized, based on the published findings as mentioned before, that the temperature changes would induce sorbate mass transfer within the system by following possible means: (1) giving up some of the water molecules that are sorbed in the material during adsorption, or gaining back some of the water molecules that have evaporated from the material during desorption within sorption sites, and (2) inducing moisture evaporation or condensation due to temperature gradient on the way of heat transfer, as a response to the extremity of temperature change to offset the damage to the system, governed by Le Chatelier's principle.

The hypothesis can be interpreted qualitatively from thermodynamic point of view. The chemical potential and water activity of the water vapor in equilibrium with the material are designated as μ_0 and a_{w0} for an isothermal system under the ideal circumstance (i.e., no 'heat accumulation or evacuation' incurred during sorption). In this case, temperature is constant at T_0 throughout the material, and $\mu_0 = RT_0 \ln(a_{w0})$, where R is the universal gas constant. In the presence of 'heat accumulation or evacuation', the local temperature, T_l, of the vapor in equilibrium with the sorbed water in the material would be either higher or lower than T_0 depending on adsorption or desorption processes. Assuming that the chemical potential and water activity of the water vapor at changed temperature were μ_l and a_{wl}, then $\mu_l = RT_l \ln(a_{wl})$. At equilibrium,

$$\mu_l = \mu_0 \tag{1}$$

or,

$$RT_l \ln(a_{wl}) = RT_0 \ln(a_{w0}) \tag{2}$$

It is generally considered that T_l is equal to T_0 in the present theoretical system, so $a_{wl} = a_{w0}$ applies for the equilibrium. However, this is only true for an ideal system where the variation of local temperature is not considered. In a real system, T_l is different from T_0. Thus, a_{wl} will be higher than a_{w0} in adsorption and lower than a_{w0} in desorption, in order to maintain $\mu_l = \mu_0$. In response to such a situation, local evaporation has to take place to lower $\ln(a_{wl})$ in adsorption or vice versa in desorption. This results in a decrease in the equilibrium moisture content of material in adsorption and an increase in the equilibrium moisture content of material in desorption at a given water activity. This causes the hysteresis.

The same conclusion would be reached from eqn (3) (Hill, 1952):

$$\phi = \mu_{pa} - \mu_a = RT \int_0^P \frac{N_l}{N_a} d \ln(P) \tag{3}$$

where ϕ is surface potential or spreading pressure, defined as the difference between the chemical potential of the sorbent containing sorbed water (μ_{pa}) and that of the pure sorbent (μ_a), T is the temperature at which sorption occurs, P is the pressure of the system, and N_l and N_a are the moles of the sorbed water and the sorbent, respectively. As long as equilibrium is established between the sorbed water and vapor phase after the sorbent has gone through previous sorption processes, the state parameters such as P and T are stable, and ϕ is kept at a constant value until the incoming sorption processes initiate. According to Le Chatelier's principle, any factors causing change in a system would simultaneously cause the system to respond in such a way that the changes would be reduced to a minimum. In this case, the factor causing the change was the temperature alteration as a result of sorption. The system could only respond to this change by decreasing in adsorption or increasing in desorption the value of N_l (the moles of sorbed water), since the system pressure P and the moles of the sorbent N_a in eqn (3) remain constant. This might be why adsorption isotherms normally lie below the desorption isotherms to yield hysteresis.

A MATHEMATICAL MODEL TO QUANTIFY SORPTION HYSTERESIS

A mathematical model in terms of the principles of heat and mass transfer has been developed based on the hypothesis described above.

Some assumptions regarding the heat and mass transfer patterns were made. Although in principle the mass transfer mode includes evaporation, condensation, diffusion, mixing, and other possible means, the mode for sorbate phase change, i.e., evaporation and condensation, were considered in this study as two major ways of moisture redistribution induced by temperature ingredients. It is assumed that conduction was the predominant mode for the excessive heat released or absorbed during sorption to be transferred through the material. In adsorption, water molecules that are absorbed onto the material could be regarded as a continuously distributed spherical energy source with a radius r_0 that instantaneously provided a pulse of energy $g_0(r_0,t_0)$ at time t_0. The resulting heat would transfer through the material that could be taken as an infinite body in relation to the dimension of the spherical surface source. The transient heat conduction in the material can be regarded as radial flow in a spherical system. In spherical polar coordinates, temperature is only a function of time and the radius, but independent of polar angles. In desorption, the assumptions are similar to those considered in adsorption, except that the instantaneous source has an energy equal to $-g_0(r_0,t_0)$. The heat conduction in spherical coordinate system is governed by the following equation (Carslaw and Jaeger, 1959; Beck *et al.*, 1992):

$$\frac{1}{r} \frac{\partial^2(rT)}{\partial r^2} + \frac{g(r,t)}{k} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \tag{4}$$

where k is thermal conductivity of a substance in W/m K, α is thermal diffusivity and equals $k/(\rho c)$ where ρ is the density of the substance in kg/m^3 and c its specific heat in kJ/kg K, and $g(r,t) = \delta(t-t_0)\delta(r-r_0)g(r_0,t_0)/(4\pi\rho_0^2)$ where δ is the Dirac delta function. The initial condition is $T(r,0) = T_0$. The temperature on the surface of the material ($r \rightarrow \infty$) is assumed to be T_0.

There are many possible ways to solve eqn (4). However, solutions in the form of Green's function (GF) is flexible, powerful and systematic. They also contain straightforward physical meanings that would help understand the conduction process better. The solution to eqn (4) in terms of GF is given as follows (Beck *et al.*, 1992):

$$T(r,t) = T_i(r,t) + T_g(r,t) + T_{b,c}(r,t) \tag{5}$$

where $T_i(r,t)$ is the contribution of initial condition to $T(r,t)$ and it is in the form:

$$T_i(r,t) = \int_0^{\infty} 4\pi GF(r,t|r_0,t_0)T(r_0,0)r'^2 dr' \tag{6}$$

$T_g(r,t)$ is the contribution of internal generation to $T(r,t)$ and it assumes the following form:

$$T_g(r,t) = \int_{\tau=o}^{t} \int_{r'=o}^{\infty} \frac{4\pi\alpha}{k} GF(r,t|r_0,t_0)g(r_0,t_0)r'^2 dr' d\tau \tag{7}$$

$T_{b,c}(r,t)$ is the contribution of boundary conditions and it is equal to zero in this case. The GF for spherical radial flow of heat in an infinite body can be written as follows (Beck *et al.*, 1992):

$$GF(r,t|r_0,t_0) = \frac{1}{8\pi r r_0\sqrt{\pi\alpha(t-t_0)}} \left\{ \exp\left[-\frac{(r-r_0)^2}{4\alpha(t-t_0)} \right] - \exp\left[-\frac{(r+r_0)^2}{4\alpha(t-t_0)} \right] \right\} \tag{8}$$

Integration of eqns (6) and (7) incorporating eqn (8) yields:

$$T_i(r,t) = T_0$$

and

$$T_g(r,t) = \frac{g_0(r_0,t_0)}{\rho c} \frac{1}{8\pi r r_0\sqrt{\pi\alpha(t-t_0)}} \left\{ \exp\left[-\frac{(r-r_0)^2}{4\alpha(t-t_0)} \right] - \exp\left[-\frac{(r+r_0)^2}{4\alpha(t-t_0)} \right] \right\} \tag{9}$$

Thus,

$$T(r,t) = T_0 + \frac{g_0(r_0,t_0)}{\rho c} \frac{1}{8\pi r r_0\sqrt{\pi\alpha(t-t_0)}} \left\{ \exp\left[-\frac{(r-r_0)^2}{4\alpha(t-t_0)} \right] - \exp\left[-\frac{(r+r_0)^2}{4\alpha(t-t_0)} \right] \right\} \tag{10}$$

Equation (10) can be rewritten as:

$$T(r,t) = T_0 + \frac{g_0(r_0,t_0)}{\rho c} GF(r,t|r_0,t_0) \tag{11}$$

Rearranging eqn (11) gives

$$GF(r,t|r_0,t_0) = \frac{\rho c}{g_0(r_0,t_0)} [T(r,t) - T_0] \tag{12}$$

Equation (12) suggests that the Green Function is equal to the temperature rise as the result of energy pulse divided by the strength of the source and multiplied by ρc, at the spherical surface $r = r_0$ at time t_0.

In the case of point source ($r_0 \rightarrow 0$), eqn (10) reduces to

$$T(r,t|r_0,t_0) = T_0 + \frac{g_0(0,t_0)}{\rho c} \frac{1}{[4\pi\alpha(t-t_0)]^{1{\cdot}5}} \exp\left[-\frac{r^2}{4\alpha(t-t_0)}\right] \tag{13}$$

or,

$$T(r,t|r_0,t_0) = T_0 + \frac{g_0(0,t_0)}{\rho c} GF(r,t|0,t_0) \tag{14}$$

As the result of internal instantaneous generation or evacuation of energy (ΔE), the temperatures both inside and outside the spherical source (within the material boundary) would be increased in adsorption and decreased in desorption. One part of ΔE contributed to the temperature variation inside the spherical source and the other to the temperature change of the region between the spherical source and the boundary of the material. As hypothesized before, mass redistribution would take place within the spherical source and along the path of heat transfer. Separate approaches were taken to deal with the mass transfer in the source and the rest of the material.

Mass redistribution within the spherical source

The spherical source contains solely sorbate at a radius r_0. The average temperature change in the spherical source, T_{ave}, can be calculated as follows:

$$T_{\text{ave}} = \frac{\int_0^{r_0} rT(r,t)dr}{\int_0^{r_0} rdr} \tag{15}$$

After introducing eqn (10) into eqn (15) and integrating eqn (15) by referring to the integrals and functions in Beck *et al.* (1992), we have

$$T_{\text{ave}} = T_0 + \frac{g_0(r_0,t_0)}{4\pi r_0^3 \rho_w c_w} \left\{ 2\operatorname{erf}\left[\frac{r_0}{\sqrt{4\alpha_w(t-t_0)}}\right] - \operatorname{erf}\left[\frac{2r_0}{\sqrt{4\alpha_w(t-t_0)}}\right] \right\} \tag{16}$$

where ρ_w is the density of sorbate in liquid state, c_w its specific heat, and α_w its thermal diffusivity.In the case of a point source, the temperature T_p at the origin (where the point source was situated) after an impulse can be obtained from eqn (13) by setting $r \rightarrow 0$.

$$T_p = T_0 + \frac{g_0(0,t_0)}{\rho_w c_w} [4\pi\alpha_w(t-t_0)]^{-\frac{3}{2}} \tag{17}$$

If a fraction of the impulse energy, $\beta\Delta E$ where β is a coefficient between 0 and 1, contributes to the temperature change from T_0 to T_{ave}, the heat balance inside the source can be written as:

$$\beta\Delta E = m_0 c_w (T_{ave} - T_0) \tag{18}$$

where m_0 is the mass of the sorbate in the spherical source. It is noted that m_0 could always be expressed as $4\pi r_0^3 \rho_w/3$ according to the definition of spherical source. As hypothesized earlier, an amount of sorbate would be responsively de-sorbed or re-sorbed to offset the effect of temperature variation. The amount of energy carried by the responsively de-sorbed or re-sorbed sorbate should equal to $\beta\Delta E$. Accordingly, eqn 18 can be rewritten as:

$$h_i L_{T_{ave}} = m_0 c_w (T_{ave} - T_0) \tag{19}$$

where h_i is the amount of redistributed sorbate within the spherical source in either adsorption or desorption, and $L_{T_{ave}}$ the latent heat of vaporization or condensation at T_{ave}. Replacing $T_{ave} - T_0$ in eqn (19) by eqn (16), we have

$$h_i = \frac{m_0 g_0(r_0,t_0)}{4\pi r_0^3 \rho_w L_{T_{ave}}} \left\{ 2\mathrm{erf}\left[\frac{r_0}{\sqrt{4\alpha_w(t-t_0)}} \right] - erf\left[\frac{2r_0}{\sqrt{4\alpha_w(t-t_0)}} \right] \right\} \tag{20}$$

Equation (20) is a general form accountable for the hysteresis either in adsorption or desorption. The term $g_0(r_0,t_0)$ is positive in adsorption (denoted by $g_{0,a}(r_0,t_0)$ and negative in desorption (denoted by $g_{0,d}(r_0,t_0)$. $L_{a,Tave}$ and $L_{d,Tave}$ are used to differentiate the latent heat of condensation (adsorption) and the latent heat of vaporization (desorption) of water, respectively, although they would be the same in most cases.

The overall hysteresis within the spherical source, H_i, is the sum of h_i in both adsorption and desorption, and thus has the following form:

$$H_i = \left[\frac{(m_0)_a g_{0,a}(r_0,t_0)}{L_{a,T_{ave}}} + \frac{(m_0)_d |g_{0,d}(r_0,t_0)|}{L_{d,T_{ave}}} \right] \frac{1}{4\pi \rho_w r_0^3} * \left\{ 2\mathrm{erf}\left[\frac{r_0}{\sqrt{4\alpha_w(\mathrm{t}-\mathrm{t}_0)}} \right] \right.$$

$$\left. - \mathrm{erf}\left[\frac{2r_0}{\sqrt{4\alpha_w(t-t_0)}} \right] \right\} \tag{21}$$

Similarly, for point source, the hysteresis in either adsorption or desorption, $h_{p,i}$, is

$$h_{p,i} = \frac{m_0 g_0(0,t_0)}{\rho_w L_{T_p}} [4\pi\alpha_w(t-t_0)]^{-\frac{3}{2}} \tag{22}$$

and the overall hysteresis, $H_{p,i}$, is

$$H_{p,i} = \left[\frac{(m_0)_a g_{0,a}(0,t_0)}{L_{a,T_p}} + \frac{(m_0)_d |g_{0,d}(0,t_0)|}{L_{d,T_p}} \right] \frac{1}{\rho_w} [4\pi\alpha_w(t-t_0)]^{-\frac{3}{2}} \tag{23}$$

where $g_{0,a}(0,t_0)$, $g_{0,d}(0,t_0)$, $L_{a,Tp}$ and $L_{d,Tp}$ have similar meanings to the notations for spherical source. Recall that m_0 was interchangeable with $4\pi r_0^3 \rho_w/3$. Replacing $(m_0)_a$ and $(m_0)_d$ with $4\pi r_0^3 (\rho_w)_a/3$ and $4\pi r_0^3 (\rho_w)_d/3$, respectively, and assuming $(\rho_w)_a = (\rho_w)_d = \rho_w$, eqn 23 becomes

$$H_{p,i} = \left[\frac{g_{0,a}(0,t_0)}{L_{a,T_p}} + \frac{|g_{0,d}(0,t_0)|}{L_{d,T_p}} \right] \frac{4\pi r_0^3}{3} [4\pi\alpha_w(t-t_0)]^{-\frac{3}{2}} \tag{24}$$

Mass redistribution outside the spherical source

To aid the derivation of hysteresis expression in the region outside the spherical source where both sorbent and sorbate are contained, a spherical shell of infinitely small thickness dr is taken at a radius r. The volume of this thin shell is $4\pi r^2 dr$. Assuming that the specific heat and the density of the material contained in it are c_s and ρ_s, the amount of material in the thin shell is $4\pi\rho_s r^2 dr$. As described earlier, the amount of energy impulse $(1-\beta)\Delta E$ will contribute to the mass redistribution outside the spherical source. An amount of sorbate, dh_r, would be responsively evaporated (in adsorption) or condensed (in desorption) due to the variation in temperature at a radius r, i.e., $T(r,t|r_0,t_0) - T_0$. The following relationship exists:

$$dh_r L_T = 4\pi\rho_s c_s [T(r,t|r_0,t_0) - T_0] r^2 dr$$

or,

$$dh_r L_T = \frac{g_0(r_0,t_0)}{2r_0\sqrt{\pi\alpha_s(t-t_0)}} \left\{ \exp\left[-\frac{(r-r_0)^2}{4\alpha_s(t-t_0)} \right] - \exp\left[-\frac{(r+r_0)^2}{4\alpha_s(t-t_0)} \right] \right\} r dr \tag{25}$$

where L_T is the latent heat of either vaporization or condensation of sorbate at the temperature T corresponding to a radius r and α_s the thermal diffusivity of the material. Remember that h_r varies from 0 to h_0 (the amount of redistributed mass that is equal to the hysteresis amount in this region either in adsorption or desorption) and r from r_0 to ∞, and we have:

$$h_0 = \int_{r_0}^{\infty} \frac{g_0(r_0,t_0)}{2r_0 L_T \sqrt{\pi\alpha_s(t-t_0)}} \left\{ \exp\left[-\frac{(r-r_0)^2}{4\alpha_s(t-t_0)} \right] - \exp\left[-\frac{(r+r_0)^2}{4\alpha_s(t-t_0)} \right] \right\} r dr \tag{26}$$

Using the intermediate-value theorem of integration, eqn (26) becomes:

$$h_0 = \frac{g_0(r_0,t_0)}{2r_0 L_\Gamma \sqrt{\pi\alpha_s(t-t_0)}} \int_{r_0}^{\infty} \left\{ \exp\left[-\frac{(r-r_0)^2}{4\alpha_s(t-t_0)} \right] - \exp\left[-\frac{(r+r_0)^2}{4\alpha_s(t-t_0)} \right] \right\} r dr \tag{27}$$

where L_Γ is the latent heat of vaporization or condensation at an intermediate temperature Γ, corresponding to the radius r_Γ ($r_0 < r_\Gamma < \infty$). Integration eqn (27) gives:

$$h_0 = \frac{g_0(r_0,t_0)\sqrt{\alpha_s(t-t_0)}}{2\sqrt{\pi} r_0 L_\Gamma} \left\{ 1 - \exp\left[-\frac{r_0^2}{\alpha_s(t-t_0)} \right] + \frac{2r_0 erfc(r_0)}{\sqrt{\alpha_s(t-t_0)}} \right\} \tag{28}$$

where $erfc(r_0)$ is the complementary error function. Similarly, h_0 accounts for the hysteresis in the region outside the spherical source in either adsorption or desorption. The total hysteresis in this region, H_0, is

$$H_{\Theta}=\left[\frac{g_{0,\mathrm{a}}(r_0,t_0)}{L_{\mathrm{a},\Gamma}}+\frac{|g_{0,\mathrm{d}}(r_0,t_0)|}{L_{\mathrm{d},\Gamma}}\right]\frac{\sqrt{\alpha_{\mathrm{s}}(t-t_0)}}{2\sqrt{\pi}r_0}\left\{1-\exp\left[-\frac{r_0^2}{\alpha_{\mathrm{s}}(t-t_0)}\right]+\frac{2r_0erfc(r_0)}{\sqrt{\alpha_{\mathrm{s}}(t-t_0)}}\right\} \tag{29}$$

For point source, the total hysteresis, $H_{\mathrm{p},\theta}$, can be found by taking limit of eqn (29) as $r_0 \rightarrow 0$. This operation is equivalent to the following:

$$Lim_{r_0\rightarrow 0}\frac{1-\exp\left[-\frac{r_0^2}{\alpha_{\mathrm{s}}(t-t_0)}\right]+\frac{2r_0erfc(r_0)}{\sqrt{\alpha_{\mathrm{s}}(t-t_0)}}}{r_0}=\frac{2}{\sqrt{\alpha_{\mathrm{s}}(t-t_0)}} \tag{30}$$

Thus,

$$H_{\mathrm{p},\theta}=\frac{1}{\sqrt{\pi}}\left[\frac{g_{0,\mathrm{a}}(0,t_0)}{L_{\mathrm{a},\Gamma}}+\frac{|g_{0,\mathrm{d}}(0,t_0)|}{L_{\mathrm{d},\Gamma}}\right] \tag{31}$$

At this point, the total hysteresis in the entire material for spherical source, H, can be calculated by addition of H_{i} (eqn (21)) and H_{θ} (eqn (29)); that is,

$$H=H_{\mathrm{i}}+H_{\theta} \tag{32}$$

Similarly, the total hysteresis in the entire material for point source, H_{p}, was eqn (24) plus eqn (31); that is,

$$H_{\mathrm{p}}=H_{\mathrm{p,i}}+H_{\mathrm{p},\theta} \tag{33}$$

DISCUSSION

Factors affecting hysteresis

From eqn (21), eqn (29), eqn (32) and eqn (33), it can be seen that the magnitude of hysteresis depended on (1) excessive heat involvement due to sorbent–sorbate interactions ($g_0(r_0,t_0)$), (2) the amount of sorbate undergoing phase change (m_0), (3) thermophysical properties of the material and sorbate (α_{s}, c_{s}, α_{w}, c_{w}, L, ρ_{s} and ρ_{w}), (4) equilibration time (t), and (5) temperature (by way of m_0 and complementary error function), which will be discussed later.

Interpretation of r_0 and m_0

The physical meaning of r_0 is, as defined previously, the radius of a spherical source. The spherical source can be theoretically considered as a collection of sorbate all over a sorbent, although the sorbate might become sorbed in the sorbent at different locations. Therefore, r_0 should accordingly be regarded as an equivalent radius of the collection of sorbate contained in the sorbent.

When there was no sorption, $r_0 = 0$. At low relative pressures, r_0 was small due to limited sorption. As sorption increases with relative pressure, r_0 also increases until at extremely high relative pressure when it approaches the dimension of the material (infinite body), i.e., $r_0 \rightarrow \infty$. Therefore, r_0 actually relates to different regions of an isotherm and can be expressed with respect to relative pressure by certain functions. One possible function (eqn (34b)) is the relationship that resembles the Kelvin's equation (Kapsalis, 1981) (eqn (34a)), if a sorption process is perceived as the case of liquid spreading over or contracting from a solid surface.

$$RT \ln\left(\frac{p}{p_0}\right) = -\frac{2\sigma V \cos\theta}{r_0} \tag{34a}$$

or

$$r_0 = -\frac{2\sigma V \cos\theta}{RT \ln(p/p_0)} \tag{34b}$$

where p/p_0 is the relative pressure at temperature T, σ the surface tension, V the molar volume of the sorbate, θ the angle of contact, and R the universal gas constant.Since m_0 is the mass of the spherical source with a radius r_0 that could, as mentioned earlier, be related to different regions of an isotherm, m_0 could also be expressed in relation to relative pressure. Relationships similar to the published isotherm models such as the BET (Brunauer *et al.*, 1938), GAB (Anderson, 1946), Halsey (1948), Oswin (1946), Henderson (1952) and Chung–Pfost (1967) equations could be used in this regard.

Hysteresis when $r_0 \to \infty$

From eqn (32), namely, eqn (21) and eqn (29), it can be found that H was equal to zero when $r_0 \to \infty$. This can be perceived as the case when sorbate occupied the entire material, an infinite body ($r \to \infty$), as hypothesized before. This corresponded to the isothermal region at extremely high water activity. In this region, most substances show zero or very small hysteresis. This model predicts such a common hysteresis behavior.

Hysteresis when $r_0 \to 0$

This is the case of sorption at the isothermal region close to zero water activity. Two situations need to be distinguished. One is the case of no sorption at all. In this case, no mass is involved in phase change ($m_0 = 0$) and no heat is released or absorbed ($g_0(r_0,t_0) = 0$). The other is the case of sorption during which heat is still released or absorbed, but the mass involved in phase change is so small that it can be taken as infinitesimal. This is a point source case where m_0 is infinitesimal (but still other than zero), r_0 could be taken as 0, and $g_0(0,t_0)$ is not zero. The magnitude of $g_0(0,t_0)$ depends upon the intensity of the interactions between sorbent and sorbate. The intensity in turn depends on the chemical composition, structure, and related properties of the sorbent and sorbate. From eqn (32), it is obvious that $H = 0$ when there was no sorption at all. However, there existed hysteresis in the case of point source, as shown by eqn (33) (i.e., eqn (24) and eqn (31)). It can be seen that the magnitude of hysteresis in the case of point source was related to material and sorbate properties (α_s, ρ_s, c_s, α_w, ρ_w and c_w) and the heat involvement, such as $g_0(r_0,t_0)$ and L_{Tp}. If the energy pulse $g_0(r_0,t_0)$ is negligibly small, H_p will be next to zero. However, if $g_0(r_0,t_0)$ is high, H_p will end up assuming a value different from zero. This could explain, to some extent, why a big hysteresis gap exists for air-dried apple even at water activities close to zero (Wolf *et al.*, 1972). This is possibly because intense heat involvement exists during hydrogen bonding between the sugar in apple and water molecules.

Time-dependent characteristics

Both eqn (32) and eqn (33) clearly show that hysteresis is time-dependent. At $t \rightarrow t_0^+$, that is, immediately following the instant of energy pulse, the following can be derived from eqn (32):

$$H = \left[\frac{(m_0)_a g_{0,a}(r_0,t_0)}{L_{a,T_{ave}}} + \frac{(m_0)_d |g_{0,d}(r_0,t_0)|}{L_{d,T_{ave}}} \right] \frac{1}{4\pi \rho_w r_0^3} + \left[\frac{g_{0,a}(r_0,t_0)}{L_{a,\Gamma}} + \frac{|g_{0,d}(r_0,t_0)|}{L_{d,\Gamma}} \right] \frac{1}{\sqrt{\pi}} erfc(r_0) \tag{35}$$

For point source, H_p at $t = t_0$ is undecided due to the infinitesimal r_0^3 and $t - t_0$ (eqn (33) and eqn (24)). Whether H_p has a certain value or infinity depends on the speed of r_0^3 and $t - t_0$ to approach zero. Three possibilities exist. One possibility is that the limit of $[r_0^3/(t-t_0)^{3/2}]$ is zero when both r_0 and $(t-t_0) \rightarrow o$. Then,

$$H_p = H_{p,o} = \frac{1}{\sqrt{\pi}} \left[\frac{g_{0,a}(0,t_0)}{L_{a,\Gamma}} + \frac{|g_{0,d}(0,t_0)|}{L_{d,\Gamma}} \right] \tag{36}$$

The second possibility is that this limit is unity. Then,

$$H_p = \frac{1}{6\sqrt{\pi \alpha_w^3}} \left[\frac{g_{0,a}(r_0,t_0)}{L_{a,T_p}} + \frac{|g_{0,d}(r_0,t_0)|}{L_{d,T_p}} \right] + \frac{1}{\sqrt{\pi}} \left[\frac{g_{0,a}(r_0,t_0)}{L_{a,\Gamma}} + \frac{|g_{0,d}(r_0,t_0)|}{L_{d,\Gamma}} \right] \tag{37}$$

The third possibility is that this limit approaches infinity. In such a case, H_p is infinite. This result can be interpreted as the situation when the sorption is so little while the heat involvement is so significant that the redistributed mass over the infinitesimal time $t - t_0$ was phenomenally huge as compared to the infinitesimal phase-change mass.

When $t \rightarrow \infty$, i.e., $(t - t_0) \rightarrow \infty$, eqn (32) approaches eqn (38) as $(t - t_0) \rightarrow \infty$.

$$H = \frac{1}{\sqrt{\pi}} \left[\frac{g_{0,a}(r_0,t_0)}{L_{a,\Gamma}} + \frac{|g_{0,d}(r_0,t_0)|}{L_{d,\Gamma}} \right] erfc(r_0) \tag{38}$$

For point source,

$$H_p = \frac{1}{\sqrt{\pi}} \left[\frac{g_{0,a}(r_0,t_0)}{L_{a,\Gamma}} + \frac{|g_{0,d}(r_0,t_0)|}{L_{d,\Gamma}} \right] \tag{39}$$

The case of $(t - t_0) \rightarrow \infty$ actually reflects the situation when a material is left in an isothermal chamber to equilibrate with a sorbate for an infinite time. This case deserved special attention due to the fact that the published isotherms were generally obtained by equilibrating a sorbate with a sorbent at a constant temperature for a length of time that is long enough for equilibrium to be reached. This could be approximately regarded as the case of $(t-t_0)\rightarrow\infty$, so eqn (38) and eqn (39) were applicable to the real isothermal cases.

It is interesting to note that when $(t-t_0)\rightarrow\infty$, the first term of eqn (32) becomes zero. This suggests that the effect of mass redistribution within the spherical source on hysteresis approaches zero as time approaches infinity. However, the effect of mass redistribution outside the spherical source on hysteresis, namely, the second term of eqn (32), still remains. This contributes to the final hysteresis magnitude as time approaches infinity. Furthermore, the difference between the spherical (eqn (38)) and point source (eqn (39)) was $erfc(r_0)$. In the case of point source, H_p is only affected by material and sorbate properties and the heat involvement during sorption. In the case of spherical source, H also varies with r_0 in addition to the effect of material properties and the heat involvement. As discussed earlier, r_0 relates to the region of an isotherm at different relative pressures. Therefore, eqn (38) is applicable to describing the hysteresis at every region of an isotherm.

The shape of hysteresis loop

It has been well known that the hysteresis loop of most substances exhibits a skewed bell shape. Equation (32) could predict such a unique characteristics of hysteresis. For the purpose of simplification, eqn (38), which is close to the real situation as mentioned earlier, is taken as example. Since $g_{0,a}(r_0,t_0)$ and $g_{0,d}(r_0,t_0)$ are the excessive heat released or absorbed by the spherical source during adsorption and desorption, respectively, their magnitudes can be expressed as $(m_0)_a^*\Delta E_a$ and $(m_0)_d^*\Delta E_d$, where ΔE_a and ΔE_d are the net enthalpy change (or excessive heat involvement) in adsorption and desorption, respectively. Replacing $g_{0,a}(r_0,t_0)$ and $g_{0,d}(r_0,t_0)$ with $(m_0)_a^*\Delta E_a$ and $(m_0)_d^*\Delta E_d$, and substituting r_0 in eqn (38) with eqn (34b), we have

$$H=\frac{1}{\sqrt{\pi}}\left[\frac{(m_0)_a\Delta E_a}{L_{a,\Gamma}}+\frac{(m_0)_d|\Delta E_d|}{L_{d,\Gamma}}\right]erfc\left[-\frac{2\sigma V\cos\theta}{RT\ln(p/p_0)}\right] \tag{40}$$

Since

$$\left[\frac{(m_0)_a\Delta E_a}{L_{a,\Gamma}}+\frac{(m_0)_d|\Delta E_d|}{L_{d,\Gamma}}\right]$$

in eqn (40) always varies with relative vapor pressure in an ascending trend between 0 (when $p/p_0\rightarrow 0$) and a positive value, and

$$erfc\left[-\frac{2\sigma V\cos\theta}{RT\ln(p/p_0)}\right]$$

always varies with relative vapor pressure between 1 and 0 in a descending trend, their product thus yielded a peaked-curve of skew bell shape. Figure 1A depicts such a relationship for four typical shapes of

$$\left[\frac{(m_0)_a\Delta E_a}{L_{a,\Gamma}}+\frac{(m_0)_d|\Delta E_d|}{L_{d,\Gamma}}\right]$$

vs. p/p_0, i.e., concave (case 1), convex (case 2), straight line (case 3), and sigmoid (case 4). The product of

$$\left[\frac{(m_0)_a \Delta E_a}{L_{a,\Gamma}} + \frac{(m_0)_d |\Delta E_d|}{L_{d,\Gamma}}\right]$$

and *erfc* all resulted in peaked-curves of skew bell shape.

According to the experimental evidence observed so far, hysteresis loops of most substances can be categorized into three major shapes (Wolf *et al.*, 1972; Kapsalis, 1981), i.e., those with their peaks located towards low relative pressures (exemplified by Garnet wheat (Babbitt, 1945); air-dried apple, carrots, and haddock (Wolf *et al.*,

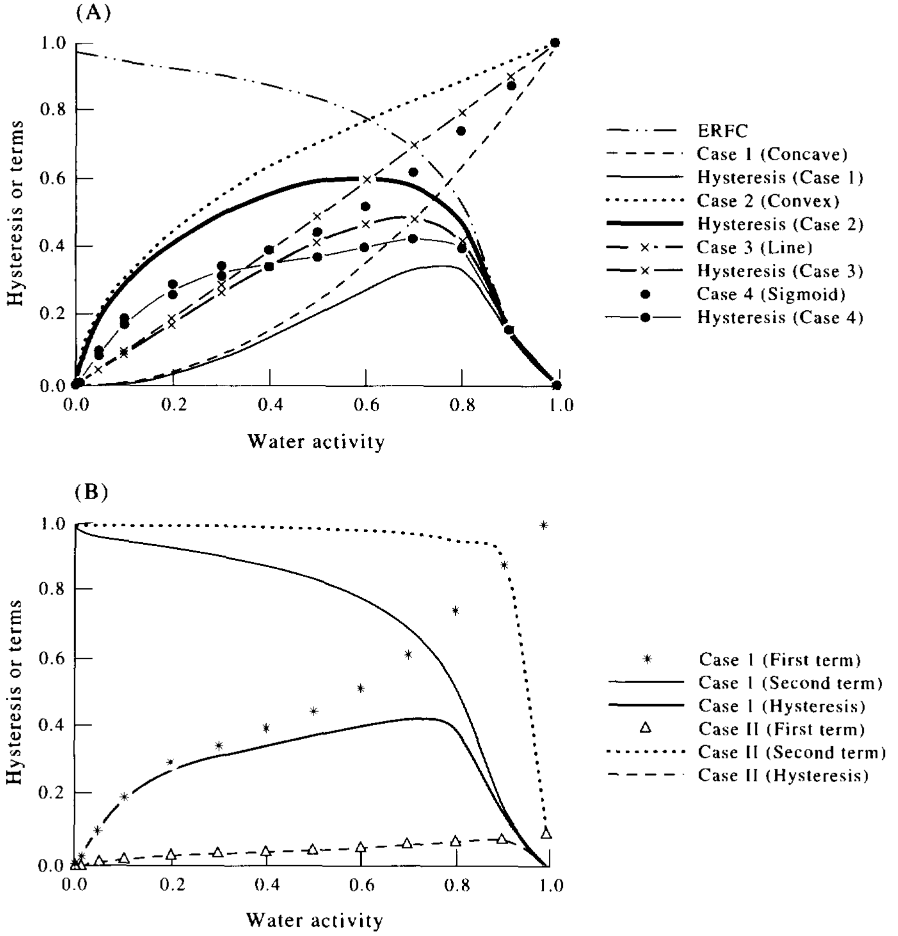

Fig. 1. Illustrations to show the shape of hysteresis loop (A) and the effect of temperature on the magnitude of hysteresis (B).

1972)), appearing in intermediate relative pressure range (exemplified by flour and freeze-dried gluten (Bushuk & Winkler, 1957); beef (Wolf *et al.*, 1972)), and oblique to intermediate-high relative pressures (exemplified by potato and rice (Wolf *et al.*, 1972); potato starch (Bizot *et al.*, 1985); millet (Ajisegiri & Sopade, 1990)). From eqn (40) it can be seen that the orientation of the peak and the shape of the hysteresis loop were controllable by the factors such as ΔE (i.e., $(\Delta E)_a$ and/or $(\Delta E)_d$), m_0, ρ_w, c_w, ρ_s, c_s, L_Γ, σ, V, θ, and T, predominantly by the magnitude of ΔE and m_0 in one or both of adsorption and desorption. For example, the skewness of the hysteresis loop of high sugar and pectin foods towards low relative pressures (Wolf *et al.*, 1972) may be a result of intense ΔE in this relative pressure range because of hydrogen bonding. High ΔE causes the hysteresis loop to peak in the low relative pressure range. For potato starch (Bizot *et al.*, 1985), it may be that the solubility of starch increases in the capillary condensation region which opens up more sorption sites so that both ΔE and m_0 increase in this region. This causes the hysteresis loop to peak at the capillary condensation region.

Experimental evidence shows that some materials exhibit no hysteresis or disappearance of hysteresis after repeated adsorption–desorption cycles (Kapsalis, 1987). Equation (40) could also predict this hysteresis behavior. From eqn (40), it can be seen that the hysteresis is zero when ΔE is equal to zero, regardless of other parameters in the equation. As mentioned earlier, ΔE is the net enthalpy change during sorption. Zero ΔE means no excessive heat generation or 'evacuation' involved. This condition can be satisfied if a sorbent behaved like a 'sponge', i.e., absorbed or released sorbate that underwent only phase change without involving in any sorbent–sorbate interactions that would generate ΔE. In other words, if a sorption involves only a reversible change in enthalpy (i.e., the latent heat due to phase change) without any irreversible enthalpy change due to sorbent–sorbate interactions, there would be no hysteresis observed. Since successive adsorption–desorption cycles might 'deactivate' or 'make blunt' any originally active sorption sites (Rao, 1941, 1942; Kapsalis, 1981), it could turn out that no more enthalpy-altering interactions between the sorbent and the sorbate occur in deactivated sorbents. Hysteresis thus disappeared after multiple adsorption–desorption cycles.

Effect of temperature

Published information in this regard suggests that an increase in temperature results in a decrease in the amount of hysteresis. This can be explained by eqn (40).

Recall that m_0 is the sorbate mass condensed from vapor in adsorption or evaporated into vapor in desorption during sorbate phase change when $g_0(r_0,t_0)$ is generated. The mass of equivalent vapor is also m_0, which can be related to the temperature (T), pressure (P), molecular mass of sorbate (M) and volume of sorbate (V) by the gas law. Generally speaking, sorbate vapor should be treated as a non-ideal gas and its volume needs correction. There are relevant theories that can be used readily. However, for simplicity sorbate vapor is approximated by an ideal gas, and the following relationship applies:

$$m_0 = (PVM)/(RT) \tag{41}$$

From eqn (41), it is obvious that m_0 is reversely proportional to T. So is H.

On the other hand, the complementary error function

$$erfc\left[-\frac{2\sigma V\cos\theta}{RT\ln(p/p_0)}\right]$$

becomes closer and closer towards unity as the temperature increases towards infinity. The value of

$$erfc\left[-\frac{2\sigma V\cos\theta}{RT\ln(p/p_0)}\right]$$

becomes less and less dependent on p/p_0 as temperature increases. In other words, the more the temperature, the more the magnitude of hysteresis depends on the first term of eqn (40), i.e.,

$$\left[\frac{(m_0)_a\Delta E_a}{L_{a,r}}+\frac{(m_0)_d|\Delta E_d|}{L_{d,r}}\right],$$

and the less it depends on the second term of eqn (40), i.e.,

$$erfc\left[-\frac{2\sigma V\cos\theta}{RT\ln(p/p_0)}\right].$$

This explains the phenomenon that hysteresis magnitude generally decreases with the increase of equilibration temperature.

Figure 1B depicts the relationship described above, where the temperature in case II is presumably 10 times that in case I (all other parameters are assumed the same in both cases). It can be seen, the hysteresis in case II is much smaller than that in case I.

MODEL VERIFICATION

Since all the published hysteresis is, as mentioned earlier, obtained in the condition that could be regarded as $(t-t_0)\rightarrow\infty$, eqn (40) is used for model verification.

To further simplify eqn (40), it is assumed that the net enthalpy change in adsorption and desorption was about the same, i.e., $(\Delta E)_a\approx(\Delta E)_d=\Delta E$. Since the latent heat of vaporization of water ($L_{d,r}$) is generally the same as the latent heat of condensation ($L_{a,r}$) at the same temperature and pressure, eqn (40) becomes

$$H=\frac{\Delta E}{\sqrt{\pi}L_r}(m_{0,a}+m_{0,d})erfc\left[-\frac{2\sigma V\cos\theta}{RT\ln(p/p_0)}\right] \tag{42a}$$

where $m_{0,a}$ and $m_{0,d}$ denote the m_0 for adsorption and desorption, respectively. They could, as discussed earlier, be expressed as a function of p/p_0 (or a_w) by published isotherm models. Through m_0, the hysteresis representation is linked to the present theoretical system of sorption isotherms. Equation (42a) can be further simplified by assuming that the mean of $m_{0,a}$ and $m_{0,d}$, m_c, follows the isotherm equations as well, that is,

$$H=A'm_c erfc[-B\ln^{-1}(a_w)] \tag{42b}$$

where A' and B equal to

$$\frac{2\Delta E}{\sqrt{\pi}L_{\Gamma}}$$

and

$$\frac{2\sigma V\cos\theta}{RT},$$

respectively.

The hysteresis data of Garnet wheat (Babbitt, 1945), air-dried apple (4·4°C), stored haddock, unstored beef, rice (37·8°C) and unstored potato (Wolf *et al.*, 1972), flour and freeze-dried gluten (Bushuk & Winkler, 1957), and millet (Ajisegiri & Sopade, 1990) were digitized from the figures by these authors and used for model verification in this study. These data represent three main categories of the shape of hysteresis loop. Non-linear regression was performed using the computer package 'TableCurve 2·02' (Jandel Scientific, 1994) to fit eqn (42b) to the hysteresis data. For simplicity temperature effect was not considered in this study. The isotherm models used in curve fitting were: the Langmuir (Brunauer *et al.*, 1938), BET (Brunauer *et al.*, 1938), Harkins and Jura (1944), GAB (Anderson, 1946), Hailwood and Harrobin (1946), Oswin (1946), Smith (1947), Halsey (1948), Henderson (1952), Kuhn (1964), Chung and Pfost (1967), Caurie (1970), Mizrahi *et al.* (1970), and Chen (1971) equations. Among these isotherm models, 11 equations, i.e., the BET, Chung–Pfost, GAB, Hailwood–Harrobin, Halsey, Henderson, Kuhn, Langmuir, Mizrahi *et al.*, Oswin and Smith, were found to perform better than the rest. Table 1 lists the 11 best performing hysteresis equations that emerged after the 11 isotherm equations were incorporated into eqn (42b). For convenience, the hysteresis equations were named after the same name of the isotherm equation. Statistical criteria, i.e., coefficient of determination (R^2), standard error of residuals (SD), coefficient of variation (CV%), and residual distribution pattern in terms of the number of runs (RUN) (Swed & Eisenhart, 1943; Beck & Arnold, 1977), are used to evaluate the goodness-of-fit of eqn (42b) to the hysteresis data (Table 2). To exemplify the goodness-of-fit of eqn (42b) to the hysteresis data, Figs 2–4 show the predicted curve vs. the hysteresis data for one material in each hysteresis category using one of the best-performing equation for this material (i.e., the Halsey for air-dried apple in hysteresis peak category I, the Oswin for freeze-dried gluten in hysteresis peak category II, and the Halsey for unstored potato in hysteresis peak category III). Equation (42b) predicted fairly well both the magnitude and shape of sorption hysteresis falling into each of the three categories. The coefficient of variation (CV%) for the best hysteresis equation corresponding to each material, i.e., the Kuhn for air-dried apple, the Chung–Pfost for Garnet wheat, the Langmuir for Haddock and freeze-dried gluten, the Oswin for flour, the Mizrahi *et al.* for unstored beef, the Henderson for millet, the Halsey for rice, and the Smith for unstored potato, ranged from 3·53 to 13·09 (Table 2). The coefficient of determination (R^2) for the same equations ranged from 0·935 to 0·991, suggesting that most of the variation in hysteresis data were explained by these equations. The number of runs (RUN) for most top-ranking equations corresponding to each material were close to the expected number of runs calculated from the number of data points,

TABLE 1
Hysteresis Models Based on Eqn (42b) and 11 Isotherm Equations

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1. BET: $H = \dfrac{ACa_w}{(1-a_w)(1-a_w+Ca_w)}\, erfc\left[-\dfrac{B}{\ln(a_w)}\right]$

2. Chung-Pfost: $Pfost{:}H = A\left\{C - \dfrac{1}{D}\ln\left[-\ln(a_w)\right]\right\} erfc\left[-\dfrac{B}{\ln(a_w)}\right]$

3. GAB: $H = \dfrac{ACDa_w}{(1-Ca_w)(1-Ca_w+CDa_w)}\, erfc\left[-\dfrac{B}{\ln(a_w)}\right]$

4. Hailwood-Harrobin: $H = \dfrac{A}{C+Da_w+E/a_w}\, erfc\left[-\dfrac{B}{\ln(a_w)}\right]$

5. Halsey: $H = A\left[-\dfrac{C}{\ln(a_w)}\right]^{\frac{1}{D}} erfc\left[-\dfrac{B}{\ln(a_w)}\right]$

6. Henderson: $H = A\left[-\dfrac{\ln(1-a_w)}{C}\right]^{\frac{1}{D}} erfc\left[-\dfrac{B}{\ln(a_w)}\right]$

7. Kuhn: $H = A\left[\dfrac{C}{\ln(a_w)} + D\right] erfc\left[-\dfrac{B}{\ln(a_w)}\right]$

8. Langmuir: $H = A\left(\dfrac{Ca_w}{1+Da_w}\right) erfc\left[-\dfrac{B}{\ln(a_w)}\right]$

9. Mizrahi *et al.*: $H = \left(\dfrac{Aa_w - C}{1-a_w}\right) erfc\left[-\dfrac{B}{\ln(a_w)}\right]$

10. Oswin: $H = A\left(\dfrac{1-a_w}{a_w}\right)^{-\frac{1}{C}} erfc\left[-\dfrac{B}{\ln(a_w)}\right]$

11. Smith: $H = [A - C\ln(1-a_w)]\, erfc\left[-\dfrac{B}{\ln(a_w)}\right]$

TABLE 2
Parameters and Statistics for the Hysteresis Models

Isotherm Equation	R^2	*SD*	*CV%*	*RUN*	*A*	*B*	*C*	*D*	*E*
I. Hysteresis loop peaked in the monolayer sorption area									
1. Air-dried apple (Wolf et al., 1972), data points: 13									
Kuhn	0.991	0.225	3.53	4	3.3318	0.8029	−5.6859	0.4245	
Smith	0.988	0.249	4.01	5	5.0166	0.8548	41.1403		
Halsey	0.986	0.283	4.70	5	16.1592	0.7775	1.2214	1.2087	
Mizrahi	0.985	0.283	5.40	5	35.6754	0.9288	−5.2087		
Chung-Pfost	0.955	0.519	10.33	4	8.4778	0.6244	1.5370	1.7374	
2. No. 1 Garnet wheat (Babbitt, 1945), data points: 12									
Chung-Pfost	0.991	0.220	9.44	6	5.9466	0.4475	1.4641	1.7852	
Oswin	0.990	0.221	9.61	6	9.5347	0.4359	4.6398	1.7852	
Henderson	0.989	0.240	12.23	6	7.9389	0.4152	0.4080		
Halsey	0.988	0.255	19.95	5	12.0817	0.5642	0.9120		
BET	0.966	0.401	12.97	6	5.6268	0.4862	690.8300		
3. Haddock (Wolf et al., 1972), data points: 13									
Hailwood-Harrobin	0.947	0.294	14.92	6	8.9898	0.7524	0.6637	−1.5279	0.2997
Langmuir	0.935	0.291	13.09	5	30.3707	0.2916	4.9932		
Henderson	0.898	0.386	17.66	6	5.9774	0.3565	0.8927	2.1094	
BET	0.891	0.378	19.18	5	3.7123	0.4397	10.5199		
Chung-Pfost	0.888	0.404	16.92	6	3.7240	0.3213	1.0649	1.8628	
II. Hysteresis loop peaked in the multilayer sorption region									
1. Flour (Bushuk & Winkler, 1957), data points: 10									
Hailwood-Harrobin	0.954	0.188	5.98	5	4.5512	0.3215	2.8228	−3.1062	0.0549
BET	0.953	0.161	5.69	5	1.5813	0.2963	43.9486		
Oswin	0.939	0.182	5.41	4	2.7691	0.2483	3.0605		
Halsey	0.939	0.198	6.31	5	5.6117	0.2850	0.2811	1.4905	
Henderson	0.934	0.205	5.54	5	3.6096	0.2320	1.5841	2.7108	
2. Freeze-dried gluten (Bushuk & Winkler, 1957), data points: 10									
Hailwood-Harrobin	0.985	0.111	4.49	5	8.0695	0.3091	2.5485	−1.5067	0.3944
Langmuir	0.983	0.099	3.50	5	16.5462	0.2814	3.7296		
Henderson	0.983	0.110	5.62	5	4.3967	0.3185	1.3366	2.1155	
Oswin	0.982	0.105	6.25	5	3.3875	0.3371	2.4126		
BET	0.981	0.106	7.06	5	2.0325	0.3778	14.0529		
3. Unstored beef (Wolf et al., 1972), data points: 13									
Mizrahi	0.986	0.116	8.33	8	5.4448	0.4291	−0.6894		
Smith	0.979	0.144	14.12	8	0.5955	0.3637	7.1534		
Halsey	0.962	0.203	10.89	8	11.3579	0.4424	0.4835	0.7540	
Oswin	0.926	0.269	15.70	6	5.8197	0.3802	1.4610		
BET	0.919	0.297	18.57	4	6.8952	0.3471	0.9770	1.2990	
III. Hysteresis loop peaked in the capillary condensation region									
1. Millet (Ajisegiri & Sopade, 1990), data points: 11									
Oswin	0.980	0.194	8.22	6	2.6230	0.1450	1.1259		
BET	0.980	0.196	8.81	6	2.1746	0.1492	1.5514		
Halsey	0.980	0.205	10.85	6	5.8302	0.1774	0.3939	0.7434	
Mizrahi	0.978	0.199	10.59	6	2.4113	0.1581	−0.1208		
Henderson	0.976	0.225	7.61	6	4.4042	0.1223	1.0799	0.8210	
2. Rice (Wolf et al., 1972), data points: 9									
Halsey	0.967	0.276	6.39	5	8.6658	0.2677	0.4047	1.0156	
Hailwood-Harrobin	0.965	0.317	7.61	6	3.3554	0.3192	1.2051	−1.5098	0.0733
BET	0.962	0.272	7.59	5	2.4922	0.2425	15.5463		
Oswin	0.948	0.318	9.07	5	4.6372	0.2246	1.9044		
Henderson	0.932	0.398	10.17	5	5.7611	0.2008	1.0715	1.6400	
3. Unstored potato (Wolf et al., 1972), data points: 12									
GAB	0.958	0.414	12.00	4	21.6996	0.3485	1.1104	0.0855	
Smith	0.952	0.421	10.78	7	1.1911	0.1884	8.0867		
Mizrahi	0.942	0.461	12.54	7	5.2612	0.2575	−1.3686		
Halsey	0.941	0.493	12.89	6	10.7458	0.2361	0.4807	1.0140	
Henderson	0.927	0.548	17.07	6	7.1792	0.1359	0.9781	1.7996	

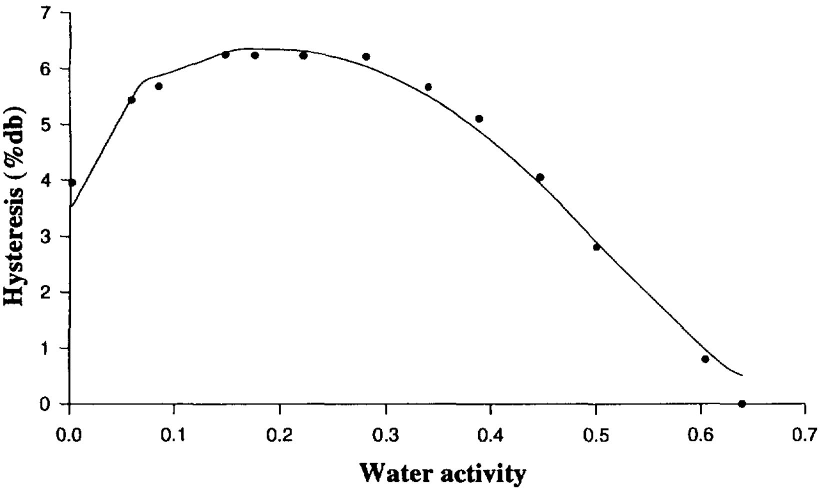

Fig. 2. Hysteresis magnitude for air-dried apple (Wolf *et al.*, 1972). The solid curve is predicted by the hysteresis model based on eqn (42b) and the Halsey isotherm equation (Table 1), with parameters and statistics listed in Table 2.

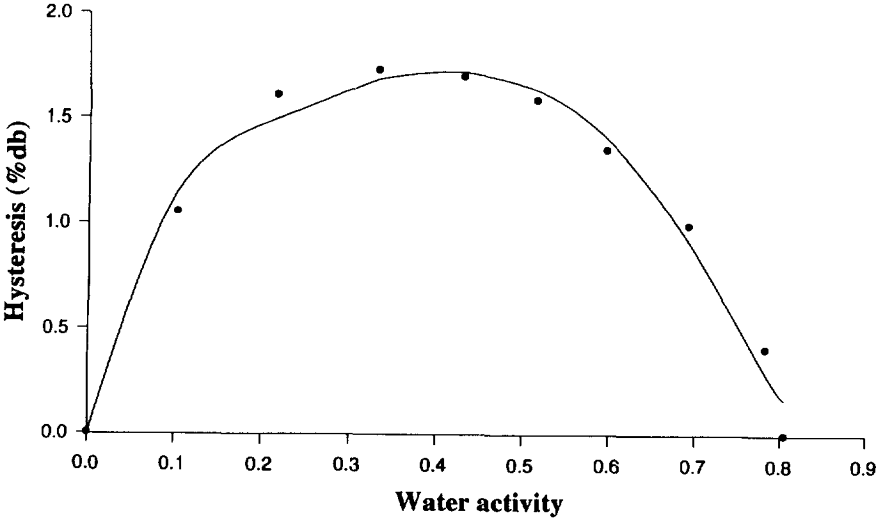

Fig. 3. Hysteresis magnitude for freeze-dried gluten (Bushuk & Winkler, 1957). The solid curve is predicted by the hysteresis model based on eqn (42b) and the Oswin isotherm equation (Table 1), with parameters and statistics listed in Table 2.

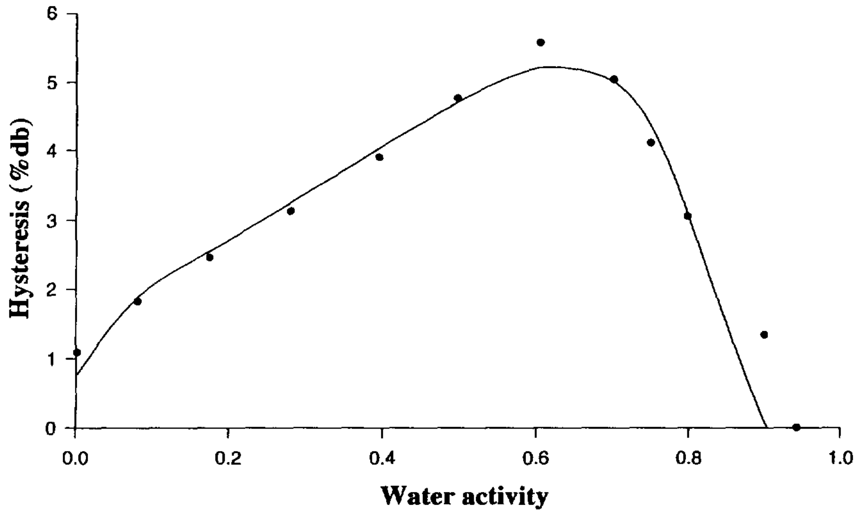

Fig. 4. Hysteresis magnitude for unstored potato (Wolf *et al.*, 1972). The solid curve is predicted by the hysteresis model based on eqn (42b) and the Halsey isotherm equation (Table 1), with parameters and statistics listed in Table 2.

signifying randomly distributed residuals. It can be seen from Figs 2–4 that eqn (42b), together with one of the 11 top performing isotherm models, was capable of approximating closely all types of the hysteresis loop.

A good agreement between eqn (42b) and the experimental data supports the hypothesis proposed in this study to explain the fundamental causes for sorption hysteresis.

CONCLUSION

A hypothesis has been proposed to account for the origin of sorption hysteresis. Based on the proposed hypothesis, a general mathematical model was developed to quantify the hysteresis loops. The theoretical hysteresis model was verified with published hysteresis data to be capable of predicting closely the hysteresis loop of a food material in all three major occasions of its orientation.

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