# Water activity and moisture sorption isotherms of foods

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### Abstract

Moisture sorption isotherm is a valuable tool for food scientists and technologists because it can be used to predict potential changes in food stability. It can be used for storing method determination, packaging selection and ingredient selection. Moisture sorption isotherm of foods shows the equilibrium relationship between water activity and moisture content of the food at a constant temperature and pressure. A critical value of water activity also exists below which no microorganisms can grow. For most foodstuffs, it is in the range of 0.6 - 0.7. Generally, temperature has important influence on water activity and consequently on course of moisture sorption isotherms. By using the Clausius-Clapeyron equation, the dependence of water activity on temperature can be predicted.

*Clausius-Clapeyron equation, equilibrium moisture content, microorganism, prediction*

## Introduction

Parameter of water activity ($a_w$) is incorporated into the legislative standards for foods in a number of countries. Commission Decision No. 92/447/EEC on the limit value of $a_w$ for selected meat products applies in the EU. The $a_w$ limit value of 0.93 is also stipulated in the Decree No. 326/2001 Coll., of the Ministry of Agriculture of the Czech Republic, as amended. This decree stipulates that a meat product must have $a_w \leq 0.93$ if it is to be considered “dry” or “durable”. Dry meat products may be stored at a higher temperature than other meat products and also have a longer shelf life (a minimum of 21 days) thanks to their low $a_w$ which is achieved by ripening, smoking, drying or fermentation. The Czech National Standard CSN ISO 21807 and Commission Regulation No. 2073/2005 on Microbiological criteria for foodstuffs are also in force. Use of $a_w$ as one microbiological criteria is also recommended in the application of procedures based on HACCP principles.

The aim of this study is to clarify parameter of $a_w$ and to present its importance for food industry; to show how $a_w$ is influenced by temperature, moisture content and relative humidity of near ambient air; and to supplement presented facts by basic theories.

### Water activity

Foods are mostly wet, predominantly hygroscopic, materials. They are generally heterogeneous multi-component mixtures. Only two components need to be considered from the viewpoint of water sorption – moisture and dry matter, i.e. the components that are separated by drying. Moisture content (MC) is variable and depends on temperature and humidity of the near ambient air. A moist hygroscopic substance can never be perfectly dried if it is in contact with surrounding environment containing water vapour. The food absorbs or desorbs moisture until the partial pressure of water vapour above the food balances the partial pressure of water vapour in the near ambient air. Stabilised value of MC of wet material at constant temperature and relative humidity (RH) of surrounding environment is known as equilibrium moisture content (EMC). If the dried material is placed in wet air, it will accept water until a new EMC is attained according

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to its hygroscopic properties. This phenomenon is known as adsorption or moistening. Water being released from a material is known as desorption, i.e. drying. The equilibrium state of moist material in an environment of certain temperature, humidity and pressure is thermodynamically characterised as zero heat and mass transfer between the material and its surroundings. The EMC is influenced primarily by RH, temperature, composition of the material and its handling, too. EMC is the basic parameter in determining conditions for the storage and packing of foodstuffs.

General conditions of equilibrium of multi-component systems with several phases can be formulated using thermodynamic parameter chemical potential ($\mu$), with the system being in equilibrium if the chemical potentials of any component are the same in all phases. Differences in $\mu$ are the cause of all changes that take place in the system until this system reaches a state of equilibrium; heat and mass transfer is equal zero, e.g. Langová 2015. The chemical potential $\mu$ is expressed by the equation:

$$\mu = \mu_0 + RT \ln a \; [J \cdot mol^{-1}] \qquad (1),$$

where $\mu_0$ is chemical potential corresponding to the standard state, $R$ is universal gas constant [J·mol$^{-1}$ K$^{-1}$], $T$ is the temperature [$K$] and $a$ [-] is the thermodynamic activity of the specific component. For the particular component $i$ in the system, the activity $a_i$ is defined by ratio of fugacity ($f$). The $f$ is a function of partial pressure ($p_p$) of the specific component. The $a_i$ may then be expressed as the ratio:

$$a_i = \frac{f_i}{f_i^0} = \frac{p_p}{p_p^{\,0}} \; [-] \qquad (2).$$

This activity enables comparisons of the properties of the system in a certain real state with the properties of the same system in its standard state. It is the measure of chemical potentials between these two states and function of all variables that determine the state of the system studied. On the basis of equations (1) and (2), the $a_w$ of foods is defined by the ratio of partial pressures of water vapour above the food and saturated water vapour in the air under the same conditions:

$$a_w = \frac{p_p}{p_p^{\,0}} = \frac{ERH}{100} = \frac{\varphi}{100} \; [-] \qquad (3),$$

where $p_p$ is the partial pressure of water vapour above the food and $p_p^{\,0}$ the partial pressure of saturated water vapour at a constant temperature and pressure. The ERH is the equilibrium relative humidity of the near ambient air ($\varphi$). This determination applies only in case that the state of equilibrium has been attained. The EMC is the basic condition for $a_w$ definition. Furthermore EMC is limiting parameter for analyses and description of drying processes. Several equations are used to describe the drying characteristics for food materials. The decreasing drying rate model suggested by Hall (1957) is still widely used in the literature to predict the drying rate:

$$\frac{dM\,(t)}{dt} = k[M(t) - M_e] \qquad (4).$$

The $M(t)$ is the moisture content of the material at the time $t$, $M_e$ is equilibrium moisture content (EMC) of the material and $k$ is the drying constant. This equation is widely used in varying modifications in literature sources to predict the drying rate and to analyse the water sorption process.

## Moisture sorption isotherms

Moisture adsorption (desorption) isotherms represent graphical or mathematical dependence of water adsorbed (desorbed) by a hygroscopic material in various near ambient air humidities at given temperature and pressure (Fig. 1). Each point of the moisture sorption isotherm corresponds with EMC of the wet material under near ambient air conditions. The MSI of biological materials, including foods, shows the equilibrium relationship between MC of the material and $a_w$ at constant temperature and pressure. At equilibrium, $a_w$ is related to the ERH of near ambient air, see equation (3).

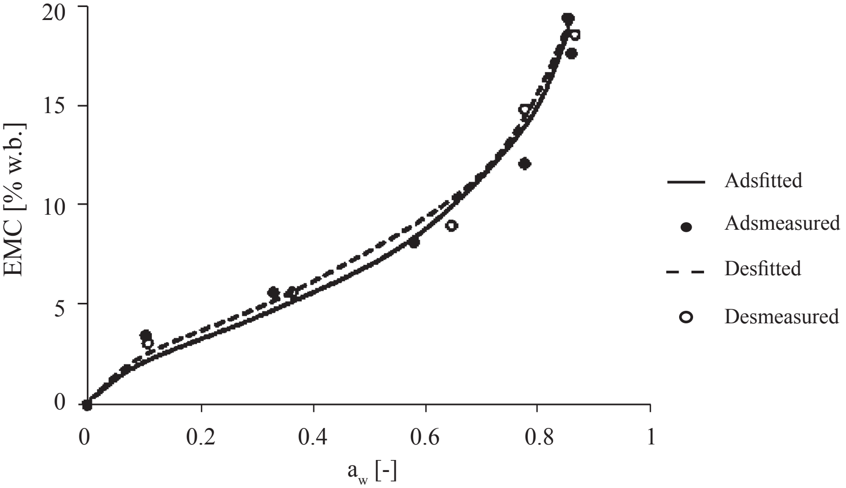

Fig. 1. Adsorption and desorption MSI (Oswin's model) accompanied by the measured data for whole milk powder at 5 °C (Langová and Štencl 2014)

The MSI of biological materials, especially of foods, are usually described as a plot of amount of sorbed water on $a_w$. Most of these materials follow the sigma-shaped curve represented as a type II BET classification, e.g. Langová 2015. The curve is the result of the additive effect of Raoult´s law, capillary effect, and surface – $H_2O$ interactions. Two bends are noted, one around $a_w$ of 0.1 – 0.3 and another at 0.7 – 0.9. These are the result of the changes in magnitude of the separate physical-chemical effects. The type I isotherm, e.g. an adsorption isotherm for pure crystalline sugar, shows very little moisture gain until $a_w$ goes above 0.7 – 0.8. This is because the only effect of water is hydrogen-bonding to the –OH groups that stick out on the surface of the crystal. Since this is a surface effect, grinding the sugar to smaller particles will increase the moisture content at low $a_w$´s by the amount of surface increase.

## Materials and Methods

Procedures for obtaining $a_w$ and MSI in foods have been described by several authors, e.g. Langová 2015. The principal methods are gravimetric and manometric; their modification is then the hygrometric method. Gravimetric methods are methods with continuous or discontinuous registration of weight changes in a static or dynamic system (Štencl et al. 1998). Manometric methods are based on the measurements of vapour pressure of water in equilibrium state with a food sample at given moisture content by a sensitive manometric device; $\varphi$ is usually used, see equation (3), e.g. Langová 2015. The MSI provides a graphical representation of the water adsorbed (desorbed) by a hygroscopic material at various near-ambient air humidity at a given temperature and pressure. Each point of the MSI corresponds to the EMC of the wet material under near-ambient air conditions.

Under these circumstances, the heat and mass exchange between the material and surrounding atmosphere does not occur. At equilibrium, $a_w$ is related to the ERH of the near-ambient air as mentioned above. There are numerous models for MSI and for predicting the relationship between EMC and $a_w$ at a constant temperature in literature sources. These models are theoretical, namely BET and GAB, semi-empirical, e.g. Halsey, Henderson, Chung-Pfost, and Oswin (Table 1), and typically, an empirical model is e.g. Peleg (Schuchmann et al. 1990). These models are most often used to describe and predict the moisture sorption properties of foods.

Table 1. Mathematical models describing the shape of MSI

| Type of model | Equation | |
|---|---|---|
| BET | $w_e = \dfrac{w_0 c a_w}{(1 - a_w)[1 + (c - 1)a_w]}$ | (5) |
| GAB | $w_e = \dfrac{w_0 c k a_w}{(1 - k a_w)[1 + (c - 1)k a_w]}$ | (6) |
| Chung-Pfost | $w_e = \dfrac{1}{A}\ln\left(\ln a_w \dfrac{(B - t)}{C}\right)$ | (7) |
| Halsey | $w_e = \left(\dfrac{\exp(A + Bt)}{-\ln a_w}\right)^C$ | (8) |
| Henderson | $w_e = \left(\dfrac{\ln(1 - a_w)}{A(t + B)}\right)^C$ | (9) |
| Oswin | $w_e = (A + Bt)\left(\dfrac{a_w}{1 - a_w}\right)^C$ | (10) |

$w_e$ = EMC [% w.b.]; $w_0$ = monomolecular moisture [% w.b.]; $t$ = temperature [°C]; c, k = constants related to the interaction between the first layer and additional layers of water molecules at individual sorption sites; A, B, C = constants used by individual models

## Results and Discussion

The MC of the biological material, temperature and pressure of near ambient air affect $a_w$ and course of the MSI. Generally, an increase in temperature causes an increase in $a_w$ of foods for the same MC and, if $a_w$ is kept constant; an increase in temperature causes a decrease in the amount of absorbed water. It indicates that the food becomes less hygroscopic at higher temperatures, e.g. Langová and Štencl 2014. Changes of $a_w$ in dependence on temperature can be predicted using Clausius-Clapeyron equation. These calculations evaluate internal energy changes of the sorption process from a thermodynamic standpoint, calculating the heat of sorption $q^{st}$ (Štencl et al. 2010). Since several different $q^{st}$ have been defined, it is necessary to clarify, which one is being considered. The reason for confusion stems from the fact, that the gas phase is characterized by three out of four variables $p$, $V_g$, $T$, and number of moles $n_g$. Depending of which variables are kept constant during the experiment or a theoretical derivation it results different heat of sorption. For example, there are two isothermal heats of sorption.

The first corresponds to adsorption at constant $V_g$. The experimental set up could be represented by a constant volume calorimeter with a specified amount of adsorbent, the whole in a constant temperature bath. The case is to describe by the first law of thermodynamics as it applies to closed system:

$$q^{st} = \Delta u - a \qquad (11).$$

No work $a$ is exchanged with the surroundings. The heat of sorption $q^{st}$ is then equal internal energy $\Delta u$.

The second isothermal heat of sorption corresponds to adsorption at constant $T$, $p$ and $n_f$. It involves a calorimeter, in which pressure $p$ is kept constant through a movable piston. For such system is valid:

$$q_n^{st} = \Delta u + p\,\Delta v = \Delta h_p \qquad (12).$$

In this case the heat evolved is called net isosteric heat of sorption:

$$q_n^{st} = \Delta h_p = n_f\,(h_g - h_f) \qquad (13).$$

where $h_g$ and $h_f$ are enthalpy of gas and adsorbed phase, respectively. The interest of this paper is focused in the net isosteric heat of sorption $q_n^{st}$, because it explains the energy relationships as a function of MC or $a_w$ and temperature, and it is also important for energy consumption optimization in praxis. For a system in equilibrium made up of saturated or unsaturated water vapour, on the bases of equal chemical potential in both phases, the Clausius-Clapeyron equation (19) is valid in general. It is possible to express it as follows:

$$\frac{d\ln\dfrac{p}{p_0}}{dT} = \frac{d\ln a_w}{dT} = \frac{q_n^{st}}{RT^2} \qquad (14),$$

$$q_n^{st} = h_G - h_f \qquad (15).$$

It is obvious that $a_w$ is a function of partial pressures, see equation (2).

The application of this method requires the measurement of sorption isotherms at least at three temperatures. On the other hand, the integration of equation (15) allows theoretically calculation of $q_n^{st}$ by taking measurements at only two temperatures:

$$\frac{\ln a_{w2} - \ln a_{w1}}{T_2 - T_1} = \frac{q_n^{st}}{RT_1T_2} \qquad (16).$$

It is possible to express $q_n^{st}$ using equation (16):

$$q_n^{st} = \frac{RT_1T_2\ln\dfrac{a_{w2}}{a_{w1}}}{T_2 - T_1} \qquad (17)$$

or

$$q_n^{st} = R\left[\frac{T_1T_2}{T_2 - T_1}\right]\left[\ln\frac{a_{w2}}{a_{w1}}\right] \qquad (18).$$

Integrating equation (14), assuming that the $q_n^{st}$ is temperature independent, gives the following equation:

$$\ln a_w = -\left(\frac{q_n^{st}}{R}\right)\frac{1}{T} + K \tag{19}$$

Heat of sorption can be determined from calorimetric measurements or from moisture sorption data. The second method is more convenient, given that MSI are determined routinely. The usual procedure to evaluate the $q_n^{st}$ consists in plotting the sorption isostere as $a_w$ versus $\frac{1}{T}$ and determining the slope, which is equal $\frac{q_n^{st}}{R}$. The $q_n^{st}$ shows the temperature dependence of $a_w$, see equations (16), (17), (18), and (19). Knowledge of its values can be used for water activity prediction. If the $a_w$ of a foodstuff is known at one temperature but the foodstuff is stored and handled at any other temperature, the responsible value of water activity can be computed using Clausius-Clapeyron equation. For example the $a_w$ of whey powder spray can be measured $a_{w1} = 0.7$ at $t_1 = 20$ °C in the laboratory. The product can consequently be handled at outdoor summer temperature $t_2 = 35$ °C. At this higher temperature the computed value of water activity $a_{w2} = 0.83$ (Štencl et al. 2010).

## Conclusions

Meaning of $a_w$ and MSI lies first of all in the possibility to determine stability conditions for foodstuffs during storage and packaging. The $a_w$ significantly affects the development of microorganisms (MO). This parameter is used in predictive microbiology, too. Minimum requirement for microbial growth is $a_w = 0.62$, which enables the development of xerophilic

Table 2. Minimum limits of $a_w$ for growth of MO significant to human health (Beuchat 1981)

| Microorganism | Min. $a_w$ for growth | Min. $a_w$ for production of toxins |
|---|---|---|
| *Shigella, E. coli, Proteus, Bacillus cereus* | 0.95 | - |
| *Clostridium botulinum* | 0.93 – 0.97 | 0.94 – 0.97 |
| *Bacillus subtilis* | 0.90 | - |
| *Lactobacillus* | 0.90 | - |
| *Staphylococcus aureus* | 0.86 | 0.87 – 0.97 (enterotoxin A, B) |
| *Pichia* | 0.92 | - |
| *Saccharomyces cerevisiae* | 0.90 | - |
| Osmophilic yeasts | 0.64 | - |
| *Stachybotrys atra* | 0.94 | 0.94 (stachybotryn) |
| *Trichothecium roseum* | 0.90 | - |
| *Aspergillus clavatus* | 0.85 | 0.99 (patulin) |
| *Aspergillus flavus* | 0.78 – 0.80 | 0.83 – 0.87 |
| *Aspergillus ochraceus* | 0.77 – 0.83 | 0.83 – 0.87 (ochratoxin) |
| *Aspergillus parasiticus* | 0.82 | 0.87 (aflatoxin) |
| *Penicillium cyclopium* | 0.82 – 0.87 | 0.97 (penicillanic acid) |
| *Penicillium expansum* | 0.83 – 0.85 | 0.99 (patulin) |
| *Penicillium martensii* | 0.79 – 0.83 | 0.99 (penicillanic acid) |
| *Penicillium patulum* | 0.81 – 0.85 | 0.85 – 0.95 (patulin) |
| *Penicillium viridicatum* | 0.83 | 0.83 – 0.86 (ochratoxin) |

moulds. A further $a_w$ increase allows the growth of yeasts and other moulds, while a high $a_w$ value leads to the development of bacteria (Roos 2002). The optimal $a_w$ value for development of majority of bacteria falls within the range of 0.995 – 0.999 (Smith 1990). Production of toxins generally occurs only within a range of $a_w$ values considerably higher than the values necessary for the growth of MO. Optimal conditions of temperature, pH, oxygen and the availability of nutrients are necessary for the reproduction of MO and production of their toxins at a reduced $a_w$ value (Beuchat 1981). Minimum limit values of $a_w$ for selected MO are given in Table 2. These limits are absolute, i.e. the given MO is not able to grow or reproduce beneath the given limit value of $a_w$ even if the other factors are optimal.

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