

Keywords: Water activity

Concept of water content & water activity

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1. Introduction

The water activity concept came into common usage in the 1970s, gaining official recognition with its incorporation into Community regulations, with a special focus on meat products. It adds a thermodynamic (ability to react and diffuse) qualitative property to the concept of water quantity, but can still be used to identify, for instance, a product's storability, given the wide range of mechanisms brought into play by all the constituents that are not necessarily in a state of equilibrium.

2. Water content & water activity

2.1. Water-Product relationship

The original structure of pure water gives it certain special properties. Water is a small molecule with electrical charges distributed between the oxygen and hydrogen atoms in a tetrahedral geometry. This configuration enables water molecules to interact among themselves or with other polar or hydrophilic molecules via the formation of hydrogen bonds. These are weak electrostatic bonds (with ten times less energy than a covalent bond), the existence of which helps to explain the properties of liquid water and water mixed with solids.

According to the latest scientific theories, the structure of liquid water is based on a mixture of single molecules and fluid microgels that can explain the original features of this liquid, such as its minimum density at 4°C. However, the structured liquid rapidly breaks down in the presence of solutes; water behaves like a normal liquid in solutions with 10% or more of solutes.

2.2. Water activity A_w of a product

The "water activity" parameter is used to estimate the quantity of available water in a product. In the biological systems used by the animal feed industries, this parameter is equivalent to equilibrium relative moisture (ERH).

At constant temperature and pressure, (the reference state) water is in equilibrium with its saturation vapour.

In other words, it is a product in a closed system in equilibrium with the confined atmosphere. The partial vapour pressure in equilibrium with the product is generated by the strength of the bonds between the water molecules and the material, and the number of water molecules present.

The product's water activity A_w can thus be defined as:

$$A_w = \frac{ERH}{100} \text{ where}$$

ERH = equilibrium relative moisture

Product water activity varies from 0 to 1. In a very dry, lyophilised product, water activity may be less than 0.05.

This therefore provides a tool that can be used to evaluate the amount of available water in a product, and that correlates fairly well with the technological, microbiological, and physiological behaviours used to control the procedures.

The main drivers of a reduction in water activity are:

1. The dispersion of water molecules among other molecules (e.g.: colligative properties of solutions).
2. The effects of specific interactions between molecules may overlap. In a solution, this involves the hydration shell of ions and the deviation from the laws governing ideal solutions. In a solid, this involves interactions at polar or hydrophilic sites.
3. Lastly, macroscopic phenomena may occur, i.e. a reduction in condensed water vapour pressure in small diameter capillary tubes (Kelvin's law).

2.3. Water content of a product

This is expressed by the ratio between the mass of the water in the product and the mass of the dry matter or the total mass of matter. Laboratories normally use dry matter.

3. Sorption isotherms

3.1. Principles

A product's affinity for water is given by its sorption isotherm. Isotherms describe the relationship between the quantity of water fixed by a product and its water activity A_w (Figure 1).

There are many products for which the adsorption isotherm cannot be superimposed on the desorption isotherm, resulting in hysteresis.

Usually, the desorption isotherm lies above the adsorption isotherm, as if for a given water activity (A_w), a substance could hold more water when it is dried than when it is hydrated.

While these variations remain fairly low (a few percent at the widest part of the hysteresis loop), they hinder the determination of water content in relation to water activity.

3.2. Using sorption isotherms

The water activity concept enables more effective control over storage in silos than the water content concept. Apart from a few slight differences, the A_w value correlates better with the development of bacteria, yeasts, moulds and with enzymatic system activity (Figure 2), irrespective of the product involved.

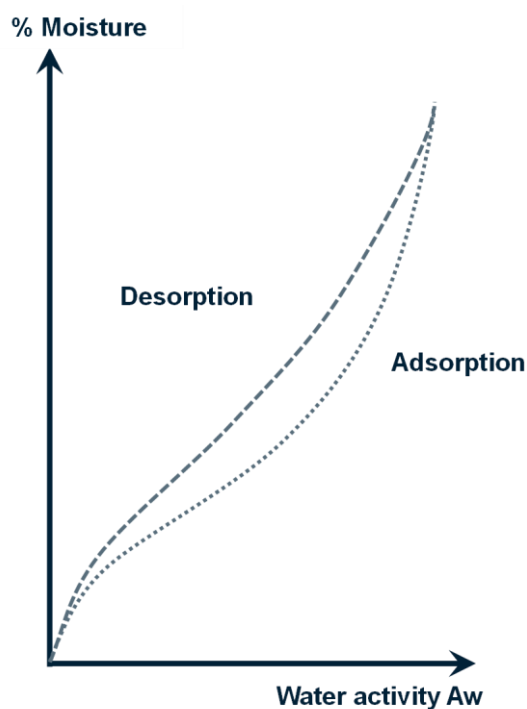


Figure 1: Sorption isotherm illustrating hysteresis

All reactions are conditioned by water activity; the optimum zone for Maillard reactions lies around 0.65, while lipid oxidation is enhanced at low A_w . Conversely, protein denaturation occurs at high A_w . A_w is a general idea, largely independent of the product (composition, structure, etc.), which is why it is able to improve control over product storage, etc. A single A_w value "replaces" 50 water content values corresponding to 50 different products.

In terms of the drying process, it is not always easy to integrate the sorption isotherm as a drying design parameter. Instead, drying rates are used, i.e. the quantity of water that evaporates per unit of time. This is proportional to the product's surface area, to a transfer coefficient that is characteristic of the surface state and to the difference between the water vapour pressure in equilibrium with the product and the water vapour pressure of the air within the dryer.

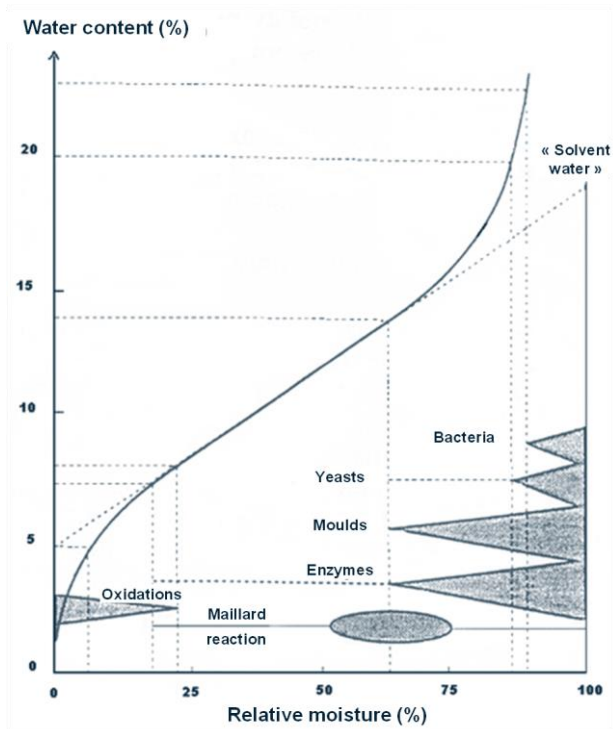


Figure 2: Wheat water desorption curve at 20°, and activity area of the relative moisture factor on the main causes of alteration (according to Cahagnier, 1996)

Water activity can be used to alter enzymatic reactions when water is one of the reactants. Lastly, there is anecdotic evidence that A_w decreases in frozen products, thereby contributing to their conservation.

4. Measurement methods

4.1. Water content

It is difficult to obtain an accurate measurement of a product's water content as the water may be confused with volatile or reducing substances. The heating required to dry the product may also modify the water content during an oxidation or hydrolysis reaction.

Generally, in the absence of a better solution, current standards are used to classify the studied product, even if there are doubts over their accuracy.

There are several classes of method: basic benchmarks, practical benchmarks and practical methods.

4.2. Measuring water activity A_w

In practice, these measurements are made using sensors that can detect variations in the conductivity of an electrolyte gel. ERH (equilibrium relative moisture) is measured after 3 to 4 hours once the product is in equilibrium with the sensor. These sensors need to be calibrated, which is easy to achieve using saturated salt solutions.

5. Identifying sorption isotherms

5.1. Operating procedure

The operating procedure involves preconditioning (drying or wetting), then conditioning with saturated salt solutions and various water activities until equilibrium is reached, and finally, measurement of the water content, generally using standardised methods.

5.2. Processing experimental data

5.2.1. Modelling

The results can be refined by adjusting mathematical models to around ten of the experimental plots obtained at the chosen temperature.

Without a doubt, the most popular model is that designed by Guggenheim, Anderson and De Boer, referred to as the G.A.B. model (1966). Widespread use of this model was promoted by Van den Berg (Van den Berg, 1975).

This model gives a satisfactory representation of sorption isotherms within a wide activity range (0.05-0.9) using only three parameters that can be interpreted physically in adsorption theories. It has the advantage of smoothing experimental data effectively and is based on assumptions of an adsorption mechanism that is localised (on sites), homogenous (all the sites are identical), and multimolecular (more than one layer of water molecules at the primary adsorption site).

The most widely recognised form of the G.A.B. equation is given below:

$$W = \frac{c \cdot K \cdot A_w \cdot W_m}{(1 - K \cdot A_w)(1 - K \cdot A_w + c \cdot K \cdot A_w)}$$

WHERE

W is the total quantity of water adsorbed

W_m is the quantity of water adsorbed in the form of a monolayer

K characterises the difference in activity energy between pure water and water adsorbed in a multilayer.

c characterises the excess energy with which the first layer of water interacts with primary adsorption sites.

5.2.2. Statistical treatment

Mathematical precision suggests using non-linear regression methods on the equation (Samaniego-Esguerra & al., 1991). For practical reasons, usually at a given temperature, it would appear simpler to use graphics software that makes it possible to adjust simple functions with separate parameters after changing a variable.

6. Conclusion

The limits of the water activity concept are set by the notion of thermodynamic equilibrium, which is seldom observed in natural or industrial goods.

Despite this, water activity remains the best qualitative approximation currently available, whether using A_w measurements for the formulation, or sorption isotherms for issues involving storage and, possibly, drying.

7. Bibliography

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