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A new method to determine “equilibrated” water activity and establish sorption isotherm by erasing surface history of the samples

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ABSTRACT

Building sorption isotherms usually requires several weeks for the samples to equilibrate at different relative humidities. Such experimental durations are very long in view of present industrial timeframes. In this work, we propose a rapid and robust method using wise thermal treatment that significantly accelerates equilibration of samples without inducing chemical or physical degradation. To demonstrate the relevance of our approach, we used maltodextrin powders considered as model systems and coupled experimental work with theoretical prediction of water diffusion. By testing different temperatures, we prove that a thermal treatment at T_g for approximately 2 h before measuring a_w allows in most cases getting rid of moisture gradients within the powders; hence, we propose to introduce the notion of apparent vs. equilibrated water activity. By using equilibrated water activity data we find sorption isotherms which are less curved in the low water activity range in comparison with classical methods and propose to discuss the differences in view of the long time it takes for powders to fully equilibrate without thermal treatment. These results impact not only the methods and the accuracy of the data but also their practical use for instance in predicting shelf-life stability or modelling drying processes.

1. Introduction

In food, the sorption isotherm is supposed to be the unique relationship describing the equilibrium between the water activity (a_w) and the moisture content expressed in dry basis (M_{db}) of a product stored at a given temperature (Barbosa-Canovas et al., 2007; Bell and Labuza, 2000).

The water activity (a_w) is commonly defined as the ratio of partial pressure of water vapour at the surface of the product (p) to the partial pressure of pure water at the same temperature (p_0) (Barbosa-Canovas et al., 2007):

$$a_w = \frac{p}{p_0} \tag{1}$$

In practice, it is equivalent to the relative humidity (RH) of the product in equilibrium with its headspace:

$$a_w = \frac{RH[\%]}{100} \tag{2}$$

Consequently, the robustness of such measurements relies on at least two major assumptions for dry powders. First, the sample must be fully homogenous in terms of moisture distribution. Secondly, whatever measurement device is used, the water activity of the sample must be in equilibrium with the relative humidity of the measuring chamber.

The moisture content (M_{db}) expressed in percentage is the mass of moisture in the product divided by the mass of dry product:

$$M_{db} = \frac{m_{moisture}}{\left(m_{sample} - m_{moisture}\right)} \cdot 100 \tag{3}$$

Sorption isotherms are widely used in food science and technology for instance to predict the shelf-life stability and moisture transfer between ingredients or to optimize drying processes and packaging.

Sorption isotherms sound relatively easy to establish knowing that it is routine analysis for analytical laboratories to measure

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moisture content and water activity. However, in practice many experimental inaccuracies may occur leading to different shapes of sorption isotherm. This can certainly explain the intense scientific controversy which has been going on for decades around this topic from both an experimental and a modelling point of view (Barbosa-Canovas et al., 2007; Bell and Labuza, 2000; Timmermann et al., 2001; Joupilla and Ross, 1994; Trujillo et al., 2003; Baucour and Daudin, 2000; Schmidt and Lee, 2012; Furmaniak et al., 2009; Meinders and van Vliet, 2009).

The most common method to build sorption isotherm consists in storing samples in desiccators or in dynamic sorption device until equilibrium is reached. The water activity is supposed to be given by the relative humidity of storage while the moisture content is assessed by various methods (e.g. thermogravimetry, Karl-Fisher titration). To our opinion, the major source of experimental discrepancy in this method is related to the notion of equilibrium which is not always accurately achieved. Depending on the experimentalist, the storage time may vary from few days up to several months while the relative sample mass variation differs from few tens of percentage up to 0.1% (Schmidt and Lee, 2012; Meinders and van Vliet, 2009; Ghorab et al., 2014). Additionally the influence of the sample structure, sample composition and potential interactions between samples stored in the same desiccators are to our knowledge rarely discussed.

To illustrate our concerns, we compared the equilibration behaviour of maltodextrin powders having different molecular weights stored in the same series of desiccators (Fig. 1a and b). Each desiccator contains a different saturated salt solution imposing a different RH. It may be first noticed thanks to the logarithm scale that none of the samples actually reached proper equilibrium after 21 days. Some bumps may also be observed in the curves which may evidence complex dynamics of mass transfer between the headspace and the samples in combination with the opening frequency of the desiccators. Finally, it looks like maltodextrin DE40 (low molecular weight, see materials) is globally further away from equilibrium although the samples were stored under similar conditions (i.e. in the glassy state). This could be explained by reduced water diffusion in densely packed material composed of both polysaccharides and maltose such as maltodextrin DE40 (Ubbink et al., 2007). These observations evidence the difficulties to give general recommendations about optimal equilibration time in desiccators.

Another method that is sometimes used, mostly by the industry, is to sample the powder at different stages of the drying process. It allows getting the range of water content that is needed to establish the isotherm. Each sample has to be measured for water content and water activity. In our opinion the major source of experimental discrepancy in this method is related to the a_w measurement since the samples may exhibit substantial moisture gradients several days after production and also need to be exposed to the lab conditions before analysis. Fig. 2 illustrates our concerns. Experimental data were assessed by collecting whole milk powders at different stages of the post-drying process performed in a fluid-bed connected to the spray-drier. The samples were stored for several weeks in sealed aluminium cans before analysis. It may be noticed that for a sample containing 3.20 ± 0.03% of water, the corresponding water activity varies between 0.138 and 0.201 at 25 °C. This is not consistent with the notion of equilibrium for which there should be only one correct value. As a consequence, the shape of the sorption isotherm depends on the robustness of the experimental data that are considered for the fit.

From the examples discussed above, it becomes obvious that an important aspect to take into consideration when measuring a_w or building sorption isotherm is the diffusion of water needed to reach true equilibrium. It is well known that this diffusion strongly depends on composition, structure, and temperature (Tromp et al., 1997a; Gianfrancesco et al., 2012). In this study we investigated the influence of the surrounding relative humidity, the sample temperature, the processing parameters, the composition and the micro-structure. Based on our finding we propose a new method to obtain robust a_w measurement and sorption isotherm.

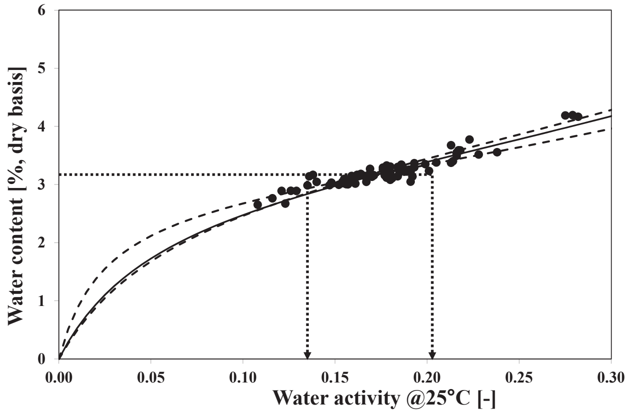

Fig. 2. Sorption isotherms obtained by sampling whole milk powder from the production line. (●): experimental data. (Continuous line): average BET fit taking all data into consideration. (Dotted line): extreme BET fits obtained using different sets of data.

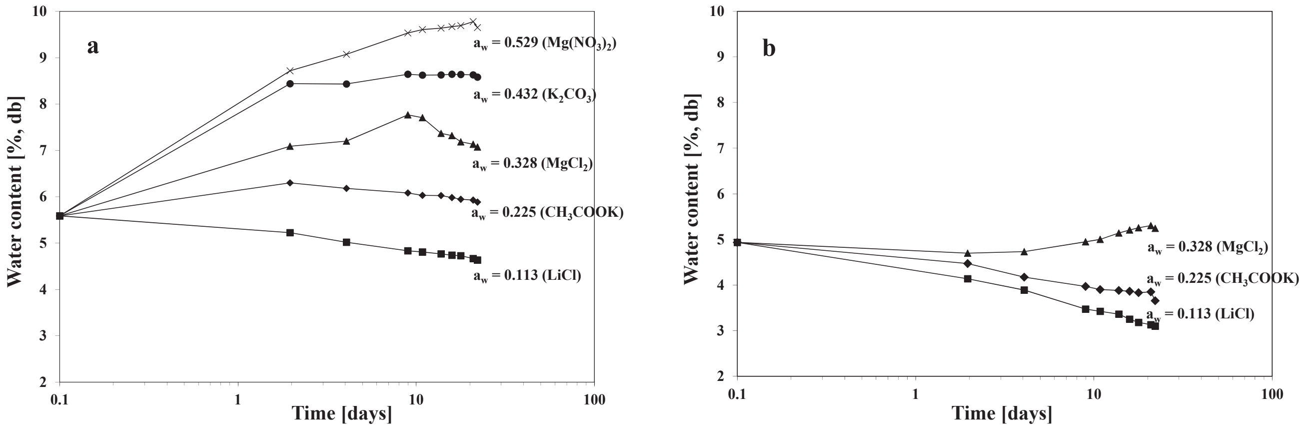

Fig. 1. Equilibration behaviour of maltodextrin DE12 (1a) and DE40 (1b) at 25 °C under various relative humidities (imposed by saturated salt solutions in desiccators) which guarantee that the samples remain in the glassy state. Graphs are plotted as logarithm of time to best highlight difficulties to reach equilibrium.