

Water activity and hydration of dairy powders

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Abstract – Water is often the main component of many food products and their stability strongly depends on water interactions with other molecules. In the case of dehydrated products and especially milk powders, their use properties (flow properties, keeping quality and reconstitution properties) are closely dependent on the modes of water binding to the other constituents (proteins and lactose in particular). The water relations of milk powders strongly depend on drying process conditions and on their composition. They are well represented by sorption isotherms. However, to understand some mechanical properties (flowing, caking) it is necessary to take into account the glassy transition phenomenon. The water activity concept, water vapour sorption isotherms and glassy transition are redefined. A brief presentation of methods for characterising water properties and measuring hydration is done. Finally, explanation of the mechanisms of lactose hydration and of its crystallographic changes allows the linking of the use properties of dairy powders to their manufacturing technology.

Milk / dairy powder / water activity / hydration / functional property

Résumé – **Activité de l'eau et hydratation des poudres laitières.** L'eau est le constituant majeur des produits alimentaires et leur stabilité dépend des interactions de l'eau avec les autres molécules. Dans le cas des produits déshydratés et notamment des poudres de lait, leurs propriétés d'usage (propriétés d'écoulement, de conservation et de reconstitution) sont étroitement dépendantes des modalités de liaison de l'eau avec les autres constituants (protéines, lactose, notamment). La notion d'activité de l'eau, l'exploitation des isothermes de sorption de vapeur d'eau et le concept de transition vitreuse sont redéfinis. Une rapide présentation des méthodes de caractérisation de l'eau et de mesure de l'hydratation est ensuite effectuée. Enfin l'explication des mécanismes de l'hydratation du lactose et de ses changements cristallographiques permet de relier les propriétés d'usage des poudres d'origine laitière à leur technologie de fabrication.

Lait / poudre laitière / activité de l'eau / hydratation / propriété fonctionnelle

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1. ROLE OF WATER IN FOODS

Water is the major component of many food materials (Tab. I). Food biochemical stability depends on the ability of water to act as a solvent, and to permit reactions by diffusion of molecules [22]. Moreover, water can be alternatively anti-oxidant at low humidity or pro-oxidant at intermediate humidity [10].

Many operations in food processing use physical properties dependent on water content or state transition of water: specific heat, conductivity and thermal diffusivity, and mass transfer. These properties are involved in thawing, concentration, drying, osmotic dehydration and salting.

Glass transition as a function of temperature and water activity is a key factor: it determines the textural properties of cookies and chips [18] and ice creams [32]. It is also involved in food preservation of dehydrated foods, i.e. dairy powders.

Water content determination is therefore a major criterion for evaluating food quality and food preservation. Hydration will influence many functional properties of food components [33], such as swelling, viscos-

ity, thickening and gelling properties of proteins. In the case of protein powders, water will act on particle-particle interactions on which flowability properties depend; powder reconstitution properties such as dispersibility or solubility will depend on particle-water interactions [20].

2. WATER MOLECULE PROPERTIES AND STATE OF WATER IN FOODS

Water in foods can be qualified as “bound” water (or non-freezing water) and “retention water” (free water and capillary water). “Bound” water will correspond to structural water while water retained in a protein matrix like casein micelles or casein gels will be designed “retention” water.

These definitions will depend on the techniques employed; in other words, on the bond energy or chemical potential involved in water interactions.

2.1. The water molecule

The water molecule is characterised by its ability to form hydrogen bonds. In a liquid state, Nemethy and Sheraga [27] hypothesise a structural model based upon an equilibrium between free water molecules and clusters whose structure is reminiscent of that of ice. Close to 0 °C, the clusters’ size increases when reciprocity is obtained near boiling point. However, Franks [13] proposed making this schematic model more precise by measuring potential energy between water molecules as a function of the distance separating two molecules or two oxygen atoms. In ice (common in terms of pressure and temperature), the tetrahedral structure of water molecules leads to four hydrogen bonds: two as donors (from hydrogen) and two as acceptors (from oxygen). Hydrogen bond energy is about 20 kJ·mol⁻¹ when the covalent O-H bond is broken at about 460 kJ·mol⁻¹ (Tab. II).

Table I. Water content (%) of food materials [25].

Food materials	Water content (%)
Milk powder	4
Almonds	5
Dehydrated vegetables	10–12
Macaronis	12
Butter	15
Honey	23
Mayonnaise	< 40
Avocado	65
Cheeses	55–80
Beef	68
Potatoes	76
Apples	84
Fruits	~ 90
Liquid dairy products	87–91
Cucumber	96

Table II. The energy of water interactions.

Type of interactions	Energy (kJ·mol ⁻¹)
Covalent bond	460
Hydrogen bond in ice	23
Hydrogen bond in water	< 20
Melting heat at 0 °C	6
Vaporisation latent heat:	
at 25 °C	44.5
at 100 °C	40.7
Sublimation heat at 0 °C	50.9
Polar sites binding (BET monolayer)	4–6
Binding with the 2nd water layer	1–3
Van der Waals forces	~ 0.5
Capillary forces	~ 0–0.3
Isosteric heat of sorption (10–40 °C, dependent on water content)	0–40

2.2. Interactions of water with other components

Interactions of water with other components are related to the presence of ions or ionisable groups and residues able to produce hydrogen bonds. For proteins, Bull and Reese [5] showed that global hydration is correlated well to the sum of polar residues (hydroxyl, carboxyl and basic groups) minus amide residues. Kuntz [21], using RMN techniques to study synthetic polypeptides' hydration showed that "bound" water (*A*) can be calculated by the following relation:

$$A = X_i + 0.4 X_p + 0.2 X_{ap}$$

where X_i , X_p and X_{ap} represent ionised (i), polar (p) and apolar (ap) amino acids.

Theoretically, the ability to retain water should be calculated through the knowledge of the amino-acid sequence of proteins. However, tridimensional conformation of proteins and exposition of hydration sites also depend on the solvent (pH, ionic force, dielectric constant and ions activity). Thus, it is still difficult to evaluate the hydration of casein, of casein micelles and, all the more so, of a milk powder particle.

The determination of global hydration is obtained by measuring the water amount or by evaluating the energy of water bonds under defined temperature and pressure conditions. Water vapour adsorption and desorption phenomena are widely studied in the food industry by water activity (a_w) measurements.

3. WATER ACTIVITY AND SORPTION ISOTHERMS

3.1. Water activity

Water content knowledge is not sufficient to evaluate food stability during storage. Water activity has been developed to take into account interactions of water with the other food components. For a solution when the solvent is in equilibrium with the vapour phase, a_w is defined as:

$$a_w = f/f_0$$

where f is the solvent fugacity in solution and f_0 , the pure solvent fugacity.

It is demonstrated that for water vapour assimilated to ideal gas, a_w can be estimated from:

$$a_w = p/p_0$$

where p and p_0 are water pressure in the solution and water pressure in pure water respectively.

Fennema [11] insists on the inadequacy of the last a_w definition when strong interactions exist between solute and solvent molecules. This is evident from experiments showing the growth of reference micro-organisms as a function of a_w adjusted by addition of solute [7] showing that water vapour relative pressure cannot completely explain micro-organism growth.

Water activity depends on temperature related to the Clausius-Clapeyron equation:

$$\left(\frac{d \ln a_w}{d(1/T)} \right)_{Y_i} = \frac{-\Delta H}{R}$$

with T , absolute temperature, R , ideal gas constant, ΔH , net isosteric heat of sorption

at a given water content, Y_i . The net isosteric heat of sorption corresponds to the heat necessary for food dehydration in addition to pure water vaporisation heat.

A ΔH calculation can be made by using sorption isotherms at different temperatures. ΔH value (kJ) increases with dehydration degree (Tab. III). These values can be compared to pure water vaporisation heat (L) which is equal to $44.5 \text{ kJ}\cdot\text{mol}^{-1}$ at $25 \text{ }^\circ\text{C}$. According to Tsami [39], positive values of sorption heat at low water content are mainly due to hydrogen bond importance in the mono-layer water molecule formation.

Negative values can be explained by endothermic dissolution of sugars and minerals [35]. At low water content, the energy necessary for complete dehydration can be twice the pure water vaporisation heat.

Table III. Isosteric heat values of sorption and adsorption (a), or desorption (b), adapted from Rahman [29].

	Water content (kg water·kg ⁻¹ dry matter)	t (°C)	ΔH (kJ·mol ⁻¹)
Lyophilised coffee	0.05	25–45	4.3 (a)
	0.025	25–45	–8 (a)
	0.25	25–45	0.4 (a)
	0.45	25–45	0.1 (a)
Milk	0.05	14–34	–8.8 (a)
	0.10	14–34	7 (a)
	0.15	14–34	0.6 (a)
Rice	0.10	0–30	8 (a)
	0.20	0–30	2.5 (a)
Onion	0.10	30–60	37.4 (b)
Pineapple	0.04	10–30	7 (a)
	0.08	10–30	5 (a)
	0.16	10–30	2 (a)
	0.32	10–30	0.7 (a)
Emmental	0.01	10–30	5 (a)
	0.02	10–30	6 (a)
	0.08	10–30	1.5 (a)
	0.16	10–30	1 (a)
Carrots	0.08	30–60	29 (b)
	0.20	30–60	15.7 (b)

3.2. Water vapour sorption isotherms

Food water content (g water per g dry matter) as a function of vapour pressure at equilibrium (p/p_0), at a constant temperature, is designated a sorption isotherm. From sorption isotherms, major information is obtained to optimise formulation, concentration and dehydration processes, packaging, microbial growth conditions, and the physical and chemical stability of the product as a function of its water content.

An isotherm curve is usually sigmoidal but in some cases (state change with

crystallisation and component dissolution) artefact can occur (Fig. 1). The case of milk powder is significant: apparent disappearance of water during the first cycle of adsorption at about a_w 0.4 has been explained by the lactose state change from amorphous to crystallised, with consumption of 2 mol of water per mol of lactose (Fig. 2). This transition, observable by electron microscopy (Fig. 3), corresponds to structural changes of milk powder particles with consequently large variation of water sorption properties and difficulties in using predictive models.

Figure 1. Sorption isotherm profiles (20 °C, except 1: 40 °C) (1): confectionery, (2): chicory dehydrated extract, (3): roasted Columbia coffee, (4): pancreas dehydrated extract, (5): rice starch, adapted from Van der Berg and Bruin [40].

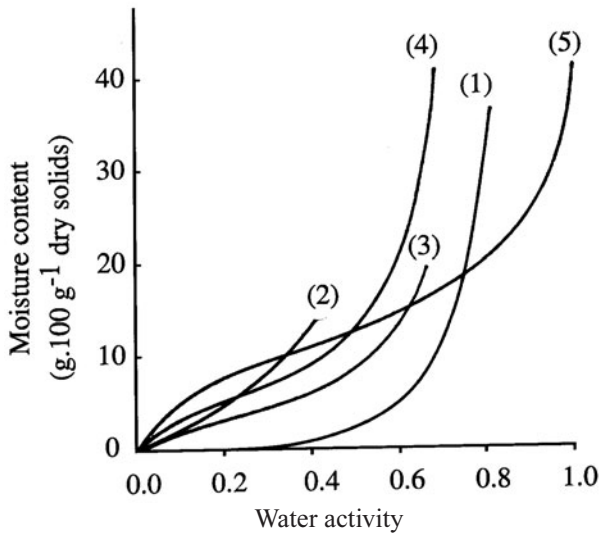


Figure 2. Adsorption isotherm of four whey powders, adapted from Berlin et al. [3].

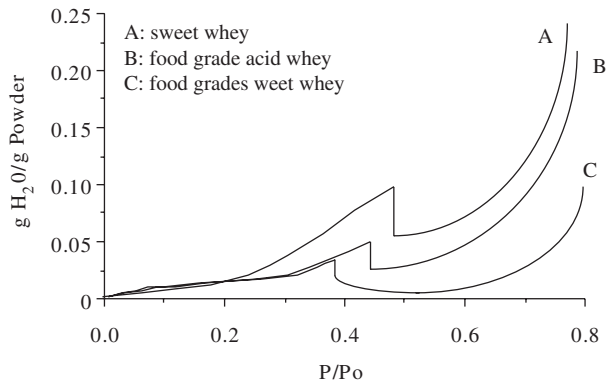




Figure 3. Electron microscopy photograph from the surface of milk powder particles after lactose crystallisation.

A considerable number of empirical and theoretical equations have been provided to describe water adsorption and desorption. The first one is the Brunauer, Emmet and Teller (BET) model (1938) that describes only the concave portion of the curve [4]. One of the best models is the GAB model developed by Guggenheim [14], Anderson [2] and De Boer [9] (Tab. IV). The relation between general curve profile and the mechanisms of water fixation onto the dry product is well-interpreted in terms of ad- and ab-sorption [15]. At low water content, fixation is mainly governed by bond energy between the water molecules and adsorbant surface. It concerns bond formation with polar and ionic groups of proteins and polysaccharides. Bond energy is about 4 to 6 kJ.mol⁻¹. At intermediate water content, other water molecules interact with the first ones by hydrogen bonding. Bond energy is about 1 to 3 kJ.mol⁻¹. The last convex portion of the curve, at the higher water content, is the result of water molecules retained by capillary forces (energy from 0 to 0.3 kJ.mol⁻¹). All the studies based upon

Table IV. Some descriptive models of water sorption isotherm curves.

Authors	Model
Brunauer, Emmett, Teller (BET), [4]	$\frac{a_w}{m(1 - a_w)} = \frac{1}{m_1 c} + \frac{c - 1}{m_1 c} \cdot a_w$ with m: water content m ₁ : monolayer water content c: constant dependent on ΔH
Guggenheim, Anderson, De Boer (GAB) [2, 9, 14, 23]	$m = \frac{m_1 YK \cdot a_w}{(1 - Ka_w)(1 - Ka_w + KYa_w)}$ K and Y, dependent temperature constants
Peleg [28]	$m = Aa_w^C + Ba_w^D \quad (C < 1 \text{ and } D > 1)$
Smith [38]	$m = A + B \ln(1 - a_w)$ valid from 0.5 to 0.95

energy measurements show a continuous spectrum of bond energy increasing with decreasing water content. In foods with high solutes content, which is the case for milk powder containing lactose, models are complex in relation to solubilisation or crystallisation. In fact, these phenomena can be interpreted by using a state phase diagram with the emphasis on the glass transition zone.

4. HYDRATION AND GLASS TRANSITION

During the last twenty years, many works have been published on the glass transition phenomenon observed in foods by analogy with the properties of glass heated to melting point. Fennema [11] underlined the importance of the molecular mobility concept with the works initiated by Franks [12] and developed since 1986 by

Levine and Slade [24] and many others. The works of Roos [32] are an important contribution to the comprehension of the physical and chemical mechanisms of state transition in products containing lactose.

With refrigeration or a decrease in water content, all or part of food components are found in a glass state. Molecular mobility is then greatly affected and all the diffusion-limited reactions are stopped. Simatos et al. [37] underlined that the "glass transition" zone is characterised by rapid changes in physical and chemical properties when temperature and also solute concentration seem to go across the line separating, in the state diagram, the saturated or sur-saturated solution of the glass solid state (Fig. 4). If T_g corresponds, for a defined composition, to the transition temperature, little variations below and above T_g will then considerably modify mechanical and textural food properties. Physical and chemical processes that occur during food preservation

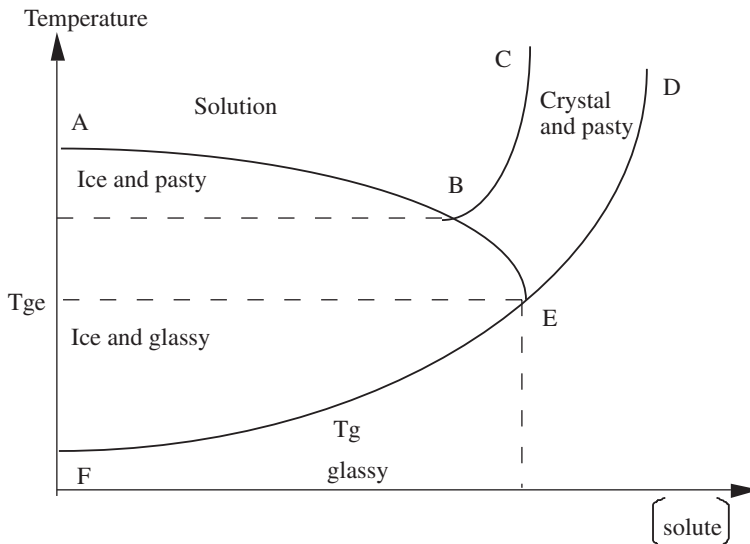


Figure 4. State diagram showing the freezing curve AB, the solubility curve BC, the eutectic point B, the glass transition line DEF, the glass transition temperature T_{ge} at the maximum of concentration of the frozen solution.

and that correspond to diffusion-controlled reactions, will depend upon the storage temperature position compared to T_g .

Simatos et al. [37] specified that T_g cannot explain all food behaviour as a low molecular mobility should still exist at temperatures below T_g . It must also be specified that, outside the glass transition zone, a_w represents the most significant parameter for predicting food behaviour during its conservation. Two more remarks are necessary. The decreasing rate of temperature plays a role in the crystallisation rate of solutes and thus in T_g . Moreover, products containing high proportions of triglycerides are concerned in glass transition mechanisms, especially for a mix of low and high melting point triglycerides showing inter-solubility. For milk powders, transition from an amorphous to a crystallised state can take a long time, the duration depending upon temperature and a_w conditions. Lactose T_g varies with a_w , from 35 °C at an a_w of 0.3 to 100 °C at a zero value of a_w [26].

5. WATER AND INTERACTION DETERMINATION

It is well known that any technique gives a definitive answer to the question of "which sites are involved in fixation of water molecules and what is the bond energy on these sites?". However, a combination of several selected techniques can contribute to a better understanding of adsorbed water by food or food components in a non-equilibrium phase.

5.1. Measurement and prediction of a_w

The usual methods employed to evaluate total water content, relative humidity or a_w , and freezing or non-freezing water by thermal analysis techniques, give global information on the food system. In a first approach, these elements are useful for pre-

dicting food stability in storage. The Raoult law permits the prediction of a_w for an ideal solution from the molar fraction. However, this relation is not yet useful for macromolecules in solution nor for non-ideal solutions where intermolecular forces (Van der Waals), solvation of ions, solute-solute interactions in a ternary system, and capillary phenomena when the solution is trapped in a porous matrix occur. Even the order of adding solutes can interfere.

This is the reason why many authors made models applied to specific applications. The Ross model (1975) [31] is always used to predict a_w in formulation. The Grover model (1947) is employed in confectionery. The model of Lilley and Sutton (1991) is a generalisation of the Ross model. Recently, Roa and Tapia [30] published a model for a_w prediction in multi-component mixes. Another approach is based upon the contribution group concept. This concept was introduced in order to predict thermodynamic properties of pure components and is therefore generalised for solutions. The usual methods used are ASOG and UNIFAC. They are largely used to describe the a_w of sugar and mineral solutions [36]. For an instrumental determination of a_w , methods developed during the last twenty years are based upon the hygrometry determination of air in equilibrium with the product. The interest of sorption isotherm determination rather than of the single a_w value has been recognised.

5.2. New techniques for water characterisation

Chinachoti [6] made a rapid synthesis of the new techniques used for water characterisation. Dielectric relaxation in the frequency region from 10 Hz to 50 MHz permits the measurement of dipole orientation in an electric field in order to acquire information on mobility loss by water molecules. Cornillon et al. [8] determined the glass transition temperature (or mobility

temperature) for various foods by this technique.

If nuclear magnetic resonance (NMR) of the proton combined with deuterium and O^{17} gave rise to considerable works, it is still a complex technique for specialists. According to Hills [17], combined relaxation of proton and deuterium distinguished three types of water in foods (free water, bound water with rapid orientations and trapped water).

NMR imaging is also interesting for quantifying water content, water distribution and diffusion and should be adapted to mass and heat transfer determination [19, 34]. Coupled with conventional microscopy, NMR should permit the study of biological material structures.

Other spectroscopic methods gave rise to specific uses in complex food systems but with many problems of interpretation. Raman spectroscopy, X-ray diffraction, molecular probe diffusion, spin electronic resonance, and light diffusion techniques are also adapted to water characterisation.

5.3. Measurement of hydration as a functional property

Water retention by food or some of the food components constitutes an interesting technological property. Two main approaches are used for its determination: the measurement of water absorption ability and of water retention capacity. The first one depends on swelling and is determined by the ability to take in vapour water (see isotherm sorption) or liquid water (Baumann apparatus). The second one corresponds to trapped water in the food matrix submitted to compression, depression, centrifugation or osmotic pressure. This water fraction can be assimilated into the sum of the capillary water and of water bound via hydrogen bonds.

Hermansson [16] gave an overview of the usual methods and underlined the im-

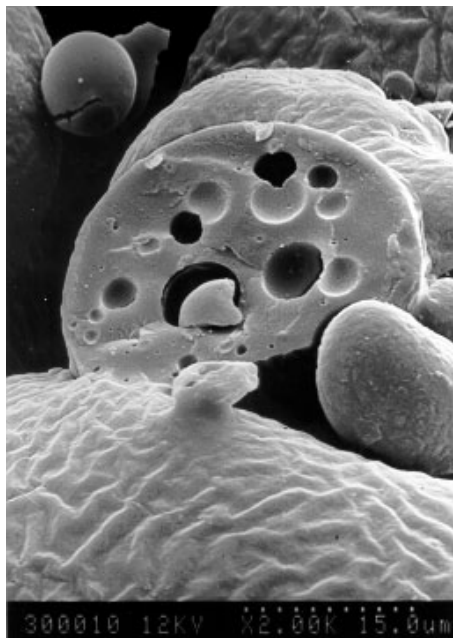


Figure 5. Electron microscopy photograph showing the internal porosity of milk powder particles.

portance of preserving the sample structure, especially gels and tissues, in order not to alter the water retention properties. In the case of powders, the previous methods are of little interest considering the porosity of the powder bulk and of each particle (Fig. 5), then the dissolution-dispersion phenomena in the aqueous phase. The functional properties of reconstituted powder (dispersibility and solubility) are therefore preferably studied.

5.4. Hydration and functional properties of dairy powders

Water and dairy powder interactions can be considered at a particle-particle level which mechanical properties depend on, and at a particle-water level which reconstitution properties depend on.

(a) Caking, characterised by powder solidification due to higher particle-particle

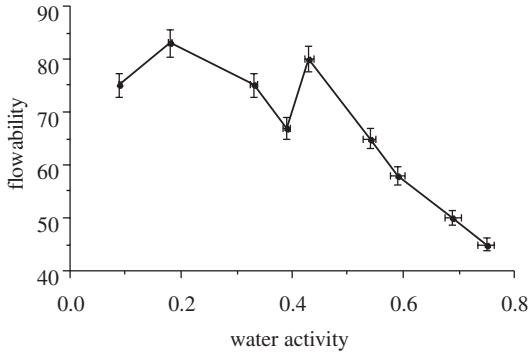


Figure 6. a_w influence on flowability properties of skim milk powder.

interactions (in intensity and number), can occur during packaging, storage and transport. In these cases, surrounding hygrometry and temperature fluctuations (night/day) in relation to climatic variations are not controlled. The nature of the adhesion forces between particles involved in caking phenomena is variable [1]. Thus, for fine particles ($< 10 \mu\text{m}$), Van der Waals forces (about 10^{-7}N), capillary forces (about 10^{-5}N) and electrostatic forces are largely responsible for cohesion. For milk powder with a particle size equal to about $150 \mu\text{m}$, a non-negligible fraction of particles are sensitive to these types of interactions. Adhesion forces coming from dissolution-recrystallisation (amorphous and α -monohydrate lactose forms) or fusion (whole milk powder) influence even more caking. In a particular system, the number of contact points between particles is very significant.

Water absorption by the particle surface and capillary condensation at contact points can produce liquid bridges evolving into solid bridges by subsequent evaporation. To avoid caking, knowledge of the sorption isotherms of milk powder and of each component, as well as the fusion temperature for lipids in whole milk powder, is indispensable. Before drying is completed, a high concentration of α -crystallised lactose, present as little crystals homogeneously distributed in particles, will permit the prevention of caking.

(b) The flowability aptitude of skim milk powders is largely influenced by water state and water content. Figure 6 (unpublished works of our laboratory) shows the variation of flowability aptitude (Powder Tester PT-R, Hosokawa, Japan) of a skim milk powder as a function of a_w . It can be noticed that this property is altered above the a_w zone of lactose crystallisation. Flowability loss is explained by a large number of “hanging points” (Fig. 6) induced by particle asperities and by liquid bridges at higher a_w just before dissolution. The addition of silica particles permits the improvement of flowability.

6. CONCLUSION

In this introduction of the session on “modelling, simulation and state of the art concerning water migration during drying and reconstitution of milk powder”, we chose to present the knowledge that scientists, engineers and students should acquire to understand interactions between a simple molecule like water and other components in foods.

For dairy powder industries, where concentration and dehydration are commonly used, the most useful knowledge concerns the state of water associated with other components, the equilibrium between materials and water in the surrounding vapour

phase, and the kinetics of dehydration and of water transfer during powder storage. Thus, the hydration state of powders represents a master parameter for explaining particle-particle interactions.

For industry using milk powders in order to formulate traditional or novel foods, understanding of interactions between particles and liquid water containing solutes (or not) is fundamental. A recent review made in our laboratory show that the mechanisms involved in the sequence of rehydration-dissolution-dispersion are not yet elucidated. Global or empirical property measurements cannot permit the understanding of the mechanisms of reconstitution. The link between powder manufacturers and end users has to be made. The studies on water interactions should therefore permit the development of common investigation methods.

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