Article:

Farshchi, A, Hassanpour, A orcid.org/0000-0002-7756-1506, Ettelaie, R orcid.org/0000-0002-6970-4650 et al. (1 more author) (2019) Evolution of surface micro-structure and moisture sorption characteristics of spray-dried detergent powders. Journal of Colloid and Interface Science, 551. pp. 283-296. ISSN 0001-8686

https://doi.org/10.1016/j.jcis.2019.04.069

Evolution of surface micro-structure and moisture sorption characteristics of spray-dried detergent powders

Amin Farshchi [1*], Ali Hassanpour [1], Rammile Ettelaie [2], Andrew Bayly [1]

[1]School of Chemical and Process Engineering, University of Leeds, Leeds,
LS2 9JT, UK

[2] Food Colloids Group, School of Food Science and Nutrition, University of
Leeds, Leeds, LS2 9JT, UK

* Corresponding author, E-mail: amin.farshchi@hotmail.com

1. Introduction

Globally, detergent powders are mainly manufactured by spray drying. This process involves the rapid removal of water from slurry droplets giving rise to particles with a complex multi-scale structure. The dried particulate product formed by typical detergent formulations, using typical conditions, consist of a porous matrix of surfactant, binder and sub-micron crystals of inorganic salts, in which larger crystals of inorganic salts and vacuoles are dispersed (Farshchi et al., 2019). Many granular products produced by chemical, pharmaceutical and food industries, are known to have a tendency to cake and agglomerate particularly during storage in humid conditions. Several mechanisms have been proposed for the powder caking phenomenon, these include van der Waals forces, electrostatic forces, liquid bridge forces, surface roughness and plastic deformation (Zafar et al., 2017). However, at increased levels of environmental humidity the stickiness and caking of powders is often associated with the formation of liquid bridges between the powders (Peleg, 1977). The formation of liquid bridges, increases the molecular mobility and this consequently induces a number of detrimental physico-chemical changes leading to crystallisation, stickiness and hence caking (Shrestha et al., 2007). The mechanism of caking is also governed by the intermolecular structure of the components within the powders. Many spray-dried powders contain a complex mixture of amorphous and crystalline ingredients. Amorphous components are considered as non-equilibrated glassy solids which remain stable due to their high viscosity, below their critical relative humidity-induced glass transition, for long periods of time (Aguilera et al., 1995). With increasing equilibrium moisture content resulting from higher relative humidity of the surrounding air, the glassy solid undergoes a transition to a rubbery phase promoted by water plasticisation. This allows the less viscous liquid-like material to flow and therefore increases the susceptibility of the powder surfaces to stickiness (Carter and Schmidt, 2012). In contrast, crystalline materials do not to absorb water, and only surface adsorption occurs at low relative humidity conditions. However, if the relative humidity exceeds the deliquescence relative humidity, the surface dissolves and a saturated solution is formed on the particle surface. This surface dissolution can subsequently induce a variety of physical changes and lead to the sintering, stickiness and caking (Ahlneck and Zografi, 1990).

Water uptake may therefore adversely affect the functional properties of these powders during storage or transport to the customer if the environmental RH is above a critical point. Water sorption isotherms are widely used to describe the interactions between materials and water vapour molecules, and to predict product stability during storage. The sorption behaviour of food and pharmaceutical powders prepared by spray drying has been extensively reported in many studies. However, studies on detergent products are limited.

The aim of the current study is to investigate the effects of composition and micro-structure on the sorption behaviour of spray-dried detergent powders. Simple, model formulations were used in the study. The laundry detergent powders contained the sodium salt of linear alkyl benzene sulphonate (NaLAS) and sodium sulphate; however, their formulation varied depending on either the initial water content (30.0 or 63.0 wt %) of the slurry, giving a different micro-structure but identical composition or the addition of sodium silicate, a commonly used binder. NaLAS is the most important functional component in spray-dried detergent powders, due to its role in the removal of dirt and soils from fabrics. The liquid crystalline phases of NaLAS were previously shown to have a tendency to swell with increasing relative humidity. However, surprisingly interlamellar water layer thickness was found to decrease in detergent powders containing sodium silicate at humid conditions, which was explained by the hygroscopic nature of sodium silicate (Farshchi, 2018). It was suggested that the sodium silicate was likely to undergo humidity-induced structural changes leading to the exposure of a greater number of silanol groups (Si-OH) which consequently enhances the hygroscopic characteristics.

Sodium silicates are widely used in detergent products because of their good buffering capacity. Also, they can soften water by exchanging sodium ions for divalent cations, and hence augment the detergency performance of anionic surfactants (Smulders and Rähse, 2000). In the current study, the aqueous sodium silicate solutions, also referred to as "water-glass", have a composition characterised by molar SiO_2:Na_2O ratio of 2.35. In such a system, a dispersion of monomer, dimer, cyclic trimer and polysilicates are thought to be in chemical equilibrium (Yang et al., 2008). Böschel et al. (2003) also confirmed that concentrated sodium silicate solutions with SiO_2:Na_2O ratios > 2 contain mainly polymeric ions. The polysilicates are considered to possess a highly polymerised dense structure with various populations of surficial functional groups, e.g. silanol (Si-OH), siloxide (SiO-) and siloxane (Si-O-Si). Upon drying of concentrated sodium silicate solutions, the removal of water gives rise to a decrease in the volume of interstitial solution until the aggregates are forced into close contact and form a transparent, solid and amorphous structure (Roggendorf et al., 2001). Consequently, it can be inferred that spray-dried sodium silicates have numerous hydroxyl groups but not all of the functional groups are accessible to water molecules. Buried hydrophilic binding sites can be subsequently exposed in a sufficiently high relative humidity due to the plasticising effect of water molecules. Also, the resulting dried phase has been demonstrated to possess a heterogeneous structure on the nano-scale, due to a random packing of the aggregates which results in the formation of voids and hence a capillary pore system (Roggendorf et al., 2015). Considering the above-mentioned characteristics, the storage of spray-dried powders containing sodium silicate is likely to induce significant physical and chemical changes in granule surface structure by enhancing the moisture uptake which can be detrimental to the stability and functional properties in spray-dried detergent powders. On the other hand, the initial water content of the slurry was previously shown to have profound effect on the morphology and micro-structure of the resulting detergent powders. Powders produced from nil-silicate, high-water content slurries produce powders with a more irregular structure, roughed surfaces, different surface composition and different micro-structure in comparison to their equivalents made from low water content slurries. This in turn can influence the water sorption capacity of the powders.

Therefore, the objectives of the present work were to determine the moisture sorption isotherms of the detergent powders, and to evaluate the ability of various mathematical models for prediction of the experimental data. Furthermore, the effect of water sorption as a function of the relative humidity on micro-structural evolution of the detergent powders was examined using X-ray diffraction studies, microscopic observations and ATR-FTIR spectroscopy. X-ray micro-CT was also used to show the morphology of the granules as a function of the initial water content of the slurry.

2. Materials and methods

2.1. Materials

Detergent granules were produced using a pilot-scale spray dryer located at Procter & Gamble’s Newcastle Innovation Centre. The conditions were chosen to be representative of the large scale and to give powders with similar properties. Conditions were kept consistent between formulations, with an air inlet temperature of 280 ° and air outlet temperature ~100 °C. Further details are given in Farshchi (2018). The spray-dried detergent powder contained the sodium salt of linear alkylbenzene sulphonate (NaLAS) and sodium sulphate; however, their formulation varied depending on either the initial water content (30 or 63 wt%) of the slurry or the addition of sodium silicate. Detergent powders containing silicate species were produced by the addition of commercial sodium silicate with the SiO_2:Na_2O molar ratio of 2.35

to the detergent slurries. The compositions of the slurries are given in Table 1. The following abbreviations are used, throughout this paper, to identify the formulations: LW: low-water content slurry; HW: high-water content slurry; LW+2.35R: low-water content slurry containing sodium silicate with a SiO_2:Na_2O molar ratio of 2.35. Prior to the microscopic observations, ATR-FTIR and XRD measurements, the samples were conditioned by storing 2.0 g of sieve cuts (300-350 µm) of the sample powders in desiccators with a specific relative humidity, i.e. 11, 33, 54, and 75% at 21 ±1°C for four weeks. The specific relative humidities were created using saturated solutions of lithium chloride, magnesium chloride, magnesium nitrate hexahydrate, and sodium chloride respectively.

Table 1. Composition of the detergent slurry formulations

2.2. X-ray diffraction (XRD) measurements

In these series of experiments, the existence of polymorphs of anhydrous sodium sulphate was investigated by X-ray diffraction, XRD, (D8 Advance, Bruker AXS, Karlsruhe, Germany) using a Cu Kα X-ray source. The samples were packed tightly in a sample holder with a 2mm indent. The scanning region of the diffraction angle was between 10 -70° (2θ).

2.3. Microscopic observations

The surface micro-structure of the detergent powders was examined using SU8230 Hitachi scanning electron microscopy (SEM). Prior to SEM observation, sputter coating was conducted to form an ultra-thin coating of gold which inhibits charging during SEM examination.

2.4. X-ray micro computed tomography (micro-CT)

The internal structure of spray-dried detergent powders was qualitatively examined using a Phoenix Nanotom CT scanner (GE Measurement and Control, Wunstorf, Germany). This provides good insight into the distribution of high density and low density phases within the powder. The high density regions are due to initially undissolved inorganic salts, i.e. sodium sulphate crystallites, and low density regions are pores and vacuoles.

Sieved size cuts (300-350 µm) of the sample powders were mounted on a rotating stage between an X-ray source and X-ray detector. Samples were then scanned in the full range of 0–360°. A series of X-ray micrographs was obtained and three-dimensional volumes were reconstituted using the VGStudio software package (Volume Graphics GmbH, Heidelberg, Germany). The spatial resolution, i.e. voxel size, of the reconstructed 3D images was 1.76 µm. To improve the 3D data visualisation, a number of different image processing tools including filtration and segmentation, were applied to the X-ray micrograph data using the Avizo software 8.0 (FEI, Oregon, USA). A non-local means filtration was applied to the grey scale projections to reduce image noise. The segmentation of highly dense regions, corresponding to initially undissolved sodium sulphate particles, from the matrix was conducted using an interactive thresholding tool in Avizo.

2.5. ATR-FTIR measurements

The infrared spectra were recorded with a Nicolet iS10 FT-IR Spectrometer (Thermo Fisher Scientific, USA) using the attenuated total reflection (ATR) method. The detergent powders were mounted on the top of a high-refractive index ATR crystal and then slightly pressed by a pre-mounted sample clamp. The infrared information was obtained by measuring the infrared light which is entirely internally reflected in the medium of ATR crystal. Background corrected spectra were measured over a range of 550-4000 cm^{-1} with 4 cm^{-1} resolution.

2.6 Dynamic vapour sorption

The dynamic sorption behaviour and isotherms of spray-dried detergent powders were gravimetrically determined using a dynamic vapour sorption (DVS) technique (DVS Advantage, Surface Measurement Systems, Middlesex, UK). The instrument can be considered as a humidity and temperature controlled incubator equipped with ultra-sensitive microbalances which enable measurement of changes in sample mass to a resolution as low as one part in ten million. The samples were loaded in a sample pan (100 µl) and an empty pan was used as a reference. The instrument is fully automated, allowing pre-programming of sorption and desorption isotherms. The DVS profiles were obtained by raising humidity from 0% to 70% RH and back to 0% RH in increments of 10% RH steps. At each RH step the sample was allowed to reach a gravimetric equilibrium, when the change in mass (dm/dt) is lower than 0.002 mg/min, and then the sample progressed to the next RH step. The experiments reported here were run at 25 ˚C.

The sorption isotherms were modelled using the Brunauer–Emmett–Teller (BET), Guggenheim–Anderson–de Boer (GAB) and Oswin equations. The BET equation is an effective method for estimating the amount of water molecules bounded to specific hydrophilic groups in dehydrated multi-component systems, even though its application is restricted to a limited range of water activities (~ 0.05 - 0.35). This is due to deviation of the linearity of BET graphs at larger relative humidity values (Basu et al., 2006). The BET equation can be written as follows:

$$M_e = \frac{M_b C a_w}{(1- a_w)[1+ (C-1)a_w]} \qquad (1)$$

Where M_e is the equilibrium moisture content (dry basis), M_b is the BET monolayer moisture content (dry basis), representing the amount of water molecules which are tightly bound to the hydrophilic and polar groups, a_w is water activity, and C is a constant related to the affinity of the solid components with the adsorbate, i.e. water molecules, and hence to the net of heat of sorption. The GAB model, with a sound theoretical foundation, is a more developed version of the BET model (Lewicki, 2009). This model is one of the most widely used equations to describe the experimental adsorption isotherms of water in a wide range of water activities from 0 to 0.9. The GAB equation can be expressed as follows:

$$M_e = \frac{M_g C K a_w}{[(1-Ka_w)(1-Ka_w+CKa_w)]} \qquad (2)$$

Where once again M_e is the equilibrium moisture content, M_g is the GAB monolayer moisture content, a_w is water activity, C a constant related to the heat of sorption of water molecules adsorbed as a monolayer, and K the correcting constant which takes into account the energies of interaction between the first and following water layers. The model parameters can be obtained by rescaling the above equation in a second-order polynomial form, of the GAB equation (Kelly et al., 2016, Timmermann et al., 2001) (Eq. 3):

$$\frac{a_w}{M_e} = \alpha a_w^2 + \beta a_w + \gamma \qquad (3)$$

Parameters of the above quadratic expression, i.e. α, β and γ, can be determined by non-linear regression analysis of the experimental values of a_w/M_e as a function of $a_{w.}$ From the values of α, β, γ obtained in this way, the original GAB parameters can be determined through the following set of equations:

$$M_g = \frac{1}{\sqrt{\beta^2-4\alpha\gamma}} \qquad (4)$$

$$K = \frac{\beta-\left(\frac{1}{M_g}\right)}{-2\gamma} \qquad (5)$$

$$C = \frac{1}{M_g K \gamma} \qquad (6)$$

The Oswin model is a two-parameter empirical model which is a series expansion for the sorption isotherms having sigmoidal-shaped profile. The equation has been successfully used for many related food products containing polymeric compounds, e.g. starch, protein, and can be conveniently expressed as follows (Labuza and Altunakar, 2007):

$$M_e = A\left(\frac{a_w}{1-a_w}\right)^B \qquad (7)$$

Where A and B are the parameters of the model, M_e is the equilibrium moisture content and a_w is the water activity. The parameters can be determined by plotting a log (M_e) versus log ($a_w/1-a_w$).

The accuracy of prediction of each sorption model was evaluated by calculating the mean percentage deviation modulus (E), where E value correlates the predicted and experimental data, and is defined as

$$E = \frac{100}{N}\sum_{i=1}^{n}\left|\frac{m_{ei}-m_{pi}}{m_{ei}}\right| \qquad (8)$$

For the above equation m_e is the experimental moisture content, m_p is the predicted moisture content, and N is the number of experimental data used in the analysis. According to the literature, a sorption model is considered acceptable for practical purposes if the E values are lower than 10% (Kaymak-Ertekin and Gedik, 2004, Peng et al., 2007). The coefficient of determination (R^2) was used to evaluate the goodness of fit of each sorption model (Bonner and Kenney, 2013). The coefficient of determination can be defined as

$$R^2 = 1 - \frac{\sum(m_{ei}-m_{pi})^2}{\sum(m_{ei}-\bar{m}_{ei})^2} \qquad (9)$$

3. Results and discussion

3.1. Microscopic observation

These experiments show the influence of relative humidity on the evolution of the surface structure and morphology of spray-dried detergent powders during storage. Fig. 1a and b illustrates two distinct surface morphologies of LW particles as a function of relative humidity. Freshly-produced LW granules have been shown to be mainly covered with a non-crystalline and smooth skin, although there may also be some shallow wrinkles on the surfaces (Farshchi et al., 2019). Fig. 1a illustrates that the surface micro-structure of a typical granule after 4 weeks of storage at 33% RH is unchanged. Moreover, no significant structural changes on the particle surface are seen at 54% RH (not shown). However, exposure to a higher water activity, 75% RH, resulted in a considerable change in surface morphology (Fig. 1b). Considering the micrograph, small embedded crystals of sodium sulphate are now more apparent at the surface, though still covered by a continuous layer of NaLAS. This is either due to an increase in mobility in the NaLAS phase which might have receded inward or growth of the sodium sulphate crystals perhaps due to Ostwald ripening.

SEM analysis of fresh spray-dried detergent powders produced from high-water content, HW, slurry has shown that they possess a more crystalline surface (Farshchi et al., 2019). These powders were stable and did not develop any noticeable humidity-induced structural change at 33% (Fig. 1c) or 54% RH. Upon exposing of spray-dried powders to 75% RH, the surface of powders also became rougher and a considerable amount of sodium sulphate crystals were observed on the surfaces (Fig. 1d).

The reason for the differences between the surface evolutions of the above-mentioned detergent powders can be explained by the fact that the matrix of NaLAS and sub-micron sodium sulphate crystals which forms the surface differ in composition due to the initial water content of the slurry(Farshchi et al., 2019). Based on these previous results the matrix composition of detergent powders produced from the LW formulation, was estimated to be rich in NaLAS surfactant, 56 wt%, while the NaLAS content of the matrix decreased to 20 wt% in the case of the HW formulation, leading to a more crystalline appearance in the resulting detergent powders and the distinct differences under storage at high humidities.

Figure 1. High-magnification SEM micrographs of spray-dried detergent powders. (a) a typical surface morphology of a detergent granule produced from the LW slurry, stored at 33% RH, and its equivalent at 75% RH (b). (c) shows a typical crystalline surface of a detergent granule produced from HW slurry, stored at 33% RH, and (d) illustrates the micro-structural evolution of these powders as a consequence of the increased relative humidity (75% RH).

For freshly-produced detergent powders containing sodium silicate, LW+2.35R, two distinct morphological features have been observed on the granule surface. In these powders, some regions are relatively smooth and similar to those observed in spray-dried powder produced from low-water content, nil-silicate LW slurry. Other regions have a crystalline appearance, and a considerable amount of nano-sized prismatic crystals can be observed on the surface. Upon storing these powders at 33% RH, the morphological characteristics of both regions remained unchanged, Fig. 2a and c. However, unlike the nil-silicate formulations, the LW+2.35R powder was susceptible to humidity-induced structural changes at 54% RH. As seen in Fig. 2b, at 54% RH, both deep and shallow wrinkles/folds can be observed on the surface, and in a similar fashion to the LW formulation the crystals are now more apparent at the surface. Additionally, it was found that the crystalline regions have undergone a noticeable morphological change at this level of relative humidity. The initial nano-sized prismatic crystals were transformed to larger crystals, signifying a moisture-induced crystal growth of sodium sulphate (Linnow et al., 2006). Comparing the surface evolution of these powders with those in the absence of sodium silicate, it can be concluded that it is the presence of sodium silicate that increases the susceptibility of detergent powders to the surface structural changes at 54% RH. A possible explanation for this observation may be the availability and mobility of water in this formulation due to the greater water sorption capacity of silicate containing detergent powders, arising from the hygroscopic nature of sodium silicates. In this study, the influence of sodium silicate on the structural profile of the adsorbed water molecules in spray-dried detergent powders has been further investigated with a FTIR spectroscopy, and will be discussed in section 3.4.

Figure 2. High-magnification SEM micrographs of a spray-dried detergent granule containing sodium silicate showing two distinct morphological features, i.e. smooth regions (a) and crystalline regions (c), at 33% RH. The smooth regions showed some deep, as well as shallower wrinkles/folds after storage at 54% RH (b). In (d) the transformation of nano-sized crystals of sodium sulphate to relatively larger crystals at 54% RH is quite noticeable

Fig. 3 displays the morphological features of the LW+2.35R powder exposed to a higher relative humidity value (75% RH). It can be seen that relatively large crystalline structures of a comparable size to the overall granule diameter, exist on the surfaces, Fig. 3a, b. Fig. 3c shows that the granule surface is progressively covered by small prismatic crystals. Moreover, rather interestingly, SEM micrographs reveal the presence of a different crystal habit on the surfaces, which is distinct from those observed in other stored powders, Fig. 3 d,e,f. Fig. 3f depicts the detailed morphology of these crystals. The morphology of these elongated crystals corresponds more closely to that of mirabilite, i.e. sodium sulphate decahydrate, when compared with the reported habits in other studies (Atzeni et al., 1995, Rodriguez-Navarro et al., 2000) showing efflorescence of thin, straight whiskers. Wide-angle X-ray diffraction (WAXS) was therefore carried out to reveal the nature of these nano-structures.

Figure 3. SEM micrographs of a typical detergent granule containing sodium silicate with the SiO_2:Na_2O molar ratios of 2.35, stored at 75% RH. The arrows highlight the presence of relatively large crystalline structures on the granule surface (a). Figure (b) shows the presence of a typical large crystalline structure. Figure (c) shows the growth of sodium sulphate crystals covering the granule surface. The emergence of a new crystal habit (d), also shown in higher magnification images (e) and (f), is clearly visible. This illustrates the presence of bundles of elongated crystals and morphological characteristic of a single crystal (see insert).

3.2. X-ray diffraction measurements (XRD)

In this section the influence of relative humidity on the stability of Na_2SO_4 polymorphs against phase transition is evaluated. The XRD patterns of detergent powders stored at 33 % RH show well-defined, sharp diffraction peaks which are characteristic of the well-ordered crystal lattices of sodium sulphate (Figures 4 and 5a) and are consistent with previously reported diffraction patterns of the model formulations reported by Farshchi et al. (2019).

Two stable polymorphs of sodium sulphate, i.e. Na_2SO_4 (V) and Na_2SO_4 (III), were identified in spray-dried detergent powders. In general, these anhydrous polymorphs have been shown to crystallize out of a supersaturated solution of sodium sulphate upon evaporation, among which phase V (thenardite) is considered to be the most stable anhydrous phase at room temperature (25 °C). Na_2SO_4 (III) is a metastable phase which remains stable for considerable periods of time at room temperature (25 °C) and dry conditions. However, depending on its environment, this polymorph has been observed to either deliquesce at RH > 80 - 83.5% or undergo a solid state transition to phase V. (Rodriguez-Navarro et al., 2000, Linnow et al., 2006).

Figure 4. Typical wide-angle X-ray diffraction (WAXS) patterns of spray-dried powders produced from LW and HW formulations, showing the stability of two anhydrous polymorphs, i.e. III and V, exposed at 75% RH.

After 4 weeks of storage, the XRD patterns of nil-silicate powders exhibited no change even at the highest relative humidity (75% RH), which suggests that the anhydrous polymorphs were quite stable (Fig. 4) and no transition from phase III to V is seen. More precisely, the well-defined Bragg peaks remained intact and no amorphous phase was identified at the highest RH value, nor were any new peaks observed. In studies on the crystallization of sodium sulphate in Na_2SO_4 – H_2O systems (Linnow et al., 2006), it has been demonstrated that the deliquescence or hydration of phase III and phase V start at 80 - 83% RH. Therefore, the stability of the anhydrous polymorphs was expected since the relative humidity in this study was significantly below this transition point.

In the case of detergent powders containing sodium silicate, the diffraction peaks similarly remained unchanged up to 54% RH, Fig. 5b, and no phase change is observed. However, for the samples stored at an RH of 75%, examination of the XRD patterns revealed the presence of a number of new peaks at 22.1, 24.2, 26.4, and 30.9 ° 2θ, Fig 5b, signifying a phase transition at such humid conditions. Interestingly, as the samples were desiccated back to 33% RH the aforementioned peaks disappeared and the powder exhibited the same diffraction patterns as they showed initially under dry conditions. The disappearance of these new peaks after desiccation at 33% RH is evidence of the formation of a hydrated crystal form of sodium sulphate. Comparing the diffraction patterns, as well as SEM images, with previous scientific studies on the crystallization of sodium sulphate, it can be concluded that it was decahydrate $Na_2SO_4.10\ H_2O$ (mirabilite) that was formed during the storage at 75% RH. The formation of mirabilite at a relative humidity far below the deliquescence of sodium sulphate can be explained by a solid-state reaction pathway. Rodriguez-Navarro et al (2000) showed that the conversion of anhydrous polymorphs of sodium sulphate to mirabilite at enhanced relative humidity can take place through a solid-solid transition reaction at which the hydration of anhydrous polymorphs proceeds smoothly without actual solvation of the solid phase. Moreover, in this series of experiments, the reason for the susceptibility of anhydrous polymorphs to solid-solid transition reaction, and hence mirabilite formation in the presence of sodium silicate, can be attributed to the hygroscopic nature of sodium silicate. This point will be discussed in next section.

Figure 5. (a) A typical wide-angle X-ray diffraction (WAXS) pattern of spray-dried powders containing sodium silicate 2.35R SiO_2:Na_2O, showing the presence of two anhydrous polymorphs, i.e. III and V at 33% RH. (b) a selected region, highlighted in (a**)**, of the patterns exposed to various RH values from 33% to 75% RH at 21±1 $^{\circ}$C followed by a desiccation to 33% RH. The arrows indicate the emergence of new peaks at a high relative humidity (75% RH).

3.3. Dynamic vapour sorption (DVS) measurements

3.3.1. Characteristics of moisture sorption

The total running time taken to reach equilibrium moisture content (EMC) values throughout sorption and desorption cycles indicates the ability of a product to adsorb water vapour from the surrounding air. Step-wise moisture sorption-desorption profiles of the spray-dried detergent powders are shown in Fig. 6. It can be seen from Fig. 6a that, for the nil-silicate LW powder, the equilibration times are very short (~ 20 min) for RH values up to 50%. Also, a near-linear increase in EMC value is evident in its corresponding sorption isotherm. However, at higher relative humidity the isotherm deviates from the linear behaviour. The EMC value increases significantly more and reaches its maximum value of 1.72 % at 70% RH. The sorption isotherms of these powders were similar to type II sigmoidal curves according to Brunauer classification (Brunauer et al., 1940), indicating adsorption on macroporous adsorbents with strong adsorbent-adsorbate interactions (Aranovich and Donohue, 1998).

The noticeable increase in EMC values above 50% RH, signifies a change in mechanism of water sorption. Several mechanisms have been proposed for the interactions between water vapour and adsorbent molecules which mainly include: surface adsorption, bulk adsorption, hydration, gelation, and deliquescence (Ouyang et al., 2015). It has been suggested that, at low relative humidity values, water vapour sorption is an entropy-controlled process which is associated with the number of available sorption sites, as well as randomness of the motion of water molecules. As relative humidity increases, the more polar available sites are occupied which in turn increases the order of the system, giving rise eventually to the formation of subsequent layers of adsorbate (Bonilla et al., 2010). Therefore, the relatively lower moisture uptake up to 50% RH can be explained by the mechanism of surface adsorption which is a function of the powder micro-structure. However, at medium and high relative humidity values it is the bulk water sorption which predominantly occurs. This can be accompanied by interactions between the sorbate and sorbent, leading to some structural changes, e.g. deliquescence, swelling and glass transition, which therefore allow water molecules to penetrate into the interior of the structures (Maher et al., 2014). Smith (1947) studied the water sorption properties of many polymers and suggested that the swelling behaviour of polymeric substances results in the development of free volumes within the gel structure which progressively increases the effective sorbing surfaces of the polymer. In the current study, the progressively increased EMC values at RH > 50% can be partially attributed to structural changes, e.g. swelling, of LAS lamellar phases, allowing the absorption of larger quantities of water molecules into the matrix structure.

Figure 6. Equilibrium moisture sorption-desorption profiles for spray-dried detergent powders produced from low-water (LW) content (a) and high-water content (HW) slurry (c), and detergent slurries containing sodium silicate (LW+2.35R) (e). Panels (b), (d) and (f) show the corresponding sorption isotherms for the aforementioned samples respectively.

Spray-dried detergent powders produced from HW slurry displayed similar step-wise moisture sorption-desorption profile (Fig. 6c), though the total running time was relatively longer (462 min) and the EMC value was considerably larger at any given relative humidity. The reason for the higher moisture uptake, despite an identical composition, can be attributed to the micro-structure, morphology and surface characteristics of these samples. It was previously demonstrated that a greater initial water content in detergent slurries gives rise to formation of a more irregular structure and a rougher surface. SEM observations of the microtome-polished cross-sections of these powders also revealed the presence of irregular open pores with some degree of connectivity within the granule matrix (Farshchi et al., 2019). The typical external appearance of these powders was also shown in an earlier micrograph (Fig. 1c). X-ray microtomography technique can provide good insight into the internal structures of these powders. Typical examples of the internal morphology as a consequence of the initial water content are illustrated in Fig. 7. The reconstructions illustrate that a significant amount of sodium sulphate in the LW powder is present as large crystals, Fig. 7b, where as in the HW case this sulphate is present within the matrix structure and due to its sub-micron size cannot be resolved by the micro-CT. It is also clear from Fig. 7d that the increased water content has led to the formation of a “foam-like” structure. These structural changes increase the effective surface area exposed to the water vapour, as well as enhance the permeability of the powder to water vapour.

A small sorption hysteresis in the HW isotherm below 30% RH could be attributed to the failure to establish true equilibrium during the desorption process; the level of water being desorbed being higher than the LW case. However, it may also be indicative of a structural change within micro-porous HW matrix, perhaps caused by movement of crystals as observed on the surface of the powder, as discussed earlier and see in Fig. 1b and d. The slight dip in the sorption curve at RH = 70%, Fig. 6c, is also indicative of a change in material structure and supports this hypothesis.

Figure 7. 3D X-ray tomograph (voxel size: 1.76 µm) comparing LW and HW powders. (a) shows a typical detergent granule produced from LW slurry; and (b) shows its 3D central cross section (52.8 µm thick) illustrating the distribution of voids and sodium sulphate crystallites (blue regions). (c) shows a typical detergent granule produced from HW slurry; and it’s corresponding cross section (56.8 µm thick) (d).

Interestingly, the addition of sodium silicate to the slurry causes considerable differences in the moisture sorption-desorption profile, total running time, EMC values and sorption hysteresis. From Fig. 6e, three distinct regions can be identified in the sorption-desorption profile, namely 0-30% RH, 30-50% RH and RH > 50%. At low relative humidity region, i.e.

0-30% RH, the equilibration times are relatively short (~ 37 min), though still considerably longer than those of silicate-free powders. At intermediate level of relative humidity, i.e. 40-50% RH, a prolonged equilibration time (350 min) can be detected. Above 50%, the EMC value progressively increases until it reaches the maximum value, 12.10 % at 70% RH. In this region, LW + 2.35R powders displayed a considerably larger EMC value at any given RH as compared with the nil-silicate powders, indicating a stronger ability of these powders to interact with water vapour molecules. Additionally, in contrast to nil-silicate detergent powders, as seen in Fig. 6f, all desorption points between 0 and 60% RH are located above the sorption points, i.e. the desorption branch does not coincide with the adsorption branch, thus indicating a hysteresis loop.

Dried sodium silicates have numerous hydroxyl groups, but not all of the functional groups are accessible to water vapour molecules. Therefore, a likely explanation for the increased capacity of moisture uptake can be attributed to structural changes in sodium silicate which probably occur above 40% RH. This leads to the increased exposure of the hydrogen binding sites, and consequently hydration and swelling of the hardened glassy silicate. These plausible alterations are also reflected in the step-wise moisture sorption-desorption profile (Fig. 6e), where the structure responds to its new physico-chemical state by requiring a noticeably prolonged equilibration time between 40 and 50% RH (Hill et al., 2010). At 25 °C, the relative humidity value of 40%, can be considered as a critical threshold above which the physical properties of sodium silicate change from a rigid glassy state into a rubbery state. After this phase transition, the subsequent desorption occurs from a highly hydrated and swollen matrix which has a different physical state from that initially present during the sorption stage of the process. This phenomenon manifests itself as hysteresis (Hill et al., 2009) which is clearly noticeable in Fig. 6f.

The increased moisture uptake as a consequence of the phase transition may concomitantly induce surficial hydroxylation reactions in sodium silicates. These consequently enhance the sorption capacity of the powders. As water vapour molecules diffuse into the interstitial spaces of the matrix, hydrogen bonding with surficial hydroxyl groups, forces water molecules to form an ordered water monolayer. At a sufficiently high relative humidity, surficial hydroxylation may occur due to the opening of siloxane rings (Warring et al., 2016). This consequently alters the chemistry of the absorbent, thereby increasing its hydrogen bonding capacity. ATR-FTIR studies of these samples, stored at various RH values, can provide some clues as to the origin of the aforementioned changes in kinetics of water sorption at high relative humidity conditions. This point will be discussed in section 3.4.

3.3.2. Data modelling

Table 2 shows the estimated model parameters and statistical results obtained from the fitting of the isotherms. Amongst the models capable of describing the sorption isotherms throughout the entire range of relative humidity (0-70 % RH), the GAB model provided the closest fit to the experimental moisture data for the nil-silicate powders. Statistically, the GAB model demonstrated the lowest mean percentage deviation modulus (E %) and the highest coefficient of determination (R^2) for both the adsorption and desorption isotherms.

The estimated value of the monolayer water (M_g) obtained by applying the isotherm models, is of significant interest as it shows the amount of water which is tightly bound to specific hydrophilic sites. Such information helps to determine the appropriate storage conditions of the powders (Shrestha et al., 2007). The GAB monolayer value for the LW powder was significantly smaller than the HW powder, this can be attributed to a greater surface area as was discussed earlier.

It has been shown that for $C \geq 2$ and $0 < K < 1$ the GAB model describes properly sigmoidal-shaped isotherms type II under the Brunauer classification (Ben Abdelhamid et al., 2016, Blahovec, 2004). GAB constant C is a measure of the difference of free enthalpy of the sorbate molecule in the first sorption layer and the layer above the monolayer, while the constant K is related to the difference of free enthalpy of the sorbate molecule in the pure liquid and those in the multilayers. In the current study, for the LW powder, K is slightly higher (K=1.06) than the limiting value of 1. At low K values water molecules are highly structured in multilayer domains. As K value approaches unity, water molecules are least bound to the monolayer region and have almost bulk liquid characteristics (Timmermann et al., 2001). K values higher than 1 are not feasible since the heat of adsorption of water molecules in the second and upper layers should be less than the heat of liquefaction (Arthur et al., 2016). Nonetheless, evidence for this overshooting of the limit on the K has been reported in many other studies (Kaymak-Ertekin and Gedik, 2004, Moraga et al., 2004, Vega-Gálvez et al., 2008). Pérez-Alonso et al. (2006) suggested that in some cases the GAB parameters may lack any physical meaning and exceeding the limits can be justified due to the mathematical relationships between the parameters which exist in any curve fitting scenario. Even though in the current study the mean values of K were only very slightly higher than 1, some K parameters were found within the adequate range and reasonably below the unity, e.g. ~ 0.97. This may imply an extremely low difference between molecules in the bulk and those residing in multilayer. Thus, one may conclude that the multilayers have the characteristics very similar to bulk liquid (Quirijns et al., 2005). A possible reason for this can be attributed to partial hydrophobicity of the granules surfaces arising from the presence of surfactant molecules. It has been suggested that the formation of multilayer domains on the hydrophobic surfaces are not energetically favourable. In the first sorption stage, adsorption onto hydrophobic sites, e.g. methyl groups, occurs due to dispersion forces which are energetically weak. In subsequent layers, water molecules have no interactions with the hydrophobic surface (Zettlemoyer, 1968). This consequently decreases the ordering of water molecules and causes water molecules to behave like bulk liquid. On the contrary, strongly hydrophilic surfaces have a tendency to favour multilayer growth (Sears, 2001).

Table 2. Estimated model parameters and fit criteria for water sorption and desorption experimental data, at 25 °C.

For the LW and HW samples, the Oswin model also shows a good fit with the experimental data with $R^2 > 0.97$ and $E < 6\%$, though it was still less successful in describing the isotherms as compared with the GAB equation. In contrast, for spray-dried detergent powders containing sodium silicate, both OSWIN and GAB equations were found to be unsuitable in describing the adsorption isotherms; E values, measuring deviation between fitted and actual results, were >15%. As can be seen in Fig. 8e, these models deviated from the real sorption isotherm at relative humidities larger than 50% RH. This deviation can be attributed to the changes in arrangements of molecular structure in polymeric sodium silicate, which is not accounted for in the GAB theory.

On the contrary, these models showed better fits for the desorption data. This may be expected since the sample has already experienced a substantial transition from the glassy to rubbery state during the absorption process, which might not have been reversible simply by desiccating the sample (Carter and Schmidt, 2012). In the absence of any major changes in the structural arrangement of molecules during the desorption part of process, one may expect a significantly better fit of the models to the experimental data.

The BET model provided a good description of the isotherms of the powders in the range of RH < 40%. The largest M_b value can be found in the detergent powder containing sodium silicate. This considerably larger moisture content in the initial monolayer region signifies a greater number of hydrophilic binding sites which strongly hold water molecules by hydrogen bonds (Cadden, 1988). As mentioned earlier, this hydrophilic characteristic can be attributed to the presence of silanol groups (Si-OH) of sodium silicate. This higher affinity of water molecules in this system is also evident from the relatively larger C parameter suggesting more favourable interaction energies. Interestingly, for all samples, both C parameter and M_b value significantly increased for desorption isotherms as expected. Once again, this was due to the humidity-induced structural changes that had already occurred during the adsorption part of the experiment, as was discussed above.

Figure 8. Experimental and predicted sorption isotherms for spray-dried detergent powders produced from LW (a) and HW slurry (c), and LW+2.35R slurry (e). Panels (b), (d) and (f) show the corresponding desorption isotherms. Temperature 25 ºC.

3.4. ATR-FTIR measurements

The microscopic observations demonstrated that the presence of sodium silicate increases the susceptibility of the powder surfaces to the humidity-induced morphological changes. Returning to the dynamic vapour sorption data in Fig. 6f, it was shown that EMC value abruptly increased at RH > 40%, which was explained by the moisture sorption-induced glass transition, in turn leading to the exposure of a greater number of active binding sites within the matrix. The changes in hygroscopic characteristics of this powder as a result of the moisture sorption phase transition can be better elucidated by probing the O-H stretching vibrations in the 3000-3800 cm^{-1} region (Fig. 9). In this region the absorption intensity can be associated with the extent of adsorbed water molecules. The O-H stretching absorption is known to be composed of three components assigned to sites differing in intermolecular bonding. It is generally accepted that a vibrational peak, with the highest energy, at ~3200 cm^{-1} is attributed to "bound water" or "ice-water" structure where the oxygen atoms of water molecules have four bounds including the covalent and hydrogen bonds. This leads to the formation of tetrahedral arrangements as can be seen in crystalline ice structures. The lowest energy peak around 3640 cm^{-1} is assigned to "free water", when the oxygen atoms are only covalently bound to two hydrogen atoms. The medium-energy peak around 3450 cm^{-1} is assigned to "multi-layer water", when the oxygen atoms on average are bound to three hydrogen atoms. These water molecules are partially structured, and hence are sometimes referred to as intermediate water (Barnette et al., 2008)

Figure 9. ATR-FTIR spectra (3000-3800 cm^{-1}) for sprayed-dried detergent powders produced from the LW formulation (a) and those containing sodium silicate, LW+2.35R (b), showing the structural evolution of water molecules at different relative humidity. The dashed lines show the O-H stretching vibration positions of bound water, multi-layer water and bulk water.

The infrared spectra of the nil-silicate LW powder, stored at different relative humidity values are shown in Fig. 9a. A broad absorbance can be seen at 11% RH value, with its intensity increasing as the relative humidity is elevated. This broad 3000-3700 cm^{-1} absorbance is apparently composed of two broad bands at ~ 3450 and ~ 3620 cm^{-1}. A considerably smaller peak also appears around 3200 cm^{-1}. It can be observed that the most intense band is at 3450 cm^{-1}, which is attributed to the multi-layer water. This noticeably changes with increasing relative humidity. By 75% RH, the multi-layer water peak dominates the absorbance profile of the O-H stretching region, while the intensities of the high and low-energy peak of the bound and free water remain relatively unchanged. This increase in population of multi-layer water molecules is thought to be associated with the swelling of liquid crystalline phases of NaLAS (Farshchi, 2018).

The spray-dried detergent powder containing sodium silicate, however, showed remarkable changes in the shape of its spectra. It can be seen that the intensity of the bands at 3200 cm^{-1} is higher than those in the nil-silicate LW powder, even at the lowest relative humidity (11% RH). This observation is consistent with the values of monolayer water obtained by BET model, suggesting the existence of a greater population of water molecules which are strongly bound to the hydrophilic binding sites. This band grows in intensity even with a small increase in relative humidity, i.e. 33% RH, becoming a well-defined strong band at 75% RH. This change was concomitant with a significant increase in the intensity of the bands at 3450 and 3620 cm^{-1}. The abrupt increase in O-H stretching absorption between 33% and 54% RH signifies a change in the molecular configuration of the water and a structural change in the sodium silicate as was earlier reflected in the sorption isotherms. There are two possible scenarios which can potentially explain these humidity-induced structural changes. Firstly, the increased relative humidity might have increased the molecular mobility of the amorphous sodium silicate and therefore have exposed the additional active surface area and hence buried hydrophilic silanol groups. Secondly, the increased moisture content may also concomitantly result in the conversion of siloxane (Si-O-Si) to silanol (Si-OH) groups (Warring et al., 2016), thereby enhancing the moisture sorption capacity.

4. Conclusion

For the first time an investigation into the impact of increased water activity on the surface morphology, micro-structure and moisture sorption of spray-dried detergent powders has been reported. Simple model formulations were used to understand the important role of powder micro-structure and silicate on the powder behaviour which was probed by microscopy and sorption isotherm measurements. The solid state of the water was found to be key to the observed behaviour and further elucidated via X-ray diffraction and IR absorbance.

Two spray-dried detergent powders, made from different slurry moisture contents, had the same composition but different morphology and micro-structure and were found to have significant different moisture sorption behaviour. Powder produced from high-water content slurry, having a more porous structure with an increase level of sub-micron sulphate crystals, than the same powder composition made from low-water content slurry, showed an increased moisture uptake, with almost double the level of water absorbed at the same RH. This was attributed to the matrix morphology which has a higher effective surface area. For both these nil-silicate samples, BET, GAB and Oswin models described the experimental moisture isotherms well.

Sodium silicate was found to play a key role in the response of the powder to increased moisture activity and in the evolution of powder micro-structure and morphology. The amorphous structure conferred by the sodium silicate was found to significantly increase the hygroscopicity of the powder and the level of moisture absorbed. For this formulation, the GAB and Oswin models were unable to describe the sorption isotherms. This was due to an increase in the moisture uptake above 40% RH which the GAB and Oswin models are not able to account for. This upturn indicated that a structural change in the sodium silicate was occurring and was thought to be due to a moisture initiated phase transition from an amorphous glassy state to a rubbery state. This relaxation of the structure was also thought to expose a greater number of hydrophilic groups, including buried silanol groups, and consequently enhance the moisture sorption capacity of the sodium silicate species and hence the spray-dried powder. These humidity-induced structural changes were also reflected in ATR-FTIR results which also suggested an evolution of water structure between 33 and 54% RH.

The increased moisture sorption capacity and water mobility in the silicate formulation also had a significant impact on the response of the surface, morphology and micro-structure to increased humidity. SEMs of the granule surface showed significant surface structure and morphology changes at the relatively low RH of 54% where significant crystal growth was seen. In contrast the nil-silicate formulations showed no obvious change at 54% RH and required exposure to 75% RH before a similar change was observed. At 75 % RH dramatic changes in powder morphology of the silicate formulation occurred and large scale changes in powder morphology, driven by crystal growth, were observed. X-ray diffraction analysis confirmed the emergence of sodium sulphate decahydrate at these humidities. This was accompanied by the continued growth of sodium sulphate crystals covering the entire granule surface. Again, in contrast, no hydrate formation or sulphate polymorph changes were seen in the nil-silicate formulations even at this higher humidity of 75% RH.

Although, spray-dried detergents have complex multi-scale structures, the findings of the current work give valuable insights into of the influence of slurry formulation on their water sorption properties and potential storage and caking behaviour. This understanding can help product and process developers design, engineer and optimise these important formulated products and their associated manufacturing processes.

Acknowledgement

The authors would like to thank the Advanced Manufacturing Supply Chain Initiative (AMSCI) for funding the project. AMSCI is a government supply chain fund which is helping to rebuild British manufacturing processes. We also acknowledge the input of Sam Tantawy, Joel Caragay and Paul Gould of Procter and Gamble for production of materials and their support throughout the project.

References

AGUILERA, J., DEL VALLE, J. & KAREL, M. 1995. Caking phenomena in amorphous food powders. Trends in Food Science & Technology, 6**,** 149-155.

AHLNECK, C. & ZOGRAFI, G. 1990. The molecular basis of moisture effects on the physical and chemical stability of drugs in the solid state. International Journal of Pharmaceutics, 62**,** 87-95.

ARANOVICH, G. & DONOHUE, M. 1998. Analysis of Adsorption Isotherms: Lattice Theory Predictions, Classification of Isotherms for Gas–Solid Equilibria, and Similarities in Gas and Liquid Adsorption Behavior. Journal of Colloid and Interface Science, 200**,** 273-290.

ARTHUR, E., TULLER, M., MOLDRUP, P. & DE JONGE, L. W. 2016. Evaluation of theoretical and empirical water vapor sorption isotherm models for soils. Water Resources Research, 52**,** 190-205.

ATZENI, C., CABIDDU, M. G., MASSIDDA, L. & SANNA, U. 1995. Crystallization of sodium sulphate in polymer impregnated plasters. Cement and Concrete Composites, 17**,** 3-8.

BARNETTE, A. L., ASAY, D. B. & KIM, S. H. 2008. Average molecular orientations in the adsorbed water layers on silicon oxide in ambient conditions. Physical Chemistry Chemical Physics, 10**,** 4981-4986.

BASU, S., SHIVHARE, U. S. & MUJUMDAR, A. S. 2006. Models for Sorption Isotherms for Foods: A Review. Drying Technology, 24**,** 917-930.

BEN ABDELHAMID, M., MIHOUBI, D., SGHAIER, J. & BELLAGI, A. 2016. Water Sorption Isotherms and Thermodynamic Characteristics of Hardened Cement Paste and Mortar. Transport in Porous Media, 113**,** 283-301.

BLAHOVEC, J. 2004. Sorption isotherms in materials of biological origin mathematical and physical approach. Journal of Food Engineering, 65**,** 489-495.

BONILLA, E., AZUARA, E., BERISTAIN, C. I. & VERNON-CARTER, E. J. 2010. Predicting suitable storage conditions for spray-dried microcapsules formed with different biopolymer matrices. Food Hydrocolloids, 24**,** 633-640.

BONNER, I. J. & KENNEY, K. L. 2013. Moisture sorption characteristics and modeling of energy sorghum (Sorghum bicolor (L.) Moench). Journal of Stored Products Research, 52**,** 128-136.

BÖSCHEL, D., JANICH, M. & ROGGENDORF, H. 2003. Size distribution of colloidal silica in sodium silicate solutions investigated by dynamic light scattering and viscosity measurements. Journal of Colloid and Interface Science, 267**,** 360-368.

BRUNAUER, S., DEMING, L. S., DEMING, W. E. & TELLER, E. 1940. On a Theory of the van der Waals Adsorption of Gases. Journal of the American Chemical Society, 62, 1723-1732.

CADDEN, A.-M. 1988. Moisture Sorption Characteristics of Several Food Fibers. Journal of Food Science, 53, 1150-1155.

CARTER, B. P. & SCHMIDT, S. J. 2012. Developments in glass transition determination in foods using moisture sorption isotherms. Food Chemistry, 132, 1693-1698.

FARSHCHI, A. 2018. The influence of slurry formulation on the multi-scale structure and functional properties of spray dried detergent powders. University of Leeds.

FARSHCHI, A., HASSANPOUR, A. & BAYLY, A. 2019. The structure of spray-dried detergent powders. Powder Technology, Under Review.

HILL, C. A. S., NORTON, A. & NEWMAN, G. 2009. The water vapor sorption behavior of natural fibers. Journal of Applied Polymer Science, 112, 1524-1537.

HILL, C. A. S., NORTON, A. J. & NEWMAN, G. 2010. The water vapour sorption properties of Sitka spruce determined using a dynamic vapour sorption apparatus. Wood Science and Technology, 44, 497-514.

KAYMAK-ERTEKIN, F. & GEDIK, A. 2004. Sorption isotherms and isosteric heat of sorption for grapes, apricots, apples and potatoes. LWT - Food Science and Technology, 37, 429-438.

KELLY, G. M., O'MAHONY, J. A., KELLY, A. L. & O'CALLAGHAN, D. J. 2016. Water sorption and diffusion properties of spray-dried dairy powders containing intact and hydrolysed whey protein. LWT - Food Science and Technology, 68, 119-126.

LABUZA, T. P. & ALTUNAKAR, B. 2007. Water activity prediction and moisture sorption isotherms. Water activity in foods: fundamentals and applications, 109, 154.

LEWICKI, P. P. 2009. Data and models of water activity. II: Solid foods. Food properties handbook, 68-143.

LINNOW, K., ZEUNERT, A. & STEIGER, M. 2006. Investigation of Sodium Sulfate Phase Transitions in a Porous Material Using Humidity- and Temperature-Controlled X-ray Diffraction. Analytical Chemistry, 78, 4683-4689.

MAHER, P. G., ROOS, Y. H. & FENELON, M. A. 2014. Physicochemical properties of spray dried nanoemulsions with varying final water and sugar contents. Journal of Food Engineering, 126, 113-119.

MORAGA, G., MARTíNEZ-NAVARRETE, N. & CHIRALT, A. 2004. Water sorption isotherms and glass transition in strawberries: influence of pretreatment. Journal of Food Engineering, 62**,** 315-321.

OUYANG, J., WANG, J., WANG, Y., YIN, Q. & HAO, H. 2015. Thermodynamic study on dynamic water and organic vapor sorption on amorphous valnemulin hydrochloride. Frontiers of Chemical Science and Engineering, 9**,** 94-104.

PELEG, M. 1977. FLOWABILITY OF FOOD POWDERS AND METHODS FOR ITS EVALUATION — A REVIEW. Journal of Food Process Engineering, 1**,** 303-328.

PENG, G., CHEN, X., WU, W. & JIANG, X. 2007. Modeling of water sorption isotherm for corn starch. Journal of Food Engineering, 80**,** 562-567.

PÉREZ-ALONSO, C., BERISTAIN, C. I., LOBATO-CALLEROS, C., RODRÍGUEZ-HUEZO, M. E. & VERNON-CARTER, E. J. 2006. Thermodynamic analysis of the sorption isotherms of pure and blended carbohydrate polymers. Journal of Food Engineering, 77**,** 753-760.

QUIRIJNS, E. J., VAN BOXTEL, A. J. B., VAN LOON, W. K. P. & VAN STRATEN, G. 2005. Sorption isotherms, GAB parameters and isosteric heat of sorption. Journal of the Science of Food and Agriculture, 85**,** 1805-1814.

RODRIGUEZ-NAVARRO, C., DOEHNE, E. & SEBASTIAN, E. 2000. How does sodium sulfate crystallize? Implications for the decay and testing of building materials. Cement and Concrete Research, 30**,** 1527-1534.

ROGGENDORF, H., BÖSCHEL, D. & TREMPLER, J. 2001. Structural evolution of sodium silicate solutions dried to amorphous solids. Journal of Non-Crystalline Solids, 293-295**,** 752-757.

ROGGENDORF, H., FISCHER, M., ROTH, R. & GODEHARDT, R. 2015. Influence of Temperature and Water Vapour Pressure on Drying Kinetics and Colloidal Microstructure of Dried Sodium Water Glass. Advances in Chemical Engineering and Science, Vol.05No.01**,** 11.

SEARS, W. M. 2001. Isosteric Heat of Adsorption of Water Vapor on Bismuth Iron Molybdate Measured by the Method of Constant Surface Conductance. Langmuir, 17**,** 5237-5244.

SHRESTHA, A. K., HOWES, T., ADHIKARI, B. P. & BHANDARI, B. R. 2007. Water sorption and glass transition properties of spray dried lactose hydrolysed skim milk powder. LWT - Food Science and Technology, 40**,** 1593-1600.

SMITH, S. E. 1947. The Sorption of Water Vapor by High Polymers. Journal of the American Chemical Society, 69**,** 646-651.

SMULDERS, E. & RÄHSE, W. 2000. Laundry Detergents, 3. Production, Testing and Economic Aspects. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA.

TIMMERMANN, E. O., CHIRIFE, J. & IGLESIAS, H. A. 2001. Water sorption isotherms of foods and foodstuffs: BET or GAB parameters? Journal of Food Engineering, 48**,** 19-31.

VEGA-GÁLVEZ, A., PALACIOS, M., LEMUS-MONDACA, R. & PASSARO, C. 2008. Moisture sorption isotherms and isosteric heat determination in Chilean papaya (Vasconcellea pubescens). Química Nova, 31**,** 1417-1421.

WARRING, S. L., BEATTIE, D. A. & MCQUILLAN, A. J. 2016. Surficial Siloxane-to-Silanol Interconversion during Room-Temperature Hydration/Dehydration of Amorphous Silica Films Observed by ATR-IR and TIR-Raman Spectroscopy. Langmuir, 32**,** 1568-1576.

YANG, X., ROONASI, P. & HOLMGREN, A. 2008. A study of sodium silicate in aqueous solution and sorbed by synthetic magnetite using in situ ATR-FTIR spectroscopy. Journal of Colloid and Interface Science, 328**,** 41-47.

ZAFAR, U., VIVACQUA, V., CALVERT, G., GHADIRI, M. & CLEAVER, J. A. S. 2017. A review of bulk powder caking. Powder Technology, 313**,** 389-401.

ZETTLEMOYER, A. C. 1968. Hydrophobic surfaces. Journal of Colloid and Interface Science, 28**,** 343-369.