Surface energy analysis (SEA) and rheology of powdered milk dairy products

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Abstract

Results of inverse gas chromatography adsorption/desorption experiments **using** selected probes on skimmed milk, whey and demineralised whey powder materials are presented. T**he** dispersive component of surface energy **was found to be dominant, indicating** low polarity character. Surface energy profiles **of demineralised whey and skimmed milk showed a characteristic** steep exponential decrease **from** approximately 170 mJ/m^2 to 60 **mJ/m^2 and 140** mJ/m^2 to 45 **mJ/m^2, respectively, whereas whey** powder exhibited **a constant (non-**

exponential) surface energy at approximately 45 mJ/m^2**. **The** dispersive surface energy **of demineralised whey and skimmed milk powder showed a broad distribution** ranging **from 40 mJ/m^2 t**o 120 mJ/m^2 **and 175 mJ/m^2, respectively**. **In contrast, the dispersive** surface energy distribution for whey **was very narrow, ranging** from **only** 42.8 mJ/m^2 to 45 mJ/m^2. **The determined** yield locus and Mohr´s circles **indicated** that demineralised whey **exhibited** free flowing powder characteristics, **whereas skimmed** milk and whey **exhibited** cohesive **powder** flow behaviour.

1. Introduction

Powdered milk is a major precursor for many food products. Its value has been enhanced **in recent years** by **the** relatively large amount of research **conducted to** support the development and commercialisation of dairy-based products with an increasing variety of **flavours, textures and shelf-lives** (Osorio, Monjes, Pinto, Ramirez, Simpson & Vega, 2014, Saffari & Langrish, 2014, Crowley, Gazi, Kelly, Huppertz & O´Mahony, 2014, Bolenz, Romisch & Wenker, 2014, Romeih, Abdel-Hamid & Awad, 2014, Martinez-Padilla, Garcia-Mena, Casas-Alencaster & Sosa-Herrera, 2014, Zhou, Liu, Chen, Chen & Labuza, 2014, Nilufer-Erdil, Serventi, Boyacioglu & Vodovotz, 2014). The colloidal nature of cow's milk is a crucial structural feature that affects **its** final product quality as well **as processing** behaviour (Fox & McSweeney, 1998, Gaucheron, Famelart, Mariette, Raulot, Michel & Legraet, 1997). It can be divided into two compositional **domains: the** casein micelle and the milk fat globule. These colloidal domains comprise nearly 80% of the approximate 12.7 g total solids per 100 g [1] in milk. **Therefore, investigation of** the structure and interactions of these colloidal particles **continues** to be **an** important **area of** milk research. Dried milk powders (e.g. whole, skimmed or retentate), dried buttermilk, and other dairy **powders (e.g.**

cheese whey powder (WP), whey protein concentrates (WPC), whey protein isolates (WPI), caseinates and **lactose)** are products made from milk **or** whey where practically all the water is removed, i.e. to < 4 g per 100 g [1] of water (Tamime, Robinson & Michel, 2007). These dried products have a very long shelf-life, they can be stored at ambient **temperature and** can be **readily** exported to countries that have a shortfall in milk production. After rehydrating milk powders, the reconstituted products may be similar to fresh milk (whole or **skimmed),** **whereas th**e **remaining** dairy powders have different applications in the dairy, food and pharmaceutical industries.

In this **study, the** term skimmed milk powder defines a dairy product obtained by removing the water from skimmed milk, with a maximum fat content of 11%, a maximum moisture content of 5% and protein content not less than 31.4% of non-fatty dry extract. Skimmed milk powder is by far the most important of **all milk powders** and the most widely used form of milk protein in the food industry. Skimmed milk production firstly involves its evaporation to a concentration of about 50% of total solids. Thereafter, the evaporated skimmed milk can be dried in any of the various types of spray drier available. Two types of powder **can** therefore **be distinguished: roller-dried powder** and spray-dried powder. **Moreover, skimmed** milk powder **represents a** significant source of protein (35%) and carbohydrate (lactose, 50%) and can be used as a food ingredient, for reconstitution and as an animal feed. **As a** food **ingredient, it performs** three **main** functions: (i) contributes to a desirable dairy flavour, (ii) affects food **texture, and** (iii) enhances the development of desirable colour and flavour compounds (Tamime, Robinson & Michel, 2007, **Ranken, Kill & Baker**, 1997).

Whey is a general term describing the translucent liquid part of milk that remains following the process (isoelectric or rennet coagulation) of cheese manufacturing (Hoffman & Falvo, 2004, Manso & Lopez-Fandino, 2004). Whey prepared by isoelectric precipitation

or rennet coagulation is called acid whey (dry whey with **0.35%** or higher titratable acidity on a reconstituted basis) **or** sweet (rennet) whey (dry whey not over **0.16%** titratable acidity on a reconstituted basis), respectively. Whey contains nearly 50% of the total solids found in whole milk, including essentially **all the** lactose and whey proteins (Fundamentals of cheese, 15). The content of total essential amino acids and branched-chain amino acids is **high** in whey protein than in most **other** dietary proteins (Helaine, Valdemiro, Dias, Borges, & Tanikawa, 2001). Whey and whey products are commonly used in animal feed, dietetic foods (infant food), bread, confectionery, candies and beverages. The composition of whey products varies depending on several factors, including the source of the milk, production method, type of cheese and manufacturer's specifications. Whey and whey components contain a number of valuable minerals **such as calcium, magnesium, manganese, phosphorus, copper, iron, zinc, sodium and potassium.**

The main component of whey is lactose (70-**75%), while** the major component of whey solids **are** whey proteins **(10-13%), mainly** lactalbumin and globulins. Practically all the mineral elements found in whey are essential for nutrition. Condensed whey, dried whey, dried modified whey, whey protein concentrate and isolates, as well as lactose (**crystallised** and dried) are the **most** often **reported** whey products. Whey can also be processed into a number of valuable **products, as** well as some that are considered waste products. **Examples of** whey types include reduced lactose whey, demineralised whey, acid **whey, sweet** whey and whey protein concentrate. Whey protein is a complete, high quality protein with a rich amino acid profile. Whey proteins refer to a group of individual proteins or fractions that separate out **from casein** during cheese-making. These fractions are **usually** purified to different **concentrations depending** on the end composition desired **and vary** in their content of protein, lactose, carbohydrates, **immunoglobulins**, minerals and fat (Tamime et al., 2007).

Demineralised whey powder is produced from whey by selective removal of most of the minerals.

The properties of surfaces and interfaces **characterised** by surface or interfacial tension and surface energy **have attracted increasing attention** in recent years. **Such** properties **affect** many phenomena **associated with** adhesion, wetting, spreading and **wicking, which play an important role in everyday** life, natural processes **and numerous** industrial applications. These processes **are important in** various **materials, for** instance biopolymers (Lapčík, Lapčík, De Smedt, Demeester & Chabreček, 1998, Collins, 2014), synthetic polymers, wood (Lapčík, Lapčík, Kubíček, Lapčíková, Zbořil & Nevěčná, 2014), paper, stone, soils (Lapčík, Lapčíková, Krásný, Kupská, Greenwood & Waters, 2012), cereals and **textiles**, **encompassing** all possible types of surface **from** polar **to non-polar (Gamble et al., 2012). However, the surfaces of such materials are usually** rough **rather** than smooth **and may** even **be porous, making their** surface **characterisation challenging**. Despite the **difficulties, several methods are applicable for characterising** powder and fibrous materials (Gajdošíková, Lapčíková & Lapčík, 2011), such as **the** capillary rise method, thin-layer wicking **and Wilhelmy** plate method. **In particular, a surfa**ce energy analysis technique based on inverse gas chromatography has been found to be very effective **for characterising** wetting phenomena on powders and fibres (Mohammadi-Jam & Waters, 2014, Lapčík, Otyepková, Lapčíková & Otyepka, 2013, Lazar, P. et al., 2014)

2. Methods

2.1.*Theoretical background*

The surface free energy of a solid can be described **by** the sum **of dispersive** and specific contributions. Dispersive (apolar) interactions, also known as Lifshitz-van der Waals

interactions, consist of London **interactions originating** from electron density changes but may **also** include both Keesom and Debye interactions (Gajdošíková et al, 2011). Other forces influencing the magnitude of surface energy are Lewis acid-base **interactions, which** are generated between **an** electron acceptor (acid) and electron donor (base). They **occur in compounds** containing hydrogen bonds - strong secondary bonds between atoms of hydrogen and a highly electronegative element such as F, O, N and Cl or other compounds **that can interact with** Lewis acids and bases. Details of the **most** widely accepted theoretical treatment **for estimation** of solid surface free **energies from** selective wetting measurements are **given** in our **recent** review article (Gajdošíková et al., 2011).

The dispersive component of the surface energy γ_S^D can be calculated from the retention **times** obtained from inverse gas chromatography measurements of a series of n-alkane probes injected at infinite dilution (concentration within the **Henry region** of the adsorption **isotherm)** (Belgacem, Gandini & Pefferkorn, 1999). For evaluation of these d**ependencies, two approaches have been used, as described by Equations (1)** (Schultz, Lavielle & **Martin, 1987) and (2) (Dorris & Gray, 1980)**:

$$RT \ln V_N \quad a\left(\gamma_L^D\right)^{1/2} 2N_A \left(\gamma_S^D\right)^{1/2} + C \qquad (1)$$

where R is the universal gas constant, N_A is Avogadro´s number, γ_L^D is the dispersive component of surface free energy of the liquid probe, γ_S^D is the dispersive component of the surface free energy of the solid, V_N is the retention volume and C is a constant, and

$$\gamma_S^D = \frac{\left[RT \ln\left(V_{N(C_{n+1}H_{2n+4})} / V_{N(C_nH_{2n+2})}\right)\right]}{4 N_A^2 a_{CH_2}^2 \gamma_{CH_2}} \qquad (2)$$

where a_{CH_2} is the surface area of a CH_2 unit (~0.6 nm^2) and γ_{CH_2} is its free energy (approximately **35.6 mJ**/m^2).

2.2.Experimental

Inverse gas chromatography was conducted using a **surface energy analyser** (SEA) (Surface Measurement Systems, UK). Samples were placed in 4 mm (internal diameter) **columns to** give a total surface area of approximately 0.5 m^2. The following eluent vapours were passed through the column: **nonane, octane, hexane and heptane.** All reagents were obtained from Sigma Aldrich **(USA) and** were of analytical grade. The injection of vapours was controlled **in order** to pass a set volume of eluent through the column to give pre-determined fractional coverage of the sample in the column. **Using this method, the** retention time of the vapours **through** the particles gives an indication of the surface properties of the material, including the surface energy. By gradually increasing the amount of vapour injected, it is possible to build up a surface heterogeneity plot.

Specific surface area measurements were made using a Micromeritics TriStar 3000 surface area and porosity analyser (USA) **combined with** the nitrogen BET technique.

Thermogravimetry (TG) and differential thermal analysis (DTA) experiments were performed on **a** Netzsch STA 449 C Jupiter **simultaneous thermal analyser** (Netzsch, Germany). **Samples were weighted to aluminium pans and measured. Each measurement was repeated 3 ×. Conditions of measurement: Heat flow 10 °C/min and dynamic atmosphere of nitrogen (N_2 50 ml/min), range of temperature measurement was from 35 °C to 300 °C.** Throughout the experiment, the sample temperature and weight-heat flow changes were continuously monitored.

Scanning electron microscopy (SEM) images were captured on a Hitachi 6600 FEG microscope (Japan) operating in the secondary electron mode and using an accelerating voltage of 1 kV.

Powder rheology measurements were **acquired** on **a** FT4 Powder rheometer (Freeman Technology, UK). All experiments were performed **under the** laboratory ambient temperature **of 23 °C** and air relative humidity **or 43%**.

The moisture content of the powdered samples was as follows: skimmed **milk 3.7 wt.%, whey 2.0 wt.% and demineralised whey 2.4 wt.% (Moravia** Lacto, Czech Republic). **The powdered** milk samples were **stored under** dry conditions in desiccators (at **an** ambient temperature of **23 °C**) for 2 weeks prior to **the** experiments.

3. Results and discussion

A typical SEM **image for the powdered** milk materials under study **is presented** in Figure 1, **showing that the particles had a spherical shape**. **The** individual **particle** diameter of **the powdered** skimmed milk **sample** was found to be 15.1 μm, **compared to** 80.0 μm and **88.0 μm** for **the powdered whey and** demineralised whey **samples, respectively**. All samples were characterised by thermogravimetric and DSC measurements **over a** temperature range of +35 to **+300 °C** to evaluate moisture content and thermal stability. **The observed** TG and DSC temperature dependencies are shown in Figures 2 and 3. **It can be seen from these scans** (Figure **2) that the powdered** skimmed milk **and whey** samples **exhibited** three step weight loss patterns. **The first** TG weight loss step **occurred from** 35 to 150 °C **and corresponded to a** weight loss of 4.6 **wt.%** for **the** skimmed milk **and 3.1 wt.%** for **the** whey **sample, representing** moisture release of physically retained water molecules by casein or whey proteins. **As** all samples were conditioned **at the same**

198 **humidity** prior to the experiments**, the** linear zero moisture behaviour in the case of
199 demineralised whey **is likely due** to its low **mineral** content in comparison to the other two
200 materials (**skimmed** milk and whey). **The second** TG degradation step **occurring over the**
201 **temperature range 150 to 248 °C** was **attributed** to the thermo-destruction of casein and
202 whey **proteins** (Mocanu, Moldoveanu, Odochian, Paius, Apostolescu & Neculau, 2012). The
203 thermal stability of **the** studied milk dairy products **can be described** by the initial
204 temperature of thermal degradation (2. **region), which wa**s 150 °C. **At this temperature, the**
205 weight loss for all samples was approximately 25 to 32 **wt.%**. The third degradation step was
206 initiated at 248 °C for **skimmed** milk and whey and at 236 °C for demineralised whey. **The**
207 residual masses were 62.9 **wt.%** for **powdered** skimmed milk, 56.9 **wt.%** for **powdered**
208 whey and 60.9 **wt.%** for demineralised **powdered** whey. As evident from Figure 2, the
209 weight lost **pattern** of skimmed milk **during the third degradation step** was inverted
210 (**became** the lowest) in comparison to the first and second degradation regions. We ascribed
211 this behaviour to the higher residual mass of lactose in comparison to the milk fats. **The**
212 **thermal** characteristics of milk powder are significantly affected by fat and lactose content
213 (**Rahman, Al-Hakmani, Al-Alawi & Al-Marhubi**, 2012). However, the tangent of the
214 sample weight at 200 °C **was** higher for the whey products in comparison to the skimmed
215 milk, **indicating that milk fats have a** lower degradation **resistivity in** comparison **to lactose**
216 **in** skimmed milk. **As milk** is a multi-component **mixture, it** would be difficult to **attribute**
217 its thermal **behaviour to particular** components **as** complex individual as well as synergistic
218 effects **need to be taken into account**.

219 Based on **the** DSC data (Figure **3), the** first exothermic peak at approximately 170 °C can
220 be **assigned to lactose crystallisation** and **the** second **huge peak to** the non-enzymatic
221 browning advanced Maillard reaction between proteins and **lactose, which is** initiated at **a**
222 temperature of 220 °C (Vuataz, Meunier & Andrieux, 2010, **Rahman et al.**, 2012)). The last

third degradation region **is likely to correspond to oxidation** of milk fats **and lactose** degradation (Raemy, Hurrell & Löliger, 1983).

The specific surface areas of the studied samples were identical for all materials under **study. Although the** obtained value of 0.6 m^2/g was relatively low, **it was** in excellent agreement **with data** available in **previous** literature (Berlin, Howard & Pallansch, 1964).

Surface energy profiles and their components of **the** studied milk products powders based on **the** inverse gas chromatography **measurements are** shown in Figure 4. T**he** surface energy profiles of **skimmed** milk and demineralised whey **clearly differed from that of whey. The** first two materials (**skimmed** milk and demineralised whey) **showed a characteristic steep** exponential decrease **in** surface energy **from approximately 170 mJ/m^2 to 60 mJ/m^2 and 140 mJ/m^2 to 45 mJ/m^2, respectively, between a coverage of 0% to approximately 2% (skimmed milk)** and **5% (demineralised whey), reflecting the** relatively **low** number of high energy sites **on** the surface of **these** materials. **In contrast, for a surface coverage of 5%** up to **20%, the** surface energy **profiles plateaued** at 45 mJ/m^2 **(skimmed milk)** and 60 mJ/m^2 **(demineralised whey)**. As clearly visible from Figure **4, the** dispersive component **dominated the** surface **energy, thus** reflecting **the** non-polar nature of the surface active sites in **both skimmed** milk and demineralised **whey powders**. The same hydrophobic character was **also found for** the third material under **study, i.e.** whey. However, in contrary to the above mentioned skim milk and demineralised whey materials, a surface energy coverage dependence exhibited stable non-exponential (linear) pattern with the magnitude of the observed surface energy approximately 45 mJ/m^2, thus reflecting high homogeneity of acting energetic surface sites**. For all three tested materials, **the** polar component of the surface energy was negligible in comparison to the dispersive component. **For both the whey and demineralised whey powders, its value** was **independent of coverage at approximately 5 mJ/m^2, thus suggesting a** high uniformity of surface structural

components responsible for this kind of behaviour. **However, the polar component of skimmed milk showed an** exponential **decay, ranging from 30 mJ/m^2 for a coverage of 0% coverage up to 5 mJ/m^2 for coverages of 3% up to 20%, which indicates a** broader distribution **of energetic** sites responsible for such behaviour due to the **increased** complexity of the main **milk constituents. It was also evident that** the polar surface active sites **were** of relatively low energy in all **the** studied powders, **providing further evidence of** their low polarity character. Such behaviour can be attributed to the presence **of milk** fat components at the surface interface (Jensen, Ferris & Lammi-Keefe, 1991).

The measured dispersive surface energy **(Figure 5), showed a characteristically** broad **distribution for both skimmed** milk **(40 mJ/m^2 to 175 mJ/m^2) and** demineralised whey **(40 mJ/m^2 to 120 mJ/m^2),** thus reflecting **the large** number of structural elements responsible for this behaviour. **However**, the dispersive surface energy distribution **of** whey **was** very **narrow (see** Figure 5 - **inset), ranging** from **only** 42.8 mJ/m^2 to 45 **mJ/m^2, with** relatively the same area increment occupancy of 2% as for demineralised whey. In **contrast, the area** increment occupancy for **skimmed** milk was 3 times **higher, reaching 6%**. **This** SEA pattern behaviour **may be due to** the **greater concentration** of inorganic salts in whey in comparison **to milk** and demineralised whey, which might successfully screen the most energetic **surface sites** (at the lowest surface coverage) by binding surrounding water molecules remaining as residual moisture content.

The macroscopic powder flow behaviour **was also investigated by determining the** yield locus and flow function dependencies at different stress levels for **the** studied **samples.** Results of the powder rheological measurements are shown in Figure **6, which presents** the yield locus and Mohr´s circles of **the** tested powder milk dairy products. **The results show** that demineralised whey exhibited free flowing powder **characteristics, as** indicated by **the** observed friction coefficient **of** 11.7. **In contrast, the friction** coefficients of **the skimmed**

milk and whey powders **ranged from 3.3** to 4.5, **which are** values characteristic for cohesive powders behaviour. **The** unconfined yield strengths **ranged** from 1.37 kPa (demineralised whey) to 4.48 kPa (**skimmed** milk) and 4.69 kPa (whey). The unconfined yield **strength.** σ_c, **can be obtained** from the stress circle tangential to the yield locus **and passing** through the origin (minor principal stress $\sigma_2 = 0$). Because the largest Mohr stress circle **indicated** a state of steady-state flow, the internal friction angle can be regarded as a measure of the internal friction at steady-state flow (**Lapčík et** al., 2012). For **the** studied **samples, the** angle of internal friction **ranged** from **26.5°** for whey up to 36.4 and **40.4°** for demineralised whey and **skimmed milk, respectively**. **The relatively** low value of the angle of internal friction observed for whey **is consistent with** the observed friction factor of 3.3 characteristic for cohesive powders. The relevant consolidation **stress,** σ_1, **can be obtained from** the major principal stress of the Mohr stress **circle tangential** to the yield locus and **intersecting** the point of steady flow. **The major principle** stress for all **the** tested powders was about 16 to 18 kPa. The latter stress circle represents the stresses in the sample at the end of the consolidation procedure (stress at steady state flow). It corresponds to the stress circle at the end of consolidation **in** the uniaxial compression test.

In addition to the above shear **testing, powder** aeration tests were performed, allowing consideration of the fluidisation capability of the studied powders. **The** aeration ratio **was found to range** from 32.4 for whey to 12.7 (demineralised whey) and 8.98 for **skimmed milk, whereas the** aerated **energy varied** from 4.8 mJ (whey) to 10.1 mJ (demineralised whey) and 14.4 mJ (**skimmed** milk). **The aeration** data **indicated** that **whey showed the lowest cohesion of all the samples tested, i.e.** highest aeration **ratio** in combination with the lowest aerated energy. All **the** tested powders **exhibited** complete fluidisation **at 4** mm/s air **velocity, with** basic flowability energy ranging from 127 mJ (**skimmed** milk and demineralised whey) to 157 mJ for whey.

Conclusions

The results showed that **the** surface energy **of the studied milk product powders was dominated by the** dispersive **component, indicating their** low polarity **character.** Surface energy profiles of **skimmed** milk and demineralised whey **showed a characteristic steep** exponential decrease of the surface energy from approximately 170 mJ/m^2 to 60 mJ/m^2 (demineralised whey) and of 140 mJ/m^2 to 45 mJ/m^2 (**skimmed milk), reflecting the** relatively **small** number of high energy sites located at the surface of the studied materials. **From 5%** up to **20%** surface **coverage, the** surface energy **profiles reached a plateau** at 45 mJ/m^2 for **skimmed** milk and 60 mJ/m^2 for demineralised **whey. Whey** powder surface energy coverage dependence exhibited stable non-exponential (linear) pattern with the magnitude of the observed surface energy approximately 45 mJ/m^2, thus reflecting high homogeneity of acting energetic surface sites. For all three tested materials, **the** polar component of the surface energy was negligible in comparison to the dispersive component. It was **found that** the polar surface active sites **were** of relatively low energy in all **the** studied powders, **confirming** their low polarity character. **The observed** dispersive surface energy **showed characteristically broad** distributions for **skimmed** milk and demineralised whey ranging from 40 mJ/m^2 to **175** mJ/m^2 and **120** mJ/m^2**, respectively**, thus reflecting **the large** number of structural elements responsible for this behaviour. **In contrast, the dispersive** surface energy distribution **of** whey **was very narrow, ranging** from **only** 42.8 mJ/m^2 to 45 mJ/m^2. **The macroscopic** powder flow behaviour of **the** studied materials **was analysed by examining the** yield locus and flow function dependencies at different stress levels. **The determined** yield locus and Mohr´s circles **indicated** that demineralised whey exhibited free flowing powder characteristics (observed friction coefficient 11.7). However, **the friction**

coefficients of **the skimmed** milk and whey powders were in the **range 3.3** to 4.5, **which are** values characteristic for cohesive **powders**. All tested powders **allowed** complete fluidisation **at 4 mm**/s air **velocity, with** basic flowability **energies** ranging from 127 mJ (**skimmed** milk and demineralised whey) to 157 mJ for whey.

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421

422 **Figures captions**

423

424 Figure 1. SEM images of studied powders: A) skimmed milk, B) **whey, and** C) demineralised
425 whey.

426 Figure 2. Thermogravimetric **analysis of** studied powder milk products: full line **– powdered**
427 skimmed milk, **dotted** line **powdered** whey, short dashed line **–** demineralised **powdered**
428 whey.

429 Figure 3. DSC pattern of studied powder milk products: full line **– powdered** skimmed milk,
430 dot line **– powdered** whey, short dashed line **–** demineralised **powdered** whey.

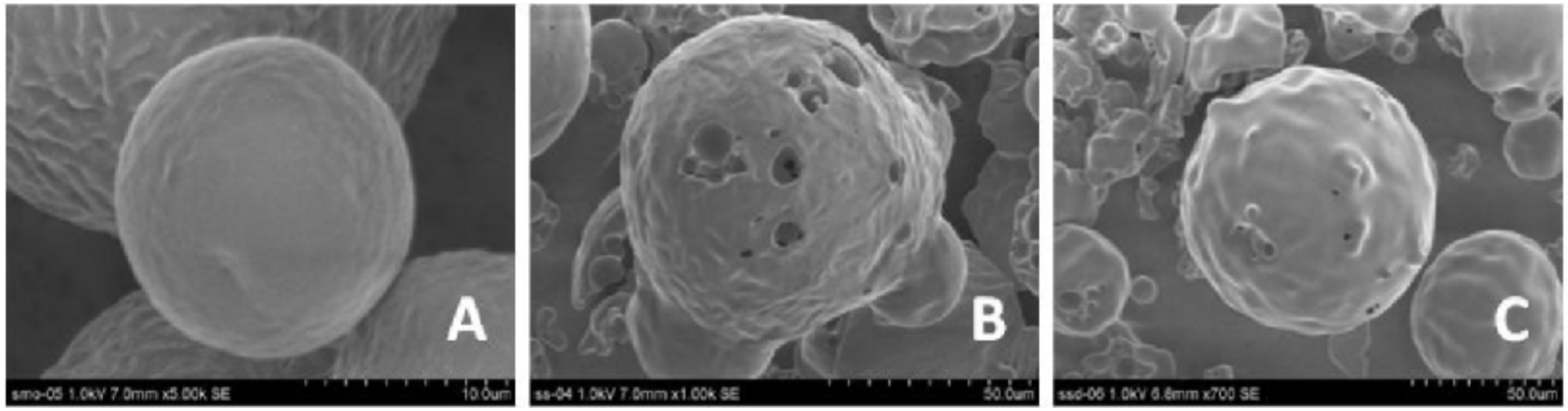
431 Figure 4. Surface energy and its **component** profiles **of powdered** milk products: circle **–**
432 **powdered** whey, **triangle –** demineralised **powdered** whey, diamond – **powdered skimmed**
433 **milk, black**– dispersive component of the surface energy (SFE), **red** polar component of
434 **SFE, green** colour **–** total SFE.

435 Figure 5. Dispersive surface energy distribution **of** demineralised **powdered** whey (circle),
436 **powdered skimmed** milk (triangle down) and **powdered** whey (triangle up). **Inset:**
437 **expanded** dispersive surface energy distribution **of** whey sample.

438 Figure 6. Yield locus and Mohr´s circles of studied **powdered** milk products: full square –
439 **skimmed** milk, full triangle up whey, empty circle demineralised whey (measured at 24
440 °C).

441

Figure(s)



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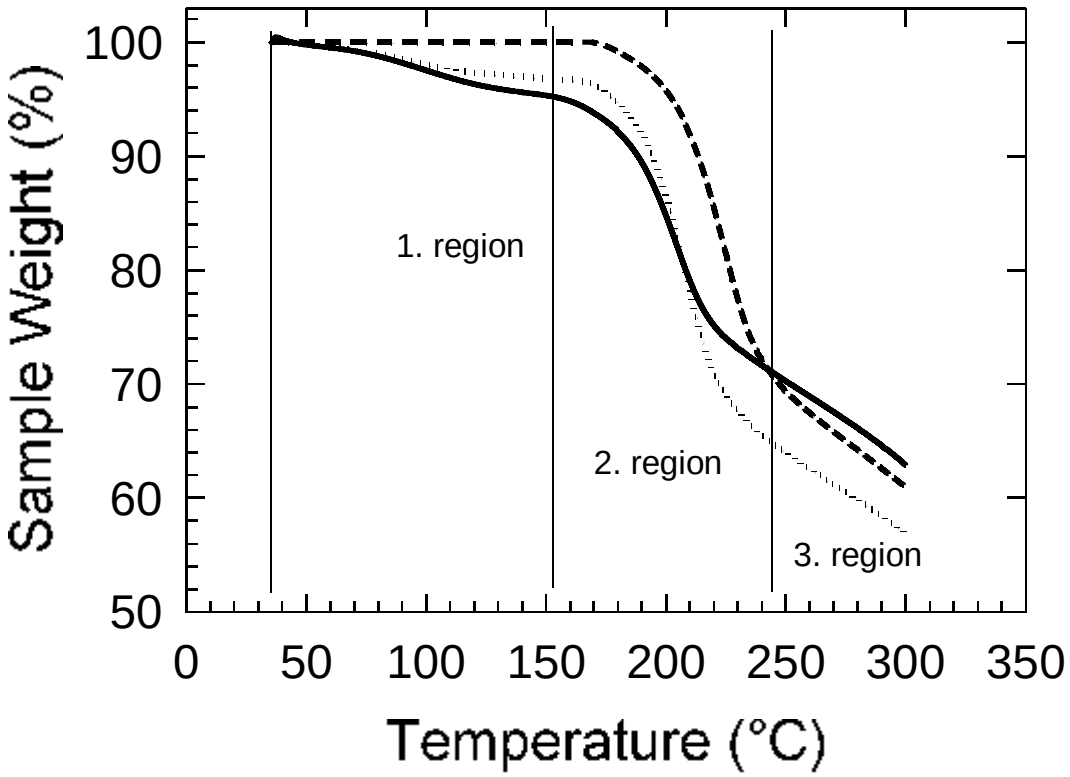

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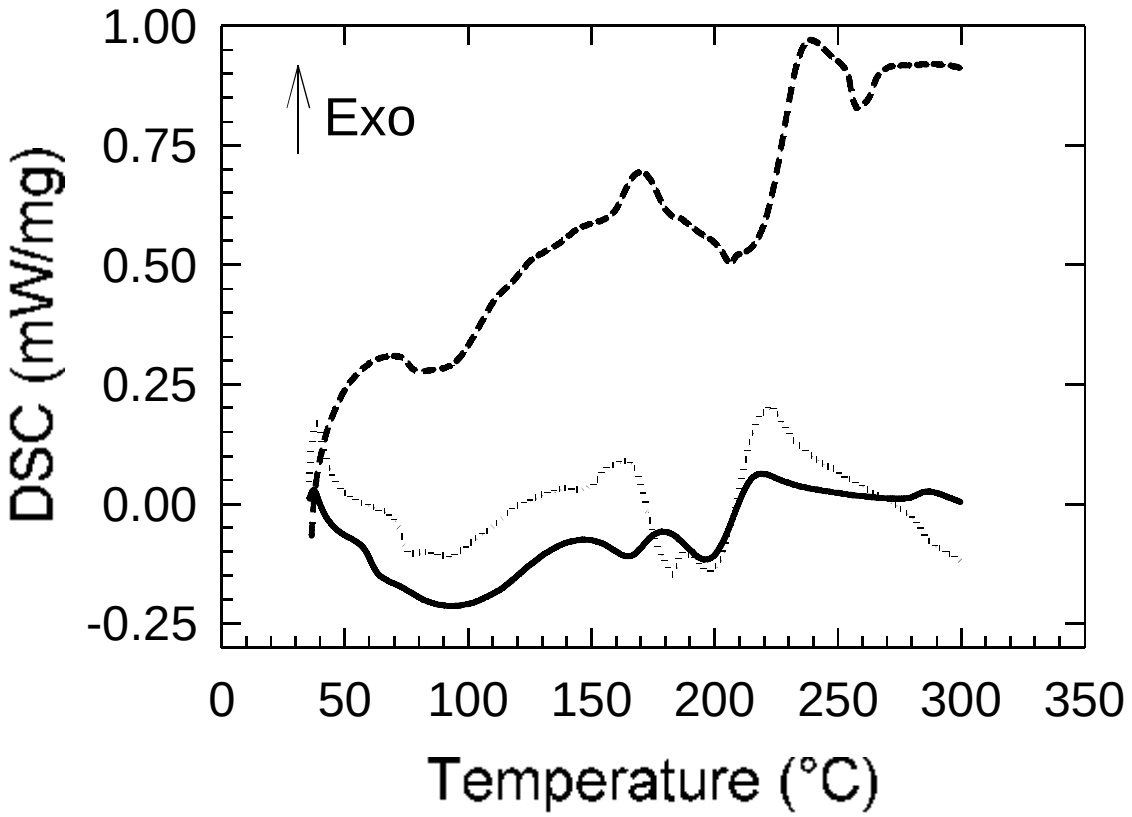

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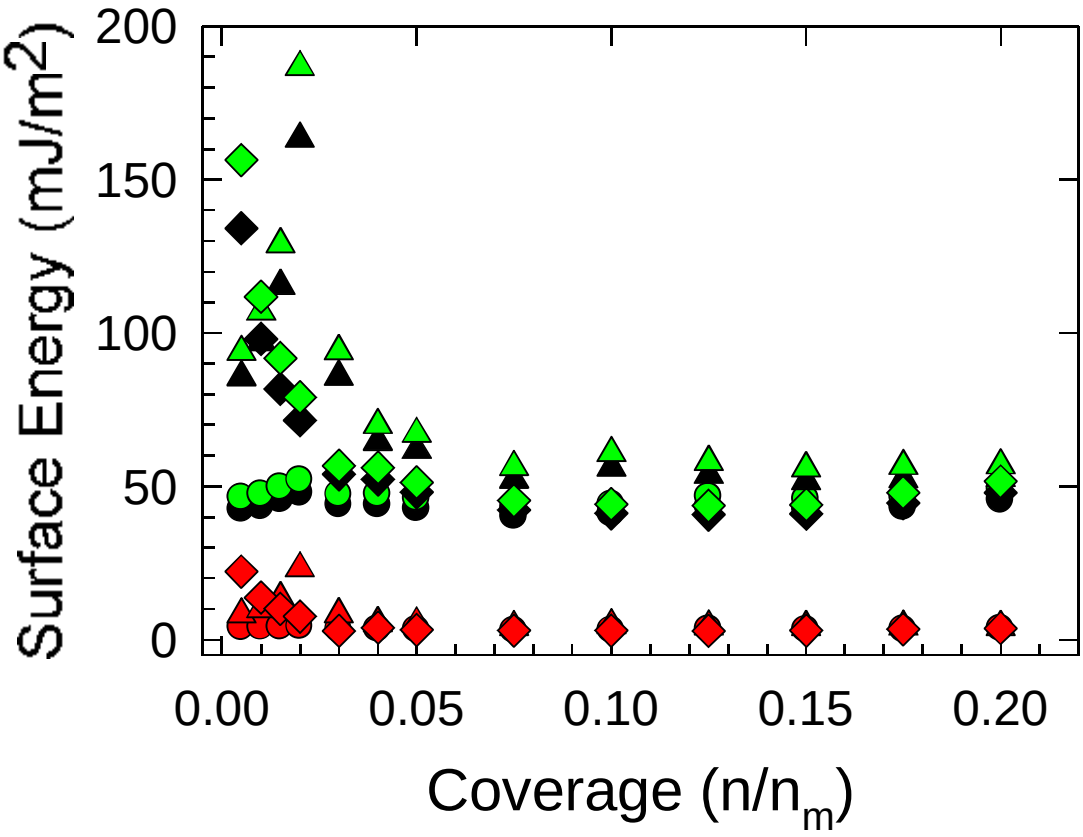

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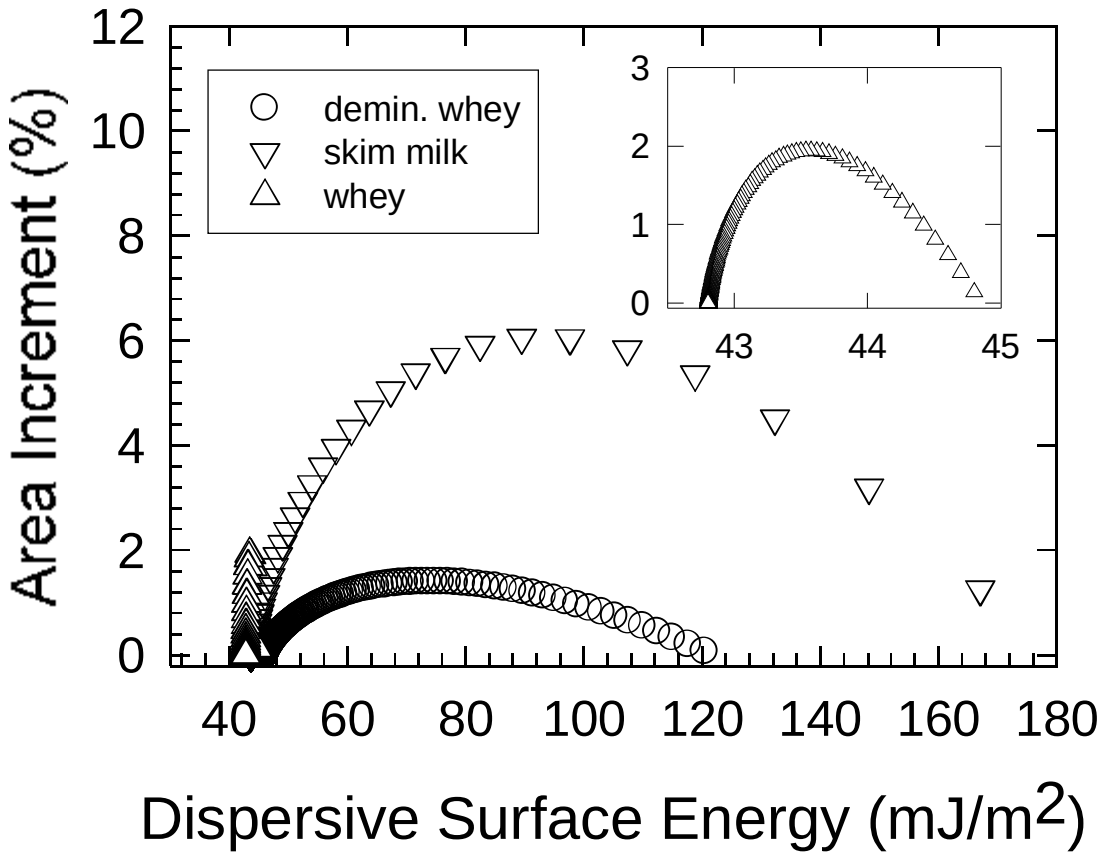

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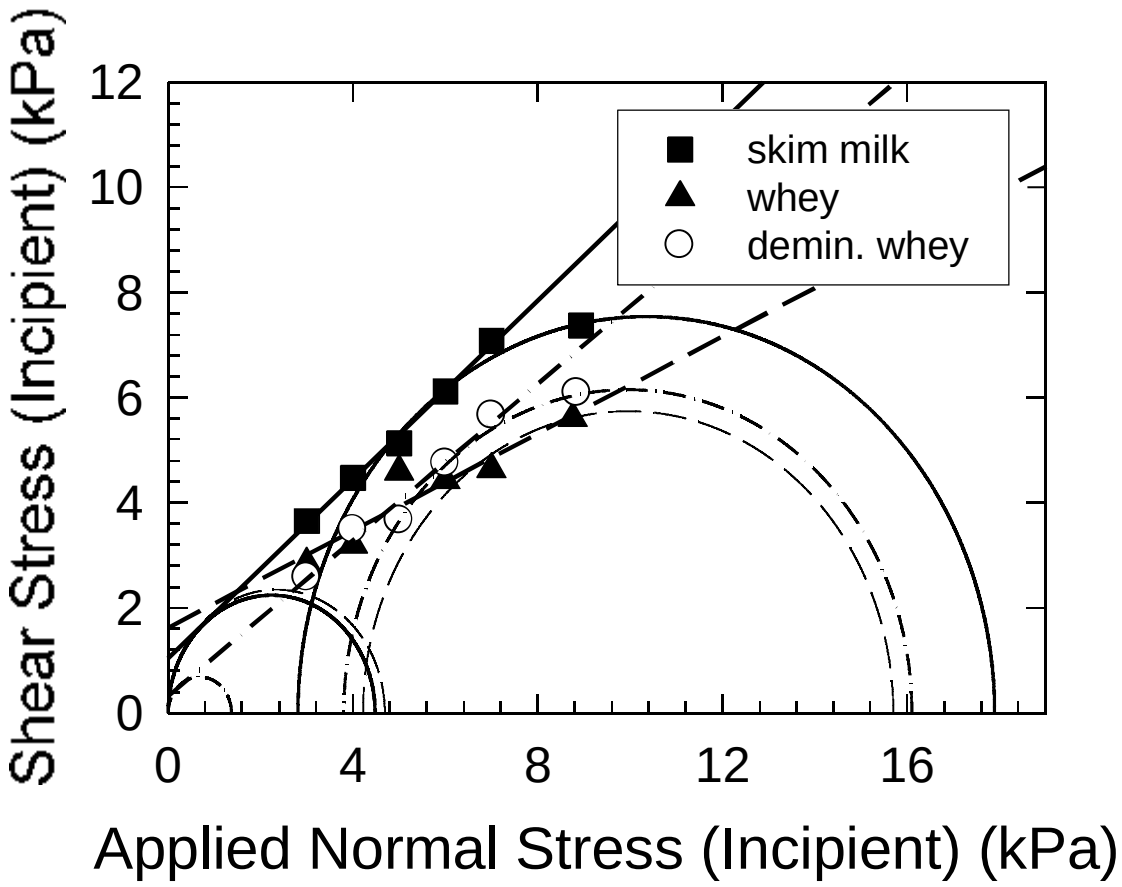

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