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WATER SORPTION ISOTHERMS OF SKIMMED MILK POWDER WITHIN THE TEMPERATURE RANGE OF 5–20 °C

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Abstract

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Moisture sorption isotherms (MSI's) of skimmed milk powder in the temperature range of 5–20 °C were determined using manometric method. MSI's, which show the water content versus water activity (Aw) at a constant temperature, are used to describe relationships between water content and equilibrium state relative vapour pressure (RVP). The equilibrium moisture content (EMC) of skimmed milk powder samples is growing with an increase of Aw at a constant temperature both for water adsorption and desorption. Isotherms were found to be type II of Brunauer-Emmett-Teller classification. It is the type most common for foods. The shape of created isotherms was sigmoid. Structural modifications of crystals were observed during adsorption in the microscope, too. Critical value of EMC of tested samples corresponding to the Aw equal to 0.6 for adsorption was 6.50% MC (w.b.) at temperature 5 °C, 9.15% MC (w.b.) at temperature 10 °C, and 7.71% MC (w.b.) at temperature 20 °C. These values determine optimal conditions for storage from the point of view microorganisms grow, Aw<0.6.

skimmed milk powder, water activity, sorption curve

Skimmed milk powder is defined as a product obtained by removing water from milk, with a maximum fat content of 11 g/100 g, a maximum moisture content of 5 g/100 g, and a protein content not less than 31.4 g/100 g of non-fatty dry extract (Tamime, 2009).

Aw is a useful value of water availability for growth of various microorganisms and physicochemical stability of low-moisture dairy products. Aw is equal to the equilibrium RVP of water in the surrounding atmosphere. Equation (1) defines that Aw is a ratio of vapour pressure in a solution to that of pure water at the same temperature. Therefore, the equilibrium state Aw is related to equilibrium relative air humidity (ERH) corresponding to the equilibrium RVP of the surrounding atmosphere (Roos, 2002).

$$Aw = \frac{p}{p''}. \quad (1)$$

Critical Aw also exists below which no microorganisms can grow. For most foods, this is in the 0.6–0.7 Aw range. Thus, with knowledge of the MSI, one can predict the maximum moisture that the food can be allowed to gain during storage. Of course, higher Aw's can be allowed if other factors such as pH, salt, antimicrobial agents, and temperature are taken into consideration (Labuza, 1984). Understanding the moisture relationships of a powder allows the moisture content that the powder should be dried to, in order to prevent sticking problems during storage, to be determined (Foster *et al.*, 2005).

Typical sorption isotherms of dairy powders are often sigmoid curves, which exhibit hysteresis for water adsorption and desorption. These powders may contain amorphous lactose and milk and whey proteins. Amorphous lactose in dairy powders is unstable and it tends to crystallize during storage above a critical water content or Aw. Such crystallization is observed by a time-dependent loss of sorbed water and a break in the sorption isotherm. The water sorption properties of the hydrophylic, crystalline lactose differ significantly from the water sorption properties of amorphous lactose. Therefore, crystallinity and crystalline forms of lactose may greatly affect on sorption properties and one of the most significant differences between dairy powders with glassy or precrystallized lactose is their water sorption behaviour. Amorphous lactose is very hygroscopic and it may sorb high amounts of water at low relative humidities (Roos, 2002).

Characterization of surface properties of milk powders is important as these properties determine the behaviour of powders during their storage, handling, transportation, and processing. Stickiness and cake formation in food powders have been recognized as significant problems (Özkan *et al.*, 2002).

Milk powders produced by spray drying are predominantly amorphous and the glass transition temperature is one of the distinctive properties of an amorphous material. Below the glass transition temperature, an amorphous material behaves as a glass with a very high viscosity ($>10^{12}$ Pa s) due to the limited molecular movement at low temperatures (Özkan *et al.*, 2002).

Glass transition can be described as a change that occurs in amorphous materials from a high viscosity, „frozen“ glassy state to a lower viscosity, rubbery state. The material in the glassy state behaves like a brittle solid but without crystalline structure and only short ranges of order. The glass transition concepts that have long been understood in the field of polymer science can also be applied to food polymers (Carter and Schmidt, 2012).

The objective of this study was to determine the effect of near ambient air temperature on adsorption and desorption isotherms of skimmed milk powder within 5–20 °C, to determine equations of sorption curves, and to observe glass transition samples tested.

MATERIAL AND METHODS

Skimmed milk powder was commercial produced and purchased in a market. The initial dry basis mass was about 95% and content of fat was declared minimal 5% on the label. The commercial package was vacuum-packaged after each sampling to measure and stored at recommended storage conditions, it means below temperature 24 °C and relative air humidity up to 70%.

The manometric method was used (Iglesias and Chirife, 1982) for sorption tests in the temperature regime 5, 10 and 20 °C. Sorption tests were performed using the Aw-meter Novasina. Moisture content of samples, both for water adsorption and desorption, were determined in the range of ERH between 11 and 97%. Six certified hygroscopic salts of Novasina with ERH 11%, 33%, 58%, 75%, 84%, and 97% were used for sorption tests. The procedure of each test was as follows: after reaching the EMC of each sample at certain ERH and constant temperature, the ERH (corresponding salt) was changed; with increasing ERH for water adsorption and with decreasing ERH for water desorption. Each of the tests was repeated three times.

Moisture content of samples were determined gravimetrically with use of halogen moisture analyzer Mettler Toledo HB-43. The experimental data were processed in the statistical software UNISTAT 4. Measured data both for EMC and Aw were tested by paired t-test and 2-Tail Probability, and consequently equations describing the course of MSI's were created.

Selected samples of skimmed milk powder were also structurally analyzed. Structure of crystal modification in skimmed milk powder was monitored and recorded using USB Digital Microscope (20 × –200 ×) V2.0.

RESULTS AND DISCUSSION

Several authors developed MSI's of milk products (Kirn and Bhowmik, 1994; Kaya and Öner, 1996; Jouppila and Roos, 1997; Foster *et al.*, 2005; Lin *et al.*, 2005).

The EMC of skimmed milk powder samples increased with an Aw increase at a constant temperature both for water adsorption and desorption, as shown on Figs. 1, 2 and 3.

MSI's give a characteristic S-shaped curve, which is typical for sorption isotherms of foods (Kaymak-Ertekin and Sultanoğlu, 2001).

Differences between the course of adsorption and desorption were tested using paired t-test. There were find no statistically significant differences at all temperatures measured, i.e. 5, 10, and 20 °C. Equations (2), (4), (6) and (3), (5), (7) are for water adsorption and desorption, respectively.

Temperature 5 °C:

$$EMC = 155.64(Aw)^3 - 182.12(Aw)^2 + 65.703Aw - 0.9783 \quad (2)$$

$$EMC = 176.59(Aw)^3 - 217.46(Aw)^2 + 82.989Aw - 1.4211 \quad (3)$$

Temperature 10 °C:

$$EMC = 150.42(Aw)^3 - 173.9(Aw)^2 + 61.935Aw + 2.1042 \quad (4)$$

$$EMC = 156.99(Aw)^3 - 190.49(Aw)^2 + 73.077Aw + 0.6027 \quad (5)$$

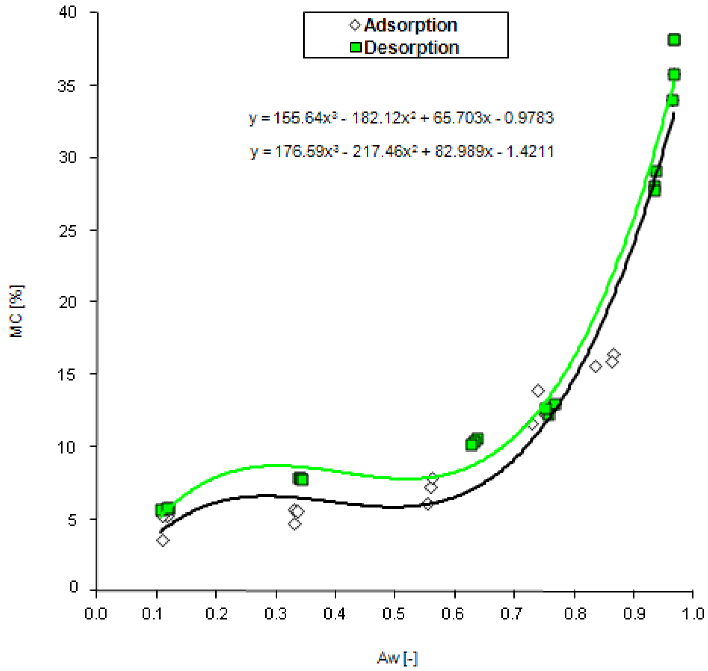
Temperature 20 °C:

$$EMC = 195.13(Aw)^3 - 236.92(Aw)^2 + 88.65Aw - 2.3368 \quad (6)$$

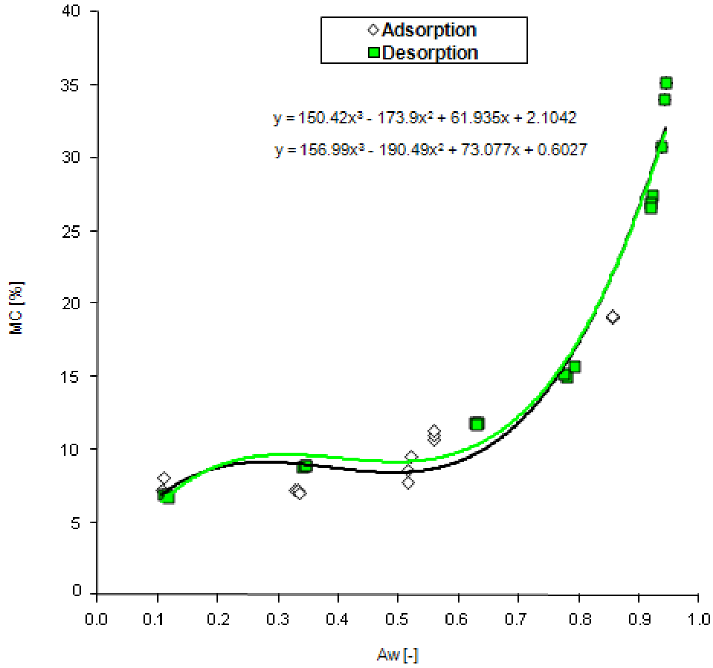
$$EMC = 181.68(Aw)^3 - 210.78(Aw)^2 + 77.601Aw - 0.8834 \quad (7)$$

Statistical characteristics of tested samples are given in tables I, II, and III.

Moisture plays an important role in glass transition and crystallization behaviour of amorphous powders, which determines flowability,



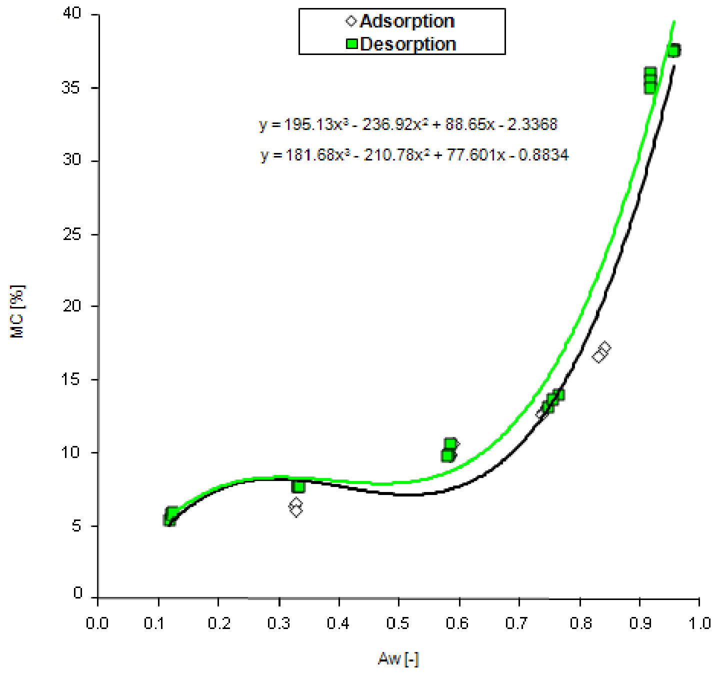
1: *MSI's for skimmed milk powder at temperature 5 °C*



2: *MSI's for skimmed milk powder at temperature 10 °C*

stickiness or caking, and storage stability (Shrestha *et al.*, 2007). The glass transition corresponding to the predetermined values of Aw and temperature for selected samples were monitored. There is the structure of skimmed milk powder after opening the package in the Fig. 4. The following figures, i.e. Figs. 5–10 present the modification of the structure of crystals. There are re-crystallization and glass transition in dependence on temperature and ERH visible.

Glass transition occurs between 33 and 75% EMC (w.b.) at temperature 10 °C, and between 58 and 75% EMC (w.b.) at temperature 20 °C, both for adsorption. Ozmen and Langrish (2002) found that the glass transition temperature decreased as the moisture content increased, as expected (low moisture content 1.65 g/100 g of dry powder basis, glass transition temperature 87.7 °C; high moisture content 4.52 g/100 g of dry powder, glass transition temperature 46.7 °C). The glass transition



3: *MSI's for skimmed milk powder at temperature 20 °C*

I: *Statistical characteristics for tested samples at temperature 5 °C*

Statistical parameter	Adsorption	Desorption
Residual Sum of Squares	7.0687385e + 001	4.3792281e + 001
Standard Error	2.3318429e + 000	1.7086502e + 000
Mean of Y	1.2159638e + 001	1.7935602e + 001
Stand Dev of y	9.6151641e + 000	1.2333604e + 001
R-squared	9.5221314e – 001	9.8400644e – 001
Adjusted R-squared	9.4118540e – 001	9.8080773e – 001
F (3,13)	8.6347096e + 001	3.0762591e + 002
Significance of F	0.0000	0.0000
Durbin-Watson Statistic	2.6055687e + 000	2.3713103e + 000

II: *Statistical characteristics for tested samples at temperature 10 °C*

Statistical parameter	Adsorption	Desorption
Residual Sum of Squares	7.0127139e + 001	4.0597581e + 001
Standard Error	2.2380977e + 000	1.7028879e + 000
Mean of Y	1.4452805e + 001	1.7183147e + 001
Stand Dev of y	9.6859913e + 000	1.0024337e + 001
R-squared	9.5603075e – 001	9.7623489e – 001
Adjusted R-squared	9.4660877e – 001	9.7114236e – 001
F (3,13)	1.0146811e + 002	1.9169960e + 002
Significance of F	0.0000	0.0000
Durbin-Watson Statistic	2.8671761e + 000	2.6297996e + 000

temperature was found to be virtually the same as the sticky-point temperature measured using a thermo-mechanical test.

CONCLUSIONS

Food powders are often prone to sticking and caking problems. Since water is one factor responsible for such problems, MSI's are a useful tool for understanding the moisture relationship

III: *Statistical characteristics for tested samples at temperature 20 °C*

Statistical parameter	Adsorption	Desorption
Residual Sum of Squares	6.7166094e + 001	5.2051108e + 001
Standard Error	2.1903375e + 000	1.9281951e + 000
Mean of Y	1.4968664e + 001	1.8441940e + 001
Stand Dev of y	1.1168456e + 001	1.3493237e + 001
R-squared	9.6832513e – 001	9.8318299e – 001
Adjusted R-squared	9.6153765e – 001	9.7957935e – 001
F (3,13)	1.4266357e + 002	2.7283016e + 002
Significance of F	0.0000	0.0000
Durbin-Watson Statistic	2.8189688e + 000	3.5762527e + 000

4: *Skimmed milk powder before measurement of samples*

5: *Skimmed milk powder at 58% ERH, and at temperature 5 °C*

6: *Skimmed milk powder at 75% ERH, and at temperature 5 °C*

7: *Skimmed milk powder at 58% ERH, and at temperature 10 °C*

8: *Skimmed milk powder at 97% ERH, and at temperature 10 °C*

9: *Skimmed milk powder at 58% ERH, and at temperature 20 °C*

10: *Skimmed milk powder at 97% ERH, and at temperature 20 °C*

of a powder and consequently its stability problem. The critical value of EMC of tested samples corresponding to the Aw equal to 0.6 (Beuchat, 1981), was 6.50% MC (w.b.) at temperature 5 °C, 9.15% MC (w.b.) at temperature 10 °C, and 7.71% MC (w.b.) at temperature 20 °C, all for adsorption. Thus skimmed milk powder should be optimally stored under the presented conditions to prevent the development microorganisms.

SUMMARY

The aim of this paper was to determine effect of near ambient air temperature on adsorption and desorption isotherms of skimmed milk powder within the temperature range of 5 and 20 °C, and subsequently determine equations for sorption curves. The next aim was to observe glass transition of skimmed milk powder at temperatures 5, 10, and 20 °C, and ERH's from 11 to 97%. It is possible to predict the maximum moisture that the biological material can be allowed to gain during the storage under precisely defined ambient air conditions with knowledge of MSI. Skimmed milk powder was commercial produced and purchased in supermarket. The manometric method was used for sorption tests in the temperature regime 5, 10, and 20 °C. EMC's of samples, both for water adsorption and desorption, were determined in range of ERH 11 and 97%. Six certified hygroscopic salts of Novasina with EMC (w.b.) 11%, 33%, 58%, 75%, 84%, and 97% were used for sorption tests. Differences between courses of adsorption and desorption were tested using paired t-test, statistically significant differences were not found. Knowledge of the MSI's could be used for possible grow of microorganisms prediction. Critical value of Aw for microorganisms grow is Aw = 0.6. Measured and analysed values of temperature, RH, EMC, and Aw could serve for optimisation of storing and transport conditions for tested skimmed milk powders.

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