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Moisture sorption isotherms of whole milk powder in the temperature range of 5–35 °C and critical values of water activity prediction

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Abstract

The study presents results of water sorption tests of whole milk powder in the temperature range of 5–35 °C and water activity (a_w) from 0.11 to 0.97. The experimental procedure used was the manometric static method. Four sorption models recommended in literature sources (Chung-Pfost, Halsey, Henderson, Oswin) were analysed and evaluated with the aim of a_w prediction. The modified Oswin's equation was the best model for moisture adsorption and desorption of the whole milk powder. Critical values of the equilibrium moisture content (EMC) from the viewpoint of microorganism growth corresponding to the a_w = 0.6 were calculated for the temperature range tested. The critical EMC was 7.82% and 8.51% wet basis (w.b.), for water adsorption and desorption, respectively, at the temperature of 20 ºC. Sorption capacity of samples tested decreased as temperature increased, and vice versa. The differences between the EMC values at a constant a_w were small in the temperature range measured, and rehydration of the dried material resulted in hysteresis but this effect was non-significant.

Sorption isotherm, moisture content, modelling, microbial growth

Water activity (a_w) is a useful measure of water availability for the growth of various microorganisms (Roos 2002) and physicochemical stability of biological materials in general. Relationships between a_w and growth of moulds, yeasts and bacteria were described by Beuchat (1981); the microbial proliferation starts at about a_w = 0.6. Moisture adsorption (desorption) isotherms provide a graphical representation of the water adsorbed (desorbed) by a hygroscopic material at various near-ambient air humidity at a given temperature and pressure. Each point of the moisture sorption isotherm (MSI) corresponds to the equilibrium moisture content (EMC) of the wet material under near-ambient air conditions. Under these circumstances, the heat and mass exchange between the material and surrounding atmosphere does not occur. At equilibrium, the a_w is related to the equilibrium relative humidity (ERH) of the near-ambient air (Rao and Rizvi 1995). Moisture sorption isotherm of biological materials, especially of food, is usually described as a plot of an amount of water adsorbed/desorbed as a function of a_w. Most of these materials follow a sigma-shaped curve corresponding to type II of the BET classification (Rao and Rizvi 1995). The course of the curve is the result of the additive effect of the Raoult's law, the capillary effect and surface–water interactions. There are two inflections, one around an a_w value of 0.1–0.3, and the other at 0.7–0.9. These are the results of changes in the magnitude of separate physicochemical effects. There are numerous models for MSI and for predicting the relationship between EMC and a_w at a constant temperature in literature data. These models are theoretical, namely BET and GAB and semi-empirical. For instance, Halsey, Henderson, Chung-Pfost, and Oswin, and typically, an empirical model is Peleg (Schuchmann et al. 1990). These models are often used to describe and predict the moisture sorption properties of foods. The MSI of dried food powder products

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is mainly described by equations such as BET, GAB, Oswin's, and Halsey's. Kaymak-Ertekin and Sultanoğlu (2001) tested pepper powder and concluded that the Halsey and Oswin models provided the best fit to the experimental sorption data for a wide range of a_w while the BET was limited; it gave the best fit for the a_w range of 0.1–0.5. Sinija and Mishra (2008) measured green instant tea powder and granules and presented the best results with the Peleg model for a_w range 0.11–0.90. Similar tests were carried out by Lin et al. (2005) with milk powders and presented the best results using the GAB model. In the same direction, Stencl (1999) evaluated the modified Oswin equation as a good model for moisture adsorption and desorption of skimmed milk powder.

Knowledge of MSI and a_w is important and useful for optimisation of storing conditions and determination of ways of packaging in order to guarantee the long-term quality and microbial stability of whole milk powder. The required period of shelf-life of this product is usually one year or longer.

The objectives of the present study were to determine the effect of temperature on the moisture adsorption and desorption isotherms of the whole milk powder under conventional storing conditions in the range of temperatures 5–35 °C. To also analyse four sorption isotherm equations available in the literature and to determine a model corresponding to the sorption behaviour of the samples tested. The other objective was to calculate the critical value of $a_w = 0.6$ in terms of microbial growth.

Materials and Methods

Industrial whole milk powder as an instant product (26% of fat) was taken for the laboratory experiments. The temperature for storing the samples tested was about 20 °C and relative humidity (RH) up to 70% before the sorption measurements. Static manometric method (Iglesias and Chirife 1982) was used for the EMC determinations. The MSI of powders was measured at 5, 15, 20, 25, 30, and 35 °C and in the a_w range from 0.11 to 0.97. The moisture content (MC) of whole milk powder was about 3.9% w.b., before sorption tests started. Six saturated salt solutions, LiCl, $MgCl_2$, NaBr, NaCl, KCl, and K_2SO_4, ensured constant air humidity in the measuring chamber and corresponded to RH values 11, 33, 53, 75, 84, and 97%, respectively. The EMC values of the samples were determined gravimetrically using the halogen moisture analyser. Measurements for each test were done in triplicate and mean EMC were taken for further computation. Four selected semi-empirical three-parameter models (Table 1) were evaluated by determining the best fit to the data measured.

All calculations were done using non-linear regression of the least square method, using Unistat 6.0.07 and Microsoft Excel 2007. The quality of fitness of sorption models was evaluated by calculating statistical indicators used for MSI in literature: the root mean square error, RMSE (Chowdhury and Das 2012; Kaushal and Sharma 2013); analysis of variance, *F*-test (Myers 1990); Durbin-Watson statistic (significant points d_L=1.18; d_U=1.65), *d* (Draper and Smith 1981); R-square, R^2 (Akanbi et al. 2006); standard error of the mean, SEM (Oluwamukomi 2009), and also probability, *P* (Mandel 1964).

Table 1. Moisture sorption equations analysed (Madamba et al. 1993; Chen and Morey 1989).

Model	Model equation	
Chung-Pfost	$w_e = \frac{1}{A}\ln\left(\ln a_w \frac{(B-t)}{C}\right)$	(1)
Halsey	$w_e = \left(\frac{\exp(A+Bt)}{-\ln a_w}\right)^C$	(2)
Henderson	$w_e = \left(\frac{\ln(1-a_w)}{A(t+B)}\right)^C$	(3)
Oswin	$w_e = (A+Bt)\left(\frac{a_w}{1-a_w}\right)^C$	(4)

w_e, = equilibrium moisture content, % (w.b); a_w = water activity, -; t = temperature, °C; A, B and C = model constants

Results

Equations (1)–(4) as presented in Table 1, which model the dependence of EMC of whole milk powder on a_w in the temperature range of 5–35 °C, were investigated and reviewed. Analyses of residuals and correctness of fit tests were carried out after

Table 2. Comparison of Halsey, Henderson and Oswin models for the adsorption and desorption of whole milk powder in physical units as explained in Table 1.

Model	RMSE	*F*-test	*d*	R^2	*P*
Halsey adsorption	14.242	0.0000	1.7533	1.1618	1.0000
Halsey desorption	15.010	0.0000	1.7571	1.3487	1.0000
Henderson adsorption	12.703	0.0000	1.7162	0.7199	1.0000
Henderson desorption	14.013	0.0000	1.7268	1.0472	1.0000
Oswin adsorption	2.1386	380.52	1.2906	0.9513	< 0.0001
Oswin desorption	1.9721	449.64	0.9751	0.9595	< 0.0001

RMSE = root mean square error; *F*-test = analysis of variance; *d* = Durbin-Watson statistic; R^2 = R-square; *P* = probability

determination of indicators. The comparison of Halsey, Henderson and Oswin models for water adsorption and desorption is given in Table 2. Chung-Pfost model did not achieve convergence. Oswin's equation (4) gave the best results. The statistical values showed that this model, both for water adsorption and desorption, had the smallest RMSE and the highest R^2. The standardized residuals of this model were uncorrelated (Durbin-Watson test), (Draper and Smith 1981). *F*-test and *P* (probability) were acceptable. These values determine the relevance of the regression function. *F*-test (Myers 1990) should be the highest as possible, and *P* value (Mandel 1964) should be the lowest as possible. Halsey's and Henderson's equations had high RMSE (Chowdhury and Das 2012) and undesirable values of *F*-test, *d*, *P* and R^2 (Akanbi et al. 2006).

Table 3. Values of indicators in Oswin's model of EMC for whole milk powder.

Constants for ads	Estimate	SEM	Constants for des	Estimate	SEM
A	7.2631	0.5210	A	7.7896	0.4916
B	-0.3463	0.0905	B	-0.3063	0.0891
C	0.5617	0.0273	C	0.5267	0.0237

ads = adsorption; des = desorption; SEM = standard error of the mean

Adsorption and desorption indicators estimated for the Oswin's model of EMC for whole milk powder are shown in Table 3. The following Table 4 shows fitted values of EMC, according to the Oswin's model, for corresponding RH values and temperatures measured. Moisture sorption isotherm for adsorption and desorption of the whole milk powder based on the Oswin's model at temperatures 5 °C and 35 °C are presented in Figs. 1 and 2, respectively. The influence of temperature on the course of MSI, based on Oswin's model for water adsorption is shown in Fig. 3. The critical values for the EMC of the samples tested, corresponding to an a_w value of 0.6 (Beuchat 1981), were calculated for temperatures measured as presented in Table 5.

Discussion

Four semi-empirical three-parameter models recommended in the literature (Chung-Pfost, Halsey, Henderson, and Oswin) were tested in determining the best fit for experimental data corresponding to moisture adsorption and desorption by whole milk

Table 4. Equilibrium moisture content values [% w.b.] of whole milk powder according to the Oswin's model for particular RH at temperatures measured

RH	5 °C	15 °C	20 °C	25 °C	30 °C	35 °C
11%	2.04	1.98	1.94	1.84	1.73	1.58
33%	4.60	4.38	4.28	4.11	3.81	3.56
53%	8.22	7.27	7.60	6.39	5.73	5.07
75%	13.80	12.01	11.35	10.71	10.20	9.37
84%	18.35	18.05	15.95	14.27	13.41	11.96
97%	18.85	27.77	36.56	30.85	27.52	30.75
84%	19.61	17.85	21.08	17.17	14.97	13.50
75%	14.24	12.87	12.22	9.62	11.11	10.51
53%	10.17	8.14	7.50	7.07	6.40	5.87
33%	5.55	5.12	4.67	4.72	4.42	4.22
11%	2.40	2.39	2.31	2.12	2.05	1.95

RH = relative air humidity

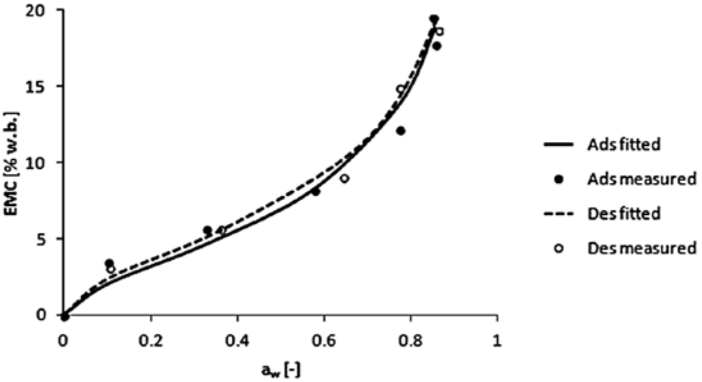

Fig. 1. Adsorption and desorption moisture sorption isotherm (Oswin's model) accompanied by the measured data for whole milk powder at 5 °C

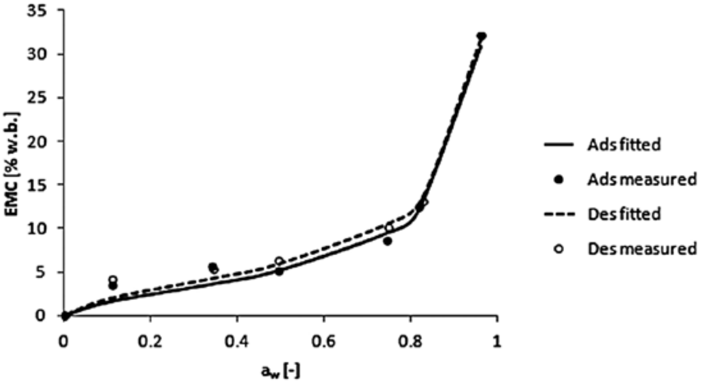

Fig. 2. Adsorption and desorption moisture sorption isotherm (Oswin's model) accompanied by the measured data for whole milk powder at 35 °C

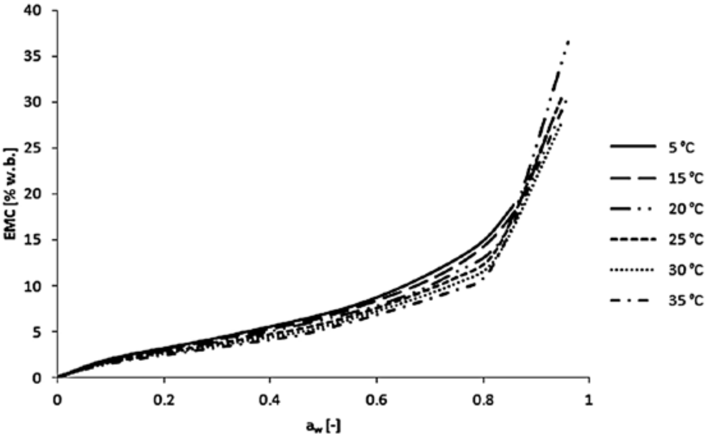

Fig. 3. Adsorption moisture sorption isotherms for whole milk powder at different temperatures, Oswin's model

Table 5. Critical equilibrium moisture content values [% w.b.] of whole milk powder for a_w = 0.6 at 5, 15, 20, 25, 30, and 35 °C.

Temperature	Adsorption	Standard error	Desorption	Standard error
5 °C	8.69	5.26	9.26	1.24
15 °C	8.25	1.20	8.89	0.79
20 °C	7.82	0.72	8.51	0.29
25 °C	7.38	0.12	8.13	0.63
30 °C	6.95	0.45	7.75	0.05
35 °C	6.51	0.11	7.37	0.53

powder. Of those tested, the Oswin's equation was found to be in the best accordance with statistical indicators analysed. Moisture sorption isotherm measured for the whole milk powder showed sigmoid shapes that corresponded to the type II BET classification (Rao and Rizvi 1995). Although moisture sorption curves were generated for both water adsorption and desorption, the hysteresis effect was negligible. The point of inflection was at a_w » 0.5 (Figs 1–3). The increase in temperature caused an increase in the value of a_w, for the same MC. For constant values of a_w, an increase in temperature caused a decrease in the amount of water adsorbed, indicating that the material becomes less hygroscopic at higher temperatures. This effect was considerable for both adsorption and desorption (Table 4 and Figs 1–3). Such observations are important for determining the proper conditions for different technological processes, especially for drying, storage, and packaging.

The semi-empirical three-parameter Oswin's mathematical equation for the functional dependence of EMC on a_w was verified. The diagrams of the sorption isotherms over the temperature range 5–35 °C were developed for this purpose. There are several models for predicting the relationship between EMC, a_w and temperature (Rao and Rizvi 1995). For instance, Van den Berg and Bruin (1978) suggested the following requirements for EMC equations: (1) the experimental curve must be described mathematically for practical applications such as drying, storage, and packaging; (2) the equation should have a simple form and require the least possible number of parameters to describe the data adequately;

(3) the parameters should be physically significant; and (4) the effect of hysteresis should be considered. The three-parameter model is generally preferred over two-parameter models on the basis of these criteria. The third constant is added to the model to allow its application over a wide range of a_w values (up to 0.9) and temperature (Osborn et al. 1989; Schuchmann et al. 1990). In a three-parameter model, the first constant is a scale factor for the overall capacity towards sorption of the material (especially at low a_w values). The second constant is an approximate measure of the isotherm shoulder, while the third constant is a measure of the steepness of the slope over high a_w regions (Schuchmann et al. 1990).

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