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WATER ACTIVITY OF SKIMMED MILK POWDER IN THE TEMPERATURE RANGE OF 20 – 45 °C

J. ŠTENCL

Mendel University of Agriculture and Forestry, Brno, Czech Republic

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Abstract

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Water activity data for adsorption and desorption of moisture from skimmed milk powder were investigated at temperatures in the range of 20 – 45 °C and moisture content of the material tested from 3.2 to 20 % (wet basis). The experimental procedure used was a gravimetric dynamic method with continuous registration of sample weight changes. Four mathematical models of sorption isotherms (Chung-Pfost, Halsey, Henderson, and Oswin) were evaluated to determine the best fit for the experimental data. The modified Oswin equation was a good model for moisture adsorption and desorption of skimmed milk powder. Water sorption capacity decreased as temperature increased. The critical value of equilibrium moisture content of milk powder tested, corresponding to the water activity equal 0.6, was 11 % (wet basis) at the temperature of 20 °C. Repeated rehydration of the material brought an increase in the original equilibrium moisture content 3.2 % (wet basis) to 6.3 – 8.1 % (wet basis) in relation to the temperature. It was also demonstrated that an increase in equilibrium moisture content was very small (about 4 % wet basis) in the range of water activity 0.1 to 0.9. Higher levels of water activity than 0.9 resulted in a marked increase of equilibrium moisture content and susceptibility to spoilage by microorganisms. The hysteresis effect between moisture adsorption and desorption was insignificant.

Adsorption, desorption, microbial food stability, milk powder, modeling, water activity

The moisture sorption isotherm is an extremely valuable tool for food scientists and technologists because it can be used to predict potential changes in food stability; it can be used for storing method determination, packaging selection and ingredient selection. The moisture sorption isotherms of foodstuffs show usually the equilibrium relationship between water activity (a_w) and moisture content (MC) of the food at constant temperatures and pressures. A critical a_w also exists below which no microorganisms can grow (Beuchat 1981). For most foodstuffs, this is in the range of 0.6-0.7 a_w. In general, dehydrated foods have a_w's less than 0.6; semi-moist foods, such as cereal grains, raisins, dates, syrups, and intermediate-moisture pet foods usually have a_w between 0.62 and 0.92. Cheeses, jams, jellies, meat, fish etc. have a_w's greater than 0.92. Thus, with knowledge of the moisture sorption isotherm, we can predict the maximum moisture that the food can be allowed to gain during storage (Kieslingerová and Bartl 1993). Of course, higher a_w's can be allowed if other factors such as pH, salt, antimicrobial agents, and temperature are taken into consideration. Table 1 lists minimum a_w values for growth and toxin production by pathogens (Beuchat 1981).

Generally, temperature has important influence on a_w. Investigations of water adsorption/desorption isotherms have been the subject of study for numerous products due to the development of modern techniques for their processing and storage.

Procedures for obtaining water sorption isotherms in foods were described in detail by

Address for correspondence:
Doc.Ing. Jiří Štencl, CSc.
Department of Postharvest Technology and Engineering
Mendel University of Agriculture and Forestry
Zemědělská 1, 613 00 Brno, Czech Republic

Phone: ++420 5 45132116
Fax: ++420 5 45212044
E-mail: stencl@mendelu.cz
http://www.vfu.cz/acta-vet/actavet.htm

Table 1
Minimal aw limits for some microorganisms of significance to public health

Microorganism	Minimal a_w for	
	Growth	Toxin Production
Aspergillus clavatus	0.85	0.99 (patulin)
A. flavus	0.78-0.80	0.83-0.87
A. ochraceus	0.77-0.83	0.83-0.87 (ochratoxin)
A. ochraceus	0.76-0.81	0.80-0.88 (penicillic acid)
A. parasaticus	0.82	0.87 (aflatoxin)
Bacillus cereus	0.93-0.95	
Byssochlamys nivea	0.84	
Clostridium botulinum	0.93(A)-0.95(A)	0.94-0.95(A)
	0.93-0.94(B)	0.94(B)
	0.95(E)-0.97(E)	0.97(E)
Clostridium perfringens	0.93-0.95	
Penicillium cyclopium	0.82-0.87	0.97 (penicillic acid)
P. cyclopium	0.81-0.85	0.87-0.90 (ochratoxin)
P. expansum	0.83-0.85	0.99 (patulin)
P. islandicum	0.83	
P. martensii	0.79-0.83	0.99 (penicillic acid)
P. patulum (patulin)	0.81-0.85	0.85-0.95
P. viridicatum (ochratoxin)	0.83	0.83-0.86
Salmonella spp.	0.92-0.95	
Stachybotris atra	0.94	0.94 (stachybotryn)
Staphylococcus aureus	0.86	0.87-0.90 (enterotoxin A)
		0.97 (enterotoxin B)
Trichothecium roseum	0.90	
Vibrio parahaemolyticus	0.94	

Wolf et al. (1990), Troller and Christian (1978) and Gal (1975). The principal methods are gravimetric, manometric and hygrometric. The gravimetric method is the most common type of sorption test. It is possible to obtain MC changes of samples continuously or periodically using a static system (usually a closed jar containing saturated salt solutions or sulphuric acid solutions which give a certain equilibrium relative humidity) or a dynamic system (circulated air with a constant flow rate). The dynamic system with continuous registration of weight changes is technically more complicated than the static one but the flow of air around the sample makes the wetting and drying processes faster. Moreover, this system gives better results in cases of layered materials (Labuza et al. 1976).

Numerous models for predicting the relationship between equilibrium moisture content (EMC), a_w and temperature have been developed. Iglesias and Chirife (1976) reviewed several equations for modelling equilibrium MC and reported that some models were adequate to characterize the sorption behaviour of particular foods for the given range of temperature and a_w or relative humidity (r.h.). Chen and Morey (1989a) evaluated four models (Chung-Pfost Halsey, Henderson and Oswin) for their ability to fit data from 18 grain and seed crops. The modified Henderson and Chung-Pfost equations were good for fibrous and starchy materials while the modified Halsey fitted well for high oil and

protein materials. A study by Mazza and Jayas (1991) revealed that the Guggenheim-Anderson-De Boer (GAB) model was superior to three other models (Chung-Pfost, Halsey and Henderson) in characterizing the sorption behaviour of sunflower seed, hulls and kernels. A recent study by Štencl et al. (1998) concluded that the modified Henderson equation characterized very well the moisture adsorption and desorption of dried blood flour in the temperature range of 20-50 °C.

Many other agricultural products have been investigated from the aspect of MC/a_w (or equilibrium relative humidity, ERH) relationship, e.g. rice (Banaszek and Siebenmorgen 1990 (Pixton and Warburton 1975), onion (Mazza and Le Maguer 1978), figs (Pixton and Warburton 1976), apple (Resnik and Chirife 1979), walnuts (Vaidya et al. 1977), malt (Pixton and Henderson 1981). The Chung-Pfost, Halsey, Henderson, and Oswin models are commonly used to describe the sorption behaviour of a wide range of biological materials.

The precision of fit of a model has been determinated using several statistics: the standard error of the estimate for equilibrium MC, SEE (Mazza and Jayas 1991; Chen and Morey 1989a; Hutchinson and Otten 1984), the mean relative percentage deviation, P (Mazza and Jayas 1991; Chen and Morey 1989ab), the Durbin-Watson statistic, d (Draper and Smith 1981), the plot of residuals (Štencl et al. 1999; Madamba et al. 1994; Mazza and Jayas 1991; Chen and Morey 1989a; Sokhansanj et al. 1986) and also coefficient of determination, R^2 (Madamba et al. 1994; Banaszek and Siebenmorgen 1990; Chen and Morey 1989a, 1989b).

The objective of this study is to determine the effect of temperature on the moisture adsorption and desorption isotherms of skimmed milk powder in the temperature range of 20 – 45 °C, to analyze four sorption isotherm equations available in the literature and to determine a model corresponding to the isotherms measured. Furthermore to establish critical a_w and to carry out microbial analysis of the material tested.

Materials and Methods

A fully computerized laboratory drying device with special control software was developed for the purpose of sorption tests (Štencl et al. 1995). The apparatus consists of two main function parts: an air duct with electronically controlled temperature, velocity and relative humidity, and an electronic balance.

Tested samples of skimmed milk powder were taken directly from a spray dryer; the quality was as follows (Table 2):

Table 2
Quality of the tested skimmed milk powder

Milkfat	Minerals	Lactose	MC (wet basis)	Protein	Molds (CFU·g^{-1})	Yeast (CFU·g^{-1})	Bacterial estimate (CFU·g^{-1})	Titratable acidity
1.17%	8.5%	52%	3.2%	35%	0	0	$<10^4$	0.11%

Samples were without coliform organisms, *Staphylococcus, Salmonella*, neutralizing agents and free from antibiotics.

Moisture equilibrium data for adsorption and desorption of water from skimmed milk powder were investigated at temperatures in the range of 20 – 45 °C in 5 °C steps and a_w ranging from 0.4 to 1.0 in 0.1 steps. The procedure of each of the tests was as follows: after reaching the equilibrium moisture content (EMC) of the sample at a certain a_w (at a constant air temperature, velocity and pressure), the a_w was automatically increased (adsorption) or decreased (desorption) and a new equilibrium was obtained under these conditions. Each test was repeated three times with material of the same sampling.

The experimental EMC data were processed using the specially developed software and analyzed using the nonlinear regression procedure of UNISTAT (1995). Four equations (Madamba et al. 1994; Chen and Morey 1989a) describing relation between EMC and ERH were evaluated for their ability to fit data for skimmed milk powder:

Chung-Pfost $w_e=1/A*\ln(\ln a_w*(B - T)/C)$ (1)
Halsey $w_e= (\exp(A + B*T)/(-\ln a_w))(C$ (2)
Henderson $w_e= (\ln(1 - a_w)/(A*(T + B)))(C$ (3)
Oswin $w_e= (A + B*T)*(a_w/(1 - a_w))(C$ (4)
where:
a_w = water activity
w_e = equilibrium moisture content (EMC)
T = temperature
A, B, C = constants for the particular equation.

Results

Equations (1) - (4) to model the dependence of EMC of skimmed milk powder on a_w in the temperature range of 20 – 45 °C were investigated and reviewed. Analysis of residuals and goodness of fit tests were carried out after parameter determination. The comparison of Chung-Pfost, Halsey, Henderson and Oswin models is given in Table 3.

The following statistics were compared: SEE - standard error of estimate, P - mean relative percentage deviation, d - Durbin-Watson statistic (significant points d_L= 1.63; (d_U= 1.72) (Draper and Smith 1981), chi-square (Hanke and Reitsch 1991) and R^2 - coefficient of determination. Best results have been received with the Oswin's equation (4), Table 3.

Table 3
Comparison of Chung-Pfost, Halsey, Henderson and Oswin models for adsorption and desorption of skimmed milk powder

Model	SEE	P	d	Probable chi-square	R^2
Chung-Pfost ads	0.5029	1.4967	1.6347	0.074	0.9675
Halsey ads	0.4379	1.2462	1.6759	0.469	0.9768
Henderson ads	0.5760	1.6798	1.6360	0.119	0.9599
Oswin ads	0.3828	1.1144	1.9511	0.277	0.9823
Chung-Pfost des	0.4688	1.2482	1.0433	0.291	0.9721
Halsey des	0.4230	1.1922	1.4799	0.448	0.9773
Henderson des	0.4888	1.3397	1.3525	0.327	0.9697
Oswin des	0.3405	0.9701	1.8069	0.689	0.9853

Notes: ads = adsorption
des = desorption

Parameter estimation for the Oswin's model of EMC for skimmed milk powder both for adsorption and desorption is indicated in Table 4.

Table 4
Parameter determination for Oswin's model of EMC for skimmed milk powder

Parameter ads	Estimate	Std.Error	Parameter des	Estimate	Std.Error
A	12.5473	0.2009	A	13.1745	0.1812
B	-0.0951	0.0056	B	-0.1022	0.0051
C	0.1283	0.0027	C	0.1204	0.0024

Notes: ads = adsorption
des = desorption

Figures 1 and 2 were generated to illustrate adsorption and desorption models of skimmed milk powder given by equation (4) using fitted parameters in Table 4.

Significant quality changes in the samples tested have not been found after realization of sorption tests. An increase of MC to the level 8.1% (wet basis) at 20 °C was important if compared with the original material (Table 2). Further quality parameters were equal. The value of a_w was approximately 0.1 at the final moisture content, i.e. a risk of growth of molds and yeast does not exist. The critical value of EMC was about 11% ($a_w = 0.6$) at the temperature 20 °C.

Discussion

Most biological products follow a sigmoid curve representing the type II isotherm BET classification (Labuza 1984). The resulting curve is caused by the additive effects of Raoult's law, capillary effects, and surface water interactions. Two bends are noted, one around an a_w of 0.03 and other at 0.95. These are the result of changes in the magnitude of the separate physical-chemical effects.

Part of sorption isotherms measured shows the type II BET classification shape. An increase in temperature causes an increase in water activity for the same MC and, if a_w is kept constant, an increase in temperature causes a decrease in the amount of absorbed water. This indicates that the material becomes less hygroscopic at higher temperatures. These effects are considerable especially up to water activity (0.95 both for adsorption and desorption (Figs 1 and 2). The diagrams show that the repeated rehydration of the material tested brought an increase of original EMC 3.2% (wet basis) on the level of 6.3 - 8.1% (wet basis) in relation to the temperature. This fact is important especially from the aspect of packaging and long-term storing of the skimmed milk powder. It has been further demonstrated that an increase of EMC was very small (about 4% MC wet basis) in the range of a_w from 0.1 to 0.9. Higher levels of a_w than 0.9 resulted in increase of EMC and susceptibility to spoilage by microorganisms. As mentioned in Materials and Methods, the moisture sorption curves have been generated from adsorption and desorption processes (Figs. 1 and 2) but the hysteresis effect was insignificant.

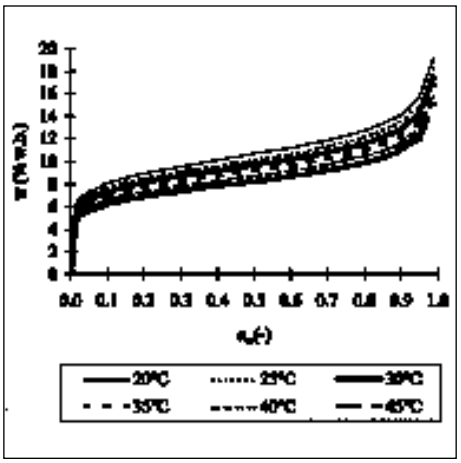

Fig. 1. Adsorption isotherms of skimmed milk powder

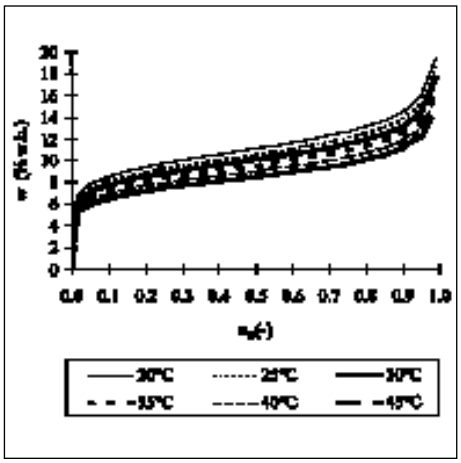

Fig. 2. Desorption isotherms of skimmed milk powder

Vodní aktivita sušeného odstředěného mléka v teplotním rozsahu 20 – 45 °C

Sorpční izotermy vlhkosti jsou významným nástrojem pro predikci možných změn v mikrobiální stabilitě biologických produktů, zvláště potravin. Jejich znalost může být využívána při stanovování podmínek skladování, balení a různých technologických

procesů, především dehydrataci, např. sušením. Sorpční izotermy potravin vyjadřují závislost mezi vodní aktivitou a rovnovážným obsahem vlhkosti vzorku při konstantní teplotě. Hodnoty vodní aktivity pro adsorpci a desorpci vlhkosti sušeného odstředěného mléka byly zkoumány v teplotním rozsahu 20 – 45 °C a vlhkosti materiálu od 3.2 do 20 %. Pro experimentální měření byla použita gravimetrická dynamická metoda s kontinuální registrací změn hmotnosti vzorku. Pro matematický popis sorpčních izoterem byly, na základě literárních zdrojů, statisticky porovnávány čtyři modely: Chung-Pfost, Halsey, Henderson a Oswin. Modifikovaná rovnice podle Oswina představovala nejlepší řešení jak pro adsorpci, tak pro desorpci vlhkosti pro sušené odstředěné mléko. U testovaných vzorků docházelo ke snižování rovnovážné vlhkosti se vzrůstající teplotou. Kritická hodnota rovnovážné vlhkosti odpovídající vodní aktivitě 0,6 činila 11 % při teplotě 20 °C. Opakovaná adsorpce a desorpce vlhkosti testovaného materiálu způsobovala nárůst původního rovnovážného obsahu vlhkosti 3,2 % na hodnoty 6,3 – 8,1 % v závislosti na teplotě. Výsledky měření dále ukázaly že nárůst rovnovážných vlhkostí byl velmi malý, asi 4%, v rozsahu vodní aktivity od 0,1 do 0,9. Při vyšší vodní aktivitě než 0.9 nastal rychlý nárůst rovnovážné vlhkosti a tím i prudké zvýšení náchylnosti k degradaci mikroorganismy. Efekt hystereze mezi adsorpcí a desorpcí vlhkosti byl nevýznamný.

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