

CHARACTERISTICS OF SORPTION PROPERTIES OF SELECTED POWDERED FOOD PRODUCTS

Millena Ruszkowska, Piotr Palich

Department of Organization of Tourist and Hotel Services
Maritime Academy in Gdynia

Key words: full-fat milk powder, powdered soybean drink, sorption isotherms, water activity, sorption kinetics.

Abstract

The goal of this study was to evaluate sorption properties of two selected powdered food products – full-fat milk powder and powdered soybean drink.

The sorption properties of these products were determined with the static method based on the evaluation of water vapor sorption isotherms and with the dynamic method by assaying water vapor sorption kinetics. The mathematical interpretation of the course of water vapor sorption isotherms was conducted with the use of the Brunauer, Emmett and Teller (BET) equation in a water activity range of $0.07 \leq a_w \leq 0.33$.

The kinetics of water vapor sorption was determined in the environment with relative humidity of $a_w = 0.33, 0.64, 0.98$, within 48 h.

Results achieved in the study demonstrated that the differences in the sorption properties of the analyzed products were determined, most of all, by various technological processes applied by particular producers and by different chemical composition of the investigated products.

CHARAKTERYSTYKA WŁAŚCIWOŚCI SORPCYJNYCH WYBRANYCH PRODUKTÓW ŻYWNOŚCIOWYCH W PROSZKU

Millena Ruszkowska, Piotr Palich

Katedra Organizacji Usług Turystyczno-Hotelarskich
Akademia Morska w Gdyni

Słowa kluczowe: izoterma sorpcji, pojemność warstwy monomolekularnej, kinetyka sorpcji pary wodnej.

Abstrakt

Celem badań była ocena właściwości sorpcyjnych dwóch wybranych produktów żywności w proszku – mleka w proszku pełnego oraz proszku napoju sojowego.

Oceny właściwości sorpcyjnych dokonano metodą statyczną na podstawie oceny izoterm sorpcji pary wodnej i metodą dynamiczną przez wyznaczenie kinetyki sorpcji pary wodnej. Do matematycznej interpretacji przebiegu izoterm sorpcji pary wodnej zastosowano równanie BET w zakresie aktywności wody $0,07 \leq a_w \leq 0,33$.

Kinetykę sorpcji pary wodnej wyznaczono w środowisku o wilgotności względnej – $a_w = 0,33$; 0,64; 0,98 w czasie 48 godzin.

Na podstawie przeprowadzonych badań stwierdzono, że różnice właściwości sorpcyjnych badanych produktów w proszku determinowane były przede wszystkim odmiennym procesem technologicznym zastosowanym przez poszczególnych producentów badanych produktów, jak również różnicami w składzie chemicznym badanych produktów.

Introduction

Food powders available on the food market are examples of convenient and stable foodstuffs characterized by diversified composition as well as physical and hygroscopic properties. Their assortment is being increased through multiple modifications of the already existing products and through the introduction of novel products targeted at a specified segment of consumers, e.g. vegetarians.

Plant-based powdered beverages are gluten-free and lactose-free products used to prepare hot or cold dairy drinks or applied as coffee additives. An example of such an innovative plant product is a powdered soybean drink being an alternative for lactose-intolerant consumers unable to use food products based on cow's milk powder.

Food powders produced by, e.g. spray drying are characterized by a low initial water activity at a level of $a_w = 0.15 \div 0.40$, as well as by hygroscopicity and easy water absorption from the environment, which affects their quality and storage stability (KOWALSKA et al. 2011). This study was aimed at evaluating sorption properties of two selected food powders – full-fat milk powder (product of animal origin) and powdered soybean drink (product of plant origin), by determining sorption kinetics and plotting water vapor sorption isotherms.

Material and Methods

The experimental materials were powdered food products: product I – full-fat milk powder produced by Dairy Cooperative Mlekpól' Grajewo, and product II – powdered soybean drink, Soymil produced by SVEN, made in the Czech Republic and imported by GOMIX enterprise from Białystok.

The purchased products were stored in their original packages, in a dry and cool place (following producers recommendations provided on packages, temp. $\geq 20^{\circ}\text{C}$, the relative air humidity $\geq 75\%$). The experimental part of this study was carried out at the laboratory of the Maritime Academy in Gdynia.

The investigated products were characterized by different chemical composition and ingredients, as declared by respective producers on the package (Table 1). Product II was characterized by a lower energy value and protein content and by higher contents of carbohydrates and fat, compared to product I.

Table 1
Chemical composition of the analyzed powdered dairy drinks, declared by producers on the unitary package

Product	The raw material composition	Parametr	The value (100 g)
I	–	energetic value [kcal] protein [g] carbohydrates [g] fat [g]	496 26.5 38.0 26.5
II	corn syrup, soybean oil, sodium caseinate, mono- and diglycerides of fatty acids, soybean lecithin, emulsifier, natural dye – annatto	energetic value [kcal] protein [g] carbohydrates [g] fat [g]	450 2.4 66.1 28.1

Methods

Determination of water content. Water content was determined by drying the samples (ca. $2\text{ g} \pm 0.0001\text{ g}$) at a temperature of 105°C for 1 h (KREŁOWSKA-KUŁAS 1993).

Determination of water activity. Water activity was determined in the AquaLab apparatus, with an accuracy of ± 0.003 (Series 3 model TE, Decagon Devices USA) at a temperature of $25 \pm 1^{\circ}\text{C}$.

Determination of sorption kinetics. Kinetics of water vapor sorption in products I and II were determined by the dynamic method, using a measuring stand that enabled keeping a constant temperature of the measurement at 25°C and stable water activity of the environment at the level of $a_w = 0.33, 0.64,$ and 0.98 . The water vapor sorption kinetics were determined for 48 h. Kinetic curves represented graphic description of changes in the quantity of water (g/100 g d.m.) adsorbed in time.

Determination of sorption isotherms. The course of water vapor sorption isotherms in products I and II was determined with the static-exsiccator method. The assay was conducted in a water activity range of $0.07 \div 0.98$, at a temperature of 25°C , in 3 replications (TYSZKIEWICZ 1987).

The time necessary to reach system equilibrium reached 45 days. Crystalline thymol was introduced into the exsiccators with water activity above 0.7 to prevent microflora growth in the samples. The initial weight of the product and changes in water content enabled calculating the equilibrium water content and plotting sorption isotherms with the use of EXCEL program.

Determination of sorption properties based on BET model. For the mathematical description of empirically-determined sorption isotherms and for the determination of sorption properties of the analyzed food powders, the sorption isotherms were transformed using the Brunauer, Emmett and Teller (BET) equation in a water activity range of $0.07 \leq a_w \leq 0.33$ (PADEREWSKI 1999, TYSZKIEWICZ 1987).

$$a = \frac{v_m \cdot c \cdot a_w}{(1 - a_w)[1 + (c - 1) \cdot a_w]} \quad (1)$$

where:

a – adsorption [kg kg^{-1}];

v_m – water content in the monolayer [$\text{g H}_2\text{O}/100 \text{ g d. m.}$];

c – constant, related in an exponential way with the difference between adsorption heat on the first and following layers, accepted as stable and equal to the condensation heat;

[Pa]; a_w – water activity [-] (OŚCIK 1983).

The specific surface of adsorbent was computed based on the following formula:

$$a_{sp} = \omega \frac{v_m}{M} N \quad (2)$$

where:

a_{sp} – sorption specific surface [$\text{m}^2/\text{g d. m.}$];

M – water molecular mass [18 g/mol];

N – Avogadro number, (6.023×10^{23} molecules/mol);

ω – water setting surface, ($1.05 \times 10^{-19} \text{ m}^2/\text{molecule}$) (PADEREWSKI 1999).

Results and Discussion

The study included determinations of water content and water activity in the analyzed products I and II. Based on the evaluation of the products sampled directly from packages, a higher initial water content and a lower water activity were determined in product II – powdered soybean drink (Table 2).

Table 2
Moisture content and water activity of investigated powder products I and II

Product	Water content [g /100 g d. m.]	SD	Coefficient of variation	Water activity [-]	SD	Coefficient of variation
I	2.57	0.02	0.78	0.254	0.002	1.00
II	3.35	0.02	0.66	0.151	0.005	3.67

SD – standard deviation

In the analyzed products the above parameters were, probably, determined by technological processes applied by their producers as well as by the resultant of water content in the products and the extent of its binding with a product's matrix.

The kinetics of water vapor sorption is influenced by many factors. A powdered food product is a heterogenous material in terms of both the chemical composition and water vapor sorption ability. The kinetics of sorption is additionally affected by the character of raw material, diversified surface of the product as well as by the relative air humidity and temperature (MARZEC and LEWICKI 2004, RUSZKOWSKA 2010).

The evaluation of the course of sorption kinetic curves, in the environment with water activity of $a_w = 0.64$; 0.98 , within 48 h of measurement, demonstrated an increase in water content compared to its initial value in both analyzed products (Figure 1).

In the case of product I, the course of water vapor sorption kinetics indicated the occurrence of water vapor adsorption within 48 h in the medium with water activity of $a_w = 0.33$ and 0.98 . Product I was characterized by a higher water vapor adsorption ability compared to product II. In the environment with water activity of $a_w = 0.64$, the greatest changes in water content of product I, corresponding to the process of adsorption, were observed within the first 9 h of the measurement (9.04 g/100 g d.m.). Afterwards, the product was successively releasing water and after 48 h its water content reached 8.09 g /100 g d.m. (Figure 1).

The evaluation of the course of water vapor sorption kinetics in product II demonstrated that in the environment with water activity of $a_w = 0.33$ within 48 h of measurements, water vapor was subject to the desorption process and the analyzed soybean milk powder reached a lower water content (3.28 g /100 g d.m.) compared to its initial level (3.35 g/100 g d.m.). In the studied water activities of the environment: $a_w = 0.64$; 0.98 , it was noted that the course of water vapor sorption kinetics of product II was similar to that of product I (Figure 1). However, at the evaluated water activities ($a_w = 0.69$; 0.98) product II was characterized by an insignificantly lower kinetics of the water vapor

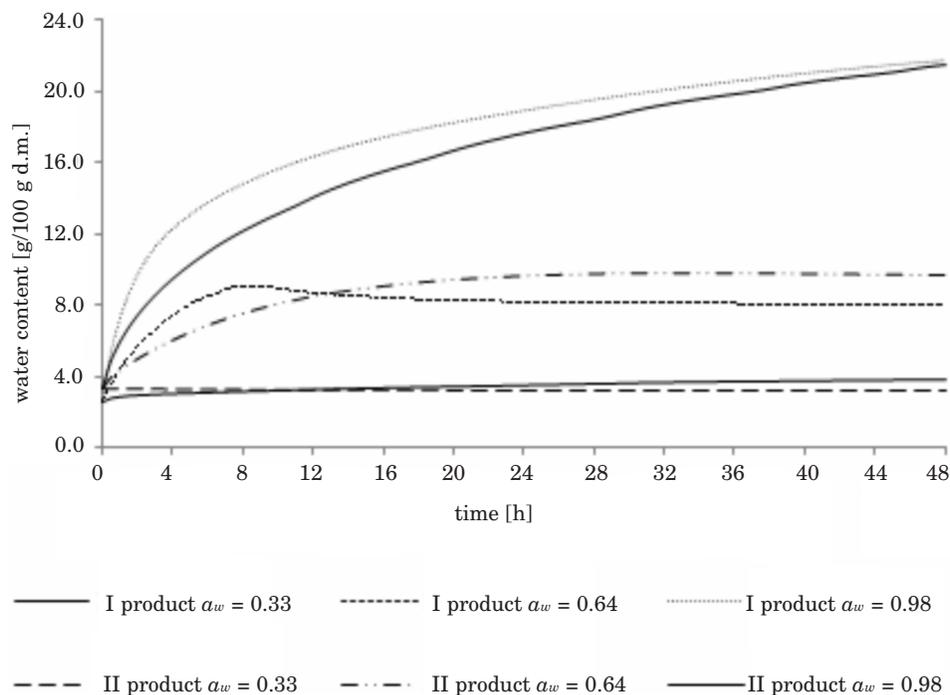


Fig. 1. Vapor sorption kinetics of product I and II, in an environment with a water activity of $a_w = 0.33$; 0.69 ; 0.98

sorption process, compared to product I. Consequently, after 48 h of measurements of water vapor sorption kinetics, a lower water content was demonstrated in product II (powdered soybean drink) – Figure 1.

Based on the comparative analysis of the kinetic curves (Figure 1), it was concluded that their course was significantly affected by the ratio of product water content and environment humidity, as the differences in the water content of a food product and humidity of the environment determine the difference in humidity potential and propelling force of the process. Therefore, the higher the water activity of the environment ($a_w = 0.64$; 0.98) the samples were kept in, the higher their water absorbability.

The course of the sorption process kinetics was also, probably, influenced by the thermodynamic status of the analyzed system that had been determined by the affinity of the investigated products to water, whereas diversity of raw materials used in the production process of product II was affecting the intensity of the course of the sorption phenomenon (Table 1) (OCIECZEK et.al. 2015).

This study included also determinations of water content in products I and II that was assayed after 48 h of sorption kinetics from water vapor sorption isotherm.

The comparative evaluation of experimental results (Table 3) demonstrated that after 48 h of the process in the environment with water activity of $a_w = 0.33, 0.64, 0.98$, the content of water in the analyzed products I and II was lower than the equilibrium water content determined from the course of the sorption isotherm (Table 3). The results achieved showed that after 48 h, the examined products did not reached the state of the real thermodynamic balance with the environment. This indicates that the state of the real equilibrium of relative humidity of the analyzed products I and II can only be reached in a longer process.

Table 3
The data of equilibrium water content achieved in the steam kinetics process determined from the steam adsorption isotherms in product I and II

Product	$a_w = 0.33$		$a_w = 0.64$		$a_w = 0.98$	
	A	B	A	B	A	B
I	3.28	4.64	9.64	11.15	21.56	27.70
II	3.91	4.87	8.09	14.86	21.75	32.50

A – Water content after 48 h sorption kinetics [g/100 g d. m.]

B – Equilibrium water content calculated from the sorption isotherms [g/100 g d. m.]

Sorption isotherms constitute graphical display of correlations between moisture content of the analyzed product and water activity in a specified temperature, thus being a tool to determine thermodynamic interactions between water molecules and a food matrix. The preliminary evaluation of sorption isotherms of products I and II was conducted by comparing the mutual location of the isotherms (Figure 2). The analyzed products I and II were characterized by the sigmoidal course of water vapor sorption isotherm.

In the water activity range of $a_w = 0.07 \div 0.98$, the highest sorption capacity was determined for product II – soybean drink powder (Table 4). The shape of sorption isotherm of product I, in the water activity range of $a_w = 0.33 \div 0.44$, was characterized by the interruption of curve continuity manifested by a decreased level of equilibrium moisture content of this product (Table 4). It is likely that water absorption was accompanied by structural changes resulting from the increased degree of ordering of particular components of product I. The water content and water activity achieved by product I in the environment with water activity of $a_w = 0.33 \div 0.44$, were indicative of the ongoing process of lactose crystallization, i.e. its transition from the amorphous into the crystalline state. The decrease of the equilibrium water content in product I occurred at the simultaneous increase of water activity in the product (Table 4). A possible reason for the discontinuity was a phase transformation of lactose as one of the most important milk constituents. Storage stability and its deriva-

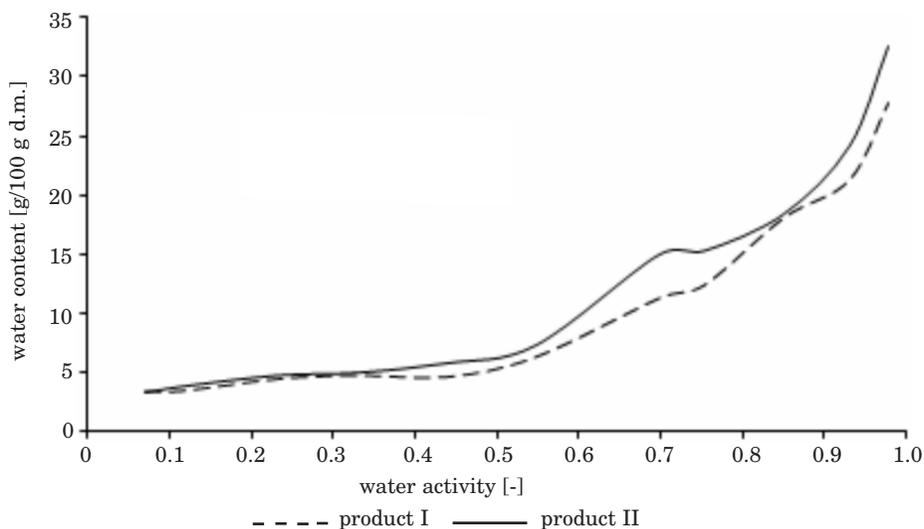


Fig. 2. Sorption isotherms of product I and II

tive, i.e. the nutritional quality of powdered milk, largely depend on the physical state of lactose which may be amorphous or crystalline. As a result of the rapid removal of water from milk during drying, fully-hydrated lactose in an amorphous state and of low viscosity is stabilized while transformed into a glassy amorphous state. This state is unstable at temperatures below the temperature of glass transition (T_g). Hydration of a product or exceeding the T_g temperature is a factor that favours glass transition and crystallization of lactose. Under such conditions, a glassy state transforms into a viscoelastic state, which is also called rubber-like, which results in a substantial increase in the mobility of lactose particles and leads to its gradual crystallization (OCIECZEK 2014, OLKOWSKI et al. 2012). The occurrence of crystalline lactose results in a balance between water content and its activity being set at a new level, which is reflected in a disruption of the continuity of a sorption isotherm. The phase transformation of lactose causes substantial changes in the nutritional quality of powdered milk due to an increase in the oxidation rate of other milk constituents, for instance, milk fat, non-enzymatic browning and a reduced capacity for rehydration (OCIECZEK 2014, FITZPATRICK et al. 2007). As a result of lactose crystallization, water is released, which favours lactose hydrolysis to glucose and galactose.

No decrease in water content was observed in product II in the environment with the water activity of $a_w = 0.33 \div 0.44$, whereas after 45 days of water vapor sorption isotherms determination this product reached higher content and activity of water, compared to product I (Table 4).

The course of sorption isotherms in the water activity range of $a_w = 0.07 \div 0.33$ enabled determining parameters of the BET equation (V_m , a_w) by assaying the degree of its fit (r^2 , FitStdErr) to empirical data. Respective results were presented in Table 5. The capacity of the monolayer (V_m) determined based on the BET equation describes the accessibility of polar sites to water vapor and indicates the volume of water that is strongly adsorbed by the specific sites and is considered optimal to ensure a high stability of food products. The analysis of the achieved capacity of the monomolecular layer of the powdered soybean drink (product II) suggest that changes proceeding in this product during storage will be less intensive than in product I – full-fat milk powder.

Table 4
The moisture and water activity of the products I, II, after 45 days of storage

Water activity of the environment [-]	Product I		Product II	
	water content [g/100 g d. m.]	water activity [-]	water content [g/100 g d. m.]	water activity [-]
0.07	3.311	0.126	3.161	0.113
0.11	3.293	0.140	3.654	0.131
0.23	4.317	0.285	4.626	0.279
0.33	4.636	0.341	4.874	0.330
0.44	4.514	0.461	5.667	0.434
0.53	6.200	0.551	7.178	0.521
0.64	11.154	0.743	14.857	0.773
0.75	12.290	0.781	15.187	0.805
0.84	17.974	0.833	18.298	0.841
0.93	21.200	0.880	24.066	0.889
0.98	27.698	0.937	32.499	0.952

Table 5
The BET equation parameters

Product	v_m	a_w	R^2	FitStdErr	Specific surface of sorption asp [$m^2 g^{-1}$]
I	3.19	0.220	0.936	0.250	112
II	3.39	0.216	0.934	0.218	119

R^2 – determination coefficient; FitStdErr – standard error

The observed differences in monolayer capacity (V_m) were probably a consequence of the physical state of particular components rich in polar sites, but also a consequence of their varying physical state and to the occurring interactions that contribute to the formation of additional hydrogen bonds.

The V_m value enabled calculating the specific surface of sorption. The results achieved (Table 5) demonstrated product II ($a_{sp} = 119 m^2 g^{-1}$) to be characterized by a greater specific surface, than in product I ($a_{sp} = 112 m^2 g^{-1}$).

Conclusions

The study demonstrated that the course of kinetic curves was determined by the ratio of products moisture content and environment humidity, which constituted the propelling force of the process. The course of sorption process kinetics enabled concluding that the examined powders I and II tended to reach the state of humidity balance with the surrounding atmosphere.

The shape of water vapor sorption isotherms plotted for the analyzed products was typical of the products with a complex composition. Minimal differences in the shape of sorption isotherms of the products were, probably, due to changes in the conformation of macromolecules determined by various technological processes. The process of lactose crystallization in product I, proceeding in the environment with $a_w = 0.33 \div 0.44$, contributed to diminished equilibrium water content and increased water activity in the analyzed products.

Results achieved in the study enable concluding that the differences in the sorption properties of the analyzed products were determined, most of all, by various technological processes applied by particular producers and by differences in their chemical composition. It can be expected that the sorption properties of the tested products were determined, inter alia, type of protein in the milk powder – casein, and caseinate and soy product having improved properties of affinity for water.

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