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Determination of the moisture sorption behavior of osmotically dehydrated mackerel fillets by means of binary and ternary solutions

Silvina Paola Agustinelli¹, Viviana Olga Salvadori² and Maria Isabel Yeannes²

Abstract

In this study, the moisture sorption isotherm of osmotically dehydrated mackerel fillets (*Scomber japonicus*) was experimentally determined. The fillets were osmotically dehydrated with solutions of salt (NaCl) (120 and 180 g per liter of solution) or in combination with sugar (350 to 700 g per liter of solution). The sorption isotherms were determined using the static gravimetric methodology with six salts for the water activity range of 0.33–0.98 at 5 °C and 25 °C. All the sorption curves were found to be type III. Temperature and the final tissue salt content had significant ($p < 0.05$) effects on the sorption isotherms. A regression program was used to fit the Halsey, Oswin and Smith moisture sorption isotherm models. Oswin equation gave the best fit for the whole range of water activity and temperatures. The Smith equation only presented valuable results for the mackerel fillets samples with the higher salt content.

Keywords

Scomber japonicus, sorption isotherm, salt–sugar–water solutions, salt–water solutions, mathematical modeling

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INTRODUCTION

Traditional fish processing techniques (salting, smoking, marinating) had in common an immersion stage in concentrated solutions with different solutes like salt, sugar and acids among others or in direct contact with them (dry salting). Osmotic dehydration (OD) is characterized by a fairly complex mass transfer process (Yao and Le Maguer, 1996). Different salts and sugars can be used alone or in mixtures as dehydrating agents in OD processes. The benefit of using these mixtures instead of using only salt has been demonstrated by Collignan and Roult-Walk (1994) in dewatering and salting cod and by Medina-Vivanco et al. (2002) in OD of tilapia fillets. By using sucrose it is possible

to reduce solute gain and allow further dehydration. The sucrose remains as a solution, thus limiting salt uptake, increasing the concentration gradient between the food and the solution and promoting water release (Collignan et al., 2001).

The product obtained after the OD process presents certain microbiological and sensorial stability that

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depends on the water content available for biochemical reactions and microbiological growth. This can be estimated by the water activity (a_w) value. With the introduction of the a_w concept, it is possible to describe the relationship between a_w and food moisture content, that is, the moisture sorption isotherm (Barbosa-Cánovas et al., 2007). The knowledge of sorption isotherms is of great importance for the design and optimization of processing and storage of dried or intermediate moisture content products (Delgado and Sun, 2002). According to the shape of these sorption curves, they are divided into five general types within the classification made by Brunauer et al. (1940) for different materials.

Due to the complex food composition, theoretical prediction of water sorption isotherms is difficult, and many times sorption data are determined from experimental data. However, several theoretical models have been studied and developed by many authors to reproduce the sorption behavior as an approach to reality. Boquet et al. (1978) and Chirife and Iglesias (1978) classified these correlations (logarithmic or power ones) to describe the isotherms of food and food products. The Halsey (Iglesias and Chirife, 1976) and Oswin (cited by Boquet et al., 1978) equations were recommended as the best fit for the meat group. Hadrich et al. (2008) and Guochen et al. (2009) obtained good results with the Oswin model describing accurately the sorption isotherms of Tunisian Sardine (*Sardinella aurita*) and shrimp (*Pandalus borealis*), respectively. Also, Aktaş and Gürses (2005) found good results with the Halsey equation studying the moisture adsorption properties of dehydrated slices of Pastirma (Turkish dry meat product).

In this context it is important to mention that there are few authors that studied the sorption isotherms behavior of fish and fish products and the information is in general scarce. Moreover, very few studies were found on the sorption behavior of osmotically treated fish products (Bellagha et al., 2005; Curran and Poulter, 1983).

Mackerel is a pelagic fish that lives in the Southwest Atlantic Ocean from 22° in Brazilian waters to 39° S in Argentine waters and has been classified within the underutilized species in the Southwest Atlantic Ocean (CFP, 2009). This condition encourages researchers to develop new products with traditional or alternative technologies. The OD process is presented as a possible alternative to produce intermediate or final fish products and gives a potential barrier to implement the Hurdle Technology in the fish product development (Yeannes, 2006).

Therefore, it is relevant to study the moisture sorption characteristics of OD mackerel fillets, in order to know the behavior of this product when treated with

different OD solutions. The knowledge of the sorption isotherms will be an aid to properly define the endpoint of a drying process, and maintaining the food quality. Taking this into account and considering that there is no information on sorption characteristics for mackerel fillets, the research proposed in this study will give a knowledge contribution and can lead to various practical applications. Hence, the aims of this work were: (1) to determine the sorption isotherms of OD mackerel fillets at two different temperatures (5°C and 25°C); (2) to study the influence of salt and sucrose concentration of osmotically treated fillets on water sorption behavior and (3) to fit suitable models for describing the sorption characteristics.

MATERIAL AND METHODS

Raw material

The samples for this research were caught in September using lampara nets by a commercial fishing trawler around latitude 38° S.

Captured fishes were chilled with flake ice and were placed in plastic containers. In these conditions, the samples temperature was near to 0°C but above the freezing point. The fish boxes were transported to the factory and the successive stages of washing, classifying, gutting and filleting were performed, to get two fillets with skin from each specimen. The weight range for each individual fillet was 90–120 g and the average length was 22.1 ± 1.67 cm. The water and fat contents of the fresh mackerel were: $69.20 \pm 0.45\%$ and $9.71 \pm 0.56\%$ in wet basis, these values were determined using AOAC (1990) method and Bligh and Dyer (1959) technique, respectively.

Osmotic treatment

The OD method was carried out with aqueous solutions of sodium chloride (120 and 180 g in a liter of water) and mixed solutions of these sodium chloride concentrations and sucrose (350 and 700 g in a liter of water). The solutions compositions are presented in Table 1. These solute mixtures were selected in order to ensure solutions with low a_w values and sufficient driving force for the mass transport process (Corzo and Bracho, 2003; Medina-Vivanco et al., 2006). The values of sucrose were within a concentration range that would not lower the osmotic effect (above 900 g/L), considering that fish tissue is susceptible to high levels of this solute (Collignan and Roult-Walk, 1994).

Fillets and solutions were previously conditioned in incubator at 20°C. Afterwards, the fillets were placed in plastic containers with a fish: solution ratio of 1:4, which is an appropriate relation for the wet salting process (Medina-Vivanco et al., 2006). The temperature

Table 1. Hypertonic Solution

OD Solution	NaCl g/l	Sucrose g/l
S1	120	–
S2	120	350
S3	120	700
S4	180	–
S5	180	350
S6	180	700

was controlled by placing the containers in an incubator at $20 \pm 0.5^\circ\text{C}$ with automatic control. After 6 h of immersion, two fillets were taken from each solution. Prior to weighing and homogenization of fillets, these were superficially dried with absorbing paper in order to remove surface moisture. The flesh fillets samples were homogenized with an Omni-Mixer (Omni International Inc.) on an ice bath, until a homogeneous paste was obtained. Fish homogenate was used to analyze the content of salt, sucrose, moisture contents, water activity and sorption isotherm.

Salt content

The salt content was determined in duplicate as chloride using the Mohr method adapted to foods (Kirk et al., 1996). Samples were prepared by diluting the dry residue with distilled water, obtained from the moisture content determination. The solution was boiled for 5 min and then filtered and made up to 250 mL. Titration was performed in three aliquots for each extract with AgNO_3 solution to get AgCl compound which precipitates during the process. The endpoint is noticed when no more Cl^- is available, therefore free Ag^+ binds to the CrO_4^{2-} of the indicator and becomes Ag_2CrO_4 compound that gives a brick red color to the solution.

Sucrose content

The sugar concentration was determined in duplicate by an enzymatic kit (Boheringer Mannheim/R-Biopharm, Germany) measuring the absorbance ($\lambda = 340\text{ nm}$) of the solutions extracted from the samples.

Samples extracts were prepared according to the supplier instructions for samples containing fat. First the samples were treated with hot water, and then they were cooled to allow the fat to be separated by filtration. Sucrose determination was done on three aliquots for each extract using the prepared reagents according to the manufacturer's instructions.

The content of sucrose was calculated and expressed as a percentage (%).

Moisture content

The moisture content was determined in triplicate by drying 5 g of minced fish at $105 \pm 1^\circ\text{C}$ until a constant weight was reached (AOAC, 1990).

Water activity

At the end of each immersion stage, liquid samples from the immersion solutions were taken in order to measure their water activity value. The water activity of the solutions was measured in duplicate with a digital hygrometer Aqualab, model CX-2T at 25°C (Decagon, Pullman, WA, USA).

Additionally, predictive models were used to correlate and calculate these values. Sereno et al. (2001) reviewed several equations proposed for a_w prediction, and they recommended the Ross equation (equation (1)) for multicomponent mixtures.

Ross (1975) equation for multicomponent mixtures

$$a_w = \prod_i^n (a_{wi}^0) \quad (1)$$

where a_{wi}^0 represent the water activity of each component of the multicomponent solution. Since the studied OD solutions are prepared using electrolytes and nonelectrolytes solutes, other predictive models for each component have to be used (Baeza et al., 2010; Chirife, 1978).

The equations are described below:

Pitzer (1973) equation, for binary solutions containing electrolytes:

The contribution of NaCl to the solution water activity was predicted using this model

$$a_w = \exp(-0.802\phi\Sigma_i m_i) \quad (2)$$

where m represents the molality of the electrolyte and ϕ , the osmotic coefficient for aqueous electrolytes, is calculated by equation (3)

$$\phi = 1 + |Z_m Z_x| F + 2m \left[\frac{u_m u_x}{u_{total}} \right] B_{mx} + 2m^2 \left[\frac{u_m u_z}{u_{total}} \right]^{3/2} C_{mx} \quad (3)$$

$$F = -A \left[\frac{I^{1/2}}{1 + I^{1/2} B} \right] \text{ and } I = 1/2 \Sigma (m_i Z_i^2) \quad (4)$$

where u_m and u_x are the number of ions, u_{total} being the total number of ions:

$$u_{total} = u_m + u_x \quad (5)$$

Z_i is the ionic charge and B_{mx} is the second virial coefficient calculated from $B_{mx}(0)$ and $B_{mx}(1)$, and their values for NaCl are 0.0765 and 0.2664, respectively (Barbosa-Cánovas et al., 2007).

$$B_{mx} = B_{mx}(0) + B_{mx}(1) \exp(-\alpha I^{0.5}) \quad (6)$$

C_{mx} is the third virial coefficient (0.00127 for NaCl), and I represents the ionic strength of the solution. A and B are Debye–Huckel coefficients (0.392 and 1.2 at 25 °C, respectively).

Norrish (1966) model:

The contribution of the sucrose component to the final solution water activity was predicted using equation (7) for nonelectrolyte solutions.

$$a_w = X_w \left[e^{(KX_s^2)} \right] \quad (7)$$

where X_w = mole fraction of water, X_s = mole fraction of solute, and K is the empirical constant equal to -6.47 for sucrose, supposed to be related to its chemical structure (Norrish, 1966).

Moisture sorption isotherm

The equilibrium moisture content of osmotic dehydrated fish was obtained through the standard gravimetric method recommended by the COST90 project (Spiess and Wolf, 1987) with the modifications suggested by Trujillo et al. (2003). They proposed changes in the sorption container geometry, the distance between the sample and the liquid and the sample shape. The container size was big enough to contain a single sample and the container height was approximately equal to the container diameter. A sample of 2 g of minced mackerel was placed in a pre-weighed mesh at 4 mm above the liquid surface, in order to minimize the external resistance. These modifications reduce the time to reach equilibrium and also avoid spoilage, especially when perishable samples are involved.

Seven plastic flasks with the previously described characteristics were used; each one contained a super saturated salt solution in order to provide a range of a_w from 0.33 to about 0.98. Their water activities at 5 °C and 25 °C were taken from Spiess and Wolf (1987) and Barbosa-Cánovas et al. (2007) and are given in Table 2. Four repetitions were made for each water activity. The closed flasks were kept in an incubator and a

Table 2. Water activities (a_w) of saturated salt solution at 5 and 25 °C

Salt	5 °C	25 °C
K ₂ SO ₄	0.985	0.973
KNO ₃	0.963	0.936
KCl	0.877	0.843
(NH ₄) ₂ SO ₄	0.824	0.803
NaCl	0.756	0.753
KI	0.733	0.689
MgCl ₂	0.336	0.328

refrigerator equipped with temperature control systems to provide the desired constant temperatures of 25 °C and 5 °C, respectively. The mesh containing the sample were weighed using an analytical balance until a weight change equal or less than 0.002 g was recorded on two consecutive weightings, when the sample was assumed to be at equilibrium. Weighing time was reduced to less than 30 s. About 5–7 days were required for the samples to reach this state. Moisture content of the sample was measured immediately after reaching the equilibrium using the previously described method in ‘Moisture content’ section.

Modeling sorption isotherm curves

Three isotherm equations, recommended by Boquet et al. (1978) and Lioutas et al. (1984) for fitting water sorption isotherms of different meat and fish products were used. The equations are presented in Table 3.

Data analysis

Analysis of variance (ANOVA) was carried out to determine the effects of osmotic solutions concentrations on the final fish muscle contents of NaCl, sucrose and moisture. Difference between means was analyzed using Tukey’s test for post hoc comparison ($p < 0.05$).

A non-linear regression analysis was used to calculate the best fitted values of constants in equations (8) to (10) in Table 3 using Microsoft excel 2003 (Microsoft Corp., USA), Origin 8.0 (OriginLab Corporation, Northampton, MA, USA) and MATLAB Version 7.4 (Release 2007a) (Mathworks, Inc., Natick, MA). Performance of the isotherm models was evaluated using parameters for non-linear regression such as the coefficient of determination (R^2), the root-mean-square error (RMSE) of the deviations and the residual plots. The RMSE was estimated as follows:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (\varepsilon_i)^2} \quad (11)$$

Table 3. Sorption models tested in this work

Reference	Equation	Parameters
Smith (1947)	$X = E - F \cdot \ln(1 - a_w)$ (8)	E: the quantity of water in the first sorbed fraction. F: is the quantity of water in the multilayer moisture fraction
Oswin (cited by Boquet et al. (1978))	$X = A \cdot \left(\frac{a_w}{1 - a_w} \right)^B$ (9)	A, B: model parameters
Halsey - Iglesias & Chirife (1976) simplification	$X = \left(\frac{-C}{\ln(a_w)} \right)^{(1/D)}$ (10)	C, D: model parameters

Table 4. NaCl, sucrose and water contents* in osmotic dehydrated mackerel fillets

OD Solution	NaCl (g/100 g w.b.)	Sucrose (g/100 g w.b.)	Water (g/100 g w.b.)
S1	4.26 ± 0.01 ^b	nc	67.76 ± 0.86 ^a
S2	2.74 ± 0.07 ^d	4.49 ± 0.32 ^b	60.37 ± 0.99 ^b
S3	1.34 ± 0.17 ^e	7.56 ± 0.11 ^a	56.01 ± 1.10 ^c
S4	5.61 ± 0.12 ^a	nc	62.02 ± 0.53 ^b
S5	3.68 ± 0.04 ^c	4.97 ± 0.27 ^b	61.15 ± 0.95 ^b
S6	1.12 ± 0.10 ^e	7.55 ± 0.15 ^a	54.24 ± 0.65 ^c

mean value ± SD. Effect of experimental conditions, means with different lower case superscripts in each column are significant different by analysis of variance (ANOVA) (1-way) and Tukey's pairwise comparison test if $p < 0.05$. nc: not containing.

where ε_i the residual of predicted and measured values and n is the number of data. The equation giving the smallest $RMSE$ and the highest R^2 *adj.* value was considered to be the best fitted equation. Regarding the residual plot, acceptance of a model is based on its randomness, that is, the data points tend to fall in a horizontal band around zero, showing no clear pattern.

The significance of the models variables was tested by comparing their p -values for the t -test with $\alpha = 0.05$. The statistical analysis was done with the open-source software R (R Development Core Team, 2005).

RESULTS AND DISCUSSION

Physicochemical analysis

Mean values of NaCl, sucrose, and water contents of dehydrated fillets, measured immediately after 6 h of immersion, are presented in Table 4. The analysis of these results indicates that the concentration and composition of the solution influence both the solutes gain and water loss.

Samples treated only with salt solutions – S1 and S5 – had the highest sodium chloride concentration. The statistic analysis (ANOVA) pointed a positive and significant effect of the initial sodium chloride

solution concentration. On the other hand, the initial sucrose concentration (ternary solutions) presented significant effect on the fillet salt content: high sucrose solutions resulted in a fish muscle with low salt content. As it was studied in gels and fish products, sucrose hinders salt entrance due to the formation of a concentrated superficial coat layer (Collignan and Roult-Walk, 1994; Emam-Djomeh et al., 2001; Medina-Vivanco et al., 2002).

Sucrose gain depends on the initial sucrose concentration of the osmotic ternary solution: higher the solution sucrose concentration is higher the final fish muscle sucrose content is. In contrast, the sodium chloride concentration did not present significant effect over sucrose gain. This fact is in accordance with the results reported by Medina-Vivanco et al. (2002). They concluded that sucrose content in tilapia fillet was negatively influenced by the increase in NaCl solution concentration in the range of 0–25 g for 100 g of water, but over this range the effect disappeared.

With respect to the water content of treated fillets, the experimental results showed that the samples treated with the highest concentrated solutions (S3 and S6) presented, as it was expected, the lowest water contents. Furthermore, water content clearly depends on the

sucrose concentration of the osmotic (ternary) solutions. On the contrary, salt concentration effect is observed only when binary solutions were used. Collignan et al. (2001) explained that sucrose's high molecular weight may cause a slow penetration in tissue, remaining in liquid phase, and hence creating a gradient concentration between the product and the solution and enhancing water release.

The comparison between salt and sucrose effects over water kinetics was completely studied in several fish products and it was related to the differences in molecular size of ionized salt versus larger and unionized sugar (Collignan and Rault-Walk, 1994; Medina-Vivanco et al., 2002).

Predicted versus experimental a_w of OD solutions

Figure 1 shows the experimental and predicted water activities of the hypertonic solutions (see 'Water activity' section). The linear fit presented an R^2 value close to 1 and an RMSE below 0.01. This RMSE value was lesser than the ones presented by Sereno et al. (2001) for prediction of water activity in ternary solutions.

Furthermore, an ANOVA (one-way ANOVA) with Tukey's test was used for means comparison between experimental values and theoretical ones. The results indicates that the means difference is not significant at the 0.05 level, with p -values in the range of 0.06001–0.3390.

According to these analysis and considering that experimental values were measured at the end of the immersion stage and theoretical values were calculated with initial solution concentration, it can be assumed

that the 1 : 4 (fish: solution) ratio was appropriate. This implies a constant driving force to remove water from tissue, avoiding dilution of the osmotic solution. In fact this is important because water activity (i.e. chemical potential), which is a function of soluble solids, is the driving force for mass transport (Corzo and Bracho, 2003; Czerner and Yeannes, 2010).

Sorption isotherms

Experimental equilibrium moisture content values of the samples at 5 °C and 25 °C are plotted in Figure 2. The shape of the isotherms was type-III, typical for food materials, within the five general types of sorption isotherms classified by Brunauer et al. (1940). Similar results for systems with crystalline soluble compounds such as sugars or salts are reported in the literature (Curran and Poulter, 1983).

From the data shown in Figure 2, it can be observed that the temperature effect is noticeable only in samples with lower salt content ($C_{\text{NaCl}} = 1.34\%$ and 1.12%). In these samples, a decrease in temperature induces an increase in the equilibrium moisture content at a fixed a_w value as expected.

The effect of immersion solution concentration (sucrose and/or salt) can be analyzed through the effect of final tissue salt content. As it was explained by Lewicki (1997), NaCl has a greater ability to catch water molecules than other components because of the ionic interaction. Binary immersion solutions produce samples with higher salt content; in consequence at a fixed a_w the equilibrium water content is high. When ternary immersion solutions are used, the salt content decreases inversely to sucrose solution

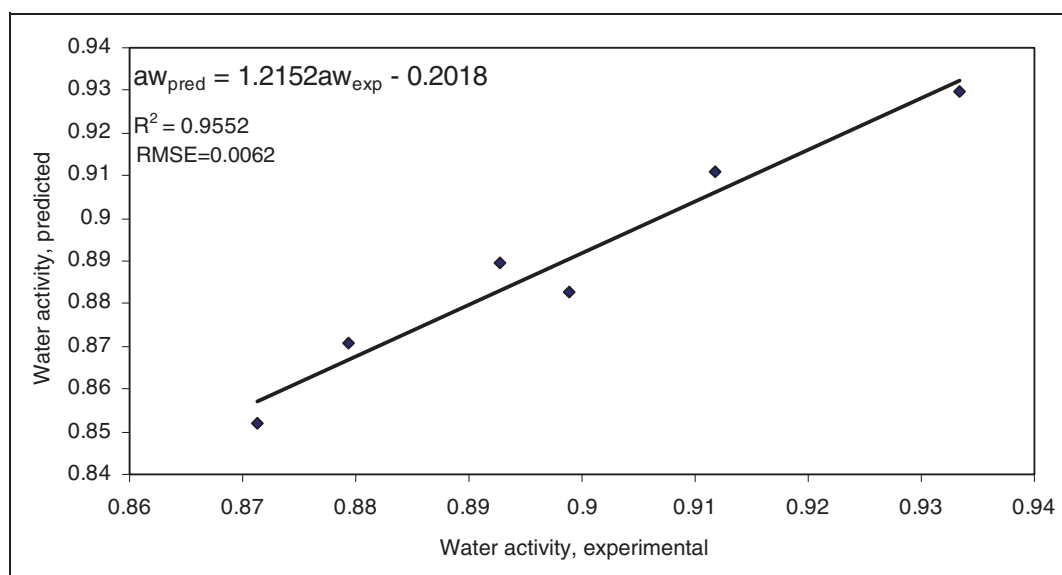


Figure 1. Water activity of sucrose–NaCl osmotic solutions: predicted vs. experimental water activities.

concentration, therefore at a fixed a_w value, the equilibrium moisture content diminishes.

Fitting sorption models

Table 5 summarizes the results for a non-linear regression of the sorption models described in Table 3. The regression procedure was repeated using different initial values to find the best solution.

According to the statistical analysis, the Smith regression coefficients were significantly different from zero ($p < 0.05$) only for the fitting procedure with experimental data from samples treated with salt–water binary solutions (S1 and S4). This model also showed the greater R^2 values and the lower RMSE

for these treatments. Lioutas et al. (1984) obtained good results with this model in meat–salt mixtures and Kabil et al. (2012) in OD beef samples with NaCl and NaCl + NaNO₂. This model was widely used as an empirical equation for fitting water sorption isotherms of foods (Al-Muhtaseb et al., 2002; Chirife and Iglesias, 1978). On the contrary, some authors like Palou et al. (1997) and Aktaş and Gürses (2005) also found that the Smith equation was not acceptable for describing the sorption behavior of food products with different chemical composition.

On the other hand, Oswin and Halsey models were statistically significant at a $p < 0.05$ level (Table 5) for all the studied conditions; the respective p -value (close to 0.00) indicates the high significance of the

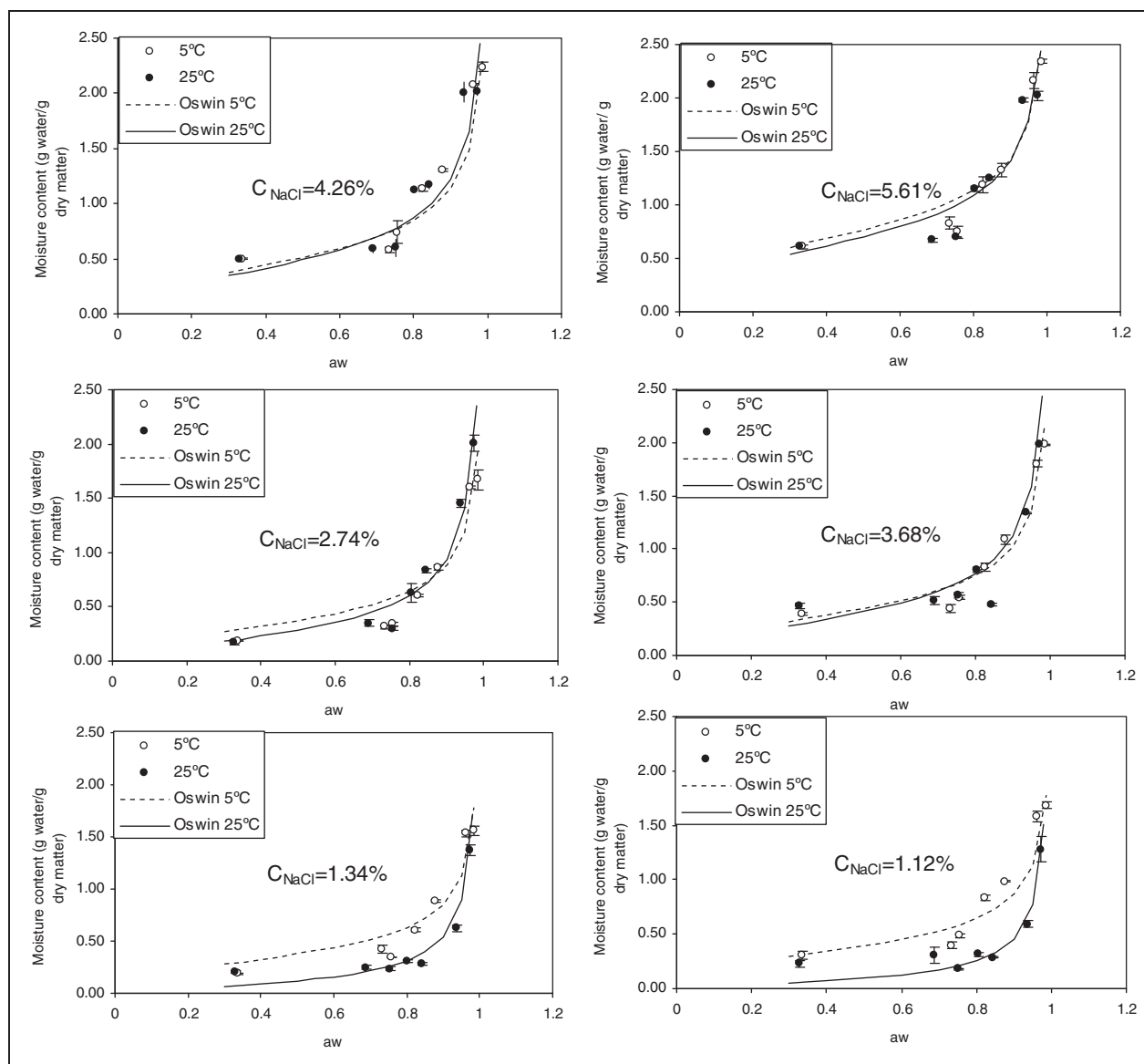


Figure 2. Experimental data and predicted isotherms of osmotic dehydrated mackerel fillets, at 5°C and 25°C.

Table 5. Estimated Smith, Oswin and Halsey constants for OD mackerel fillets at 5 and 25 °C

T (°C)	Smith				Oswin				Halsey					
	Parameters	p-value	R ²	RMSE	Parameters	p-value	R ²	RMSE	Parameters	p-value	R ²	RMSE		
S1	5	E = 0.13	3.96E−02	0.931	0.156	A = 0.616	1.97E−02	0.899	0.188	C = 0.197	3.96E−02	0.890	0.197	
		F = 0.53	2.77E−04			B = 0.327	1.32E−03			D = 2.892	2.77E−04			
		E = 0.089	6.68E−03			A = 0.592	2.15E−02			C = 0.209	6.68E−03			
	25	F = 0.577	1.65E−03	0.86	0.206	B = 0.370	4.53E−03	0.827	0.229	D = 2.526	1.65E−03	0.817	0.235	
		5	E = −0.217	1.33E−01	0.94	0.135	A = 0.297	4.40E−03	0.905	0.169	C = 0.063	1.33E−01	0.895	0.178
			F = 0.493	1.97E−04			B = 0.450	1.73E−03			D = 2.120	1.97E−04		
E = −0.318	6.41E−02		A = 0.278	5.18E−04			C = 0.095	6.41E−02						
25	F = 0.622	2.07E−04	0.938	0.142	B = 0.563	3.81E−04	0.949	0.129	D = 1.676	2.07E−04	0.942	0.138		
	5	E = −0.083	4.99E−01	0.927	0.128	A = 0.346	7.21E−03	0.872	0.170	C = 0.060	4.99E−01	0.858	0.178	
		F = 0.423	3.12E−04			B = 0.386	3.10E−03			D = 2.460	3.12E−04			
E = −0.183		3.22E−01	A = 0.104			1.94E−05	C = 0.041			3.22E−01				
25	F = 0.356	6.78E−03	0.757	0.176	B = 0.713	9.75E−05	0.957	0.074	D = 1.342	6.78E−03	0.967	0.065		
	5	E = 0.231	1.27E−02	0.942	0.141	A = 0.690	1.43E−02	0.922	0.163	C = 0.256	1.27E−02	0.917	0.168	
		F = 0.525	1.80E−04			B = 0.308	5.94E−04			D = 3.065	1.80E−04			
E = 0.224		2.59E−02	A = 0.667			2.02E−02	C = 0.251			2.59E−02				
25	F = 0.533	1.52E−03	0.865	0.186	B = 0.332	3.26E−03	0.839	0.203	D = 2.798	1.52E−03	0.833	0.207		
	5	E = −0.002	9.89E−01	0.931	0.145	A = 0.462	8.03E−03	0.904	0.170	C = 0.109	9.89E−01	0.896	0.177	
		F = 0.491	2.78E−04			B = 0.366	1.24E−03			D = 2.591	2.78E−04			
E = 0.026		8.61E−01	A = 0.344			3.78E−04	C = 0.119			8.61E−01				
25	F = 0.504	1.71E−03	0.917	0.17	B = 0.487	1.75E−04	0.904	0.084	D = 2.126	1.71E−03	0.978	0.103		
	5	E = 0.027	8.25E−01	0.924	0.13	A = 0.430	8.15E−03	0.880	0.164	C = 0.081	8.25E−01	0.868	0.172	
		F = 0.421	3.50E−04			B = 0.347	2.27E−03			D = 2.730	3.50E−04			
E = −0.135		4.46E−01	A = 0.111			1.07E−04	C = 0.038			4.46E−01				
25	F = 0.323	9.23E−03	0.726	0.172	B = 0.674	3.83E−04	0.926	0.090	D = 1.417	9.23E−03	0.939	0.081		

corresponding parameter. Moreover, the high determination coefficients (R^2) values obtained for the Oswin ($0.826 < R^2 < 0.957$) and Halsey equations ($0.817 < R^2 < 0.978$) indicates that both were good models to explain the sorption isotherm of the dehydrated mackerel fillets. To complete the statistical analysis, the residual plots obtained with Oswin and Halsey models were performed. Both plots presented in Figure 3 followed a random and equivalent pattern. Even though both models seem to fit the raw data with similar accuracy, the Oswin model showed in general the greatest values of R^2 and the lower values of RMSE. These results endorse the evaluations made by Boquet et al. (1978) about the fitting abilities of the Oswin equation. They established that the Oswin model gives good fitting description of meat and proteins isotherms. In terms of fishery products, Bellagha et al. (2005) found good fit results explaining the sorption isotherms of salted sardine; Hadrich et al. (2008) in fresh Tunisian sardine fillets, and Guochen et al. (2009) in the study of Shrimp sorption behavior. Therefore, the Oswin model was selected to perform a thorough analysis of the sorption isotherms, concerning the influence

of the final tissue salt content. As the temperature effect is significant at low salt content (Figure 2 and statistical analysis, results not shown), the fitting was done with two groups of data: 5 °C and 25 °C.

In consequence, the dependence of the Oswin parameters on tissue salt content C_{NaCl} was investigated. Second-order polynomials were used to fit each set of raw data of the osmodehydrated mackerel fillets, with C_{NaCl} varying from 1.12 to 5.62 and water activity range from 0.32 to 0.98 at each temperature, 5 °C and 25 °C. Fitting equations are presented as follows:

At 5 °C

$$X = (0.0333 \cdot C_{NaCl}^2 - 0.1404 \cdot C_{NaCl} + 0.5069) \cdot \left(\frac{a_w}{1 - a_w} \right)^{(-0.0133 \cdot C_{NaCl}^2 + 0.0718 \cdot C_{NaCl} + 0.2972)}$$

At 25 °C

$$X = (0.0064 \cdot C_{NaCl}^2 + 0.0915 \cdot C_{NaCl} - 0.0148) \cdot \left(\frac{a_w}{1 - a_w} \right)^{(0.0054 \cdot C_{NaCl}^2 - 0.1234 \cdot C_{NaCl} + 0.8405)}$$

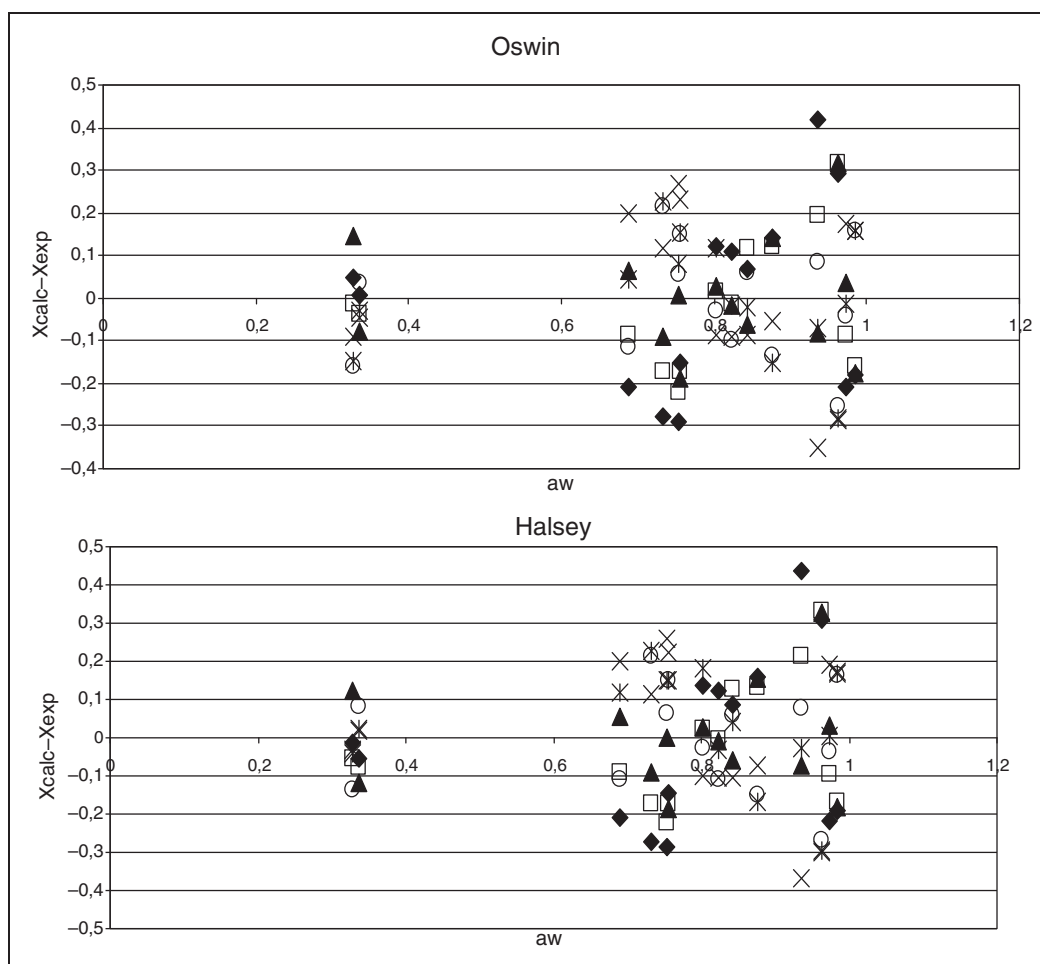


Figure 3. Residual plot for Oswin and Halsey models including temperature effect. (♦) S1, (□) S2; (▲) S3; (x) S4; (★) S5; (○) S6.

Experimental and predicted (Oswin model) values of desorption isotherms of osmodehydrated mackerel fillets obtained at 5°C and 25°C are also shown in Figure 2. These results indicate that the water activity of the OD fillets strongly depends on their final salt content, independently of the solution's sucrose concentration as it is presented in the Oswin modified model at each temperature.

CONCLUSION

In this work, the sorption behavior of osmotic dehydrated mackerel (*Scomber japonicus*) fillets has been studied; the sorption curves were within the type III in the BET classification. Temperature effect was significant only at low final tissue salt content. Instead, the final salt content strongly influences the water activity of the OD fillets, being lower as its salt content is higher.

The experimental data were fitted to three isotherm models. The Oswin model showed the best performance

of the three analyzed models, describing the relationship between water activity, moisture content and final salt concentration of osmodehydrated mackerel fillets treated in binary and ternary solutions.

The results obtained in this work presented valuable information for the design of drying stages of salted mackerel fillets, establishing the conditions of dehydration and defining the endpoint of the process.

CONFLICT OF INTEREST

None declared.

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REFERENCES

- Aktaş N and Gürses A. (2005). Moisture adsorption properties and adsorption isosteric heat of dehydrated slices of Pastirma (Turkish dry meat product). *Meat Science* 71: 571–576.
- Al-Muhtaseb AH, McMinn WA and Magee TRA. (2002). Moisture sorption isotherm characteristics of food products: a review. *Food Bioprocess Technology* 80: 118–128.
- AOAC. (1990). *Official Methods of Analysis*, 15th ed. Washington, DC: Association of Official Analytical Chemists.
- Baeza R, Pérez A, Sánchez V, Zamora MC and Chirife J. (2010). Evaluation of Norrish's equation for correlating the water activity of highly concentrated solutions of sugars, polyols, and polyethylene glycols. *Food and Bioprocess Technology* 3: 87–92.
- Barbosa-Cánovas GV, Fontana AJ, Schmidt Jr SJ and Labuza TP. (2007). *Water Activity in Foods: Fundamentals and applications*. Oxford, UK: Blackwell Publishing Ltd.
- Bellagha S, Sahli A, Glenza A and Kechaou N. (2005). Isohalic sorption isotherm of sardine (*Sardinella aurita*): experimental determination and modelling. *Journal of Food Engineering* 68: 105–111.
- Bligh EG and Dyer WJ. (1959). A rapid method for total lipid extraction and purification. *Canadian Journal of Biochemistry and Physiology* 37: 911–917.
- Boquet R, Chirife J and Iglesias HA. (1978). Equations for fitting water sorption isotherms of foods: II. Evaluation of various two parameter models. *Journal of Food Technology* 13: 319–327.
- Brunauer S, Deming LS, Deming WE and Teller E. (1940). On a theory of the Van der Waals adsorption of gases. *Journal of American Chemical Society* 62: 1723–1732.
- Chirife J. (1978). Prediction of water activity in intermediate moisture foods. *Journal of Food Technology* 13: 417–424.
- Chirife J and Iglesias HA. (1978). Equations for fitting water sorption isotherm of foods: Part I: a review. *Journal of Food Technology* 13: 159–174.
- Collignan A, Bohuona P, Deumier F and Poligné I. (2001). Osmotic treatment of fish and meat products. *Journal of Food Engineering* 49: 153–162.
- Collignan A and Roult-Walk AL. (1994). Dewatering and salting cod by immersion in concentrated sugar/salt solutions. *Lebensmittel-Wissenschaft und-Technologie-Food Science and Technology* 27: 259–264.
- Comaposada J, Gou P, Pakowski Z and Arnau J. (2000). Desorption isotherms for pork meat at different NaCl contents and temperatures. *Drying Technology* 18: 723–746.
- CONSEJO FEDERAL PESQUERO – CFP. (2009). Resolución n. 18, de 22 de Octubre de 2009. Captura Máxima Permitida para la especie caballa. Boletín Oficial, Argentina.
- Corzo O and Bracho N. (2003). Effects of brine concentration and temperature on equilibrium distribution coefficients during osmotic dehydration of sardine sheets. *Lebensmittel-Wissenschaft und-Technologie* 37(4): 475–479.
- Curran CA and Poulter RG. (1983). Isohalic sorption isotherms. III. Application to a dried salted tropical fish (*Xenomugil thoburni*). *International Journal of Food Science & Technology* 18: 739–746.
- Czerner M and Yeannes MI. (2010). Brining kinetics of different cuts of anchovy (*Engraulis anchoita*). *International Journal of Food Science & Technology* 45: 2001–2007.
- Delgado AE and Sun DW. (2002). Desorption isotherm for cooked and cured beef and pork. *Journal of Food Engineering* 51: 163–170.
- Emam-Djomeh Z, Djelveh G and Gros J-B. (2001). Osmotic dehydration of foods in a multicomponent solution, Part I. Lowering of solute uptake in agar gels: diffusion considerations. *Lebensmittel-Wissenschaft und-Technologie* 34: 312–318.
- Guochen Z, Arason S and Arnason SV. (2009). Dehydration property of Shrimp (*Pandalus borealis*) undergoing heat-pump drying process. *International Journal of Agriculture and Biological Engineering* 2: 92–97.
- Hadrich B, Boudhrioua N and Kechaou N. (2008). Experimental and mathematical study of desorption isotherms of Tunisian sardine (*Sardinella aurita*). *ICChem, Food and Bioprocess Processing* 86: 242–247.
- Iglesias HA and Chirife J. (1976). A model for describing the water sorption behaviour of foods. *Journal of Food Science* 41: 984–992.
- Kabil E, Aktaş N and Balcı E. (2012). Effect of sodium chloride, sodium nitrite and temperature on desorption isotherms of previously frozen beef. *Meat Science* 90: 932–938.
- Kirk R, Sawyer R and Egan H. (1996). *Composición y Análisis de Alimentos de Pearson*, 2nd ed. México: Continental S.A. C.V.
- Lewicki PP. (1997). Water sorption isotherms and their estimation in food model mechanical mixtures. *Journal of Food Engineering* 32: 47–68.
- Lioutas TS, Bechtel PJ and Steinberg MP. (1984). Desorption and adsorption isotherms of meat-salt mixtures. *Journal of Agricultural and Food Chemistry* 32: 1382–1385.
- Medina-Vivanco M, Sobral PJ do A and Hubinger MD. (2002). Osmotic dehydration of tilapia fillets in limited volume of ternary solutions. *Chemical Engineering Journal* 86: 199–205.
- Medina-Vivanco M, Sobral PJ do A and Hubinger MD. (2006). Kinetic aspects of salting tilapia fillets using small volumes of brine. *Brazilian Journal of Food Technology (ITAL)*, Campinas 9: 9–18.
- Norrish RS. (1966). An equation for the activity coefficients and equilibrium relative humidities of water in confectionery syrups. *Journal Food Technology* 1: 25–39.
- Palou E, Lopez-Malo A and Argaz A. (1997). Effect of temperature on the moisture sorption isotherms of some cookies and corn snacks. *Journal of Food Engineering* 31: 85–93.
- Pitzer KS. (1973). Thermodynamics of electrolytes: I. Theoretical basis and general equations. *Journal of Physical Chemistry* 77(2): 268–277.
- R Development Core Team. (2005). *R: A Language and Environment for Statistical computing*. Vienna,

- Austria: R Foundation for Statistical Computing. ISBN 3-900051-07-0. R website.
- Ross KD. (1975). Estimation of water activity in intermediate moisture foods. *Food Technology* 29: 26–34.
- Sereno AM, Hubinger MD, Comesaña JF and Correa A. (2001). Prediction of water activity of osmotic solutions. *Journal of Food Engineering* 40: 103–114.
- Smith SE. (1947). The sorption of water vapour by high polymers. *Journal of the American Chemical Society* 69: 646–651.
- Spiess WEL and Wolf W. (1987). Critical evaluation of methods to determine moisture sorption isotherms. In: *Water activity: Theory and Applications to Food* (L.B. Rockland and L.R. Beuchat, eds.), pp. 215–233. New York: Marcel Dekker.
- Trujillo FJ, Yeow PC and Pham QT. (2003). Moisture sorption isotherm of fresh lean beef and external beef fat. *Journal of Food Engineering* 60: 357–366.
- Yao Z and Le Maguer M. (1996). Mathematical modelling and simulation of mass transfer in osmotic dehydration processes. Part I: conceptual and mathematical models. *Journal of Food Engineering* 29: 349–360.
- Yeannes MI. (2006). Aspectos Científicos y Tecnológicos en Preservas de Productos Pesqueros. Facultad de Ciencias Agrarias. UCA. ISBN: 987-05-1523-1.