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Sorptional behaviour of rosehip leather formulations added with sucrose or polydextrose

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The sorptional behaviour of two formulations intended to develop rosehip leathers, both based on rosehip fruit pulp, was assessed experimentally. One formulation had sucrose added, while polydextrose was added to the other to reduce the calorie intake. Isotherms were measured by the static gravimetric method at 10, 20, 40 and 60 °C. The GAB equation and a model proposed by Leiva Díaz, Giannuzzi, and Giner (2009) gave the best representation of data for sucrose- and polydextrose-added formulations, respectively. A detailed statistical analysis revealed an interaction between composition and temperature effects on isotherms. Sucrose proved to be more effective than polydextrose to lowering the water activity of the formulation, except in conditions that favour the formation of sucrose crystals. In general, the water activity of the polidextrose-added formulation, which did not experience crystallisation, increased with increasing temperature for a given moisture content. However, the temperature effect on the isotherms of the sucrose-added matrix was more complex, possibly being affected by crystallisation.

1.   Introduction

Eating behaviours have been modified in recent decades, affected by more intense and diversified working days and other changes in lifestyle. More people are eating at work or consuming food while walking on the street. Thus, the time devoted to cooking or eating has generally shortened (Trichopoulou & Naska, 2002). Many resort to eating fast food or snacks, although such products do not always provide nutritional quality, since carbohydrates and fats prevail in their compositions. A challenge for food industry is to develop a wider variety of snacks or ready-to-eat products to satisfy

consumer's needs whilst attending their nutritional requirements. Fruit leathers are a good example of such products, being a practical vehicle to incorporate fruit solids. They are dehydrated, fruit-based products eaten as candy or snacks, usually presented as flexible stripes or sheets that remain stable for 7 months or longer without refrigeration, as shown by Quintero Ruiz, Demarchi, Massolo, Rodoni, and Giner (2012) for apple leathers. The consumption of fruit leathers adds variety to the diet and allows the intake of dietary fibre, vitamins and minerals, while providing a substantial energy input.

In the present work, two formulations intended to develop rosehip leathers were studied. Rosehip fruit pulp, the main ingredient, is an important source of minerals, anthocyanin,

Nomenclature		W	moisture content (kg [water] kg^{-1} [dry matter])
		W_i	experimental moisture content (kg [water] kg^{-1} [dry matter])
Symbols		W_{ic}	calculated moisture content (kg [water] kg^{-1} [dry matter])
A	Halsey model parameter		
a_w	water activity	W_M	monolayer moisture content in GAB model (kg [water] kg^{-1} [dry matter])
C	GAB model parameter		
C_1, C_2, C_3	Leiva Díaz model parameters	W_m	average moisture content (kg [water] kg^{-1} [dry matter])
D	Oswin model parameter		
E_{RMS}	root mean square error	y_i	experimental value in a data set
F	Oswin model parameter	y_{ij}	every experimental value
f	statistical value for comparison of data sets	$\hat{y}_i$	value predicted by the model for each data set
k	GAB model parameter	$\hat{y}_{ij,c}$	every value predicted by the model for combined data
m	number of data sets to be compared in the F-test		
n	number of experimental data	ϕ_D	sum of degrees of freedom for each data set fit
n_j	number of data in each set	ϕ_{Dc}	degrees of freedom for combined data fit
p	number of fitting parameters		
R	Halsey model parameter	*Abbreviations*	
r^2	coefficient of determination	PAF	polidextrose-added formulation
S_{Dc}	combined sum of squared deviations	SAF	sucrose-added formulation
S_{Dj}	sum of squared deviations in each set of data		
T_g	glass transition temperature		

carotene and, particularly, of vitamin C (from 10 to 40 mg [ascorbic acid] g^{-1} [dry matter]) (Erenturk, Gulaboglu, & Gultekin, 2005; Pirone, Ochoa, Kesseler, & De Michelis, 2007; Yilmaz & Ercisli, 2011), while providing the natural high-methoxyl pectins required for the "saccharide–acid–pectin" gelation mechanism by which leathers are formed (Rinaudo, 1996). The saccharide content was increased by adding sucrose to the natural sugars previously existing in the fruit, while the natural pH of the pulp was adjusted with citric acid. To develop an alternative, reduce-calorie rosehip leather formulation, suitable for health conscious consumers, the sucrose added to the original formulation was replaced by polydextrose. This polysaccharide provides soluble fibre and yields only 4.18 kJ g^{-1}, i.e., a quarter of the energy input of sugars (Achour et al., 1994). Polydextrose is non-cariogenic, acts as a prebiotic polymer and is suitable for diabetics (Zhong Jie et al., 2000). Unlike sucrose, polydextrose does not crystallise at the concentrations used in dehydrated rosehip leathers (Ribeiro, Zimeri, Yildiz, & Kokini, 2003). Also, the higher glass transition temperature (T_g) of polydextrose compared with sucrose (94 °C and 62 °C, respectively) may increase the storage stability (Slade & Levine, 1991). Addition of this polymer has successfully replaced the incorporation of sucrose in apple leathers previously prepared in our laboratory, leading to the expected characteristics on the final product. Although the effect of polydextrose on drying kinetics was studied (Demarchi, Quintero Ruiz, Concellón, & Giner, 2013), no research was focused on the influence of this polysaccharide on the sorption equilibrium characteristics of leather formulations. Isotherms represent the relationship between moisture content and water activity (a_w) of a product at constant temperature. The shapes of the isotherms reflect the way in which water interacts with food solids. As these curves are noticeably affected by the amount and type of soluble solids, and also by food microstructure (Giovanelli, Zanoni, Lavelli, & Nani, 2002; Goula, Karapantsios, Achilias,

& Adamopoulos, 2008; Labuza & Altunakar, 2007), they are unique for each product and must be properly determined to design new formulations, predict drying endpoints and select process and storage conditions. An important issue to be evaluated in alternative preparations, such as sucrose- and polydextrose-added formulations presented here, is the safe moisture content, i.e., the value at which the product is microbiologically stable, for instance at $a_w = 0.7$. The effect of temperature on isotherms is particularly important in food while, from the research viewpoint, constitutes a challenging subject as it encompass various competing mechanisms in matrices with high-soluble solids content (Ayranci, Ayranci, & Doğantan, 1990; Labuza & Altunakar, 2007; Saravacos, Tsiourvas, & Tsami, 1986; Tsami, Marinos-Kouris, & Maroulis, 1990; Yu, Mazza, & Jayas, 1999).

Based on the preceding considerations, the aims of this work were (1) to construct experimental desorption isotherms of two rosehip formulations, one added with sucrose and the other, with polydextrose, in the range of temperature from 10 to 60 °C; (2) to find mathematical models that provide an accurate prediction of the isotherms; and (3) to evaluate the effect of composition and temperature on the sorptional behaviour of rosehip formulations.

2. Materials and methods

2.1. Fruit processing

Ripe rosehip fruits (*Rosa rubiginosa* L., syn. Rosa *eglanteria* L.) harvested in El Bolsón, Province of Río Negro, Argentina, were boiled for 30 min in an industrial cooker, adding 0.2 kg of drinking water per each kg of whole fruit. The softened fruits were processed with a pulping machine and passed through a 0.5 mm sieve to remove seeds and non-edible matter. A homogeneous pulp was obtained which was concentrated by

evaporation to 14 °Brix. Then the pulp (average moisture content 85.4 g [water] 100 g^{-1} [pulp] or 5.85 decimal, dry basis) was cooled, frozen and stored at −20 °C until using.

2.2. Sucrose- and polydextrose-added formulations

For preparing 100 g of the sucrose-added formulation (SAF), 75 g of the thawed rosehip pulp were mixed with 20 g of commercial sucrose and 5 g of a citric acid solution (5.8 g [citric acid] 100 g^{-1} [solution], concentration equivalent to that in lemon juice). The mixture thus attained was manually stirred for 3 min until obtaining a homogeneous fluid-like formulation. With regard to the polydextrose-added formulation (PAF), the only difference with the SAF was that 20 g of polydextrose powder (Winway® I, China) were added instead of sucrose. After 5 min of manual stirring, a homogeneous mixture was obtained.

2.3. Initial moisture content and water activity

The rosehip formulations were stored in sealed jars at 4 °C for 24 h, to allow for the total dissolution of added saccharides. Then, aliquots of each formulation were taken and allowed to equilibrate with room temperature for determination of initial moisture content and water activity (a_w). Moisture content was measured in 5 g samples introduced in a Mettler LP16 moisture analyser set at 105 °C, until reaching constant weight, according to the AOAC method 984.25 (AOAC, 1998). In turn, a_w was determined at 25 °C by the AOAC hygrometric method 978.18 (AOAC, 1998), using a temperature-controlled AquaLab 3TE water activity meter (Decagon Devices, Inc., USA). Four replicates were measured for each determination.

2.4. Determination of desorption isotherms

The rosehip formulations studied were intended to form leathers by drying, so only desorption isotherms were of interest. The static gravimetric method as described by Rahman and Sablani (2008) was chosen to determine isotherms at 10, 20, 40 and 60 °C for both formulations. The selected temperature range encompasses both storage (refrigerated and room conditions) and drying processes. Ten saturated salt solutions (slurries), generating constant a_w atmospheres, were prepared in order to equilibrate the samples, according with the AOAC method 978.18 (AOAC, 1998). Their water activities at the experimental temperatures are shown in Table 1. The solutions were placed in flasks, leaving a layer of salt crystals in the bottom of the containers. A plastic structure was then put inside each flask to support the sample. Then, a 2 g sample of formulation was deposited in open glass dishes, placed onto the plastic supports. The flasks were then sealed to allow for vapour transfer between sample and solution. For environments with a_w above 0.75, a small open container with toluene was left inside the flask to prevent microbial growth. All isotherms were determined in triplicate, using an individual flask for each sample. One set of flasks was maintained at 10 °C in a cold store, while, at 20 °C, samples were placed in a temperature-controlled room. For the material corresponding to 40 and 60 °C, a convection culture oven with automatic temperature control was utilised. Flasks were periodically open

Table 1 – Saturated salt solutions and their water activities at 10, 20, 40 and 60 °C. (Adapted from Greenspan (1977), Kiranoudis, Maroulis, Tsami, and Marinos-Kouris (1993) and TAPPI (2002)).

Saturated salt solutions utilized	Water activity			
	10 °C	20 °C	40 °C	60 °C
LiCl	0.113	0.113	0.112	0.109
KCH$_3$COO	0.245	0.234	0.208	0.160
MgCl$_2$	0.340	0.330	0.320	0.300
K$_2$CO$_3$	0.431	0.432	0.433	0.432
Mg(NO$_3$)$_2$	0.574	0.544	0.484	0.440
NaNO$_2$	0.654	0.654	0.614	0.593
NaCl	0.760	0.754	0.747	0.745
KCl	0.879	0.867	0.843	0.819
BaCl$_2$	0.919	0.904	0.884	0.840
K$_2$SO$_4$	0.982	0.976	0.964	0.964

to weigh the samples. Equilibrium was assumed as variations in moisture content of samples (calculated by weighing, considering constant dry matter), became less than 0.003 kg [water] kg^{-1} [dry matter], which is the accepted error for oven-moisture determinations (Lomauro, Bakshi, & Labuza, 1985).

2.5. Mathematical description of desorption isotherms

Table 2 describes the equations proposed to represent the sorptional behaviour of rosehip formulations for isothermal conditions. In all equations, the moisture content (W, kg [water] kg^{-1} [dry matter]) is expressed as a function of the water activity (a_w). The Halsey model (Eq. (1)) presents two fitting parameters, A and R, and is usually adequate for fruits and oilseeds (Demarchi, Quintero Ruiz, De Michelis, & Giner, 2013; Giner & Gely, 2005). This expression takes into account multilayer sorption and the parameter R characterizes the type of interaction between vapour and solids (Al-Muhtaseb, Mcminn, & Magee, 2002). The Guggenheim, Anderson, De Boer (GAB) model (Eq. (2)), based on the theory of multi-layer adsorption, has been suggested to be the most versatile sorption model available in the literature (Bizot, 1983; Labuza & Altunakar, 2007; Van den Berg & Bruin, 1981). In this equation W_M represents the monolayer moisture content in dec., dry basis, while C and k are parameters related to the sorption

Table 2 – Mathematical models fitted to the experimental desorption isotherms.

Model	Equation	
Halsey	$W = \left(\dfrac{-A}{\ln(a_w)} \right)^{1/R}$	(1)
GAB	$W = \left(\dfrac{W_M C k a_w}{(1 - k a_w)(1 - k a_w + C k a_w)} \right)$	(2)
Leiva Díaz et al. (2009)	$W = C_1 \exp\left(C_2 a_w^{C_3} \right)$	(3)
Oswin	$W = \left(\dfrac{D}{((1/a_w) - 1)^F} \right)$	(4)

W: moisture content (kg [water] kg^{-1} [dry matter]); a_w: water activity; A, R, W_M, C, k, C_1, C_2, C_3, D and F: fitting parameters of the models.

Table 3 – Characteristics of the roseship formulations

	Sucrose-added formulation	Polydextrose-added formulation
Water activity[a]	0.966 ± 0.004	0.972 ± 0.002
Moisture content[b]	68.56 ± 1.31	68.71 ± 0.29
Total carbohydrates[c]	30.04	30.04
Sugars[c]	22.70	2.70
Fibre[c]	1.00	21.00
Proteins[c]	0.24	0.24
Total fat[c]	0.05	0.05
Ashes[c]	0.80	0.80

[a] Experimental data (no units) expressed as average ± standard deviation.
[b] Experimental data (g 100 g^{-1} [formulation]) expressed as average ± standard deviation.
[c] Calculated data (g 100 g^{-1} [formulation]).

dynamic equilibrium. Eq. (3) is a phenomenological model for J-shaped curves, with three fitting parameters C_1, C_2 and C_3, purpose-developed for apple leathers by Leiva Díaz, Giannuzzi, and Giner (2009), which accurately predicted sorption isotherms for apple, rosehip and tomato formulations intended for leathers (Demarchi et al., 2013). Finally, the empirical model developed by Oswin (Eq. (4)) was tested. Equations were fitted to the data using the nonlinear least-squares criterion, which was conducted in OriginPro 8 software (Origin, 2009). Goodness of fit was evaluated by two indices: coefficient of determination, r^2 (Eq. (5)), and the root mean square error, E_{RMS}, which takes into account the number of fitting parameters (Eq. (6)).

$$r^2 = 1 - \frac{\sum_{i=1}^{n}(W_i - W_{ic})^2}{\sum_{i=1}^{n}(W_i - W_m)^2} \tag{5}$$

$$E_{RMS} = \sqrt{\frac{\sum_{i=1}^{n}(W_i - W_{ic})^2}{n-p}} \tag{6}$$

where W_i, W_{ic} and W_m are the experimental, calculated and average moisture contents respectively, n is the number of experimental data points and p, the number of fitting parameters.

2.6. Statistical analysis

In order to evaluate the effect of composition and temperature on the isotherms, the curves were compared applying a

method described by Green and Margerison (1978, chap. 12). As the method requires the use of models, the most accurate equation for each condition was selected to carry out the analysis. This procedure is adequate to compare the general sorptional behaviour, as it evaluates whether or not various sets of data are different enough to be represented by various groups of model parameters. In this test, the statistic f calculated by Eq. (7) is compared with the tabulated F-Snedecor value corresponding to $\phi_{Dc} - \phi_D$ degrees of freedom for numerator and ϕ_D degrees of freedom for denominator.

$$f = \frac{\left(S_{Dc} - \sum_{j=1}^{m} S_{Dj}\right) \Big/ (\phi_{Dc} - \phi_D)}{\sum_{j=1}^{m} S_{Dj}/\phi_D} \tag{7}$$

where

$$S_{Dc} = \sum_{ij}\left(y_{ij} - \widehat{y}_{ij,c}\right)^2 \tag{8}$$

$$S_{Dj} = \sum_{i=1}^{n}\left(y_i - \widehat{y}_i\right)^2 \tag{9}$$

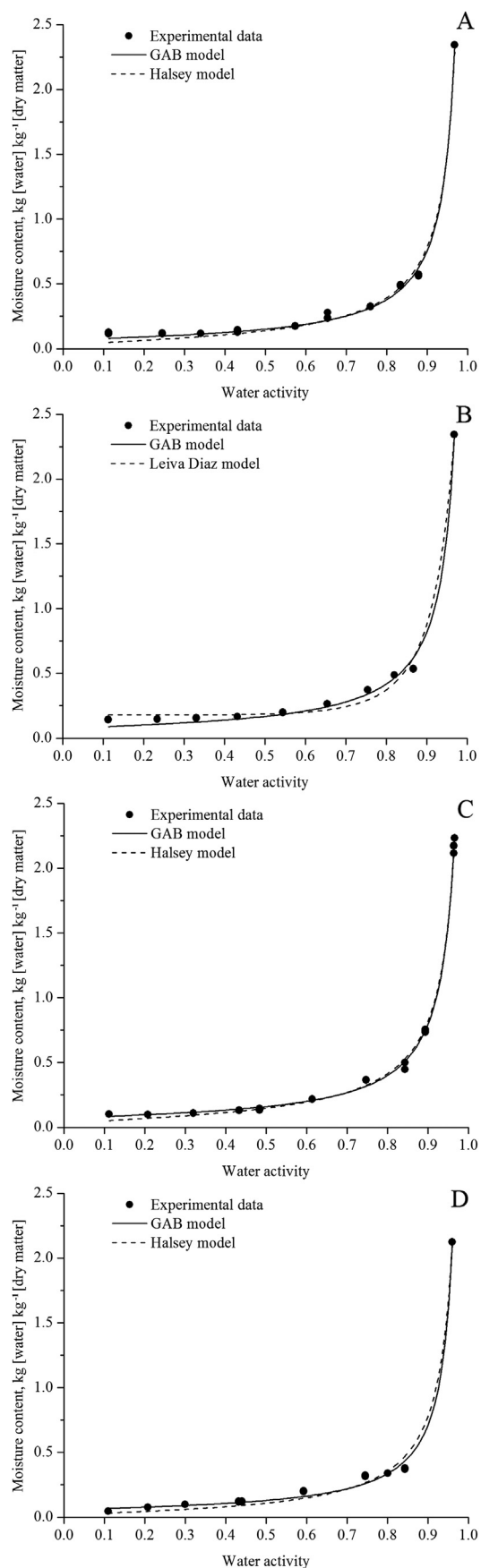$$\phi_{Dc} = \sum_{j=1}^{m} n_j - p \tag{10}$$

$$\phi_D = \sum_{j=1}^{m} n_j - p*m \tag{11}$$

As shown in Eq. (8), S_{Dc} is the combined sum of squared deviations, considering all data fitted by a single group of parameters, where y_{ij} is every experimental value of moisture content and $\hat{y}_{ij,c}$ is the corresponding model-calculated value for combined data. On the other hand, S_{Dj} (Eq. (9)) is the sum of squared deviations in each set of data (i.e., for a given temperature or composition), being y_i the experimental moisture content and $\hat{y}_i$ the value predicted by each group of fitting parameters. The degrees of freedom are calculated by Eqs. (10) and (11), where n_j is the number of data in each set, p is the number of fitting parameters and m is the number of data sets to be compared.

To provide a detailed comparison of curves at specific a_w levels, a two-way analysis of variance (ANOVA) with $\alpha = 0.05$ was conducted point-by-point in the range of a_w from 0.11 to 0.86 (i.e., an ANOVA for every data set corresponding to each a_w level). Such analysis allows the evaluation of data in

Fig. 1 – Photographs of rosehip fruits (A), sucrose-added formulation (B) and a rosehip leather obtained by hot-air drying (C).

Fig. 2 − Desorption isotherms for sucrose-added formulation at 10 °C (A), 20 °C (B), 40 °C (C) and 60 °C (D). Symbols represent experimental data and lines, the two most accurate models for each data set.

particular zones of the curve, especially those where product stability is critical. When significant differences were detected by ANOVA, the mean moisture contents were compared by the Fisher test ($\alpha = 0.05$).

3.   Results and discussion

3.1.   Characteristics of the rosehip formulations

The rosehip formulations added with sucrose or polydextrose are described in Table 3. Their compositions, except moisture content, were calculated by mass balances using as data the contents of components in the ingredients. The composition of the rosehip pulp was experimentally determined, while added sucrose (sugars), polydextrose (soluble fibre) and citric acid were considered as total carbohydrates. Differences between the sum of components and the theoretical total (100%) were lower than the standard deviation of moisture content for each formulation. This indicates that calculated data were reliable. The amount of total carbohydrates was the same for both formulations. Nevertheless, soluble solids in SAF were mainly simple sugars (those from rosehip pulp plus added sucrose), while carbohydrates in PAF were predominantly polysaccharides (mostly soluble fibre provided by polydextrose). Applying a t-test with 95% confidence level, no significant difference was found between the initial moisture content of both formulations. However, the water activity of SAF did prove to be significantly lower than that of PAF ($p = 0.03$), which suggest that interactions between water and solids depend on the saccharide used. Fig. 1 shows photographs of rosehip fruits, sucrose-added formulation and a rosehip leather obtained by hot-air drying.

3.2.   Experimental desorption isotherms

The time elapsed until reaching practical equilibrium (see Section 2.4) varied between 7 days for isotherms measured at 60 °C, and 90 days at 10 °C. Experimental data for the rosehip formulation added with sucrose at every temperature is shown in Fig. 2, while the corresponding data for polydextrose-added formulation is presented in Fig. 3. The two most accurate model predictions for each curve are also illustrated. Experimental isotherms were J-shaped, corresponding to type III in the BET classification (Brunauer et al., 1940), as expected for matrices containing a high-soluble solids content (Iglesias & Chirife, 1982). For all formulations and temperatures, water activities were extremely sensitive to changes in moisture content, in the low water activity range. However, a less pronounced variation of a_w was observed as moisture content changes in the range of high
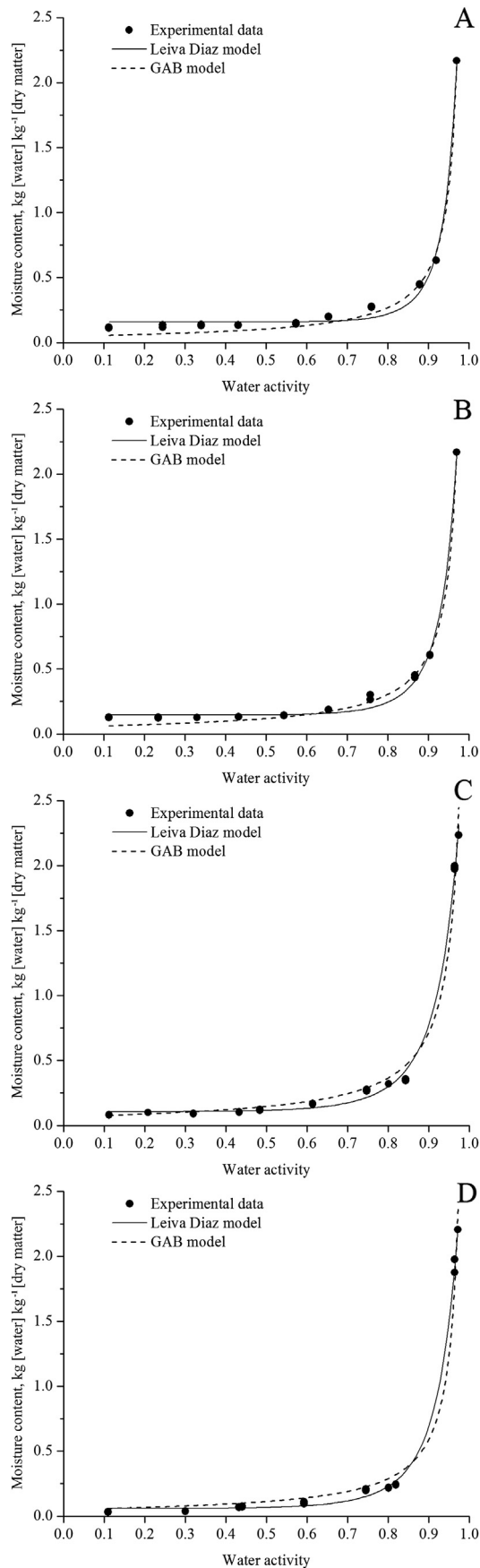
water activities. A similar sorptional behaviour has been reported for several fruits and high-sugar foods (Djendoubi Mrad, Bonazzi, Boudhrioua, Kechaou, & Courtois, 2012a; Kaya & Kahyaoglu, 2005; Tsami et al., 1990; Vullioud, Márquez, & De Michelis, 2006).

3.3. Output of mathematical models

Table 4 includes parameters of the models tested for representing the observed behaviour, along with their corresponding goodness-of-fit indices. For all the temperatures studied, the GAB model gave the best representation of experimental data (maximum r^2 and minimum E_{RMS}) for the sucrose-added formulation, whereas the Leiva Díaz et al. (2009) model (hereafter "Leiva Díaz model") revealed as the most accurate (same criteria) for the polydextrose-added formulation. In spite of presenting the best fitting for SAF, the GAB model showed a slight underestimation of the moisture content around the food security zone (a_w from 0.6 to 0.8) at all temperatures (see Fig. 2). The same was observed for the Leiva Díaz model in PAF (Fig. 3). Illustrations show clearly that the GAB equation could also be used to predict the safe moisture content of PAF at 10 °C and 20 °C (Fig. 3A and B). However, at higher temperatures the Leiva Díaz model is still the best option for PAF, as the GAB estimations are higher than experimental data (Fig. 3C and D). Table 5 lists the values of safe moisture content, i.e., the values calculated for $a_w = 0.7$, predicted by the two most accurate models, for each formulation and temperature. Fitting has revealed that parameter k from the GAB equation is very close to unity so that, in practice, the GAB and BET models tend to coincide for these formulations. Given that moisture content increases sharply for a_w above 0.9, values of k higher than unity can be determined by the fitting procedure. Such values bear no physical meaning, as they correspond to an isotherm whose moisture content tend to infinity for a_w lower than unity (Chirife, Timmermann, Iglesias, & Boquet, 1992). For that reason, and especially in J-shaped isotherms, the use of the GAB model is recommended for a_w below 0.95 (Labuza & Altunakar, 2007). Values of $k > 1$ were nevertheless reported without comment by Bronlund and Paterson (2004) for amorphous lactose powder, Djendoubi Mrad et al. (2012a) for pears and apples, Giovanelli et al. (2002) for dried tomato products, and Kim, Kim, Kim, Shin, and Chang (1998) for strawberry jam, among others.

3.4. Effect of composition on isotherms

When comparing the isotherms of sucrose- and polydextrose-added formulations in Fig. 4, a similar effect was observed for all temperatures: curves for PAF were always below those of SAF, i.e., the polydextrose-added matrix showed lower moisture contents than the sucrose-added formulation for given a_w. Results of the statistical F-test ($P < 0.01$) confirmed that the

Fig. 3 – Desorption isotherms for polydextrose-added formulation at 10 °C (A), 20 °C (B), 40 °C (C) and 60 °C (D). Symbols represent experimental data and lines, the two most accurate models for each data set.

Table 4 – Fitting parameters of the models which describe the desorption isotherms for both formulations at the studied temperatures. Values in parenthesis are the standard deviations of the corresponding parameters.

Formulation	Model	Temperature (°C)			
		10	20	40	60
Sucrose-added	**Halsey**				
	A	0.0808 (0.0015)	0.0854 (0.0020)	0.0845 (0.0010)	0.0829 (0.0018)
	R	1.0880 (0.0216)	1.1620 (0.0280)	1.1001 (0.0148)	0.9570 (0.0251)
	r^2	0.989	0.983	0.998	0.985
	E_{RMS}	0.0446	0.0554	0.0325	0.0496
	GAB				
	W_M	0.0760 (0.0018)	0.0853 (0.0027)	0.0809 (0.0014)	0.0647 (0.0022)
	C	100.000 (0.000)	100.000 (0.000)	100.000 (0.000)	100.000 (0.000)
	k	0.9995 (0.0008)	0.9953 (0.0012)	0.9982 (0.0006)	1.0099 (0.0010)
	r^2	0.995	0.990	0.999	0.993
	E_{RMS}	0.0306	0.0430	0.0243	0.0349
	Leiva Díaz				
	C_1	0.1510 (0.0129)	0.1797 (0.0131)	0.1384 (0.0120)	0.1173 (0.0158)
	C_2	3.3818 (0.0799)	3.1730 (0.0703)	3.4111 (0.0789)	3.6832 (0.1170)
	C_3	6.5271 (0.4353)	6.5833 (0.4446)	5.9514 (0.3574)	5.9245 (0.5957)
	r^2	0.986	0.985	0.995	0.980
	E_{RMS}	0.0524	0.0531	0.0502	0.0588
	Oswin				
	D	0.1194 (0.0086)	0.1447 (0.0115)	0.1282 (0.0071)	0.0921 (0.0086)
	F	0.8670 (0.0243)	0.8086 (0.0272)	0.8550 (0.0176)	0.9821 (0.0325)
	r^2	0.980	0.969	0.995	0.978
	E_{RMS}	0.0615	0.0752	0.0486	0.0615
Polydextrose-added	**Halsey**				
	A	0.0628 (0.0018)	0.0667 (0.0018)	0.0711 (0.0022)	0.0636 (0.0015)
	R	0.9881 (0.0399)	1.0418 (0.0364)	1.0862 (0.0407)	0.9346 (0.0314)
	r^2	0.968	0.982	0.986	0.992
	E_{RMS}	0.0746	0.0618	0.0818	0.0573
	GAB				
	W_M	0.0527 (0.0022)	0.0604 (0.0022)	0.0747 (0.0046)	0.0571 (0.0041)
	C	100.000 (0.000)	100.000 (0.000)	100.000 (0.000)	100.000 (0.000)
	k	1.0057 (0.0010)	1.0021 (0.0010)	0.9954 (0.0020)	1.0039 (0.0014)
	r^2	0.985	0.992	0.987	0.987
	E_{RMS}	0.0503	0.0404	0.0786	0.0731
	Leiva Díaz				
	C_1	0.1576 (0.0108)	0.1455 (0.0094)	0.1077 (0.0116)	0.0592 (0.0089)
	C_2	3.6235 (0.0775)	3.4975 (0.0637)	3.5515 (0.0925)	4.1832 (0.1301)
	C_3	10.7056 (0.6254)	8.5180 (0.4208)	5.5691 (0.4076)	5.0427 (0.4122)
	r^2	0.988	0.994	0.996	0.997
	E_{RMS}	0.0467	0.0357	0.0415	0.0322
	Oswin				
	D	0.0691 (0.0102)	0.0850 (0.0112)	0.1054 (0.0118)	0.0652 (0.0075)
	F	0.9789 (0.0479)	0.9252 (0.0420)	0.8714 (0.0337)	1.0116 (0.0339)
	r^2	0.955	0.970	0.986	0.992
	E_{RMS}	0.0883	0.0784	0.0832	0.0566

composition has a significant effect on the sorptional behaviour for every temperature studied, indicating that sucrose was more effective than polydextrose for lowering a_w at the same moisture content. This could be explained by the water-binding capacity per unit mass of the disaccharide, which is higher than that of the polymer. Sucrose has a molar mass of 342 g mol^{-1}, with 8 hydroxyl groups available for binding water molecules by hydrogen bonds. However, in the highly

Table 5 – Values of safe moisture content, expressed as kg [water] kg^{-1} [dry matter], predicted for $a_w = 0.7$ by the two most accurate models for each formulation and temperature (the corresponding models are indicated in parenthesis).

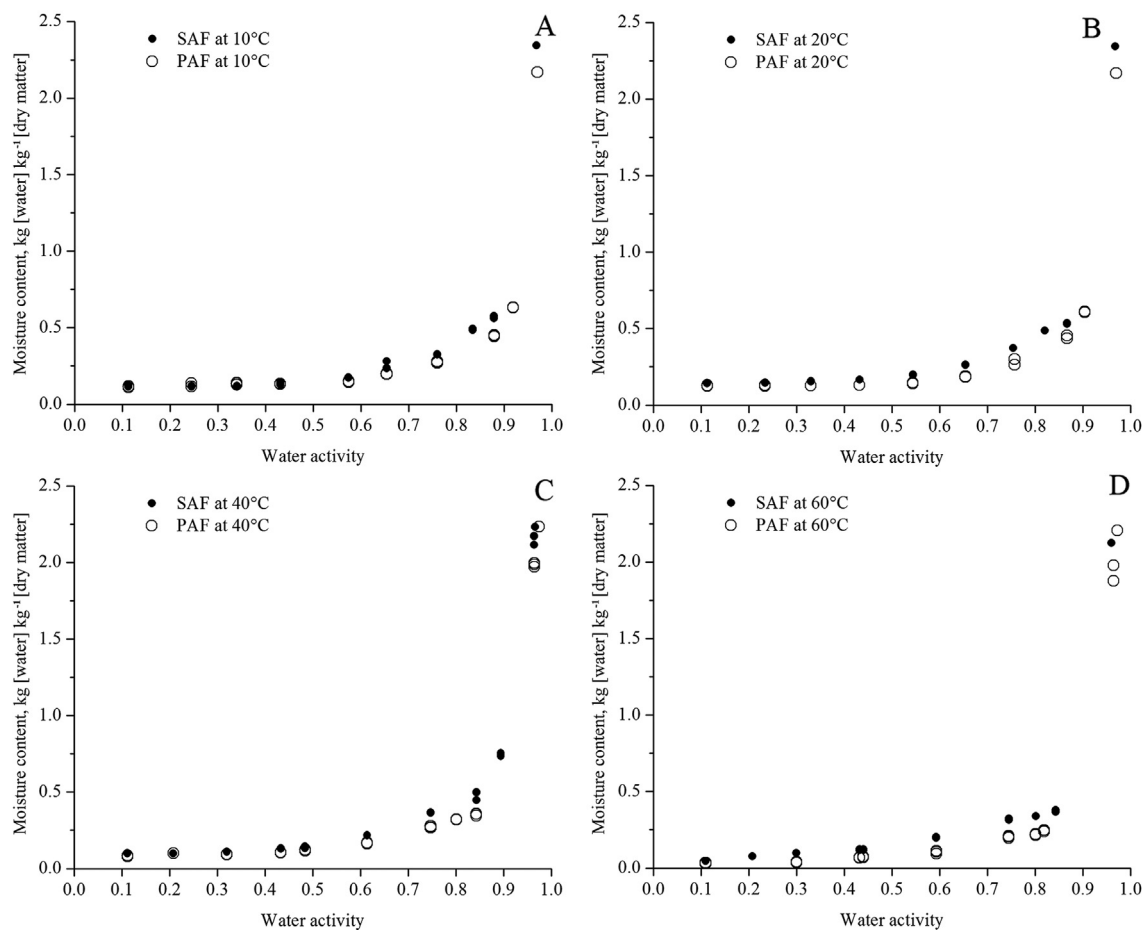| Formulation	Temperature (°C)			
	10	20	40	60
Sucrose-added	0.252 (GAB)	0.280 (GAB)	0.267 (GAB)	0.220 (GAB)
	0.256 (Halsey)	0.243 (Leiva Díaz)	0.270 (Halsey)	0.218 (Halsey)
Polydextrose-added	0.171 (Leiva Díaz)	0.172 (Leiva Díaz)	0.175 (Leiva Díaz)	0.118 (Leiva Díaz)
	0.177 (GAB)	0.201 (GAB)	0.245 (GAB)	0.191 (GAB)

Fig. 4 – Desorption isotherms obtained for rosehip formulations added with sucrose (solid symbols) and polydextrose (open symbols) at 10 °C (A), 20 °C (B), 40 °C (C) and 60 °C (D).

branched molecule of polydextrose, many of the hydroxyl groups of glucose are implicated in the random links between glucose units, as can be seen in Fig. 5. This illustration shows 11 glucose monomers randomly connected by 10 glycosidic bonds, which result in a 1800 g mol^{-1} unit with 34 free hydroxyl groups. The ratio of hydroxyl groups to molar mass is therefore of 0.0234 in sucrose, and 0.0189 in polydextrose. Moreover, this ratio varies in polydextrose from 0.0172 for a
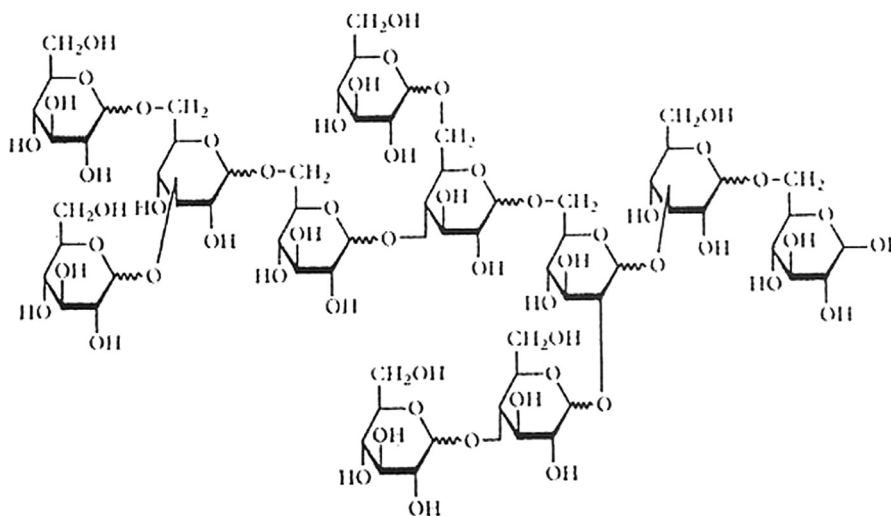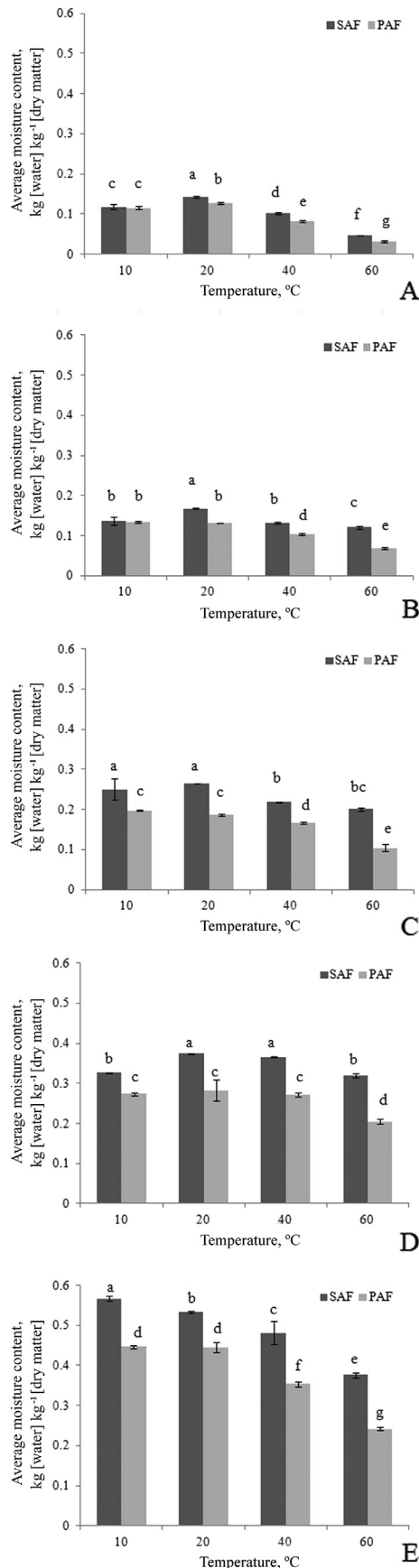

Fig. 5 – Molecular structure of polydextrose (R=H, glycosyl group or more branched polymer).

highly branched zone of the polymer to 0.0210 for linearly linked glucose units, but never reaches the value of sucrose. So, for a given moisture content and temperature, a specific mass of sucrose is likely to bind more water than the same mass of polydextrose, resulting in lower a_w. This trend was also observed by Kaymak-Ertekin and Gedik (2004) when comparing desorption isotherms of high-sugar samples, as grapes (78–82 g [sugar] 100 g^{-1} [dry solids]), and polysaccharide-rich matrices, as potatoes (77–84 g [starch] 100 g^{-1} [dry solids]). A more detailed analysis was conducted by the ANOVAs and Fisher tests performed point-by-point. The outcome was that the interaction of composition and temperature effects was significant ($P < 0.05$) in the range of a_w from 0.11 to 0.86. Isotherms at 10 °C were not affected by composition for a_w lower than 0.432 (see Fig. 4A). As the equilibration time for isotherms at 10 °C was relatively long (56–90 days), it is possible that a substantial sucrose crystallization occurred in moderate and low water activity samples, reducing the water-binding capacity of SAF for a_w lower than 0.432 (Chinachoti & Steinberg, 1984). Thus, no differences between the two formulations were found at 10 °C in this range of a_w. Additionally, this kinetic phenomenon would also justify the results obtained when analysing the temperature effect on isotherms (following section). For isotherms at 20, 40 and 60 °C the effect of composition was significant for the entire a_w range and also increased with a_w. Moreover, the effect of composition was slightly stronger at 60 °C. Although these results can be deduced from the isotherms in Fig. 4, the differences between formulations can be more easily seen from the interaction plots (Fig. 6A–E), where the average moisture content for every formulation and temperature is represented at various a_w levels. As the food security zone is affected by composition, the final moisture content for drying, or drying endpoint of the rosehip leather prepared with the sucrose-added formulation, will be higher than that of the alternative polydextrose-added product. Even for the same a_w value, the polydextrose-added leather might be more stable than the sucrose-added matrix during storage, because of its lower moisture content and likely higher glass transition temperature (Roos & Karel, 1991).

3.5. Effect of temperature on isotherms

In Fig. 7A and B isotherms were grouped by composition in order to visualise the sorption behaviour as affected by temperature. Since the difference between curves was not clear, a change of scale was proposed in Fig. 7C and D, considering the range of a_w from 0.11 to 0.80. For the polydextrose-added formulation, the effect of temperature seems to be mostly as expected, with lower moisture contents retained by isotherms measured at higher temperature, at constant water activity. Isotherms for sucrose-added formulation seem to be very close

Fig. 6 – Average moisture content for every formulation and temperature at diverse a_w levels: a_w = 0.112 (A), a_w = 0.432 (B), a_w = 0.629 (C), a_w = 0.751 (D) and a_w = 0.855 (E). The error bars correspond to the standard deviation and different letters indicate significantly different values ($P < 0.05$).
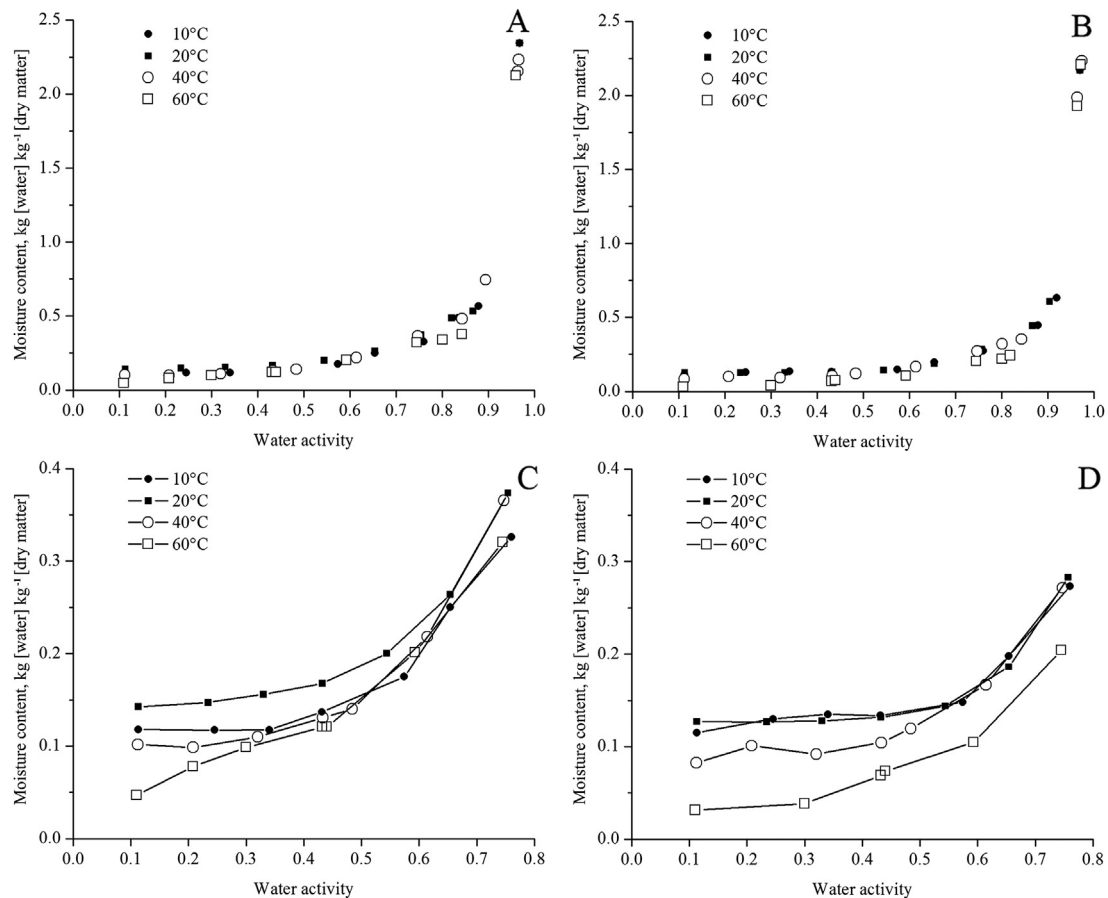
Fig. 7 — Desorption isotherms obtained for rosehip formulations added with sucrose (A) and polydextrose (B) at various temperatures, in the complete range of water activities. (C) and (D) are the corresponding versions for a narrower water activity range (from 0 to 0.8). Symbols represent experimental data. In (C) and (D), symbols were connected by straight line segments for an easier inspection of the data trend.

one to another, although that corresponding to 60 °C showed a lower moisture content. The results of the F-test ($P < 0.01$) revealed that the effect of temperature was more noticeable on PAF, for which isotherms measured at all temperatures were significantly different, than on SAF, for which only the isotherm at 60 °C differed from the others. When the F-test was performed in a reduced a_w range, from 0.11 to 0.80 (see Fig. 7C and D), the results were not the same ($P < 0.01$): isotherms for SAF at all temperatures were found to be different, with a crossover observed around a_w of 0.65. In turn, curves for PAF at 10 °C and 20 °C did not differ significantly, as observed clearly in Fig. 7D and also in Fig. 6, which illustrate the results of ANOVAs and Fisher tests performed point-by-point. This detailed analysis showed that the temperature effect seems to be stronger at lower a_w values. Moreover, for a_w from 0.6 to 0.8, only the isotherm for PAF at 60 °C differed from the other PAF curves. As we said before, isotherms for sucrose-added formulation did not present a clear tendency on relation to temperature. This may happen because curves are affected by the sugar crystallization, a kinetic phenomenon, so the effect of time on these isotherms prevails over the conventional effect of temperature. At 60 °C, when practical equilibrium is quickly reached by desorption (7–10 days), the rapid water loss and consequent increase in the viscosity of the matrix (already

accentuated by added sucrose), may be sufficient to reduce the mobility of sugar molecules and thus avoid crystallization (Chinachoti & Steinberg, 1986). Conversely, as sorption equilibrium is slowly reached by desorption at 10 °C (56–90 days), although the mobility of sugar molecules is reduced by temperature, the time may be sufficiently long to allow the transition from amorphous to crystalline, less hygroscopic form (Djendoubi Mrad, Bonazzi, Boudhrioua, Kechaou, & Courtois, 2012b). This may explain why the SAF desorption isotherm at 10 °C exhibited a lower moisture content than expected (see Fig. 7C). As polydextrose does not crystallize, the effect of temperature on PAF isotherms was easier to follow, explained by the higher mobility of water molecules at higher temperatures, in agreement with predictions of the widely accepted theory of physical adsorption.

4.   Conclusions

Experimental desorption isotherms for rosehip leather formulations with added sucrose or polydextrose were all J-shaped, corresponding to type III in the BET classification. The GAB equation and the Leiva Díaz model gave the best representation of data for SAF and PAF, respectively, in the temperature range

from 10 to 60 °C. Both models showed a slight underestimation of the safe moisture content, which is in any case conservative for food safety, and were highly accurate in general for describing the sorptional behaviour of the material under study. A given mass of sucrose proved to be more effective than the same mass of polydextrose for lowering the water activity of the formulation, except under conditions that may lead to sugar crystallization. A conventional effect of temperature was observed on isotherms of the polydextrose-added matrix, which remains in amorphous form. However, the temperature effect on the sorptional behaviour of SAF was affected by sucrose crystallization at low a_w values. As fruit leathers have a shelf life of several months, sucrose crystals may appear in dehydrated rosehip leathers during storage. This feature should be investigated further as it would affect the sorption properties of rosehip leathers.

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