Moisture sorption isotherms and thermodynamic properties of mexican mennonite-style cheese

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Abstract Moisture adsorption isotherms of fresh and ripened Mexican Mennonite-style cheese were investigated using the static gravimetric method at 4, 8, and 12 °C in a water activity range (a_w) of 0.08–0.96. These isotherms were modeled using GAB, BET, Oswin and Halsey equations through weighed non-linear regression. All isotherms were sigmoid in shape, showing a type II BET isotherm, and the data were best described by GAB model. GAB model coefficients revealed that water adsorption by cheese matrix is a multilayer process characterized by molecules that are strongly bound in the monolayer and molecules that are slightly structured in a multilayer. Using the GAB model, it was possible to estimate thermodynamic functions (net isosteric heat, differential entropy, integral enthalpy and entropy, and enthalpy-entropy compensation) as function of moisture content. For both samples, the isosteric heat and differential entropy decreased with moisture content in exponential fashion. The integral enthalpy gradually decreased with increasing moisture content after reached a maximum value, while the integral entropy decreased with increasing moisture content after reached a minimum value. A linear compensation was found between integral enthalpy and entropy suggesting enthalpy controlled adsorption. Determination of moisture content and a_w relationship yields to important information of controlling the ripening, drying

and storage operations as well as understanding of the water state within a cheese matrix.

Keywords Mexican Mennonite-style cheese · Adsorption isotherms · Thermodynamic properties · Compensation theory · Sorption models · Weighed non-linear regression

Nomenclature

A	constant of the eq. (8) (J/mol).
A_m	area that occupies one single water molecule at monolayer ($1.06 \times 10^{-19} \text{ m}^2$).
a_w	water activity (dimensionless).
a_{Oswin}	Oswin parameters (dimensionless).
b	
a_{Halsey}	Halsey parameter (dimensionless).
r	
C_G	GAB parameter (dimensionless).
C_B	BET parameter (dimensionless).
$C_{G,0}$	pre-exponential factor in C_G (dimensionless)
E	mean relative percentage deviation modulus (%).
H_1	molar enthalpy of sorbed molecules in the monolayer (kJ/mol).
H_m	molar enthalpy of sorbed molecules in the multilayer (kJ/mol).
H_L	molar enthalpy of condensation of bulk liquid water (kJ/mol).
k	Boltzmann constant ($1.38 \times 10^{-23} \text{ J/K}$).
$k_{G,0}$	pre-exponential factor in k_G (dimensionless).
k_G	GAB parameter (dimensionless).
m	moisture content of cheese sample (g of water/g of solid).
MSI	moisture sorption isotherm.
m_e	experimental moisture content.
m_p	predicted moisture content.
m_0	pre-exponential factor in $m_{0,G}$ (dimensionless).

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$m_{o,G}$	monolayer moisture content obtained with GAB eq. (g of water/g of solid).
$m_{o,B}$	monolayer moisture content with BET eq. (g of water/g of solid).
N	number of experiments.
n	number of isotherms.
R	universal gas constant (8.32 J/mol K).
R^2	coefficient of determination.
SE	standard error
T	absolute temperature (K).
T_B	isokinetic temperature (K).
T_{hm}	harmonic temperature.
ΔH_k	difference in enthalpy between bulk liquid water and multilayer (kJ/mol).
ΔH_C	difference in enthalpy between monolayer and multilayer (kJ/mol).
ΔH_m	constant to express temperature dependence of $m_{o,G}$ (kJ/mol).
ΔH_{is}	isosteric enthalpy of sorption (J/mol).
ΔH_{in}	integral enthalpy of sorption (J/mol).
ΔS_{is}	isosteric entropy of sorption (J/mol K).
ΔS_{in}	integral entropy of sorption (J/mol K).
Φ	spreading pressure (J/m ²).

Introduction

Mexican Mennonite-style cheese or Chihuahua cheese is a typical product of the northern of Mexico. It is mildly flavoured semihard cheese and it is usually consumed within 6 months after manufacture (Van Hekken et al. 2006). This cheese is widely consumed in Mexico through the retail and food service sectors to prepare cheese-based products and processed cheeses. As an ingredient, Chihuahua cheese is usually blended with other ingredients using thermal and mechanical treatments, such as to portioning, shredding, heating, and freezing.

Searching alternatives for extending the applicability of Chihuahua cheese, several authors have characterized its manufacturing procedures (Tunick et al. 2008), rheological (Van Hekken et al. 2007), sensorial, and texture properties (Van Hekken et al. 2006). The response of these properties to a particular treatment determinates the final cheese application. Consequently, the functionality of cheese is strongly influenced by the water content and how water molecules interact with other cheese components (Guinee 2002). The relationship between water content and its degree of availability within a food system has a critical role in food engineering applications. A graphical representation of this relationship at constant temperature is known as moisture sorption isotherms (MSI) (Bell and Labuza 2000). An investigation of low fat cheese made with resistant starch as

fat replacer showed that MSI can be used to evaluate the water binding capacity within cheese matrix. More importantly, using MSI at different temperatures, the authors were able to separate the water binding contribution of casein proteins from the starch (Duggan et al. 2008). Others authors have develop empirical models to estimate a_w during salting and ripening steps of Emmental cheese (Pajonk et al. 2003a,b; Saurel et al. 2004). In their models, the MSI obtained at various temperatures, positions and processing stages were correlated to NaCl content and free NH_2 group concentration. These authors concluded that these models can be used to simulate heat and mass transfer in Emmental cheese production.

Fundamental thermodynamic of an idealized system has been used to understand the role of water on food surfaces and to calculate the energy requirements for heat and mass transfer operations (Alam and Singh 2011; Jain et al. 2010; Fasina 2006). This approach is based on the estimation of sorption energy from MSI moisture sorption by applying the Clausius-Clapeyron and Gibbs-Helmholtz theories. The energy of sorption is expressed in terms of isosteric enthalpy (ΔH_{is}) and entropy (ΔS_{is}) of sorption, integral enthalpy (ΔH_{in}) and entropy (ΔS_{in}) (Benado and Rizvi 1985). In addition to this approach, changes in sorption energy can be related by the compensation or isokinetic theory, which yields a linear relationship between enthalpy and entropy.

Experimental data on sorption isotherms are essential for controlling ripening, drying and storage operations as well as understanding of the water state within a cheese matrix. In addition, moisture adsorption isotherms of Mexican Mennonite-style cheese have not been reported. Therefore, the objectives of this work were to determine experimental sorption isotherm data of Mennonite-style cheese, to evaluate the applicability of existing sorption models and to use the best fitted sorption model to estimate the thermodynamic functions.

Materials and methods

Sample preparation and compositional analysis

The Mexican Mennonite-style cheeses used in this study were manufactured in a local dairy plant using pasteurized milk. Cheeses from the same batch were stored at 4 °C and divided in two groups, one was kept for 10 d (fresh cheese) and the other was kept for 6 m (ripened cheese). A sample of each group was tested for pH, moisture, fat, protein, salt, and water activity (a_w). The pH was measured using an electrode with stainless steel blade for cheese penetration (Microprocessor pH meter 210, Hanna Instruments, Ronchi di Villafrance, Italy). Cheese moisture was determined in 5 g of cheese with

moisture analyzer (Sartorius Model MA145, Goettingen, German). Fat, protein, and salt content were determined using a Milko scan FT 120 (Foss Electric, Hillerød, Denmark). The a_w was measured with a hygrometer (Novasina IC-500AW-Lab, Talstrasse, Switzerland) (precision ± 0.001). Cheeses samples from fresh and ripened were hand shredded, freeze-dried (Model 794080, Labconco Corporation, Kansas City, MI) and stored in a desiccator at room temperature until used.

Moisture sorption isotherms

The gravimetric static method was used to determine the MSI of fresh and ripened cheeses. The methodology guidelines are described by Bell and Labuza (2000). Freeze-dried cheeses, 3 ± 0.05 g, were placed in a dessicator at different controlled relative humidity regulated by saturated salt aqueous solutions. Nine saturated salts were used to provide the desirable humidity in the range of 8–96 % and were prepared by dissolving predetermined quantities of NaOH, CH_3COOK , MgCl_2 , K_2CO_3 , NaBr, NaCl, KCl, BaCl_2 and KH_2PO_4 (J.T. Baker, USA) in distilled water. The systems, cheese and saturated salt, were stored in temperature controlled room (4, 8 or 12 °C) until reach equilibrium (30 d). Once the equilibrium was reached, the samples were weighed to determinate the moisture content. All experiments were done in triplicate. The equilibrium moisture content, expressed as g water/g of solids, were plotted against a_w to obtain MSI. The MSI were estimated by fitting GAB, BET, Oswin and Halsey equations to experimental data.

$$m = \left(\frac{m_{o,G} C_G k_G a_w}{(1 - k_G a_w)(1 - k_G a_w + k_G C_G a_w)} \right) \quad (1)$$

$$m = \left(\frac{m_{o,B} C_B a_w}{(1 - a_w)(1 - a_w + C_B a_w)} \right) \quad (2)$$

$$m = a_{\text{Oswin}} \left(\frac{a_w}{(1 - a_w)} \right)^b \quad (3)$$

$$m = \left(\frac{a_{\text{Halsey}}}{\ln a_w} \right)^{1/r} \quad (4)$$

Where m is equilibrium moisture content (g of water/g of solid); m_o is the monolayer moisture content (g of water/g of solid) obtained by either GAB or BET equations; C_G and k_G are constants of GAB equation; C_B are constants of BET equation; a_{Oswin} and b are constants of Oswin equation; a_{Halsey} and r are constants of Halsey equation.

Thermodynamic properties

Differential properties

The isosteric enthalpy (ΔH_{is} , kJ/mol) and entropy (ΔS_{is} , J/mol K) of sorption were estimated using the equation of Gibbs-Helmoltz in the form (Fasina et al. 1999):

$$(\ln a_w)_m = -\frac{\Delta H_d}{RT} + \frac{\Delta S_d}{R} \quad (5)$$

Where R is the universal gas constant (8.31 J/mol K); T is the absolute temperature (K). After plotting $\ln(a_w)$ against $1/T$ for a given moisture content, the ΔH_{is} and ΔS_{is} could be determined directly from the slope and intercept of the curve, respectively.

Integral properties

According to Benado and Rizvi (1985), the integral enthalpy (ΔH_{in} , kJ/mol) and entropy (ΔS_{in} , J/mol K) should be calculated at constant spreading pressure (Φ , J/m²). The Φ of Mennonite-style cheese at different temperatures can be calculated using the eq. (6):

$$\phi = \frac{kT}{A_m} \int_0^{a_w} \frac{m}{m_0 a_w} \quad (6)$$

Where k is Boltzman constant (1.38×10^{-23} , J/K); A_m is the area that occupies one single water molecule at monolayer (1.06×10^{-19} m²). Combining eq. (6) with (1), Liebanes et al. (2006) mathematically expressed the Φ in the form of GAB equation:

$$\phi = \frac{kT}{A_m} \ln \left[\frac{1 - k_G a_w + k C_G a_w}{1 - k_G a_w} \right] \quad (7)$$

Using the Clausius-Clapeyron equation in the form of eq. (8), the ΔH_{in} and ΔS_{in} were obtained from the slope and the intercept after plotting $\ln a_w$ against $1/T$ at constant Φ (Fasina 2006; Liebanes et al. 2006).

$$-(\ln a_w)_\phi = \frac{\Delta H_{in}}{RT} + \frac{\Delta S_{in}}{R} \quad (8)$$

Compensation theory

The isokinetic theory correlates the ΔH_{in} and ΔS_{in} values obtained from equation (8) according to following equation (Madamba et al. 1996):

$$\Delta H_d = T_B (\Delta S_d) + A \quad (9)$$

Where T_B is the isokinetic temperature and A is a constant (J/mol) at T_B . (Krug et al. 1976) reported that T_B

should be compared to the harmonic mean temperature (T_{hm}):

$$T_{hm} = \frac{n}{\sum \left(\frac{1}{T}\right)} \quad (9)$$

Where n is the total of number of used isotherms.

Statistical analysis

The regression parameters were calculated through weighed non-linear regression analysis using Sigmaplot software V11 for windows (SPSS Inc., Chicago, IL, USA). The predictive capability of the individual models was assessed by the coefficient of determination (R^2), standard error (SE), and mean relative percentage deviation modulus (E) expressed by:

$$E = \frac{100}{N} \sum \frac{|m_e^i - m_p^i|}{m_e^i} \quad (10)$$

Where m_e is the experimental value of moisture content; m_p is the predicted moisture content and N is the number of experiments. All data were collected in triplicate and are reported as mean values and standard deviation. Tukey test was used to differentiate between samples.

Results and discussion

Cheese composition

Table 1 shows compositional characteristics of fresh and ripened cheese. No important compositional differences between fresh and ripened samples were observed, except for pH and a_w parameters. As expected, higher pH and a_w values were observed in ripened. During ripening, a progressive hydrolysis of *para*-casein leads to a formation of α -carboxylic and α -amino groups, increasing the water binding capacity of cheese matrix which reduces the free water or a_w (Kaya and Oner 1996; McSweeney et al. 2006). The values of moisture, fat, protein, salt, and pH are similar to those reported by Van Hekken et al. (2007). Tunick et al. (2008) found manufacturing protocols of Mexican Mennonite-style cheese are quite diverse between dairy plants, depending on equipment availability.

Moisture sorption isotherms

Moisture sorption isotherms of fresh and ripened cheese at 4, 8 and 12 °C are shown in Fig. 1. The experimental curves of both samples were sigmoid in shape following a type II isotherm. In addition, experimental data showed a relatively large variance at high a_w (>0.80). This phenomenon is not

surprising since it is difficult to reach equilibrium at such a_w levels as reported by several authors (Coskun-Dalgic et al. 2011; Quirijns et al. 2005a; Maroulis et al. 1988; Samaniego-Esguerra et al. 1991). This type of isotherms is characteristic of a localized multilayer adsorption in which two macroscopic phases are distinguished: solid and gas. Water molecules are adsorbed in layers whose thickness increases with increasing a_w (Quirijns et al. 2005b). At low a_w levels, the initial water adsorption results from a combination of chemical and physical forces. The proteins hydration and salts solubilisation within cheese surface form the first shell of water (monolayer), which is function of the availability and amount of hydrophilic or low energy sorption sites (Jena and Das 2011; McMinn and Magee 1997). At high a_w , the water is progressively adsorbed in subsequent layers (multilayer) by physical forces such hydrogen bonds, van der Waals and ionic attractions, having less interaction with the sorbent surface and exhibiting more properties of bulk liquid (Myers 2002).

Figure 1 also shows the effect of temperature on moisture sorption isotherm. As the temperature increases, the moisture content decreases for a given a_w value. Exceptions to this generalization were observed in fresh and ripened cheese at 8 °C and 0.96 of a_w , where the moisture content was higher than the moisture content at 4 °C and 0.96 of a_w . Similar temperature effect on adsorption isotherm was reported in Sbrinz (Ruegg 1985) and Gaziantep (Kaya and Oner 1996) cheeses. It appears that the temperature influences the excitation state and mobility of water molecules. As temperature increases, the distance between adsorbed and sorption site increases, consequently, reducing the attractive forces (van der Waals forces) and lowering the moisture content (Quirijns et al. 2005a).

Sorption isotherms modeling

The GAB, BET, Oswin and Halsey models were fitted to experimental data through weighed non-linear regression analysis and the results are given in Table 2. The R^2 , SE, and E are commonly used in the literature to evaluate the goodness of fit of sorption models (Rakshit et al. 2011; Arslan and Togrul 2006). R^2 indicates how well the variability has been explained by the given model, the SE is a measure of how precisely the parameters have been estimated and E values are indicative of reasonable good fitting when $E < 10\%$. The GAB and Oswin models present the best fitting performance throughout the entire experimental domain (having the highest R^2 , and lowest SE and E values), followed by BET and Halsey models. In addition, the standardized residual against predicted values obtained with GAB and Oswin models showed no systematic pattern (graph not shown), allowing the estimation of model parameters, error standard, and prediction of new observation

Table 1 Comparison of compositional parameters of samples used in this study with values reported in the literature for Mexican Mennonite-style cheese

Parameters	Fresh	ripened	Reported values by Van Hekken et al. (2007)
Moisture (%)	42.2±1.51a	41.1±1.24a	42.1±1.46
Fat (%)	31.7±1.55a	32.3±0.56a	31.5±0.84
Protein (%)	23.8±0.97a	24.9±0.31a	25.2±1.22
pH	5.04±0.11a	5.00±0.09b	5.15±0.19
Salt (%)	1.9±0.96a	1.7±0.74a	NR
Water activity	0.96±0.001a	0.95±0.002b	NR
Ripening index	20.5±1.66a	49.4±0.91b	NR

Mean±standard deviation ($n=3$) within each row with different letters (a–b) are significantly different ($P<0.05$). NR—not reported.

without abnormality in the methodology. These results indicate that GAB and Oswin models are statistically appropriate to describe the water adsorption within the experimental domain. Almost no distinction on fitting performance was detected between Oswin and GAB model;

nevertheless García-Pérez et al. (2008) recommended that an ideal sorption model would be one whose parameters have physical meaning and adequate statistical indexes. Unlike Oswin, the GAB model has theoretical background and its parameters can provide important information on sorption thermodynamics. GAB model has been reported to satisfactory represent the moisture sorption isotherms in Emmental (Saurel et al. 2004), Gaziantep (Kaya and Oner 1996), Cheddar (Ruegg 1985), and imitation (Duggan et al. 2008) cheeses.

GAB analysis of sorption isotherms

The adsorption isotherms shown in Fig. 1 imply a multilayer adsorption: an absorbent molecule lies somewhere on the solid-gas inter-phase covering the primary sorption sites, and then, adsorbent molecules form subsequent layers. These layers can be characterized by their own thermodynamics properties. Thus, a more detailed analysis of the GAB parameters could provide important information on enthalpy and entropy effects on adsorption of water by a cheese matrix. Therefore, the C_G , k_G , and m_{o-GAB} parameters from Table 2 were analyzed using the following equations (11–15), and the results are showed in Table 3.

$$C_G = C_{G,o} \exp\left(\frac{\Delta H_C}{RT}\right) \quad (11)$$

$$k_G = k_{G,o} \exp\left(\frac{\Delta H_k}{RT}\right) \quad (12)$$

$$m_{o,G} = m_o \exp\left(\frac{\Delta H_m}{RT}\right) \quad (13)$$

$$C_{G,o} = \exp\left(\frac{\Delta S_1}{R}\right) \quad (14)$$

$$k_{G,o} = \exp\left(\frac{\Delta S_m}{R}\right) \quad (15)$$

Where: $C_{G,o}$, $k_{G,o}$, and m_o —pre-exponential factors (dimensionless) in C_G , k_G and m_{o-GAB} , respectively; ΔH_C —

Fig. 1 Moisture sorption isotherms of Mexican Mennonite-Style cheese at 4, 8, and 12 °C: (a) fresh and (b) ripened cheese

Table 2 Estimated parameters and fitting performance of sorption models for fresh and ripened Mexican Mennonite cheese

Parameters	Fresh cheese			Ripened cheese		
	4 °C	8 °C	12 °C	4 °C	8 °C	12 °C
GAB Equation						
C_G	7.6±1.4	5.1±0.51	3.3±0.29	4.5±0.92	3.5±0.37	3.1±0.28
k_G	0.95±0.001	0.96±0.005	0.96±0.005	0.94±0.01	0.97±0.005	0.97±0.005
$m_{o,G}$	0.029±0.00	0.024±0.001	0.017±0.001	0.035±0.003	0.025±0.001	0.018±0.001
R^2	0.96	0.98	0.98	0.95	0.98	0.98
E (%)	12.5	9.0	8.7	14.9	8.7	8.8
BET Equation						
C_B	9.9±1.27	8.8±0.86	5.3±0.87	6.3±0.83	5.8±0.99	5.1±0.83
$m_{o,B}$	0.026±0.001	0.018±0.001	0.013±0.001	0.029±0.001	0.019±0.001	0.013±0.001
R^2	0.97	0.93	0.94	0.97	0.94	0.94
E (%)	15.6	17.9	23.5	20.0	21.8	24.0
Halsey Equation						
a_{Oswin}	0.012±0.001	0.014±0.001	0.012±0.001	0.014±0.002	0.017±0.002	0.013±0.001
r	1.2±0.04	1.1±0.03	1.0±0.03	1.2±0.04	1.0±0.003	1.0±0.03
R^2	0.92	0.92	0.89	0.89	0.90	0.89
E (%)	8.3	16.4	15.8	10.4	15.6	15.7
Oswin Equation						
a_{Halsey}	0.051±0.001	0.041±0.001	0.025±0.001	0.052±0.001	0.038±0.001	0.026±0.001
b	0.59±0.01	0.66±0.01	0.71±0.01	0.63±0.01	0.71±0.01	0.73±0.01
R^2	0.95	0.98	0.98	0.94	0.98	0.98
E (%)	11.7	7.2	6.7	13.7	7.3	7.1

Table 3 GAB parameters describing enthalpy and entropy of water adsorption of fresh and ripened Mexican Mennonite cheese

Parameters ^a	Fresh cheese	Ripened cheese
$C_{G,o}$ (dimensionless)	1.54×10^{-12}	9.14×10^{-6}
$k_{G,o}$ (dimensionless)	1.59	2.28
m_o (dimensionless)	1.81×10^{-10}	2.27×10^{-10}
ΔH_C (kJ/mol)	67.38	30.17
ΔH_k (kJ/mol)	−1.18	−2.02
ΔH_m (kJ/mol)	43.66	50.34
H_1 (kJ/mol)	109.21	72.85
H_m (kJ/mol)	41.83	42.67
ΔS_1 (J/mol K)	−226.12	−96.47
ΔS_m (J/mol K)	3.86	6.85

^a $C_{G,o}$, $k_{G,o}$, and m_o —pre-exponential factors; ΔH_C —difference in molar enthalpy between monolayer and multilayer; ΔH_k —difference in molar enthalpy between bulk liquid water and multilayer; ΔH_m —constant to express temperature dependence of $m_{o,GAB}$; H_m —molar enthalpy of sorbed molecules in the multilayer; H_1 —molar enthalpy of sorbed molecules in the monolayer; H_L —molar enthalpy of condensation of bulk liquid water; ΔS_1 —difference in molar entropy between sorption vacant site and adsorbent molecule in multilayer; ΔS_m —difference in molar entropy between adsorbent molecule in multilayer and adsorbent molecule in standard state.

difference in molar enthalpy between monolayer and multilayer= H_m-H_1 (kJ/mol); ΔH_k —difference in molar enthalpy between bulk liquid water and multilayer= H_L-H_m (kJ/mol); ΔH_m —constant to express temperature dependence of $m_{o,GAB}$ (kJ/mol); H_m —molar enthalpy of adsorbed molecules in the multilayer (kJ/mol); H_1 —molar enthalpy of adsorbed molecules in the monolayer (kJ/mol); H_L —molar enthalpy of condensation of bulk liquid water (kJ/mol); ΔS_1 —difference in molar entropy between sorption vacant site and adsorbed molecule in multilayer (J/mol K); ΔS_m —difference in molar entropy between adsorbent molecule in multilayer and adsorbent molecule in standard state (J/mol K).

Tables 2 and 3 show the estimated GAB parameters for fresh and ripened cheese samples at different temperatures. For both cheese samples the values of C_G , k_G and $m_{o,G}$ parameters were $\ll 1$, ≈ 1 , and >0 , respectively. In addition, C_G and $m_{o,G}$ decreased gradually with increasing temperature, while k_G increased slightly, being consistent with the thermodynamics meaning. Kaya and Oner (1996) reported different values of C_G and $m_{o,G}$ (close to 1 and 0.944 g water/g solid, respectively) for Gaziantep cheese at 12 °C. Gaziantep cheese is salted by immersion in brine, a procedure that may affect the compositional parameters, resulting in different surface properties. As for low fat cheese made with different concentration of starch, Duggan et al. (2008)

reported C_G and $m_{o,G}$ values at 25 °C that ranged from 62 to 442 and 0.048 to 0.059, respectively. These variations were attributed to the influence of starch concentration on structuring water in cheese surface. For Gaziantep and imitation cheeses, the k_G values were similar to the k_G values found in this work.

In thermodynamics terms, C_G represents the difference in chemical potential between water molecules that have been adsorbed in the first layer and water molecules adsorbed in the subsequent layers. C_G has an enthalpic nature and it is a measure of how strong the water molecules are bound to the primary sorption sites (Quirijns et al. 2005b). On the other hand, k_G represents the difference in chemical potential between bulk liquid water molecules and molecules adsorbed in the multilayer. k_G has an important entropic contribution which arise from the relative higher number of possible configuration and degree of mobility of water molecules in bulk liquid state compared with water molecules structured in the multilayer (Quirijns et al. 2005b). $m_{o,G}$ is the amount of water needed to cover and form a continuous adsorbed layer over food surface. Water molecules in this region are held by polar sites in food surface through strongly hydrophilic bonds (Sanchez et al. 1997).

The fresh Chihuahua cheese has C_G values $\gg 1$ and k_G values approaching to 1, indicating that the water molecules are strongly bound to the primary sorption sites forming a strong monolayer whose properties are quite different from the multiyear and bulk liquid water. The combinations of C_G and k_G values also indicate that subsequent layers are slightly structured in multilayer having properties comparable with bulk liquid water. In the case of ripened Chihuahua cheese, C_G and k_G indicate that water molecules are less strongly bound in the monolayer compared with fresh samples, and the subsequent structured layers have similar properties to liquid water. It is important to highlight that the GAB model might fail to represent k_G values at high temperatures. This is because the $k_{G,o}$ are greater than one. One possible explanation is that the cheese matrix at 12 °C changes its viscosity, affecting its adsorption properties.

The estimated values of ΔH_C for fresh and ripened cheese had large positive values (67.38 and 30.17 kJ/mol, respectively). These values represent the heat of sorption of the monolayer and are expected to be positive due to its strongly hydrophilic bonds between adsorbed water molecules and the primary sorption sites of cheese surface. On the other hand, the estimated values of ΔH_k for both cheese samples were negative (−1.18 and −2.02 kJ/mol, respectively), indicating that water molecules are less firmly bound in multilayer (Samaniego-Esquerro et al. 1991; Simal et al. 2007). The $m_{o,G}$ values showed a tendency to decrease with increasing temperature, according to eq. (7). As the temperature increases, the solubility of constituents of low molecular weight produced by the hydrolysis of caseins is

increased, modifying the strength and number of hydrophilic interactions and greatly reducing the amount of vacant sites for water adsorption (Simal et al. 2007).

The pre-exponential factors $C_{o,G}$ and $k_{o,G}$ obtained with the equations (11) and (12) are entropic expressions of adsorption process whose nature and numerical values are controversial (Timmermann 2003). Nevertheless, some authors consider that pre-exponential factors can be attributable to entropic effects of adsorption including the degree of availability and mobility of absorbed water between the first and multilayer, and between the multilayer and the bulk liquid (Yadav et al. 2009; Pradas et al. 2004). Pradas et al. (2004) using a statisticomechanical approach related the $C_{o,G}$ and $k_{o,G}$ to the molar entropy of water adsorption in water-synthetic polymer systems through eq. (14) and (15).

The difference in molar entropy between the first and multilayer (ΔS_1), and between the multilayer and the bulk liquid (ΔS_m) are presented in Table 3. These entropic values are in agreement with their thermodynamic meaning. For both samples, the ΔS_1 showed negative values that can be explained by the restricted rotational motion of adsorbed molecules in the cheese surface and significant changes in protein conformation that occurs during adsorption. The entropy is lost (giving negative values) because of a reduction in the number of ways that the energy can be dispersed in the cheese surface. In general, the ΔS_m showed small positive values indicating that water molecules adsorbed in the multilayer are less restricted than the molecules adsorbed in the monolayer (Yadav et al. 2009).

Isosteric enthalpy and entropy of adsorption

Using the data presented in Tables 2 and 3, a new set of isotherms of fresh and ripened cheeses were generated using the GAB equation within the experimental domain ($4 \leq T \leq 12$ °C and $0.08 \leq a_w \leq 0.096$) from which the ΔH_{is} and ΔS_{is} were calculated, according to eq. (6). The resulted values are average isosteric heat and entropy of adsorption of Mennonite-Style cheese and their values expressed as function of moisture content are showed in Fig. 2.

For both samples, the ΔH_{is} values are positive indicating that adsorption of water molecules by cheese matrix is an endothermic process. Figure 2a shows a decreasing tendency in ΔH_{is} values from the highest ΔH_{is} obtained at low moisture content. These results are indicators of the attraction forces between water molecules and sorption sites (Simal et al. 2007). At low moisture contents, the sorption sites that are highly hydrophilic are more available and accessible to being adsorbed by water molecules resulting in higher energetically attraction forces. These attractive forces from which the monolayer is formed are strongly depended on the distance between food surface and adsorbed molecule. As the adsorption takes place, the distance from the food surface to

Fig. 2 Average isosteric enthalpy (a) and entropy (b) of adsorption of fresh and ripened Mexican Mennonite-Style cheese

water molecule increases because the sorption sites are already occupied, consequently, the attraction forces are progressively decreased (Quirijns et al. 2005a,b).

The obtained ΔH_{is} were correlated to moisture content through an exponential equation of the form:

$$\text{For fresh sample : } \Delta H_d = 133.4 * \exp\left(\frac{-m}{0.035}\right) \quad (16)$$

$$R^2 = 0.986$$

$$\text{For ripened samples : } \Delta H_d = 91.8 * \exp\left(\frac{-m}{0.037}\right) \quad (17)$$

$$R^2 = 0.987$$

Several authors have reported similar mathematical expressions for different agricultural and food materials

(Basu et al. 2011; Al-Muhtaseb et al. 2002; Goula et al. 2008; Tsami et al. 1990; Wang and Brennan 1991).

On the other hand variations in ΔS_{is} with moisture content are presented in Fig. 2b. The results for fresh and ripened cheeses were exponential in shape, having similar trend to ΔH_{is} (Fig. 2a). For both cheese samples, the ΔS_{is} approaches asymptotically to zero after a lowest value at low moisture content has reached. The ΔS_{is} values were negative within the evaluated moisture content. Negative values are explained by the lost of entropy due to restricted mobility of adsorbed water molecules at given moisture content. At low moisture content, the water molecules are adsorbed on the most accessible sorption sites, reducing its motion and losing its entropy. As the moisture content increases, the sorption sites are less accessible causing that water molecules form different layers whose spatial arrangements allow more molecular motion of adsorbed molecules, increasing the entropy (Benado and Rizvi 1985).

According to Quirijns et al. (2005a), for properly establishing the type of water and their thermodynamic functions, the sorption knowledge obtained from GAB isotherm needs to match with the isosteric enthalpy of sorption. In that respect, the highest value of ΔH_{is} for fresh and ripened cheese (101.7 and 76.3 kJ/mol, respectively) was obtained at 0.01 g water/g solid. This moisture content is significantly different from the calculated monolayer value obtained from the GAB equation ($0.015 \leq m_{o,G} \leq 0.029$ and $0.018 \leq m_{o,G} \leq 0.034$ for fresh and ripened cheese, respectively). These ΔH_{is} values are rather close to the monolayer enthalpy (109.2 and 72.8 kJ/mol, respectively) derived from the

Fig. 3 Enthalpy-entropy relationships for water adsorption in fresh and ripened Mexican Mennonite-Style cheeses

Fig. 4 Spreading pressure isotherms as function water activity of Mexican Mennonite-Style cheese at 4, 8, and 12 °C: (a) fresh and (b) ripened

GAB isotherm. It is seen that an underestimation of the true monolayer value is responsible for these differences. Among the assumptions of GAB equation are that the sorption sites are identical, distinguishable, and independent (Nikitas 1996; Quirijns et al. 2005a). In porous surfaces (cheese surface) heterogeneity and lateral interaction of adsorbed molecules might create a first sub-monolayer, leading to an underestimation of the monolayer value obtained with GAB equation (Nikitas 1996).

Enthalpy-entropy compensation theory

Figure 3 shows the enthalpy-entropy relationship for water adsorption in fresh and ripened cheese samples. These plots were generated using the predicted ΔH_{is} and ΔS_{is} values at different moisture content. For both samples, a linear relation was obtained ($R^2 \geq 0.98$) and from which the isokinetic temperature (T_β) was derived according to Eq. (5). The T_β was 294.6 and 297 K for fresh and ripened, respectively.

According to Krug et al. (1976), a linear relationship between enthalpy and entropy values does not necessarily imply that compensation exists; instead, the harmonic temperature (T_{hm}) must be different to T_β in order to claim that compensation occurs. The T_{hm} value (281.1 K), which is significant different from the T_β values, confirms the

Fig. 5 Net integral enthalpy (a) and entropy (b) of adsorption of Mexican Mennonite-Style cheese at low ripening and high ripening stage as function of moisture content

applicability of the compensation theory for water adsorption by Mexican Mennonite-Style cheese. In addition, the compensation theory suggests that adsorption of water by cheese matrix is enthalpy driven, since $T_{\beta} > T_{hm}$. These results also implied that there is an isokinetic temperature for adsorption of water at different moisture contents, indicating that adsorption follows one mechanism and the cheese does not suffer significant structural modification during the adsorption.

Spreading pressure and net integral enthalpy and entropy

The spreading pressure (Φ) curves of fresh and ripened at 4, 8, and 12 °C are presented in Fig. 4. For both cheese samples, the spreading pressure increases with increasing a_w . These plots also showed that the spreading pressure values decrease with increasing temperature. Similar values and trends have been reported in black tea (Arslan and Togrul 2006), sesame seed (Kaya and Kahyaoglu 2006), olive oil by products (Liebanes et al. 2006), loquat and quince fruits (Moreira et al. 2008), sweet potato (Fasina 2006), melon seed and cassava (Aviara and Ajibola 2002), safflower petals and tarragon (Kaya and Kahyaoglu 2007), starch powder and dried garlic (Madamba et al. 1996).

In ripened samples (Fig. 4b), the effect of temperature on the spreading pressure values is less pronounced. This could be attributed to changes in cheese matrix structure induced by protein hydrolysis. It has been reported that the protein matrix in goat cheese changes from an irregular open structure to a more regular dense and compact structure as the ripening advance. These changes might lead to release of water that is strongly bound to the cheese surface due to a reduction on the surface area. Consequently, the area of adsorbed molecule is greater in ripened samples, lowering its spreading pressure values and neglecting the temperature effect.

The curves of Fig. 5 were used to estimate the integral enthalpy (ΔH_{in}) and entropy (ΔS_{in}) at constant spreading pressure. The variations in ΔH_{in} with moisture content for fresh and ripened are shown in Fig. 5a. For both fresh and ripened cheese the ΔH_{in} decreases with increasing moisture content. The ΔH_{in} reaches highest values for fresh and ripened (62.11 and 25.77 kJ/mol, respectively) at low moisture content (0.02 g water/g solid). Then, ΔH_{in} gradually approaches to zero at high moisture content. Similar decreasing trends have been reported by other authors (Fasina et al. 1999; Liebanes et al. 2006; Moreira et al. 2008). The curves of ΔH_{in} as function of moisture content represent a measure of accessibility of sorption sites and location of bound water. At low moisture content, the high-energy sorption sites that are more accessible are firstly occupied until the monolayer is completely covered and greater water-solid interaction is observed. As the moisture content is further increased, the solid matrix has less accessible sites

to cover, consequently, forming subsequent layers of adsorbed water which decreases the ΔH_{in} values.

Contrarily, the ΔS_{in} values of fresh and ripened were negative in magnitude, having low values (−197.71 and −70.97 kJ/mol K, respectively) at low moisture content (0.02 g water/g solid) and values that approaching to zero at high moisture content. At low moisture content, the highly negative value at low moisture content implies that the entropy is lost due to restricted mobility of localized adsorption sites. As the moisture content increases, the ΔS_{in} values are explained due to structural transformation arising from solubilization and swelling that allows more mobility of absorbed molecules (Benado and Rizvi 1985).

Conclusions

For the first time, adsorption of water by fresh and ripened Mexican Mennonite-style cheese has been studied in a temperature and water activity range of 4–12 °C and 0.08–0.96, respectively, yielding the followings outcomes:

- The adsorption isotherms of fresh and ripened were sigmoid in shape resembling type II isotherms.
- GAB and Oswin models were found to be statistically adequate to represent the adsorption of fresh and ripened samples within the experimental domain. Using the parameters of GAB model, the existence of different classes of adsorbed water (monolayer, multilayer, and free water) was established for fresh and ripened.
- The variations in isosteric enthalpy on moisture content were adequately described by an exponential equation. The isosteric entropy variations were found to be analogous to isosteric enthalpy.
- Enthalpy-entropy compensation theory was successfully applied and suggests that adsorption of water by cheese matrix is enthalpy driven.
- The integral enthalpy gradually decreased with increasing moisture content after reached a maximum value, while the integral entropy increased with increasing moisture content after reached a minimum value.

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