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Thermodynamics of Moisture Vapor Sorption and Mechanical Characterization of Methylcellulose and Ethylcellulose Based Films

G. Velazquez[1] · A. Y. Guadarrama-Lezama[2] · R. Viveros-Contreras[3] · M. O. Martin-Polo[4] · D. Diaz-Bandera[2] · J. Castaño[5]

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Abstract

The thermodynamic parameters of moisture sorption isotherms and the mechanical behavior of ethylcellulose and methylcellulose based films were studied. The GAB equation was used to describe the sorption isotherms. The thermodynamic analysis showed that the minimum integral entropy value was found in the 0.1–0.6 range of water activity (*aw*) in both types of films, being the lower range for methylcellulose. Compensation enthalpy–entropy theory showed that the water vapor sorption was mainly driven by entropy at low *aw* values. Mechanical analysis of films equilibrated under different *aw* conditions (0.22–0.90) showed constant values of tensile strength and elongation to break for films in the region where the minimum of entropy was reached, indicating that thermodynamic properties could be used as one criterion to describe the mechanical stability of films intended for food packaging applications.

Keywords Ethylcellulose · Methylcellulose · Films · Thermodynamic properties · Mechanical properties

Introduction

The use of plastic bags and synthetic materials to preserve foods has increased in the last decade. Some practical studies mention that the time of use for a packaging material after bought is 30 min. As a consequence, high amounts of materials based on petroleum are disposed. In this regard, food science and technology have been increasingly interested in developing biodegradable and edible films intended for food packaging also known as bio-based packaging i.e., packaging materials based on organic or natural components [1].

Several biopolymers have been considered for this purpose such as chitosan, polyvinyl alcohol, pullulan, sodium alginate, zein, and ethylcellulose, among others [2–5].

Methylcellulose and ethylcellulose are derivatives of cellulose in which some of the hydroxyl groups on the repeating glucose units are substituted by methyl ether or ethyl ether groups, respectively. Both are non-toxic and they are used as film-forming materials, emulsifiers, thickeners, or glue derivates in several applications. Methylcellulose is soluble in water meanwhile ethylcellulose is soluble in methanol due to its hydrophobicity.

Biodegradable films are generally studied concerning various important properties such as transparency, color, solubility, oxygen barrier properties, water vapour permeability, glass transition temperature, mechanical properties, antimicrobial characteristics, or interaction with water [6]. The main functions of packaging materials are to protect foods from mechanical damage and to prevent degradative reactions. In this sense, packaging materials from biopolymers have been demonstrated to be a good alternative to protect the quality attributes of foods without compromising the environment.

✉ G. Velazquez
gvelazquezd@ipn.mx

✉ A. Y. Guadarrama-Lezama
ayguadarramal@uaemex.mx

1 Instituto Politécnico Nacional, CICATA, Unidad Querétaro, Cerro blanco 141, Colinas del Cimatario, CP 76090 Santiago de Querétaro, Querétaro, Mexico

2 Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colón esq. Paseo Tollocan s/n, Col. Residencial Colón, C.P. 50120 Toluca, Estado de México, Mexico

3 Centro de Investigaciones Biomédicas, Universidad Veracruzana, Doctor Castelazo Ayala S/N, Industrial Animas, 91190 Xalapa Enríquez, Veracruz, Mexico

4 Independent Consultant, Santiago de Querétaro, Mexico

5 Facultad de Ingeniería Arquitectura y Diseño, Universidad San Sebastián, Lientur 1457, 4080871 Concepción, Chile

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As a packaging material, the ability of biodegradable films to restrict moisture transfer between the food and its environment is an important characteristic. The interaction of water molecules with biopolymeric materials modifies the physical properties of the films and leads to considerable changes when the moisture content reaches a critical level. Consequently, it is extremely important to analyze water sorption properties under various environmental conditions, such as temperature and relative humidity of equilibrium (RHeq) through the water vapor sorption isotherms [7].

In fresh food preservation, low-temperature conditions impose an environment of high relative humidity mainly due to water vapor transpiration because of the metabolic activity. These conditions significantly affect the performance of the film in terms of the changes induced in the physicochemical properties, which are mainly attributed to a plasticization of the polymeric matrix of films, caused by the interaction of water molecules with the biopolymeric chains. Therefore, environmental conditions need to be controlled to ensure the efficiency and integrity of the biodegradable film when used as packaging material for food preservation.

Thermodynamic parameters are calculated from moisture sorption isotherms, and they are regarded as a reliable guideline to determine the stability of the physical properties of films while stored or when they are used as a food packaging material.

This research work was carried out in four stages: (1) fitting the moisture sorption isotherms data reported in the literature for methylcellulose (water soluble) or ethylcellulose (ethanol soluble) based films, (2) assessing the thermodynamic parameters of the films, (3) describe the mechanism of water vapor sorption through compensation enthalpy–entropy theory, (4) correlate the thermodynamic and mechanical properties in order to describe its stability.

Materials and Methods

Materials

Methylcellulose (MC) (Methocel A15-LV Premium, from Dow Chemical Midland, MI, United States) and ethylcellulose (EC) (Sigma-Chemical Co., St Louis, MO, United States) were used to prepare the films. Ethanol was purchased from Fermont, Mexico. K_2CO_3, $MgCl_2$, KCl, NaCl, NaBr, and $BaCl_2$ (Jalmek Científica, Monterrey, México) were used to prepare the oversaturated salt solution for the microclimates.

Methods

Films Preparation

Films from MC and EC were prepared following the procedure described by De La Cruz et al. [8]. Briefly, 4.25 g of MC was dissolved in 75 mL of ethanol:water (2:1, v/v) or ethanol for MC or EC, respectively, and kept under reflux while stirring at 75 °C for 20 min. The filmogenic solution was cast on glass molds (200 × 200 mm) using a thin chromatography spreader. The spreading thickness was fixed to 1 mm and the coated plates were dried at 75 ± 1 °C for 45 or 30 min for MC or EC, respectively in a forced-convection oven (Binder model 810). After drying, the films were peeled, placed in plastic bags inside a desiccator with silica gel, and stored at room temperature.

Mechanical Properties

Tensile strength (TS) and percentage of elongation (%E) of MC and EC films were assessed in samples conditioned at 9 or 25 °C under several RHeq values following the specifications of the ASTM D882-12 [9]. Film samples (10 × 100 mm) were cut and placed for one week into desiccators containing oversaturated solutions of different salt solutions supplying RHeq values of 22.6, 43.8, 57.7, 75.3, and 90.3% at 25 °C, using K_2CO_3, $MgCl_2$, NaBr, NaCl, and $BaCl_2$, respectively [10], equivalent to water activity (aw) in the 0.22–0.90 interval ($aw \approx$ HReq/100) [11]. A texture analyzer (TA-HD Microstable Systems) was used to measure the mechanical properties. The initial separation of the mechanical grips was set at 50 mm and a crosshead speed of 1 mm/s was used for the test. Seven replicates were analyzed for each film. Before evaluating the mechanical properties, the thickness was measured on 7 random points in the film using a digital micrometer (model 345, Elcometer Instruments Ltd). The thickness of the films was 24.82 ± 3.86 mm for MC and 30.05 ± 2.66 mm for EC films.

Fitting of Moisture Sorption Isotherms Data

Moisture sorption isotherms data obtained from De La Cruz et al. [8] were fitted to the Guggenheim–Anderson–De Boer (GAB) model. To calculate the best fitting parameters, the polynomial form of the GAB model [12] (Eq. 1) was used to calculate M_o (Eq. 2), C (Eq. 3), and K (Eq. 4).

$$\frac{a_w}{M} = \alpha + \beta a_w + \gamma {a_w}^2 \tag{1}$$

$$M_o = \frac{1}{\beta^2 - 4\alpha\gamma} \tag{2}$$

$$C = 2 + \frac{\beta}{K\alpha} \tag{3}$$

$$K = \frac{\sqrt{\beta^2 - 4\alpha\gamma} - \beta}{2\alpha} \tag{4}$$

These parameters were used as initial values to solve the non-linear form of the GAB model (Eq. 5) using the Solver add-on of MS Excel which allows performing the fitting of all data sets at the same time. This approach seems to be more effective to calculate the parameters of the GAB model when dealing with multiple moisture sorption isotherms. The fitting was verified using Kaleida Graph from Synergy software (Reading PA, USA).

$$M = \frac{M_0 C K a_w}{\left(1 - K a_w\right)\left(1 - K a_w + C K a_w\right)}, \tag{5}$$

where M is the equilibrium moisture content (g H_2O/100 g of dry solids (d.s.)), M_0 is the moisture content in the monolayer (g H_2O/100 g d.s.), C is the Guggenheim constant, and K is the constant correcting the properties of the multilayer molecules with respect to the bulk liquid. To assess the accuracy of the fitting with the GAB model, the coefficient of determination (R^2) and the mean relative deviation modulus (E) were used.

Sorption Properties of Films

Determination of Sorption Area The sorption area on the solid surface determines the water bond capacity of the materials and it can be calculated from the monolayer moisture content (M_0) using Eq. 6 [11, 13].

$$S_0 = M_0 \frac{1}{M_w} N_0 A_{H_2O} = 3.5 \times 10^3 M_0, \tag{6}$$

where M_0 is the moisture content in the monolayer expressed as g H_2O/g d.s. (dry basis), M_w is the water molecular weight (g/mol), N_0 is the Avogadro number (6.022×10^{23} molecules/mol), and A_{H2O} denotes the water molecule area (1.06×10^{-19} m^2).

Thermodynamic Properties

The enthalpy and entropy parameters were used to assess the region for mechanical stability of the EM and MC films. The criterion of minimum integral entropy as the point of maximum stability has been applied and confirmed experimentally in several studies [14–16]. In the studied films, the region of minimum entropy was considered as the zone where the maximum stability of mechanical properties was reached. The changes of the integral enthalpy $(\Delta H_{int})_T$ (kJ/mol) at the different water activities were calculated using the model of Othmer [17] (Eq. 7).

$$\frac{\partial \ln P_v}{\partial \ln P_v^0} = \frac{H_v(T)}{H_v^0(T)}, \tag{7}$$

where P_v(atm) is the water vapor pressure in the sample, H_v(T) (kJ/mol) is the integral molar heat of adsorption, P_v^0 (atm) is the vapor pressure (atm) of pure water at the temperature of adsorption, and H_v^0(T) (kJ/mol) is the condensation heat of pure water.

The water vapor pressure as a function of temperature was calculated using the Arden Buck model (Eq. 8) [18].

$$P_v = 6.1121 * \frac{e^{\left(\frac{18.678 - T}{234.5}\right) * \left(\frac{T}{257.14 + T}\right)}}{10} \tag{8}$$

As all terms depend on the temperature, Eq. 7 can be integrated as follows:

$$\ln P_V = \left[\frac{H_V(T)}{H_V^0(T)}\right]_{\phi} \ln P_V^0 + A, \tag{9}$$

where ϕ (kJ/mol) is the surface potential or diffusion pressure, and A is the adsorption constant. A straight line is obtained in a plot of $\ln P_v$ versus $\ln P_v^0$ when the ratio $H_v(T)/H_v^0(T)$ is constant in the temperature range studied.

At the same pressure of diffusion for each isotherm, the molar integral enthalpy $(\Delta H_{int})_T$ was calculated using Eq. 10 [19].

$$\left(\Delta H_{int}\right)_T = \left[\frac{H_V(T)}{H_V^0(T)} - 1\right]_{\phi} H_V^0(T) \tag{10}$$

$$\phi = \mu_{ap} - \mu_a = RT \frac{W_{ap}}{W_V} \int_0^{a_W} M d\ln\left(a_W\right), \tag{11}$$

where μ_{ap} and μ_a (kJ/mol) are the chemical potential of the pure adsorbent and that in the condensed phase, respectively, meanwhile, W_{ap} and W_v (kg/mol) are the molecular weight of the adsorbent and of the water, respectively.

The integral enthalpy at different temperatures was obtained after calculating $H_v(T)/H_v^0(T)$ from Eq. 9 and substituting it into Eq. 10 using the estimation of $H_v^0(T)$ proposed by [20].

$$H_V^0(T) \mathrm{J/mol^{-1}K^{-1}} = 6.15 \times 10^4 - 94.14T + 17.74 \times 10^{-2} T^2 - 2.03 \times 10^{-4} T^3 \tag{12}$$

From the values of $(\Delta H_{int})_T$, the changes in the integral molar entropy $\left(\Delta S_{int}\right)_T$ were calculated using Eq. 13.

$$\left(\Delta S_{int}\right)_T = S_s - S_L = -\frac{\left(\Delta H_{int}\right)_T}{T} - R\ln a_w, \tag{13}$$

where S_L (kJ/mol K) is the molar entropy of liquid water in equilibrium with vapor; S_S=S/N_1 (kJ/mol K) is the integral entropy of the water adsorbed. In this last expression, S (kJ/mol K) is the total entropy of the adsorbed water and N_1 is the moles of adsorbed water.

Compensation Theory

The enthalpy–entropy compensation theory assumes that there is a linear relationship between enthalpy and entropy. The ΔH_{int} and ΔS_{int} values are correlated in the compensation law Eq. 14.

$$\Delta H_{int} = -T_\beta \Delta S_{int} + \Delta G_\beta, \tag{14}$$

where T_β is the isokinetic temperature at which all reactions take place at an equal rate; ΔS_{int} is the integral entropy; ΔG_β is the free energy at the isokinetic temperature. When $\Delta G_\beta <$ 0, the sorption of water is occurring spontaneously. The isokinetic temperature is an important physical parameter because it represents the temperature at which all reactions are carried out at the same rate [21].

The comparison of T_β (isokinetic temperature) with the harmonic mean temperature (T_{hm}), defined by Eq. 15, is used to corroborate the compensation theory [22].

$$T_{hm} = \frac{N}{\sum_{i=1}^{n} \frac{1}{T}} \tag{15}$$

The compensation theory can be applied only when $T_\beta \neq T_{hm}$.

Statistical Analysis

The results were reported as mean values ± standard deviation (SD). One-way ANOVA was carried out using the Minitab software (Minitab Inc., State College, PA, USA). To determine the statistically significant difference between means, the Fisher test ($p \leq 0.05$) was applied.

The coefficient of determination (R^2) and the mean relative deviation modulus (E) given by Eq. 16 were used to assess the fitting of the GAB model to moisture adsorption isotherm.

$$E = \frac{100}{n} \sum \left| \frac{M_i - M_{Ei}}{M_i} \right|, \tag{16}$$

where M_i is the moisture content, M_{Ei} is the estimated moisture content and n is the number of experimental points. Values of $E < 10\%$ indicate an acceptable fit [14–16, 23].

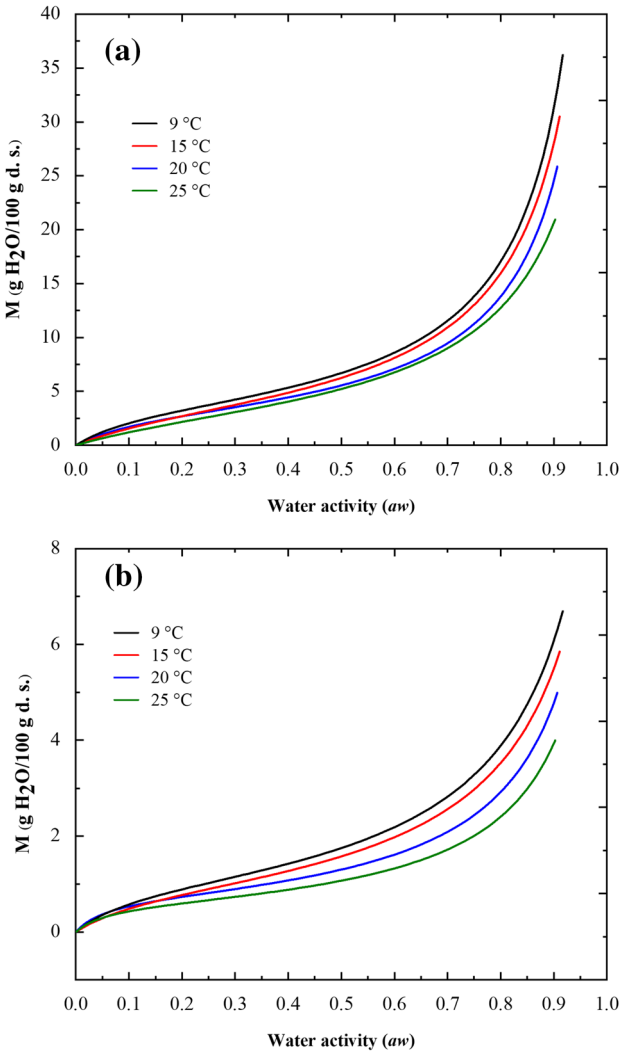

Fig. 1 Moisture sorption isotherms on **a** methylcellulose and **b** ethylcellulose films

Results and Discussion

Moisture Sorption Isotherms

Figure 1 shows the moisture sorption isotherms of MC and EC films at 9, 15, 20, and 25 °C. The MC and EC isotherms had a typical type II sigmoid shape. Similar isotherm shapes have been reported in the literature for cellulosic materials [24, 25]. Noticeable differences between the isotherms of both films were observed. Films from MC were more hydrophilic, whereas the EC films presented the lowest equilibrium moisture contents mainly due to differences in the affinity for water molecules determined by the substituting functional groups in MC and EC. In both cases, at a constant water activity value, the moisture content of equilibrium decreased as the temperature increased, thus indicating that films become less hygroscopic. This behavior is due

Table 1 Estimated parameters of the GAB equation for MC and EC films

Film	Temperature °C	M_0 (g H_2O/100 g of dry solid)	C	K	R^2	E (%)
Methylcelullose (MC)	9	3.862 ± 0.12^a	8.412 ± 0.05^a	0.975 ± 0.10^a	0.999	3.490
	15	3.908 ± 0.14^a	5.343 ± 0.07^b	0.960 ± 0.12^a	0.999	3.855
	20	3.229 ± 0.12^b	8.541 ± 0.03^c	0.967 ± 0.06^a	0.999	2.183
	25	3.540 ± 0.05^c	4.363 ± 0.04^d	0.928 ± 0.05^b	0.999	1.387
Ethylcelullose (EC)	9	1.061 ± 0.13^a	9.524 ± 0.03^a	0.920 ± 0.10^a	0.998	2.502
	15	0.979 ± 0.12^b	7.998 ± 0.05^b	0.918 ± 0.12^a	0.996	6.092
	20	0.729 ± 0.10^c	18.707 ± 0.07^c	0.942 ± 0.06^b	0.999	1.090
	25	0.601 ± 0.17^d	17.445 ± 0.01^d	0.942 ± 0.05^b	0.999	2.764

Results are presented as means ± SD (n = 3). Values with different letters in the same column indicate significant difference ($p \leq 0.05$)

MC methylcelullose; *EC* ethylcelullose; M_0 moisture content of the monolayer (g water/100 kg d.s); C and K GAB model constants; *aw* water activity; R^2 coefficient of linear determination; E mean relative deviation modulus (%)

to an increase in the kinetic energy of the water molecules and that of the functional groups in the sorption sites as a result of higher calorific energy when the temperature increases leading to a lower amount of water molecules interacting with the material [26]. This phenomenon was more noticeable in EC films. Also, this behavior could be explained by the chemical structure of the molecules, while MC has methyl groups in its side main chain, the EC has ethyl groups, which changes the availability of hydrophilic regions of each polymer to bind water. The moisture content of MC films at water activity of 0.60 was approximately five folds higher than that of EC films, indicating that the MC was more hydrophilic as observed by De La Cruz et al. [8].

The experimental moisture sorption data reported by De La Cruz et al. [8] were well fitted to the GAB equation. Table 1 summarizes the values for M_0, C, and K calculated at the four temperatures studied for MC and EC films. The coefficients of determination (R^2) were higher than 0.995 for all temperatures. In general, the R^2 values obtained were higher than those reported by De La Cruz et al. [8]. E values were ≤ 10%, indicating a good fit to the GAB model [14–16, 23]. The monolayer (M_0) moisture content shows the amount of water strongly adsorbed at specific binding sites in the material and it is considered as the optimum moisture content to reach the maximum stability of polymeric materials [15]. The monolayer values for MC were in the narrow range from 3.229 to 3.908 g H_2O/100 g d.s. For EC, the M_0 values decreased as the temperature increased from 1.061 to a minimum of 0.601 g H_2O/100 g d.s. attributed to an increase in the kinetic energy of the water molecules and that of the functional groups of the binding sites promoting the distance apart [5].

According to the type of sorption and the classification of Brunauer et al. [27], the isotherms for MC and EC were type II, presenting C values higher than 2. This means that the attraction forces between the adsorbate and the adsorbent were larger than those between adsorbate molecules in the liquid state [28]. The C parameter describes the adsorption energy of water molecules in the multilayers and the monolayer [29, 30].

The C values (Table 1) for films ranged from 4.363 to 18.707. Not a clear trend was observed for MC, meanwhile, the C values for EC increased in general as the temperature increased probably because of the hydrophobic character of EC films.

The K values close to 1 indicate a reduction of the adsorption energy which suggests a disruption of the multilayer to a bulk liquid-like domain [31]. In this work, the K values calculated for EC films were, in general, lower than those for MC films, indicating the formation of a lower number of water layers in MC films.

The values of M_0 and K obtained in this work were similar to those reported by De La Cruz et al. [8] although, higher R^2 and lower E values were obtained in this work.

Sorption Properties of Films

Surface area of sorption influences the sorption properties of films. The surface area of sorption for MC and EC films is shown in Table 2. The surface area values for MC did not show a clear trend to increase or decrease, meanwhile, those of EC decreased as the temperature increased as a consequence of an increase in the kinetic energy of the molecules involved in the sorption process resulting in a lower amount of water molecules absorbed in the binding sites and also, because of the decrease in the binding sorption energy associated to the monolayer and multilayer [32].

The films prepared from MC had the highest values of surface area compared to EC films (Table 2). The behavior is related to the functional groups in MC. As the number of carbon atoms and hydrogen groups in the substituting groups

Table 2 Surface area of sorption (m^2/g) for MC and EC films

Films	9 °C	15 °C	20 °C	25 °C
MC	138.58 ± 4.15^a	141.13 ± 4.23^a	117.37 ± 3.52^b	125.47 ± 3.76^c
EC	37.63 ± 3.58^a	34.70 ± 2.52^a	25.85 ± 2.10^b	21.33 ± 3.10^d

Values with different letters in the same row indicate significant difference ($p \leq 0.05$)

MC methylcelullose; *EC* ethylcelullose

increases, its affinity to water is reduced. Then, because of the presence of ethyl groups, EC films have hydrophobic behavior. Since the superficial area refers to more available sites to bind water, the calculated values indicate that MC films have a higher water bonding area.

Thermodynamic Properties of Films

Integral Enthalpy

Integral enthalpy $(\Delta H)_{int}$ indicates the degree of interaction between water molecules and the film. The integral enthalpy for MC and EC films increased to a maximum value and then, it gradually decreased when water activity increased (Fig. 2). For the MC films, the integral enthalpy reached a maximum (approximately 25 kJ/mol) at *aw* values lower than 0.1 for all tested temperatures suggesting a strong interaction with water. The integral enthalpy for EC films had noticeable differences among temperatures. The maximum level of energy reached was almost equal at each temperature (about 13 kJ/mol) but as the temperature increased, the water activity where the maximum value was reached, increased in a range from 0.30 to 0.70 *aw*. This behavior indicates that, as the temperature increased, the film had a weaker interaction with water. The maximum enthalpy value achieved by films indicates that the strongest binding sites and the greatest water-film interactions are reached. The low enthalpy values at the low water activity region are a good indication of the degree of occupation of water binding sites in the films.

The quick decrease of the energy to bind water at *aw* values higher than 0.1 observed in MC films is due to the formation of multilayers, where the interaction water-water with lower interaction energies is favored while EC is able to bind water at higher water activity levels (in the range from 0.3 to 0.7). It is possible that the covering of fewer binding sites is being favored promoting the formation of multi-layers. The difference in the integral enthalpy indicates that, under the same sorption conditions, the MC and EC films bind water in a different way. Films from EC can keep the water molecules bound, meanwhile MC films bind water with slightly stronger energy, but they are not able to keep it when the water activity increases. This behavior could

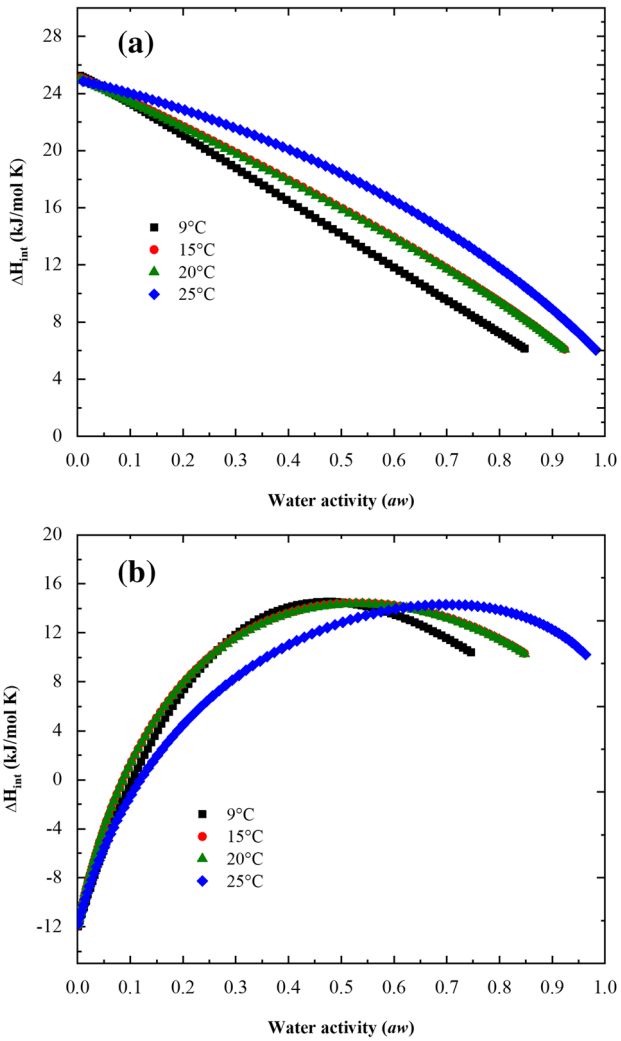

Fig. 2 Integral enthalpy changes of sorbed water on **a** methylcellulose and **b** ethylcellulose films as a function of water activity

be attributed to the chemical structure of both macromolecules [33]. The binding energy is kept at higher levels in a wider range of water activity for EC compared to MC films (Fig. 2). The enthalpy values in which water vapor is being absorbed on films indicate that a physisorption phenomenon is taking place in MC and EC films.

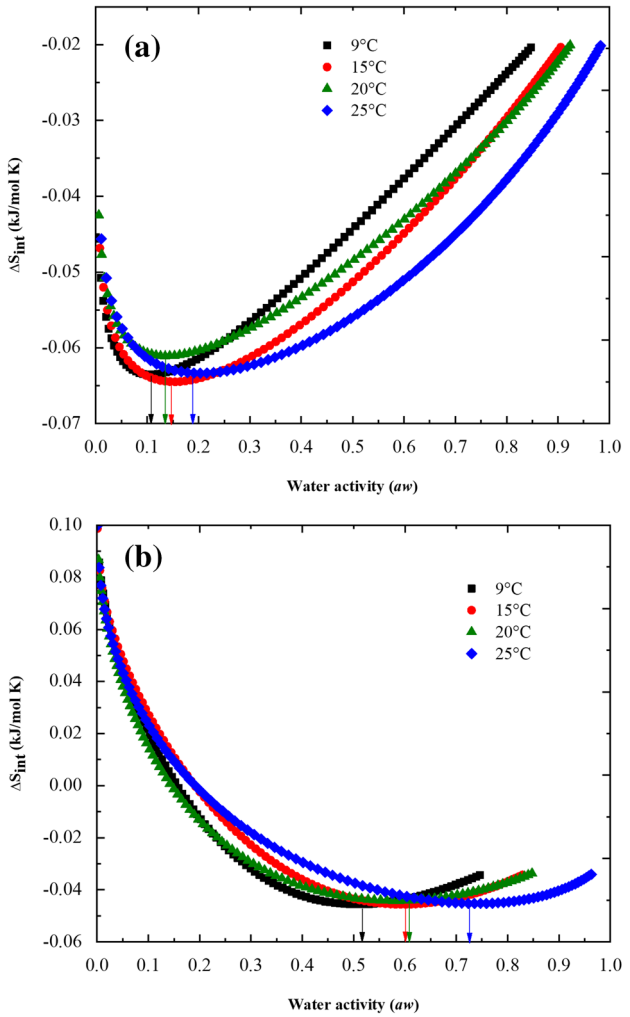

Fig. 3 Integral entropy changes of sorbed water on **a** methylcellulose and **b** ethylcellulose films as a function of water activity

Integral Entropy

Integral entropy $(\Delta S)_{int}$ describes the arrangement of water molecules on solids that is taking place during the sorption process, having an important effect on the stability of the systems. Then, $(\Delta S)_{int}$ is considered as the maximum stability point. The values of minimal integral entropy depend on the mechanism of sorption as a consequence of the chemical composition and the physicochemical properties of the material [30]. At this point, water molecules have a more ordered arrangement and form strong interactions with the material (MC or EC films). Thus, water is less available, and it does not participate in other processes [14, 23].

Figure 3 shows the integral entropy of MC and EC films as a function of water activity at 9, 15, 20, and 25 °C. The integral entropy decreased until reaching a minimum point and then increased as the water activity increased. The decrease in integral entropy indicates a diminution in the mobility of water molecules promoting the saturation of binding sites and, therefore, higher energy is required for the sorption process. On the other hand, the increasing of integral entropy implies that the water molecules can form multilayers or clusters. At high moisture contents, entropy will be approximately the same as that of liquid water [34].

In the case of MC and EC films, there are not just minimum values referred to as the minimal entropy, but a zone of minimum entropy (Fig. 3). For MC films, the water activities with the minimum of entropy ranged from 0.1 to 0.2 for all studied temperatures. The water activities for maximum stability of EC were in the range from 0.52 to 0.73 at the different temperatures studied. In both films, as the temperature increased, the values of *aw* where the minimal integral entropy was reached, also increased. For MC, the range of minimum of entropy is presented in very closer values but in EC, a wider range was observed, suggesting that films prepared from EC, because of their hydrophobic behavior, can be stored or applied at higher water activities compared to MC.

This value of the minimum entropy could gain much importance in the conformation of films and their application in the manufacturing industry because it is a parameter that is important for processing and handling of materials.

Compensation Enthalpy–Entropy

The calculation of the compensation enthalpy–entropy allows knowing if the water sorption process is driven mainly by an enthalpy or entropy mechanism based on the isokinetic (T_B) and the harmonic medium temperature (T_{hm}) [35]. The compensation theory applies when the isokinetic temperature (T_B) is different from the harmonic mean temperature (T_{hm}) according to the Krug test criteria [22, 36]. The isokinetic compensation for the sorption of water on MC and EC films was confirmed. The T_{hm} calculated for the studied temperatures was 290.27 °C.

The values of T_B and T_{hm} for MC and EC films are shown in Fig. 4. Two lines for each film are shown, indicating water sorption regions, related to low and high values of water activity. The arrows indicate the direction of water sorption from lowest to highest equilibrium moisture content. T_{B1} and T_{B2} represent the integral isokinetic temperature at low and high *aw* values, respectively.

Results show that at lower water activity values, the phenomenon was mainly driven by entropy, while at high values of water activity it was mainly controlled by enthalpy for MC and EC based films. These results indicate that the sorption mechanism was driven by the physical structure of the films in the first stage, when the water activity was lower (0.1–0.2 for MC and 0.1–0.4 for EC), whereas, at intermediate and high values of water activity (0.2–0.6

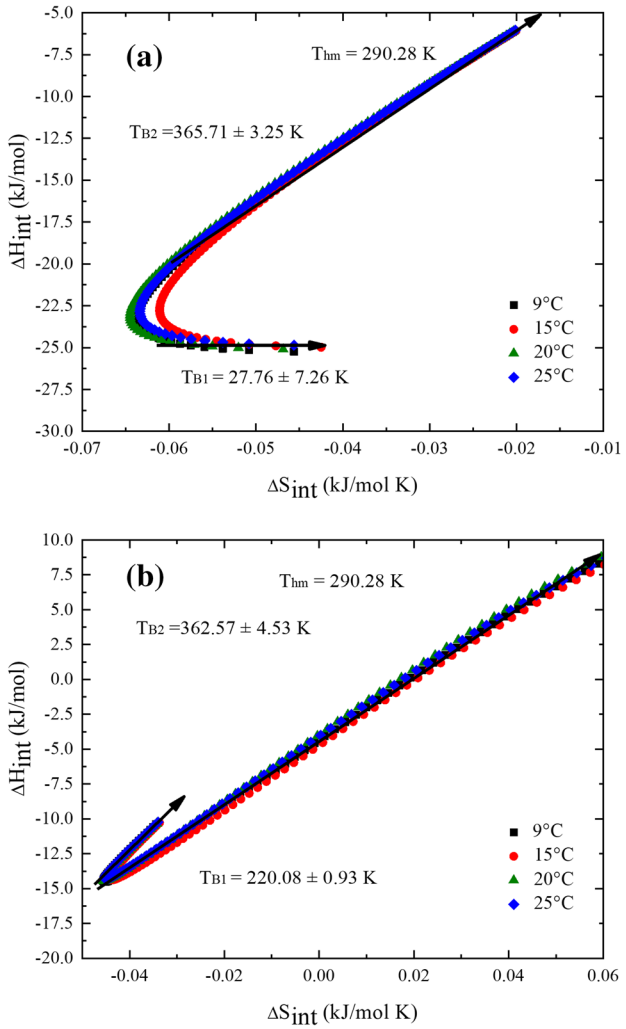

Fig. 4 Compensation theory of **a** methylcellulose and **b** ethylcellulose films

for MC and 0.6–0.9 for EC), the mechanism was driven by energetical interactions which depend on the chemical composition of the polymers conforming the films.

Mechanical Properties

The mechanical properties of films showed a strong dependence on water activity. For MC at 9 °C (Fig. 5a), the maximum tensile strength (around 58 MPa) was observed at water activity values lower than 0.2, after this, a step-like decrease was displayed until 0.9 of water activity, where the minimum value was observed (around 6 MPa). This could be related to a plasticizing effect exerted by the water molecules. The attraction forces between water molecules and functional groups in the film matrix imply high interaction forces promoting the swelling and plasticization of the polymer and, consequently, a relaxation of the polymer chains [37]. Elongation at break (EB) was almost invariable at least up to 0.8 of water activity and only a maximum (12.5%) was reached at 0.9 of water activity. No significant differences were found when the EB values between 0.1 and 0.8 of *aw* were compared. It is noticeable the constant value of tensile strength (TS) and EB in the range where the zone of minimum entropy was also found (Fig. 5a). In the case of the MC equilibrated at 25 °C, TS and EB were constant up to 0.6 of water activity (Fig. 5b) where no significant differences were observed. This is attributed to the capacity of MC to bind water molecules at lower activities but as the water activity increases a weaker interaction takes place between water and the material conforming the films. This behavior was evident in the integral enthalpy (describing the strong interaction of water molecules with the film at lower values of water activity). Also, the values for TS and EB remained invariable in the range of minimum of integral entropy confirming the stability of films in this region of water activity. A minimum value (30 MPa) for TS and maximum (12.5%) for EB was displayed at 0.9 of water activity where the deformation of the film is attributed to a higher mobility of water molecules. Previous reports associated the decrease of tensile strength and the increase in the percent of elongation at break of the polymers with a plasticizing process [38–40].

The TS values for EC films at 9 °C remained constant in all the range of water activity from 0.1 to 0.60 of *aw* (Fig. 6a) where no statistical differences were found. At 25 °C the mechanical properties remained constant in the 0.1–0.75 range of *aw* (Fig. 6b); in the case of EB, there was an increase for EC at 9 and 25 C as the water activity increased; however, a steep increase was observed for films equilibrated at 9 C in a range from 0.6 to 0.9 of water activity, indicating that, under these conditions, the material is more flexible. This is attributed to the capacity for EC to form strong interactions with the water as evidenced in the integral enthalpy (Fig. 2) at 0.6 of water activity. In hydrophilic materials, the adsorption of water promotes structural changes modifying the mechanical properties because the small water molecules can penetrate the structure, acting as a lubricant, and interrupting the interactions between polymeric chains, leading to fragile materials [41]. However, the mechanical properties at 25 °C and the TS at 9 °C of EC show that the minimum of entropy cannot be considered as the only parameter to define the maximum mechanical stability since these properties were constant in the entire range of water activity.

The mechanical properties of MC and EC films were modified to different extent when exposed to different conditions of the relative humidity of equilibrium. This effect was more noticeable at water activities higher than 0.4 for MC films equilibrated at 9 and 25 °C.

Results from this study indicate that the point at which the mechanical properties suddenly decrease could be

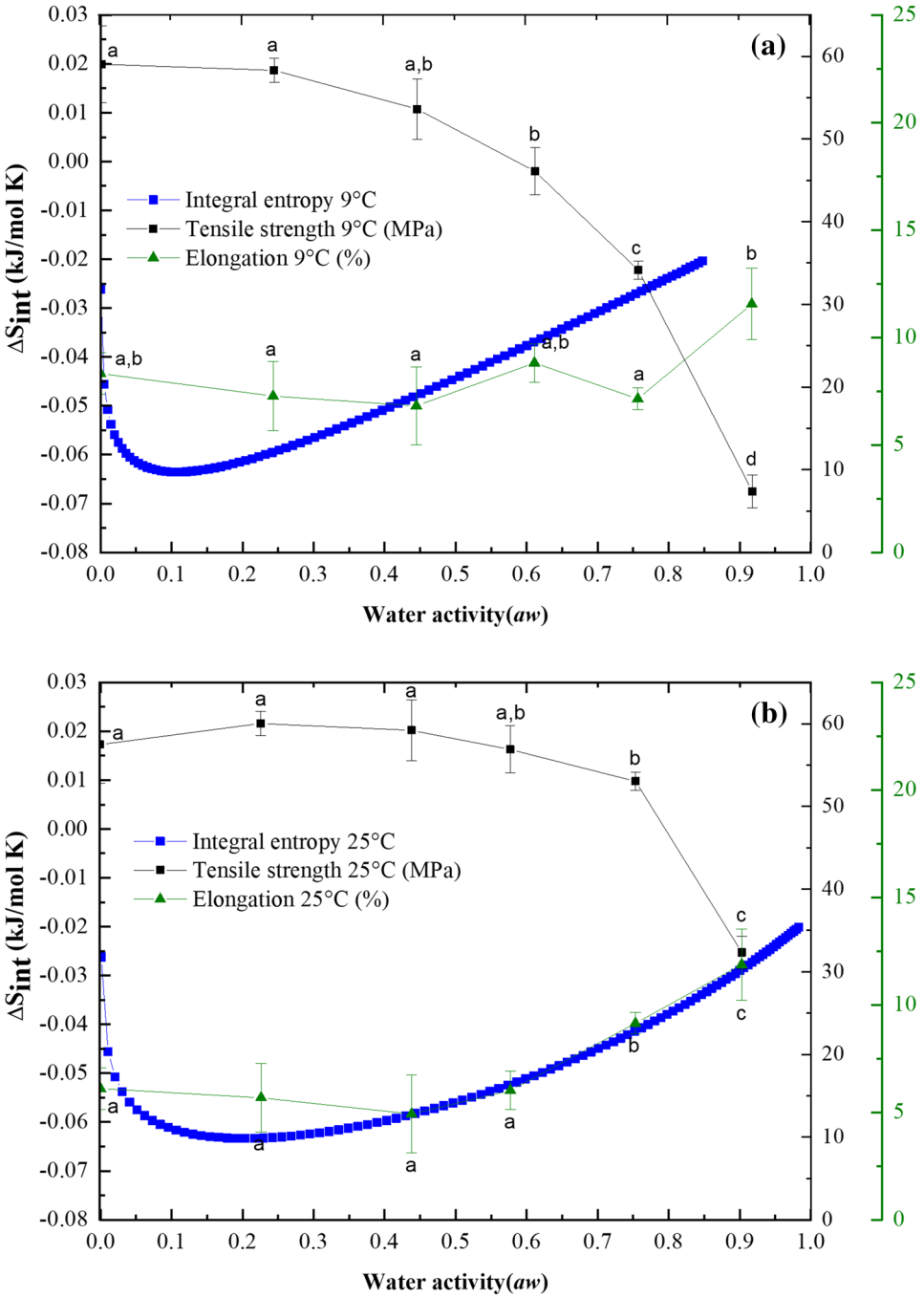

Fig. 5 Mechanical properties of methylcellulose films at **a** 9 °C and **b** 25 °C as a function of water activity. Different letters in the same parameter indicate significant difference ($p \leq 0.05$)

considered as an indication of excessive hydration in presence of water molecules. There are important changes in the mechanical properties when the hydrophilic materials are excessively hydrated. This was corroborated in this work because TS and EB drastically changed their values at 0.4 of water activity for MC films.

In both types of films (MC or EC) the mechanical properties remained quasi-constant in the minimum of the entropy, suggesting that this criterion should not be considered as the only parameter defining the point of maximum stability especially for EC films where TS and EB remained constant at 25 °C, as well as the TS values at 9 °C for MC films. The determination of TS and EB are important parameters that combined with the minimum of entropy could help to confirm that in such conditions, films can be stable materials for food packaging.

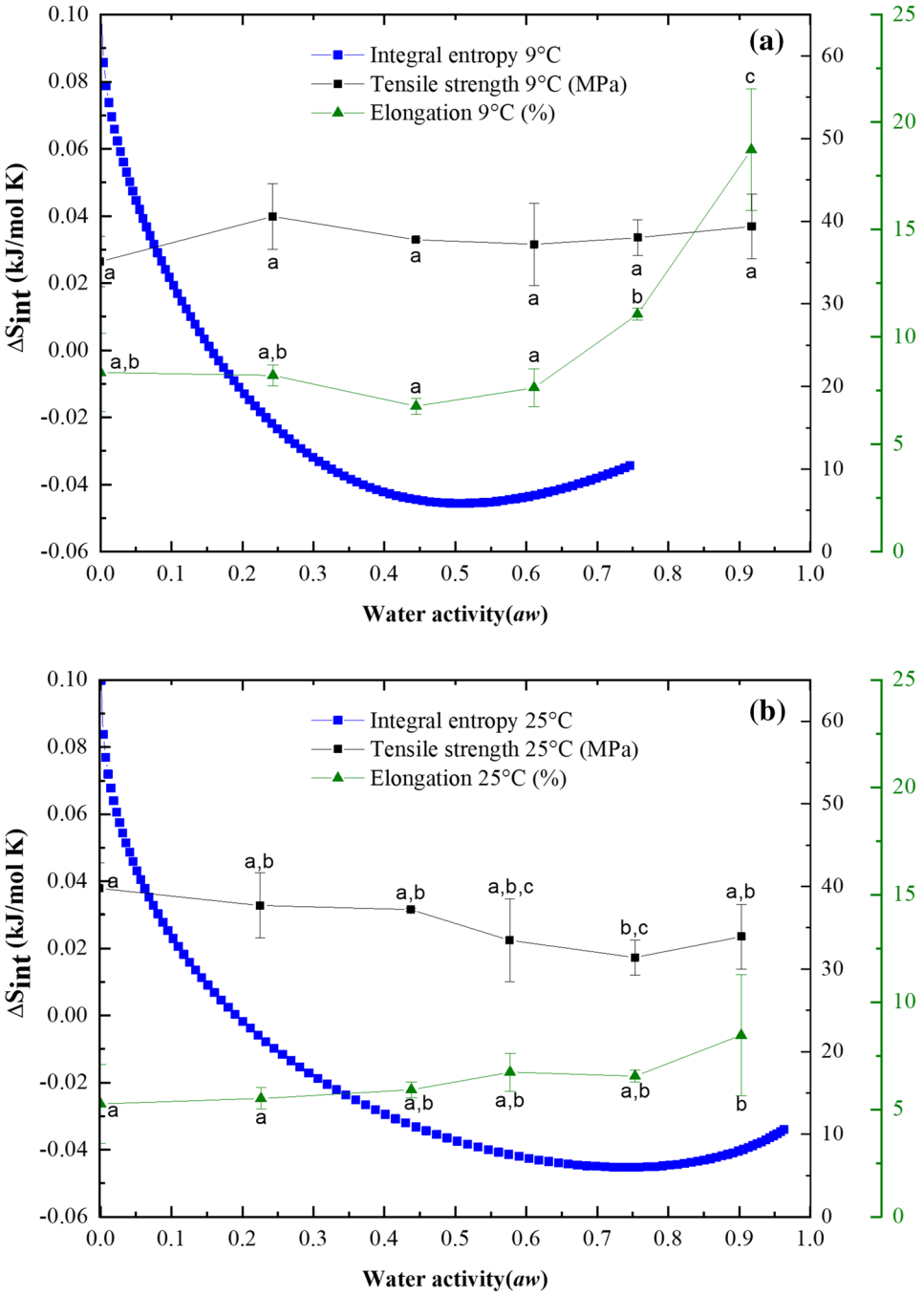

Fig. 6 Mechanical properties of ethylcellulose films at **a** 9 °C and **b** 25 °C as a function of water activity. Different letters in the same parameter indicate significant difference ($p \leq 0.05$)

Conclusion

Moisture sorption isotherms for MC and EC based films were well fitted ($R^2 > 0.999$) to the GAB model and they presented a typical sigmoidal shape. The minimum of integral entropy, regarded as the point of maximum physical stability in films, ranged from 0.1 to 0.2 of water activity for MC, whereas those values for EC ranged from 0.30 to 0.70 of *aw*. The thermodynamic behavior indicates that, under the same sorption conditions, the MC and EC films bind water in a different way mainly due to the chemical difference between the polymers. The EC films may be stored at higher *aw* values than the MC films. The compensation theory evidenced that at lower *aw* values the sorption is prevalently governed by entropy, whereas at high *aw* values, the phenomenon is mainly driven by enthalpy. Some mechanical properties presented constant values where the zone of minimum integral entropy was displayed indicating that the thermodynamic properties could be used as one of the parameters defining the stability of films, however, it should

not be considered as the only parameter defining the point of maximum stability, especially hydrophobic materials as the mechanical properties of EC films remained constant in the entire range of water activity.

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Declarations

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