Thermodynamic sorption of red cabbage extract (*Brassica oleracea* L. var. *capitata* L. f. *rubra*) encapsulated by spray drying

Anahi Bernstein¹ · Caciano P. Zapata Noreña¹

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Abstract Red cabbage aqueous extract acidified with 2 % citric acid was spray-dried using gum Arabic as encapsulating agent. The concentration of anthocyanin in the powder was 253.45 ± 10.82 mg/100 g of dry basis and antioxidant activity of 4.6 ± 0.2 mmol trolox/kg of dry basis. The sorption isotherms were determined at 15, 25 and 35 °C, and the GAB model was the one that best adjusted to the experimental data. The differential enthalpy and entropy for moisture levels up to 2 g of water/g of dry basis decreased to a minimum value of -4.36 kJ/mol and -0.019 kJ/molK respectively, and then increased in magnitude with the rise in moisture content to levels close to the free moisture with a spontaneous process, governed by the entropy. The spreading pressure increased with the rise in water activity for all temperatures, while net integral enthalpy and entropy decreased with the rise in moisture content reaching levels close to 10 kJ/mol and 0.025 kJ/molK, respectively.

Keywords Thermodynamic properties · Sorption isotherms · Gum Arabic · Water activity · Anthocyanin

Introduction

Studies related to the influence of the red cabbage in the human health have verified its activity in the prevention of heart diseases as well as its effects against some types of

cancer (Charron et al. 2007; Dyrby et al. 2001; Wu et al. 2004). Among the substances present in red cabbage responsible for these properties are the glucosinolates (van Poppel et al. 1999) and the polyphenols (Cooke et al. 2005; Singh et al. 2006; Charron et al. 2007), as well as the anthocyanins, the class of phenolic compounds in greatest abundance (Charron et al. 2007; Dyrby et al. 2001; Wu et al. 2004; Wu and Prior 2005).

Anthocyanins are very unstable during processing and storage due to their sensibility to temperature, light, pH, oxygen and other factors (Tonon et al. 2010). In order to minimize these factors, the encapsulating technique has been widely used by the food industry; encapsulation via spray drying is the most commonly used method (Desai and Park 2005; Cai and Corke 2000).

Different wall materials can be used, but gum Arabic is considered an encapsulant by excellence, and its most important properties include the formation of emulsions, the formation of films at the interface, its low hygroscopicity, low viscosity and its subtle sensory properties (Madene et al. 2006).

The knowledge of sorption data is important for many aspects related to food technology, such as prediction of microbiological, enzyme and chemical stability, selection of packing material, design of drying and concentration material and the selection of the best storing conditions (Mrad et al. 2012).

Water sorption properties in food are influenced by composition, processing, temperature and relative humidity (Iglesias and Chirife 1976). The effect of temperature on sorption isotherms is of great importance because the foods are exposed to different temperatures during processing and storage, which can affect the mobility of water molecules and the dynamic equilibrium between steam and adsorbed phase (Al-Muhtaseb et al. 2004a).

✉ Caciano P. Zapata Noreña
czapatan@ufrgs.br

¹ Institute of Food Science and Technology, Federal University of Rio Grande do Sul, Porto Alegre, RS, Brazil, Av. Bento Gonçalves, n° 9500, CEP 91501-970

Food thermodynamic properties relate the water concentration in the food with its partial pressure, which is crucial for the analysis of heat and mass transfer during the drying process (Aviara et al. 2002). Regarding the later, they help determine the final moisture content until which the food must be dehydrated in order to obtain a stable product, and also the minimum energy requirements for the water removal (Arslan and Togrul 2005).

Some thermodynamic parameters can be estimated based on the sorption isotherm, and this information is useful to understand the physicochemical connection of the water when the product is subjected to different temperatures and relative moisture levels (Azuara and Beristain 2006). Properties such as enthalpy, entropy and Gibbs free energy, which represent the quantity of energy, the order or the excitement state and the chemical balance of molecules inside the material, respectively, are useful to explain the reactions and phenomena in the molecular level of the materials (Brovchenko and Oleinikova 2008).

The differential enthalpy or sorption heat (Δh) supplies the energy needed to remove the moisture from food (strength of water-solid connection) (Aviara et al. 2004). The differential entropy (ΔS) of a given material is related to the number of sorption sites available at a specific energy level (Madamba et al. 1996). In addition, the concept of order/disorder, which is useful to interpret processes that occur during the moisture sorption, such as dissolution, crystallization and swelling, is also related to entropy (Aviara et al. 2002).

Net integral proprieties allow for quantitative interpretation of the sorption phenomenon. They describe the degree of disorder or the disorganized movement of water molecules, as well as the energy involved in the sorption process. These functions derive from the first thermodynamic law, applied for the pure adsorbent material (Rizvi 1986).

Therefore, net integral enthalpy (Δh_{int}) indicates the strength of the water molecules connection with the food particles and can be considered a measure for water-food affinity (Aviara et al. 2004). Variations in net integral enthalpy can also offer information on energy change variation after the mixture of water molecules with the adsorbent during the sorption process (Telis et al. 2000). On the other hand, net integral entropy (ΔS_{int}) describes the degree of disorder or randomness of water molecule movements, and also quantifies the mobility of the water molecules adsorbed (Mazza and LeMaguer 1978).

This work aimed to determine the differential and integral thermodynamic proprieties of sorption of red cabbage extract, obtained through extraction with water at 2 % of citric acid, encapsulated by atomization using gum Arabic as wall material.

Material and methods

Raw material

The red cabbage was purchased from the Central Supply of Rio Grande do Sul (CEASA) in Porto Alegre. The cabbage heads were selected considering the absence of visible injuries and infections, and then washed, dried and stored in perforated polyethylene bags at refrigeration temperature (7 ± 2 °C) until the time of processing.

Experimental procedure

The red cabbage was cut in slices of approximately 0.5 cm and subjected to steam blanching during 4 min, followed by an ice bath. Anthocyanin extraction followed the method described by Chandrasekhar et al. (2012), with a few changes. The blanched cabbage was macerated in acidified water with citric acid at 2 % for 16 h under no illumination, and after this time the mixture was vacuum filtered. 15 % of gum Arabic (p/v) was added, and the solution was mixed with a homogenizer (Ultra Turrax IKA T25, Germany) for 5 min at 4000 rpm (Saénz et al. 2009).

The suspension was atomized in a spray dryer with a double-fluid nozzle (MDS 1.0, Labmaq, Ribeirão Preto, Brazil), with a supply nozzle of 1.0 mm of diameter, drying temperature of 140 °C, atomization pressure between 2 and 4 kgf/cm², drying air flow of 1.0 m³/min and mean feeding flow of 0.6 L/h. The powder product was collected and conditioned in aluminum foil envelopes inside polyethylene plastic bags, which were sealed and stored in a dissector containing silica gel until the moment of analysis.

The quantification of anthocyanins and the antioxidant activity in the extract and in the atomized powder were performed using the spectrophotometric pH differential method as described by Xu et al. (2010) and the DPPH radical method of Brand-Williams et al. (1995) with a few changes, respectively. In the powder, color was measured by direct reading in a Minolta colorimeter (CR400/410, Minolta Sensing Inc., Osaka, Japan) through the three-dimensional system $CIEL^*a^*b^*$ (Palou et al. 1999); the solubility in water at 25 °C was realized by the method of Caparino et al. (2012), and the microstructure was observed via scanning electron microscopy (JSM 6060, Tokyo, Japan) using the method recommended by Toneli et al. (2008).

Sorption isotherms

The sorption isotherms were determined by the gravimetric method as described by Nayak and Rastogi (2010) and Shrestha et al. (2007). One gram of encapsulated powder was placed in glass beakers (duplicate) inside hermetic pots containing different solutions saturated by salts at the different

temperatures studied. The saturated solutions used were lithium chloride, potassium acetate, magnesium chloride, potassium carbonate, sodium chloride, potassium chloride and barium chloride (Greenspan 1977; Stokes and Robinson 1949).

In order to prevent fungi from growing in the recipient, a beaker containing 1.5 mL of toluene was placed in the environments that contained relative humidity higher than 50 % (McMinn and Magee 2003). The samples were weighted every 7 days until constant weight (equilibrium) was obtained after 7 weeks. For each isotherm, the sorption data in equilibrium were adjusted to different sorption models (Table 1).

The differential and integral thermodynamic properties were calculated based on the model that best adjusted to the experimental data. The effectiveness of the adjustment to the best model was assessed using the determination coefficient (R^2) and root mean square error (RMSE) (Torres et al. 2012):

$$RMSE = \left[\frac{1}{N} \sum_{i=1}^N (X_{exp} - X_{pred})^2 \right]^{1/2} \quad (6)$$

where N is the number of experiments; X_{exp} and X_{pred} represents the moisture content experimental and predicted, respectively.

Differential properties of sorption

The differential enthalpy or isosteric heat of sorption Δh (J/mol) and the differential entropy of sorption ΔS (J/mol.K) were determined using Clausius-Clapeyron equation, in conditions of equilibrium moisture content constant (Tsami 1991):

$$\Delta h = -R \left[\frac{\partial \ln(a_w)}{\partial (1/T)} \right]_x \quad (7)$$

Table 1 Models of the sorption isotherms used to fit the experimental data

Name of equation	Equation	
GAB (Van der Berg 1985)	$X = \frac{X_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)}$	(1)
Oswin (Lomauro et al. 1985)	$X = A \left(\frac{a_w}{1 - a_w} \right)^B$	(2)
Chung and Pfof (1967)	$\ln(a_w) = -A \exp(-B \cdot X)$	(3)
Smith (1947)	$X = A + [B \cdot \log(1 - a_w)]$	(4)
Halsey (1948)	$a_w = \exp\left(-\frac{A}{X^B}\right)$	(5)

X equilibrium moisture (g water/g dry matter); a_w water activity; X_m monolayer moisture; A , B , C , K equation constants

After integration, the Eq. (8) relates the differential enthalpy and entropy.

$$\ln(a_w)_x = -\frac{\Delta h}{RT} + \frac{\Delta S}{R} \quad (8)$$

where R represents the universal gas constant (8.314 J/mol.K), T is the absolute temperature (K), a_w is the water activity and X is the equilibrium moisture (g water/g dry basis).

The angular coefficient, represented by $-\Delta h/R$, and the linear coefficient, represented by $\Delta S/R$, were both obtained using regression analysis $\ln(a_w)$ as a function of $1/T$ at constant moisture. Differential enthalpy (Δh) and differential entropy (ΔS) were respectively obtained by $-\Delta h/R$ and $\Delta S/R$ (McMinn and Magee 2003).

Compensation theory

The enthalpy-entropy compensation theory (or isokinetic theory) is used to assess physical and chemical phenomena such as sorption reactions and propose a linear relation between Δh and ΔS (McMinn et al. 2005):

$$\Delta h = T_\beta \cdot \Delta S + AG \quad (9)$$

where T_β is the isokinetic temperature (K), representing the temperature at which all reactions occur at the same speed and where AG is Gibbs free energy (kJ/mol). Both functions are calculated via linear progression analysis. Gibbs free energy indicates the affinity of the sorbents by water and verifies whether the adsorption occurs as a spontaneous process (Telis et al. 2000).

Krug et al. (1976) recommend a test to validate the compensation theory, which consists on comparing mean harmonic temperature (T_{hm}) and isokinetic temperature. If $T_\beta \neq T_{hm}$, then the theory can be applied. T_{hm} is calculated by the equation:

$$T_{hm} = \frac{n}{\sum_{i=1}^n \left(\frac{1}{T} \right)} \quad (10)$$

Net integral properties of sorption

Sorption net integral enthalpy (Δh_{int}) and net integral enthalpy (ΔS_{int}) were obtained in a similar way for differential properties, but using spreading pressure rather than water equilibrium (X). Spreading pressure (φ) represents the free energy in the adsorption surface and can be considered as the difference in surface tension between the sorption sites available in solid means and the molecules adsorbed (Al-Muhtaseb et al. 2004b).

The spreading pressure (φ , kJ/m²) was determined from the equation described by Iglesias and Chirife (1976) and Fasina et al. (1999):

$$\varphi = \frac{K_B \cdot T}{A_m} \cdot \int_0^{a_w} \frac{X}{X_m \cdot a_w} \cdot d(a_w) \quad (11)$$

where K_B is the Boltzmann constant (1.38×10^{-23} J/K); A_m is the surface area of a water molecule (1.06×10^{-19} m²); X_m is the monolayer moisture content and X is the equilibrium moisture content (Mazza 1980).

The value of $a_w=0$ will make the integral of Eq. (11) to be indeterminate. Therefore, the lower limit was taken as $a_w=0.05$ (Iglesias et al. 1976). After substitution of the GAB equation (Eq. 1) in Eq. (11) and integration, the spreading pressure was calculated from:

$$\varphi = \frac{K_B T}{A_m} \cdot \ln \left[\frac{1 + C \cdot k \cdot a_w - k \cdot a_w}{1 - k \cdot a_w} \right]^{q_w}_{0.05} \quad (12)$$

For each isotherm, from values of φ obtained from Eq. (12), as a function of a_w , the data were adjusted to the following equation:

$$\varphi = \frac{d \cdot e \cdot f \cdot a_w}{(1 - f \cdot a_w)(1 - f \cdot a_w + e \cdot f \cdot a_w)} \quad (13)$$

where d , e and f are constants that were calculated for regression analysis.

The Eq. (14) was used in order to obtain the a_w values at the condition of constant spreading pressure (Aviara et al. 2004):

$$a_w = \frac{2 + e \left(\frac{d}{\varphi - 1} \right) - \left[\left(2 + e \left(\frac{d}{\varphi - 1} \right) \right)^2 - 4(1 - e) \right]^{1/2}}{2f(1 - e)} \quad (14)$$

The net integral enthalpy and entropy values were calculated from the equation (Hill and Rizvi 1982):

$$\ln(a_w)_\varphi = -\frac{\Delta S_{\text{int}}}{R} - \frac{\Delta h_{\text{int}}}{R} \cdot \frac{1}{T} \quad (15)$$

Results and discussion

The concentration of anthocyanin resulting of the extraction with acidified water was 261.02 ± 14.48 mg/100 g of dry basis (d.b.), and in the atomized powder was 253.45 ± 10.82 mg/100 g of dry basis. The antioxidant activity of the extract in acidified water was approximately 7.4 ± 0.3 mmol trolox/kg (d.b.) and in dehydrated products decreased to 4.6 ± 0.2 mmol trolox/kg (d.b.). In addition, the solubility of the powder was 99.3 ± 0.5 %; the $CIEL^*a^*b^*$ color values were 75.8 ± 0.1 , 30.1 ± 0.1 and -4.1 ± 0.1 for L^* , a^* and b^* , respectively. In

Fig. 1 Electron microscopy image of the red cabbage extract atomized with 10 % of gum Arabic at 140 °C (a). Magnification of 3,000×

Fig. 1 is possible to observe that the particles are spherical in shape and contain many concavities and the adhesion of smaller particles to the bigger ones. According to Osorio et al. (2010), the formation of concavities in the powders atomized with gum Arabic may be a result of the particle shrinking that takes place due to the rapid evaporation during the drying process.

Sorption isotherms

In Fig. 2 it is observed that the equilibrium moisture rises with the increase in water activity, with equilibrium values for water activity ranging from 0.119 to 0.905. According to Mrad et al. (2012), moisture rises linearly with the water activity in cases of low and medium water activity (region of multilayered sorption), and rises quickly with the water activity in

Fig. 2 Experimental values for the equilibrium moisture as a function of water activity and sorption isotherms at the different temperatures. (▼) 15 °C; (■) 25 °C; (●) 35 °C; (—) GAB model 15 °C; (---) GAB model 25 °C; (····) GAB model 35 °C

cases of high water activity (region of capillary condensation). Fernandes et al. (2014) observed that the equilibrium moisture content in treatments formulated using gum Arabic rose strongly when exposed to relative humidity levels higher than 0.60. On the other hand, Ayranci et al. (1990) indicates that water can be adsorbed in the surface of carbohydrates in polar sites in cases of low values of water activity, while carbohydrate dissolution takes places in cases of high water activity.

The sorption isotherms belonged to type III, similarly to what was observed for the other products encapsulated with gum Arabic, such as rosemary essential oil (Fernandes et al. 2014), chicken meat hydrolyzed protein (Kurozawa et al. 2009), pineapple pulp (Gabas et al. 2007) and açai juice (Tonon et al. 2009).

The experimental data was adjusted to the models shown in Table 1, and the parameters obtained by regression analysis, as well as the determination coefficients and RMSE are shown in Table 2. In Table 2 it can be seen that GAB model was the one that best adjusted to the experimental data ($R^2=0.99$ e $RMSE=0.0356$ a 0.0761), followed by Oswin and Halsey models.

Table 2 also shows that the values of GAB C constant decreased with the rise in temperature, which suggests an expected tendency for a reduction of bond energy of the first

adsorbed layer with the rise of temperature (Al-Muhtaseb et al. 2004a). Such decrease indicates an increasingly shorter residence time of the molecules adsorbed on the first layer, and an adsorption process less strongly localized (Resio et al. 1999). We can assume the existence of strong adsorbent-adsorbate interactions favored by low temperatures, causing a rise in parameter C with temperature decrease (Pérez-Alonso et al. 2006). Gabas et al. (2007) also observed that samples of powder pineapple with gum Arabic showed a decrease in the value of C with the temperature rise.

The monolayer moisture content (X_m) increased with the rise in temperature, similarly to what was observed by Togrul and Arslan (2007) in a study using walnut tree seed. Although this is not a very common behavior, it can be justified by two mechanisms, as observed by Ferreira and Pena (2003) in peach-palm flour adsorption isotherms. A rise in temperature may cause changes in the product's physical structure, providing a higher number of active sites with affinity for water molecules; or a rise in the solubility of solutes intrinsic to the product, causing a higher number of water molecules to be retained in the monolayer.

It is also observed that K values were close to 1. According to Cano-Higueta et al. (2013), the K value provides a measure for interaction between the molecules in multilayers and the adsorbent, and tends to be situated between the energy value of molecules in multilayer and in the liquid water. If K equals to 1, the multilayer has liquid water properties.

Quirijns et al. (2005) suggests that the low values of C (lower than 2) and high values of K (higher than 0.9) indicate that the monolayer and multilayer molecules are not so different and that the multilayer molecules behave more like liquid molecules.

Differential thermodynamic properties

The values of differential enthalpy and entropy calculated for the red cabbage extract powder as a function of moisture content are shown in Fig. 3. Differential enthalpy was negative for all moisture values at the temperature used. These values indicate the existence of strong forces of attraction in the water-wall material mixture, which apparently commanded the connection between the extract and the wall material (Pérez-Alonso et al. 2006). According to Rizvi and Benado (1984), the wall materials may present active sites with different activation energies in their surface. Therefore, the water molecules are adsorbed preferably at active sites with stronger forces, producing the most negative enthalpy value (4.36 kJ/mol).

As the water content increases, the water molecules penetrate the matrix of the wall material and occupy all accessible active sites. The differential enthalpy decreased to a minimum negative value (4.36 kJ/mol) with the rise in moisture content, and then rose gradually in magnitude as the water content

Table 2 Estimated values for the coefficients obtained from the fit of the sorption models

Model	Constant	Temperature		
		15 °C	25 °C	35 °C
GAB	X_m	0.8857	1.9283	3.3805
	C	1.4017	0.3264	0.1899
	K	0.9980	0.9609	0.9308
	R^2	0.9999	0.9997	0.9994
	$RMSE$	0.0356	0.0514	0.0761
Halsey	a	3.3571	3.4375	3.4873
	b	-4.1636	-3.9243	-3.7454
	R^2	0.9754	0.9729	0.9714
	$RMSE$	0.4977	0.5227	0.5372
Oswin	a	0.9969	0.9834	1.0319
	b	0.9835	1.0473	1.0666
	R^2	0.9997	0.9985	0.9976
	$RMSE$	0.0541	0.3949	0.3721
Chung & Pfof	a	0.0203	0.0249	0.0293
	b	5.1872	5.0249	4.8869
	R^2	0.9705	0.9636	0.9606
	$RMSE$	0.5453	0.6053	0.6300
Smith	a	-0.9392	-1.1612	-1.7588
	b	-8.5950	-9.8624	-10.4295
	R^2	0.9367	0.9483	0.9543
	$RMSE$	0.7985	0.7219	0.6790

Fig. 3 Differential enthalpy and differential entropy as a function of the equilibrium moisture content. (●) enthalpy; (▼) entropy

went up. The rise of the differential enthalpy corresponds to an endothermic process that may be associated to the swelling of the polymer matrix, which exposes new active sites where new water molecules can be adsorbed by an exothermic process that compensates for the endothermic heat (Pérez-Alonso et al. 2006). When the moisture content rises, the availability of highly polar water adsorption sites decreases, causing enthalpy to decrease as well (Aviara et al. 2002; Kaya and Kahyaoglu 2006).

The differential entropy also decreased to a minimum negative value (0.019 kJ/molK) and then rose in magnitude with the rise in water content. According to McMinn and Magee (2003), this value of minimum entropy is possibly caused by water fixation (loss of freedom of rotation and randomness) due to the strong connection between the water molecules with the solid mean. According to Madamba et al. (1996), the differential entropy is proportional to the number of sorption sites available at a specific energy level, and the changes in entropy may be associated to the connection and repulsion forces in the system. ΔS may also be related to the degree or randomness order of the water-adsorbent system and is useful for interpreting processes such as dissolution, crystallization and tumescence (Beristain et al. 1996; Aviara et al. 2002).

Compensation theory

Krug's test (1976) was used to assess the compensation theory and indicated that the value of harmonic mean temperature (297.93 K) was significantly different from the isokinetic temperature (190.08 K), which confirms the theory. Because the value obtained for T_β was lower than the one obtained for T_{hm} , this indicated that the adsorption process is controlled by entropy.

Gibbs free energy value was -0.48 kJ/mol, indicating that the adsorption process is spontaneous ($\Delta G < 0$) and suggesting that the product spontaneously adsorbs moisture from the

environment (Apostopoulos and Gilbert 1990). According to Rizvi (2005), negative values for ΔG suggest strong intermolecular or connection interactions (related to enthalpy), which leads to a higher reduction of freedom in the configuration of water molecules, and consequently to a higher order in the system (related to entropy). Cano-Higueta et al. (2013) also obtained negative values of approximately -8 kJ/mol for ΔG in a study using mango pulp atomized with maltodextrin.

Net integral thermodynamic properties

Figure 4 shows the spreading pressure variation as a function of water activity. It can be observed that the spreading pressure rises along with the water activity for all temperatures studied, but there is little temperature effect on φ values, as verified by Torres et al. (2012) in a study using different gums, and by McMinn et al. (2004) in a study using starch gels. The spreading pressure represents the excess of free energy on the surface and provides an indication of the superficial tension increase on sorption sites due to the molecules adsorbed (Fasina et al. 1999).

Figure 5 shows the values of net integral enthalpy and entropy as function of the moisture content. It is possible to observe that the net integral enthalpy decreases with the rise in moisture content. A similar behavior was observed by Torres et al. (2012) in a study using guar gum, locust bean gum and xanthan gum. The net integral enthalpy occurs due to the primary and highly polar water adsorption sites present on the surface of the material (Fasina et al. 1999). In low moisture content, water is adsorbed in the most accessible sites of the solid surface, and then the net integral enthalpy starts to decrease as less favorable places are covered and multiple layers of adsorbed water are formed (Al-Muhtaseb et al. 2004b). When the equilibrium moisture content are too low, the water molecules are adsorbed forming a monolayer over the

Fig. 4 Spreading pressure as a function of the water activity for the different temperatures. (▼) 15 °C; (■) 25 °C; (●) 35 °C

Fig. 5 Net integral enthalpy and net integral entropy as a function of the equilibrium moisture content. (●) enthalpy; (▼) entropy

adsorption sites and the adsorption system gains energy. After the monolayer is formed, the net integral enthalpy decreases as the adsorption sites are occupied by relatively weak connections of water molecules forming successive layers (Kaya and Kahyaoglu 2006).

Net integral entropy decreases with the rise in moisture content. Rizvi and Benado (1983) observed that there are two opposed entropic contributions regarding the adsorption of moisture in food: a loss in entropy due to the water location and a rise in entropy due to the structural transformation caused by solubilization and swelling.

Conclusion

The sorption data for the red cabbage extract encapsulated with gum Arabic were adjusted to the GAB model and the isotherms obtained belonged to type III.

The differential enthalpy and entropy for moisture content up to 2 g of water/g of dry basis decreased until they reached a minimum negative value of 4.36 and 0.019 kJ/mol, respectively. They increased in magnitude with the rise in moisture content until up to values closer to free moisture.

The use of the compensation theory was proven, with isokinetic temperature of 190.08 K, and the process was governed by enthalpy ($T_{\beta} < T_{hm}$). The values of Gibbs free energy were negative (−0.48 kJ/mol), which proves the process is spontaneous.

Regarding the integral properties, the spreading pressure increased with the rise in water activity for all temperatures studied, while net integral enthalpy and entropy decreased with the rise of moisture content, reaching values close to 10 kJ/mol and 0.025 kJ/molK, respectively.

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