

## 5. HEAT EFFECTS OF WATER SORPTION BY CHITOSAN AND ITS BLENDS WITH HPC

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### 1. Introduction

Polymers are characterised by a significant ability to sorb low-molecular substances. Their sorption abilities are related to the chemical structure and material non-homogeneity. Studies of sorption by polymers cover a broad spectrum of phenomena, including kinetics of the sorption of liquids at constant or changing temperature, migration of plastifiers and other additives in a polymer, elution of components from polymer blends, dissolution of polymers and other substances in the polymers, swelling, etc. Sorption studies enable calculation of sorbent diffusion coefficients, and provide information on thermodynamic properties of a system.

Water sorption by polymers has been a subject of researchers' interest for many years. Water sorption by both natural polymers such as cellulose, wool, silk, or proteins (casein, albumin), and synthetic polymers – polyamides, poly(vinyl) alcohol, polybutyral was analysed [1 - 3].

In this paper studies on water sorption by chitosan and its hydroxypropylcellulose blends in the form of films with different weight fractions of components are presented and thermal effects accompanying the sorption process are determined.

### 2. Theoretical

Gas adsorption on a solid surface is a spontaneous, exothermal process, accompanied by a decrease of free energy of the entire system.

Depending on the type of water bonding with material, thermal effect of the adsorption process is different. The highest heat of sorption, reaching hundreds of kJ/mol

water, is characteristic of chemisorption. In this case, the amount of moisture in the material is determined by stoichiometric ratios of the reacting substrates (water and adsorbent). During physical adsorption, water is bound to the material by so-called adsorption bonds and released heat is of the order of dozens kJ/mol water. The weakest thermal effect occurs when the so-called “free water” is bound due to condensation.

The adsorption equilibrium in the solid-water system is most often described by so-called adsorption (sorption) isotherms that determine the dependence of the mass of water adsorbed on the surface of 1 kg of the adsorbent, on water activity over the solid body, at constant temperature. Basing on the determined sorption isotherms, we can define the heat of sorption released when water is bound to the material.

Water sorption isotherms [4 - 6] can be described by the so-called GAB equation in the form:

$$\frac{X}{X_m} = \frac{c \cdot k \cdot a_w}{(1 - k \cdot a_w) \cdot [1 + (c - 1) \cdot k \cdot a_w]} \quad (1)$$

where:

$a_w = p/p_s$  – water activity, defined as the ratio of vapour pressure over water (p) to vapour pressure over the tested sample ( $p_s$ )

$k = e^{d/RT}$  – parameter in the equation

$X$  – amount of water in the sample

$d$  – energy needed to transport water inside a multimolecular absorbent layer

$X_m, c$  – parameters of the GAB equation,

$T$  – process temperature

$R$  – gas constant

Parameters  $c$  and  $X_m$  in the above equation, are determined from experimental data, using a linear form of the GAB equation:

$$\frac{a_w}{X \cdot (1 - k \cdot a_w)} = \frac{1}{X_m \cdot c \cdot k} + \frac{c - 1}{X_m \cdot c} \cdot a_w \quad (2)$$

The GAB model describes precisely sigmoidal isotherms to water activity up to ca. 0.9.

Parameters of the equation should be then in the range:  $0.24 < k \leq 1$  and  $5.67 \leq c < \infty$  [7].

Parameter  $c$  in the GAB isotherm equation is used to calculate the mean heat of adsorption of the first layer of gas molecules ( $E_1$ ):

$$c = \frac{a_1 \cdot b_2}{b_1 \cdot a_2} \cdot e^{(E_1 - E_2)/RT} \quad (3)$$

where:

$a_1, a_2, b_1, b_2$  – constants independent of the amount of water adsorbed in the first and second layer, respectively

$T$  – temperature

- $R$  – gas constant  
 $E_I$  – heat of adsorption in the first layer  
 $E_L$  – molar heat of adsorptive vapour condensation

Since relation  $(a1 \cdot b2)/(b1 \cdot a2)$  is close to unity, a formula for pure molar heat of adsorption ( $q$ ), corresponding to the difference of heat of adsorption in the first layer ( $E_I$ ) and molar heat of water vapour adsorption ( $E_L$ ), is as follows:

$$q = E_I - E_L = R \cdot T \cdot \ln c \quad (4)$$

An increase of temperature is disadvantageous for the sorption process because it causes a decrease of material sorptivity, i.e. moisture content  $X$  at a constant value of  $a_w$ .

By a direct analysis of experimental isotherms that describe water sorption by a given adsorbent at different temperatures, we can define thermal effect which accompanies a transformation which takes place in isothermal and isobaric conditions, i.e. the so-called isosteric heat of adsorption  $q_{st}$ . From adsorption isotherms we can determine isosteres – the lines representing the dependence of water activity on temperature at a constant amount of adsorbed gas [8, 9].

When isosteres describing the relation:  $\ln(a_w) = f(1/T)$  are the straight lines, pure molar isosteric heat of adsorption is calculated from slopes of straight lines of particular isosteres, using the equation:

$$q_{st}^o = -R \cdot \left( \partial \ln a_w / \partial \frac{1}{T} \right)_x \quad (5)$$

### 3. Experimental

#### 3.1. Materials

Chitosan is a natural copolymer of glucosamine and N-acetylglucosamine. It is formed during deacetylation of chitin, a polysaccharide that occurs in the shells of crabs, shrimps, lobsters, insects and other crustaceans, and also in fungi parenchyma and cell walls of microorganisms.

Hydroxypropylcellulose is an ester of cellulose obtained due to binding propylene oxide to hydroxyl groups of alkylcellulose.

Both polymers, as high-molecular polysaccharides, can sorb water easily by formed hydrogen bonds using hydroxyl and amide groups that exist in their structures. Chitosan (CH) is a copolymer, a partly deacetylated derivative of chitin coming from various natural sources. An object of this study was the sample of chitosan (from krill) with deacetylation degrees (DD) 78% and  $M_w = 2.1 \cdot 10^5$  purchased from the Sea Fishery Institute in Gdynia, where it was produced.

A polymer used for physical modification of chitosan was hydroxypropylcellulose (HPC) of  $M_w=1 \cdot 10^5$  purchased from the Sigma – Aldrich Chemie, Germany. A water solution of 1% acetic acid was used as a chitosan solvent.

### 3.2. Film preparation techniques

Chitosan is insoluble in water, but with acetic acid it forms a water-soluble salt called chitosan acetate. Chitosan of deacetylation degree  $DD = 78\%$  in the form of powder, was dissolved in 1% acetic acid to obtain 2% solutions. The process of chitosan dissolution took place at room temperature (ca.  $24\text{ }^\circ\text{C}$ ) for about 48 h. The resultant bright yellow solutions with different viscosities were then carefully filtered.

In order to obtain blends of CH78 with HPC of proper weight fractions of the components, appropriate amounts of 2% chitosan solution were mixed with 2% (water) solution of hydroxypropyl cellulose (Table 1).

**Table 1.** Determination of chitosan and chitosan hydroxypropylcellulose blends;  $w_f$  – weight fraction of chitosan.

Sample	$w_f$
CH78	1
CH78/HPC/0.8	0.8
CH78/HPC/0.6	0.6
CH78/HPC/0.4	0.4
CH78/HPC/0.2	0.2
HPC	0

The solutions of chitosan CH78, HPC and their blends (CH78/HPC) were cast onto glass plates and left for 3 days to evaporate water. Strictly specified amounts of the solutions were used to produce films of comparable thicknesses equal to about  $15\text{ }\mu\text{m}$ . Prior to the investigations, the films of CH78, HPC and their blends were air-dried for 24 h.

### 3.3. Research methods

The kinetics of water sorption by tested samples was investigated by the gravimetric method using an analytical balance.

Analysis of water sorption was carried out at the temperatures  $25^\circ$ ,  $35^\circ$  and  $45^\circ\text{C}$  ( $\pm 1^\circ\text{C}$ ) in 9 desiccators equipped with a hygrometer and thermometer, each of them containing saturated solution of a different salt (Table 2) in order to obtain variable air humidity (water activity).

Prior to proper water sorption measurement, the tested samples were dried at the temperature around  $100^\circ\text{C}$  to constant mass. Next, they were placed in the desiccators

containing saturated solutions of the above mentioned salts. Every several minutes the samples were taken out, their mass was measured. The measurements were made until reaching the state of equilibrium (ca. 4 h).

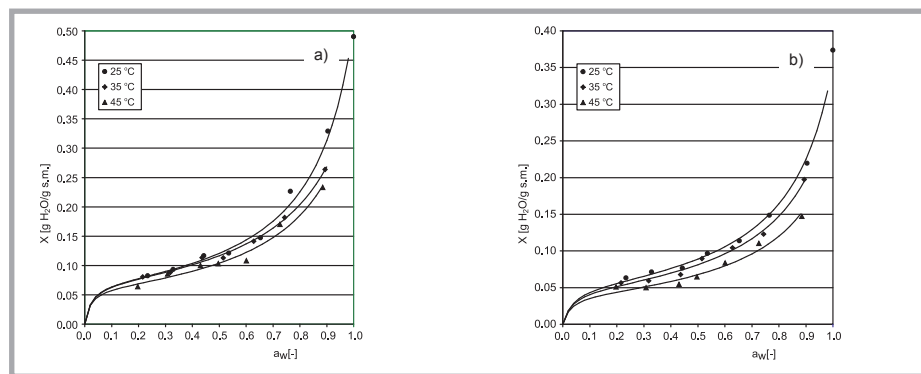
The estimated error of gravimetric measurements was about 10%. The error resulted primarily from the experimental method that consisted in taking the samples out from the desiccator to weigh them which disturbed thermodynamic equilibrium of the system for a short time. Similar measurements were triplicated. Desorption studies were performed by scanning calorimetry in a Mettler DSC FP90.

**Table 2.** Water activities over saturated solutions of various salts;  $a_w$  – water activity.

salts	$a_w$
CH <sub>3</sub> COOK	0.234
MgCl <sub>2</sub>	0.329
K <sub>2</sub> CO <sub>3</sub>	0.443
Mg(NO <sub>3</sub> ) <sub>2</sub>	0.536
NaNO <sub>2</sub>	0.654
NaCl	0.765
KCl	0.846
BaCl <sub>2</sub>	0.904
H <sub>2</sub> O	1.000

#### 4. Results and discussion

Figures 1a) and b) show examples of sorption isotherms obtained at three temperatures, at which the process of sorption was carried out.



**Figure 1.** Sorption isotherms: a) CH78, b) CH78/HPC/0,6; points – experimental data, lines – isotherms according to GAB equation.

The shape of isotherms suggests that water adsorption by chitosan films is a strong phenomenon. The higher is the fraction of hydroxypropylcellulose in chitosan blend, the lower is sorption ability of the films.

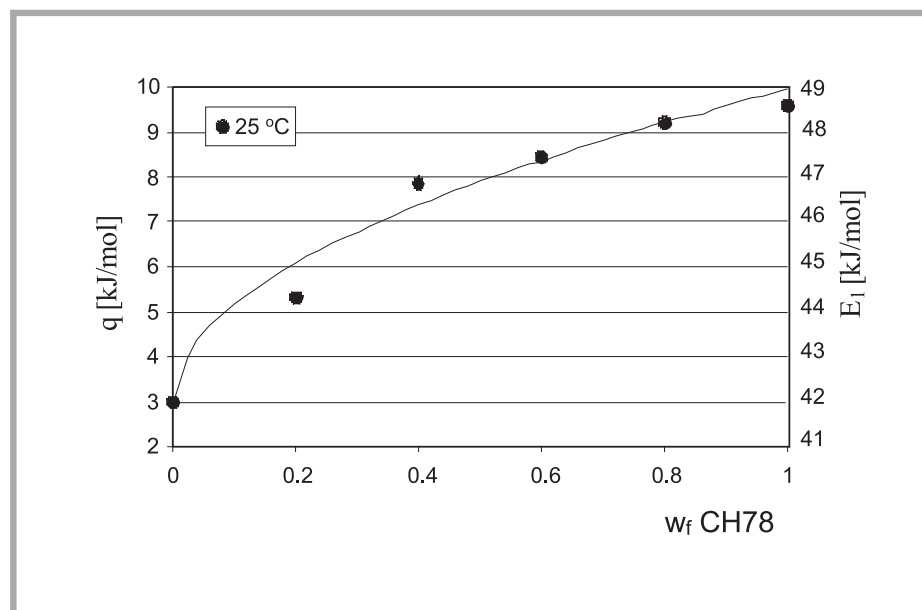
With temperature increase the adsorption becomes less efficient, which results in a decrease of sorption isotherm curves.

With temperature growth there is an increase of energy of adsorbed water molecules, which allows some of them to leave active centres of the adsorbent. As a result, the amount of adsorbed moisture decreases [10].

#### 4.1. Determination of pure molar heat of adsorption $q$ and mean heat of adsorption $E_1$ in the first layer of water molecules

Pure molar heat of adsorption ( $q$ ) and mean heat of adsorption of the first layer of water molecules ( $E_1$ ), were determined from equation (4).  $E_L$  – the heat of water vapour condensation at sorption temperature, was taken from literature [11] as known and equal to  $E_L=38.7$  kJ/mol.

Determination of the dependence of  $q$  and  $E_1$  on weight fraction ( $w_f$ ) of chitosan in the blend with HPC is shown graphically in Figure 2.



**Figure 2.** Dependence of pure molar heat of water sorption ( $q$ ) and mean heat of adsorption of the first layer of water molecules ( $E_1$ ), on chitosan weight fraction  $w_f$  in the blend;  $T=25^\circ\text{C}$ ; points – values calculated from equation (4)

When analysing the above relations, it is found that both  $E_I$  and  $q$  increase with an increase of chitosan weight fraction  $w_f$  in the blend according to the formulae:

$$q = 7.0 \cdot w_f^{0.6} + 3.0 \text{ and } E_I = 7.0 \cdot w_f^{0.6} + 41.7$$

#### 4.2. Calculation of partial isosteric heat of water adsorption $q_{st}$

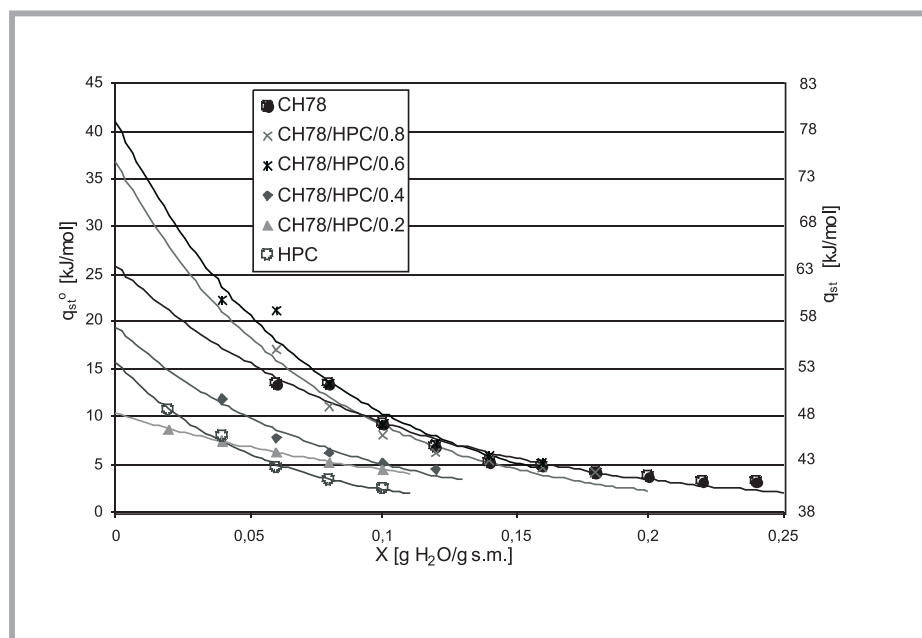
Isosteric heat of water adsorption is a measure of energy that binds water molecules with adsorbent surface [11]. It is also identified with the energy required to remove moisture from material [12, 13].

Since the process of adsorption is accompanied by vapour condensation, to estimate the total energy effect of the process, to the pure partial isosteric heats of water sorption (eq. (5)) one should add mean heat of water vapour condensation (for the analysed temperature range: 25 - 45 °C,  $E_L=38.7$  kJ/mol). Consequently, the partial isosteric heat of water adsorption  $q_{st}$  is obtained:

$$q_{st} = q_{st}^0 + E_L \quad (6)$$

Using Riedl equation [8], which represents a change in water activity  $a_w$  with temperature T (7):

$$\ln \left[ \frac{a_w(T_2)}{a_w(T_1)} \right]_X = A \cdot e^{(-b \cdot X)} \cdot \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (7)$$



**Figure 3.** Dependence of pure isosteric heat of water adsorption ( $q_{st}^0$ ) and isosteric heat of water adsorption ( $q_{st}$ ) on the amount of adsorbate, chitosan and hydroxypropylcellulose blend

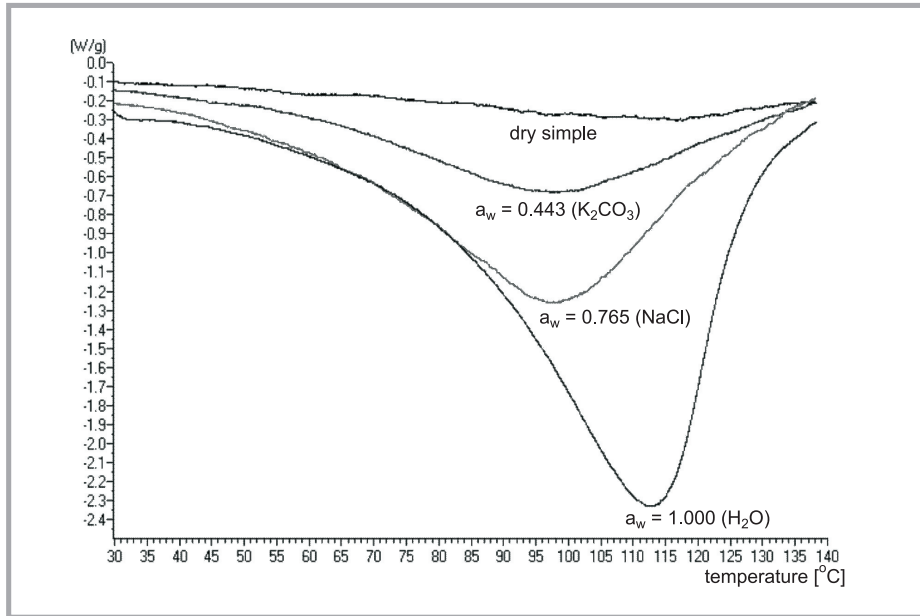


Figure 4. DSC peaks of water desorption for CH78, sorption at  $T=25\text{ }^{\circ}\text{C}$ .

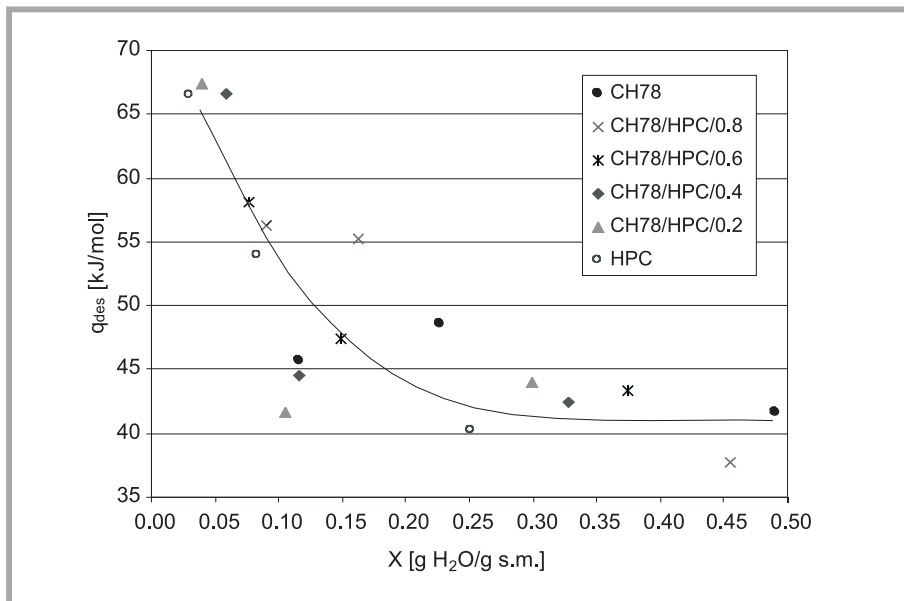


Figure 5. Dependence of the heat of water desorption ( $q_{des}$ ) on the amount of water adsorbed by polymer films ( $X$ ) at temperature  $25\text{ }^{\circ}\text{C}$ . Points - experimental data; lines - calculated from equation (8),  $C=40$ ,  $b=12$ ,  $E_L=41$ .



where:  $A, b$  – constants,

isosteric heat of adsorption  $q_{st}$  was described [12] as a function of water content in the material  $X$  in the following way:

$$q_{st} = C \cdot e^{(-b \cdot X)} + E_L \quad (8)$$

$C = R \cdot A$  – constant, ( $R$  – gas constant).

It follows from equation (8) that with an increase of the amount of adsorbed water, heat  $q_{st}$  released during the process decreases, tending to the heat of condensation  $E_L$ . The biggest thermal effect occurs at the beginning of the process (the first layer), then it decreases exponentially.

Figure 3 illustrates this tendency of heat of water adsorption decrease with an increase of  $X$ . From analysis of this Figure it follows that the highest thermal effect accompanies water adsorption by films made from CH78 and its blends of high CH78 content. Least heat is released during water sorption by films with a prevailing fraction of hydroxypropylcellulose.

#### **4.3. Determination of thermal effect of water desorption by the differential scanning calorimetry method (DSC)**

Water desorption is an endothermal process. Film samples with sorbed water at different activity  $a_w$  were heated in a DSC calorimeter. Thermal energy used for water evaporation, was recorded as a curve that formed an endothermal peak, whose surface area presents the heat of desorption of water bound in the sample. Figure 4 shows examples of water desorption curves obtained by the DSC method.

Dependence of the heat of desorption on the amount of water adsorbed at the temperature 25°C is shown graphically in Figure 5.

As in the case of adsorption, also water desorption from the surface of films made from chitosan, HPC and their blends is characterised by an increase of thermal effect with a decrease of moisture content in the sample. This means that the biggest amount of energy is required to remove water layers bound directly with the adsorbent surface. With an increase of absorbed water, the heat of desorption decreases tending to the value of the heat of water evaporation  $E_\gamma = 36.1$  kJ/mol (for  $T = 100$  °C).

## **5. Conclusions**

Measurements of water sorption by films made from chitosan, hydroxypropylcellulose and their blends performed by the gravimetric method, show superiority of chitosan to absorb water from the gas phase over HPC. Water sorption is the more effective the bigger is the chitosan content in the film composition.

Water sorption efficiency decreases with temperature growth, which is represented graphically as a decrease of sorption isotherms for  $X = \text{const}$ . With temperature increase adsorption becomes less efficient. As a result, sorption isotherm curves decrease.

With an increase of temperature, the energy of adsorbed water molecules increases and allows some of them to leave active centres of the adsorbent. A consequence is a decrease of the amount of adsorbed moisture.

For majority of water-polymer film systems, the description of experimental points by the GAB isotherm equation appeared to be suitable, the matching error of sorption curves to experimental data did not exceed 10%.

From parameter  $c$  in the GAB equation, the mean heat of adsorption of the first monomolecular layer of water molecules ( $E_1$ ), and pure molar heat of adsorption ( $q$ ) were determined. Results obtained lead to the following conclusions: at each analysed temperature, the highest thermal effect accompanied water sorption by chitosan films, and the least heat was released during sorption in the hydroxypropylcellulose-water system. It can be observed that the heat of adsorption of the first layer of water molecules ( $E_1$ ) exceeds the heat of water vapour condensation ( $E_L$ ).

The isosteric heat of water adsorption by polymer films ( $q_{st}^0$  and  $q_{st}$ ) was calculated by direct analysis of sorption isotherms, using the Clausius-Clapeyron relation. Graphs representing relation  $q_{st} = f(X)$  show that with an increase of adsorbed water, heat released during the process decreases, tending to the heat of condensation ( $E_L=38.7$  kJ/mol). This biggest thermal effect occurs at the beginning of the process; then it decreases exponentially. While analysing the isosteric heat of adsorption, we should note that the biggest thermal effect determined in this way is characteristic of water adsorption by films made from CH78 and its blends of high CH78 content, while least heat is released during the sorption of water molecules on the surface of films with a prevailing percentage of hydroxypropylcellulose. Differences in the heat of adsorption for films with different composition diminish with an increase of water adsorbed ( $X$ ), because the contribution of water vapour condensation characterised by heat  $E_L$ , constant for the analysed temperature range, grows during the process.

Thermal effect of the process of water desorption from polymer films was analysed by the differential scanning calorimetry method (DSC). As in the case of adsorption, also water desorption from the surface of films made from chitosan, HPC and their blends, is characterised by an increased thermal effect observed along with moisture content decrease in the sample. This means that the biggest amount of energy is required to remove water layers bound directly to the adsorbent surface.

With an increase of adsorbed water, the heat of desorption decreases, tending to the value of the heat of water evaporation  $E_V=36.1$  kJ/mol (for  $T=100^\circ\text{C}$ ).

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