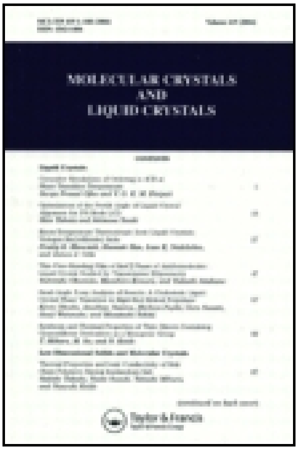

Molecular Crystals and Liquid Crystals

Study of Adsorption and Desorption Heats of Water in Chitosan and its Blends with Hydroxypropylcellulose

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Study of Adsorption and Desorption Heats of Water in Chitosan and its Blends with Hydroxypropylcellulose

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The aim of this work was to carry out a spectroscopic (FTIR) and calorimetric (DSC) study of water adsorption and desorption processes for chitosan (CH) and its blends with hydroxypropylcellulose (HPC). The amount of water adsorbed by samples was obtained from gravimetric measurements and sorption isotherms were prepared. Through the analysis of adsorption/desorption heats, states of water in films were identified.

Keywords: chitosan; hydroxypropylcellulose; isotherm; isosteric heat; water adsorption

INTRODUCTION

Water adsorption in polymers affects their physicochemical properties and determines degradability of macromolecules in the environment, e.g. by enzymes transported by water. It also plays a key role in drug delivery behavior [1]. Water adsorbed by polymers is divided into two main types [2–4]. The first one is bound water: adsorbate molecules are strongly bonded to individual hydrophilic material active sites making a first monomolecular layer or few molecular layers. This kind of water cannot freeze at the usual freezing point. The second one is free water which can freeze close to its freezing point (0°C). Adsorption of free water occurs due to condensation of additional monomolecular adsorbate layers.

Other researchers [5–8], basing on calorimetric measurements, identified third state of water in polymers, called freeazble bound water. This type of water tends to freeze below freezing point.

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Chitosan (CH) is a natural polymer obtained from chitin – a linear polysaccharide which is present e.g. in crustacean shields. A chemical process of converting chitin into chitosan – deacetylation, occurs at high temperature (over 383 K) and pressure in the presence of a strong alkali solution. The relation of obtained amino groups to primary acetyl groups of chitin is called deacetylation degree (*DD*). Chitosan finds applications in biomedicine, agriculture and environmental protection, since it has both hydroxyl and amino groups (Fig. 1A) that can be modified easily.

Hydroxypropylcellulose (HPC) is a cellulose ether. It is obtained by attaching propane oxide molecules to hydroxyl groups of cellulose (Fig. 1B). This polymer is used mainly in food production technologies and medicine (especially for drug delivery systems [9]).

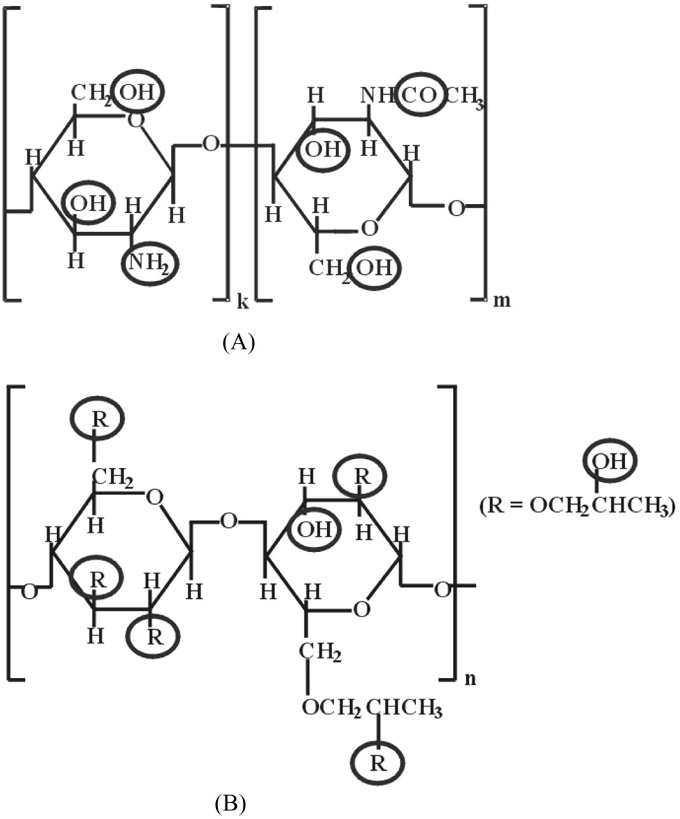


FIGURE 1 Chemical structure of chitosan (A) and hydroxyproylcellulose (B); water binding groups are marked.

Both chitosan and hydroxypropylcellulose are biodegradable and adsorb water easily. Groups which are capable to bind water molecules are marked in Fig. 1.

Blends of CH and HPC form homogeneous complexes due to hydrogen bonds. Addition of HPC to chitosan films makes them more flexible and reduces the amount of water adsorbed by them. This complexes can find many applications as matrices for drug delivery systems and food packing materials.

MATERIALS AND METHODS

Chitosan (CH) of deacetylation degree $DD = 78.5\%$ was purchased from the Sea Fishery Institute in Gdynia, Poland. Hydroxypropylcellulose (HPC) was produced by Sigma Aldrich Chemie GmbH, Steinheim, Germany. We used 1% acetic acid as a chitosan solvent and distilled water as a HPC solvent.

Films of chitosan, HPC and their blends of various compositions were prepared by casting 2% solutions onto Plexiglas plates and evaporating solvent at room temperature. Thickness of the obtained films was: 10 μm for FTIR and 40 μm for gravimetric analysis.

The films adsorbed water from vapor phase in dessicators which contained saturated salt solutions of different water activities (ranging from 0.2 up to 0.9) at three temperatures: 25°C, 35°C and 45°C. The effect of adsorption was analyzed either by gravimetric or infrared spectroscopy (FTIR) methods. Before the adsorption process, samples were dried at 90°C for 1 h to constant mass and the dry mass of the polymer films was determined.

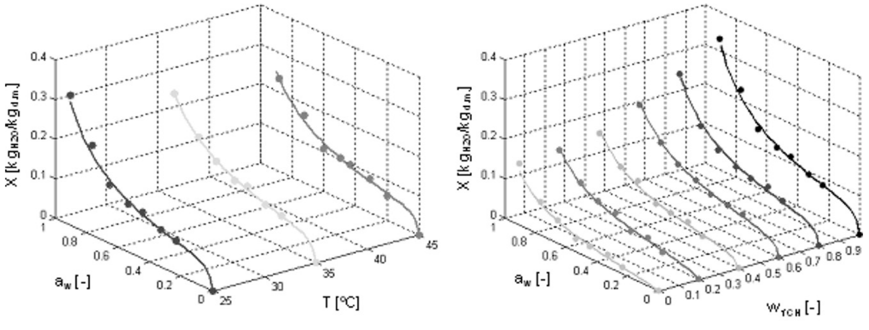
Desorption of water was studied by differential scanning calorimetry (DSC). The samples were heated at the rate 10°C/min from −30°C up to 185°C. This temperature range allowed us to identify the states of water present in the films.

RESULTS AND DISCUSSION

Adsorption Isotherms

Figure 2 shows water adsorption isotherms of the samples under study. Equilibrium of water adsorption by biomaterials is usually well described by the GAB model (Eq. (1)) [10].

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



(A) (B)

FIGURE 2 Water adsorption isotherms $X = \mathrm{f}(a_w,T,)$, $X = \mathrm{f}(a_w,w_f,)$ taken for: (A) CH at different adsorption temperatures ($T = 25°\mathrm{C}$, $T = 35°\mathrm{C}$, $T = 45°\mathrm{C}$). (B) CH/HPC blends at $T = 25°\mathrm{C}$; (points – experimental data, lines – GAB equation).

where X – amount of adsorbed water $[\mathrm{kg_{H_2O}/kg_{dry\ mass}}]$; X_m – adsorbate forming complete monolayer on the adsorbent surface $[\mathrm{kg_{H_2O}/kg_{d.m.}}]$; c – parameter related to adsorption heat, > 5.67; k – parameter ranging from 0.24 to 1; a_w – water activity [–].

It can be concluded that the higher adsorption temperature, the less water molecules are adsorbed by samples (Fig. 2A). On the other hand, a decrease of chitosan weight fraction in blend with hydroxypropylcellulose causes an increase of the amount of adsorbed water by film (Fig. 2B).

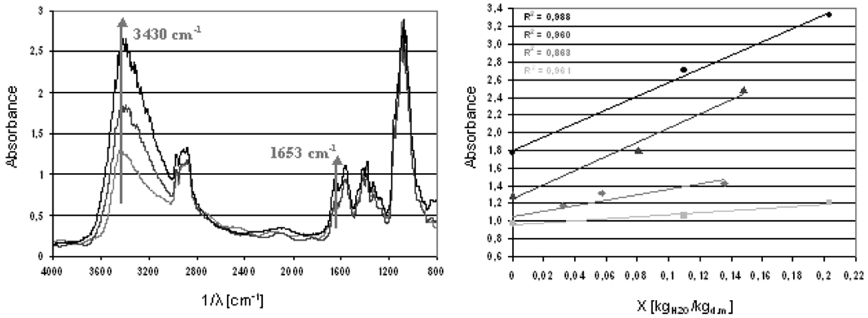
FTIR Spectra

Thin polymer films (of 10 µm thick) were analyzed by infrared spectroscopy. The most characteristic bands for chitosan and HPC which are affected by water, are: amino group (NH) at $1596\,\mathrm{cm^{-1}}$, C=O in amide group at $1653\,\mathrm{cm^{-1}}$ and hydroxyl group (OH) at $3430\,\mathrm{cm^{-1}}$. The chosen FTIR spectra are shown in Figure 3.

With an increasing amount of adsorbed water, intensity of absorbance in the band related to the hydroxyl group increases remarkably in all investigated samples. Water adsorption affects also IR absorbance in the band related to chitosan amide group (Fig. 3B).

Calorimetric Measurements (DSC)

The DSC thermograms show that whole water adsorbed by samples from vapor phase (up to 0.32 $[\mathrm{kg_{H_2O}/kg_{dry\ mass}}]$, see Fig. 2) is well



(A) (B)

FIGURE 3 (A) FTIR spectra for chitosan blend with HPC ($w_f = 0.6$) for different water amount: 1. $X = 0.148$ [$\mathrm{kg_{H_2O}/kg_{d.m.}}$]; 2. $X = 0.081$ [$\mathrm{kg_{H_2O}/kg_{d.m.}}$]; 3. $X = 0$ (dry sample). (B) Dependence of IR absorbance on the amount of adsorbed water: 1. OH group ($3430\,\mathrm{cm^{-1}}$) in chitosan; 2. OH group ($3430\,\mathrm{cm^{-1}}$) in CH/HPC blend ($w_f = 0.6$); 3. OH group ($3430\,\mathrm{cm^{-1}}$) in hydroxypropylcellulose; 4. amide group ($1653\,\mathrm{cm^{-1}}$) in chitosan.

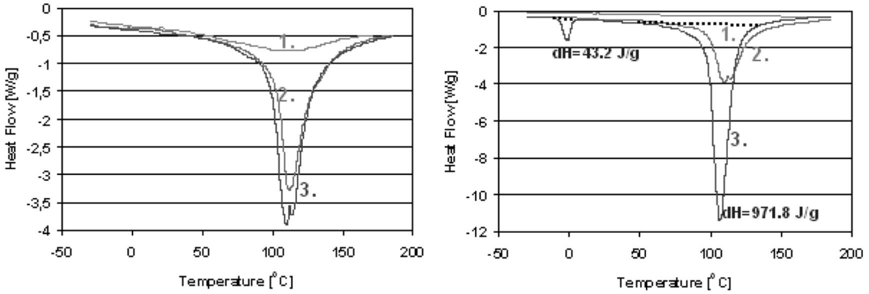
distributed on pore surfaces of the sample due to the interactions of hydrogen bonds and does not freeze at the freezing point (no water melting peak in Fig. 4A). With an excess water concentration > 0.54 [$\mathrm{kg_{H_2O}/kg_{dry\ mass}}$] for chitosan and > 0.62 [$\mathrm{kg_{H_2O}/kg_{dry\ mass}}$] for its blend with HPC ($w_f = 0.6$) freezing water is detected (Fig. 4B). In another paper [11] on chitosan powder ($DD = 80\%$) similar results were reported. To prepare the swelling samples with a higher amount of water, they were dipped in a vessel with distilled water for about a minute and then gently wiped with paper tissue.

Heat Effect of Water Adsorption/Desorption

DSC investigations of water evaporation from chitosan, HPC films and their blends are presented in Fig. 5A. Total heat needed to evaporate adsorbed water (dH) was detected as the area of wide endothermic peaks ranging from 50°C up to 150°C. Values of water desorption heat q_{des} were calculated per mole of water (Fig. 5B).

Isosteric heat of adsorption (q_{ads}) was calculated from sorption isotherms $X = f(a_w)$. It was determined for a narrow range of temperatures (25°C – 45°C), using the Clausius-Clapeyron equation (Eq. (2)). Basing on the values of c (GAB parameter), heat of adsorption of first monomolecular water layer (E_1) was also calculated (Eq. (3)).

$$\frac{d\ln(a_w)}{d[1/T]} = -\left(\frac{q_{ads} - E_L}{R}\right) \tag{2}$$



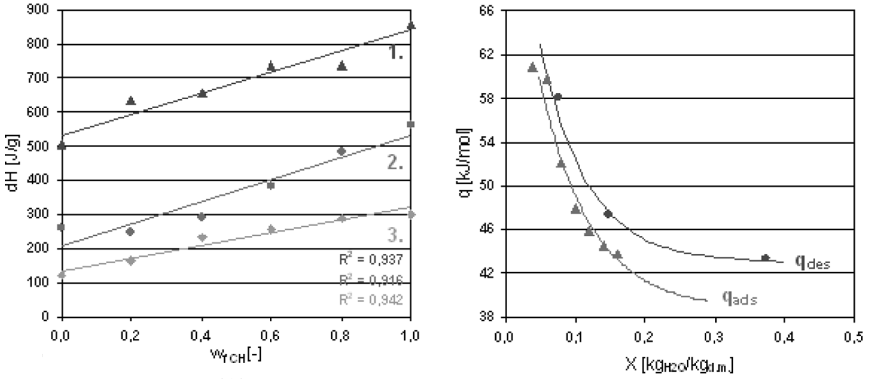
(A) (B)

FIGURE 4 (A) DSC curves for: 1. HPC ($X = 0.148\,\mathrm{kg_{H_2O}/kg_{d.m.}}$); 2. CH/HPC ($w_f = 0.6$; X $= 0.296\ \mathrm{kg_{H_2O}/kg_{d.m.}}$); 3. CH ($X = 0.323\ \mathrm{kg_{H_2O}/kg_{d.m.}}$). (B) DSC curves for chitosan films: 1. $X = 0$ (dry sample); 2. $X = 0.323\,\mathrm{kg_{H_2O}/kg_{d.m.}}$; 3. $X = 0.805\,\mathrm{kg_{H_2O}/kg_{d.m.}}$ (heats of water desorption are calculated as peak areas); (X – water amount, sample moisture).

where E_L – heat of water condensation [kJ/mol]; R – gas constant [kJ/(mol K)].

$$E_1 = R \cdot T \cdot \ln(c) + E_L \tag{3}$$

Both heat of water adsorption q_{ads} and desorption q_{des} tends to decrease with an increasing amount of adsorbate (Fig. 5B) leading to



(A) (B)

FIGURE 5 (A) Dependence of evaporation heat of water (per gram of sample) on blend composition (w_f – weight fraction of chitosan in CH/HPC blends); 1. $a_w = 1.0$; 2. $a_w = 0.765$; 3. $a_w = 0.443$. (B) Dependence of water adsorption (q_{ads}) and desorption (q_{des}) heats on the amount of adsorbate (water) for CH/HPC blend film.

the value of water condensation heat E_L (39 kJ/mol). The observed excess value of heat released (higher than condensation heat) during adsorption (q_{ads}) allows us to predict that at least few molecular layers of water in sample pores are bonded strongly enough by hydrogen bonds. Thus, this water is unfreezable and can be named semibound. DSC thermograms (Fig. 4B) don't show the presence of bound freezing water in analysed samples.

Heat of adsorption of the first monomolecular water layer (E_1) versus X_m (Fig. 6) exhibits parabolic character in the range of X_m under study. X_m – the amount of water in the first monomolecular layer reaches the value up to 0.07 [$kg_{H_2O}/kg_{dry\ mass}$] for chitosan. Parabolic relation $E_1 = f(X_m)$ – (Eq. (6)) was obtained by combining dependencies of X_m and E_1 on blend composition (Eq. (4,5)) calculated previously [12].

$$X_m = 0.043 \cdot w_f + 0.026 \tag{4}$$

$$E_1 = 48.7 \cdot w_f + 42.1 \cdot (1 - w_f) + w_f \cdot (1 - w_f) \cdot 7.5 \tag{5}$$

$$E_1 = A + B \cdot X_m - C \cdot X_m^2 \tag{6}$$

where $A = 30.9$ kJ/mol; $B = 538.8$ $(kJ \cdot kg_{d.m.})/(mol \cdot kg_{H_2O})$; $C = 4054.1$ $(kJ \cdot kg_{d.m.}{}^2)/(mol\ kg_{H_2O}{}^2)$; w_f – weight fraction of chitosan.

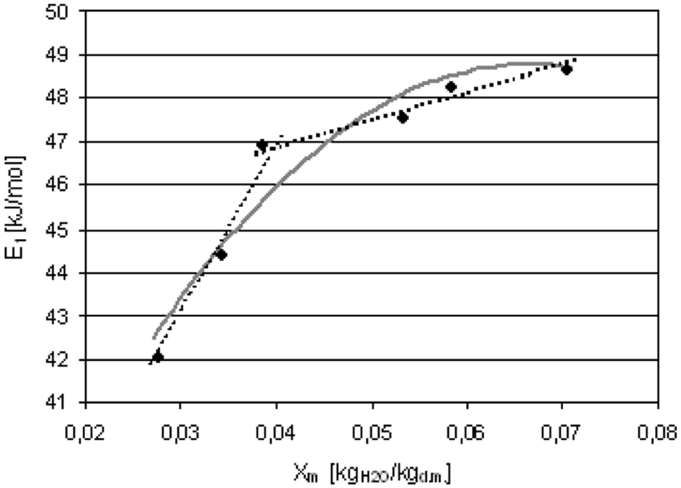


FIGURE 6 Dependence of adsorption heat of the first monolayer of water molecules (E_1) on the amount of adsorbate in that layer (X_m).

CONCLUSIONS

Chitosan films adsorb at 25°C more than 0.3 [$kg_{H_2O}/kg_{dry\ mass}$] water from vapor phase at high water activity ($a_w = 0.904$) (Fig. 2). With an increasing adsorption temperature, the amount of adsorbate decreases. The more weight fraction of HPC in the blend the less water is adsorbed.

With a rising amount of water in the blends the intensity of absorbance bands (OH stretching vibration mode at about 3430 cm^{-1} and carbonyl stretching vibration mode in chitosan amide group at 1653 cm^{-1}) related to hydrogen bonds increase remarkably (Fig. 3).

The whole water adsorbed from vapor phase by films of chitosan, HPC and their blend ($w_f = 0.6$) is certainly unfreezing, named as bound and semibound water.

Heat needed to evaporate water from CH/HPC blend films increases linearly with an increasing weight fraction of chitosan in the blend (Fig. 5A).

Heat of adsorption and desorption decreases exponentially with an increasing water amount in the sample reaching heat of water condensation ($E_L = 39$ kJ/mol) (Fig. 5B).

In a lower range of X_m values (HPC excess in the blends) E_1 changes with X_m more rapidly than in the case of higher X_m values (CH excess in the blends) (Fig. 6).

Results of our study show that different states of water are present in chitosan films and its blends with HPC. Since blends of CH and HPC are homogenous on micron level of the domains, and hydroxypropylcellulose adsorbs less water than chitosan, one can control blend hydrophilicity by matching its composition.

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