

# THE INFLUENCE OF THE DISPERSED OXIDES ON THE INTERFACE ENERGY OF THE MICROCRYSTALLINE CELLULOSE IN WATER SUSPENSION.

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## Abstract

The characteristics of water bounded layers in the hydrated powders and water suspensions of microcrystalline cellulose and thought containing SiO<sub>2</sub> or TiO<sub>2</sub> particles were investigated by <sup>1</sup>H NMR method. It is found that the concentration of strong bounded water and the  $\gamma_s$  value are in a strong dependence to the concentration of cellulose in suspension. Probably, it is dictated by strong interaction between cellulose particles. At the very high concentration of suspension concentration of water inside the cellulose filament decreases in more than 3 time and ( $\gamma_s$ ) value decreases from 9 to 31 J/g which is due to effect of surface forces. In the presence of dispersed particles of oxides, the concentration of bound water and  $\gamma_s$  value in average are decrease, aseptically in the case of suspensions with TiO<sub>2</sub> particles.

## Introduction

Cellulose is the one of the most prevalent natural polymer material which is part of the most plants. It can be isolate from the vegetable raw material as filament-like formation. This substances have a distinct crystalline structure created by space ordered elements of molecules, formed of adjacent polymer chains [1]. By chemical treatment the cellulose particles can be transferred into amorphous state which is characterized by orderless disposition of glucose elements being in the neighboring polymer chains. As the anhydro-D-glucopyranose units works as basis of filament-like polymer chains a significant amount of water molecule can be bounded with cellulose surface. Water forms a strong hydrogen bounded complexes with the hydroxyl groups of glucose. Water molecules are able to show a significant influence on interaction between cellulose particles which is reflected on the properties of the material as a whole.

The interaction of the cellulose with water molecule has been studied by a number of authors during the last decades [2-6]. The X-ray diffractometry data [3,4] shows that hydration of the surface of cellulose particles increases with decreasing of degree of crystallinity of the sample. On the basis of this statement it was shown that main part of bounded water in cellulose filament is located in amorphous zone. This conclusion have been confirmed by model calculation of the bounded water concentration on the surface of cellulose crystal [4,5]. In the corresponding with these calculations the bounded water layer with 2-3 molecular diameter in thickness might be formed on the surface of cellulose particles. However hydration of cellulose may be significantly more which is caused by filling the space between neighboring polymer chains or fibrils with water molecule. The concentration of the water molecule in such samples can get up to 30 wt % and mire [6]. Owing to non-strict structure of the cellulose the degree of hydration is not a constant and might be dependent on the external factors

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In particular the concentration of solid phase in suspension or presence of the dispersed particles being able to interact with polymer chains and affect on the hydration process.

The determination of the characteristics of the bounded water in water suspension and hydrated powders of microcrystalline cellulose (MCC) sample at the different ratio of the components were the goal of the present study as well as the influence of the dispersed oxides of silica and titania on the process of interaction between water molecule and MCC.

### Materials

Microcrystalline cellulose used in pharmaceutical industry as a component of tablet formulation was chosen for this study. A picture of powder obtained by scanning electron microscope is shown in fig. 1. In accordance with figure 1 cellulose particle have a cylindrical shape and average size is 10 x 100  $\mu\text{m}$ . Microcrystalline cellulose is the such type of cellulose which is partly hydrolyzed by HCl treatment. As a sequence main part of the amorphous sections are desolved and grows of cristallinity is observed. Dispersed silica (Aerosil 300) with surface area 300  $\text{m}^2/\text{g}$  and  $\text{TiO}_2$  with the particle size 0.1  $\mu\text{m}$  were used.

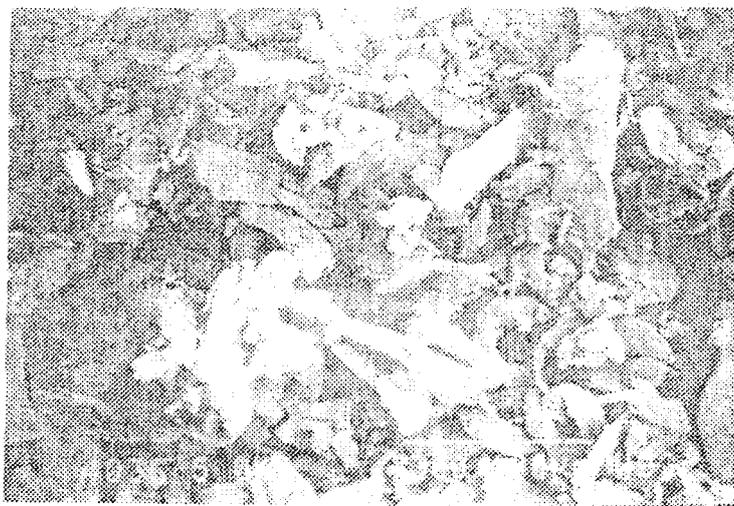


Fig. 1. Microphotography of microcrystalline cellulose, obtained by scanning electron microscope

### Method

The determinations have been done by  $^1\text{H}$  NMR spectroscopy by using a freezing of liquid phase procedure. This method has a good recommendation in the determination of the characteristics of bounded water layers in suspension of adsorbents and solutions of biopolymers [7-10].  $^1\text{H}$  NMR spectra were recorded on a high-resolution NMR spectrometer Bruker WP-100 SY (operating frequency 100 MHz: transmission band up to 50 kHz). The spectrometer sensor temperature was remained constant to an accuracy of  $\pm 1$  degree with the aid of a temperature controller BVT-1000. The integrated intensity of NMR signals was determined to an accuracy of  $\pm 10\%$  using an electronic integrator. The amounts of interfacial unfrozen water ( $C_{\text{H}_2\text{O}}$ ) in the frozen aqueous suspension of

cellulose at  $190 < T < 273$  K were estimated by comparison of an integral intensity ( $I_{uw}$ ) of  $^1\text{H}$  NMR signal of unfrozen water with that ( $I_w$ ) of water at  $T = 285$  K.

$$C_{\text{H}_2\text{O}} = (I_{uw}/I_w)(m_w / (m_c + m_w)) \quad (1)$$

Where  $m_w$  and  $m_c$  is the mass of water and cellulose in suspension before freezing.

The signals of surface hydroxyls and water molecules from ice were not detected due to features of the measurement technique and the short time ( $\sim 10^{-6}$  s) of cross relaxation of proton in solids [11]. The Gibbs free energy changes ( $\Delta G$  in kJ/mol) of the interfacial water were calculated (with relative mean error  $\pm 15\%$ ) using the known dependence of the changes of the Gibbs free energy of ice on the temperature  $\Delta G = 0.036(273 - T)$  [12]. We assume that water is frozen ( $T < 273$  K) at the interface when  $G = G_i$  and the value of  $\Delta G = G_o - G$  equals  $\Delta G_i = G_i / T = 273 - G_i(T)$  and corresponds to a decrease in the Gibbs free energy of the interfacial water due to its interaction with the solid surface ( $G_o$  denotes the Gibbs free energy of the bulk (undisturbed) ice).

To prevent the overcooling of water during freezing the measurement of signal intensity have been made at the heating of the samples preliminary cooled to  $T = 190$  K.

## Results

The dependence of  $\Delta G(C_{\text{H}_2\text{O}})$  for water suspension (curves 1-6) and hydrated powders of cellulose (curves 7,8) are presented in Fig. 2. Concentration of solid phase ( $C_{\text{sol}}$ ) in suspensions was varied from 6 to 44%. As it can be observed from Fig. 2, there is a vertical part of the curve for all dependencies which corresponds to the case of the constant concentration of unfrozen water in wide range of  $\Delta G$  changes (water adsorbed on the surface doesn't freeze in a wide range of temperature variation). For the microporous and mesoporous materials it was shown [13], that the presence of a such vertical section is caused by strong interaction between water molecule and surface. In this temperature region the decreasing of free energy caused by adsorption is larger than it caused by temperature drop. As strong bounded water is water that freezes at sufficient temperature diminution [7,13] it can be concluded in water suspension of cellulose all adsorbed water is strong bounded if concentration of cellulose  $C_{\text{sol}} \geq 20$  wt %. In diluted suspensions (Fig. 2, curve 1,2) the sections caused by weak bounded water are appeared. These sections can be characterized by changes of  $\Delta G$  value insignificantly in wide range of changes of the concentration of unfrozen water [12]. The concentration of strong and weak bounded water ( $C_{\text{H}_2\text{O}}^{\text{S}}$  and  $C_{\text{H}_2\text{O}}^{\text{W}}$  respectively) and maximum value in the decreasing of free energy in the layers of strong and weak bounded water ( $\Delta G^{\text{S}}$   $\Delta G^{\text{W}}$  respectively) can be determined by extrapolation of accordance parts of the  $\Delta G(C_{\text{H}_2\text{O}})$  dependence to the coordinate axis. In this case

$$C_{\text{H}_2\text{O}}^{\text{W}} = C_{\text{H}_2\text{O}}^{\text{max}} - C_{\text{H}_2\text{O}}^{\text{S}} \quad (2)$$

where  $C_{\text{H}_2\text{O}}^{\text{max}}$  maximum concentration of unfrozen water at  $T \rightarrow 273$  K.

The data obtained by this way are presented in Table 1. The Table also presents the interface energy  $\gamma_{\text{S}}$  value.

$$\gamma_{\text{S}} = \int_0^{C_{\text{H}_2\text{O}}^{\text{max}}} \Delta G dC_{\text{H}_2\text{O}} \quad (3)$$

Interface energy is equal to total decreasing of free energy of the water caused by presence of biopolymer/water interface. As the value of specific surface area of biopolymers is not known, as a rule, the  $\gamma$  value can be expressed in the units of free energy related to one gram of dry material.

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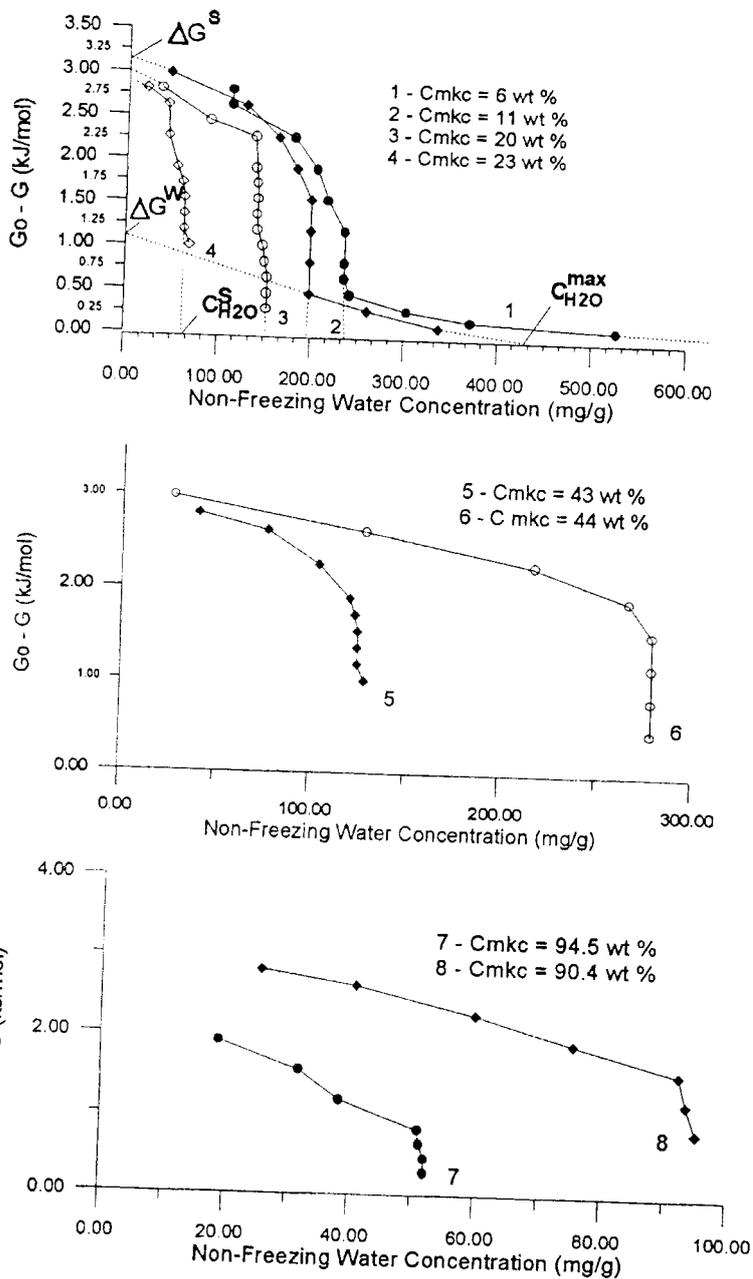


Fig. 2. The dependence of  $\Delta G(C_{H_2O})$  for water suspensions (curve 1-6) and hydrated pouders (curve 7,8) of cellulose

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Fig. 3 present the dependence of  $\Delta G(C_{H_2O})$  for hydrated powders (curves 1-3) and water suspension ( curves 4-8) for 1 : 5.7 mixture of silica and MCC and Fig 4 sows such dependencies for 1 : 3 mixture of dispersed  $TiO_2$  and MCC in the water. In the both cases the amount of powder was a half of the volume of the cellulose. The characteristics of the water bounded layers for the MCC+  $SiO_2$  +  $H_2O$  and MCC +  $TiO_2$  +  $H_2O$  systems are listed in tables 2 and 3.

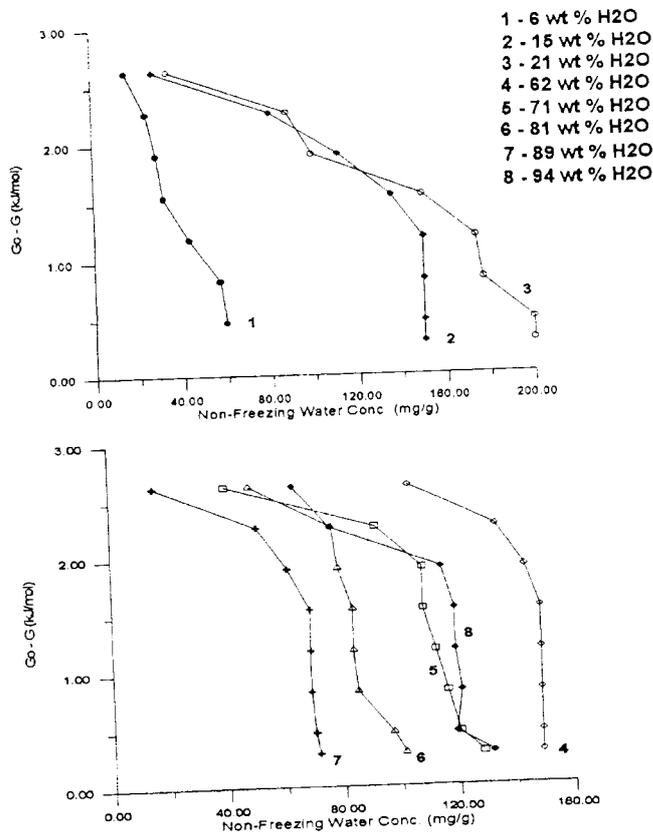


Fig. 3. The dependence of  $\Delta G(C_{H_2O})$  for water suspensions of cellulose and silica 5.6 : 1

The dependencies of interface energy from concentration of solid for water suspension for studied systems are presented on Fig. 5a. This dependencies has a complicated shape. In the beginning at  $C_{sol} \leq 20$  wt % (for systems MCC +  $H_2O$  and MCC +  $SiO_2$  +  $H_2O$ ) or  $C_{sol} \leq 10$  wt % (for system MCC +  $TiO_2$ ) as concentration of solid increases the  $\gamma_s$  value has inversely proportional decreasing. The  $\gamma_s$  value begins to increase again at more concentration. The dependencies of the concentration of strongly bound water against  $C_{sol}$  is shown on Fig. 5b. By comparison of Fig. 5a and 5b it can be concluded that observing character of dependence  $\gamma_s(C_{sol})$  caused by changing of  $C_{H_2O}^S$ . So the alteration of concentration of strong bounded water determines the interface energy value.

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**Table 1**  
 Characteristic of water bounded layers in the water suspension and hydrated powders of cellulose

| Concent. of Cellulose Wt. % | $\Delta G^s$ kJ/mol | $\Delta G^w$ kJ/mol; | $C_{H_2O}^s$ Mg/g | $C_{H_2O}^w$ mg/g | $\gamma_s$ J/g |
|-----------------------------|---------------------|----------------------|-------------------|-------------------|----------------|
| 6                           | 3.3                 | 0.7                  | 230               | 470               | 31             |
| 11                          | 3.2                 | 1.0                  | 200               | 200               | 29             |
| 20                          | 3.0                 | -                    | 160               | -                 | 23             |
| 23                          | 2.9                 | -                    | 75                | -                 | 9              |
| 43                          | 3.0                 | -                    | 125               | -                 | 17             |
| 44                          | 3.1                 | -                    | 280               | -                 | 38             |
| 90.4                        | 3.0                 | -                    | 95                | -                 | 12             |
| 94.5                        | 2.2                 | -                    | 52                | -                 | 5              |

As can be observed from Fig. 2 data the concentration of weak bounded water has a tend to decrease at  $C_{sol}$  increases. This type of bounded water has been appeared in that case when the distance between cellulose particles in suspension was more than some minimal value. So, weak bounded water is set up on the external side of the cellulose particle. For the strong bounded water different situation can be observed. Presence of the vertical sections on the dependence  $\Delta G (C_{H_2O})$  makes it similar to correspond dependence which is observed for water suspension of hydrophilic microporous adsorbents [13]. As micropores inside the cellulose particle can be either a channels formed by group of microfibrils or a free space between microfibrils available for water molecule. It can be considered that concentration of water in micropores (volume of micropores) determines by position of the vertical part of the dependence  $\Delta G (C_{H_2O})$ .

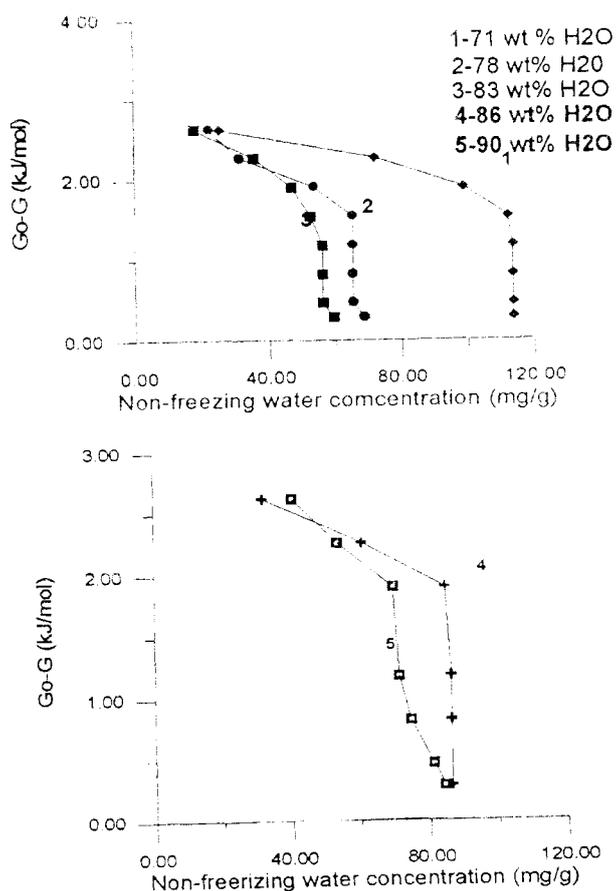
In contrast to the carbon adsorbents, the strong dependence of the volume of micropores against concentration of solid phase (Fig. 5b, Curve 1) can be observed. The volume of pores can be reduced from 250 down to 75  $\mu L/g$  that is due to influence of the neighbor particles. The most possible reason for this can be influence of the surface force on the volume of micropores. These forces acts in a big distance from the surface of cellulose particles and it can be proofed by the fact that the concentration of weak bounded water in diluted suspension may exceeds the concentration of strong bounded water inside the fibrils.

As the concentration of the strong bounded water in the cellulose filament is determined by the degree of crystallinity of the polymer [3,4] it might be suggested that surface forces of the neighboring particles affects on the crystallinity of the hydrated filament and sign of the interactions is determined by the distance between particles. If the distance is great (diluted suspension, left part of the curve 1, figure 5) then the degree

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of crystallinity increases under influence of the neighboring particles together with concentration of suspension. As a consequence the concentration of the strong bounded



**Fig. 4.** The dependence of  $\Delta G(C_{H_2O})$  for water suspensions of cellulose and titania 3 : 1 water in fibrils decreases. If the concentration of suspension (distance between particles reaches to some critical value then surface forces affects in opposite direction – the orderless structure of the polymer chains in fibrils is a result if this affection. Together with it the concentration of the strong bounded water in filaments increases ( right part of the curve 1 , fig.5). Proposed mechanism agreed with obtained in [14] dependence of cristallinity and hydration of some samples of cellulose.

The presence of the dispersed particles such as  $SiO_2$  and  $TiO_2$  in water suspension of cellulose brings the decreasing as maximal concentration of the strong bounded water as the  $\gamma_s$  value. The dependencies of the  $\gamma_s(C_{sol})$  and  $C_{H_2O}^S(C_{sol})$  become more smooth and the section which is due to increasing of the  $\gamma_s$  и  $C_{H_2O}^S$  values with concentration can be observed better ( fig.5, curves 2,3).

The begining of this section shifts to more diluted suspension side as can be easily observed in the example of the  $SiO_2$  containing samples ( fig.5, curve2). Using this diagram it might be assumed the following mechanism of the influence of the dispersed

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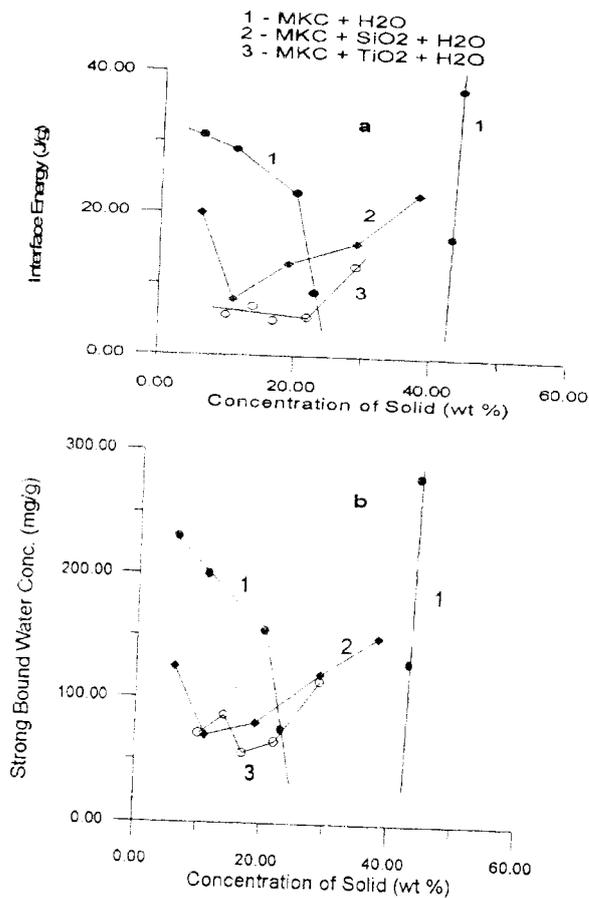


Fig. 5. The dependencies of interface energy and concentration of strong bonded water from concentration of solid for water suspension of studied systems

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oxides on the order of the polymer filaments in the cellulose fiber. The oxides dispersed in suspension affects not only on the decreasing of the interactions between cellulose particles but also can regulate the order in the polymer chain by itself. The main effect of this influence is arising of crystallinity of the filaments in presence of the dispersed oxides. This effect can be better observed for suspension containing TiO<sub>2</sub>. The observing dependencies  $\gamma_s(C_{sol})$  and  $C_{H_2O}^s(C_{sol})$  are determined as a summation of the effects of the interaction between MCC particles and MCC particles with dispersed oxides.

For each system which has been investigated the inflection of the interface energy value caused by interactions between particles may be determined as the difference between maximal and minimal value of the interface energy at the variation of concentration of the solid phase ( curve 1-3, fig. 5a). For the system containing just MCC, MCC + SiO<sub>2</sub> and MCC + TiO<sub>2</sub> this value is 22, 15 and 8 J/g respectively. On the basis of plots recorded on fig.5a the variation of the interface energy value caused by presence of the dispersed oxide can be determined. This value is defined as difference between ordinates of curves 1-2 or 1-3 when  $C_{sol}$  value is fixed.

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## Conclusions

On the basis of the investigation that have been performed it can be concluded that  $^1\text{H}$  NMR spectroscopy method together with freezing of liquid phase procedure can be used effectively to determine the bounded water concentration in water suspension of cellulose and interface energy value in suspension with different concentration.

Concentration of the strong and weak bounded water in the water suspensions changes in several times with concentration of suspension inflection. It is caused by decreasing of interface energy on the MCC/water interface. One of the possible reason for this effect might be influence of the neighboring cellulose particles on the order in the polymer chains in fibrils. When the distance between particles (diluted suspension) is big the neighboring particles would cause the ordering effect and the concentration of the strong bounded water and interface energy value decreases with arising of concentration of suspension. If the distance is less then some critical value (concentrated suspensions) a reverse regularity is occurred. The nearest molecule can cause the regulation of the polymer chains and as a consequence the  $\gamma_s$  and  $C_{H_2O}^S$  values increases.

By introduction of the dispersed oxides in suspension containing less then 20 % of the solid phase the  $\gamma_s$  and  $C_{H_2O}^S$  values have been decreased. The interface energy value has also been decreased caused by interaction between particles. It was state that the dispersed oxides particles and cellulose particles would cause the regulation of the polymer chains in fibrils.

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