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# Study of thermodynamic properties of various allomorphs of cellulose

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**Abstract :** Thermodynamic characteristics of cellulose samples having different crystallinity (X) and type of crystalline allomorph (CI to CIV) have been studied. Using methods of combustion calorimetry and DSC, the accurate values of standard enthalpy,  $\Delta_f H^\circ$ , and free energy of formation,  $\Delta_f G^\circ$ , as well as melting enthalpy of crystallites,  $\Delta H_m^\circ$ , were obtained. To avoid the use of uncertain indexes of crystallinity, a precise thermochemical method was proposed to determine the actual degree of crystallinity (X) of cellulose samples. It was found that with the decrease of crystallinity degree all linear dependences  $\Delta_f H^\circ = f(X)$  and  $\Delta_f G^\circ = f(X)$  converge at one common point,  $\Delta_f H_{am}^\circ = -942.4$  kJ/mol and  $\Delta_f G_{am}^\circ = -642.6$  kJ/mol, corresponding to amorphous phase cellulose at  $X = 0$ . This evidences that the amorphous phase in different cellulose samples has iden-

tical thermodynamic characteristics. On the other hand, the linear extrapolation of these dependences to the values corresponding to  $X = 1$  gives the enthalpy and free energy of formation of different crystalline allomorphs. Based on obtained thermodynamic characteristics, the phase stability of various crystalline forms of cellulose and amorphous cellulose (CA) was estimated; and namely, the relative stability of the allomorphs decreases in the following order: CII > CIV  $\geq$  CI > CIII > CA. These results allow to explain the structural phase transitions and reactivity of the cellulose allomorphs under certain conditions. © Trade Science Inc.

**Keywords :** Cellulose; Crystalline allomorphs; Amorphous cellulose; Thermodynamic characteristics; Phase stability; Phase transitions.

## INTRODUCTION

Cellulose is a linear, stereoregular polysaccharide composed of D-glucopyranose (anhydroglucose) units linked by chemical  $\beta$ -1,4-glycosidic bonds<sup>[1,2]</sup>. The linear macromolecules of cellulose joined by hydrogen bonds form complicated supramolecular structure of this polymer

that consists of elementary nanofibrils and their bundles called microfibrils<sup>[2,3]</sup>. Moreover, each fibril is built of ordered crystallites and low ordered non-crystalline (amorphous) domains. The crystallites having three-dimensional order are strong and inaccessible structural elements. As against, the low-ordered amorphous domains having twisted and curved segments are weak and accessible places of

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the fibrils. Molecular chains of cellulose pass through several crystallites and amorphous domains linking them by strong chemical bonds. Thereby, cleavage of glycosidic bonds at the hydrolysis occurs mainly in amorphous domains of cellulose nanofibrils that facilitates release of the crystalline particles. The formed crystalline fragments have a level-off degree of polymerization from 100 to 300 that approximately corresponding to average degree of polymerization of individual crystallites<sup>[4]</sup>.

The structural investigations of ordered constituents showed that crystallites of natural celluloses have the allomorph type CI. Furthermore it was found that crystalline unit cell of CI can be in two distinct crystalline forms: triclinic  $CI_{\alpha}$  of  $P_1$ -space group and monoclinic  $CI_{\beta}$  of  $P2_1$ -space group; where  $CI_{\alpha}$  form is characteristic for algae and bacterial celluloses, while more stable  $CI_{\beta}$  form is dominant in higher plants and tunicin<sup>[2,5,6]</sup>.

Three additional crystalline allomorphs: CII, CIII and CIV, have been identified, which are attributed to structural-modified celluloses<sup>[1-3,5,6]</sup>. Samples containing CII-crystallites can be obtained by alkaline treatment of natural cellulose or by regeneration from cellulose solutions. Cellulose samples with CIII crystalline allomorph are derived from samples of CI or CII by treatment with liquid ammonia. Samples with CIV crystalline form are prepared usually by heating of CIII-samples in hot glycerol. Various cellulose allomorphs have different parameters of crystalline unit cells<sup>[2,3,6-8]</sup>. The crystalline allomorphs of cellulose differ from each other also by shapes of crystalline unit cells. The projection of CI-unit cell has shape of parallelepiped; CIV-unit cell has square shape, while unit cells of CII and CIII have rhombic shape. Content of crystalline domains in various cellulose samples i.e. crystallinity, is different, from zero for amorphous sample to about 80% for microcrystalline cellulose<sup>[3]</sup>. Amorphous cellulose can be produced by ball-milling of semicrystalline cellulose samples or by saponification of amorphous cellulose acetate in non-aqueous medium<sup>[9]</sup>.

Due to existence of distinct crystalline polymorphs and amorphous cellulose, various studies were performed in order to estimate the phase

stability of different allomorphs. The amorphous phase state is regarded as a labile, because the amorphous cellulose can easily recrystallize in any crystalline allomorph under certain conditions<sup>[9]</sup>. This conclusion is also confirmed by the results of thermodynamic and thermochemical investigations<sup>[10,11]</sup>. In the case of crystalline polymorphs of cellulose, the problem regarding the relative stability of the phase state is not completely resolved and remains open. Study of thermodynamic and thermochemical characteristics gave reason to believe that phase state of CII is more stable than CI<sup>[11,12]</sup>. However, in another study it was concluded that the stability of phase state of various crystalline allomorphs cannot be estimated with a reasonable degree of certainty due to uncertainties in the measured characteristics<sup>[10]</sup>. As is known, the completely crystalline cellulose is absent. Therefore, to study the phase state of a crystalline allomorph, it requires the use of several samples with different crystallinity degrees. Unfortunately, the existing methods for determining the crystallinity of cellulose such as XRD and <sup>13</sup>C-NMR, give unreliable indexes of crystallinity<sup>[3]</sup>, which cannot be used in accurate thermodynamic calculations.

The aim of this paper was to study of the thermodynamic stability of four crystalline allomorphs of cellulose (CI, CII, CIII and CIV), as well as amorphous cellulose. To avoid the use of uncertain indexes of crystallinity, a precise thermochemical method was proposed to determine the actual degree of crystallinity of cellulose samples.

## EXPERIMENTAL

### Materials

Refined and bleached chemical Kraft pulp (KP) and cotton cellulose (CC) having  $CI_{\beta}$  allomorph were supplied from Buckeye Technologies, Inc. Samples of  $CI_{\beta}$  Avicel MCC PH-101 (MCC-1) and PH-301 (MCC-2) were supplied from FMC. The  $CI_{\beta}$  samples were additionally purified by extraction with organic solvents, chelating agent EDTA, boiling 2% NaOH and boiling water; then samples were rinsed with deionized water, ethanol and dried at 350 K to

constant weight. Amorphization of cellulose was carried out by ball-milling of Kraft pulp with ceramic balls for 2 (AC-1) and 8 h (AC-2); then amorphized samples were washed with ethanol and dried at 350 K to constant weight.

To obtain CII allomorph, the CI<sub>p</sub> samples were mercerized with 20% NaOH at room temperature overnight; then the samples were washed with water, neutralized with 1% HCl, washed with water to neutral pH, rinsed with ethanol and dried at 350 K to constant weight. Fibers of regenerated cellulose (RC) with CII allomorph were obtained from Rayonier Inc. The fibers of RC were additionally purified by extraction with organic solvents, chelating agent EDTA and boiling water; then samples were rinsed with ethanol and dried at 350 K to constant weight.

To prepare CIII, the Kraft pulp and cotton cellulose were treated with anhydrous liquid ammonia at 240 K for 3 h, washed with ethanol and dried. Samples with CIV allomorph were prepared by treatment of CIII samples in glycerol at 533 K for 30 min; then the treated samples were washed with water, ethanol and dried at 350 K to constant weight. The main characteristics of the samples are shown in the TABLE 1.

## METHODS

### Characterization of samples

Content of cellulose in the samples was

determined by NREL LAP 002 method<sup>[13]</sup>, while content of ash was analyzed by NREL LAP 005 method<sup>[14]</sup>. Average degree of polymerization (DP) was measured by the viscosity method using diluted cellulose solutions in Cadoxen<sup>[15]</sup>. Structural investigations of cellulose samples were carried out by XRD method<sup>[16]</sup>. Index of crystallinity (CrI) was estimated using subtraction method of amorphous scattering<sup>[17]</sup>.

### Calorimetry of wetting

The enthalpy of cellulose wetting with water ( $\Delta_w H$ ) was studied at 298.15 K by the method of precise microcalorimetry using TAM III calorimeter<sup>[18-20]</sup>. Cellulose samples were used in the form of small pieces or pellets. Typically, 100 mg of air-dry sample was weighed into a small glass ampoule and dried at 380 K to constant weight. The glass ampoule containing dry sample was sealed and introduced into one cell of the microcalorimeter. Another, reaction glass ampoule, was filled with 10 ml of distilled water, sealed and introduced into other cell of the microcalorimeter. The microcalorimeter was thermostated at 298.15 K to achieve an equilibrium state. Thereafter, the small ampoule with sample was open and quickly transferred to the reaction ampoule in order to provide wetting of the cellulose sample. To prevent the evaporation of water, the reaction ampoule was sealed again. Finally, the exothermic heat effect of cellulose wetting was measured. For each sample

TABLE 1 : Characteristics of the samples

Sample	Abbreviation	Allomorph	CrI	Cellulose, %	Ash, %	DP
Avicel PH-101	MCC-1	CI	0.65	>99	<0.01	220
Avicel PH-301	MCC-2	CI	0.67	>99	<0.01	170
Cotton cellulose	CC	CI	0.63	>99	<0.01	2700
Kraft pulp	KP	CI	0.58	>99	<0.02	1200
Amorphized cellulose, ball-milling for 2h	AC-1	CI	0.46	>98	<0.05	810
Amorphized cellulose, ball-milling for 8h	AC-2	CI	0.24	>98	<0.05	640
Mercerized CC	CCM	CII	0.48	>99	<0.01	2100
Mercerized KP	KPM	CII	0.46	>99	<0.02	1000
Regenerated cellulose	RC	CII	0.35	>99	<0.02	350
CC treated with liquid ammonia	CCA	CIII	0.33	>99	<0.01	2700
KP treated with liquid ammonia	KPA	CIII	0.30	>99	<0.02	1200
CCA treated with hot glycerol	CCAG	CIV	0.55	>98	<0.02	430
KPA treated with hot glycerol	KPAG	CIV	0.52	>98	<0.02	360

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three experiments were carried out to calculate an average enthalpy value and standard deviation. The actual crystallinity degree (X) of cellulose was calculated by the equation<sup>[20]</sup>:

$$X = 1 - (\Delta_w H^{\circ} / \Delta_w H^{\circ}_{am}) \quad (1)$$

where  $\Delta_w H^{\circ}_{am} = -27.16$  kJ/mol is enthalpy of wetting of amorphous cellulose.

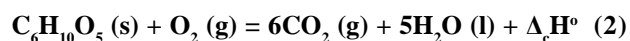
### Calorimetry of combustion

Combustion of the samples in pelletized form (cca. 1 g) was carried out in a stainless steel calorimetric bomb having volume 0.320 dm<sup>3</sup> at oxygen pressure of 3.05 MPa with 1.00 cm<sup>3</sup> of deionized water added to the bomb. The combustion measurements were carried out by an isothermal water calorimeter at 298.15 K with accuracy  $\pm 0.001$  K. The value of the energy equivalent of the calorimeter determined by standard benzoic acid was  $15802.3 \pm 0.9$  J/K. The true mass of cellulose sample used in each experiment was determined from the mass of the produced CO<sub>2</sub>. All needed corrections were introduced. Conventional procedure was used to adjust the experimental combustion energy to standard conditions: T=298.15 K and p= 0.1 MPa. For each sample five experiments were performed to calculate an average value of combustion enthalpy and standard deviation.

## RESULTS AND DISCUSSION

By means of precise measurement of wetting enthalpy, the actual degree of crystallinity (X) of cellulose samples was determined (TABLE 2) instead of unreliable crystallinity index (CrI), which was less than X.

The combustion reaction of one glucopyranose unit of cellulose is written as:



Based on this reaction, the standard enthalpy of formation of cellulose can be calculated by the equation:

$$\Delta_f H^{\circ} = 6\Delta_f H^{\circ}(CO_2, g) + 5\Delta_f H^{\circ}(H_2O, l) - \Delta_c H^{\circ} \quad (3)$$

where standard enthalpies of formation of carbon dioxide and water are:

$$\Delta_f H^{\circ}(CO_2, g) = -393.51 \text{ kJ/mol and } \Delta_f H^{\circ}(H_2O, l) = -285.83 \text{ kJ/mol.}$$

TABLE 2 : Enthalpy of wetting ( $\Delta_w H^{\circ}$ ) and actual crystallinity degree (X)

Abbreviation	Allomorph	$-\Delta_w H^{\circ}$ , kJ/mol	X
MCC-1	CI	7.61 $\pm$ 0.42	0.72 $\pm$ 0.02
MCC-2	CI	6.79 $\pm$ 0.40	0.75 $\pm$ 0.02
CC	CI	8.15 $\pm$ 0.41	0.70 $\pm$ 0.02
KP	CI	9.51 $\pm$ 0.43	0.65 $\pm$ 0.02
AC-1	CI	13.04 $\pm$ 0.42	0.52 $\pm$ 0.02
AC-2	CI	19.56 $\pm$ 0.48	0.28 $\pm$ 0.02
CCM	CII	12.22 $\pm$ 0.53	0.55 $\pm$ 0.02
KPM	CII	12.77 $\pm$ 0.40	0.53 $\pm$ 0.02
RC	CII	16.30 $\pm$ 0.51	0.40 $\pm$ 0.02
CCA	CIII	17.11 $\pm$ 0.52	0.37 $\pm$ 0.02
KPA	CIII	17.65 $\pm$ 0.42	0.35 $\pm$ 0.02
CCAG	CIV	10.86 $\pm$ 0.50	0.60 $\pm$ 0.02
KPAG	CIV	11.68 $\pm$ 0.44	0.57 $\pm$ 0.02

The results of determination of the standard combustion enthalpy ( $\Delta_c H^{\circ}$ ) of cellulose samples having different structural characteristics are given in TABLE 3.

Using the obtained values of combustion enthalpy, the standard enthalpy of formation ( $\Delta_f H^{\circ}$ ) of cellulose samples was calculated by means of equation (3) (TABLE 3). It was discovered that for samples with the same crystalline allomorph, increasing the crystallinity degree leads to a linear increase in absolute value of the formation enthalpy (Figure 1).

To calculate standard entropy, S<sup>o</sup>, the data on the temperature dependence of heat capacity of cellulose samples were used<sup>[10, 21, 22]</sup>. As a result, Gibbs free energy of formation was calculated (TABLE 3):

$$\Delta_f G^{\circ} = \Delta_f H^{\circ} - T^{\circ}(S^{\circ} - \sum S_i^{\circ}) \quad (4)$$

where  $\sum S_i^{\circ} = 1199.61$  J/(mol K) is sum of standard entropies of carbon atoms (graphite), molecules of H<sub>2</sub> and O<sub>2</sub> needed for forming one glucopyranose unit of cellulose; T<sup>o</sup> = 298.15 K.

As can be seen from Figures 1 and 2, with the decrease of crystallinity degree all linear dependences  $\Delta_f H^{\circ} = f(X)$  and  $\Delta_f G^{\circ} = f(X)$  converge at one common point,  $\Delta_f H^{\circ}_{am} = -942.4$  kJ/mol and  $\Delta_f G^{\circ}_{am} = -642.6$  kJ/mol, corresponding to X = 0. This evidences that the amorphous phase in different cellulose samples has identical thermodynamic

TABLE 3 : Standard thermodynamic characteristics of cellulose samples

Abbreviation	Allomorph	X	$-\Delta_c H^\circ$ , kJ/mol	$-\Delta_f H^\circ$ , kJ/mol	$-\Delta_f G^\circ$ , kJ/mol
MCC-1	CI	0.72±0.02	2821.0±2.0	969.2±2.0	667.0±2.3
MCC-2	CI	0.75±0.02	2819.8±1.8	970.4±1.8	668.1±2.1
CC	CI	0.70±0.02	2821.2±1.7	969.0±1.7	666.8±2.0
KP	CI	0.65±0.02	2823.6±2.2	966.6±2.2	664.6±2.5
AC-1	CI	0.52±0.02	2828.7±2.3	961.5±2.3	659.9±2.6
AC-2	CI	0.28±0.02	2837.4±2.1	952.8±2.1	652.0±2.4
CCM	CII	0.55±0.02	2823.3±1.8	966.9±1.8	664.7±2.1
KPM	CII	0.53±0.02	2824.2±2.3	966.3±2.3	664.4±2.6
RC	CII	0.40±0.02	2830.0±1.7	960.2±1.7	659.0±2.0
CCA	CIII	0.37±0.02	2836.4±2.3	953.8±2.3	652.7±2.6
KPA	CIII	0.35±0.02	2837.0±2.0	953.2±2.0	652.2±2.3
CCAG	CIV	0.60±0.02	2825.0±2.1	965.2±2.1	662.4±2.4
KPAG	CIV	0.57±0.02	2826.1±1.9	964.1±1.9	662.2±2.2

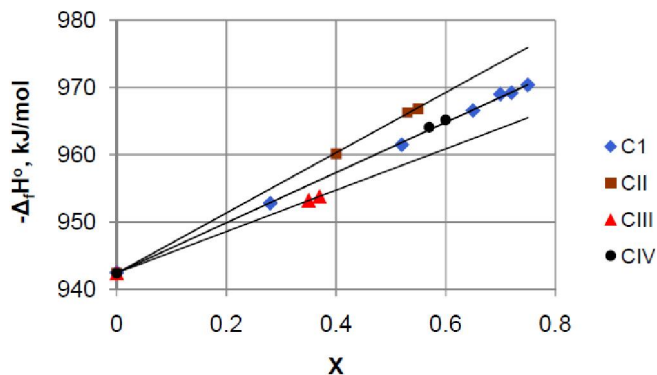


Figure 1 : Dependence of enthalpy of cellulose formation on degree of crystallinity

characteristics. On the other hand, the linear extrapolation of these dependences to the values corresponding to  $X = 1$  gives the enthalpy and free energy of formation of different crystalline allomorphs,  $\Delta_f H^\circ_{cr}$  and  $\Delta_f G^\circ_{cr}$  (TABLE 4). Furthermore, melting enthalpy ( $\Delta H^\circ_m$ ) of the cellulose crystallites was calculated:

$$\Delta H^\circ_m = \Delta_f H^\circ_{am} - \Delta_f H^\circ_{cr} \quad (5)$$

Based on the obtained results, it can be concluded regarding the thermodynamic stability of various crystalline forms of cellulose and amorphous cellulose (CA). For this purpose, the index of relative stability (IRS) was calculated, as:

$$IRS = \Delta H^\circ_m / \Delta H^\circ_m(CII) \quad (6)$$

As can be seen, the thermodynamic stability of the allomorphs decreases in the following order (Figure 3):

$$CII > CIV \geq CI > CIII > CA$$

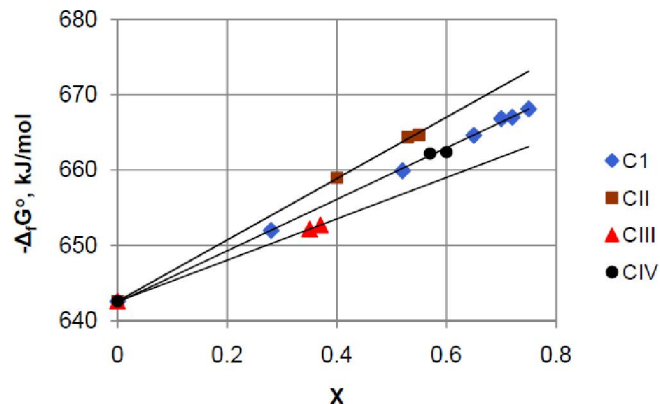


Figure 2 : Dependence of gibbs energy of cellulose formation on degree of crystallinity

On the other hand, the index of relative reactivity,  $IRR = 1 - IRS$ , of the different allomorphs decreases in the reverse order (Figure 4):

$$CA > CIII > CI \geq CIV > CII$$

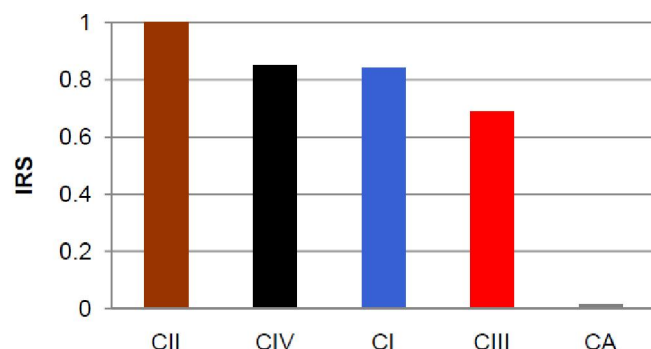
The obtained thermodynamic characteristics allow explaining the structural phase transitions and reactivity of the cellulose allomorphs under certain conditions. The amorphous cellulose is the most unstable and the most reactive; therefore it can recrystallize in any crystalline allomorph under certain conditions<sup>[10]</sup>. For instance, under action of moisture, the amorphized cellulose recrystallizes in the most stable CII allomorph<sup>[23,24]</sup>. It is also known that after regeneration from various solutions, structure of cellulose always turns to CII crystalline allomorph.

Among various crystalline allomorphs, the CII is the most stable, whereas the CIII is the most labile

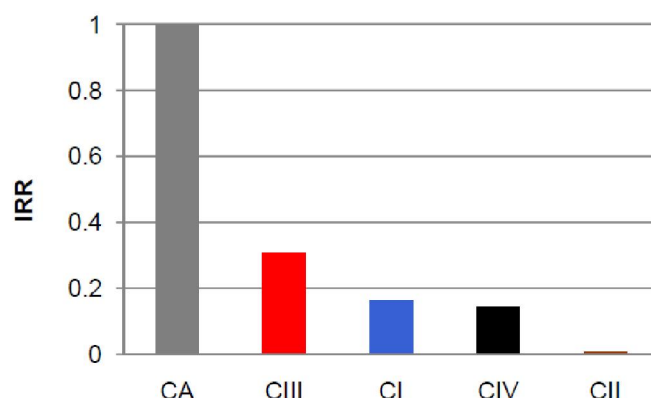
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**TABLE 4 : Thermodynamic characteristics of various allomorphs**

Allomorph	$-\Delta_f H^\circ$ , kJ/mol	$-\Delta_f G^\circ$ , kJ/mol	$\Delta H_m^\circ$ , kJ/mol
CI	979.6	676.4	37.2
CII	986.9	683.7	44.5
CIII	973.2	670.0	30.8
CIV	980.4	677.2	38.0
CA	942.4	642.6	0



**Figure 3 : Index of relative stability (IRS) of different crystalline allomorphs and amorphous cellulose**



**Figure 4 : Index of relative reactivity (IRR) of different crystalline allomorphs and amorphous cellulose**

(Figure 3, TABLE 4). Increased phase stability of the CII crystallites leads to some problems at the cellulose application. It is known that after transformation of crystalline structure CI of natural cellulose to CII, e.g. by mercerization, a decrease in solubility and reactivity of the sample is observed<sup>[25]</sup>. In particular, transparency and filterability of solutions of CII-samples declines due to forming of gel-particles. The presence of CII crystallites is a main factor that causes the low reactivity of cellulose at acetylation, nitration and forming of viscose<sup>[25-27]</sup>.

On the other hand, the transformation of crystalline structure CI of chemical pulp into labile CIII allomorph increases the reactivity of

cellulose<sup>[27]</sup>. It was also discovered that high-temperature treatment of CIII<sub>1</sub> sample in air at 480-490 K triggers the inverse transformation of CIII to CI<sup>[28]</sup>, whereas after treatment in glycerol above 533 K CIII<sub>1</sub> structure turns into CIV allomorph<sup>[29]</sup>.

## CONCLUSION

Thermodynamic characteristics of cellulose samples such as standard enthalpy of formation,  $\Delta_f H^\circ$ , free energy of formation,  $\Delta_f G^\circ$ , as well as melting enthalpy of crystallites,  $\Delta H_m^\circ$ , have been studied. The precise thermochemical method was used to determine the actual degree of crystallinity (X) of cellulose samples.

It was found that with the decrease of crystallinity degree all linear dependences  $\Delta_f H^\circ = f(X)$  and  $\Delta_f G^\circ = f(X)$  converge at one common point,  $\Delta_f H_{am}^\circ = -942.4$  kJ/mol and  $\Delta_f G_{am}^\circ = -642.6$  kJ/mol, corresponding to amorphous phase cellulose at X = 0. This evidences that the amorphous phase in different cellulose samples has identical thermodynamic characteristics. On the other hand, the linear extrapolation of these dependences to the values corresponding to X = 1 gives the enthalpy and free energy of formation of different crystalline allomorphs.

Based on obtained thermodynamic characteristics, the stability of various crystalline forms of cellulose and amorphous cellulose (AC) was estimated; and namely, the thermodynamic stability of the allomorphs decreases in the following order:

$$CII > CIV \geq CI > CIII > AC.$$

On the other hand, the index of relative reactivity of the different allomorphs decreases in the reverse order:

$$CA > CIII > CI \geq CIV > CII$$

These results allow explain the structural phase transitions and reactivity of the cellulose allomorphs. The most unstable and the most reactive amorphous cellulose can recrystallize in any crystalline allomorph under certain conditions. Among various crystalline allomorphs, the CIII is the most labile, and therefore after high-temperature treatment it can

turn into CI and CIV. Conversely, the CII is the most stable crystalline allomorph, resulting in reduced solubility and reactivity of the samples containing CII crystallites.

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