

## Thermodynamic analysis of cellulose nitration

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### Abstract

In this study, the standard formation enthalpies and entropies of cellulose and nitrocellulose samples were determined. These characteristics were used for thermodynamic analysis of bulk nitration of the entire cellulose sample and local nitration only of amorphous domains (ADs) of cellulose. It was found that the reaction of bulk nitration of cellulose up to a substitution degree (DS) of 1.5 is endothermic and determined primarily by the contribution of the temperature-entropy component to the negative Gibbs potential. However, if DS is higher than 1.5, the bulk nitration becomes exothermic and its feasibility is determined by the impact of enthalpy on the Gibbs potential. In the case of local nitration of cellulose ADs, the main contribution to the Gibbs potential is made by the reaction enthalpy that determines the feasibility of this process. It was shown that with the enhancement in DS of nitrocellulose, the negative value of the Gibbs potential of the reaction increases. Thus, the cellulose nitration to higher DS is thermodynamically favorable. Since the locally nitrated samples are copolymers of amorphous nitrocellulose and crystalline cellulose, they should be significantly less hydrophilic than cellulose. Therefore, it can be expected that the local nitration method will find a wide practical application for inexpensive hydrophobization of cellulose materials.

**Keywords:** Cellulose nitration; Bulk nitration; Local nitration; Nitrocelluloses; Degree of substitution; Thermodynamic functions; Thermodynamical analysis

### 1. Introduction

Among various cellulose derivatives, cellulose nitrates are of particular practical importance since these esters are widely used in the production of plastics, membranes, films, protective coatings, adhesives, paints, varnishes and enamels, smokeless powder, rocket fuels, explosives, etc. [1]. It was shown that the application area of use depends on the degree of substitution (DS) of the nitrocellulose (NC) sample [2]. If DS is less than 1.5, this type of NC can only be used to produce paints, varnishes, and enamels. NC having DS between 1.5 and 2.4 is used in the production of plastics and membranes. If DS exceeds 2.4, then this type of NC can be used to produce smokeless powder, rocket propellants, and explosives.

To produce high-quality NC, pure cotton cellulose with a high content of  $\alpha$ -cellulose and an increased degree of polymerization is usually chosen as the starting cellulose material [3]. The cellulose can be nitrated with concentrated nitric acid alone or with various nitrating systems, such as mixtures of nitric acid, sulfuric acid, and water; nitric acid, phosphoric acid, and phosphoric anhydride; nitric acid, acetic acid, and acetic anhydride; nitric acid and its salts; nitric acid and dichloromethane; nitric acid and ether; etc. [2, 4].

However, for the industrial production of NC, only mixtures of nitric with sulfuric acid and water are used. The cellulose nitration can be carried out at temperatures of 273-313 K for 30-60 min, at a ratio of the nitrating system to cellulose 30-50. The DS value of the resulting NC is adjusted by changing the composition of the reaction mixture, especially the water content.

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The chemical mechanism of cellulose nitration with nitric acid in the presence of sulfuric acid consists of the reaction of electrophilic substitution of protons in hydroxyl groups by the nitronium cations ( $\text{NO}_2^+$ ) [2].

Depending on reaction conditions, nitration of cellulose can occur in two main topochemical directions. The first topochemical direction is bulk nitration when the nitrating reagent quickly reacts with amorphous domains (ADs), and more slowly with the crystallites (CRs) of cellulose, resulting in cellulose decrystallization and the formation of NC with an amorphized structure [2, 5-8]. The cellulose crystallinity affects the rate of nitration but has little impact on the final degree of substitution of NC. Such a bulk nitration process of cellulose occurs if for the reaction the concentrated nitric acid or nitrating mixtures with a relatively small amount of water are used.

The second topochemical direction is local nitration of only the most accessible ADs, whereas CRs of the cellulose remain almost unreacted. Such a local nitration process can occur if nitrating mixtures contain an increased amount of water.

Although the chemical aspects of the nitration of cellulose are well known, its thermodynamics is largely unexplored. In particular, it is unclear, which component of the Gibbs potential, enthalpy, or entropy of the reaction, determines the feasibility of local and bulk cellulose nitration. This article is devoted to solving this problem.

## 2. Materials and methods

### 2.1. Materials

The original cellulose material was pure cotton cellulose (CC) having 98%  $\alpha$ -cellulose and DP=2700. Amorphous cellulose (AC) was prepared by ball-milling of CC with ceramic balls for 10 h. Samples of NC with DS=0.97 (NC-1), DS=2.03 (NC-2), and DS=2.85 (NC-3) were obtained by bulk nitration of CC. In addition, the NC (NC-4) with a DS of about 0.62 was synthesized using the method of local nitration.

### 2.2. Methods

#### 2.2.1. Nitration of cellulose

The bulk nitration of CC was carried out at 293 K with a liquid reagent system-to-cellulose ratio of 50 for 60 min using mixtures of nitric acid, sulfuric acid, and water. To achieve the DS of NC-1 of 0.97, the reagent system contained 25 wt.%  $\text{HNO}_3$ , 49 wt.% of  $\text{H}_2\text{SO}_4$  and 26 wt. %  $\text{H}_2\text{O}$ . To obtain NC-2 with DS of 2.03, the reagent system contained 28 wt.%  $\text{HNO}_3$ , 53 wt.% of  $\text{H}_2\text{SO}_4$  and 19 wt. %  $\text{H}_2\text{O}$ . NC-3 with DS of about 2.85 was synthesized using the reagent system containing 36 wt.%  $\text{HNO}_3$ , 60 wt.% of  $\text{H}_2\text{SO}_4$  and 4 wt. %  $\text{H}_2\text{O}$ . The nitrocellulose samples were washed with cold water and 1%  $\text{NaHCO}_3$  to a neutral pH value; then the samples were washed with hot water (358 K), cold water, rinsed with anhydrous methanol, and dried in a vacuum chamber at 323 K to constant weight.

The local nitration of CC to DS = 0.62 (NC-4) was carried out with the dilute reagent system containing 21 wt.%  $\text{HNO}_3$ , 44 wt.% of  $\text{H}_2\text{SO}_4$  and 35 wt. %  $\text{H}_2\text{O}$ . The temperature was 293 K, the liquid reagent system-to-cellulose ratio was 50, and the duration of nitration was 30 min.

#### 2.2.2. WAXS

In the WAXS method, the experiments were carried out on a Rigaku-Ultima Plus diffractometer ( $\text{CuK}\alpha$ -radiation,  $\lambda = 0.15418$  nm) in the  $\varphi = 2\theta$ -angle range from 5 to 50 ° using a reflection mode [9]. Collimation included a system consisting of vertical slits and Soller slits. The procedure of 0.02 ° step-by-step scanning was used to determine the exact position of the peaks. The tested specimens in the shape of tablets with a diameter of 16 mm and a thickness of 2 mm were prepared from washed and dried samples by pressing at a pressure of 50 MPa.

#### 2.2.3. Enthalpy of interaction with water

The standard enthalpy of the interaction of the dry cellulose samples with water, i.e., wetting enthalpy ( $\Delta_w H$ ) of the samples was measured using a TAM Precision Solution Calorimeter. Before starting the experiments, the air-dry sample was put into a special glass ampoule and dried in a vacuum at 378 K to constant weight. The glass ampoule containing the dry sample was sealed and introduced into the calorimetric cell filled with the liquid. The calorimeter was thermostated at 298 K to achieve an equilibrium state. Thereafter, the sealed ampoule with the dry sample was broken to ensure that the cellulose sample to contact with the liquid. The released exothermic heat effect was measured with accuracy  $\pm 0.01$  J. Three of the same samples were tested to calculate a reliable enthalpy value and standard deviation.

The degrees of cellulose crystallinity (X) and amorphicity (Y) were calculated as follows:

$$X = 1 - (\Delta_w H / \Delta_w H_{am}) \quad (1)$$

$$Y = 1 - X \quad (2)$$

where  $\Delta_w H_{am} = -27.2$  kJ/mol is the standard wetting enthalpy of completely amorphous cellulose (AC) [10].

#### 2.2.4. Enthalpies of combustion and formation

Combustion of the dry samples was carried out in a stainless-steel calorimetric bomb having a volume of 0.320 dm<sup>3</sup> at an oxygen pressure of 3.05 MPa with 1.00 cm<sup>3</sup> of deionized water added to the bomb [10]. The combustion measurements were performed using an isothermal water calorimeter at 298.15 K with an accuracy of  $\pm 0.001$  K. To adjust the enthalpy of combustion ( $\Delta H_c$ ) to standard conditions,  $T_s = 298.15$  K and  $P_s = 0.1$  MPa, the Washburn correction, as well as the correction for the change in the number of moles of gases before and after combustion was introduced. For each sample, five experiments were performed to calculate the reliable value of combustion enthalpy and standard deviation.

The standard enthalpies of formation ( $\Delta_f H$ ) of one mole of the repeating unit of cellulose and nitrocellulose can be calculated from the measured standard enthalpies of combustion ( $\Delta_c H$ ) using the equation:

$$\Delta_f H = 6 \Delta_f H(\text{CO}_2, g) + (5 - 0.5 \text{ DS}) \Delta_f H(\text{H}_2\text{O}, l) - \Delta_c H \quad (3)$$

where  $\Delta_f H(\text{CO}_2, g) = -393.51$  kJ/mol and  $\Delta_f H(\text{H}_2\text{O}, l) = -285.83$  kJ/mol are standard enthalpies of the formation of carbon dioxide and liquid water, respectively; DS is the average substitution degree of NC sample.

#### 2.2.5. Specific heat capacity and entropy

Specific heat capacities ( $C_p$ ) of dry samples were measured in the temperature range of 80–340 K using an adiabatic vacuum calorimeter [11]. Below 80 K,  $C_p$  values were estimated by the method of Kelly, et al. [12]. For each sample, four experiments were performed to calculate the reliable  $C_p$  value and standard deviation.

The entropy values of the samples at temperature T were calculated, as follows:

$$S(T) = \int_0^T \left( \frac{C_p}{T} \right) dT \quad (4)$$

If T is the standard temperature,  $T_s = 298.15$  K, then the calculated result is the standard entropy of the sample,  $S(T_s)$ .

An example of determining  $C_p$  and  $S(T)$  of the NC-3 sample is given in Table 1.

**Table 1** Averaged values of  $C_p$  and S for NC-3

T, K	$C_p$ , J/mol K	S, J/mol K
80	108.6	102.7
100	130.2	126.8
120	147.7	148.4
140	167.2	172.8
160	186.8	196.2
180	206.3	219.2
200	228.1	244.7
220	245.3	266.1
240	264.8	289.2
260	284.5	312.6

280	304.0	336.1
<b>298.15</b>	<b>316.6</b>	<b>355.0</b>
300	322.6	359.3
320	342.7	380.5
340	362.6	403.8

As can be seen, the standard entropy value of this sample is  $S(T_s) = 355$  (J/mol K).

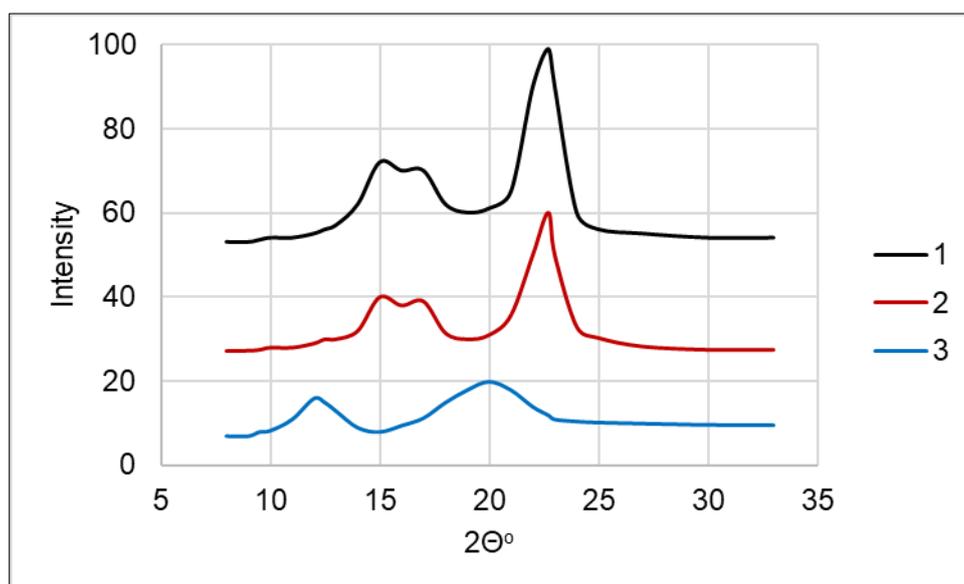
### 3. Results and discussion

#### 3.1. Structural studies of samples

X-ray patterns of the original cotton cellulose and some NC samples are shown in Figures 1 and 2. As can be seen from Figure 1, the original cotton cellulose, CC, has a pronounced crystalline structure with specific peaks at the  $2\theta$  angles of 14.7, 16.5, and 22.7 degrees. The determined crystallinity degree of CC was  $X=0.7$  and the amorphicity degree of this cellulose was  $Y=0.3$ .

As a result of bulk nitration, the crystalline structure of cellulose is disturbed and turns into an amorphized structure of NC having a wide diffuse scattering with a maximum at the  $2\theta$  angle of 20 degrees (Figure 1, X-ray pattern 3). In addition, the NC sample exhibits a diffuse peak at lower  $2\theta$  angles of 12.0-12.5° due to the forming of mesomorphous layers [13].

Unlike the NC sample obtained by bulk nitration, the NC sample obtained by local nitration retains the crystalline structure characteristic of cellulose (Figure 1, X-ray pattern 2). This is because with the local method only amorphous domains of cellulose are nitrated, while its crystallites are practically unaffected.



**Figure 1** X-ray diffraction patterns of initial cotton cellulose (1), sample of NC-4 with DS = 0.62 prepared by local nitration method (2), and sample of NC-2 with DS = 2.03 obtained by bulk nitration method (3)

#### 3.2. Thermodynamic characteristics of samples

The thermodynamic (TD) characteristics of studied cellulose and nitrocellulose samples are presented in Table 2. From the linear dependences of TD functions on DS, the TD characteristics of mono-nitrocellulose (MNC), sesqui-nitrocellulose (SNC), di-nitrocellulose (DNC), and tri-nitrocellulose (TNC) were also calculated using the following equations.

$$\Delta_c H \text{ (kJ/mol)} = -2845.1 + 45.7 \text{ DS} \quad (5)$$

$$\Delta_f H \text{ (kJ/mol)} = -945.1 + 96.8 \text{ DS} \quad (6)$$

$$S(T_s) \text{ (J/mol K)} = 190 + 57.8 \text{ DS} \quad (7)$$

**Table 2** Standard TD characteristics of samples

Sample	SD	$-\Delta_c H$ , kJ/mol	$-\Delta_f H$ , kJ/mol	$S(T_s)$ , J/mol K
*CR	0	2810.0	980.2	180
CC	0	2821.2	969.0	183
AC	0	2845.1	945.1	190
NC-1	0.97	2800.6	851.2	246
NC-2	2.03	2752.2	748.7	307
NC-3	2.85	2714.8	669.4	355
NC-4	0.62	2817.0	885.1	226
MNC	1	2799.4	848.3	248
SNC	1.5	2776.6	799.9	277
DNC	2	2753.7	751.5	306
TNC	3	2708.0	654.7	363

\*Note: data for CI crystallites (CR) were obtained by extrapolation of dependences of TD functions on crystallinity degree (X) to X=1 [14].

The melting enthalpy of CI crystallites is  $\Delta_m H = \Delta_f H \text{ (AC)} - \Delta_f H \text{ (CR)} = 35.1 \text{ (kJ/mol)}$

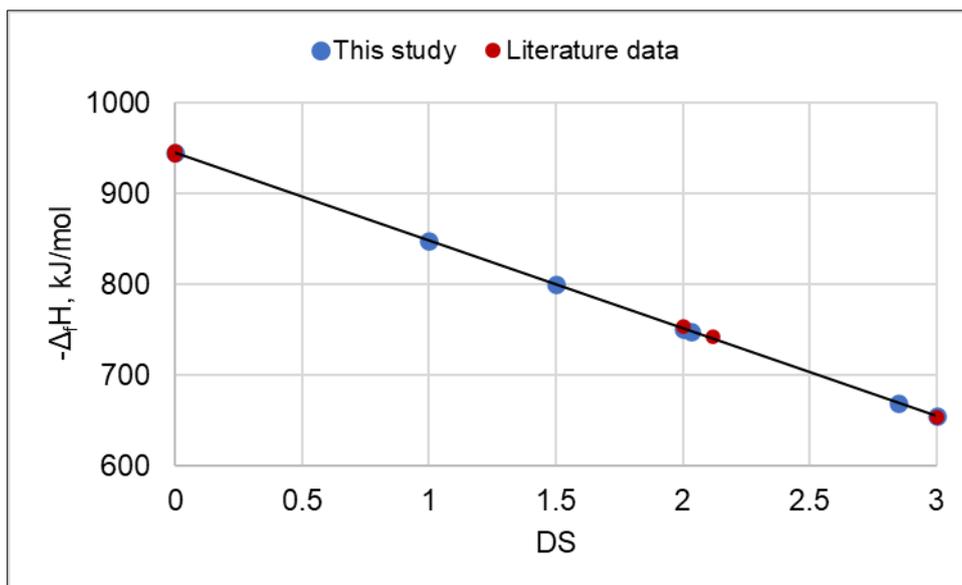
For comparison with the TD characteristics obtained in this study, some literature data were presented in Tables 3, 4, and Figures 2, 3. As can be seen, the obtained results are confirmed by literature data.

**Table 3** Standard formation enthalpy values of samples

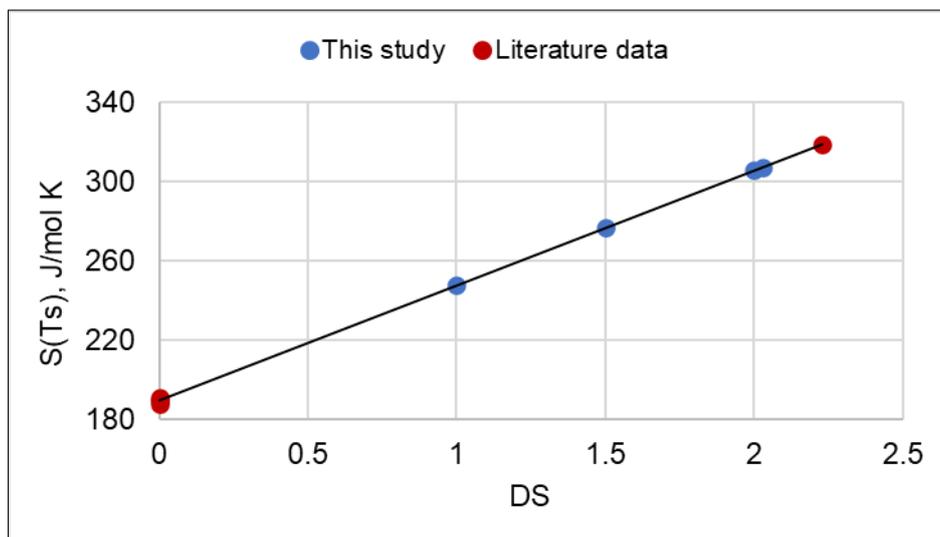
Sample	$-\Delta_c H$ , kJ/mol	$-\Delta_f H$ , kJ/mol	Reference
Cotton linter	2824.1	966.1	[15]
Amorphized cellulose	2842.8	947.4	[16]
	2845.3	945.0	[17]
	2847.8	942.4	[9]
NC, DS=2.12	2748.2	742.7	[15]
DNC	2751.6	753.3	[15]
TNC	2709.4	653.0	[15]

**Table 4** Standard entropy values of samples

Sample	$S(T_s)$ , J/mol K	Reference
Amorphized cellulose	188	[18]
	190	[10]
	191	[19]
NC, SD=2.23	319	[20]



**Figure 2** Dependence of standard formation enthalpy on degree of substitution of NC samples



**Figure 3** Dependence of standard entropy on degree of substitution of NC samples

The obtained TD characteristics of cellulose and NC samples were used for thermodynamic analysis of bulk and local nitration of cellulose to different DS values.

### 3.3. Bulk nitration of cellulose sample

The bulk nitration process is accompanied by decrystallization (melting) of cellulose crystallites and nitration of amorphized cellulose (AC) with the formation of amorphous NC. This process can be described by the following TD equations:

$$\Delta_r H(\text{CC}) = \Delta_r H(\text{AC}) + X \Delta_m H \quad (8)$$

$$\Delta_r S(\text{CC}) = \Delta_r S(\text{AC}) + X \Delta_m S \quad (9)$$

where  $\Delta_rH(CC)$  and  $\Delta_rS(CC)$  are enthalpy and entropy of CC nitration, respectively;  $\Delta_rH(AC)$  and  $\Delta_rS(AC)$  are enthalpy and entropy of AC nitration, respectively;  $X=0.7$  is the crystallinity degree of CC;  $\Delta_mH=35.1$  (kJ/mol) is the melting enthalpy of CI crystallites, and  $\Delta_mS = \Delta_mH/T_s$  is the melting entropy of CI crystallites.

The expanded forms of these equations can be expressed, as follows:

$$\Delta_rH(CC) = \Delta_rH(NC) + DS [\Delta_rH(H_2O) - \Delta_rH(HNO_3)] - \Delta_rH(AC) + X \Delta_mH \quad (10)$$

$$\Delta_rS(CC) = S(NC) + DS [S(H_2O) - S(HNO_3)] - S(AC) + X \Delta_mS \quad (11)$$

Then, the Gibbs potential for the bulk nitration reaction of CC was calculated, as follows:

$$\Delta_rG(CC) = \Delta_rH(CC) - T_s \Delta_rS(CC) \quad (12)$$

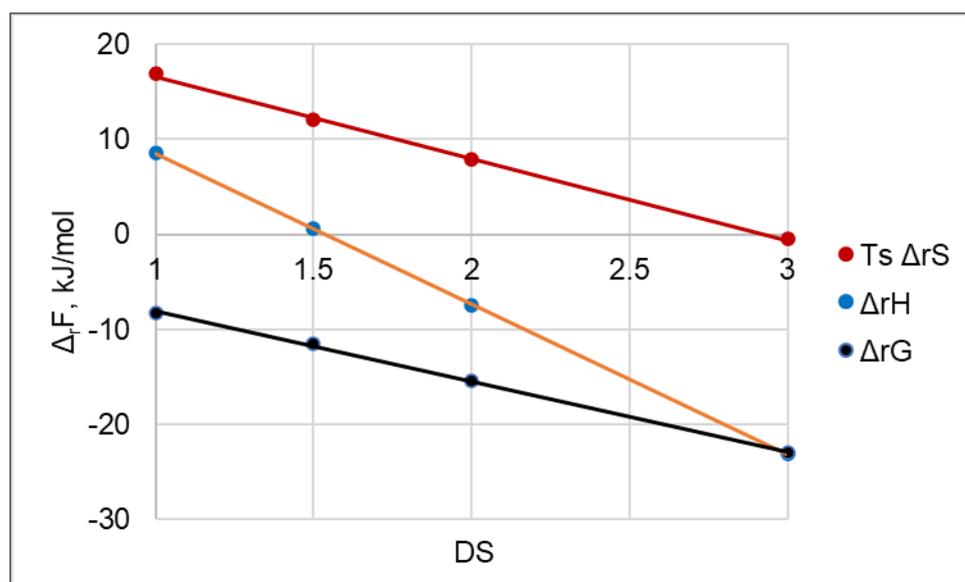
In addition to the thermodynamic characteristics of the samples (Table 2), standard TD characteristics of liquid water ( $\Delta_rH = -285.83$  kJ/mol;  $S(T_s) = 70$  J/mol K) and nitric acid ( $\Delta_rH = -173$  kJ/mol;  $S(T_s) = 156$  J/mol K) were also used for calculations.

The resulting TD functions for the reaction of bulk nitration of CC are shown in Table 3, while the dependences of these functions on DS can be seen in Figure 4.

**Table 3** TD functions of the bulk nitration reaction

NC *(B)	DS	$\Delta_rH$ , kJ/mol	$T_s \Delta_rS$ , kJ/mol	$\Delta_rG$ , kJ/mol
MNC (B)	1	8.6	16.9	-8.3
SNC (B)	1.5	0.6	12.1	-11.5
DNC (B)	2	-7.5	7.9	-15.4
TNC (B)	3	-23.5	-0.7	-22.8

\*Symbol (B) denotes the bulk nitration method



**Figure 4** Dependences of TD functions of bulk nitration reaction of CC on average substitution degree of NC samples

The obtained results show that when the DS of NC is below 1.5, the bulk nitration reaction is endothermic, and therefore, its feasibility is determined mainly by the contribution of the temperature-entropy component ( $T_s \Delta_rS$ ) to the negative Gibbs potential of this reaction. However, when the DS value exceeds 1.5, the reaction becomes exothermic and it is implemented due to the predominant contribution of the enthalpy of the process to the negative Gibbs potential.

### 3.4. Local nitration of amorphous domains of cellulose

Consider the local nitration of only the most accessible amorphous domains (AD) of cellulose when the crystalline regions (CR) of the sample remain unreacted. This process can be described by the following equation:



where  $Y = 0.3$  is the amorphicity degree,  $X = 0.7$  is the crystallinity degree of CC, and  $DS_a$  is the degree of substitution of AD.

Then the enthalpy, entropy, and Gibbs potential for the reaction of local nitration of CC can be calculated, as follows:

$$\Delta_r H(CC) = X \Delta_f H(CR) + Y \Delta_f H(NC) + Y DS_a [\Delta_f H(H_2O) - \Delta_f H(HNO_3)] - \Delta_f H(CC) \quad (14)$$

$$\Delta_r S(CC) = X S(CR) + Y S(NC) + Y DS_a [S(H_2O) - S(HNO_3)] - S(CC) \quad (15)$$

$$\Delta_r G(CC) = \Delta_r H(CC) - T_s \Delta_r S(CC) \quad (16)$$

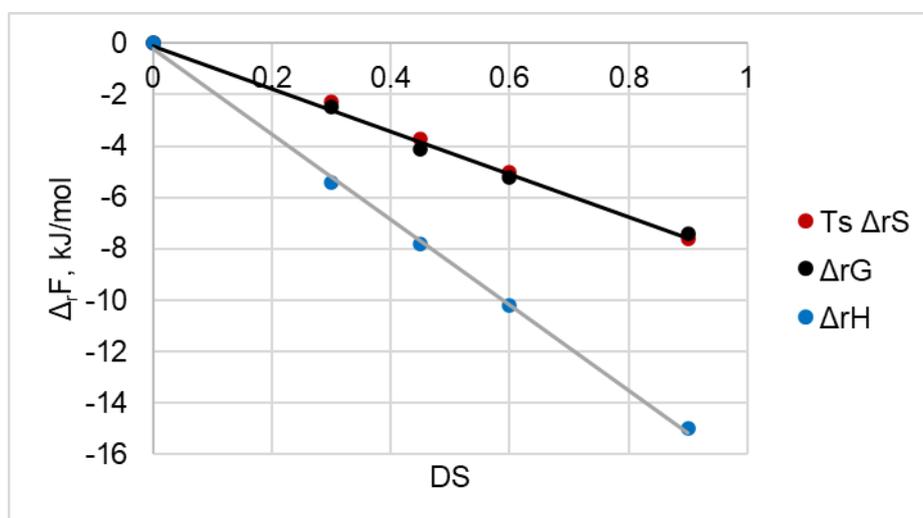
The obtained results are shown in Table 4.

**Table 4** TD functions for the local nitration process of AD

NC *(L)	DS <sub>a</sub>	DS	Δ <sub>r</sub> H, kJ/mol	T <sub>s</sub> Δ <sub>r</sub> S, kJ/mol	Δ <sub>r</sub> G, kJ/mol
MNC (L)	1	0.3	-5.4	-2.3	-3.1
SNC (L)	1.5	0.45	-7.8	-3.7	-4.1
DNC (L)	2	0.6	-10.2	-5.0	-5.2
TNC (L)	3	0.9	-15.0	-7.6	-7.4

\*Symbol (L) denotes the local nitration method;  $DS = Y DS_a$  is the average substitution degree of the NC sample

From the obtained results, it follows that for the local nitration of AD, the enthalpy of the exothermic reaction has the greatest impact on the negative Gibbs potential, while the contribution of the temperature-entropy component ( $T_s \Delta_r S$ ) to this potential is smaller. This trend can be seen more clearly in Figure 5. Thus, the feasibility of the local nitration is determined mainly by the contribution of enthalpy to the negative Gibbs potential of this process.

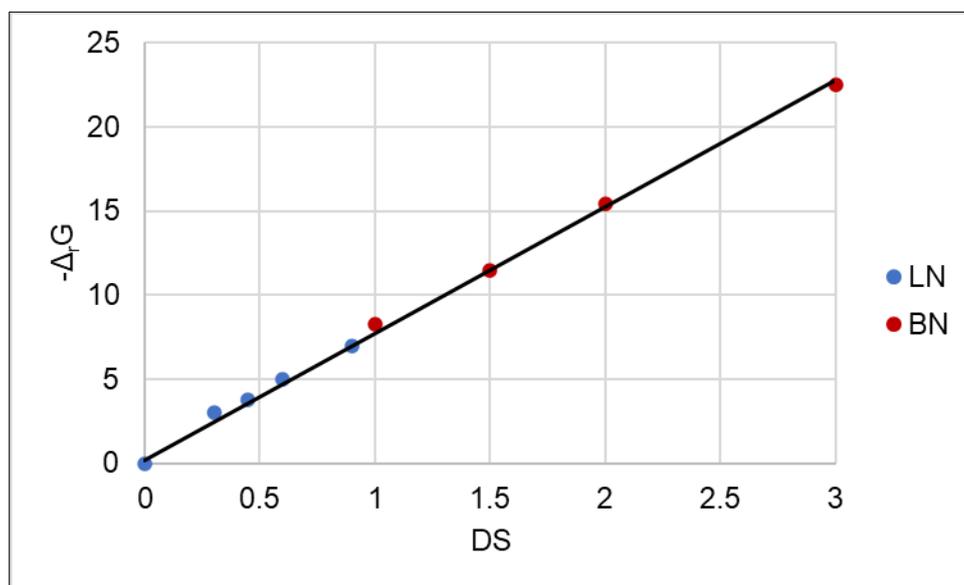


**Figure 5** Dependences of TD functions of local nitration process of AD on average substitution degree of NC samples

A specific feature of locally nitrated samples is the localization of nitro groups in amorphous domains, due to which the resulting material is a copolymer of amorphous nitrocellulose and crystalline cellulose. Since amorphous NC is hydrophobic and cellulose crystallites are water-resistant, such a copolymer should be significantly less hydrophilic than cellulose. Therefore, it can be expected that the local nitration method will find a wide practical application for inexpensive hydrophobization of cellulose fibers, films, fabrics, and papers, as well as cellulose-based fillers and excipients, namely, powdered, microcrystalline, and nano celluloses.

### 3.5. General dependence of the Gibbs potential on the average degree of substitution of NC

If plot the general graph for a dependence of the Gibbs potential on the average degree of substitution of NC for both bulk and local nitration process of cellulose, it can be seen that with increasing SD the negative value of the Gibbs potential increases (Figure 6).



**Figure 6** Dependences of Gibbs potential on average substitution degree of NC samples for local (LN) and bulk (BN) nitration process

Thus, the cellulose nitration to higher substitution degrees is thermodynamically favorable.

## 4. Conclusions

The standard formation enthalpies and standard entropies of cellulose and nitrocellulose samples were determined. These characteristics were used for thermodynamic analysis of cellulose bulk and local nitration reaction to various degrees of substitution.

It was found that when the DS of NC is below 1.5, the bulk nitration reaction is endothermic, and its feasibility is determined mainly by the contribution of the temperature-entropy component to the Gibbs potential of this reaction. However, if the DS value exceeds 1.5, the reaction becomes exothermic and it is implemented due to the predominant contribution of the enthalpy of the process to the Gibbs potential.

For the reaction of local nitration of amorphous domains of cellulose, the main contribution to the Gibbs potential is made by the reaction enthalpy that determines the feasibility of the local nitration process.

It was also shown that with the enhancement in DS of nitrocellulose, the negative value of the Gibbs potential of the reaction increases. Thus, the cellulose nitration to higher DS is thermodynamically favorable.

Since the locally nitrated samples are copolymers of amorphous nitrocellulose and crystalline cellulose, they should be significantly less hydrophilic than cellulose. Therefore, it can be expected that the local nitration method will find a wide practical application for inexpensive hydrophobization of diverse cellulose materials.

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