(RESEARCH ARTICLE)

Thermodynamics of cellulose esterification

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Abstract

This research discusses the standard enthalpies of the combustion and formation of cellulose acetates and nitrates. In addition, the standard enthalpies of cellulose esterification were calculated. For cellulose acetates, it was shown that an increase in the degree of substitution (SD) contributes to enhancing both the exothermic enthalpy of the formation and the exothermic enthalpy of the reaction. It was concluded that the feasibility of the acetylation reaction of cellulose, especially to di- and triacetates, is determined mainly by the exothermic enthalpy. The experiments with nitrocelluloses have shown that with an increase in SD, the enthalpies of combustion and formation become less exothermic. When cellulose is nitrated with dilute nitric acid to SD < 1.5, the enthalpy of the nitration reaction is endothermic. Thus, to implement the nitration process of cellulose with a dilute reagent, the contribution of the entropy to the Gibbs potential of this reaction is necessary. On the other hand, when cellulose is nitrated with more concentrated nitric acid to SD >1.5, the reaction enthalpy becomes exothermic. In this case, the feasibility of the cellulose nitration process will be determined mainly by the exothermic reaction enthalpy. As the degree of substitution increases, the specific gravity of cellulose acetates decreases, while that of nitrocelluloses increases. From experimental values of specific gravity, the degree of substitution of cellulose derivatives was calculated.

Keywords: Cellulose acetates; Cellulose nitrates; Characterization; Enthalpy of Combustion; Enthalpy of Formation; Thermodynamics of reactions

1. Introduction

Among diverse cellulose derivatives, two derivatives, namely the acetates and nitrates of cellulose, are of particular importance. To obtain acetates of cellulose, the starting cellulose material is placed in a suitable organic liquid and treated with an anhydride of acetic acid in the presence of a small amount of a catalyst [1]. If cellulose and its ester do not dissolve in the organic liquid, the esterification process is heterogeneous. In the case when the organic liquid is a solvent for cellulose and/or its ester, the reaction is carried out under homogeneous conditions. Heterogeneous acetylation of cellulose proceeds in the solid phase according to the laws of topochemical reactions, namely, rapidly in amorphous domains and more slowly inside the cellulose crystallites [2]. On the contrary, homogeneous acetylation proceeds fairly uniformly in liquid media that cause swelling or/and dissolution of cellulose.

Studies have shown that the replacement of hydroxyls of cellulose with acetate groups leads to a significant rise in the hydrophobicity of the resulting derivative [3]. In addition, when passing from monoester to triester, a noticeable enhancement of hydrophobicity is observed, since in this event all three hydroxyls in the repeating unit are replaced by non-polar groups.

Due to their performance properties, cellulose acetates can be in the production of hydrophobic fillers, and reinforcements compatible with hydrophobic polymers, as well as in the compositions of hydrophobic coatings, paints, adhesives, and other hydrophobic materials [3-7]. Moreover, these cellulose esters are applied in the production of

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thermoplastics, electronic device housings, spectacle frames, anti-fog goggles, cigarette filters, semi-permeable and separating membranes, optical films, heat, and rot-resistant fabrics, self-cleaning materials, protective coatings, and other materials

Another significant cellulose esters are nitrates. To produce nitrocelluloses the starting cellulose material can be treated with mixtures of nitric with sulfuric, or phosphoric acids [8]. In addition, mixtures of nitric acid with anhydrides of phosphoric or acetic acids can be also used for nitration [9]. Nevertheless, in industry, only mixtures of nitric with sulfuric acid are used for the production of nitrocelluloses. Cellulose nitrates are used in the production of plastics, membranes, films, protective coatings, adhesives, varnishes and enamels, smokeless powder, rocket fuels, explosives, etc. [10].

Although the chemical aspects of esterification reactions of cellulose are well known, their thermodynamics is largely unexplored. Since these reactions are carried out with a high yield (more than 80%), it is obvious that the Gibbs thermodynamic potential of these reactions is negative. However, it is unclear which component of the Gibbs potential, enthalpy, or entropy, determines the possibility of cellulose esterification. This article is devoted to solving this problem.

2. Materials and methods

2.1. Materials

The original cellulose material was pure cotton cellulose (98% α-cellulose, DP=2700) supplied from Hercules, Inc., USA. The needed chemicals (acids, anhydrides, alkalis, organic solvents, etc.) were acquired from Sigma-Aldrich Co.

2.2. Methods

2.2.1. Acetylation of cellulose

The acetylation of the initial cotton cellulose (CC) was carried out in the medium of trifluoroacetic acid (TFAA) served as a solvent and also a catalyst [3]. Cotton cellulose was mixed with TFAA while stirring at room temperature for 1 h and then treated with acetic anhydride at 323 K for 1 h using a liquid reagent system-to-cellulose ratio of 50. The molar ratio of the anhydride to cellulose was adjusted in such a manner to achieve a degree of substitution (SD) of about 1, 2, and 3. Finally, the cellulose esters were washed with water, rinsed with anhydrous ethanol, and dried in a vacuum chamber at 323 K to constant weight.

2.2.2. Nitration of cellulose

The nitration of CC was carried out at 298 K with a liquid reagent system-to-cellulose ratio of 50 for 1 h using mixtures of nitric acid, sulfuric acid, and water [11]. To achieve the SD of nitrocellulose of about 1, the reagent system was chosen containing 38 wt.% HNO_3, 35 wt.% of H_2SO_4 and 27 wt. % H_2O. To obtain dinitrocellulose (SD of about 2), the reagent system contained 43 wt.% HNO_3, 38 wt.% of H_2SO_4 and 19 wt. % H_2O. Tri-nitrocellulose (SD of about 3) was synthesized using the reagent system containing 50 wt.% HNO_3, 45 wt.% of H_2SO_4 and 5 wt. % H_2O. The nitrocellulose samples were washed with cold water and 1% NaHCO3 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.

2.2.3. Characterization of Samples

The substitution degree (SD) of cellulose acetates was studied by a method of chemical analysis [12]. It was found that the SD of obtained monoesters was 0.9-1.1, diesters 1.8-2.2, and triesters 2.8-3.0.

In the case of nitrocellulose samples, SD was calculated using the following equation [13]:

$$SD = 3.6\ N/(31.1 – N) \qquad (1)$$

where N is the percentage of nitrogen in the nitrocellulose (NIC), which was measured by the saponification of NIC with alkali [10].

The specific gravity (G) of dry samples was measured by a pycnometric method in the immersion medium of propanol [1]. The supramolecular structure of the samples was studied using a "Rigaku-Ultima Plus" diffractometer (CuK$_\alpha$ – radiation, λ=0.15418 nm). X-ray diffractograms were recorded in the 2Θ angle range from 5 to 50° [3].

2.3. 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^3 at an oxygen pressure of 3.05 MPa with 1.00 cm^3 of deionized water added to the bomb. The combustion measurements were carried out by an isothermal water calorimeter at 298.15 K with an accuracy of ±0.001 K. The value of the energy equivalent of the calorimeter determined by standard benzoic acid was 15802.3 ± 0.9 J/K. The true mass of the sample used in each experiment was determined from the mass of the produced CO_2. The correction of combustion energy for ignition, formation traces of nitric acid, and some other corrections were taken into account. To adjust the enthalpy of combustion (ΔH_c) to standard conditions, T=298.15 K and P= 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 enthalpy of formation (ΔH_f) of one mole of the repeating unit of cellulose derivatives having formula $C_aH_bO_c$ or $C_aH_bO_cN_d$ can be calculated from the measured standard enthalpy of combustion (ΔH_c) using the known Hess equation:

$$\Delta H_f = a\ \Delta H_f\ (CO_2, g) + 0.5b\ \Delta H_f\ (H_2O, l) - \Delta H_c \qquad (2)$$

where ΔH_f (CO_2, g = -393.51 kJ/mol and ΔH_f (H_2O, l) = -285.83 kJ/mol are standard enthalpies of the formation of carbon dioxide and liquid water, respectively.

For additional thermodynamic calculations, the literature data on standard formation enthalpies of the reagents and low-molecular-weight products of esterification were also used (Table 1).

Table 1 The standard formation enthalpies

Liquid Substance	-ΔH_f, kJ/mol
Nitric Acid	173.2
Acetic Anhydride	625.0
Acetic Acid	484.5
Water	285.83

3. Results and discussion

3.1. Structural studies

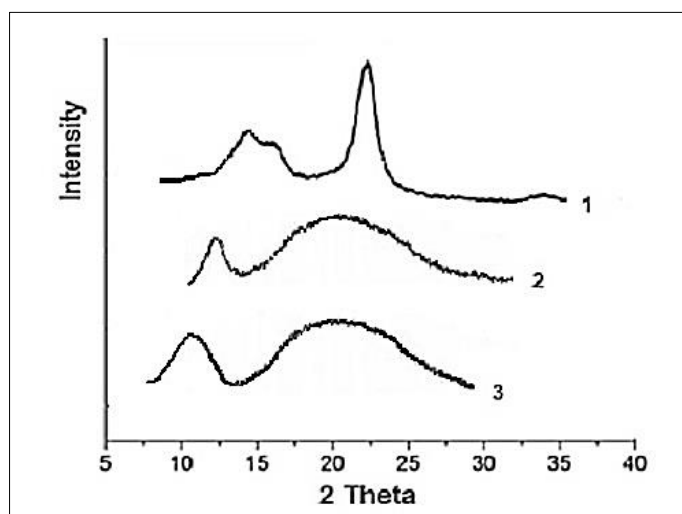X-ray patterns of original cotton cellulose and some cellulose derivatives were shown in Figure 1.

Figure 1 X-ray patterns of cotton cellulose (1), dinitrocellulose (2), and diacetate cellulose (3)

As can be seen, the original cellulose has a semi-crystalline structure with specific peaks at the 2θ angles of 14.7, 16.5, and 22.7 degrees. As a result of esterification, the crystalline structure of cellulose is disturbed and turns into a non-crystalline mesomorphic structure of cellulose derivatives with a wide diffuse scattering with a maximum at the 2θ angle of 20 degrees. In addition, these derivatives exhibit diffuse peaks at lower 2θ angles due to layered mesomorphous structure [3]. For example, a mesomorphous sample of nitrocellulose has an additional peak at the 2θ angle of 12 degrees, while mesomorphous cellulose acetate - at the 2θ angle of 10 degrees.

3.2. Study thermodynamics of preparation of cellulose acetates

The following non-crystalline samples of cellulose mono-, di-, and triacetate having a molar mass of M of the repeating unit were studied (Table 2).

Table 2 The studied cellulose acetates

Acetates of cellulose	Abbreviation	SD	Formula of unit	M	G, g/cm³
Monoacetate	MAC	1	$C_8H_{12}O_6$	204	1.38
Diacetate	DAC	2	$C_{10}H_{14}O_7$	246	1.33
Triacetate	TAC	3	$C_{12}H_{16}O_8$	288	1.28

As follows from the obtained results (Table 1, Figure 2), with an increase in the degree of substitution, the specific gravity of cellulose acetate decreases, as follows:

$$G = 1.445 - 0.056 \text{ SD} \qquad (3)$$

From eq. (3) the substitution degree (SD) can be calculated if the specific gravity (G) of the acetate was determined:
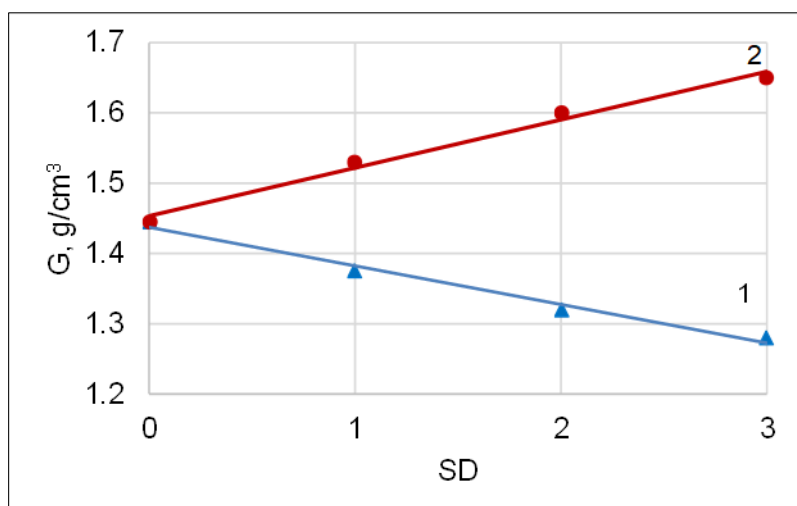
$$SD = 25.8 - 17.86 \text{ G} \qquad (4)$$

Figure 2 Dependence of specific gravity on the degree of substitution for cellulose acetates (1) and nitrates (2)
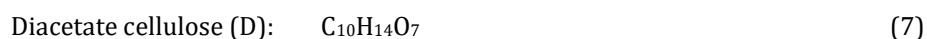
On the other hand, the theoretical specific gravity of these esters also can be calculated, as follows [1]:
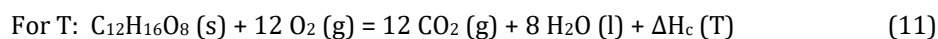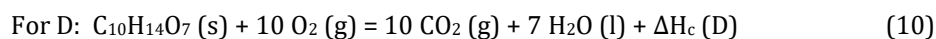
$$G = M/V_m \qquad (5)$$
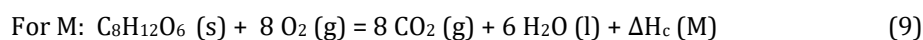
where $V_m = 112.2 + 37.2$ SD is the molar volume of the repeating unit of the cellulose acetates expressed in cm³/mol.

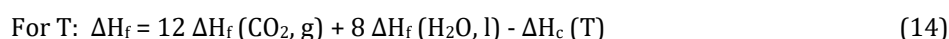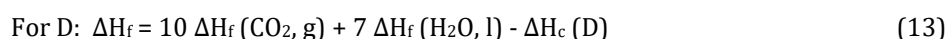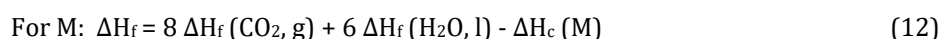Calculations according to eq. (5) were in good agreement with the experimental values of G.

The one repeating units of cellulose acetates can be described by the following general formulas.

Monoacetate cellulose (M): $C_8H_{12}O_6$ (6)

Diacetate cellulose (D): $C_{10}H_{14}O_7$ (7)

Triacetate cellulose (T): $C_{12}H_{16}O_8$ (8)

Then, the combustion process of one mole of repeating units of esters can be described by the following equations:

For M: $C_8H_{12}O_6$ (s) + 8 O_2 (g) = 8 CO_2 (g) + 6 H_2O (l) + ΔH_c (M) (9)

For D: $C_{10}H_{14}O_7$ (s) + 10 O_2 (g) = 10 CO_2 (g) + 7 H_2O (l) + ΔH_c (D) (10)

For T: $C_{12}H_{16}O_8$ (s) + 12 O_2 (g) = 12 CO_2 (g) + 8 H_2O (l) + ΔH_c (T) (11)

Accordingly, standard enthalpies of the formation of these esters can be calculated, as follows.

For M: ΔH_f = 8 ΔH_f (CO_2, g) + 6 ΔH_f (H_2O, l) - ΔH_c (M) (12)

For D: ΔH_f = 10 ΔH_f (CO_2, g) + 7 ΔH_f (H_2O, l) - ΔH_c (D) (13)

For T: ΔH_f = 12 ΔH_f (CO_2, g) + 8 ΔH_f (H_2O, l) - ΔH_c (T) (14)

where ΔH_f (CO_2, g) = -393.51(kJ/mol) is the standard enthalpy of the formation of gaseous carbon dioxide, and ΔH_f(H_2O, l) = -285.83 (kJ/mol) is the standard enthalpy of the formation of liquid water, while ΔH_c is the standard enthalpy of combustion of the ester.

The determined thermodynamic characteristics of cellulose acetates are collected in Table 3.

Table 3 Thermodynamic characteristics of cellulose acetates

Esters	SD	Formula of unit	-ΔH_c, kJ/mol	-ΔH_f, kJ/mol	-ΔH_r, kJ/mol
MAC	1	$C_8H_{12}O_6$	3747.6	1115.5	6.0
DAC	2	$C_{10}H_{14}O_7$	4647.5	1288.4	38.4
TAC	3	$C_{12}H_{16}O_8$	5547.4	1461.3	70.8

The study showed that such thermodynamic characteristics as enthalpies of combustion (ΔH_c) and formation (ΔH_f) are functions of the degree of substitution (SD):

$$\Delta H_c = \Delta H_c(Am) - 899.8 \text{ SD}$$ (15)

$$\Delta H_f = \Delta H_f(Am) - 173 \text{ SD}$$ (16)

where ΔH_c(Am) = - 2847.8 kJ/mol and ΔH_f(Am) = - 942.4 kJ/mol are standard enthalpies of combustion and formation of amorphous cellulose, respectively [14].

The obtained results showed that increasing the degree of substitution (SD) contributes to enhancing the exothermic enthalpy of the ester formation (Table 3).

The acetylation process of one repeating unit of cellulose by acetic anhydride with the formation of cellulose acetate and acetic acid can be described as follows:

$C_6H_{10}O_5 + n(CH_3CO)_2O = C_6H_{(10-n)}O_5(COCH_3)_n + nCH_3COOH$ (17)

where n is SD.

Knowing the values of the standard enthalpies of formation of the acetic anhydride, ΔH_f (AAn), and acetic acid, ΔH_f(AAc) (Table 1), cellulose ester, ΔH_f (E) (Table 3), and the original cotton cellulose ΔH_f (CC) = -969 kJ/mol [14], it is possible to calculate the standard enthalpy of the acetylation reactions, as follows:

$$\Delta H_r = \Delta H_f (E) + n\, \Delta H_f(AAc) - \Delta H_f (CC) - n\Delta H_f(AAn) \tag{18}$$

As can be seen from Figure 3, the cellulose acetylation is accompanied by an exothermic enthalpy. Moreover, the more SD, the higher the exothermic heat effect of this reaction.
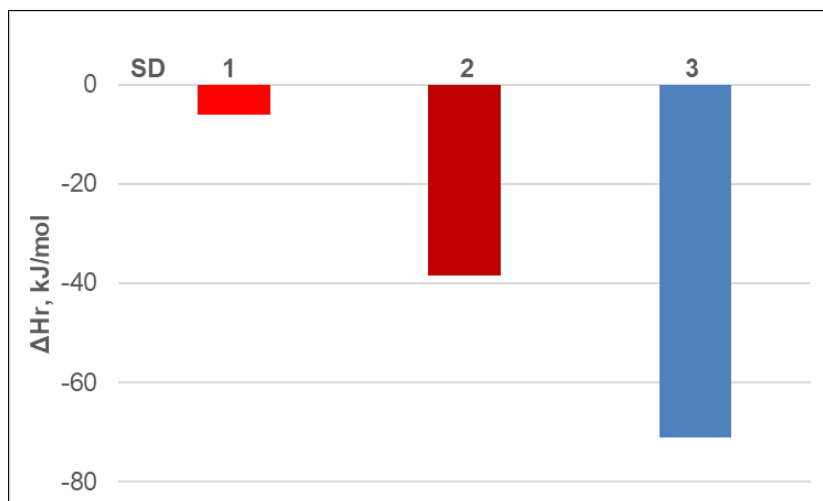

Figure 3 Enthalpy of acetylation reaction to produce monoacetate (1), diacetate (2), and triacetate (3) of cellulose

Regarding the standard entropy of the reaction (ΔS_r), it can be noted that if this entropy increases, this will contribute to the reaction implementation. However, in the event that the entropy of the reaction decreases, then the following conditions must be fulfilled for the implementation of such a reaction:

$$[\Delta H_r] > [T\, \Delta S_r] \text{ and } \Delta G_r = (\Delta H_r - T\, \Delta S_r) < 0 \tag{19}$$

where ΔG_r is the standard Gibbs potential of the reaction, and T is temperature.

Thus, thermodynamic analysis indicates that the feasibility of cellulose acetylation, especially to di- and triacetates, is determined mainly by the exothermic enthalpy of this reaction

3.3. Study thermodynamics of cellulose nitration

The characteristics of studied non-crystalline nitrocellulose samples having a formula of $C_6H_{(10-n)}O_5(NO_2)_n$ (where **n** is SD) are presented in Table 4.

Table 4 Characteristics of original cotton cellulose (CC) and samples of nitrocellulose (NIC)

Sample	Formula of unit	M	N, %	SD	G, g/cm³	-ΔH_c, kJ/mol	-ΔH_f, kJ/mol	ΔH_r, kJ/mol
CC	$C_6H_{10}O_5$	162	0	0	-	2821.2	969.0	0
Mono-NIC	$C_6H_9O_5NO_2$	207	6.72	0.99	1.54	2800.1	848.4	8
Di-NIC	$C_6H_8O_5(NO_2)_2$	252	11.21	2.03	1.60	2750.4	749.7	-6
Tri-NIC	$C_6H_7O_5(NO_2)_3$	297	13.87	2.90	1.65	2708.7	667.1	-36

In contrast to cellulose acetates, with an increase in the degree of substitution of nitrocellulose, a rise in the specific gravity of the samples was observed (Table 4, Figure 2). Therefore, after determining the specific gravity (G), it is possible to calculate the degree of substitution (SD) of the nitrocellulose using the following correlation equation:

$$SD = 14.3\ G - 20.8 \qquad (20)$$

The experiments have shown that with an increase in SD of NIC, the enthalpy of combustion (ΔH_c) becomes less exothermic (Table 3). Knowing the enthalpy of combustion, the enthalpy of NIC formation can be calculated, as follows:

$$\Delta H_f = 6\Delta H_f\ (CO_2, g + (5 - 0.5\ SD)\ \Delta H_f(H_2O, l) - \Delta H_c \qquad (21)$$

Thus, $\qquad \Delta H_f = -3790.21 + 142.915\ SD - \Delta H_c \qquad (22)$

where $\Delta H_f(CO_2, g) = -393.51(kJ/mol)$ is the standard enthalpy of the formation of gaseous carbon dioxide, and $\Delta H_f(H_2O, l) = -285.83\ (kJ/mol)$ is the standard enthalpy of the formation of liquid water

As can be seen from Table 4, with the increase in SD of NIC, the exothermic value of the formation enthalpy (ΔH_f) decreases.

The nitration reactions can be described, as follows:

$$C_6H_{10}O_5 + n\ HNO_3 = C_6H_{(10-n)}O_5(NO_2)_n + n\ H_2O \qquad (23)$$
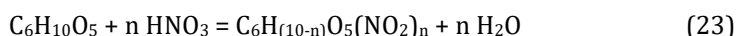
After calculating the enthalpy of the nitration reaction (ΔH_r) of cotton cellulose (CC) with dilute nitric acid (C<40%) to SD<1.5, it turned out that the value of the reaction enthalpy is positive (Figure 4), i.e., the thermal effect of this reaction is endothermic.
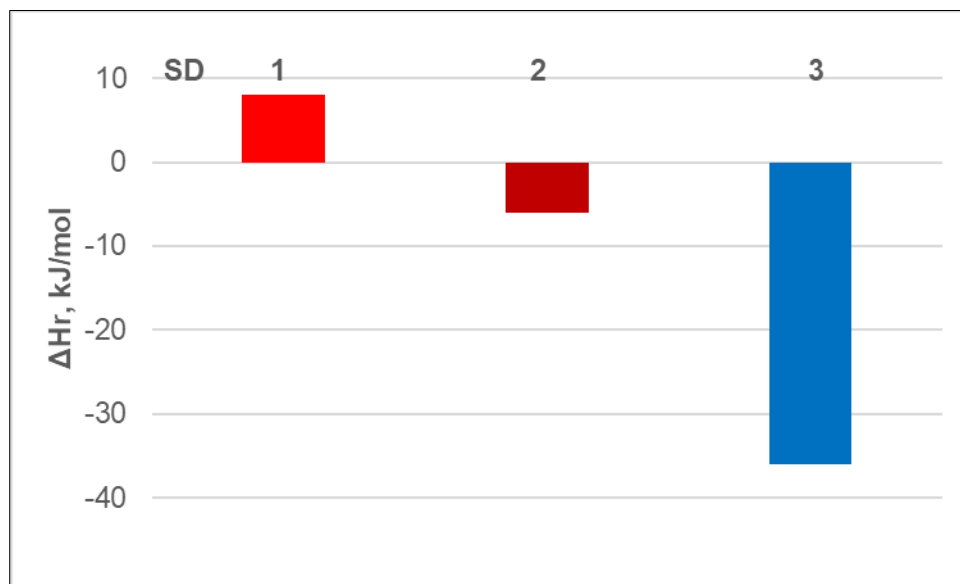

Figure 4 Enthalpy of reaction of cellulose nitration at the synthesis of mono-NIC (1), di-NIC (2), and tri-NIC (3)

If the reaction is endothermic, then its implementation requires an influx of thermal energy from the outside. However, as is known [13], nitration of the cellulose also proceeds when the reaction system is cooled to relatively low temperatures when the supply of thermal energy from the outside is difficult. In this case, the only possibility for the nitration reaction takes place is a significant increase in the reaction entropy, so that the Gibbs potential of this reaction becomes negative, as follows:

$$[T\ \Delta S_r] > [\Delta H_r]\ \text{and}\ \Delta G_r = (\Delta H_r - T\ \Delta S_r) < 0 \qquad (24)$$

Thus, thermodynamic analysis shows that the process of nitration of cellulose with dilute nitric acid (C<40 wt.%) to SD<1.5 is possible if the entropy contributes to the Gibbs potential of this reaction. On the other hand, when cellulose is nitrated with more concentrated nitric acid to SD >1.5, the reaction enthalpy becomes exothermic. Moreover, the greater the SD, the higher the exothermic thermal effect of this reaction. Thus, when the nitration of cellulose is carried out with a sufficiently concentrated nitric acid until an increased degree of substitution is reached, the feasibility of this reaction is determined mainly by the exothermic enthalpy.

4. Conclusions

The standard enthalpies of combustion and formation of non-crystalline acetates and nitrates of cellulose were determined. In addition, the thermodynamics of esterification reactions of cellulose was studied.

It was shown that an increase in the degree of substitution of cellulose acetates contributes to enhancing the exothermic enthalpy of the reaction. Thus, the feasibility of cellulose acetylation, especially to di- and triacetates, is determined mainly by the exothermic enthalpy of this reaction.

The study of nitrocelluloses has shown that with an increase in the degree of substitution, the enthalpies of combustion and formation become less exothermic. When cellulose is nitrated with dilute nitric acid to SD < 1.5, the enthalpy of the nitration reaction is endothermic. Thus, to implement the nitration process of cellulose with a dilute reagent, the contribution of the entropy to the Gibbs potential of this reaction is necessary. On the other hand, when cellulose is nitrated with more concentrated nitric acid to SD >1.5, the reaction enthalpy becomes exothermic. In this case, the feasibility of the cellulose nitration process will be determined mainly by the exothermic reaction enthalpy.

As the degree of substitution increases, the specific gravity of cellulose acetates decreases, while that of nitrocelluloses increases. From experimental values of specific gravity, the degree of substitution of cellulose derivatives was calculated.

References

[1]   Ioelovich M. Structural characteristics of cellulose esters with different degrees of substitution. Organic Polymer Mater Res. 2022; 4: 38-43.

[2]   Sassy J-F, Chanzy H. Ultrastructural aspects of the acetylation of cellulose. Cellulose 1995; 2: 111-127.

[3]   Ioelovich M. Adjustment of hydrophobic properties of cellulose materials. Polymers 2021: 13, 1241: 1-11.

[4]   Wei DW., Wei H., Gauthier AC, et al. Superhydrophobic modification of cellulose and cotton textiles: Methodologies and applications. J. Biores. Bioprod. 2020; 5: 1–15.

[5]   Edgar KJ, Buchanan CM, Debenham JS, et al. Advances in cellulose ester performance and application. Progress in Polym. Sci. 2001; 26: 1605-1688.

[6]   Filho GR, Monteiro DS, Da Silva Meireles K, et al. Synthesis and characterization of cellulose acetate produced from recycled newspaper. Carbohydrate Polym. 2008; 73: 74-82.

[7]   Fischer S, Thümmler K, Volkert B, et al. Properties and applications of cellulose acetate. Macromolec. Sympos. 2008; 262: 89-96.

[8]   Panchenko O, Tutova O. Problems and advances in production of nitrate cellulose. Chem. Plant Mater. 2005; 3: 85–88.

[9]   Cheung C. Studies of the Nitration of Cellulose – Application In New Membrane Material. Diss. Thesis. Vancouver; 2014.

[10]   Mattar H, Baz Z, Saleh A, et al. Nitrocellulose: structure, synthesis, characterization, and applications. Water, Energy, Food and Env. J. 2020; 1: 1-15.

[11]   Obolenskaya AV, Elnitskaya ZP, Leonovich AA. Laboratory Practicum on Chemistry of Wood and Cellulose. Ecology; 1991.

[12]   Freire CSR., Silvestre AJD., Neto CP., Rocha RMA. An efficient method for determination of the degree of substitution of cellulose esters of long-chain aliphatic acids. Cellulose 2005; 12: 449–458.

[13]   Stovbun SV, Nikolskiy SN, Melnikov VP, et al. Chemical physics of cellulose nitration. J. Physical Chemistry, B. 2016; 10: 245–259.

[14]   Ioelovich M. Study of thermodynamic stability of various allomorphs of cellulose. J. Basic Appl. Res. Int. 2016; 16: 96-103.