

## Thermochemistry of alkalization and etherification of cellulose

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### Abstract

In this research, the process of alkalization of cotton cellulose with solutions of sodium hydroxide of different concentrations has been studied. It was found that the enthalpy of cellulose alkalization is exothermic. Moreover, the exothermic enthalpy value of cellulose alkalization with 30-40% NaOH solutions is higher than with 16-20% alkalis. Thus, the cellulose treatment with 30-40% alkalis provides the formation of more reactive alkali cellulose. In addition, the determination of the formation enthalpy of alkali celluloses showed that this thermochemical characteristic is also exothermic, and therefore, the process of cellulose alkalization is energetically favorable. It is most likely that cellulose alkalization is a physicochemical process of forming a molecular adduct of hydrated hydroxide ions with cellulose. A study of the methylation reaction of alkali cellulose with methyl chloride to a degree of substitution of 1.3-1.8 showed that the enthalpy of this reaction is quite exothermic. This means that methylation reaction is energetically advantageous, and obtaining methylcellulose with a higher degree of substitution is preferable.

**Keywords:** Cellulose; Sodium hydroxide; Interaction; Alkali cellulose; Enthalpy of alkalization; Enthalpy of formation; Enthalpy of etherification

### 1. Introduction

Treatment of cellulose with solutions of hydroxides of alkali metals is one of the most common methods of modification of this biopolymer. Currently, treatment with aqueous solutions of sodium hydroxide is used for the improvement of luster, hygroscopic properties, and dyeing of cellulose fibers and fabrics, for cellulose activation and refining, as well as in the production of cellulose ethers [1-6].

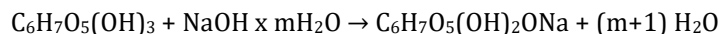
It has been established that after cellulose treatment with solutions of sodium hydroxide having a concentration of less than 10-11%, the crystalline structure of CI remains unchanged [7]. However, when cellulose is alkalized with 16-20% alkali solutions the hydrated hydroxide ions penetrate between [110] planes of the crystalline lattice of CI and transform it into the swollen crystalline lattice of alkali cellulose (AIC) containing one molecule of NaOH and three molecules of H<sub>2</sub>O per each anhydroglucose unit (AGU) in crystalline domains of cellulose.

Cellulose treatment with more concentrated solutions of sodium hydroxide leads to the transformation of CI crystalline lattice into lattices of other alkali cellulose types with lower volume and content of water molecules [7]. For example, cellulose alkalization with 35-40% NaOH causes the formation of a crystalline lattice of AIC with the composition AGU·NaOH·H<sub>2</sub>O, i.e., containing no more than one molecule of H<sub>2</sub>O per AGU. An anhydrous form of AIC with the composition AGU·NaOH was also obtained. During alkalization, the partial decrystallization of cellulose is observed [8]. It was also established that the process of cellulose alkalization is accompanied by an exothermic heat effect [9, 10].

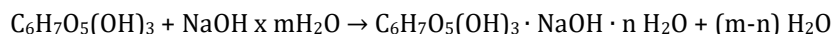
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After washing various alkali celluloses with water, hydroxide ions are replaced by water molecules resulting in the formation of the crystalline lattice of hydrate-cellulose, which after drying turns completely into the crystalline lattice of CII [11, 12].

The process of formation of alkali celluloses has been studied by various methods including sorption, XRD, NMR, FTIR, Raman spectroscopy, etc. [5, 6, 10, 13-16]. Despite these studies, the mechanism of this process is still the subject of discussion. Some researchers suggest that due to the interaction of cellulose with alkali solutions, a chemical compound similar to sodium alcoholate is formed [17].



Other researchers believe that when using aqueous solutions of alkali, the formation of such a chemical compound with cellulose is impossible, and the most probable interaction mechanism is the formation of a molecular adduct of hydrated alkali ions with cellulose [7, 18].



In this research, to elucidate the mechanism of the cellulose alkalization process, a thermochemical method was used to determine the heat effect or enthalpy of alkalization, as well as the standard enthalpy of the AIC formation. In addition, the thermodynamics of cellulose etherification process was studied.

## 2. Materials and methods

### 2.1. Materials

The original cellulose material was pure cotton cellulose, CC (98%  $\alpha$ -cellulose, DP=2700) supplied from Hercules, Inc., USA. Samples of methylcellulose (MC) with a degree of substitution of 1.3 (MC 1) and 1.8 (MC 2) were acquired from Dow Chemical Co., USA. The chemically pure sodium hydroxide was purchased from Sigma-Aldrich Co., USA.

### 2.2. Methods

#### 2.2.1. Alkalization of cellulose

The alkalization of the dry cellulose was carried out with aqueous solutions of sodium hydroxide of various concentrations at room temperature (298 K) for 2 h at a solution/cellulose ratio of 50 while stirring. After treatment, excess alkali was removed by centrifugation at 4000 rpm for 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. 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. The crystallinity degree ( $X$ ) of the samples was calculated according to the following equation [19]:

$$X, \% = 100 \int I_c d\varphi / \int I_o d\varphi$$

where  $I_c$  and  $I_o$  are the corrected and normalized intensities of diffraction from the crystalline part and whole sample, respectively.

The content of the CII-crystalline allomorph in the sample was determined using the XRD method of the inner standards [20]:

$$\text{CII, \%} = 200 I_{12} / (I_{15} + I_{16})$$

where  $I_{12}$ ,  $I_{15}$ , and  $I_{16}$  are the crystalline peak intensities on the X-ray pattern of the sample at the  $\varphi = 2\theta$  of 12, 15, and 16 degrees, respectively.

### 2.3. Absorption of alkali with cellulose

The absorption of NaOH and water molecules by dry cotton cellulose from alkali solutions of various concentrations was studied at room temperature (298 K), for 2 h at a solution/cellulose ratio of 50 while stirring. To measure the absorption values of NaOH and water, the method of differential titration of the alkali solutions containing the additive of an inert electrolyte (NaCl) before and after the absorption process was used [21]. Three of the same samples were tested to calculate an average enthalpy value and standard deviation.

#### 2.3.1. Enthalpy of alkalization

The standard enthalpy of cellulose alkalization ( $\Delta_{al}H$ ) was studied at 298 K using a TAM Precision Solution Calorimeter [22]. Before starting the experiments, the dried cellulose sample was weighed into a special glass ampoule and additionally dried in a vacuum at 378 K to a constant weight. The glass ampoule containing the dry sample was sealed and introduced into the calorimetric cell filled with an alkali solution. The calorimeter was thermostated at 298 K to achieve an equilibrium state. Thereafter, the sealed ampoule with the dry cellulose sample was broken to ensure contact of the sample with the alkali. The released exothermic heat effect was measured with accuracy  $\pm 0.01$  J. Three of the same samples were tested to calculate an average enthalpy value and standard deviation.

#### 2.3.2. Enthalpy of combustion

Combustion of the dry samples was carried out in a stainless-steel calorimetric bomb having a volume of  $0.320 \text{ dm}^3$  at an oxygen pressure of 3.05 MPa with  $1.00 \text{ cm}^3$  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  $\pm 0.001$  K. The value of the energy equivalent of the calorimeter determined by standard benzoic acid was  $15802.3 \pm 0.9 \text{ J/K}$ . The true mass of the sample used in each experiment was determined from the mass of the produced  $\text{CO}_2$ . The correction of combustion energy for ignition and some other corrections were taken into account. To adjust the enthalpy of combustion ( $\Delta_c H$ ) to standard conditions,  $T=298.15 \text{ K}$  and  $P=0.1 \text{ MPa}$ , 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.

## 3. Results and Discussion

The compositions of used alkali solutions are shown in Table 1.

**Table 1** The composition of 100 g alkali solutions of various concentrations

NaOH, %	NaOH, mol	H <sub>2</sub> O, mol	m*
6	0.15	5.22	34.8
8	0.20	5.11	25.5
10	0.25	5.00	20.0
12	0.30	4.89	16.3
14	0.35	4.78	13.6
16	0.40	4.67	11.7
18	0.45	4.55	10.1
20	0.50	4.44	8.9
30	0.75	3.89	5.2
35	0.875	3.61	4.1
40	1.00	3.3	3.3

Note: **m** is the number of H<sub>2</sub>O moles per 1 mole of NaOH in the solution

X-ray studies have shown that after treatment of the original cotton cellulose with an alkali concentration below  $C_o = 10\%$ , the structure of the CI remains unchanged. When cellulose is treated with an alkali concentration higher than  $C_o$ , the formation of the crystalline structure of alkali cellulose (AIC) begins, accompanied by a decrease in cellulose crystallinity. If the critical alkali concentration  $C_{cr} = 16\%$  is reached, the CI crystalline structure of the original cellulose

is completely transformed into the crystalline structure of AIC, which, after washing and drying, turns completely into the CII crystalline structure with reduced crystallinity (Figures 1, 2). The appearance of CII after washing and drying the alkali-treated cellulose sample indicates the formation of the crystal structure of AIC under the influence of alkali.

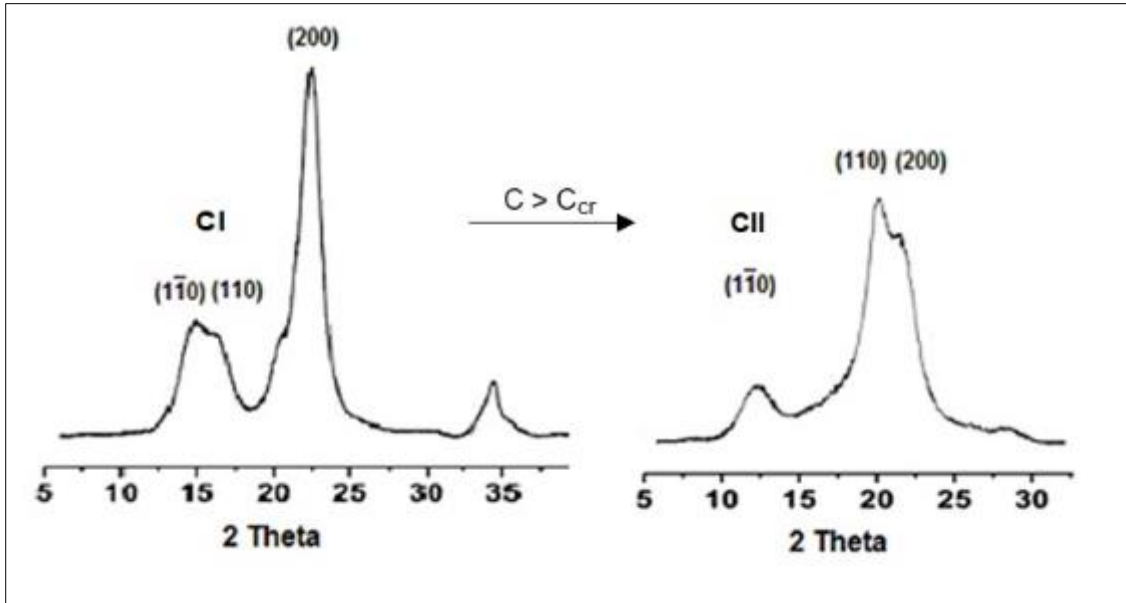


Figure 1 X-ray patterns of CI and CII

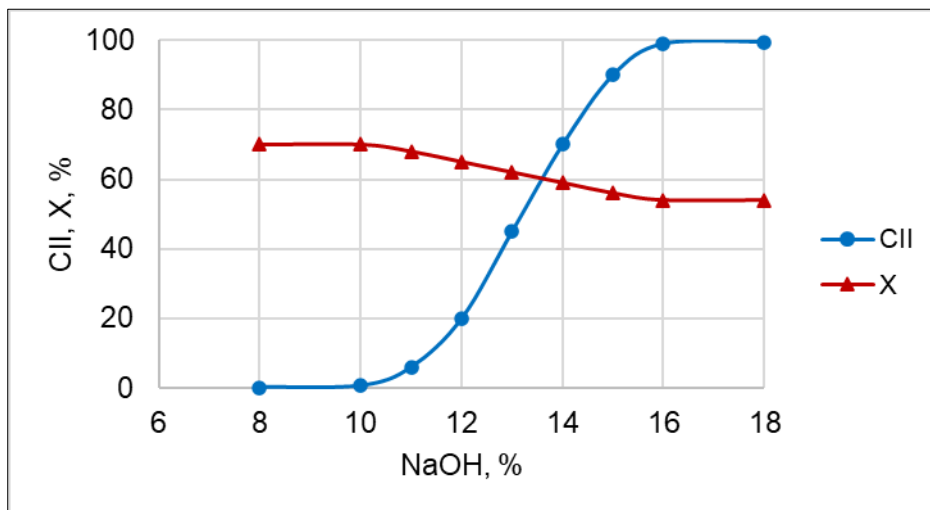
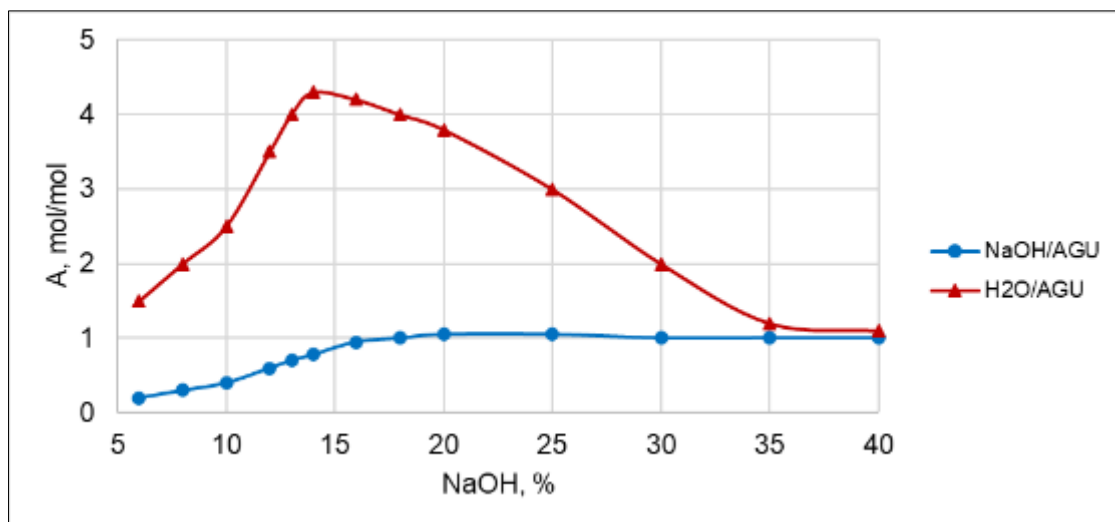


Figure 2 Dependence of CII content and crystallinity of cellulose sample on alkali concentration

A study of the absorption of hydroxide and water molecules from NaOH solutions by cellulose sample showed that AIC formed after cellulose alkalinization with alkali concentration above  $C_{cr} = 16\%$  can contain about 1 mole of NaOH and from 1 to 4 moles of water per one AGU of cellulose (Figure 3).



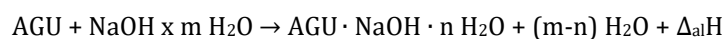
**Figure 3** Absorption of hydroxide and water molecules from alkali solutions by cellulose sample

Using the absorption results, the compositions of various alkali cellulose samples formed after the treatment of the original cellulose with alkali solutions having concentrations above  $C_{cr}$  were assessed (Table 2).

**Table 2** Estimated composition of various alkali celluloses

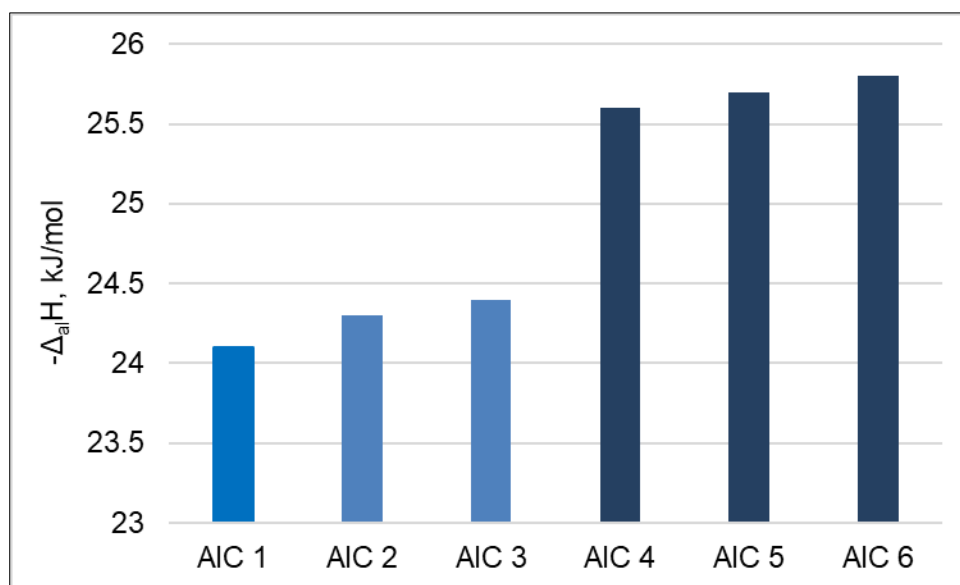
NaOH, %	AIC Label	AGU, mol	NaOH, mol	n H <sub>2</sub> O, mol
16	AIC 1	1	1	4
18	AIC 2	1	1	4
20	AIC 3	1	1	4
30	AIC 4	1	1	2
35	AIC 5	1	1	1
40	AIC 6	1	1	1

The alkalization process with the formation of alkali celluloses with modified crystalline structures can be described, as follows:



where  $\Delta_{al}H$  is the standard enthalpy of alkalization

The results showed that the formation of AIC 4-6 is accompanied by a higher value of exothermic enthalpy of alkalization than the formation of AIC 1-3 (Figure 4).



**Figure 4** Enthalpy of cellulose alkalization with the formation of various alkali celluloses

Another significant thermodynamic characteristic is the standard enthalpy of the formation of alkali cellulose from one AGU and alkali solution containing  $m$  moles  $H_2O$  per 1 mol of NaOH (Table 1).

Following Hess's law, the standard enthalpy of the formation of alkali cellulose was calculated, as follows:

$$\Delta_f H (\text{AIC}) = \Delta_f H (\text{CC}) + \Delta_f H (\text{Alkali}) - (m-n) \Delta_f H (H_2O) + \Delta_{al} H$$

where  $\Delta_f H (\text{CC}) = -969$  kJ/mol is the standard enthalpy of formation of 1 mole AGU of original cotton cellulose [24],  $\Delta_f H (H_2O) = -285.83$  kJ/mol is the standard enthalpy of formation of liquid water,  $\Delta_{al} H$  is the enthalpy of alkalization (Figure 4), while the standard enthalpy of formation of an alkali solution is:

$$\Delta_f H (\text{Alkali}) = \Delta_f H (\text{NaOH}) + m\Delta_f H (H_2O) + \Delta_{ds} H$$

Note:  $\Delta_f H (\text{NaOH}) = -426.6$  kJ/mol is the standard enthalpy of formation of crystalline NaOH and  $\Delta_{ds} H$  is the enthalpy of dissolution of 1 mole NaOH in  $m$  moles  $H_2O$  (see Table 3).

The results of the calculations are shown in Tables 3 and 4.

**Table 3** Standard enthalpy of formation of alkali solutions

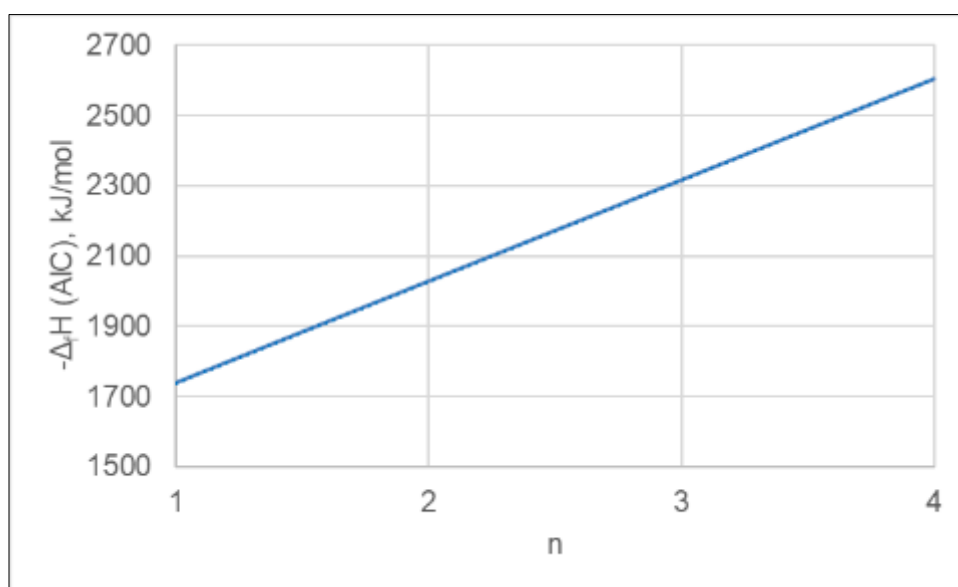
NaOH, %	$m$	$-\Delta_{ds} H^*$ , kJ/mol	$-\Delta_f H (\text{Alkali})$ , kJ/mol
16	11.7	42.6	3813
18	10.1	42.5	3356
20	8.9	42.0	3012
30	5.2	38.2	1951
35	4.1	34.5	1633
40	3.3	31.0	1401

$\Delta_{ds} H^*$  is the enthalpy of dissolution of 1 mole of dry NaOH crystals in  $m$  moles of  $H_2O$  [23]

**Table 4** Standard enthalpy of formation of various alkali celluloses

AIC Label	n	$-\Delta_{al}H$ , kJ/mol	$-\Delta_fH$ (AIC), kJ/mol
AIC 1	4	24.1	2605
AIC 2	4	24.3	2605
AIC 3	4	24.4	2605
AIC 4	2	25.6	2030
AIC 5	1	25.7	1742
AIC 6	1	25.8	1738

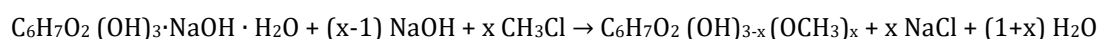
It was found that with an increase in the number of H<sub>2</sub>O molecules (n) in the AIC composition, the exothermic value of formation enthalpy of alkali cellulose increases linearly (Figure 5).

**Figure 5** Dependence of formation enthalpy of alkali cellulose on the number of H<sub>2</sub>O molecules in its composition

This dependence is expressed by the equation:  $\Delta_fH(\text{AIC}) = -288.3n - 1452$ .

From the presented results it follows that the enthalpy of the formation of various alkali celluloses,  $\Delta_fH(\text{AIC})$ , is exothermic, and thus, the process of cellulose alkalization is energetically favorable. It is most likely that alkalization is a physicochemical process of forming a molecular adduct of hydrated hydroxide ions with cellulose. In addition, since the exothermic enthalpy of alkalization,  $\Delta_{al}H$ , at the formation of the AIC 4-6 has the highest value (Figure 4), these alkali celluloses should be more reactive than the AIC 1-3 samples. Therefore, for the alkalization stage of cellulose before etherification, 30-40% alkali solutions are used, which give alkali celluloses AIC 4-6 with an increased reactivity.

Consider as an example the process of production of methylcellulose (MC). The first stage of this process is cellulose alkalization, e.g., with a 40% NaOH solution at room temperature, after which the excess alkali is removed to obtain a mass ratio of alkali to cellulose of 3:1 [25]. The resulting alkali cellulose such as AIC 6 is kept in the air at 35°C for 1-2 h, and then methylated with methyl chloride:



where  $x$  is the degree of substitution (DS) of MC. The DS of the studied MC samples, MC-1 and MC-2 was 1.3 and 1.8, respectively.

Taking into consideration the equation of the etherification process, the enthalpy of the methylation reaction of AIC 6 can be calculated, as follows:

$$\Delta_r H = \Delta_f H (\text{MC}) + x\Delta_f H (\text{NaCl}) + (1+x) \Delta_f H (\text{H}_2\text{O}) - \Delta_f H (\text{AIC 6}) - (x-1) \Delta_f H (\text{NaOH}) - x \Delta_f H (\text{CH}_3\text{Cl})$$

where  $\Delta_f H (\text{AIC 6})$  is the standard enthalpy of formation of AIC 6 (see Table 4), while  $\Delta_f H (\text{NaCl})$ ,  $\Delta_f H (\text{NaOH})$ ,  $\Delta_f H (\text{CH}_3\text{Cl})$ , and  $\Delta_f H (\text{H}_2\text{O})$  is the standard enthalpy of formation of the corresponding substance (Table 5).

**Table 5** Standard enthalpy of formation of various substances

Substance	$-\Delta_f H$ , kJ/mol
NaCl (cr)	410.9
NaOH (cr)	426.6
CH <sub>3</sub> Cl (g)	83.7
H <sub>2</sub> O (l)	285.83
CO <sub>2</sub> (g)	393.51

The standard enthalpy of formation  $\Delta_f H (\text{MC})$  for MC 1 and MC 2 samples was calculated from the standard combustion enthalpy  $\Delta_c H (\text{MC})$  of these samples:

$$\Delta_f H (\text{MC}) = (6+x) \Delta_f H (\text{CO}_2) + (5+x) \Delta_f H (\text{H}_2\text{O}) - \Delta_c H (\text{MC})$$

where  $\Delta_f H (\text{CO}_2)$  and  $\Delta_f H (\text{H}_2\text{O})$  are the standard enthalpy of formation of corresponding substances (Table 5), while the experimental value of standard combustion enthalpy of  $\Delta_c H (\text{MC1}) = -3706$  kJ/mol, and  $\Delta_c H (\text{MC2}) = -4036$  kJ/mol, respectively.

Then, the standard enthalpy of formation of MC1  $\Delta_f H (\text{MC1}) = -967.3$  kJ/mol, and of MC 2  $\Delta_f H (\text{MC2}) = -977.0$  kJ/mol

As a result, the following values of enthalpy of the methylation reaction of AIC 6 to obtain methylcellulose samples were calculated.

For MC 1 ( $x=\text{DS} = 1.3$ ):  $\Delta_r H (\text{MC 1}) = -184$  kJ/mol.

For MC 2 ( $x=\text{DS} = 1.8$ ):  $\Delta_r H (\text{MC 2}) = -287$  kJ/mol.

Since the enthalpy values of the methylation reaction of AIC 6 were quite exothermic, this means that the methylation reaction is energetically advantageous. Moreover, obtaining methylcellulose with a higher degree of substitution is preferable.

#### 4. Conclusions

The results showed that the enthalpy of the formation of various alkali celluloses,  $\Delta_f H (\text{AIC})$ , is highly exothermic, thus, the process of cellulose alkalization is energetically favorable.

It was established that the exothermic enthalpy of cellulose alkalization  $\Delta_{al} H$  at the formation of the AIC 4-6 has the highest value, and therefore these alkali celluloses should be more reactive than the AIC 1-3 samples.

It is most likely that alkalization is a physicochemical process of forming a molecular adduct of hydrated hydroxide ions with cellulose.

A study of the methylation reaction of alkali cellulose with methyl chloride to a degree of substitution of 1.3-1.8 showed that the enthalpy of this reaction  $\Delta_r H (\text{MC})$  is quite exothermic and ranges from -184 to -287 kJ/mol. This means that methylation reaction is energetically advantageous.



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