Carbohydrate Polymers 115 (2015) 658–662

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Effect of different alkaline solutions on crystalline structure of cellulose at different temperatures

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ARTICLE INFO

Article history:
Received 4 July 2014
Received in revised form 2 September 2014
Accepted 9 September 2014
Available online 28 September 2014

Keywords:
Cellulosic fiber
Alkaline solution
Dissolution
Degree of polymerization
X-ray diffraction, Solid state NMR

ABSTRACT

Effect of alkaline solutions such as 10% NaOH, NaOH/urea and NaOH/ethylene glycol solutions on crystalline structure of different cellulosic fibers (cotton linter and filter paper) was investigated at room temperature and −4 °C. The highest dissolution of cotton linter and filter paper was observed in NaOH/ethylene glycol at both temperatures. X-ray patterns of treated cotton linter with different alkaline solutions at low temperature showed only two diffractions at $2\theta = 12.5^{\circ}$ and 21.0°, which belonged to the crystalline structure of cellulose II. CP/MAS ^{13}C NMR spectra showed the doublet peaks at 89.2 ppm and 88.3 ppm representing C_4 resonance for cellulose I at room temperature, Whereas, at low temperature the doublet peaks were observed at 89.2 ppm and 87.8 ppm representing C_4 resonance for cellulose II. Degree of polymerization of cellulose plays an important role in cellulose dissolution in different alkaline solutions and temperatures, where, a low temperature gives high dissolutions percentage with change in crystalline structure from cellulose I to cellulose II forms.

1. Introduction

Study of cellulose dissolution is an interesting research area and could be used in many applications such as membrane production, paper recycling and drug delivery. Suitable solvent for cellulose dissolution plays a key role for the design and processing conditions. Generally, polymeric material does not dissolve instantaneously, and the dissolution is controlled by either the disentanglement of the polymer chains or by the diffusion of the chains through a boundary layer adjacent to the polymer–solvent interface (Cai & Zhang, 2005). On the other hand, cellulose did not dissolution at temperature lower than its degradation temperature, due to, strong intra- and inter-molecular hydrogen bonds in cellulose which prevents the dissolution in most common organic solvents (Cai & Zhang, 2005). For these reasons, cellulosic materials are regarded as un-moldable materials. Therefore, wood and cotton fibers are difficult to be refabricated as other thermosetting and thermoplastic polymers (Ruan, Zhang, Mao, Zeng, & Li, 2004). The dissolution of a polymer into a solvent involves two transport processes, namely solvent diffusion and chain disentanglement. When amorphous and glassy polymer is in contact with a compatible solvent, the solvent will diffuse onto the polymer. So, understanding the dissolution behavior of cellulose in different solvents is of particular interest for cellulose researchers and industries (Rder & Morgenstern, 1999; Ramos, Assaf, El-Seoud, & Frollini, 2005; Roy, Budtova, & Navard, 2003; Keshk, Yousef, & Omran, 2014). Effective cellulose solvents should be able to break down inter and intra-hydrogen bonding. Sodium hydroxide is the most popular solution that swells and can even dissociates cellulose in a narrow range of liquid phase (Ruan et al., 2004; Zhang, Ruan, & Gao, 2002). The maximal dissolution of cellulose with low to moderate degree of polymerization occurs with 8% to 10% sodium hydroxide solution (Kunze & Fink, 2005; Wang, Zhao, & Deng, 2008). In recent years, researchers found that, dissolution rate using sodium hydroxide with urea or ethylene glycol could be significantly improved at low temperature (Isogai & Atalla, 1998; Keshk & Sehemi, 2013). But, these reports that deal with dissolution of cellulose did not provide clear understanding of cellulose structure before and after dissolution. Furthermore, no explanation was provided for ease of dissolution of cellulose at low temperatures. On the other hand, no clear discussion for the effect of the presence of either ethylene glycol or urea with sodium hydroxide in the cellulose dissolution was studied. This work explores the behavior of different cellulosic materials in alkaline solutions at different temperatures, using X-ray diffractometer and CP/MAS ^{13}C NMR spectra. Moreover, physical structure evaluation of the cellulose dissolution at different temperatures is discussed.

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http://dx.doi.org/10.1016/j.carbpol.2014.09.045
0144-8617/

2. Experimental

2.1. Materials

Cotton linters cellulose sheets and chemicals were purchased from Sigma and Aldrich Chemical Co.

2.2. Methods

2.2.1. Alkaline solutions preparation

1. 10% NaOH.
2. NaOH/Urea solution (6 g urea with 7 g NaOH in 100 ml H_2O).
3. NaOH/Urea solution (1:1, 6 g urea with 4 g NaOH in 100 ml H_2O).
4. NaOH/Ethylene glycol (8 g ethylene glycol with 7 g NaOH in 100 ml H_2O).

2.2.2. Cellulose dissolution in alkaline solution

1.0 g of cotton linter or filter paper was rinsed in 50 ml of alkaline solution and placed in 100 cm^3 glass reactor equipped with mechanical stirrer. Cellulose dissolution was carried out at room temperature and −4 °C for 36 h. Cellulose samples were then taken and washed well with water till neutralization to prevent further dissolution, then dried well in dissector under vacuum.

2.3. Dissolution measurement

The dissolution percentage of cellulose was defined as the weight of dissociated cellulose (the difference between the original sample weight and the weight of un-dissociated residue) divided by original oven dried weight of cellulose (Eq. (1)).

$$S\,\% = \frac{W_o - W_r}{W_o} \times 100 \quad (1)$$

where S: is the dissolution percentage; W_o: is the original weight and W_r: is the weight of cellulose after dissolution.

2.4. Viscosity and degree of polymerization measurements

Viscosities of both cotton linter and filter paper were measured according to the TAPPI test method (TAPPI T 230 om-89) using cupriethylendiamine (CED) as a solvent and a capillary viscometer 3 times (Keshk, Suwinarti, & Sameshima, 2006). The degree of polymerization (DP) of the fibers was calculated as:

$$\mathrm{DP} = [0.75\,[(954 \log \mu) - 325]]^{-0.905} \quad (2)$$

where μ: is the TAPPI viscosity (cP).

2.5. X-ray diffraction

The X-ray diffraction patterns of cellulosic materials in different alkaline solutions were determined on a Shimadzu Lab-XRD-6000 diffractometer, using Nickel-filtered Cu $K\alpha$ radiation at 40 kV and 50 mA. The effect of different alkaline solutions on the degree of crystallization was determined at different temperatures.

2.6. Determination of crystallinity index

Crystallinity was calculated from the diffracted intensity data using the method of Segal, Creely, Martin, and Conrad (1959). The calculation of the crystallinity index (C.I.) followed equation,

$$\mathrm{C.I}\% = \frac{I_{200} - I_{\mathrm{am}}}{I_{200}} \times 100 \quad (3)$$

where, I_{200}: is the maximum intensity of the diffraction from (2 0 0) plane at $2\theta = 22.8^\circ$ and I_{am}: is the intensity of the amorphous background scatter measured at $2\theta = 18^\circ$.

2.7. Determination of crystallinty width

The crystallite widths of cellulosic fibers were estimated and evaluated using Scherer equation (Eq. (4)) from the peak profile of the (2 0 0) reflection at $2\theta = 22.8^\circ$ that refers to the width of the crystallite (Andersson, Serimma, Paakkari, Saranpaa, & Pesonen, 2003; Jasiukaityte, Kunaver, & Poljansek, 2012).

$$L = \frac{K\lambda}{\beta \cos\theta} \quad (4)$$

here L: is the crystallite width, θ: is the Bragg angle, λ: is the wave length of the radiation, K: is the constant, and β: is the corrected width of the peak given by specimen. A value of $K = 0.9$ at half-width of the peak profiles was used (Jasiukaityte et al., 2012).

2.8. Solid state ^{13}C NMR spectroscopy

CP/MAS ^{13}C NMR spectrum was recorded (at 292 ± 1 K) on a Joel CMX-300 instrument operating at 7.0 T. A double air-bearing probe and a zirconium oxide rotor were used. The MAS rate was in the 4–5 kHz range. Acquisition was performed with a standard CP pulse sequence using a 5 μs proton 90 pulse, a 1200 μs contact pulse and 3 s delays between repetitions. Adamantine was used as an external standard for the chemical shift scale relative to tetramethylsilane.

3. Results & discussion

From Table 1, it is clear that, the highest dissolution percentages of cotton linter and filter paper were observed (85.7% and 94.0%, respectively) at −4 °C in NaOH/ethylene glycol solution. While the lowest dissolution of cotton and filter paper was observed in 10% NaOH (48.9% and 65.0%, respectively) at room temperature. These results can be explained, as the molecular weight of cellulose is high in the beginning of dissolution and a little amount of cellulose dissociates in NaOH solution, which would increase viscosity and this leads to gelation and prevent further dissolution (Table 1). Moreover, the dissolution of cellulose in NaOH/Urea or ethylene glycol showed the best result at −4 °C compared to those at room temperature (whereas the viscosity increases at low temperature) (Table 1). Therefore, the presence of urea or ethylene glycol in NaOH increases the dissolution efficiency of NaOH at both temperatures. The mechanism for a good alkaline efficiency at low temperature (−4 °C) may be explained as, ice started to form and NaOH concentration increases in the liquid phase, that enhances the adsorption of NaOH onto cellulose fiber. In addition, at low temperature NaOH hydrate has less intermolecular hydrogen bond in the presence of urea or ethylene glycol, owing to ease of penetration onto crystalline cellulose. The crystal growth in free water induced a rapid volume expansion that could break hydrogen bonds and separate glucan chains in the highly ordered region. As NaOH gradually entered the crystalline part, cellulose crystallinity quickly decreased and an intermediate structure of Na-cellulose I with larger unit cell is formed. Na-cellulose I structure will change into cellulose II with smaller unit cell after washing and drying (Nishiyama, Langan, & Chanzy, 2002). Figs. 1–4 showed the X-ray patterns of alkali treated cotton linter and filter paper at different temperatures. The X-ray patterns of treated cotton linter and filter paper at room temperature (Figs. 1 and 3) clearly exhibits the typical diffraction peaks at 14.8°, 16.3°, 21.1° and 22.5°, which belonged to the crystalline structure of cellulose I (Nishimura & Sarko, 1991). In contrast, treated samples with NaOH/ethylene glycol exhibit the typical diffraction peaks that belonged to the crystalline structure of cellulose II (Nishiyama et al., 2002). So, NaOH/ethylene glycol solution is the best solvent for cellulosic fiber among others at room temperature. The X-ray patterns of treated cotton linter and filter paper at −4 °C (Figs. 2 and 4) show only two diffractions at $2\theta = 12.5^\circ$

Table 1
Dissolution percentage and viscosity (cP) of different cellulosic materials in different alkaline solutions at different temperatures.

Materials/solution	Blank (water)	10% NaOH	NaOH/UE[a] (1:1)	NaOH/UE[a] (mix)	NaOH/EN[b]
Cotton linter (RT)	0.0 (125)	48.9 (90)	55.7 (80)	56.1 (77)	80.4 (65)
Cotton linter (LT)	0.0	66.0 (75)	76.9 (61)	75.5 (60)	85.7 (51)
Paper (RT)	0.0 (160)	65.0 (140)	80.2 (100)	82.2 (98)	85.0 (78)
Paper (LT)	0.0	80.1 (98)	91.2 (91)	89.1 (88)	95.0 (62)

* Viscosity value in cP.
[a] UE—urea, RT—room temperature.
[b] EN—ethylene glycol, LT—low temperature.

Table 2
Degree of crystallizations index (c.i) and crystallite width (c.w) at (2 0 0) plan of different cellulosic materials in different alkaline solutions at different temperatures.

Materials/solution	NaOH (10%)		NaOH/UE[a] (mix)		NaOH/UE[a] (1:1)		NaOH/EN[b] (mix)	
	C.I.	C.W	C.I.	C.W	C.I.	C.W	C.I.	C.W
Cotton linter (RT)	58.7	2.34	40.2	2.83	60.4	2.83	70.0	2.35
Cotton linter (LT)	64.2	1.00	48.1	2.01	49.1	1.41	61.0	1.19
Paper (RT)	51.3	2.36	43.1	2.83	44.5	2.02	45.0	2.17
Paper (LT)	52.0	1.06	40.5	1.13	40.0	0.98	70.0	0.92

[a] UE—urea, RT—room temperature.
[b] EN—ethylene glycol, LT—low temperature.

and 21.0° that belong to the crystalline structure of cellulose II. The crystal type changed from cellulose I to cellulose II for treated cellulose at −4 °C (Figs. 2 and 4) rather than that at room temperature (Figs. 1 and 3). The crystallinity index of cotton linter and filter paper in different alkaline solutions at different temperatures were summarized in Table 1. It can be observed, from Tables 1 and 2 that cotton linter, which has the lowest DP and the highest crystallinity index, gave the lowest dissolution among all the cellulose samples at both temperatures. Based on these results, DP of cellulose plays a more important role in cellulose dissolution in different alkaline solutions rather than cellulose crystallinity, where cellulose with high crystallinity does not necessarily lead to high dissolution (Jasiukaityte et al., 2012). Furthermore, the X-ray pattern of treated cotton linters and filter paper at room temperature were shown in Figs. 1 and 3, the basic shape of spectra did not change (i.e. no crystal type change was found) except for a remarkable increase of the intensity of the corresponding to slight increase in crystallinity. This can be explained based on the alkali attacks on the amorphous area of cellulose. This process is relatively slow so a remarkable increase of the crystallinity was only observed after 48 h of alkali treatment at room temperature. In NaOH/ethylene glycol, however, the basic shape of spectra changes (crystal type change from I to II). This

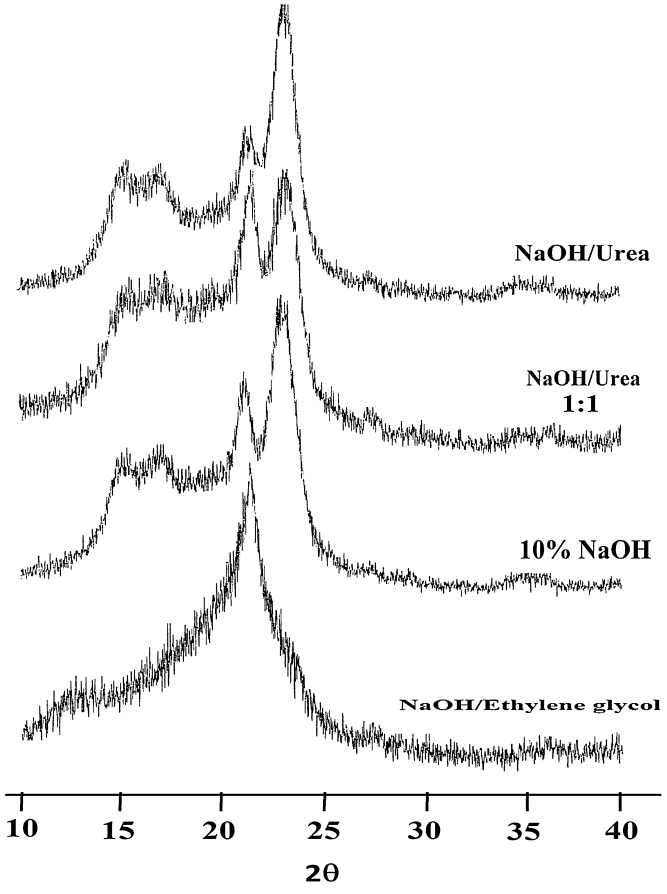

Fig. 1. X-ray pattern of cotton linter in different alkaline solutions at room temperature.

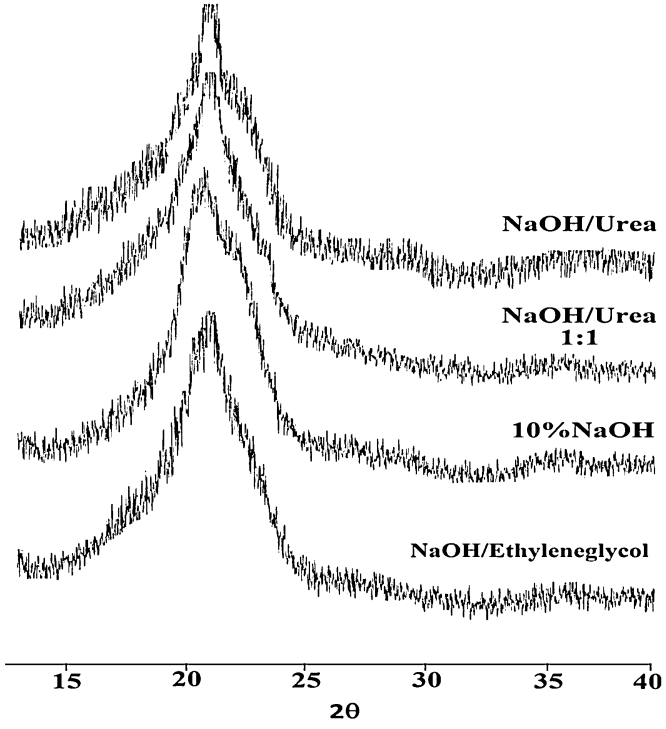

Fig. 2. X-ray pattern of cotton linter in different alkaline solutions at −4 °C.

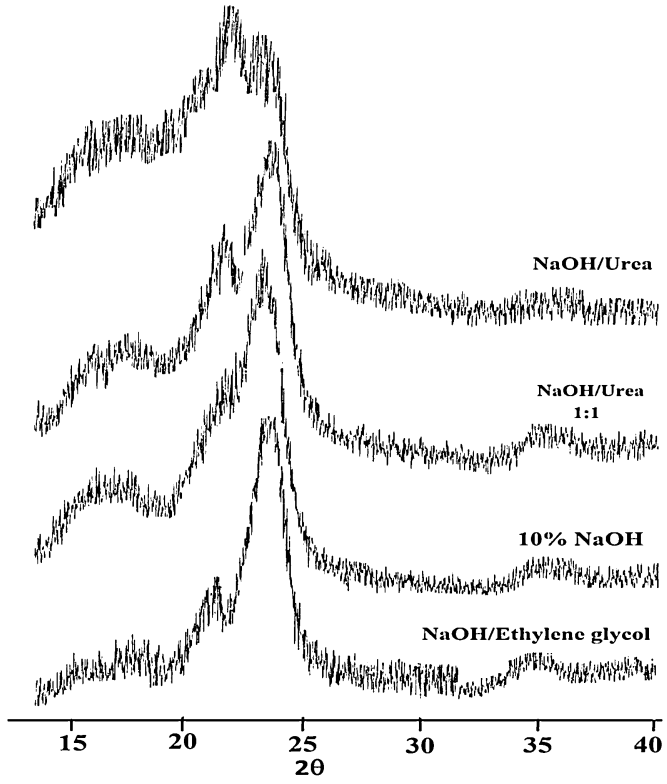

Fig. 3. X-ray pattern of filter paper in different alkaline solutions at room temperature.

can be attributed to strong efficiency of NaOH/ethylene glycol solution among other alkaline solutions. On the other hand, the crystal type change from cellulose I to cellulose II at −4 °C (Figs. 2 and 4), and the peaks shifted to lower Bragg angles, suggesting that the

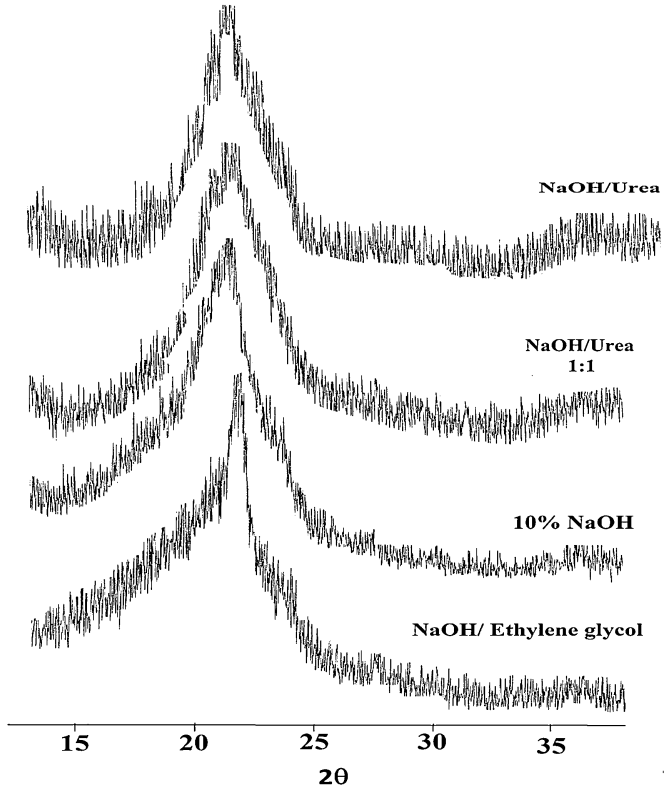

Fig. 4. X-ray pattern of filter paper in different alkaline solutions at −4 °C.

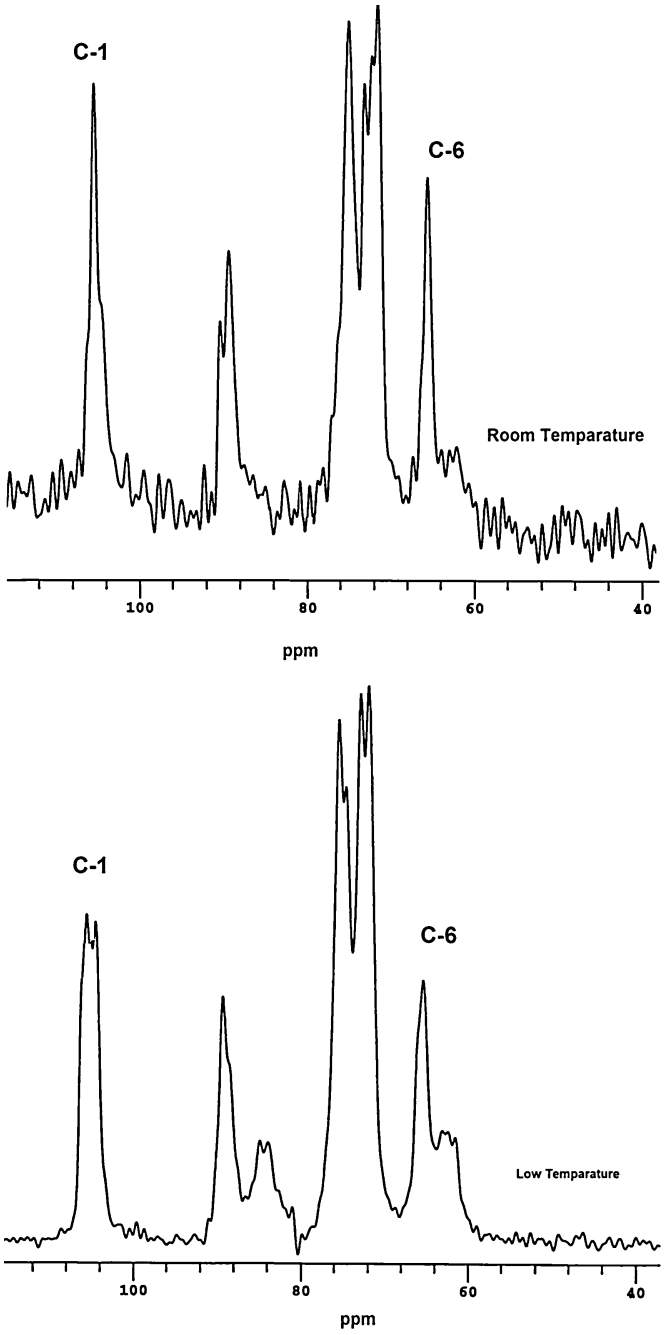

Fig. 5. CP/MAS ^{13}C NMR spectra of dissociated cellulose at both room and low temperatures.

crystallite sizes decreased with alkali treatment. Table 2, shows the crystallinity index and the crystallite widths for cotton linters and filter paper. The changes of the crystallite width followed by the significant weight loss, especially during the treatment at −4 °C which implies the crystal type change from cellulose I to cellulose II (Nishimura & Sarko, 1991).

The CP/MAS ^{13}C NMR spectra of dissociated cellulose at both room and low temperatures in NaOH/ ethylene glycol solution are depicted in Fig. 5. The dissociated cellulose at low temperature showed doublet peaks of C-1 at 105.3 ppm and 104.5 ppm and 63.2 ppm due to C-6 that correspond to cellulose II lattice (Nishiyama et al., 2002). Whereas, the dissociated cellulose at room temperature shows a singlet peak of C-1 at 106.0 ppm and that of C-6 at 65.6 ppm which corresponds to the cellulose I lattice (Fig. 5).

Furthermore, the doublet peaks at 89.2 ppm and 88.3 ppm represent C_4 resonance for cellulose I, and the doublet peaks at 89.2 ppm and 87.8 ppm represent C_4 resonance for cellulose II. These results are in a good agreement with X-ray data.

4. Conclusion

Degree of polymerization of cellulose plays an important role in cellulose dissolution in different alkaline solutions than cellulose crystallinity does. Cellulose with high crystallinity does not necessarily lead to high dissolution. The presence of ethylene glycol with NaOH is very significant compared with the presence of urea at room and low temperatures. Low temperature facilitates dissolutions of cellulose through enhancing the adsorption of NaOH onto cellulose and eases its penetration to form cellulose II.

Acknowledgement

Author would like to thank King Khalid University and King Abdul Aziz City for Science and Technology for their miscellaneous help during this study. This project (AT-34-95) was jointly supported by King Abdul Aziz City for Science and Technology (KACST).

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