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Synthesis and characterization of low sulfoethylated cellulose

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ABSTRACT

The synthesis and characterization of sulfoethyl cellulose (SEC) exhibiting low degrees of substitution ascribed to sulfoethyl groups (DS_{SE}) were reported. The effects of reaction temperature, duration, reaction mediums as well as sulfoethylating agents on DS_{SE} were investigated. The total DS_{SE} was determined via elemental analysis and the structure of SEC was elucidated by FT Raman, one- (1D-) and two-dimensional (2D-) NMR spectroscopy. Based on the characterization, SEC with diverse total DS_{SE} up to 0.65 were obtained and the primary hydroxyl groups were found to be preferably substituted. Finally, the feasibility of using FT Raman spectroscopy with the band at 1044, 811 or 747 cm^{-1} as marker band to determine total DS_{SE} of SEC was presented.

1. Introduction

Cellulose ethers are important commercial cellulose derivatives. Before almost a century carboxymethyl cellulose was first synthesized and now it has become the most important ionic cellulose derivative (Heinze & Pfeiffer, 1999; Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998). Besides carboxymethyl cellulose, there are still many other cellulose ethers, such as methylcellulose and hydroxyethylcellulose, which receive more and more attention in industry as well (Koschella, Heinze, & Klemm, 2001; Zhang, 2001; Zhou, Zhang, Deng, & Wu, 2004).

As most cellulose ethers, sulfoalkyl ethers of cellulose have such common properties like solubility in water or organic solvents, non-toxicity and chemical stability. Sulfoalkylation of cellulose can proceed as Michael addition of alkali cellulose with ethylene sulfonic acid or as substitution reaction with chloroalkane sulfonate at elevated temperature. Several sulfoalkyl ethers of cellulose have been synthesized and total DS from 0.1 to 0.3 has been reached (Klemm et al., 1998).

SEC is one of these sulfoalkyl ethers which is water-soluble and has found applications in a few fields. It is a strongly acidic cation-exchanger and could be used as a chromatographic adsorbent for inorganic ions (Shimizu, Tadokoro, Suganuma, & Hirose, 1984). As well, SEC together with chitosan, polycationic poly[dimethyl(diallyl)ammonium chloride] (PDADMAC) or cationic benzyl(dodecyl)dimethylammonium chloride could be utilized to prepare polyelectrolyte–surfactant complex membranes (Clasen, Wilhelms, & Kulicke, 2006; Schwarz, Lukáš, & Richau, 2003). The possibility of forming hollow beads from SEC and PDADMAC or chitosan that can be used in encapsulating biocatalysts and other materials has been surveyed (Rose, Neumann, Thielking, Koch, & Vorlop, 2000). Furthermore, SEC can be used as an additive in gypsum and cement compositions, as a major component in aqueous formulation for surface preparation of paper and cartons or as a superabsorbent material (Glasser & Michalek, 2006; Kiesewetter, Szablikowski, & Lange, 1993). In these investigations, SEC was normally prepared with sodium vinylsulfonate (NaVS) or halogenealkane sulfonate in slurry processes. Homogeneous synthesis of SEC was also conducted by reaction of cellulose with 2-bromoethansulfonate in the DMSO–SO_2–DEA system. The SEC was obtained with the aim of producing biodegradable polymeric surface-active substances (Talába, Sroková, Ebringerová, Hodul, & Marcinčin, 1997).

For the aim of characterizing cellulose derivatives, various analysis methods including IR and NMR spectroscopy have been used (Atalla & VanderHart, 1999; Guo & Wu, 2008). Raman spectroscopy, a rapid and non-destructive method, has been successfully applied in characterizing derivatives from cellulose and starch (Fechner et al., 2005; VanderHart, Hyatt, Atalla, & Tirumalai, 1996; Yuen, Choi, Phillips, & Ma, 2009; Zhang, Brendler, & Fischer, 2010). It demonstrates not only a qualitative analysis method but also a quantitative one with the purpose of analysing cellulose derivatives and determining the contents of substituents within these derivatives, such as carboxymethyl cellulose and cellulose sulfate (Yuen

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et al., 2009; Zhang et al., 2010). Thus, Raman spectroscopy can be another alternative for determining the total DS_{SE} in addition to elemental analysis.

A complete understanding of the structure of SEC and the distribution of sulfoethyl groups are essential for regulating the synthesis processes and the applications of SEC, e.g. for the formation of capsules with desired properties. However, few investigations have been done so far with respect to the effects of the reaction conditions on the total DS_{SE} and the distribution of sulfoethyl groups within SEC. In this report, diverse SEC with various total DS_{SE} were prepared during different synthesis routes and the structure of SEC was clarified using NMR and FT Raman regarding the above-mentioned effects. Finally, the feasibility of determining total DS_{SE} with FT Raman spectroscopy was examined.

2. Experimental

2.1. Materials

Microcrystalline cellulose (MCC) with an average DP of 276 was received from J. Rettenmaier&Söhne GmbH (Rosenberg, Germany). Sodium vinylsulfonate (NaVS, tech. 25% aqueous solution) was purchased from Alfa Aesar GmbH & Co. KG (Karlsruhe, Germany). Sodium 2-chloroethanesulfonic acid monohydrate (NaCES) was obtained from Merck Schuchardt OHG (Hohenbrunn, Germany) and sodium 2-bromoethanesulfonic acid (NaBES, 98%) from Acros Organics BVBA (Geel, Belgium). Sodium hydroxide (NaOH) in the form of tablet was purchased from Carl Roth GmbH (Karlsruhe, Germany). NaOH powder with an average diameter of particles smaller than 0.5 mm was prepared by milling NaOH tablets. Water was deionized before use. Other chemicals were all of analytical grades and used as received. The dialysis membrane with an approximate molecular weight cut off of up to 500 Da was purchased from Spectrum Laboratories Inc. (Rancho Dominquez, USA).

2.2. Preparation of SEC with NaVS

For a typical sulfoethylation of cellulose, 1 g cellulose was suspended in 50 ml organic solvent, such as isopropyl alcohol (IPA) or cyclohexane under nitrogen atmosphere. Then 8.25 ml NaVS, i.e. 3 mol per mol anhydrous glucose units (AGU), were added into the suspension and it was stirred for 20 min. Subsequently, 1.52 g NaOH tablet or powder or 10.5 ml NaOH aqueous solution (3.6N) corresponding to 6.1 mol NaOH per mol AGU were added and the mixture was stirred for another 1 h. After that, the temperature of the mixture was raised to 80 °C and the mixture was stirred at this temperature for 5 h. After cooling to room temperature (RT) and removing the solvent, the product was dissolved in 40 ml water and the solution was then neutralized with acetic acid. The product was obtained through precipitating its solution in 250 ml ethanol and followed washing with ethanol–water mixture (8/2, v/v). At the end, the product was dissolved in water, dialysed and lyophilized.

2.3. Preparation of SEC with NaCES or NaBES

1 g cellulose was suspended in 50 ml IPA under nitrogen atmosphere. Then 10.5 ml of 3.6N NaOH aqueous solution corresponding to 6.1 mol NaOH per mol AGU were added and the mixture was stirred for 3 h. After that, 3.38 g NaCES or 3.86 g NaBES equal to 3 mol sulfoethylating agents per mol AGU was added and it was stirred for further 30 min. The mixture was then heated to 80 °C and kept at this temperature for 2 h. The followed treatment to obtain SEC was carried out as described in modification with NaVS.

2.4. Measurements

The contents of carbon, hydrogen and nitrogen were determined with Elemental Analyser vario El from Elementar (Hanau, Germany). The sulphur contents were measured with Elemental Analyser Eltra CS 500 from Eltra (Neuss, Germany). The total DS_{SE} of the products can be calculated according to the following equation:

Total $DS_{SE} = (S\% \times 9)/(C\% \times 4 - S\% \times 3)$, where S% and C% are contents of sulphur and carbon determined by elemental analysis.

FT Raman spectra were recorded on a Bruker MultiRam spectrometer (Bruker Optics, Etlingen, Germany) with a liquid-nitrogen cooled Ge diode as detector. A cw-Nd:YAG-laser with an exciting line of 1064 nm was applied as light source for the excitation of Raman scattering. The spectra were recorded over a range of 3500–100 cm^{-1} using an operating spectral resolution of 3 cm^{-1} and a laser power output of 100 mW was applied. Double analysis with a total scan number of 400 was executed for each sample. An average spectrum was formed and the peak height was acquired after vector-normalization of the spectrum using the operating software OPUS Ver. 6.5 (Bruker Optics).

The ^{13}C NMR spectra were obtained at RT using a Bruker DPX 400 spectrometer (Bruker Biospin) at a frequency of 100.13 MHz and with 30° pulse width, 0.35 s acquisition time and a relaxation delay of 3 s. Solutions of the samples with concentrations of 3–5% (wt.%) were prepared in D_2O and up to 20,000 scans were accumulated.

The ^1H NMR and 2D NMR spectroscopy as COSY (^1H–^1H correlation spectroscopy), HSQC (^1H detected heteronuclear single quantum coherence) and ROESY (^1H–^1H Rotating-frame overhause effect spectroscopy) were executed at RT on a Bruker Avance III 600 spectrometer running at a frequency of 600 MHz for ^1H and 150 MHz for ^{13}C (DEPT 135 NMR). The samples were dissolved in D_2O and scans of up to 32 were accumulated.

The analysis of the data was executed with OriginPro 7.0 (OriginLab Corporation, MA, USA).

3. Results and discussion

3.1. Preparation of SEC with NaVS in IPA

SEC with various overall DS_{SE} can be prepared with NaVS in IPA. Cellulose suspension became a mixture consisting of a visibly clear solution and non-dissolved solid matter after the reaction, which suggests that the sulfoethylation of cellulose in IPA was a heterogeneous reaction. The total DS_{SE} were determined via elemental analysis and are listed in Table 1.

As shown in Fig. 1, the FT Raman spectra of SEC exhibiting diverse DS_{SE} illustrate the derivatization of cellulose and some differences can be found when comparing the Raman spectra of SEC and cellulose.

At first, new signals appear at 747, 811, 838, 1044 and 1264 cm^{-1}. Among them, the signal at 1044 cm^{-1} is due to symmetric stretching vibration of O=S=O of sulfate groups (υ_{sym}(O=S=O)), while the signal at 1264 cm^{-1} is attributed to asymmetric stretching vibration of O=S=O (υ_{asym}(O=S=O)) (Cabassi, Casu, & Perlin, 1978; Zhang et al., 2010). The band at 747 cm^{-1} can be derived from stretching vibrations of S–C groups (υ(S–C)) and the band at 811 cm^{-1} as well as a very small band around 838 cm^{-1} can be ascribed to deformation vibrations of CH_2 groups ($\delta(CH_2)$) within the sulfoethyl groups (Socrates, 2001).

Besides the emergence of new signals, the bands between 2800 and 3000 cm^{-1} representing the stretching vibrations of the CH- and CH_2-groups changed their positions and intensities. Within the Raman spectrum of cellulose, the peak at 2896 cm^{-1} is the dominant one and the other one at 2969 cm^{-1} is much smaller. However, after the sulfoethylation, the new peak at 2939 cm^{-1} within the

Table 1
SEC prepared with NaVS in IPA.

Samples	Reaction temperature (°C)	Reaction duration (h)	State of NaOH	Total DS_{SE}[a]
SECT1	80	5	3.6N solution	0
SEC1	65	5	Powder	0.58
SEC2	80	5	Powder	0.65
SEC3	65	5	Pellet	0.47
SEC4	65	24	Pellet	0.50
SEC5	80	3	Pellet	0.46
SEC6	80	5	Pellet	0.60
SEC7	80	24	Pellet	0.33

[a] Determined with elemental analysis.

Raman spectrum of SEC becomes more intensive, which is due to the introduction of the sulfoethyl groups.

Another change is notable for the bending vibration ascribed to CH_2 of cellulose backbone which displays a signal at 1481 with a shoulder at 1458 cm^{-1} within the spectrum of cellulose I. After sulfoethylation, only one peak at 1471 cm^{-1} is visible, which demonstrates a different structure as cellulose I. This shift of the Raman signal is due to the change of cellulose polymorphs, which was realised by dissolving and regeneration of cellulose during the sulfoethylation (Zhang et al., 2010).

Furthermore, the substitution positions can be analysed by NMR spectroscopy and characteristic NMR spectra of SEC can be found in Figs. 2–5. Figs. 2 and 3 present typical ^{13}C and ^{1}H NMR spectra of SEC and the signals were assigned based on the 2D NMR spectra of SEC. The 2D NMR spectra of SEC4 as COSY, HSQC and ROESY were illustrated in Figs. 4 and 5.

^{13}C NMR spectra of SEC confirm the introduction of the sulfoethyl groups into cellulose chains. The DEPT NMR spectrum of SEC4 (Fig. 2a) demonstrates the signals attributed to CH_2 of the AGU and sulfoethyl groups. These CH_2 groups are located at positions C6, C7 and C8. The signal of C6 at 59.8 ppm was shifted to 66.1 ppm after substitution at the 6-*O*-position. C7 shows a peak at 67.8 ppm and C8 at 50.5 ppm. A very small peak at 81.8 ppm may be attributed to $C2_S$ due to the reactivity of C2 that is lower than C6 but higher than C3 (Fig. 2a and b). Other signals could also be assigned according to the NMR spectra. C1 of the AGU presents a signal at 102.7 ppm, while the signals of C2, 3, 4 and 5 can be found in the region of 70–80 ppm. C2, 3, 4 and 5 have similar chemical shifts in 1D ^{13}C NMR and can be distinguished by means of 2D NMR. Regarding the HSQC of SEC in Fig. 4, the assignment of the signals ascribed to different carbons within the repeating units can be carried out. Thus, the signals attributed to C2, 3, 4 and 5 can be distinguished. The signal at 78.2 ppm is ascribed to C4, and other four adjacent peaks at 74.8, 74, 73.4 and 72.9 ppm are derived from C3, C5, C5′ (shifted signal of C5 due to the sulfoethylated 6-*O*-position) and C2, respectively. Based on these assignments, it can be concluded that the primary hydroxyl groups were substituted and only a very small part of sulfate groups could be found at other positions.

Moreover, the signals within the ^{1}H NMR spectrum of SEC can be resolved (Fig. 3) according to the ^{1}H–^{1}H COSY and HSQC of SEC in Fig. 4. All signals attributed to various protons in SEC are found to be within the range of 4.6–3 ppm and a concrete assignment of the signals was executed (Table 2). As shown in Table 2, the protons at C6/6_S/7 demonstrate two peaks which can be distinguished very well. This presence of two peaks for one substituted position is due to the non-equivalence of two protons on the same carbon, e.g. C7. Besides, this fact has also been observed within ^{1}H NMR and COSY spectra of cellulose sulfate (Kamide, 2005).

In addition, ^{1}H–^{1}H ROESY was carried out to investigate the structure of the repeating units within SEC. A characteristic ROESY of SEC is shown in Fig. 5 and the signals within the spectrum arise from the protons that are close to each other in space. The analysis of the adjacency was executed and is visible in Fig. 5. Accord-

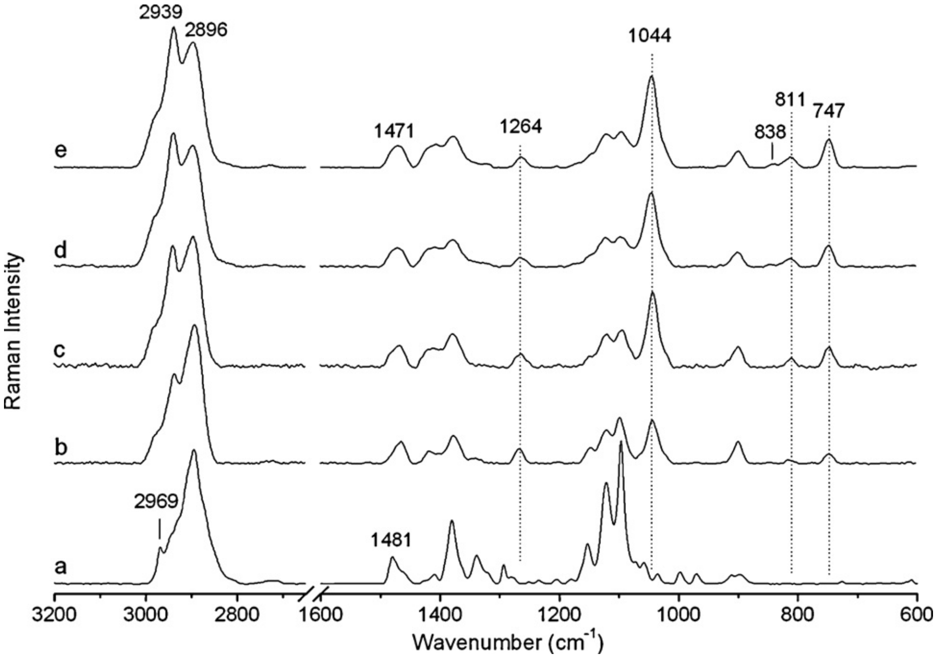

Fig. 1. FT Raman spectra (3200–600 cm^{-1}) of (a) cellulose, (b) SEC8 (DS_{SE} = 0.16), (c) SEC11 (DS_{SE} = 0.35), (d) SEC3 (DS_{SE} = 0.47) and (e) SEC6 (DS_{SE} = 0.6) at RT.

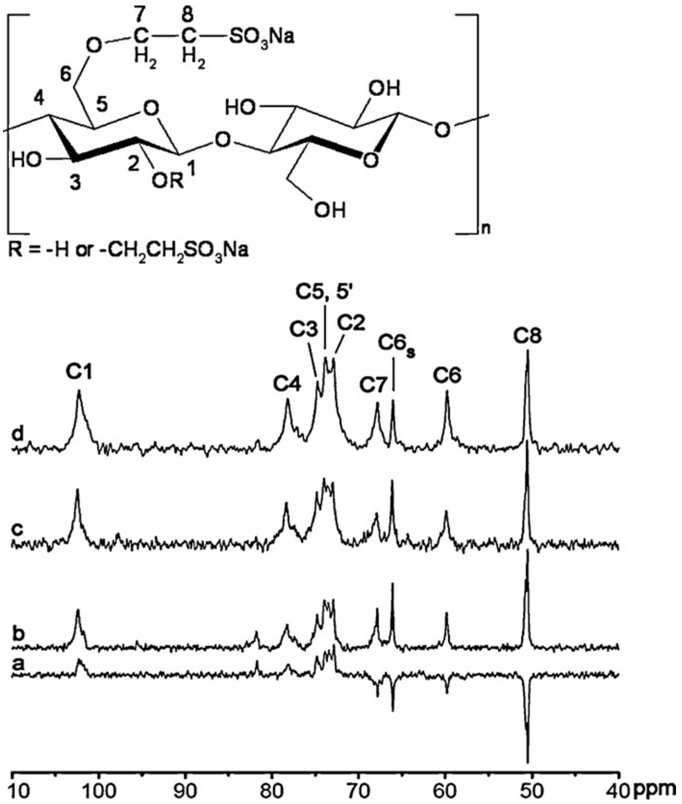

Fig. 2. Above: Simplified structure of SEC. Bottom: ^{13}C NMR spectra (110–40 ppm) of (a) SEC4 (DEPT 135) ($DS_{SE} = 0.5$), (b) SEC4 ($DS_{SE} = 0.5$), (c) SEC2 ($DS_{SE} = 0.65$) and (d) SEC12 ($DS_{SE} = 0.26$) in D_2O at RT.

ing to the analysis, protons H1/2 within the sugar rings of SEC dissolved in D_2O are near to protons H3/4/5, while the protons $H6_S$/7/8 are adjacent after substitution. Furthermore, the proton H8 is also stereoscopic close to the protons H2/4/5′. However, it should be noted, that these signals are not only ascribed to stereoscopic adjacency of protons insides the same repeating units, but also to protons within different repeating units. Especially, the interaction between the protons $H6_S$/6 is apparently derived from two different repeating units.

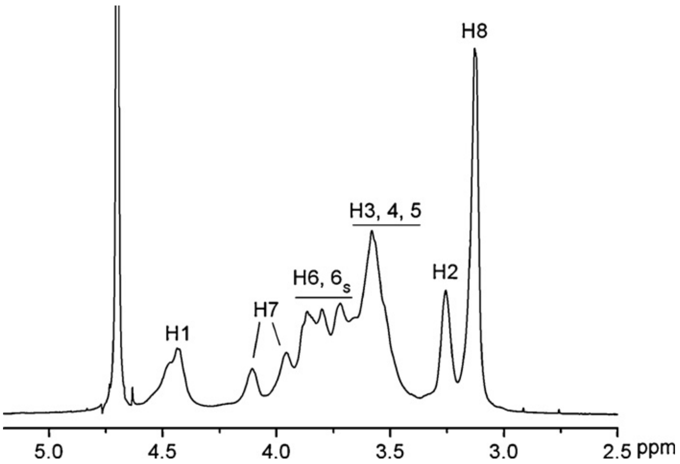

Fig. 3. ^{1}H NMR spectrum (5.2–2.5 ppm) of SEC4 ($DS_{SE} = 0.5$) in D_2O at RT.

This fact is possibly due to the formation of differently substituted AGU within the cellulose chains. Generally, there are 8 kinds of partially and totally substituted repeating units which are un-, mono-, di- or trisubstituted. During the heterogeneous

Table 2
Assignment of signals within ^{1}H NMR spectrum of SEC.

Peaks (ppm)	Protons
4.47, 4.43	H1
4.1, 3.96	H7
3.88, 3.72	$H6_S$
3.86, 3.80	H6
3.66	H5′
3.58	H4
3.56	H5
3.52	H3
3.26	H2
3.13	H8

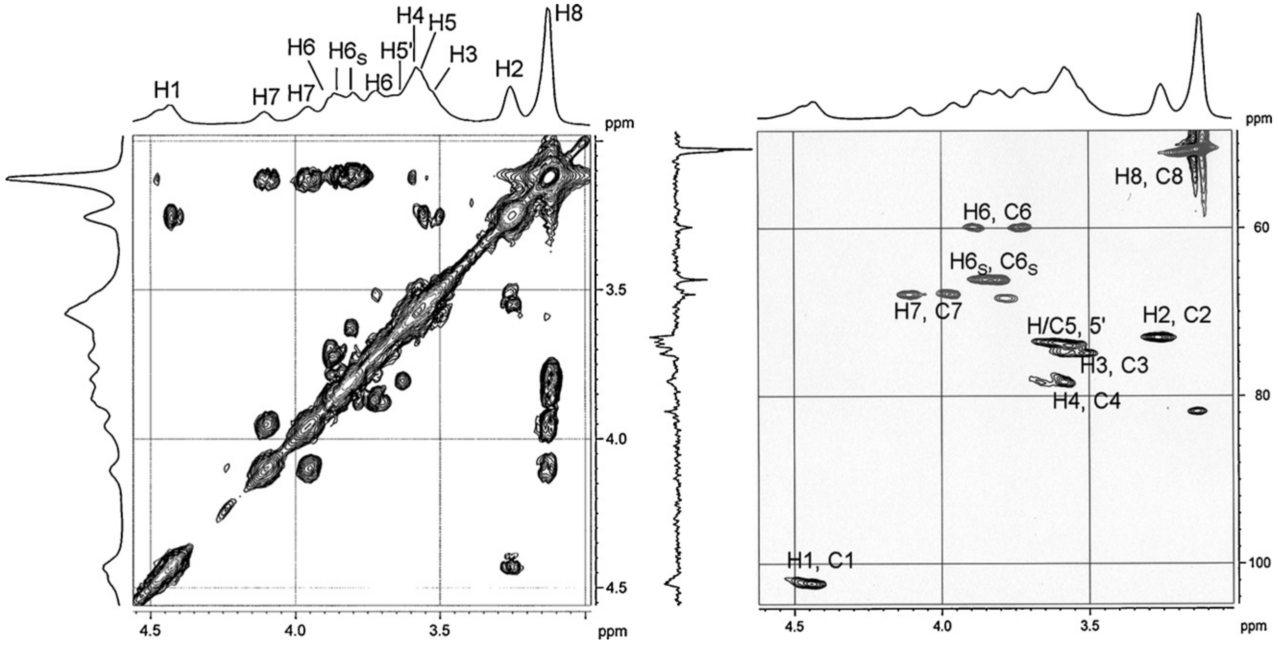

Fig. 4. ^{1}H–^{1}H COSY (left) and HSQC spectrum of SEC4 ($DS_{SE} = 0.5$) in D_2O at RT.

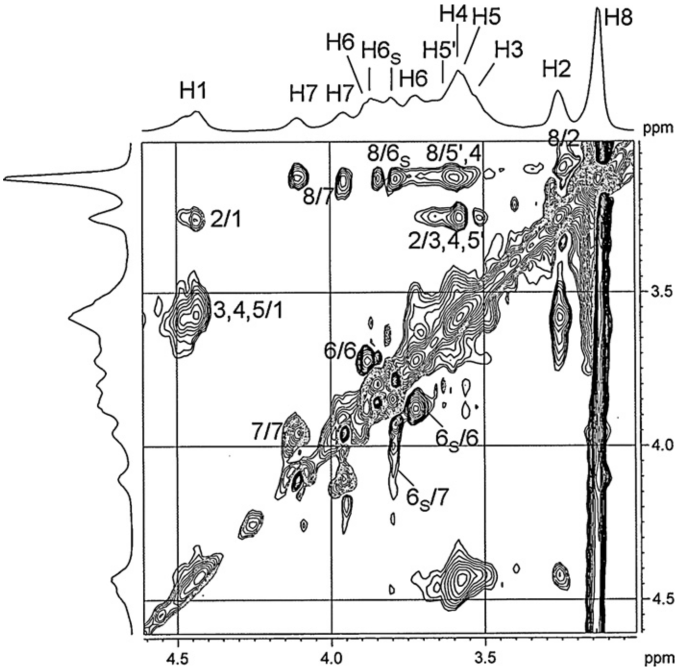

Fig. 5. ^1H–^1H ROESY spectrum of SEC4 (DS_{SE} = 0.5) in D_2O at RT.

carboxymethylation of cellulose as slurry process, carboxymethyl celluloses with all 8 kinds of repeating units were obtained. They can be analysed via HPLC after depolymerisation or via ^{13}C NMR (Baar, Kulicke, Szablikowski, & Kiesewetter, 1994). Besides, higher partial DS_{CM} at 2- and 6-*O*-position compared to 3-*O*-position were observed for such carboxymethyl celluloses (Heinze & Pfeiffer, 1999). Based on that, it can be presumed that diverse repeating units within the prepared SEC were formed during the heterogeneous etherification of cellulose.

Besides the structure, the total DS_{SE} is another important feature of SEC. Based on the results in Table 1, the reaction parameters including reaction duration, temperature and the form of NaOH can affect the total DS_{SE}. High reaction temperature, such as 80 °C, led to higher total DS_{SE} than lower temperature (e.g. 65 °C) and the total DS_{SE} increases with longer reaction durations of up to 5 h.

However, sulfoethylation at 80 °C with reaction duration of 24 h reduced the total DS_{SE} remarkably. The sulfoethylation in IPA is a heterogeneous reaction and cellulose could be strongly degraded during the reaction. It can be assumed that prolonged substitution up to 24 h resulted in hydrolysis of already modified cellulose chains and formation of by-products, which decreased the total DS_{SE} of SEC.

In addition, the form of NaOH as pellet or powder could also influence the total DS_{SE}, while a 3.6N NaOH aqueous solution could not activate the sulfoethylation with NaVS according to SECT1 (Table 1). The NaOH powder was able to raise total DS_{SE} slightly compared to pellets. This increase can be due to a stronger activation in sulfoethylation by NaOH powder that demonstrates larger contact areas to cellulose.

3.2. Preparation of SEC with NaVS in other solvents

Chemical modification of cellulose in diverse solvents can affect the properties of cellulose derivatives. Desired properties may be obtained by applying a certain solvent (El Seoud & Heinze, 2005; Köhler & Heinze, 2007; Zhou et al., 2004). Thus, other solvents were used as reaction mediums for the sulfoethylation of cellulose in addition to IPA with the aim to find out the effect of these solvents on the sulfoethylation process. The following solvents, with a rising polarity, were used for the substitution: cyclohexane, toluene, n-octanol, n-butyl alcohol, IPA and dioxane. The total DS_{SE} of SEC prepared in these solvents are visualized in Table 3.

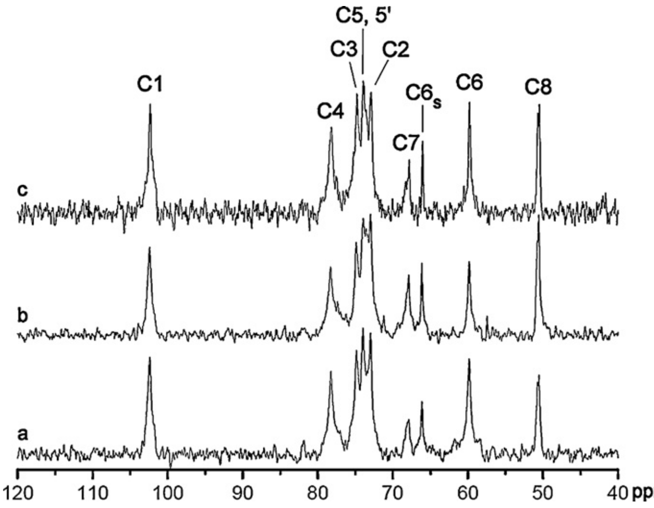

Fig. 6. ^{13}C NMR spectra (120–40 ppm) of (a) SEC18 (DS_{SE} = 0.19), (b) SEC20 (DS_{SE} = 0.34) and (c) SEC21 (DS_{SE} = 0.31) in D_2O at RT.

As shown in Table 3, other solvents besides IPA could also be used as the reaction medium for sulfoethylation of cellulose and the reaction was heterogeneous as well. According to the results, sulfoethylation in IPA led to highest total DS_{SE}, while sulfoethylation in cyclohexane exhibiting the lowest polarity caused the smallest DS_{SE} after etherification at 80 °C under other equal conditions. Otherwise, the sulfoethylation in n-butyl alcohol and dioxane having similar polarities as IPA resulted in SEC with total DS_{SE} of 0.39 at 80 °C for 5 h. Therefore, the reaction medium could also affect the total DS_{SE} and proper polarity should be considered with the purpose of preparing SEC exhibiting designated total DS_{SE}. Moreover, a higher reaction temperature of 80 °C resulted in a higher total DS_{SE} compared to 65 °C with cyclohexane as the reaction medium. At 80 °C, longer reaction duration from 2 or 3 to 5 h increased the total DS_{SE}.

The ^{13}C NMR spectrum of SEC12 in Fig. 2 illustrates that the primary hydroxyl groups were etherified, while almost no substitution of other hydroxyl groups can be observed. Thus, the sulfoethylation in other solvents should be run off in the same way as in IPA.

3.3. Preparation of SEC with NaCES and NaBES

Two other sulfoethylating agents in addition to NaVS – sodium 2-chloroethanesulfonate monohydrate (NaCES) and sodium 2-bromoethanesulfonate (NaBES) – were also applied to substitute cellulose. The total DS_{SE} of prepared SEC were determined and listed in Table 4.

Fig. 6 presents the ^{13}C NMR spectra of SEC synthesized with NaCES and NaBES. The signal of C6 was shifted from 59.8 to 66.1 ppm representing the sulfoethylation of the primary hydroxyl groups, while the signal of C1 remained a singlet, indicating no sulfoethyl groups at 2-*O*-position.

According to Table 4, the application of 3 mol NaBES or NaCES per mol AGU resulted in SEC with the total DS_{SE} within the range of 0.12–0.34. Furthermore, it is noticeable that NaBES caused higher total DS_{SE} than NaCES under other equal reaction conditions.

In addition, at higher temperature, sulfoethylation with NaCES or NaBES increased the total DS_{SE} in the same way as sulfoethylation with NaVS. Prolongation of the reaction duration to 24 h raised significantly the total DS_{SE} at 65 or 80 °C based on Table 4.

Table 3
SEC prepared in various solvents after 1 h alkaline treatment with NaOH-pellets.

Samples	Reaction mediums	Reaction temperature (°C)	Reaction duration (h)	Total DS_{SE}[a]
SEC8	Cyclohexane	65	5	0.16
SEC9	Cyclohexane	80	5	0.31
SEC10	Toluene	80	3	0.30
SEC11	Toluene	80	5	0.35
SEC12	n-Octanol	80	2	0.26
SEC13	n-Octanol	80	5	0.33
SEC14	n-Butyl alcohol	80	3	0.32
SEC15	n-Butyl alcohol	80	5	0.39
SEC16	Dioxane	80	5	0.39
SEC3[b]	IPA	65	5	0.47
SEC5[b]	IPA	80	3	0.46
SEC6[b]	IPA	80	5	0.60

[a] Determined with elemental analysis.
[b] These samples are from Table 1 and listed here for the comparison.

Table 4
SEC prepared in IPA with NaCES or NaBES as sulfoethylating agents.

Samples	Reaction temperature (°C)	Reaction duration (h)	State of NaOH	Sulfoethylating agents/molar ratio	Total DS_{SE}[a]
SEC17	80	3	Solution	NaCES/3	0.12
SEC18	80	5	Solution	NaCES/3	0.19
SEC19	65	5	Solution	NaBES/3	0.17
SEC20	65	24	Solution	NaBES/3	0.34
SEC21	80	5	Solution	NaBES/3	0.31
SEC22	80	24	Solution	NaBES/3	0.56

[a] Determined with elemental analysis.

The alkalisation of cellulose before the sulfoethylation seems to be essential for the modification, especially for the sulfoethylation with NaCES or NaBES. It should be noted that the necessary alkalisation of cellulose before sulfoethylation with NaCES or NaBES was 3 h that was much longer than NaVS with just 1 h alkalisation, but the attained total DS_{SE} by using NaVS are higher than using NaCES or NaBES as sulfoethylating agent under equal molar ratios. Thus, the reactivity of these three sulfoethylating agents can be in the order of NaVS > NaBES > NaCES with respect to obtained DS_{SE}, which is in accordance with the findings in Klemm et al. (1998).

3.4. *FT Raman spectroscopic quantification of the total DS_{SE}*

As described before, FT Raman spectroscopy can be used to determine the contents of substituents within cellulose derivatives (Fechner et al., 2005; Yuen et al., 2009; Zhang et al., 2010). In order to determine the total DS_{SE} of SEC, adequate bands attributed to sulfoethyl groups are required. For this purpose, the peak heights of bands at 1044, 811 and 747 cm^{-1} attributed to sulfoethyl groups were chosen as marker bands for the quantitative analysis. The signal at 898 cm^{-1} can be used as an internal standard because this signal arises from the vibrations of cellulose backbone and should remain independent from the sulfoethyl groups.

Representative SEC with the total DS_{SE} in the range of 0–0.65 were analysed with Raman spectroscopy and the peak heights of marker bands as well as internal standard band were determined. The total DS_{SE} of these SEC and their peak height ratios are listed in Table 5. Calibration curves obtained by plotting the peak height ratios against the total DS_{SE} are illustrated in Fig. 7. The linear regression parameters of the calibration curves are visible in Table 6.

According to Table 6, all three Raman peak height ratios based on the marker bands ascribed to sulfoethyl groups show correlation coefficients larger than 0.94 ($p < 0.001$), which suggests a strong correlation between the spectroscopic data and the total DS_{SE} determined by elemental analysis. While the signal at 811 cm^{-1} has the smallest correlation coefficient of 0.941, the marker band at 747 cm^{-1} which is ascribed to υ(S–C) exhibits the biggest cor-

Table 5
SEC with their total DS_{SE} and Raman peak height ratios between marker bands and internal standard band[a].

Samples	Total DS_{SE}	H_{1044}/H_{898}	H_{811}/H_{898}	H_{747}/H_{898}
MCC	0	0	0	0
SEC17	0.12	1.766	0.219	0.312
SEC8	0.16	1.944	0.181	0.444
SEC12	0.26	3.913	0.391	1
SEC7	0.33	4.064	0.468	1.234
SEC11	0.35	3.574	0.463	0.982
SEC15	0.39	4.224	0.469	1.204
SEC3	0.47	5.081	0.568	1.486
SEC4	0.5	5.514	0.703	1.757
SEC1	0.58	4.923	0.538	1.410
SEC6	0.6	5.486	0.629	1.714
SEC2	0.65	5.941	0.647	1.882

[a] H_{1044}/H_{898}, H_{811}/H_{898}, H_{747}/H_{898}: peak height ratios between bands at 1044, 811 or 747 and 898 cm^{-1}. These ratios were taken as 0 for MCC.

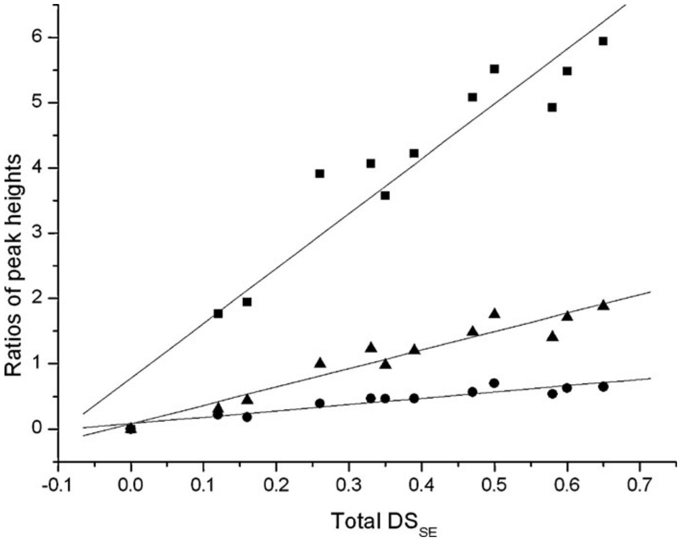

Fig. 7. Calibration curves after plotting the Raman peak height ratios against the total DS_{SE} as: (■) H_{1044}/H_{898}, (●) H_{811}/H_{898}, (▲) H_{747}/H_{898}.

Table 6
Linear regression parameters of the calibration curves in Fig. 7[a].

Peak height ratios	*a*	*b*	*r*	SD	*p*	*n*
H_{1044}/H_{898}	0.779 ± 0.336	8.409 ± 0.807	0.957	0.547	<0.0001	12
H_{811}/H_{898}	0.084 ± 0.046	0.969 ± 0.110	0.941	0.075	<0.0001	12
H_{747}/H_{898}	0.079 ± 0.105	2.828 ± 0.252	0.962	0.171	<0.0001	12

[a] $Y = a + bX$; where Y is the height ratios between the peaks at 1044, 811 or 747 cm^{-1} and the internal standard at 898 cm^{-1}. X is the total DS_{SE}, a is the Y-intercept, b is the slope, r is the correlation coefficient, SD is the standard deviation, p is the significance level and n is sample volume.

relation coefficient of 0.962 and the band at 1044 cm^{-1} displays a similar coefficient of 0.957. However, the calibration curves using the former two bands show much smaller standard deviations than the last one. Therefore, FT Raman spectroscopy can be regarded as another alternative for determining the total DS_{SE} of SEC and the marker band at 747 cm^{-1} is the most suitable Raman band for the quantitative analysis.

4. Conclusions

SEC with various DS_{SE} could be prepared using NaVS, NaCES or NaBES and an alkalisation of cellulose with NaOH was important for sulfoethylation. Sulfoethylation can be realized in various reaction mediums and reaction at 80 °C resulted in higher DS_{SE} than at 65 °C, but longer reaction duration could reduce the DS_{SE}. The reactivity of the applied sulfoethylating agents was found to be in the order of NaVS > NaBES > NaCES with respect to obtained DS_{SE}. The structure of SEC was elucidated by 1D-, 2D-NMR and FT Raman spectroscopy. Primary hydroxyl groups were found to be preferably substituted in all products. Finally, Raman spectroscopy with the bands at 747 and 898 cm^{-1} as the marker band and internal standard can be another alternative for determining the total DS_{SE} up to 0.65.

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