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Full Paper

Surprising insensitivity of homogeneous acetylation of cellulose dissolved in triethyl(n-octyl)ammonium chloride/molecular solvent on the solvent polarity

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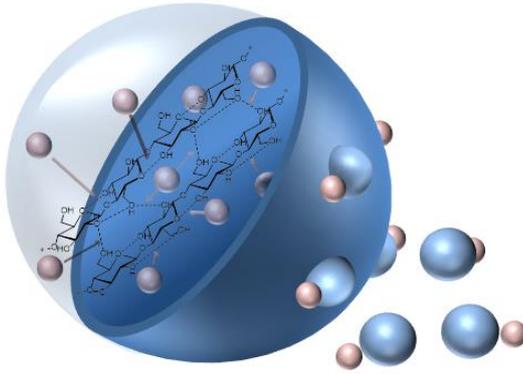
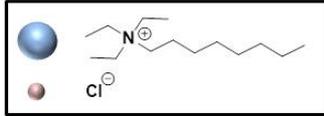
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The homogeneous acetylation of microcrystalline cellulose (MCC) by acetyl chloride and acetic anhydride in triethyl(n-octyl)ammonium chloride (N₂₂₂₈Cl)/molecular solvents (MSs) was investigated. The reaction with both acylating agents showed the expected increase of the degree of substitution (DS_{Ac}) on reaction temperature and time. Under comparable reaction conditions, however, DS_{Ac} was surprisingly little dependent on the MS employed, although the MSs differ in polarity by 7 kcal/mol as calculated by use of solvatochromic probes. The polarities of (MCC + N₂₂₂₈Cl + MS) differ only by 0.8 kcal/mol. The formation a polar electrolyte sheath around cellulose chains presumably contributes to this “leveling-off” of the dependence DS_{Ac} on the polarity of the parent MS. N₂₂₂₈Cl recovery and recycling is feasible.



1. Introduction

Cellulose is the main component of higher plants, which makes it the most abundant biopolymer in nature. Cellulose found a broad variety of applications^[1] Additionally, cellulose can be modified into a range of derivatives that are of commercial interest. Cellulose acetate (CA) with different average degree of substitution (DS_{Ac}) is used as fiber and filtration membranes. It is manufactured on a hundred kiloton scale by a heterogeneous two-step process, including complete acetylation, followed (where required) by subsequent hydrolysis to obtain product with the desired DS_{Ac} value.^[2, 3] As is usual with many heterogeneous reactions, control of the regularity of the (OH \rightarrow acetate) conversion in the anhydroglucose unit (AGU) and along the polymer backbone is difficult and may lead to products with irreproducible properties, hence performance. Thus, the solubility of seven commercial CAs with $DS_{Ac} \approx 2.5$ (1 % ,w/w) was tested; only one sample was soluble in ethyl acetate; solubility in dichloromethane-methanol (4:1, v/v) and ethyl acetate:methanol (5.7:1, v/v) differed by factors of 7, and 11.2, respectively.^[4]

A successful approach to remedy product inhomogeneity is to dissolve cellulose chemically, i.e., by forming a derivative (e.g., cellulose xanthate), or physically.^[5] Physical dissolution of cellulose is a challenge due to the intricate hydrogen bond network and hydrophobic interactions within and between cellulose chains.^[6, 7] Solvents for physical dissolution of the biopolymer include, e.g., LiCl in N,N-dimethylacetamide (DMAc);^[8] quaternary ammonium electrolytes (QAEs) in molecular solvents, both protic (aqueous tetra-(*n*-butyl)phosphonium hydroxide),^[9] and aprotic, e.g., tetra-(*n*-butyl)ammonium fluoride x 3H₂O in dimethylsulfoxide (DMSO).^[10, 11] A solvent for cellulose, which reached commercial success, is *N*-methylmorpholine-*N*-oxide (NMMO), used in the Lyocell process for production of cellulose textile fibers.^[12] Various classes of ionic liquids (ILs) emerged as efficient cellulose solvents about fifteen years ago.^[13] The use of ILs and their properties for cellulose dissolution were studied extensively.^[14-16] Several studies were conducted on the acetylation of cellulose in ILs.

In 1-allyl-3-methylimidazolium chloride (AMIMCl), products with DS_{Ac} values between 0.94-2.74 could be obtained with acetic anhydride, depending on the molar ratio used.^[17] Further imidazolium-based ILs were investigated for acetylation of cellulose; DS_{Ac} values of up to 3 have been accomplished in the presence of pyridine at 80°C for 2 hours.^[18]

The use of ILs for cellulose dissolution and derivatization is associated with some limitations including high price, reduced mass and heat transfer due to the high viscosity of the biopolymer-IL solution, and side-reactions in particular elimination of the relatively acidic C2-*H* of the imidazolium ring by bases, including the IL anion.^[19] Thus, there is impetus to introduce alternative cellulose solvents; of these quaternary ammonium electrolytes, (QAEs, e.g., halides and carboxylates) in MSs is the most extensively investigated example.^[20, 21]

Recently, triethyl(*n*-octyl)ammonium chloride ($N_{2228}Cl$) was found to be a solvent for cellulose. Various dipolar aprotic solvents may act as co-solvents without losing the ability to solubilize cellulose efficiently. Surprisingly, it was shown that $N_{2228}Cl$ can be used in combination with acetone, which otherwise is a precipitating agent (i.e., non-solvent) for cellulose; clear solutions of low viscosities were prepared.^[22] A broad range of organic solvents, which can be used in combination with $N_{2228}Cl$ for dissolution of different cellulose, including samples of high molecular weight, were recently investigated.^[23] Homogeneous acetylation of cellulose was performed in $N_{2228}Cl$ in combination with DMAc or acetone. Acetylation with acetyl chloride yielded CA with DS_{Ac} values comparable to CA obtained in DMAc/LiCl or 1-butyl-3-methylimidazolium chloride (BMIMCl) under comparable conditions.^[24]

The aim of the present study is the investigation of the effect of the molecular solvent (MS) in combination with $N_{2228}Cl$ on acetylation of cellulose. A variety of MSs with different empirical polarities (as given by $E_T(WB)$ in kcal/mol, vide infra) were used while reaction time, temperature, and reagent concentrations were kept constant. The DS_{Ac} values of the products were used as a measure for solvent effect on reactivity. Further investigations were conducted with further acylation agents under different reaction conditions. The MSs employed differ by

7 kcal/mol, hence we expected a relatively clear dependence of DS_{Ac} on $E_T(WB)$. The fact that this was not observed, may be attributed to the similarity of “microscopic or local” polarities at the surface of the biopolymer, independent of the polarity of the MS employed. This could be due to the formation of an ionic sheath around the dissolved biopolymer chain.

2. Experimental Section

2.1. Materials

Microcrystalline cellulose (MCC, Avicel PH-101, Fluka, DP_v (ISO-5351) = 135) was applied for dissolution studies. The cellulose was dried at 100°C for 2 h prior to use. Triethyl(*n*-octyl)ammonium chloride ($N_{2228}Cl$) was purchased from Orgentis Chemicals (m.p. 81°C) and was dried at 60°C over potassium hydroxide for 2 h prior to use. Acetone (VWR), 2-butanone (VWR), 3-pentanone (Sigma Aldrich), tetrahydropyran 99% (Acros), 2-methyltetrahydrofuran >99% (2-methyl-THF, Acros), 1,3-dimethyl-2-imidazolidinone 98% (Acros), *N*-methylpyrrolidone 99% (Acros), *N,N*-dimethylformamide 99.8% (Acros), DMAc 99.5% (Acros), pyridine >99.5% (Acros), acetic anhydride (Fisher Scientific), and acetyl chloride (Merck), were used as received. The solvents were purified by distillation and dried over molecular sieves prior to determination of the solvatochromic parameter $E_T(WB)$. The purity was confirmed from agreement between their experimental $E_T(WB)$ and published data.^[25-27] CA obtained from Eastman chemicals possessed a degree of substitution (DS_{Ac}) of 2.31, determined by NMR spectroscopy. 2,6-dichloro-4-(2,4,5-triphenylpyridinium-1-yl)phenolate (WB, **Figure 1**) was available from our previous studies and was synthesized following the procedure of Kessler *et al.*^[28, 29]

2.2. Cellulose dissolution in MS/ $N_{2228}Cl$ for solvatochromic measurement

A typical solution were prepared as followed: 4.67 g dry *N*-methylpyrrolidone 99% (Acros) (NMP), 4.56 g $N_{2228}Cl$ and 0.48 g MCC were transferred into a glass tube, flushed with N_2 and

vigorously stirred for 2 h at 60 °C. The completed dissolution of cellulose was confirmed by means of optical microscopy (Axioskop 40 from ZEISS with a CP-Achromat objective and cross polarization).

2.3. Synthesis

Acetylation of cellulose

Depending on the MS applied, dissolution of MCC was performed in different ways, according to previously reported studies.^[23] In a typical acetylation procedure, 1.58 g (15.5 mmol) acetic anhydride or 0.73 g (9.3 mmol) acetyl chloride were added to the dissolved cellulose (0.5 g, 3.1 mmol). In case of addition of pyridine, 0.61 g (7.75 mmol) or 1.23 g (15.5 mmol) of the base was added first. The resulting mixture was heated to 50 °C (acetyl chloride or acetic anhydride) or 70 °C (acetic anhydride) and reacted for 0.25, 0.5, 1, 3, 4.5 or 6 h under stirring. Isolation of the product was carried out by precipitation; the reaction mixture was poured into methanol (~200 mL, if $DS_{Ac} > 1.0$) or acetone (~200 mL, if $DS_{Ac} < 1.0$). The filtered solid was washed thoroughly two times with acetone or methanol (~150 mL), followed by three times washing and disintegration of the polymer with methanol (~150 mL) to ensure complete removal of $N_{2228}Cl$ and other chemicals. The product was dried at 40 °C under vacuum for 3 days.

2.4. Recycling of $N_{2228}Cl$ after acetylation

After acetylation, the filtrates and precipitation media were collected and concentrated by vacuum evaporation. The resulting liquid was diluted with $CHCl_3$ (~150 mL) followed by extraction with saturated aqueous NaCl (3x ~200 mL). The organic phase was dried over magnesium sulfate and was vacuum evaporated to receive a white, hygroscopic solid. Purity of the $N_{2228}Cl$ obtained was characterized by NMR spectroscopy.

2.5. Characterization

2.5.1. NMR spectroscopy

The NMR spectra were measured at room temperature on a Bruker Avance 250 MHz applying 16 scans $^1\text{H-NMR}$ (250 MHz) applying ample concentration of 40 mg/mL. Samples of N_{2228}Cl and perpropionylated CA were dissolved in CDCl_3 . Measurements of CA samples were conducted in $\text{DMSO-}d_6$ after the addition of trifluoroacetic acid to enable DS_{Ac} calculation.

DS_{Ac} values were calculated by integrating the AGU and CH_3 acetate moiety by equation (1):

$$\text{DS}_{\text{acetate}} = \frac{7 \cdot \int \text{CH}_3, \text{acetate}}{3 \cdot \int \text{H, AGU}} \quad (1)$$

2.5.2. Spectrophotometric determination of $E_T(\text{WB})$

The final WB concentration was $2 \cdot 5 \cdot 10^{-4} \text{ mol L}^{-1}$. UV-Vis spectra of probe solutions in the different solvents showed no changes in λ_{max} or shape of the charge-transfer band as a function of probe concentration in the range $1 \cdot 10^{-4} - 5 \cdot 10^{-4} \text{ mol L}^{-1}$. This shows that there is no detectable probe aggregation under our experimental conditions. A Shimadzu UV-2550 UV-Vis spectrophotometer was used equipped with a digital thermometer (model 4000A, Yellow Springs Instruments) that measured the temperature inside the cell-holder ($25 \pm 0.05^\circ\text{C}$). Each spectrum was recorded 3 times at a resolution of 0.2 nm and the values of λ_{max} were determined from the first derivative of the absorption spectrum. The uncertainty in $E_T(\text{WB})$ is $\pm 0.04 \text{ kcal mol}^{-1}$ (spectral range = 400 - 700 nm).

3. Results and Discussion

As reported in prior studies, triethyl(*n*-octyl)ammonium chloride (N_{2228}Cl) is an efficient cellulose solvent.^[22] In the current study, the investigations were expanded and cellulose acetate (CA) samples were prepared under different reaction conditions using a variety of molecular solvents (MS) in combination with N_{2228}Cl . The scope of the studies was to perform a detailed examination of the influence of the binary mixtures of $\text{N}_{2228}\text{Cl}/\text{MS}$ on the acetylation of

cellulose. Thus, the polarity values ($E_T(WB)$), as one of the parameters that have significant impact on the course of chemical reactions, of the solvent combinations were determined.^[30]

3.1. Preparation of CA samples

Previous investigations demonstrated that $N_{2228}Cl/acetone$ and $N_{2228}Cl/DMAc$ are suitable reaction media for the homogeneous acetylation of cellulose.^[24] However, solvents based on QAEs with fluoride as anions tend to lead to deacetylation under mild conditions.^[31, 32] Surprisingly, the deacetylation occurred preferably at position C-2 and C-3. To exclude this side reaction using $N_{2228}Cl$, different acetylation conditions were simulated, using a commercial CA possessing a DS_{Ac} value of 2.31. After the treatment, the polymer was recovered and purified to determine the DS_{Ac} (**Table 1**).

The results obtained disproved any deacetylation by the use of $N_{2228}Cl$ as solvent under the applied reaction conditions. Neither the treatment of CA in $N_{2228}Cl$ at elevated temperatures of 70 °C nor the imitation of the prior dissolution process had an influence on the DS_{Ac} . The deviation of the final DS_{Ac} values belongs to measurement uncertainty.

Required DS_{Ac} values of the prepared CA should reach a value between 1.0 and 1.5 to have suitable prerequisites for the later calculations. Therefore, different reaction conditions were investigated, varying reaction time, reaction temperature and acetylation agent (**Figure 2**). $N_{2228}Cl$ was combined with different MS, which may affect the final polarity of the solvent composition. The solvents chosen were DMF, NMP, 2-butanone, acetone, ethyl acetate, DMI, DMAc, 2-methyl-THF, THP, and 3-pentanone. In previous studies, it was demonstrated that cellulose is soluble in all of these $N_{2228}Cl/MS$ mixtures following a certain dissolution protocol and there are included different types of solvents.^[23]

In order to find the optimum conditions to achieve DS_{Ac} values between 1.0 and 1.5, cellulose was converted with acetic anhydride (Ac_2O) or acetyl chloride at different reaction time. Prior

studies demonstrated already that reactions in ILs employing acetyl chloride can achieve high DS_{Ac} values between 2.5 and 3.0 within 2 h at 80 °C.^[18] To slow down the conversion, reactions were carried out at 50 °C within 0.25 h to 3 h applying $N_{2228}Cl/2$ -butanone or $N_{2228}Cl/DMAc$ as reaction media. Whereby, $N_{2228}Cl/2$ -butanone is representing a solvent system that is uncommon for cellulose chemistry, and the DMAc based solvent belongs to the solvents normally applied for polysaccharides. The DS_{Ac} values of CA obtained depending on reaction time are presented in **Figure 3**.

In general, the DS_{Ac} values for the different reaction times were quite similar. As illustrated in **Figure 3**, a reaction time of 0.25 h led to DS_{Ac} values of 1.68 ($N_{2228}Cl/2$ -butanone) or 1.81 ($N_{2228}Cl/DMAc$). Increasing the reaction time to 3 h resulted in final DS_{Ac} of 2.22 and 2.19 applying $N_{2228}Cl/2$ -butanone and $N_{2228}Cl/DMAc$, respectively. Regarding the progress of the acetylation, both curves show a fast increase in DS_{Ac} up to a reaction time of one hour ($DS_{Ac}=2.0$ and 2.19), afterwards the values leveled off and approached their final values ($DS_{Ac}=2.19$ and 2.22). Thus, prolonging the reaction time would not result in higher DS_{Ac} . Thereby, the reactions performed in $N_{2228}Cl/2$ -butanone showed a stronger increase in DS_{Ac} depending on the reaction time, whereas, the reaction in $N_{2228}Cl/DMAc$ possessed a higher DS_{Ac} at short reaction times.

In the next set of experiments, the acetylation was carried out with acetic anhydride. As already demonstrated, the acetylation with acetic anhydride is less efficient compared to those applying acetyl chloride.^[24] Thus, a molar ratio AGU/Ac_2O of 1/5 and a reaction temperature of 70 °C were applied. Since a lower reactivity can be expected for acetic anhydride, the reaction time ranged from 1 to 6 h (**Figure 4**).

As expected, in case of acetic anhydride as acetylating agent, the resulting DS_{Ac} values were significantly lower compared to the reactions with acetyl chloride. After 6 h, the DS_{Ac} values achieved were 1.05 ($N_{2228}Cl/2$ -butanone) and 0.96 ($N_{2228}Cl/DMAc$). As summarized in **Figure 4**, the increase of the DS_{Ac} differs from those shown in Figure 3. With increasing reaction time,

the DS_{Ac} increases almost linearly. Thus, it was expected that longer reaction times would further increase the DS_{Ac} value. Drastic changes of the DS_{Ac} depending on the solvent system used were not observed (1.05 and 0.96). Again, both reaction media led to products of similar DS_{Ac} values.

Since the esterification with acetyl chloride gave products of high DS_{Ac} values after 1 h, the reactions using the entire solvent mixtures ($N_{2228}Cl/MS$) were carried out with acetic anhydride. Thus, the adjustments of the reaction conditions in order to control the DS_{Ac} values were easier to carry out. In order to be able to include the volatile acetone as one of the MS, the reactions were performed at 50 °C for 6h applying acetic anhydride. Experiments were also performed both with and without pyridine as base (**Table 2**).

As summarized in Table 2, the reaction of cellulose with acetic anhydride exhibited very low conversion. Addition of pyridine to the reaction mixture caused a significant enhancement of the reaction efficiency. The DS_{Ac} values obtained ranged from 0.69 to 0.87 (**2.1B-2.10B**). The molar ratio of AGU/ Ac_2O /pyridine of 1/5/2.5 led to *in situ* formation of acetylpyridinium ion, which renders a higher reactivity compared to acetic anhydride.^[33] Consequently, further increase of the pyridine amount gave CA with DS_{Ac} values between 0.95 and 1.31 (**2.1C-2.10C**). Thus, the reactivity was mainly controlled by the acetylpyridinium ions formed. On the contrary, the acetylation of cellulose with acetic anhydride without a base was not sufficient under the conditions investigated. It was also noticeable that the DS_{Ac} values were independent of the $N_{2228}Cl/MS$ applied, as they only varied in a narrow range for the solvent systems investigated. An exception was the reaction performed in $N_{2228}Cl/3$ -pentanone with an equimolar ratio of Ac_2O and pyridine, which gave a CA of comparably low DS_{Ac} (**2.10**). This low DS_{Ac} was attributed to low solubility of MCC in that mixture, thus, diminishing the reactivity.

3.2. Solvatochromic investigations

Unexpectedly, the DS_{Ac} values of the CA samples possessed comparable values applying the same reaction conditions, however, applying different MS (Table 2). Thus, it was of interest to study the solvent polarity. Because of the acidic nature of $N_{2228}Cl$, the solvent polarity parameter was determined employing $E_T(WB)$. For the measurements, a 1/1 ratio by weight was applied for the mixtures of $N_{2228}Cl/MS$. The corresponding cellulose solutions were obtained by adding 5 wt% MCC to $N_{2228}Cl/MS$ and subsequent stirring for at least 2 h at 60 °C; i.e., the final composition of the solution $N_{2228}Cl/MS/cellulose$ was 9.5/9.5/1 by weight. The $E_T(WB)$ values measured for the MS, $N_{2228}Cl/MS$, and for the solution of cellulose in $N_{2228}Cl/MS$ are presented in **Table 3**, as well as the DS_{Ac} values of the corresponding CA discussed in the previous section.

For the reactions, relatively polar and strongly dipolar aprotic solvents were used. DMAc and DMF are commonly employed in polysaccharide chemistry and in particular in combination with ILs, too.^[14, 34] The dependence of DS_{Ac} of the obtained esters on the nature of the MS employed was probed, as given by their empirical solvent polarity parameter $E_T(WB)$. This correlation is valid, because we showed that the reaction product (CA) was stable under the experimental conditions (see 3.1). Surprisingly, the results for acetylation in 10 MS showed little dependence of DS_{Ac} on $E_T(WB)$ of the MS (Table 3). Additional $E_T(WB)$ measurements showed that dissolution of QAE in MS resulted in a noticeable increase of medium polarity, by 3.7 ± 0.5 kcal/mol, excluding DMI. Dissolution of MCC in these $N_{2228}Cl/MS$ mixtures resulted only in a small increase of $E_T(WB)$ relative to the MS. The final polarity values of $N_{2228}Cl/MS/cellulose$ were 55.3 ± 0.4 kcal/mol, excluding acetone. That is, the increase in $E_T(WB)$ of the final solutions (relative to MS) are essentially due to interactions (electrostatic and hydrogen bonding) of the N_{2228}^+ and to a lesser degree of the hydroxyl groups of the AGU with the phenolate oxygen of WB. The unexpected relative insensitivity of DS_{Ac} to the nature of the MS showed that $N_{2228}Cl$ dominated the polarity of the final solution, not that of the pure solvents that controlled the reaction. Apparently, the relatively high molality of $N_{2228}Cl$ had a

“leveling-off” effect on medium polarity. Hence, the nature of the MS had only a minimal influence on the acetylation reaction and on the final DS_{Ac} . Furthermore, the high $N_{2228}Cl$ concentration can lead to encapsulation of the cellulose chains that is the anion interacts with the hydroxyl groups of the polymer backbone, whereas the cation forms the sheath (**Figure 5**). Due to this sheath the polarities at reaction site in different MS did not differ appreciably, thus, a slight effect of MS on the DS_{Ac} obtained can be observed. Moreover, this would also be an explanation for the solubility of cellulose in MS of low polarity combined with $N_{2228}Cl$, although the employed MS do not swell cellulose.

3.3. Recovery of $N_{2228}Cl$ after the acetylation

In order to examine the possibility to reuse the $N_{2228}Cl$, the filtrates and washings after acetylation were collected and purified to recover the QAE. The products obtained were studied by 1H -NMR spectroscopy to determine the purity of the salt (**Figure 6**).

Figure 6 illustrates that $N_{2228}Cl$ was recovered successfully depending on the MS applied, for the dissolution of cellulose. In the 1H -NMR spectra different chemical shifts of the hydrogen atoms were observed that could be attributed to the different $N_{2228}Cl$ concentrations used for the NMR spectroscopic measurements. Thus, anion coordination differed in between the samples, which led to varying electron densities at the respective hydrogen atoms.^[35] The spectrum at the top represents pure $N_{2228}Cl$. The salts, which were recovered from mixtures containing $N_{2228}Cl/2$ -butanone or $N_{2228}Cl$ /acetone, enabled the complete purification of $N_{2228}Cl$ after the reaction (Figure 6.1 and 6.2). The signals in the 1H -NMR spectra can be clearly assigned to $N_{2228}Cl$ and remaining water, the latter was caused by the hygroscopic nature of the salt. The recovery process yielded 93 % ($N_{2228}Cl/2$ -butanone) and 91 % ($N_{2228}Cl$ /acetone) of the $N_{2228}Cl$ originally applied. However, the demonstrated spectrum in Figure 6.3 contained some impurities that could be assigned to the MS NMP employed. The same observations occurred for other organic solvents possessing a comparable high boiling point, i.e., DMF, DMAc, and

DMI. Whereas solvents like acetone or 2-butanone were able to be removed by final vacuum evaporation, solvents with higher boiling point remained in the product recovered. Remaining MS in the product was responsible for preventing the crystallization of the salt. Further investigations will cover that issue by aiming an optimization of extraction of $N_{2228}Cl$.

The successful recovery of $N_{2228}Cl$ from mixtures with acetone is even more interesting considering the fact that products containing low DS_{Ac} values ($DS_{Ac} < 1.0$) were likewise precipitated in acetone. This provides new opportunities in the process flow of CA manufacture. The utilization of acetone as solvent as well as precipitation agent, and the complete recovery of $N_{2228}Cl$, could facilitate selected working steps and recycling processes, leading to a potentially cheaper CA production.

4. Conclusions

The studies presented were carried out to determine the dependence of the DS_{Ac} on the polarity value ($E_T(WB)$) of the $N_{2228}Cl/MS$ mixture applied. The results demonstrated that the solvent mixtures investigated possessed similar $E_T(WB)$ values just differing in approximately 1.5 kcal/mol. Accordingly, the DS_{Ac} achieved under the corresponding reaction conditions, showed similar values. As discussed, the DS_{Ac} -values were mainly affected by the reaction conditions and acetylation agents selected.

Further studies will prove if MS, which are proven non-solvents for MCC in combination with $N_{2228}Cl$, also show comparable polarity values and what DS_{Ac} values can be achieved in those heterogeneous mixtures. Moreover, it is necessary to decrease the concentration of $N_{2228}Cl$ in these mixtures, since a “leveling-off” effect of the electrolyte on the polarity values is expected. It is also expected that the $N_{2228}Cl$ covers the cellulose and isolate it from its environment and, therefore, makes it impervious to changes of MS. Another approach could be the utilization of another dye system, which is more sensitive for determination of polarity values, independent of the concentration of $N_{2228}Cl$.

Finally, successfully electrolyte recovery was presented for N₂₂₂₈Cl/MS mixtures employing a MS with low boiling point. These solvents could be fully separated from N₂₂₂₈Cl by extraction and evaporation after the acetylation reaction. This is an interesting result, considering the fact that CA with low DS_{Ac} <1.0 can be dissolved and precipitated in acetone. The same purification procedure did not work for solvents with higher boiling point, leading to products that still contained some impurities of MS. Hence, for MS like DMF, DMI, DMAc, and NMP further recovery investigations need to be done.

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Keywords:

Cellulose acetate, solvatochromism, solvent polarity, triethyl(*n*-octyl)ammonium chloride, homogeneous acetylation, recycling

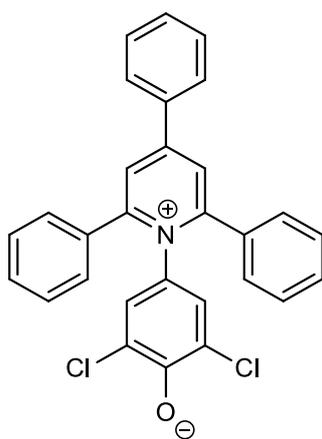


Figure 1: Structure of the dye 2,6-dichloro-4-(2,4,5-triphenylpyridinium-1-yl)phenolate (WB)

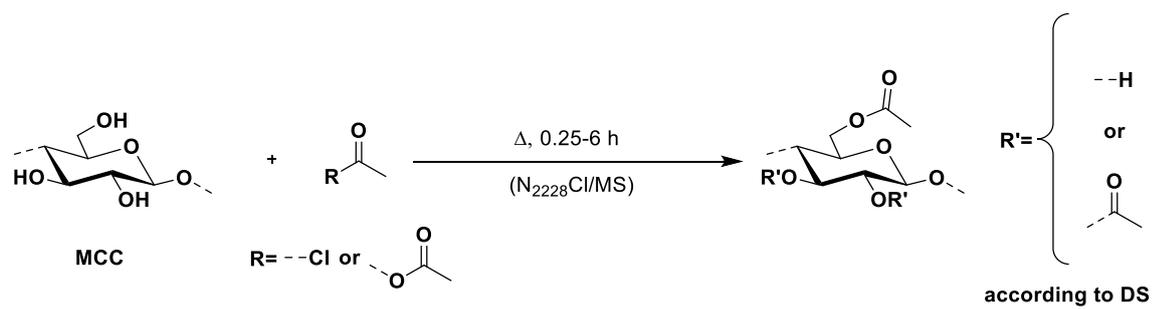


Figure 2: General reaction conditions for the synthesis of cellulose acetate

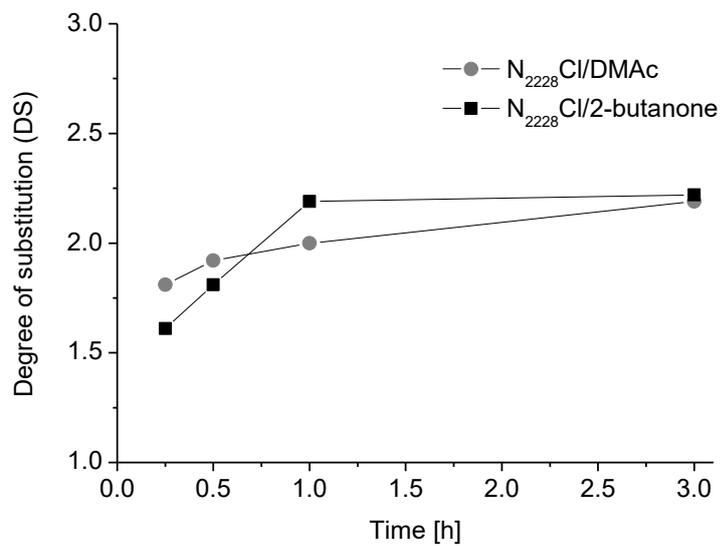


Figure 3: Degree of substitution of cellulose acetate (DS_{Ac}) synthesized in $N_{2228}Cl/DMAc$ and $N_{2228}Cl/2$ -butanone (molar ratio AGU/acetyl chloride = 1/3, 50 °C) in dependence of the different reaction times applied.

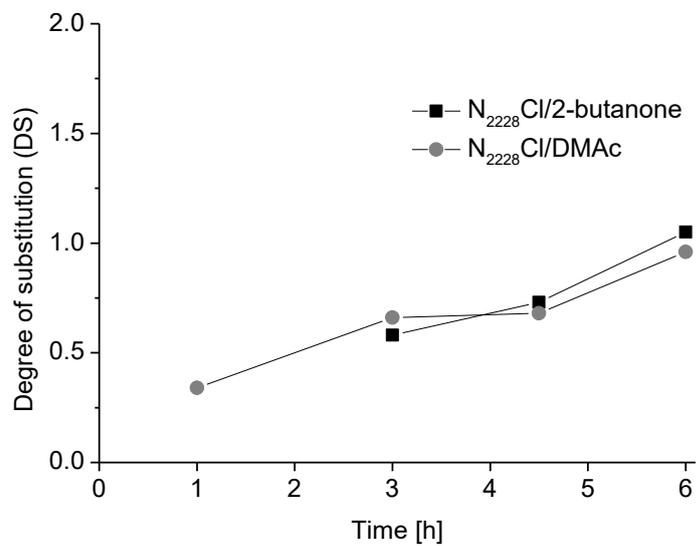


Figure 4: Degree of substitution of cellulose acetate (DS_{Ac}) synthesized in $N_{2228}Cl/DMAc$ and $N_{2228}Cl/2$ -butanone (molar ratio AGU/acetic acid anhydride = 1/5, 70 °C) in dependence of the different reaction times applied.

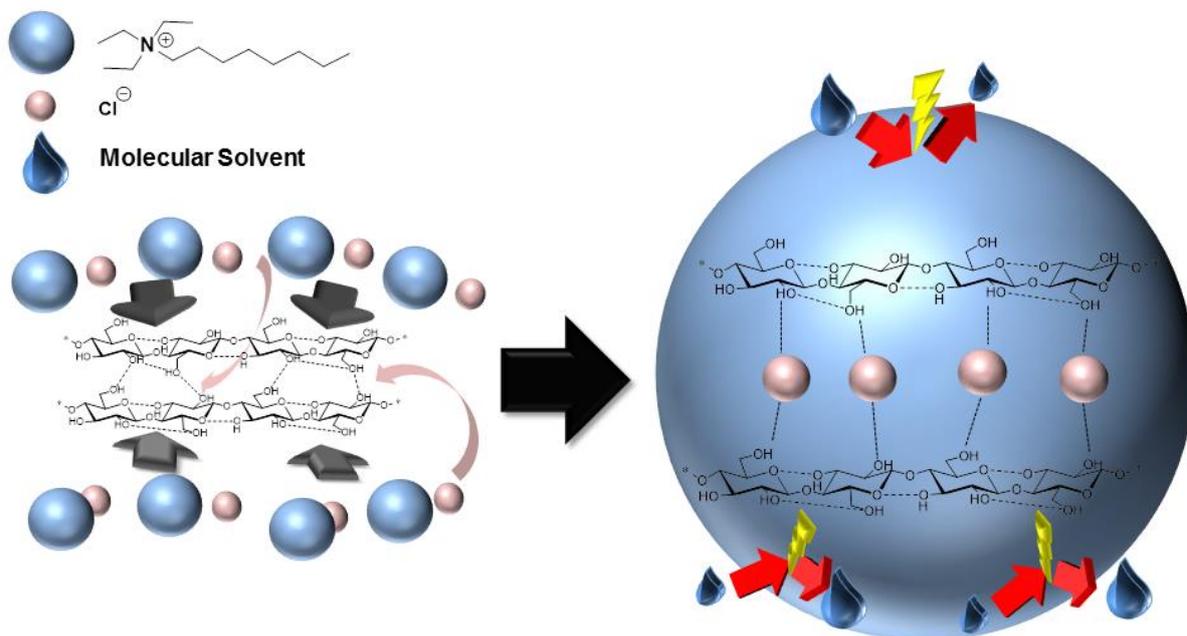


Figure 5: Potential sheath formation during cellulose dissolution. The chloride anions (bright red) interact with the hydroxyl units, the cations (bright blue) build the sheath and “isolate” the cellulose from the molecular solvent (dark blue droplet)

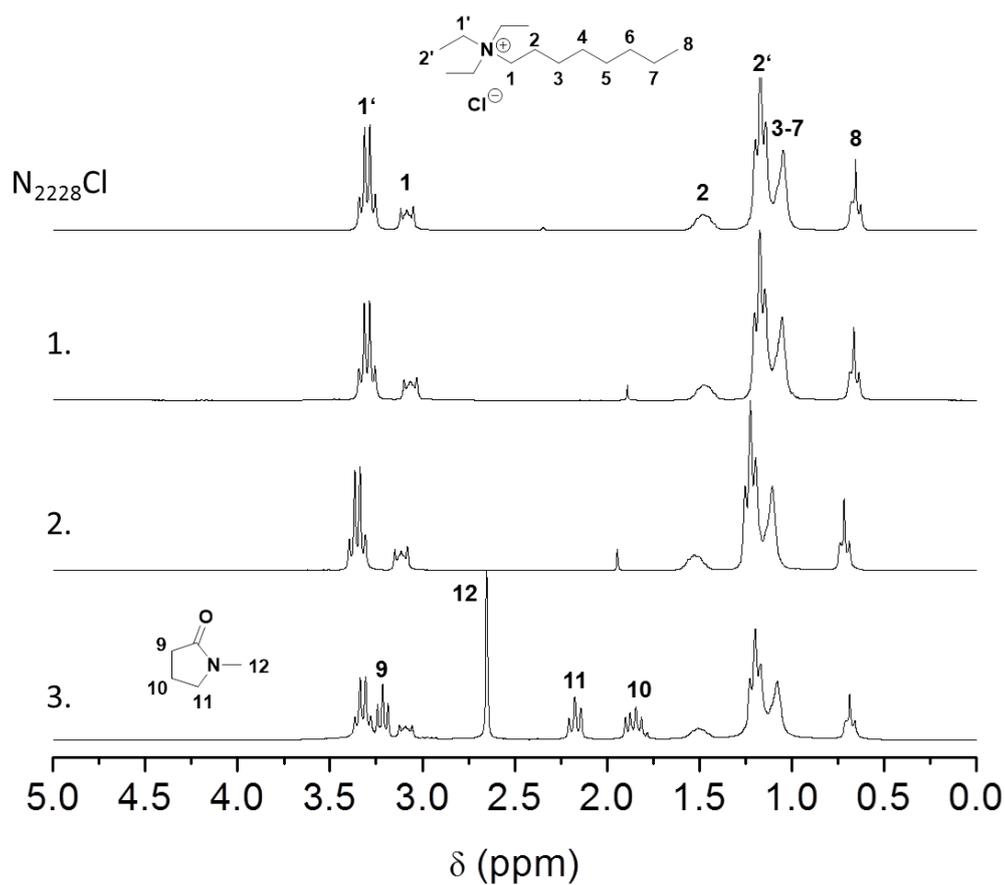


Figure 6: ¹H-NMR spectra recorded in CDCl₃ of neat N₂₂₂₈Cl (top) and recovered N₂₂₂₈Cl after acetylation from solvent mixtures N₂₂₂₈Cl/2-butanone (1.), N₂₂₂₈Cl/acetone (2.) and N₂₂₂₈Cl/NMP (3.)

Table 1: Results of deacetylation investigations applying a CA (degree of substitution, $DS_{Ac} = 2.31$) under reaction conditions applied for acetylation

No.	Solvent	Temperature [°C]	Time [h]	Resulting DS_{Ac}
1.1	N ₂₂₂₈ Cl/DMAc	RT ^a +70	18+6	2.24
1.2	N ₂₂₂₈ Cl/2-butanone	70	6	2.24
1.3	N ₂₂₂₈ Cl/DMAc	70	6	2.56

^a room temperature

Table 2: Conditions for and results of the acetylation of cellulose applying different molar ratio of anhydroglucose unit (AGU)/Ac₂O of 1/5 (A), AGU/Ac₂O/pyridine of 1/5/2.5 (B), and AGU/Ac₂O/pyridine of 1/5/5 (C) in N₂₂₂₈Cl/MS, 50°C 6h

No.	Solvent	Degree of substitution (DS _{Ac})		
		A	B	C
2.1	DMF	0.02	0.84	1.26
2.2	NMP	0.00	0.76	1.26
2.3	2-Butanone	0.22	0.77	1.19
2.4	Aceton	0.00	0.78	1.12
2.5	Ethyl acetate	0.24	0.71	1.31
2.6	DMI	0.05	0.82	1.24
2.7	DMAc	0.09	0.79	1.10
2.8	2-Methyl-THF	n.d. ^a	0.69	1.24
2.9	THP	0.58	0.87	1.21
2.10	3-Pentanone	0.24	0.77	0.95

^a-not determined

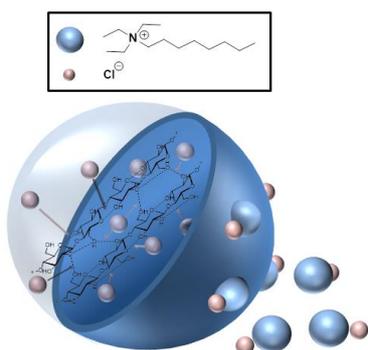
Table 3: Results of the solvatochromic investigations of different organic solvents (A), organic solvent/N₂₂₂₈Cl (B), and organic solvent/N₂₂₂₈Cl/cellulose (C) and degree of substitution (DS_{Ac}) of cellulose acetates prepared

Solvent	$E_T(\text{WB})$			No.	DS _{Ac}	
	[kcal mol ⁻¹]				AGU/Ac ₂ O/Pyridine	AGU/Ac ₂ O/Pyridine
	A	B	C		1/5.0/2.5	1/5.0/5.0
DMF	51.9	55.1	55.3	2.1	0.84	1.26
NMP	50.6	54.3	54.9	2.2	0.76	1.26
2-Butanone	50.6	54.8	55.7	2.3	0.77	1.19
Acetone	52.0	55.6	56.5	2.4	0.78	1.12
DMI	52.0	54.7	54.9	2.6	0.82	1.26
DMAc	51.5	55.1	55.1	2.7	0.79	1.10

Homogeneous acetylation of cellulose is investigated in different N₂₂₂₈Cl/molecular solvents. In order to determine if there is a dependency of the polarity of the solvent applied and the achieved DS_{Ac}, the $E_T(\text{WB})$ value of the solvent mixtures is examined. The results lead to the assumption that due to high N₂₂₂₈Cl concentration cellulose is covered by a sheat of N₂₂₂₈Cl, isolating the cellulose.

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Influence of the empirical polarity of the molecular solvent on cellulose acetylation in the presence of triethyl(n-octyl)ammonium chloride



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