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Solvent Effects on the NMR Chemical Shifts of Imidazolium-Based Ionic Liquids and Cellulose Therein

*Stephanie Hesse-Ertelt,**[1,2] *Thomas Heinze,*[1,2] *Birgit Kosan,*[1] *Katrin Schwikal,*[1]
*Frank Meister**[1]

Summary: The interactions of ionic liquids (IL) with solvents usually used in liquid-state nuclear magnetic resonance (NMR) spectroscopy are studied. The ^{1}H- and ^{13}C-NMR chemical shift values of 1-n-butyl-3-methyl (BM)- and 1-ethyl-3-methyl (EM)-substituted imidazolium (IM) -chlorides (Cl) and -acetates (Ac) are determined before and after diluting with deuterated solvents (DMSO-d_6, D_2O, CD_3OD, and $CDCl_3$). The dilution offers structural modifications of the IL due to the solvents capacity to ionization. For further investigation of highly viscous cellulose dopes made of imidazolium-based IL, solid-state NMR spectroscopy enables the reproducibility of liquid-state NMR data of pure IL. The correlation of liquid- and solid-state NMR is shown on EMIM-Ac and cellulose/EMIM-Ac dope (10 wt %).

Keywords: ^{1}H-NMR; ^{13}C-NMR; chemical shift (CS); cellulose dope; ionic liquid (IL); imidazolium; nuclear magnetic resonance (NMR)

Introduction

Ionic liquids (IL) are low-melting salts (melting point < 100 °C) forming liquids that consist only of cations and anions.[1] IL are designated as ''green'' solvents because they have extremely low vapor pressure, are noninflammable, and thermally and chemically stable. The current interest in IL as a cellulose solvent[2,3] stems primarily from the heightened awareness of their potential applications in cellulose modification,[4-6] their great potential in the manufacture of cellulose fibres and films, and the associated emphasis on clean manufacturing processes. Compared with the N-methylmorpholine oxide (NMMO) process, the direct dissolution of cellulose in IL is more easily controlled, the process is inherently safer, and it enables the production of fibres with very different properties. Moreover, the flexibility in designing fibre properties gives the potential for a wide-scale use in textile and technical applications.[7,8] For cellulose dissolution, organic salts with particularly asymmetric cations like ammonium-, pyridinium-, and imidazolium cations are able to interact with the cellulose backbone. According to the state of the art, phosphonium- and sulfonium salts are not suitable as cellulose solvents.[9] Up to now, there is no clear theory proposed concerning the interaction of IL with polysaccharides. As demonstrated with ^{13}C nuclear magnetic resonance (NMR) studies, they are considered as non-derivatizing solvents, because there are no covalent interactions involved.[6,10] Due to the difficult sample preparation by means of high sample viscosities and non-available deuterated IL, these and further NMR investigations use workarounds, e.g., low molecular weight cellulose, oligomers, or a dilution with

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[1] Thuringian Institute for Textile and Plastics Research, Breitscheidstrasse 97, D-07407 Rudolstadt, Germany
Fax: +49- 3641 9 48272; +49- 3672 379 379;
E-mail: meister@titk.de; stephanie.hesse@uni-jena.de
[2] Friedrich Schiller University of Jena, Institute of Organic Chemistry and Macromolecular Chemistry, Centre of Excellence for Polysaccharide Research, Humboldtstrasse 10, D-07743 Jena, Germany

dimethyl-d_6 sulfoxide (DMSO-d_6).[11] Nevertheless, the studies on solutions from cellulose and cellulose oligomers in 1-n-butyl-3-methylimidazolium chloride (BMIM-Cl) pointed out that the cellulose is dissolved disordered[12] and that the addition of DMSO-d_6 as a co-solvent has no impact on the chemical shifts observed in BMIM-Cl for any of the oligomers studied, even though a well known fact is that solvents are able to influence the chemical shifts of the dissolved samples therein.

In this work, the vary of the ^{1}H- and ^{13}C-NMR chemical shifts of imidazolium based IL (1-n-butyl-3-methyl (BM)- and 1-ethyl-3-methyl (EM)-substituted imidazolium (IM) -chloride (Cl) and -acetate (Ac), respectively) due to solvents (DMSO-d_6, D_2O, CD_3OD, and $CDCl_3$) will be discussed and compared with data of undiluted IL. Furthermore, the influence of the dilution with DMSO-d_6 on the chemical shifts of cellulose/1-ethyl-3-methylimidazolium acetate dope will be shown. In this regard, solid-state NMR turned out to be a good option for measuring high concentrated cellulose dopes without any dilution. Results will be verified by comparative liquid- and solid-state NMR studies.

Experimental Part

Solvents and Reagents

The polymer used was an eucalyptus prehydrolysis sulphate pulp (Eu-556) obtained from Sappi Limited (South Africa). The solvents 1-n-butyl-3-methylimidazolium chloride (BMIM-Cl), 1-ethyl-3-methylimidazolium chloride (EMIM-Cl), 1-n-butyl-3-methylimidazolium acetate (BMIM-Ac), and 1-ethyl-3-methylimidazolium acetate (EMIM-Ac) from BASF and Solvent Innovation, respectively, were used either in analytical grade (EMIM-Cl, BMIM-Cl, BMIM-Ac) or in a quality of $\geq 95\%$ (EMIM-Ac), without any pre-treatment. The solvents DMSO-d_6, D_2O, CD_3OD, and $CDCl_3$ were obtained from Fluka and Merck. All chemicals were used as delivered.

Dissolution of Cellulose in EMIM-Ac

The preparation of the cellulose solution was carried out in a special vertical kneader system, linked with a RHEOCORD 9000 (HAAKE). Temperature, torque, and revolutions per minute (rpm) vs. reaction time were determined on-line. For the dissolution process, cellulose Eu-556 was disintegrated by means of an ultra-turrax shearing step in water. It was separated from excessive water and finally transferred in the aqueous IL EMIM-Ac along with stabilizers. The stable suspension obtained was poured in the vertical kneader system. After this, the water was removed almost completely at temperatures between 90 °C and 115 °C using a reduced pressure between 700 mbar and 5 mbar and a revolution speed of 10 rpm to 80 rpm. The dissolving step was finally visible in a strong increasing of the torque. The viscous gel thus obtained was homogenized at a constant revolution speed within an after-dissolution time of 1 hour. After the dissolution process, a microscopic homogeneous cellulose dope (10 wt% cellulose in EMIM-Ac) was obtained (cellulose/EMIM-Ac dope).

The rheological characterization of cellulose solutions was performed using a rheometer HAAKE MARS with cone / plate measuring system (4° angle geometry) and electrically heated cone & plate unit with active cone heater. Zero shear viscosities were calculated from creep attempts in the rotation mode at shear stress of 90 Pa.

Liquid-State NMR Studies of IL and Cellulose/EMIM-Ac Dope

The IL were diluted with the organic solvents DMSO-d_6, D_2O, CD_3OD, and $CDCl_3$ (50 mg . mL^1); the cellulose/EMIM-Ac dope (10 wt%) was diluted with DMSO-d_6 (50 mg . mL^1) under argon atmosphere using a glove box. Undiluted IL were investigated in coaxial NMR tubes (RototecSpintec GmbH; WGS-5BL) using DMSOd_6 as an external reference having chemical shifts of 2.49 ppm (^{1}H) and 39.5 ppm (^{13}C) with respect to tetramethylsilane at 0.0 ppm.[13]

One-dimensional NMR spectra were recorded at room temperature (about 293 K) using a Bruker Avance 250 MHz spectrometer (5.9 T; Avance 250) operating at 250.13 MHz (^1H) and 62.86 MHz (^{13}C), respectively. Spectra recorded at 333 K were measured on a Bruker Avance 400 MHz spectrometer (9.4 T; Avance 400_1) operating at 400.13 MHz (^1H) and 100.58 MHz (^{13}C), respectively. 16 scans were accumulated and the recycle delay was set to 1.5 s for each ^1H-NMR experiment. In case of ^{13}C-NMR, the repetition time was 2 s; 1k scans (Avance 250) and 800 scans (Avance 400_1), respectively, were accumulated.

The heteronuclear single quantum coherence (HSQC) experiment on cellulose/EMIM-Ac dope was carried out on Avance 400_1 at 333 K; 24 scans were accumulated and the recycle delay was set to 1.5 s. The indirect time dimension consisted of 128 data points with a dwell time of 113.6 μs.

Solid-State NMR Studies of EMIM-Ac and Cellulose/EMIM-Ac Dope

The sample filling of dopes was carried out under argon atmosphere using a glove box. Both, pure IL EMIM-Ac and the cellulose dope (10 wt% cellulose in EMIM-Ac) were investigated in Kel-F inserts with 4 mm ZrO_2 rotors using adamantane as an external reference having ^{13}C-NMR chemical shifts of 29.5 ppm (CH) and 38.5 ppm (CH_2) with respect to tetramethylsilane at 0.0 ppm.[14] Experiments have been carried out at room temperature (about 293 K). The single pulse one-dimensional magic angle spinning (MAS) ^1H-NMR spectrum was recorded at 10 kHz MAS on a Bruker Avance 400 MHz (9.4 T; Avance 400_2, TU Chemnitz) operating at 400.13 MHz (^1H); 1k scans were accumulated, and the recycle delay was set to 4 s. The single pulse one-dimensional MAS $^{13}C\{^1H\}$-NMR spectrum was recorded at 11 kHz MAS on a Bruker Ultrashield 600 MHz (14.1 T; Ultrashield 600, KIT/CN: Karlsruhe Institute of Technology, Campus Nord) spectrometer operating at 150.90 MHz (^{13}C); 1k scans were accumulated, the recycle delay was set to 2 s Continuous wave proton decoupling was applied. The cross polarized MAS $^{13}C\{^1H\}$-NMR spectrum of cellulose/EMIM-Ac dope was recorded at 11 kHz MAS on a Bruker Avance 400 MHz (9.4 T; Avance 400_3, TU Darmstadt) spectrometer operating at 100.58 MHz (^{13}C); the cross polarization (CP) contact time was 1 ms, 32k scans were accumulated, and the recycle delay was set to 2 s. Two-pulse phase modulation (TPPM) was applied for proton decoupling.[15]

Results and Discussion

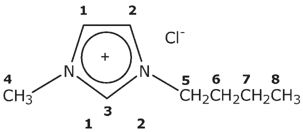
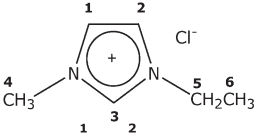
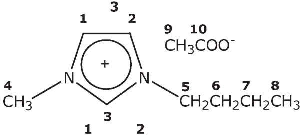
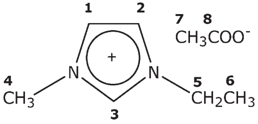
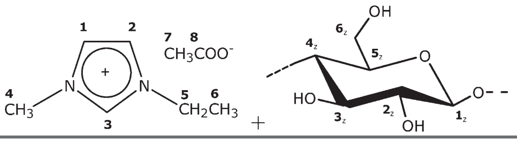
Influence of Co-Solvents on the Chemical Shifts of Ionic Liquids

Due to the high viscosity, NMR measurements of polymer dopes make high demands on the experimenter. The addition of DMSO-d_6 and other co-solvents appears to be a helpful tool to make the sample preparation much easier and to get a better resolution for the NMR chemical shifts. According to this, usually liquid-state NMR results of ionic liquids (IL) and polymer/IL dopes diluted with solvents are discussed. The influence of the co-solvent on the NMR chemical shifts of IL and dopes, however, was hardly in the focus in previous studies. Nevertheless, the detailed detection of the chemical shifts of IL may give important information about the cellulose-IL solution state.

To investigate the interactions of IL with organic solvents, deuterated protic- and aprotic liquids were used: DMSO-d_6, D_2O, CD_3OD, and $CDCl_3$. ^1H- and ^{13}C-NMR chemical shifts of the ionic liquids BMIM-Cl, EMIM-Cl, BMIM-Ac, and EMIM-Ac were determined by liquid-state NMR before and after dilution. As the NMR chemical shifts depend on the concentration of the ionic liquid, samples were always diluted by 50 mg . mL^1. The chemical structures of the imidazolium-based IL used for studies are shown in Table 1.

In principle, the ^1H-NMR chemical shifts (CS) can be easily assigned for each

Table 1.
Ionic liquids (IL) used for cellulose dissolution.

	IL	Chemical structure	NMR details
BMIM-Cl	1-n-butyl-3-methylimidazolium chloride		Avance 250, RT[a],[b]
EMIM-Cl	1-ethyl-3-methylimidazolium chloride		Avance 250, RT[a] Avance 400_1, 333 K[b]
BMIM-Ac	1-n-butyl-3-methylimidazolium acetate		Avance 250, RT[a],[b]
EMIM-Ac	1-ethyl-3-methylimidazolium acetate		Avance 250, RT[a] Ultrashield 600, RT[c]
	Chemical structure		NMR details
Cellulose/ EMIM-Ac dope (10 wt%)			Avance 400_1, 333 K[d] Avance 400_2, RT[e] Avance 400_3, RT[f] Ultrashield 600, RT[g]

RT ≡ Room temperature (about 293 K);[a]liquid-state NMR of diluted IL;[b]liquid-state NMR of undiluted IL;[c]solid-state NMR of undiluted IL;[d]liquid-state NMR of diluted cellulose/EMIM-Ac dope;[e]single pulse MAS ^{1}H-,[f]CP/MAS $^{13}C\{^{1}H\}$-, and[g]single pulse MAS $^{13}C\{^{1}H\}$-NMR of pure cellulose/EMIM-Ac dope

proton of the samples. The dilution of imidazolium based IL with different organic solvents was not relevant for basic peak assignment. Regarding the comparability of their CS values, however, the influence of the internal standard on exact signal positions became noticeable.

By means of the liquid-state ^{1}H-NMR, it is proved that the imidazolium-based proton resonances H1-H3 were significantly shifted depending on the type of organic solvent used for the dilution (Table 2). In case of BMIM-Cl and EMIM-Cl in DMSO-d_6, the proton signals of the imidazolium ring were similar to the CS values of BMIM-Ac and EMIM-Ac in DMSO-d_6, even though H3 was shifted due to the influence of the acetate ions.

Using $CDCl_3$ as organic solvent, most significant changes to the data of IL/DMSO-d_6 solutions occurred between the signals of H1-H3. Compared with results of undiluted IL, the line positions of H1-H3 diverged extensively. It should be mentioned that the most significant changes were always detected in case of the C-H acidic position H3 varied at about ±1 ppm comparing to the undiluted IL.

More precisely, position 3 appeared to be the most sensitive part of each of the imidazolium based IL that has been studied. Such an effect of co-solvents on the NMR chemical shifts of IL was also found previously. As described by Headley and Jackson,[16] H3 should be more acidic and more sensitive to solvation effects than H1 and H2, since it is bonded to a carbon located between two electronegative nitrogen atoms. Furthermore, cluster models to simulate specific interactions between IL and solvent molecules predict increasing ^{1}H chemical shifts of the H3 atom.[17] Finally, theoretical results are consistent with the existence of hydrogen-bond

Table 2.
^{1}H-NMR chemical shifts in ppm of imidazolium based IL in organic solvents.

	Solvent	H1	H2	H3	H4	H5	H6	H7	H8	H9
BMIM-Cl	DMSO	7.78	7.86	9.50	3.86	4.21 4.18 4.16	1.81 / 1.78 1.75 1.72 / 1.69	1.30 / 1.27 1.24 / 1.21 1.18 / 1.15	0.90 0.87 0.83	
	D_2O	7.35	7.40	8.64	3.82	4.15 4.12 4.09	1.83 / 1.80 1.77 1.74 / 1.71	1.31 / 1.28 1.25 / 1.22 1.19 / 1.16	0.87 0.84 0.80	
	CD_3OD	7.55	7.61	8.97	3.89	4.21 4.19 4.16	1.88 / 1.86 1.82 1.79 / 1.77	1.40 / 1.37 1.34 / 1.31 1.28 / 1.25	0.96 0.93 0.90	
	$CDCl_3$	7.45	7.61	10.44	4.00	4.25 4.22 4.19	1.85 / 1.82 1.79 1.76 / 1.73	1.33 / 1.30 1.27 / 1.24 1.21 / 1.18	0.89 0.86 0.83	
	-/-	7.75	7.88	9.63	3.49	~3.78	~1.05	~0.38	~-0.05	
EMIM-Cl	DMSO	7.81	7.91	9.60	3.86	4.26 / 4.23 4.18 / 4.15	1.41 1.38 1.36			
	D_2O	7.35	7.42	8.64	3.82	4.20 / 4.17 4.14 / 4.11	1.45 1.42 1.39			
	CD_3OD	7.62	7.69	9.04	3.96	4.35 / 4.31 4.29 / 4.26	1.58 1.55 1.52			
	$CDCl_3$	7.54	7.55	10.35	3.97	4.32 / 4.29 4.26 / 4.23	1.48 1.45 1.42			
	-/-	7.50	7.63	9.31	3.37	~3.66	~0.63			
BMIM-Ac	DMSO	7.78	7.85	10.03	3.86	4.21 4.18 4.15	1.82 / 1.80 1.77 1.74 / 1.71	1.29 / 1.26 1.23 / 1.20 1.17 / 1.14	0.89 0.86 0.83	1.59
	D_2O	7.31	7.36	8.60	3.78	4.10 4.07 4.04	1.76 / 1.75 1.72 1.70 / 1.67	1.27 / 1.24 1.21 / 1.18 1.15 / 1.12	0.86 0.83 0.80	1.79
	CD_3OD	7.58	7.65	H↔D	3.93	4.25 4.22 4.19	1.93 / 1.90 1.88 1.86 / 1.82	1.46 / 1.43 1.40 / 1.37 1.34 / 1.31	1.02 0.99 0.96	1.88
	$CDCl_3$	7.18	7.27	11.23	3.94	4.20 4.17 4.13	1.77 / 1.74 1.71 1.69 / 1.68	1.31 / 1.28 1.25 / 1.22 1.19 / 1.16	0.88 0.85 0.82	1.86
	-/-	7.99	8.14	10.31	3.64	~3.91	~1.29	~0.69	0.30 0.27 0.24	~1.46
EMIM-Ac	DMSO	7.77	7.86	10.02	3.86	4.25 / 4.22 4.19 / 4.16	1.41 1.36 1.30	1.55		
	D_2O	7.30	7.36	8.60	3.77	4.15 / 4.12 4.09 / 4.06	1.41 1.37 1.35	1.78		
	CD_3OD	7.58	7.66	9.00	3.93	4.31 / 4.28 4.25 / 4.22	1.56 1.53 1.50	1.89		
	$CDCl_3$	7.27	7.28	11.05	3.92	4.27 / 4.24 4.21 / 4.18	1.46 1.43 1.40	1.83		
	-/-	7.90	8.07	10.14	3.60	3.92 / 3.89 3.87 / 3.84	0.64 0.61 0.58	~1.09		

interactions between the acidic groups of the cation (C3-H3 and alkyl chains) and the nucleophilic atoms of the anion.

Besides resonance shifting due to the organic co-solvents, however, a replacement of protons against deuterons, so-called H-D exchanges (H↔D), can be observed. These exchanges became noticeable by the reduction or even disappearance of the respective resonance in the ^{1}H-NMR spectra, especially by a decrease of H3; while a replacement by a three-peak with coupling constants of about 40 Hz occurred in the corresponding ^{13}C{^{1}H}-NMR spectrum (Table 3). The ability of IL to H↔D was already known. As a result of CH acidity, several pure imidazolium based ionic liquids exhibit a kind of incompatibility with strong bases.[18] The acidity of the imidazolium ring is reflected in the formation of N-heterocyclic carbenes and in the readiness of these cations to exchange protons and deuterons of the aromatic ring.[19] Furthermore it has been published that methyl groups exhibit noteworthy CH acidity at imidazolium cations. Here, on one hand, H↔D could be observed and, on the other hand, deprotonation with subsequent alkylation occurs.[20]

For our samples, DMSO-d$_6$ showed minimal influence on chemical shifts and line shapes of the different IL and furthermore, no H-D exchange with the imidazolium based IL was found. On the contrary, $CDCl_3$- and CD_3OD- diluted IL showed an indication of H↔D, exhibited by three-peaks instead of a single C3 resonance (Figure 1).

The co-solvents used included protic (CH_3OH, H_2O) and aprotic (DMSO, $CHCl_3$) species. Caused by their different polarities ($H_2O > DMSO > CH_3OH > CHCl_3$) and acidities, the observed differences were thus not surprising. The occurrence of three-peaks caused by H-D exchanges apparently depended on the effective reaction time of each IL with the co-solvents; however, this was not subject of these studies. Therefore, no quantitative analyses were accomplished.

To revisit the ^{1}H-NMR chemical shift values (Table 2), the proton resonances H1 and H2 also exhibited minor shifting, while the remaining proton resonances (H4-H9) were just marginally shifted. The displacement strongly depended both, on the co-solvent and on the IL, which might be due

Table 3.
^{13}C-NMR chemical shifts in ppm of imidazolium based IL in organic solvents.

	Solvent	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
BMIM-Cl	DMSO	124.0	122.7	137.2	36.1	48.9	31.8	19.2	13.7		
	D_2O	123.5	122.2	135.8	35.6	49.3	31.3	18.8	12.7		
	CD_3OD	124.9	123.7	137.9	36.5	50.6	33.1	20.4	13.7		
	$CDCl_3$	123.7	122.0	137.7	36.4	49.6	32.1	19.3	13.1		
	-/-	123.2	122.2	136.8	35.7	48.1	31.3	18.4	12.7		
EMIM-Cl	DMSO	124.0	122.4	137.0	36.1	44.5	15.6				
	D_2O	123.5	121.9	135.6	35.6	44.8	14.5				
	CD_3OD	123.6	122.0	136.2	35.2	44.7	14.3				
	$CDCl_3$	123.6	121.9	137.3	36.4	45.0	15.6				
	-/-	123.6	122.2	137.0	36.3	44.5	15.4				
BMIM-Ac	DMSO	124.0	122.7	138.3	35.9	48.7	31.9	19.2	13.7	26.2	173.5
	D_2O	123.5	122.2	135.8	35.6	49.2	31.2	18.7	12.6	23.1	180.8
	CD_3OD	123.5	122.2	[a]	35.0	49.1	31.7	19.0	12.3	22.7	178.3
	$CDCl_3$	122.8	121.2	140.1	36.0	49.4	32.0	19.3	13.3	25.2	177.5
	-/-	123.8	122.8	138.5	34.9	48.1	31.7	18.7	12.6	24.9	174.3
EMIM-Ac	DMSO	123.9	122.4	137.9	35.9	44.4	15.6	26.6	173.5		
	D_2O	123.4	121.8	135.5	35.5	44.7	14.4	23.3	181.1		
	CD_3OD	123.5	121.9	[b]	35.0	44.6	14.2	22.9	178.7		
	$CDCl_3$	123.0	121.1	[c]	36.0	44.8	15.4	25.4	177.6		
	-/-	123.7	122.3	138.0	35.0	43.7	15.2	25.1	174.4		

[a] three-peaks 137-135.5 ppm; [b] three-peaks at about 136.0 ppm; [c] three-peaks 140-138.8 ppm

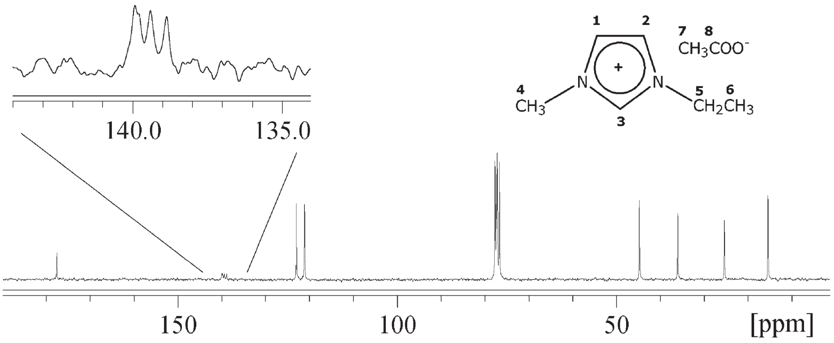


Figure 1.
$^{13}C\{^1H\}$-NMR spectrum of the ionic liquid EMIM-Ac diluted with $CDCl_3$ (Avance 250).

to strong interactions of the imidazolium ring protons with the solvent during the dilution process.

Additionally to mark is that the solvent effect led to a strong shifting of the acetate proton peaks of EMIM-Ac and BMIM-Ac of more than 0.4 ppm compared to ^1H-NMR chemical shift data of undiluted samples.

In case of both EMIM-Ac and BMIM-Ac, the acetate peaks were significantly shifted to lower fields. These liquid-state ^1H-NMR data already account for a strong impact of the co-solvent on the IL.

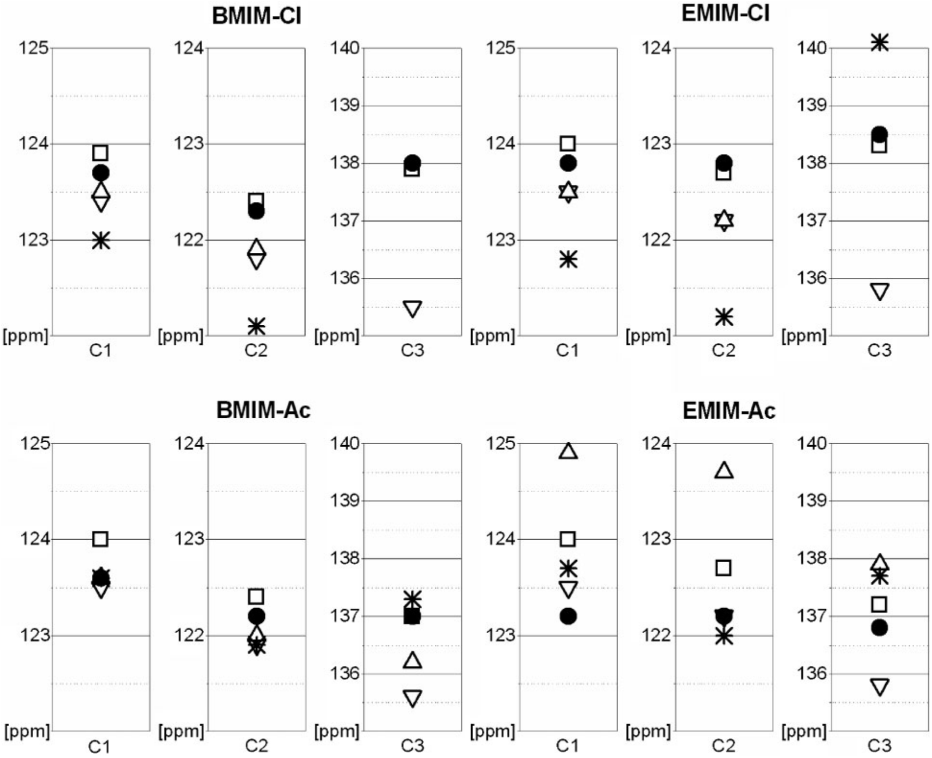
The results were then revised by $^{13}C\{^1H\}$-NMR measurements. According to the co-solvents used, carbon resonances were shifted similarly to the respective ^1H-NMR chemical shifts. But, the shift of the carbon resonances of the imidazolium ring C1-C3 was much less visible than in ^1H-NMR. A maximum shifting of more than ±2 ppm could be detected in case of C3. Considering the widths of proton and carbon NMR scales, a shift of ±2 ppm in ^{13}C-NMR did not carry as much weight as the shift of ±1 ppm in ^1H-NMR; anyway, the shifting was not negligible.

Table 3 shows an overview of the ^{13}C-NMR data of pure and diluted IL. It could be verified that the signals of C4 to C10 of the different IL were not that much affected by the organic solvent; with the exception of carbon C9 of BMIM-Ac, which exhibited differences of about ±2 ppm depending on the dilution agent.

The numerical values (Table 3) are depicted in Scheme 1, which shows the ^{13}C-NMR chemical shifts of the three imidazolium-based carbons C1, C2, and C3 of each IL, which were either undiluted or diluted with the several organic solvents.

The comparison of the NMR chemical shifts of the pure IL in coaxial NMR tubes provided identical results to the solid-state NMR data (Figures 2, 3); both ^1H-and $^{13}C\{^1H\}$-NMR spectra fit perfectly. This fact of equality was important for continuative investigations of highly viscous cellulose dopes by solid-state NMR.

The largest deviations to the solvent-free IL occurred at the D_2O- and $CDCl_3$-diluted BMIM-Cl- and EMIM-Cl- as well as the CD_3OD- and $CDCl_3$-diluted EMIM-Ac samples. The comparatively best agreement with chemical shifts of pure IL was found for DMSO-d_6-diluted IL. Because of the analysed interactions between the different IL and the co-solvents, measurements on undiluted samples are essential for the investigation of the solution state of cellulose in ionic liquids. The measurement of undiluted, high concentrated cellulose dopes using liquid-state NMR has experimental limitations, however. Therefore, the pure ionic liquids were additionally determined by solid-state NMR measurements. Figures 2 and 3 show the ^1H- and $^{13}C\{^1H\}$-NMR spectra of EMIM-Ac in the DMSO-d_6 diluted state obtained by liquid-state NMR and of undiluted EMIM-Ac obtained by solid-state NMR techniques.



Scheme 1.
^{13}C-NMR chemical shifts of the carbon atoms C1, C2, and C3 of the imidazolium-based ionic liquids BMIM-Cl, EMIM-Cl, BMIM-Ac, and EMIM-Ac, which were either undiluted or diluted with organic solvents. Legend: □ DMSO-d$_6$; ▽ D$_2$O; Δ CD$_3$OD; * CDCl$_3$; ● solvent-free.

In summary, it should be pointed out that the dilution of IL with solvents for the purpose of NMR investigations distorts chemical shift results, which might finally cause incorrect conclusions regarding structural predictions and interactions between cellulose and IL.

NMR Measurements of Cellulose Eu-556

Solid-state ^{13}C{^{1}H}-NMR measurements were initially carried out on pure pulp (Eu-556). For differentiation, each cellulose resonance was cited by an index "z". Before dissolving in EMIM-Ac, the pulp was proved to be in the crystalline state of cellulose I (approx. 51%, $I_\alpha : I_\beta \approx 1:1.4$) by line shape analysis of the C1$_z$ position, using Gaussian lines only.[21] For the crystalline parts, ^{13}C-NMR chemical shifts were found at about 101.6 ppm (C1$_z$), 85.9 (C4$_z$), 62.0 ppm (C6$_z$), and between 68 ppm and 72 ppm (C2$_z$, 3$_z$, 5$_z$). Amorphous cellulose parts were found near 80 ppm (C4$_z$ region) and around 59 ppm (C6$_z$ region).[22]

NMR Measurements of Cellulose/EMIM-Ac Dope

To study structure-property relationships, several cellulose/IL dopes of different percentage of polymer were investigated. Representative, a dope containing 10 wt% cellulose, which was made of an eucalyptus pre-hydrolysis sulphate pulp and EMIM-Ac was selected for this publication (Table 1).

Caused by its high viscosity, meaning that a zero shear viscosity of about 400 Pas at 85°C was determined at the sample, liquid-state NMR measurements could not be realized on the undiluted sample. Thus, the sample had to be diluted with DMSO-d$_6$ for first NMR experiments, keeping in mind

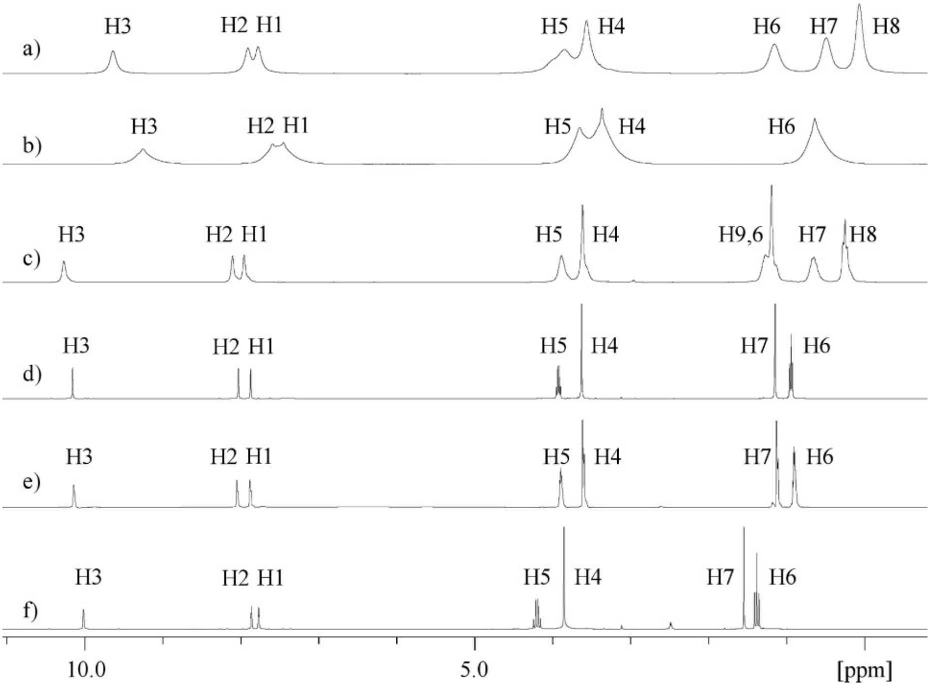


Figure 2.
^{1}H-NMR spectra of the pure ionic liquids a) BMIM-Cl, b) EMIM-Cl, c) BMIM-Ac, and d) EMIM-Ac investigated in the undiluted state in coaxial NMR tubes (a,c,d: Avance 250; b: Avance 400_1); e) solid-state NMR spectrum of EMIM-Ac (Ultrashield 600), f) NMR spectrum of EMIM-Ac in DMSO-d_6 (Avance 400_1).

that the dilution influences the NMR chemical shifts of IL.

A two-dimensional (2D) heteronuclear single quantum coherence experiment (HSQC) was carried out, which allowed the resolution and structural assignment of carbon signals to their directly attached protons. The inverse experiment utilized one-bond couplings in the range of $J = 120$-215 Hz. The ^{13}C-NMR chemical shifts were displayed in the vertical- and ^{1}H-NMR chemical shifts in the horizontal dimension (Figure 4). Cross peaks gave the shift of the corresponding proton and carbon. For a better assignment, the projections of Figure 4 present highly resolved ^{1}H- and ^{13}C{^{1}H}-NMR spectra of the cellulose/EMIM-Ac dope in DMSO-d_6. These 1D spectra were determined at 333 K and exhibit well resolved peaks of both cellulose Eu-556 and EMIM-Ac.

Finally, the proton- and carbon resonances of cellulose Eu-556 could be easily assigned using the HSQC spectrum (Table 4), even though the ^{1}H-NMR chemical shifts of cellulose were superposed by the H4 resonance of EMIM-Ac in the 1D ^{1}H-NMR spectrum. Furthermore, the diastereotopic protons $H6_Z$ and $H6_{Z'}$ exhibited different chemical shifts at 3.63 ppm and 3.74 ppm, which was caused by the influence of the chiral environments.

As measured by the spectral resolution and considering the chemical shift of $C4_Z$ at 79.3 ppm, it should be mentioned that the cellulose in EMIM-Ac was existent in the dissolved state. To investigate the process of dissolving cellulose in IL only, analyses of the undiluted cellulose/EMIM-Ac dope were required. The sample was thus studied in the original, highly viscous state using solid-state NMR spectroscopy. It should be mentioned that a decrease of the spectral resolution can be expected in ^{1}H-, but also in ^{13}C{^{1}H}-NMR spectra, depending on the strength of the static magnetic field.

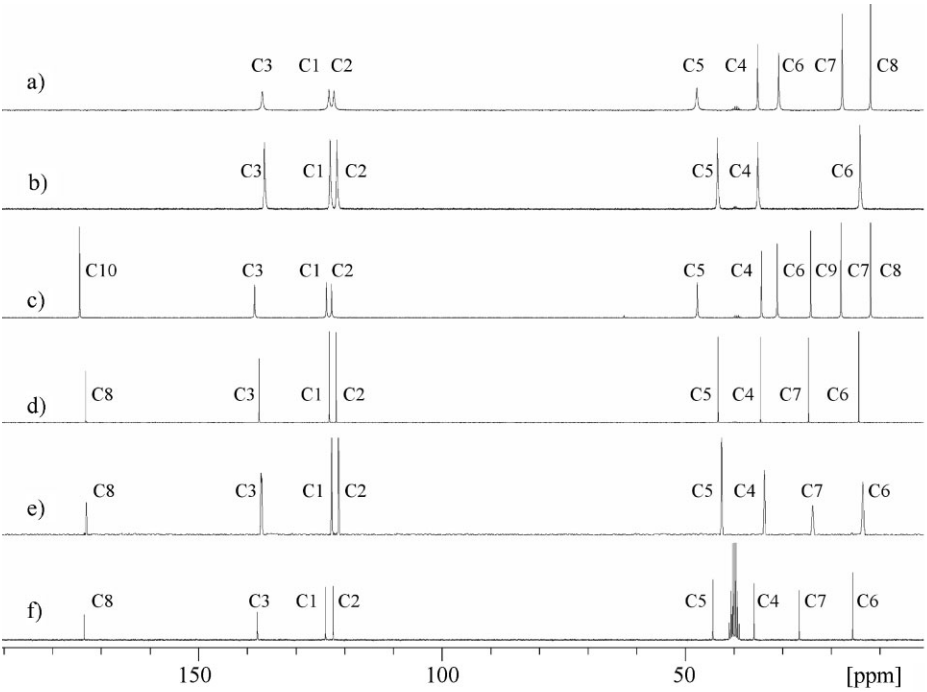


Figure 3.
$^{13}C\{^1H\}$-NMR spectra of the pure ionic liquids a) BMIM-Cl, b) EMIM-Cl, c) BMIM-Ac, and d) EMIM-Ac investigated in the undiluted state in coaxial NMR tubes (a,c,d: Avance 250; b: Avance 400_1); e) solid-state NMR spectrum of EMIM-Ac (Ultrashield 600), f) NMR spectrum of EMIM-Ac in DMSO-d_6 (Avance 400_1).

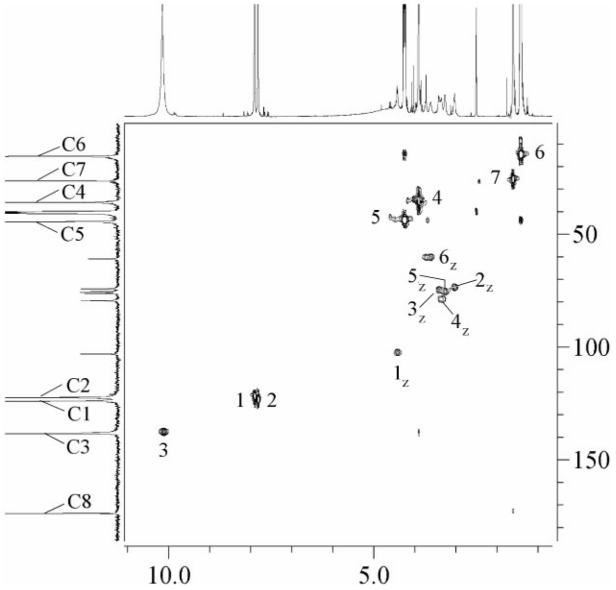


Figure 4.
HSQC spectrum of cellulose/EMIM-Ac dope (10 wt-%) diluted with DMSO-d_6 (Avance 400_1).

Table 4.

^{1}H- and $^{13}C\{^{1}H\}$-NMR chemical shifts in ppm of cellulose Eu-556 and ionic liquid EMIM-Ac in a cellulose/EMIM-Ac dope (10 wt%), which were obtained by liquid- and solid-state NMR, respectively.

	^{1}H-NMR chemical shifts of cellulose [ppm]							
	$H1_z$	$H2_z$	$H3_z$	$H4_z$	$H5_z$	$H6_z$	$H6_{z'}$	
Dope/ DMSO-d_6	4.42	3.05	3.42	3.37	3.28	3.63	3.74	
Pure dope, sp/MAS	-/-	3.14	3.34	3.32	3.24	3.50	-/-	
	^{13}C-NMR chemical shifts of cellulose [ppm]							
	$C1_z$	$C2_z$	$C3_z$	$C4_z$	$C5_z$	$C6_z$		
Dope/ DMSO-d_6	103.0	73.9	75.2	79.3	75.9	60.8		
Pure dope, CP/MAS	103.3	74 – 78	74 – 78	80.2	74 – 78	61.4		
	^{1}H-NMR chemical shifts of EMIM-Ac [ppm]							
	H1	H2	H3	H4	H5	H6	H7	
Dope/ DMSO-d_6	7.76	7.84	10.00	3.90	4.28 / 4.26 4.24 / 4.22	1.45 1.43 1.41	1.59	
Pure dope, sp/MAS	8.23	8.39	10.37	4.02	4.31	1.31	1.54	
	^{13}C-NMR chemical shifts of EMIM-Ac [ppm]							
	C1	C2	C3	C4	C5	C6	C7	C8
Dope/ DMSO-d_6	123.8	122.3	138.0	35.8	44.4	15.4	26.3	174.0
Pure dope, CP/MAS	124.6	123.2	138.5	36.2	45.0	15.9	25.8	-/-
Pure dope, sp/MAS	124.8	123.2	138.4	36.4	45.2	15.9	25.8	176.3

DMSO-d_6 = solvent; sp = single pulse, CP = cross polarization, MAS = magic angle spinning

The solid-state MAS single-pulse ^{1}H-NMR measurement on cellulose/EMIM-Ac dope (10 wt-%) was carried out with dipolar decoupling during data acquisition. The spectrum was compared with the liquid-state ^{1}H-NMR spectrum of cellulose/EMIM-Ac dope, dissolved in DMSO-d_6 (Figure 5a, b). As aforementioned, the solid-state ^{1}H-NMR spectra should be comparable to liquid-state NMR spectra of undiluted cellulose/EMIM-Ac dope.

It should be mentioned that the hygroscopic properties of the dope were strictly accounted for sample preparation. Rotor

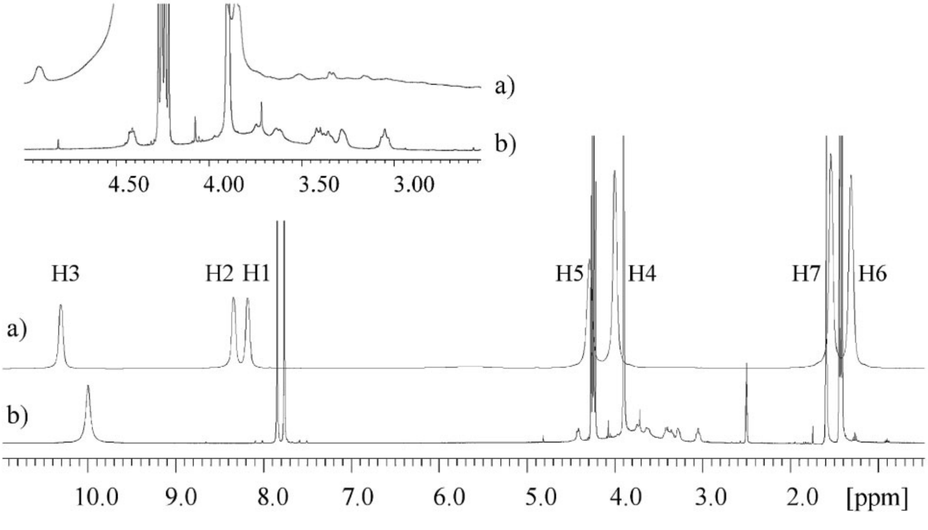


Figure 5.

^{1}H-NMR spectra of cellulose/EMIM-Ac dope (10 wt-%); a) single pulse MAS experiment (Avance 400_2) and b) liquid-state NMR of the sample diluted with DMSO-d_6 (Avance 400_1).

inserts were filled under argon atmosphere, which minimized the influence of water on the chemical shift values of the dope (Figure 5a). Considering this, it became apparent that the sample dilution by DMSO-d_6 influenced the ^{1}H-NMR chemical shifts of both cellulose and EMIM-Ac in cellulose/EMIM-Ac dopes.

The signals of EMIM-Ac and cellulose Eu-556 were well resolved in the liquid-state NMR spectrum (Figure 5b). Lines could be easily referred to the ^{1}H-NMR peak of DMSO-d_6 at 2.49 ppm; exact chemical shift data were listed in Table 4. Even though the spectra were resolved sufficiently, the solid-state ^{1}H-NMR chemical shifts of cellulose were understandably not that much separated as in liquid. Thus, the assignment of the solid-state NMR lines of cellulose was much more difficult. However, it could be shown that each resonance of the solid-state ^{1}H-NMR spectrum in Figure 5a was slightly shifted compared to the lines of the diluted sample (Table 4). Most significant changes were obtained for the cellulose resonance $H6_z$ and for the imidazolium ring protons H1-H3 of EMIM-Ac.

Comparing undiluted EMIM-Ac with the undiluted cellulose/EMIM-Ac dope, it was also noticeable that the ^{1}H-NMR chemical shifts of EMIM-Ac in dopes were shifted, too, compared to the resonance values of pure EMIM-Ac. This fact was ascribable to the influence of cellulose in its dissolved state in the dope.

In addition to ^{1}H-NMR investigations, solid-state MAS ^{13}C{^{1}H}-NMR measurements on cellulose/EMIM-Ac dope (10 wt-%) were carried out at different conditions. Data obtained were shown in Figure 6a and b. For further comparison, the same sample was diluted with DMSO-d_6 and measured by liquid-state ^{13}C{^{1}H}-NMR, too (Figure 6c).

Cross-polarized MAS investigations were used to verify cellulose signals in the range of 110 ppm to 60 ppm (Figure 6a). For cross polarization (CP) studies of the dope, 32k scans had to be accumulated to achieve a reasonably good signal to noise ratio. Even though the resolution of lines was not satisfactory, the ^{13}C-NMR chemical shifts $C1_z$-$C6_z$ of the pulp could be readily assigned by line shape analysis taking into account

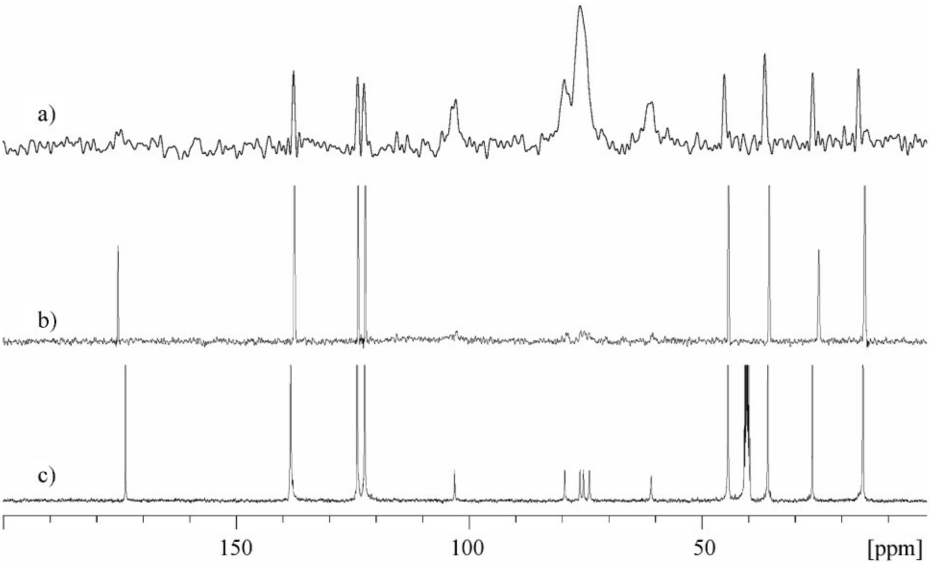


Figure 6.
^{13}C{^{1}H}-NMR spectra of cellulose/EMIM-Ac dope (10 wt-%); a) CP/MAS experiment (Avance 400_3; TPPM: ± 10°, 6 μs), b) single pulse MAS experiment (Ultrashield 600; cw-decoupling), and c) liquid-state NMR of cellulose/EMIM-Ac dope in DMSO-d_6 (Avance 400_1).

data from the literature.[23] The ^{13}C-NMR lines of cellulose Eu-556 diluted in EMIM-Ac were found at following positions: 103.3 ppm ($C1_z$), 80.2 ppm ($C4_z$), 61.4 ppm ($C6_z$), and between 74 ppm and 78 ppm ($C2_z$, 3_z, 5_z). Compared to the crystalline peaks of pure pulp Eu-556, the carbon resonances $C1_z$, $C2_z$, $C3_z$, and $C5_z$ of cellulose/EMIM-Ac dope were shifted to lower field by more than 2 ppm due to interactions with the IL, while the chemical shift of $C6_z$ remained at almost the same value. The part of $C4_z$, however, was shifted upfield by about 5 ppm. In addition, the $C4_z$ values of cellulose/EMIM-Ac dope virtually correlated with the chemical shift of disordered (amorphous) $C4_z$ of pure pulp. This fact indicated both strong interactions between cellulose and EMIM-Ac and the decrystallization of cellulose in EMIM-Ac. As the intrachain hydrogen bonds are responsible for the special geometry of the glycosidic linkage, the characteristic chemical shift of $C4_z$ resonances near 90 ppm could be observed only in crystalline cellulose.[24,25] Even though it was previously found for cellobiose[11] that the hydrogen bonding of hydroxyls with the acetate anion and imidazolium cation of EMIM-Ac is the major force for cellulose dissolution in ionic liquids, current data of the more complex cellulose system are still incommensurable. Further investigations of cellulose dissolution in IL will be published elsewhere.

The resonances of EMIM-Ac, however, could not be detected satisfactory using cross-polarized MAS experiments. Rather broad lines of low intensity were observed at about 138.5 ppm (C3), 124.6 ppm (C1), 123.2 ppm (C2), 45.0 ppm (C5), 36.2 ppm (C4), 25.8 ppm (C7), and 15.9 ppm (C6). This fact might be due to the comparatively high molecular mobility of the dope with just 10 wt% of cellulose. Those mobility inhibited polarization transfer from protons to carbons in the case of EMIM-Ac molecules. Especially the carbon peak of the acetate molecules (C8) was centred by the molecular motion. To that effect, the resonance C8 was not visible at all in the CP/MAS ^{13}C{^{1}H}-NMR spectrum. Even by varying the contact time from 0.5 ms to 5 ms, no improvement of the IL-line resolution was achieved in the cross-polarized NMR spectra.

Anyhow, it might be also possible that the coexistence of different kinds of solvent in the IL is responsible for the decrease of IF resonances in the CP/MAS ^{13}C{^{1}H}-NMR spectrum of cellulose/EMIM-Ac dope. In this regard, one moiety of EMIM-Ac, which was more or less bound to cellulose, exhibited a kind of (mobile) solid-state character and was thus partially accessible to CP. Consequently, another more liquid contribution was not visible in this way. This assumption, however, needs further investigation.

To detect each resonance of the cellulose/EMIM-Ac dope, the sample could be cooled down or experiments without polarization transfer should be chosen. Therefore, single pulse MAS ^{13}C{^{1}H}-NMR experiments with unvaried repetition times were performed, which enabled the detection of carbon lines with real intensities. The single pulse spectrum of cellulose/EMIM-Ac dope (Figure 6b) exhibited resonances of both pulp and IL. In contrast to the CP spectrum in Figure 6a, the ^{13}C chemical shifts of the IL could fully be detected with line widths of less than 70 Hz. This resolution is comparable with the resolution of the liquid-state NMR lines; meaning that ^{13}C single pulse experiments in MAS NMR proved to be a useful tool for the investigation of dopes in the solid state. Within the error limit and with the exception of carbon C8, the ^{13}C chemical shift values of the single pulse experiment: 176.3 ppm (C8), 138.4 ppm (C3), 124.8 ppm (C1), 123.2 ppm (C2), 45.2 ppm (C5), 36.4 ppm (C4), 25.8 ppm (C7), and 15.9 ppm (C6) were identical to the data obtained by CP/MAS ^{13}C{^{1}H}-NMR.

The cellulose resonances of the dope in Figure 6b were not as good resolved as in the cross-polarized MAS NMR spectrum of the same sample (Figure 6a). The frequency ranges of the carbon peaks, however, were comparable. It became apparent that a cellulose concentration of 10 wt% or less in cellulose/EMIM-Ac dopes was not sufficient for solid-state NMR research. Drastically increasing the number of scans might improve the spectral resolution of cellulose resonances.

Comparing the ^{13}C-NMR spectra obtained by solid-state NMR in Figure 6a and b with the liquid-state NMR spectrum of cellulose/EMIM-Ac dope diluted in DMSO-d_6 (Figure 6c), only slight differences in the chemical shifts were found.

This study offered another starting point for further NMR investigations on polymer/IL dopes. Especially the measurement of dopes with a higher cellulose concentration, which is interesting for a couple of fibre processes, was now accessible.

Conclusion

Pure BMIM-Cl, EMIM-Cl, BMIM-Ac, and EMIM-Ac and the IL after dilution with different solvents were investigated. It was proved that the imidazolium proton resonances H1-H3 were significantly shifted depending on the type of solvent (DMSO-d_6, D_2O, CD_3OD, and $CDCl_3$). The most significant changes of more than 1 ppm were detected for H3, while the displacement strongly depended both on the solvent and to some extend on the IL used. Furthermore, the solvent effect led to a strong shifting of the acetate proton peaks of EMIM-Ac and BMIM-Ac of more than 0.4 ppm compared to ^{1}H-NMR chemical shift data of undiluted samples. It was shown that the investigation of pure IL, poured into coaxial NMR tubes with an external reference, provided identical values to solid-state NMR data. Results obtained by liquid-state ^{1}H-NMR were confirmed by ^{13}C{^{1}H}-NMR spectroscopy. Besides resonance shifting, a proton deuteron exchange was visible in ^{1}H- and ^{13}C{^{1}H}-NMR spectra. Using HSQC in liquid-state NMR, the ^{1}H- and ^{13}C-NMR chemical shifts of cellulose and EMIM-Ac were obtained. The investigations of the undiluted cellulose/EMIM-Ac dope were achieved by MAS NMR. As for liquid-state NMR results, it became apparent that the part of $C4_z$ of cellulose/EMIM-Ac dope virtually correlated with the chemical shift of disordered (amorphous) $C4_z$ of pure pulp; meaning that the cellulose in EMIM-Ac was existent in the dissolved state. With this given methods cellulose concentration higher than 10 wt% in EMIM-Ac are possible to measure without any co-solvents. This is an important step for further investigations of the dissolution state of cellulose in IL.

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