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NMR Insights on the Properties of $ZnCl_2$ Molten Salt Hydrate Medium through Its Interaction with $SnCl_4$ and Fructose

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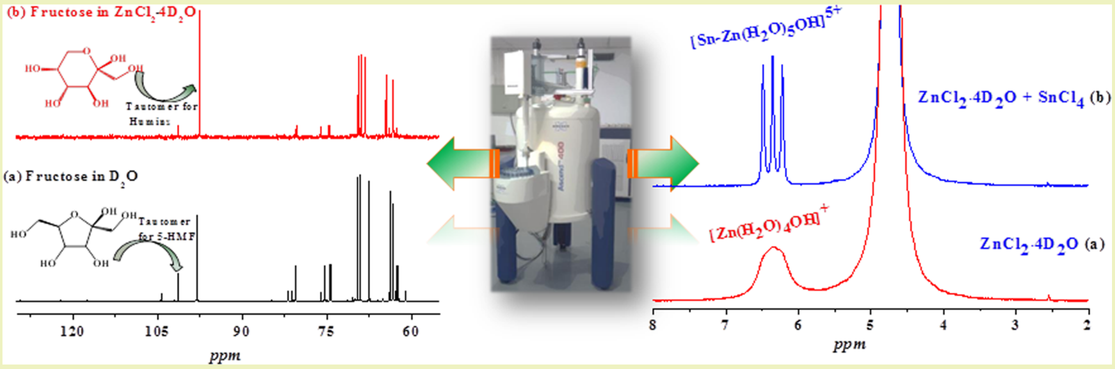
Supporting Information



ABSTRACT: The solvent properties of $ZnCl_2$ molten salt medium and its synergic effect with the Lewis acid catalyst, Sn^{4+}, for biomass conversion, were investigated by nuclear magnetic resonance. The tautomeric distribution of fructose in the $ZnCl_2$ molten salt medium was examined, and its effect for humins formation during the biomass conversion was evaluated. The ion complex composed by Sn^{4+} and Zn^{2+} indicated that there is a synergic catalytic effect between these two Lewis acid ions. ^{13}C NMR spectra of fructose in different $ZnCl_2$ molten salt hydrate concentrations revealed that the concentration of β-furanose and α-furanose tautomers, which lead to 5-HMF, were significantly decreased with increased salt concentration. Meanwhile the β-pyranose tautomer, which is correlated with humins formation, was increased significantly.

KEYWORDS: *Fructose, 5-HMF, Molten salt hydrate medium, NMR, $ZnCl_2$*

INTRODUCTION

Due to the good solubility for biomass substrate and efficient catalytic activity for biomass conversion, the molten salt hydrate medium $ZnCl_2·4H_2O$ (typically 65 wt % $ZnCl_2$ solution) has been developed successfully as an economic, nontoxic, and recyclable homogeneous reaction medium for converting inulin,[1] lignocellulosic biomass,[2−8] and chitin biomass[9] into value-added fine chemicals, such as 5-hydroxymethylfurfural (5-HMF),[7,9] levulinic acid (LA), and isosorbide.[2−5] Interestingly, according to previous experimental results, $SnCl_4$ played completely different roles in the degradation of inulin, chitin, and cellulose biomass.[9−12] For chitin biomass degradation in the $ZnCl_2$ molten salt hydrate medium, the reaction was inhibited by the addition of $SnCl_4$ due to the strong chelation between the amino groups of D-glucosamine and Sn^{4+}. However, the degradation of D-glucose and D-fructose was promoted by this Lewis acid catalyst. Even more exciting is that the distribution of products including 5-HMF and LA could be controlled in the conversion of inulin biomass, if the reaction was performed in a $ZnCl_2$ molten salt hydrate with $SnCl_4$ as the co-catalyst.[1]

However, it is unclear why the $ZnCl_2$ molten salt hydrate medium works efficiently with Sn^{4+} as co-catalyst for the lignocellulosic biomass degradation reaction; this needs to be investigated further. It has been proposed that the incompletely coordinated Zn^{2+} ion has shown catalytic activity on the isomerization of D-glucose into D-fructose and further into 5-HMF. The information for the interaction between $ZnCl_2$ and the biomass substrate and/or reaction intermediates, such as D-fructose, is still unexplored. The $ZnCl_2$ molten salt hydrate medium could provide an acidic environment, and the potential influence beyond the acidic condition on the biomass degradation reaction also needs to be elucidated. In addition, biomass degradation, in this novel reaction medium, is always hampered by the formation of humins, and consequently, the yield of the desired product is reduced significantly. The reaction pathway and mechanism for this side reaction are still unknown, and it is already the major obstacle for biomass conversion in this efficient medium.

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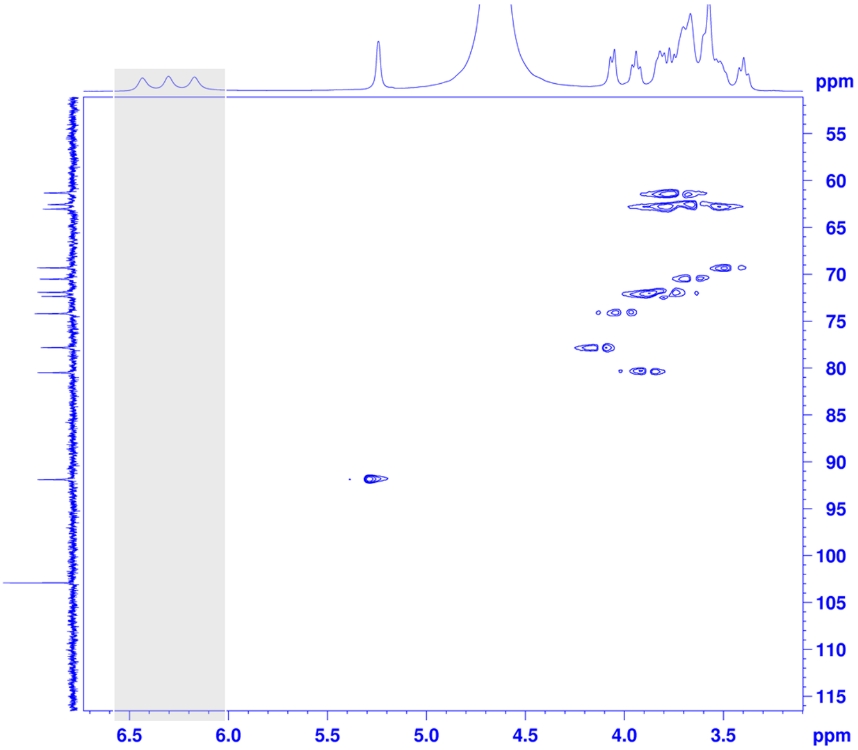

Figure 1. 2D $^1H-^{13}C$ HSQC NMR spectrum of sucrose in $ZnCl_2·4D_2O$ solution with a catalytic amount of $SnCl_4·5H_2O$ (sugar unit/Sn^{4+} = 2:1 by mole). Sucrose concentration: 1 g of sucrose per 30 g of reaction mixture.

Nuclear magnetic resonance (NMR) is a powerful technology for analysis of the molecular structure in organic chemistry. Now, it has been successfully utilized in the structural analysis of lignocellulosic biomass.[13−15] It is also a versatile technique for biomass conversion studies to identify intermediates, disclose reaction pathways, and reveal the mechanism.[16−20] Advanced *in situ* NMR could follow the biomass conversion process and acquire more detailed information under the reaction conditions without the need for quenching the reaction. Horváth and Weitz employed isotopic-labeled D-fructose to disclose the reaction pathway of 5-HMF formation in DMSO, and several intermediates were identified successfully.[21,22] Matubayasi applied ^{13}C NMR to demonstrate the solvent effects in the D-fructose dehydration reaction in DMSO, water, and methanol.[23] Han et al. showed by ^1H NMR that there is an interaction between Sn^{4+} and D-glucose, and Ma et al. followed the process of cellulose hydrolysis to D-glucose and then D-glucose dehydration into 5-HMF by ^{13}C NMR.[11,24] Yan et al. employed ^1H, ^{13}C, and ^{11}B NMR to reveal that boric acid interacts with hydroxyl groups on C_3/C_4 and C_6 of N-acetyl-D-glucosamine and forms a boron-containing complex, which will lead to the final nitrogen-containing product 3-acetamido-5-acetylfuran.[25] Recently, the NMR technique was further applied to monitor the degradation reaction of marine biomass. Quantitative ^1H NMR was employed to quantify the 5-HMF yield, and the results were found to agree well with those obtained by HPLC.[9,26,27]

In this report, 1D ^1H, ^2H, and ^{13}C NMR, as well as 2D $^1H-^1H$ correlation spectroscopy (COSY) and $^1H-^{13}C$ heteronuclear single quantum coherence (HSQC) were exploited to reveal the nature of the $ZnCl_2·4H_2O$ molten salt hydrate medium with and without Sn^{4+}. Moreover, the tautomeric distribution of fructose was studied, and its influence on humins formation was disclosed. Consequently, a deep insight into hexose biomass conversion, in this novel $ZnCl_2$ molten salt hydrate medium, was achieved.

■ EXPERIMENTAL SECTION

Materials. Fructose (analytical grade, 99.5%) and sucrose (analytical grade) were obtained from Shanghai Crystal Pure Co., Ltd. Hydrochloric acid (HCl, 37% aqueous solution), zinc chloride ($ZnCl_2$, analytical grade), and tin(IV) chloride pentahydrate ($SnCl_4·5H_2O$, analytical grade) were purchased from Beijing Chemical Reagent Company. Deuterium oxide (D_2O, 99.9 atom % D) was supplied by Cambridge Isotope Laboratory. All reagents utilized in this work were used as received without further purification. Double distilled water was used in all experiments.

Typical Procedure for NMR Measurement. 1D and 2D NMR spectra were acquired on a Bruker AV-III 400 MHz NMR spectrometer (9.39 T) equipped with autosampler at room temperature. ^1H, ^2H, and ^{13}C NMR were obtained at frequencies of 400.13, 60.42, and 100.61 MHz, respectively. The chemical shifts for ^1H NMR and ^2H NMR were referenced to 4.77 ppm of the residual protons of D_2O, and chemical shifts in ^{13}C NMR spectra were referred to the sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS). The NMR parameters for ^1H measurements are as follows: pulse program for acquisition, zg30; P1, 9.7 μs; PLW1, 18 W; AQ, 4.09 s; D1, 1.0 s; DS, 2; and NS, 16. The NMR parameters for ^{13}C measurement are as follows: pulse program for acquisition, zgpg30; P1, 9.5 μs; PLW1, 84 W; AQ, 1.36 s; D1, 2.0 s; DS, 4; and NS, 2048. The NMR parameters for ^2H measurement are as follows: pulse program for acquisition, zg2h; P1, 347 μs; PLW1, 3.0 W; AQ, 38.1 s; D1, 1.0 s; DS, 0; and NS, 10. The pulse programs for COSY and HSQC acquisition are "cosygpppqf" and "hsqcetgpsi2", respectively. The collected 1D and 2D NMR data were processed using Bruker Topspin 3.1 software.

■ RESULTS AND DISCUSSION

NMR Evidence of Interaction between Sn^{4+} and Zn^{2+}. To elucidate the interaction between Sn^{4+} and $ZnCl_2$ molten salt hydrate, the sucrose dehydration reaction mixture (1.0 g

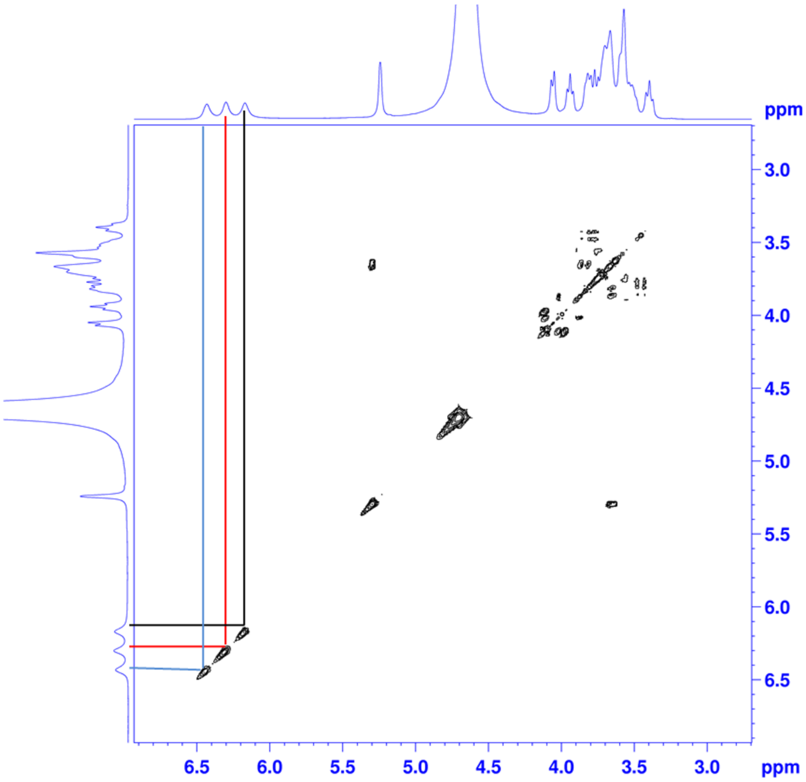

Figure 2. 2D ^1H−^1H COSY NMR spectrum of sucrose in $ZnCl_2·4D_2O$ solution with a catalytic amount of $SnCl_4·5H_2O$ (sugar unit/Sn^{4+} = 2:1 by mole). Sucrose concentration: 1 g of sucrose per 30 g of reaction mixture.

sucrose in 30 g solvent) was chosen and examined at room temperature in $ZnCl_2·4D_2O$ (65 wt % $ZnCl_2$ deuterium oxide solution), and a catalytic amount of $SnCl_4$ (sugar unit/Sn^{4+} = 2:1 by mole) was introduced. The obtained ^1H and ^{13}C spectra are listed in Figures S1 and S2 of the Supporting Information, respectively. Although high $ZnCl_2$ concentration could affect the sensitivity of NMR measurements, well-resolved signals of sucrose were observed in the ^{13}C spectrum. These signals were assigned and listed in the insertion of the ^{13}C spectrum. However, signals of the ^1H spectrum were not well resolved and approximately assigned. Besides, three notable single peaks located around 6.22−6.48 ppm were also detected (Figure S1, Supporting Information). In order to gain further insight and assign these three single peaks, HSQC (Figure 1) and COSY (Figure 2) measurements of the sucrose dehydration reaction mixture were performed, which could reveal the correlation between proton−carbon and proton−proton, respectively. According to the HSQC spectrum, no carbon atoms of sucrose are connected with protons for these three single peaks. So, these protons do not belong to carbohydrate, herein sucrose. In the condition that the strong HOD peak commonly appears at 4.70 ppm, these signals presumably belong to protons in other forms, for example, coordinated or hydrolyzed water with Sn^{4+} and/or Zn^{2+}. Then, the ^1H NMR spectra of the pure reaction medium $ZnCl_2·4D_2O$ molten salt hydrate with and without Sn^{4+} were additionally examined, and the obtained spectra are shown in Figure 3a and b. The NMR spectra showed that three single peaks were observed only in the system of $ZnCl_2·4D_2O$ with Sn^{4+} (Figure 3a), while there was a broad peak at 6.35 ppm for the $ZnCl_2·4D_2O$ solvent without Sn^{4+} (Figure 3b). In addition, ^2H NMR was performed to collect further evidence to support these above results. In the $ZnCl_2$ molten salt hydrate medium, the equilibrium between active ^1H and ^2H is occurring fast. So, ^2H signals could be observed in the corresponding positions of the ^1H signals. The obtained ^2H NMR spectra for the $ZnCl_2·4D_2O$ reaction medium with and without Sn^{4+} are listed in Figures S3 and S4 of the Supporting Information. Correspondingly, comparable spectra were obtained, which could prove our suggestion, and all these signals originate from active protons.

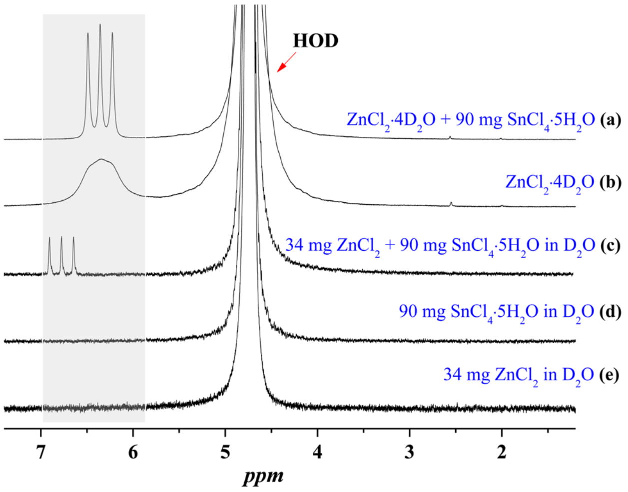

Figure 3. ^1H NMR characterization of the interaction between Zn^{2+} and Sn^{4+}. The volume of the NMR samples is 0.5 mL.

It has been proven that the Zn^{2+} ion at such high concentration (65 wt %) is incompletely coordinated, and one Zn^{2+} ion could be coordinated with four H_2O (or D_2O, HOD) molecules through the hydroxyl group to form a $Zn(H_2O)_4Cl_2$ cluster.[7] Therefore, the coordinated residual proton of the deuterated solvent could give the broad peak in the spectrum (Figure 3b). This NMR result agrees with the structure of the suggested cluster, where all four water molecules are shown in an identical chemical environment. Consequently, the broad peak at 6.35 ppm of the $ZnCl_2$ molten salt hydrate without Sn^{4+} is assigned to the HOD coordinated with Zn^{2+}.

However, the formation path for these three single peaks observed in Figure 3a is still unclear. Three NMR experiments were performed to assign three single peaks precisely. The first NMR sample, 90 mg of $SnCl_4{\cdot}5H_2O$ in 0.5 mL of D_2O (Figure 3d, 11.3 wt % $SnCl_4$) was prepared, where the concentration of Sn^{4+} is exactly the same as in a typical biomass dehydration experiment.[9] The second one contained the same mole concentration of Zn^{2+} (34 mg of $ZnCl_2$ in 0.5 mL of D_2O) as Sn^{4+} (Figure 3e, 5.8 wt % $ZnCl_2$). In the last one, 90 mg of $SnCl_4{\cdot}5H_2O$ together with 34 mg of $ZnCl_2$ were dissolved in 0.5 mL of D_2O (Figure 3c). ^1H NMR spectra of these three samples were surveyed at room temperature. It is interesting that these three single peaks were observed neither in the spectrum of $SnCl_4$ solution (Figure 3d) nor in the spectrum of the diluted $ZnCl_2$ solution (Figure 3e). Conversely, in the spectrum of Figure 3c, mixture of Sn^{4+} and Zn^{2+}, three clearly resolved single peaks could be observed. It should be highlighted that the concentration of $ZnCl_2$ in the above-mentioned experiments is only 5.8 wt % (Figure 3c and e), far lower than 65 wt % of the molten salt hydrate medium. The obtained results could perhaps support a hypothesis that the three single peaks originate from the interaction of Sn^{4+}, Zn^{2+}, and a proton (in HOD or $M(OH)_n^+$ form). Again, the ^2H NMR spectra were measured and are listed in Figures S5−S7 of the Supporting Information. The obtained spectra could approve our above-mentioned suggestion that signals for these three single peaks originate from active protons. Recently, Choudhary et al. systematically investigated the $CrCl_3$ speciation in aqueous solution.[28] Their results disclosed that three main complex ions, including $[Cr(H_2O)_6]^{3+}$, $[Cr(H_2O)_5Cl]^{2+}$, and $[Cr(H_2O)_5OH]^{2+}$, are formed in this Lewis acid solution, together with H^+ being released and pH bieng dropped. Moreover, the hydrolyzed Cr(III) complex, $[Cr(H_2O)_5OH]^{2+}$, was identified as the most active species for glucose isomerization and acts as the bifunctional Lewis acid−Brønsted base site to promote the dehydration and subsequent 5-HMF rehydration steps. Additionally, strong correlation between these three single peaks was shown in the COSY spectrum (Figure 2), and it was also shown that these protons only correlated to themselves. Hence, it is reasonable to propose that these three single peaks probably originate from the complex $[Sn{-}Zn(H_2O)_5OH]^{5+}$, which is formed from the hydrolysis of $SnCl_4$ and $ZnCl_2$. The complex $[Sn{-}Zn(H_2O)_5OH]^{5+}$ and HCl (formed in the hydrolysis of the metal chlorides) may have different effects on the hydrolysis of glycosidic bonds and promote the formation of 5-HMF and LA.[1,7,9]

NMR Insight on Interaction between Zn^{2+} and Fructose. The 5-HMF preparation from biomass employing the $ZnCl_2$ molten salt hydrate as the reaction medium usually suffers from low product yields due to the formation of polymeric substances, namely, humins (Figure S8, Supporting Information). Considering that the reaction medium could be reused several times, the humins formation is the main drawback of using this environmentally benign solvent, $ZnCl_2$ molten salt hydrate, as the reaction medium for biomass conversion.[7,9] Understanding the pathway for humins formation is an essential step in order to optimize the reaction condition and increase the yield of the desired platform compounds, such as 5-HMF and LA. A molecular level survey of the solvent/substrate interaction by the NMR approach can be used to quantify the tautomeric distribution, and it can support the understanding for the biomass degradation process in the $ZnCl_2$ molten salt hydrate clearly. Hence, ^{13}C NMR spectroscopy was employed as a characterization tool to quantify the behaviors of D-fructose in a reaction medium with different $ZnCl_2$ concentrations. The corresponding spectra are listed in Figure 4. ^{13}C NMR showed that the tautomeric composition of D-fructose was obviously different from those in D_2O without any salt (Figure 4a), and the equilibrium between furanose and pyranose forms was significantly affected by the $ZnCl_2$ molten salt hydrate medium. The five tautomers, including the open chain (indicated by 213.5 ppm for −CHO group as shown in the insert of Figure 4), α,β-pyranose, and α,β-furanose forms of D-fructose, were observed by ^{13}C NMR (Figure 4a) in the D_2O solution.[29] The β-pyranose, β-furanose, and α-furanose are the three main tautomers. In a concentrated $ZnCl_2$ solution, such as 55 wt % ($ZnCl_2{\cdot}6D_2O$) and 65 wt % ($ZnCl_2{\cdot}4D_2O$) (Figure 4b and c), β-pyranose turned out to be the absolute majority at the expense of the β-furanose concentration and disappearance of α-furanose. The abundance of each tautomer of D-fructose and even the formation of target molecules are strongly affected by the nature of the solvents condition, such as temperature and pH.[19] In the universally proposed mechanism, the fructofuranose tautomers, α-furanose and β-furanose of D-fructose, are the identified precursors for 5-HMF formation via dehydration reaction of hexose sugar.[21,22,30] Correspondingly, β-pyranose of D-fructose is believed to be responsible for formation of humins.[21,22] Therefore, higher concentration of β-pyranose in $ZnCl_2$ molten salt hydrate increases the rate and possibility of humins formation.[22] The chemical shifts of β-pyranose in different solvents are listed in Table 1. The chemical shift changes ($\Delta\delta$) of β-pyranose in the reaction medium (compared with these values in D_2O) are also presented in Table 1. According to Table 1, the chemical shift changes ($\Delta\delta$) for C_1 and C_3 of β-pyranose in 65 wt % ($ZnCl_2{\cdot}4D_2O$) are positive

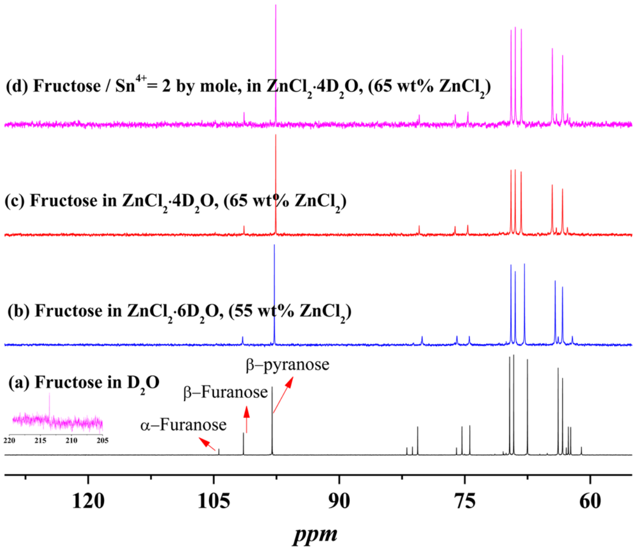

Figure 4. ^{13}C NMR spectra of fructose in different reaction media.

Table 1. ^{13}C Chemical Shifts for β-Pyranose Tautomer of Fructose in Different Reaction Media and Changes in ^{13}C NMR Chemical Shifts ($\Delta\delta$) of Each Carbon Due to the Reaction Medium Effect[a]

entry	$C_1/\Delta\delta$ (ppm)	$C_2/\Delta\delta$ (ppm)	$C_3/\Delta\delta$ (ppm)	$C_4/\Delta\delta$ (ppm)	$C_5/\Delta\delta$ (ppm)	$C_6/\Delta\delta$ (ppm)
d	64.53/0.69[b]	97.59/−0.43	68.25/0.73	69.48/−0.15	68.97/−0.19	63.29/−0.03
c	64.54/0.70	97.58/−0.44	68.26/0.74	69.48/−0.15	68.97/−0.19	63.30/−0.02
b	64.19/0.35	97.75/−0.27	67.86/0.34	69.48/−0.15	68.97/−0.19	63.38/0.06
a	63.84	98.02	67.52	69.63	69.16	63.32

[a] Entry number is same as in Figure 4. [b] $\Delta\delta$ values were obtained by comparing with the chemical shift of fructose in D_2O.

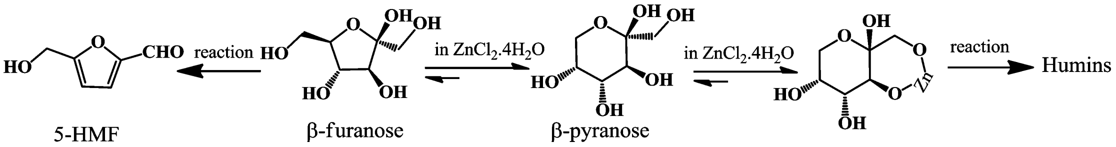

Figure 5. Proposed tautomeric equilibrium and reaction pathways for fructose in $ZnCl_2$ molten salt hydrate medium.

values (about 0.7 ppm, move to the low field). It can be reasoned that these two carbons are conjoined with, or close to, an electron-withdrawing group or ion. As mentioned above, the incompletely coordinated Zn^{2+} in the concentrated $ZnCl_2$ medium could be coordinated with H_2O (or D_2O, HOD) and/or the −OH group to form a complex. The chemical shift changes support the possibility that coordination takes place from the −OH groups of C_1 and C_3 of β-pyranose (Figure 5). Correspondingly, the chemical shift of C_2 is negative (moves to the high field) due to it being located between C_1 and C_3. These values for C_4, C_5, and C_6 are almost constant or just slightly toward the high field, suggesting that the −OH groups connected with these carbons are not engaged in the coordination. Hence, it is reasonable to conclude that the equilibrium distribution for D-fructose tautomers in a higher concentration salt hydrate medium is switched to the β-pyranose side (Figure 5) due to the complex formation. Moreover, the distribution of tautomers was not further affected by the added catalytic amount of $SnCl_4$ (Figure 4d) at high $ZnCl_2$ concentration ($ZnCl_2{\cdot}4D_2O$), so humins will always be formed during the dehydration reaction.

CONCLUSIONS

The nature of the $ZnCl_2$ molten salt hydrate medium with and without $SnCl_4$, which was utilized for inulin, lignocellulosic biomass, and chitin biomass conversion, was studied systematically by NMR technology at the molecular level. The complex $[Sn{-}Zn(H_2O)_5OH]^{5+}$ might be formed in the $ZnCl_2{-}SnCl_4$ biomass degradation reaction medium. The tautomeric distribution of D-fructose was significantly influenced by the concentration of $ZnCl_2$ according to the ^{13}C NMR spectra. The chemical shift changes suggest that the β-pyranose−Zn^{2+} complex was formed, and β-pyranose became the major component in this novel reaction medium. The influence of tautomeric distribution on the humins formation was disclosed. Our research demonstrated that the NMR approach could provide fundamental information for understanding the biomass conversion pathways and mechanisms in the $ZnCl_2$ molten salt hydrate.

ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR data of sucrose in $ZnCl_2{\cdot}4D_2O$ solution with catalytic amount of $SnCl_4{\cdot}5H_2O$, ^2H spectra, and picture of humins. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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