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Electronic Supplementary Information

Extraction of 5-HMF from the conversion of glucose in ionic liquid [Bmim]Cl by compressed carbon dioxide

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S1. Experimental Techniques

Materials

The IL 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) used in the experiment, which with purity over 98 wt% was purchased from Lanzhou Greenchem ILs, LICP, CAS, China (Lanzhou, China). The water content was determined by Karl-Fischer titration after drying it at 50 °C under vacuum conditions for 96 h, and it had water content less than 1000 ppm. CO_2 (> 99.95 %) was provided by Beijing Analysis Instrument Factory. Glucose (99%) and 5-hydroxymethylfurfural (HMF) were provided by J&K Scientific Ltd. $CrCl_2$ (98 %) was purchased from Alfa Aesar.

Dissolution of glucose in [Bmim]Cl

The dried IL (about 5.0 g) was added in a 100 ml, 3-neck, round-bottom flask, which was then immersed in an oil bath. Under the continuous stirring, glucose powder (1 wt% of the IL) was added into the flask. This mixture was heated and stirred under N_2 atmosphere. Additional glucose (another 1 wt% of the IL) was added until the solution became clear. We viewed the glucose was saturated in [Bmim]Cl when the glucose powder could not be dissolved under the certain temperature within 2 h.

Attenuated Total Reflection Fourier Transform Infra-Red (ATR-FTIR) spectra measurement of [Bmim]Cl and glucose solutions in [Bmim]Cl

The experiments were carried out using a Prestige-21 FT-IR spectrometer (Shimadzu, Japan) using a single reflection ATR cell. Acquisition was accomplished in the DTGS detector mode using an accumulation rate of 40 scans at a resolution of 4 cm^{-1} in the spectral range of 400 to 4600 cm^{-1}. Triplicates of each sample were measured.

NMR measurements of pure [Bmim]Cl, [Bmim]Cl/CO_2 and [Bmim]Cl/glucose systems

The binary systems of [Bmim]Cl and CO_2 were prepared by loading the dried IL in the high-pressure view cell, and charging CO_2 into the cell. After it was kept to equilibrate for at least 12 h, the pressure was released to 0.1 MPa to remove the redundant CO_2. The NMR sample was measured as the neat liquids using co-axial capillary containing dimethyl sulfoxide-d_6 (DMSO-d_6) as a lock solution. Then ^1H NMR and ^{13}C NMR measurements were performed on a Bruker Avance III 400 HD spectrometer operating at 400 MHz for ^1H and 100 MPa for ^{13}C.

^{13}C NMR spectra measurements of the [Bmim]Cl/glucose solution were performed on a Bruker DMX 300 spectrometer at different temperature. The solution was prepared by adding solution into a 5mm NMR tube, and then a capillary tube containing DMSO-d_6 was inserted to provide an external standard.

Determination of HMF solubility in compressed CO_2

The apparatus consisted of a high-pressure view cell with a variable volume (20-50 mL), a water bath at constant temperature controlled by a YKKY A2 digital temperature controller, a DB-80 high-pressure syringe pump, a magnetic stirrer, a gas cylinder, a gas sampler and a pressure gauge with an accuracy of ± 0.025 MPa in the pressure range of 0-22 MPa. In a typical experiment, a certain amount of HMF was loaded into the view cell and sealed. The air was removed by charging CO_2 in the cell for three times. After that, the certain mass of CO_2 was charged into the view cell that was placed in the oil bath with the desired temperature, followed by adjusting the volume to make the system be homogeneous. To adjust the volume of system sequentially, we can record the cloud point and some parameters including temperature, pressure and volume. By controlling the conditions, we can obtain a series of HMF solubility in compressed CO_2 under different temperature and pressure.

Determination of volume expansion of IL

The apparatus were similar to those described above. In a typical experiment, the desired amount of [Bmim]Cl was added in the view cell, which was placed in the oil bath at the desired temperature. We began to charge a suitable amount of CO_2 into the cell when the thermal equilibrium had been reached. After the mixing of CO_2 and IL was finished, the volume expansion can be obtained. More CO_2 was continued to charge and the volume expansion at another pressure was measured.

General procedures of the reaction for the dehydration of glucose to HMF

In a typical procedure, the desired amounts of glucose and catalyst $CrCl_2$ were added to the preheated [Bmim]Cl in a flask in an oil bath. The mixture was stirred at 100 °C. After a 3 h reaction time, the system was cooled to room temperature. The samples were then analyzed by High Performance Liquid Chromatography (HPLC).

The analysis of HMF

The amount of HMF was analyzed by HPLC with a Shimadzu LC-15C pump, a Shimadzu UV-vis SPD-15C detector at 282.0 nm, and a Supelcosil LC-18 5ìm column at 30 °C. Before analysis, the reaction mixture was diluted to 1000 mL. A methanol–water solution (30/70 v/v) was used as the mobile phase at a flow rate of 1.0 mL min^{-1}.

S2. The separation of HMF from IL

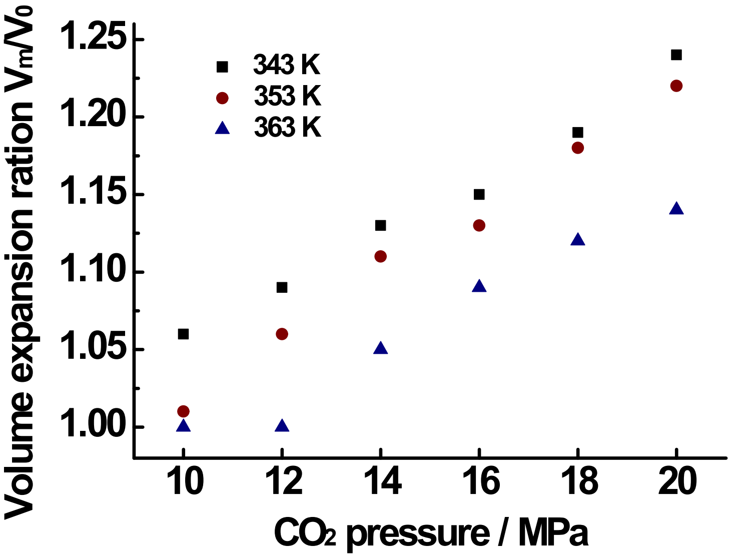

Fig. S1 The volume expansion ratio (V_m/V_0) of [Bmim]Cl after charging compressed CO_2 at different temperature.

Table S1 The separation efficiency of HMF from the conversion of glucose in [Bmim]Cl using different extraction solvents.

Entry	Solvents	Separation efficiency of HMF / %
1	compressed CO_2 [a]	69.6
2	tetrahydrofuran	42.7
3	toluene	23.5
4	ether	45.9

[a] 20 MPa at 343 K in 60 min

S3. The dissolution of glucose in [Bmim]Cl

We can obtain three linear functions (y = ax + b) for the selected wavenumbers according to Fig. 1A.

For 1082 cm^{-1}, it is $y = -0.0485\ x + 1.2657$ ($R^2 = 0.98$).

For 1427 cm^{-1}, it is $y = 0.0087\ x + 0.5156$ ($R^2 = 0.98$).

For 3132 cm^{-1}, it is $y = 0.0105\ x + 0.0619$ ($R^2 = 0.94$).

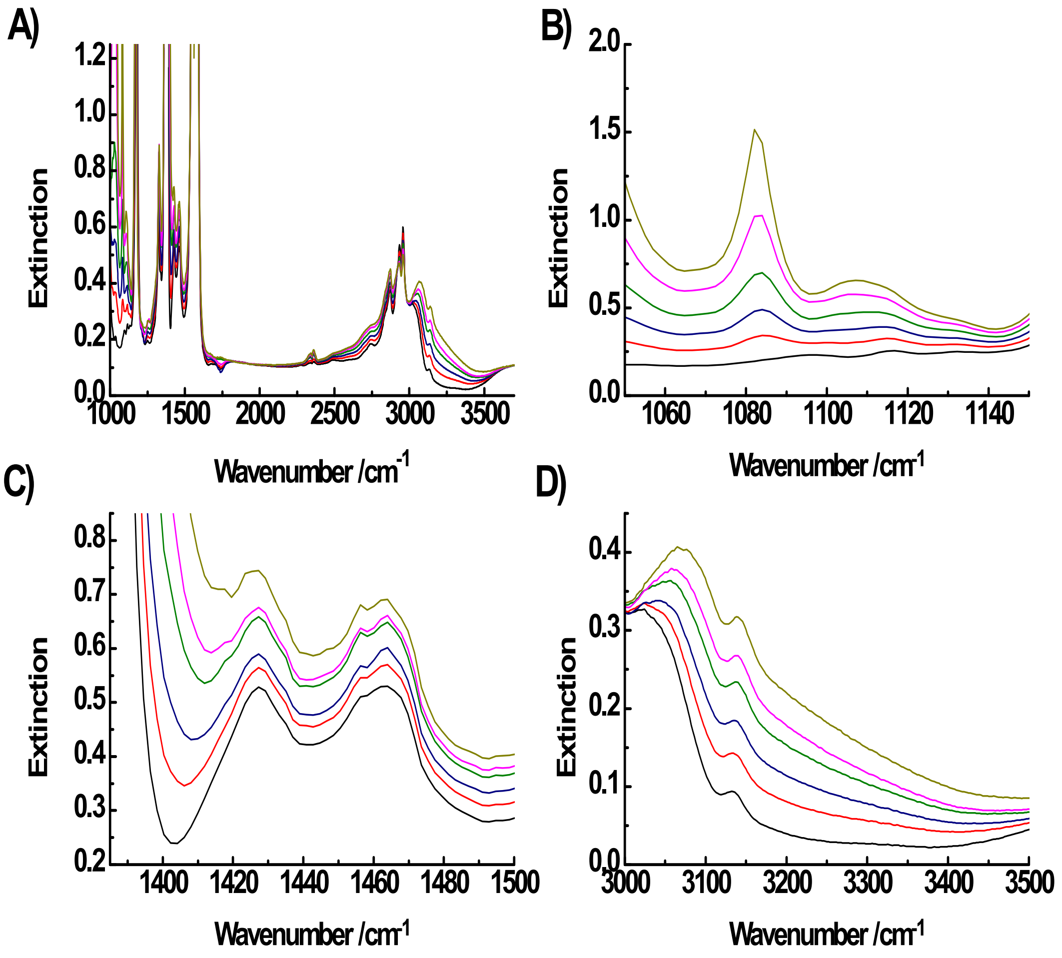

Fig. S2 ATR-IR extinction spectra of [Bmim]Cl and the solutions of [Bmim]Cl/glucose with different concentration. (From bottom to top: 0, 5, 10, 15, 20, 25 wt% glucose in [Bmim]Cl.)

S4. NMR measurement

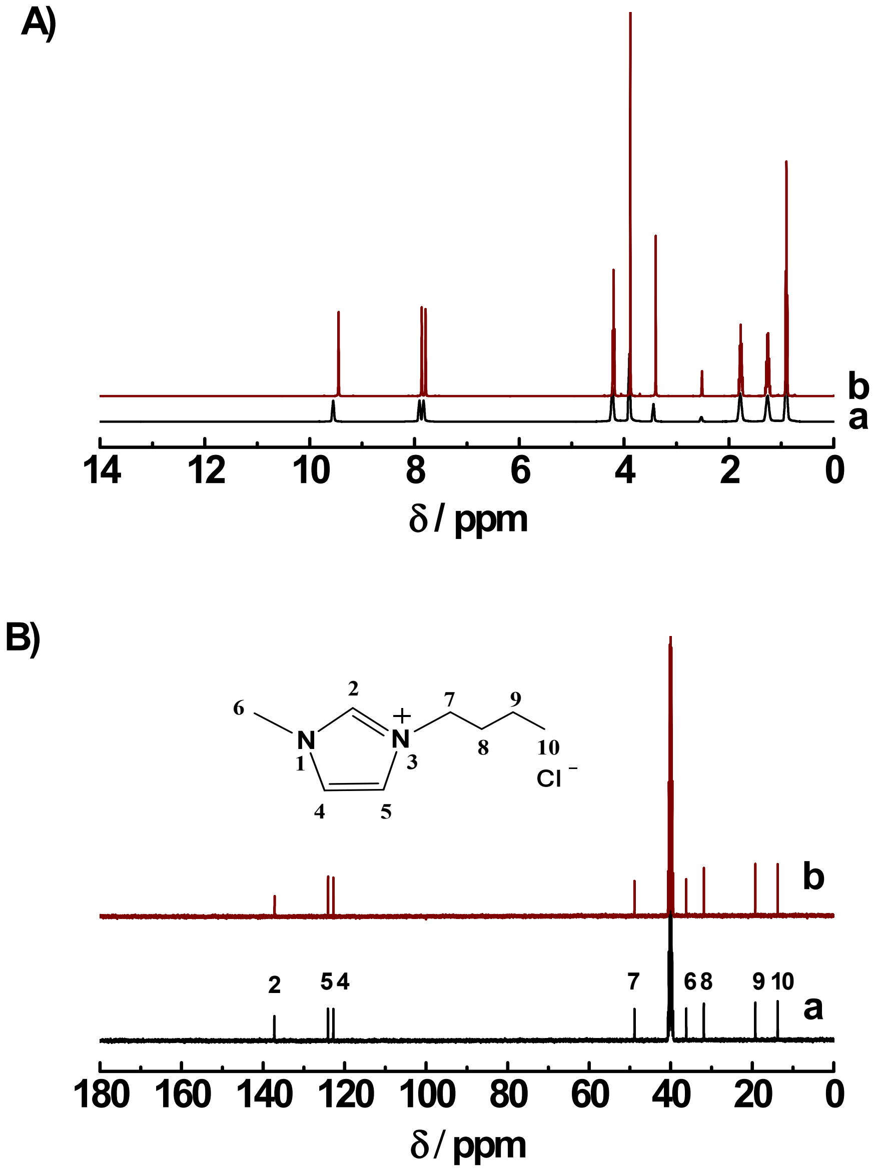

Fig. S3 ^{1}H (A) and ^{13}C (B) NMR spectra of [Bmim]Cl without (a) and with (b) charging CO_2 at 300 K.

Table S2 The relative ^{13}C NMR chemical shifts of the carbon atoms in [Bmim]Cl at different temperature, which were obtained by the differences between the NMR chemical shifts of [Bmim]Cl in [Bmim]Cl/glucose (10 wt%) and the ones of pure [Bmim]Cl.

Entry	Temperature/ K	The relative ^{13}C NMR chemical shifts of the carbon atoms in [Bmim]Cl							
		C2	C4	C5	C6	C7	C8	C9	C10
1	300	-0.15	-0.12	-0.11	-0.10	-0.11	-0.09	-0.11	-0.12
2	320	-0.17	-0.13	-0.14	-0.12	-0.14	-0.12	-0.14	-0.13
3	350	-0.24	-0.19	-0.20	-0.18	-0.16	-0.14	-0.17	-0.15
4	370	-0.30	-0.26	-0.23	-0.22	-0.20	-0.21	-0.20	-0.19