

Carbon Dioxide Capture Through 1-Hexyl-3-Methylimidazolium Acetate

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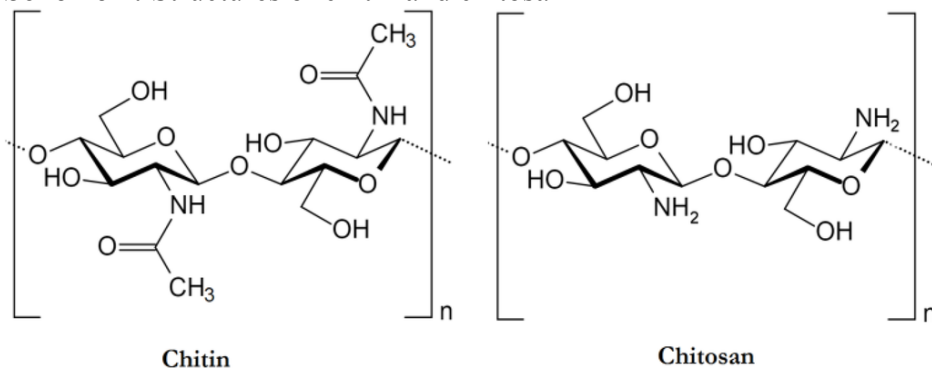
Introduction

Materials and Methods

Preparation of Materials

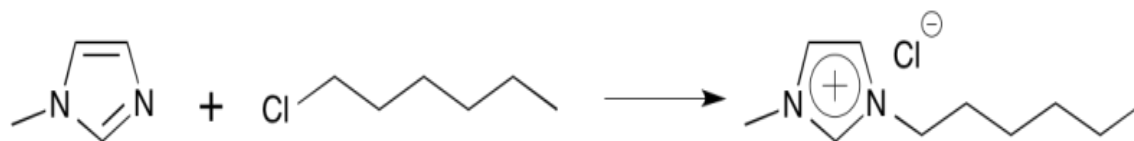
Raw crab shells were obtained by removing the crab meat. The shells, which contain chitin, were then washed and dried in open air. The shells were then decalcified, went through protein removal, and deacetylated using 5% HCl solution, 10% NaOH, and 45% NaOH, producing chitosan. The shell was ground up further after it dried. Scheme 1 shows the structures of both chitin and chitosan. The complete synthesis of chitin and chitosan can be found in the supporting information section.

Scheme 1: Structures of chitin and chitosan



1-hexyl-3-methylimidazolium acetate, or [Bmim]OAc, was synthesized by combining and cooling 1-methylimidazole with ethyl acetate, then adding 1-chlorohexane. Eventually the top layer and excess 1-chlorohexane were removed, followed by the production of [Bmim]OAc¹, with purities of over 99.9 % by weight and a water content of less than 1000 ppm.² The synthesis of [Bmim]OAc can be seen in Scheme 2. The exact synthesis of [Bmim]OAc can be found in the supporting information section.

Scheme 2: Synthesis of [Bmim]OAc



To combine both chitosan and [Bmim]OAc into one compound, chitosan was dissolved into an acidic solution (1% v/v using glacial acetic acid) to a final concentration of 1% w/v and was stirred overnight, with a pH of 3.5. 15 mL of the chitosan solution was put in Petri dishes and evaporated 50°C for 2 days. The IL was then added by 99% wt. The solution was stirred vigorously for 12 hours, producing a chitosan/IL film. The film was then neutralized in a 20 mL bath of 0.5 M NaOH solution for 10 seconds and then washed three times with bi-distilled water. The films were then dried for 24 hours at 37°C.³ The chitosan/[Bmim]OAc film was used to capture CO₂.

Capture of CO₂

A thermogravimetric analysis (TGA) instrument was used to capture CO₂. 10-15 mg of the chitosan/IL film was loaded onto the platinum pan of the TGA. To remove excess water, the IL/chitosan film was exposed to N₂ at 40°C in an isothermal mode. CO₂ was then introduced to the system, mimicking as it would in the atmosphere. It was streamed in at 5 mL/min at 25°C. Once equilibrium was reached, the IL/chitosan compound was again purged with N₂ at 80°C to release CO₂.

To determine the amount of CO₂ captured, ¹H and ¹³C NMR spectroscopy, volume expansion ratio, and solvatochromic UV-vis experiments were conducted. The experiment was conducted on a Prestige-21 FT-IR spectrometer (Shimadzu, Japan), using a single-reflection ATR cell. The instrument was used in the DTGS detector mode using an accumulation rate of 40 scans at a resolution of 4 cm⁻¹ at 25°C from 400 to 4600 cm⁻¹.

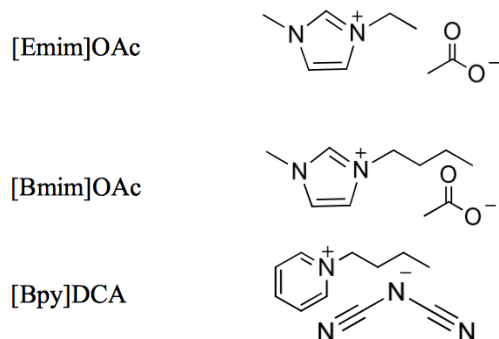
The sample was measured three times. The spectra is shown in the supporting information.

To take NMR measurements on the IL/CO₂ system, the IL/CO₂ compounds were prepared by loading each sample into the high-pressure view cell of the TGA and allowing CO₂ to enter the cell at 6.6 MPA at 25°C. Once the system equilibrated (at least 12 hours), the pressure was released to 0.1 MPA to remove excess CO₂. The NMR samples were measured as liquids using a coaxial capillary that contained (DMSO-d₆). ¹H and ¹³C NMR measurements were performed on a Bruker Avance III 400 HD spectrometer at a setting of 400 MHz for ¹H and 100 MHz for ¹³C.²

The measurement apparatus of solvatochromic parameters of the IL/CO₂ compound were carried out at various pressures. The apparatus contained a gas cylinder, a high-pressure UV-vis sample cell, a high-pressure pump, a pressure gage, and a temperature adjuster. The optical path length and inner volume of the sample cell were 21 mm and 6.5 mL. Three stock solutions were prepared by adding different dyes to methanol. The dyes were N,N-diethyl-4-nitroaniline (DENA), 4-nitroaniline (NA), and Reichard's dye 33 (RD33).⁴ The UV-vis absorbance was executed on a model TU-1201 spectrophotometer.

With the measurements from these experiments, the sorption efficiency of CO₂ with respect to two other ILs were compared to [Bmim]OAc: 1-ethyl-3-methylimidazolium acetate, [Emim]Oac, and 1-butyl-pyridinium dicyanamide, [Bpy]DCA, shown in Scheme 3. Table 1 shows that [Bmim]OAc has the highest sorption efficiency of chitosan/IL CO₂ capturing when being compared to [Emim]OAc and [Bpy]DCA. It can be seen that [Bmim]OAc has a sorption efficiency maximum at 7 n_{CO2}/n_{IL}, [Emim]DCA has a sorption efficiency maximum at 6.26 n_{CO2}/n_{IL}, and [Bpy]DCA has a sorption efficiency maximum at 5.6 n_{CO2}/n_{IL}. The environmental

conditions for this experiment were at 25°C under one atm CO₂.⁵ Also, the sorption efficiency is compared in Figure 4 between [Bpy]DCA [Bmim]DCA. It is seen that [Bmim]DCA has a larger sorption efficiency than [Bpy]DCA. It should be noted that the experimental condition factors were different in Figure 4 and Table 1.



Scheme 3: Structures of 1-ethyl-3-methylimidazolium acetate, [Emim]OAc, 1-butyl-3-methylimidazolium acetate, [Bmim]OAc, and 1-butyl-pyridinium dicyanamide, [Bpy]DCA.

Each of the three ILs were utilized in the TGA instrument with their respective chitosan compound. The measurements between these three compounds measured how long it took to absorb CO₂ in the environments. The experiment was carried out at 25°C using 6.0 wt % chitosan/IL. Figure 2 shows the results of this experiment in terms of the volume expansion ratio of CO₂ capture with [Bmim]CO₂. With the calculations of the CO₂ capturing spectra, the volume expansion ratio was calculated for each of the three ILs with respect to CO₂ pressure, which is shown in Figure 3. Here is seen that the best CO₂ capturing IL is [Bpy]DCA > [Emim]OAc > [Bmim]OAc. It is interesting that in this case, [Bmim]OAc is the least effective CO₂ capturing IL.²

While each ionic liquid shows different maximas for CO₂ absorptivity under different conditions, [Bmim]OAc is more economical than [Emim]OAc and [Bpy]DCA. Figure 5 shows that 1 gram of [Bmim]OAc is \$19.80, while 1 gram of [Emim]OAc is \$40.60 and 1 gram of [Bpy]DCA is \$63.00 (Sigma Aldrich). In each of the previous experimental examples, [Bmim]OAc does a comparative job at capturing CO₂ in the same environmental conditions as to the two other ILs. Therefore, [Bmim]OAc is a cheaper CO₂ capturing IL than [Emim]OAc and [Bpy]DCA.

Table 1: Comparison of sorption efficiency for varying 6 wt% chitosan/IL solutions at 25°C under 1 atm CO₂.

Time (min ⁻¹)	[Bmim]OAc (n _{CO2} /n _{IL})	[Emim]OAc (n _{CO2} /n _{IL})	[Bpy]DCA (n _{CO2} /n _{IL})
0	0	0	0
50	3.2	2.6	2.75
100	4.5	3.5	4.5
150	5.6	4.4	4.8
200	6.63	4.9	5.08
250	6.68	5.25	5.25
300	6.75	5.5	5.5
350	6.8	5.7	5.51
400	6.87	5.9	5.53
450	6.95	6	5.58
500	7	6.08	5.6
550	7	6.25	5.6
250	6.68	5.25	5.25

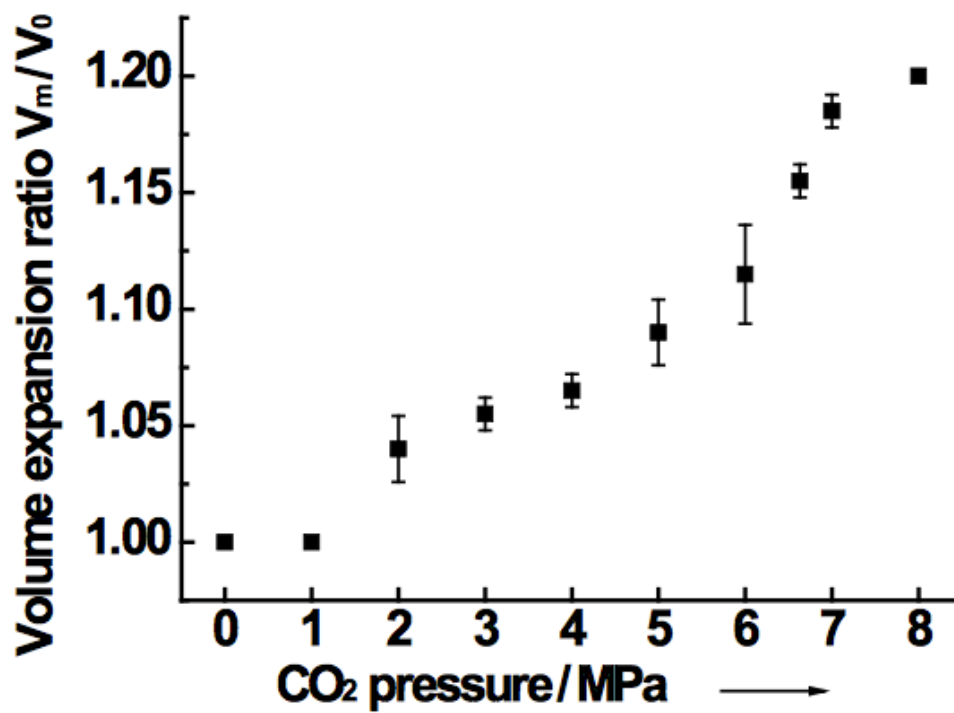


Figure 2: The volume expansion ratio (V_m/V_0) of 6.0 wt% chitosan/[Bmim]OAc solution at 25°C after charging compressed CO_2 .

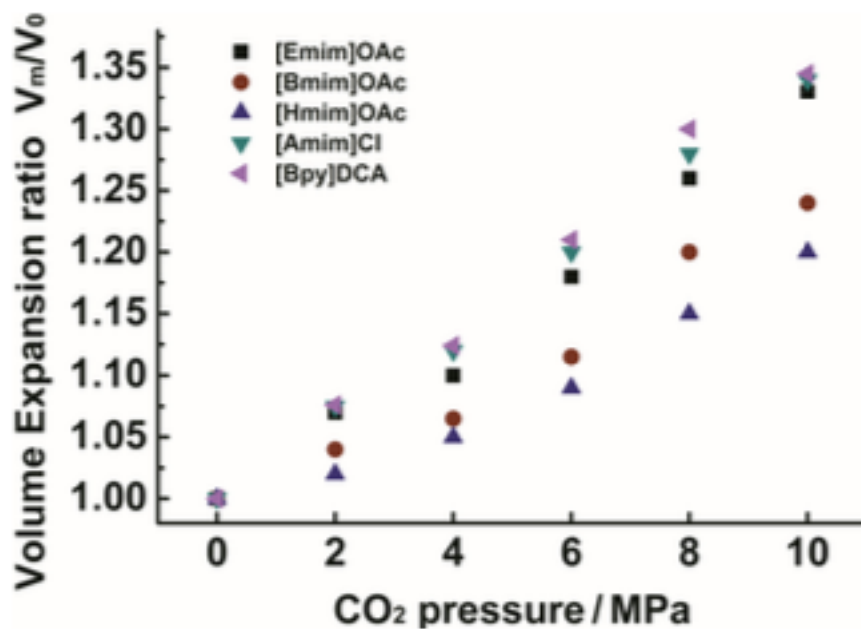


Figure 3: The three different ILs, [Emim]OAc, [Bmim]OAc, and [Bpy]DCA were compared with respect to the amount of CO₂ each can absorb. Each compound was 6.0 wt. % chitosan/IL at 25°C at varying pressures.

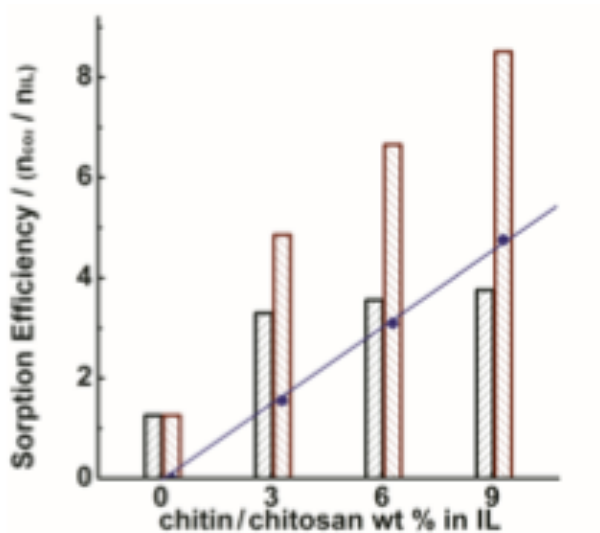


Figure 4: CO₂ saturation capacities for [Bmim]OAc (red bar) and [Dpy]DCA (black bar) with their respective chitosan solution.

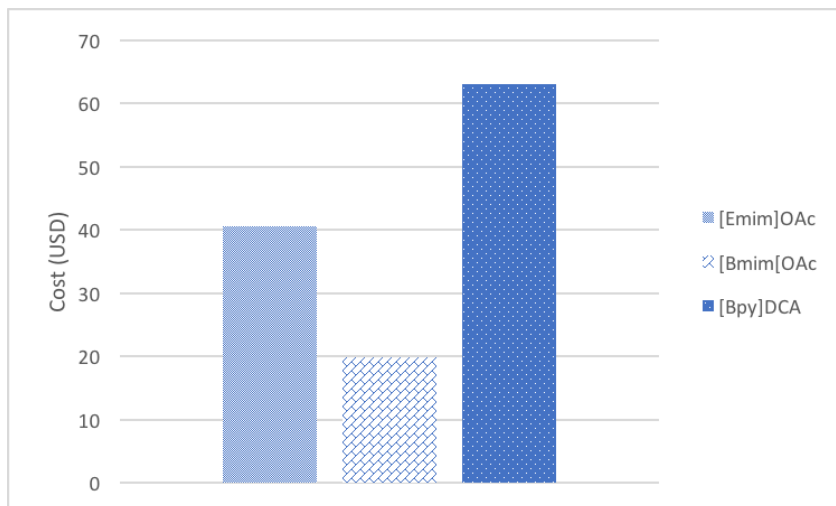


Figure 5: Cost comparison (in USD) between three ILs: [Emim]OAc, [Bmim]OAc, and [Bpy]DCA.

Results and Discussion

Conclusion

Supplementary Material Available

The appendix contains a more detailed description of the process and preparation of the substrates, as well as their characterization.

References

- ¹ Griffith, Jeraime, Tom Welton. Synthesis of 1-Hexyl-3-methylimidazolium Chloride. *ChemSpider Synthetic Pages*. **2015**, 786.
- ² Sun, Xiaofu, Chengyi Huang, Zhimin Xue, and Tiancheng Mu. An Environmentally Benign Cycle to Regenerate Chitosan and Capture Carbon Dioxide by Ionic Liquids.

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³ Dias, A. M. A., A. R. Cortez, M. M. Barsan, J. B. Santos, C. M. A. Brett, and H. C. De Sousa. Development of Greener Multi-Responsive Chitosan Biomaterials Doped with Biocompatible Ammonium Ionic Liquids. *ACS Sustainable Chemistry & Engineering*. **2013**, 1.11, 1480-492.

⁴ Oehlke, A.; Hofmann, K.; Spange, S. New aspects on polarity of 1-alkyl-3-methylimidazolium salts as measured by solvatochromic probes. *New J. Chem.* **2006**, 30, 533-536.

⁵ Sun, Xiaofu, Chengyi Huang, Zhimin Xue, and Tiancheng Mu. An Environmentally Benign Cycle To Regenerate Chitosan and Capture Carbon Dioxide by Ionic Liquids. *Energy Fuels*. **2015**, 29 (3), pp 1923–1930.

Supporting Information

Carbon Dioxide Capture Through 1-Hexyl-3-Methylimidazolium Acetate

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Synthesis of Chitin and Chitosan

Crab meat was removed and the crab shells were cleaned, dried, and ground into small pieces. The shells were demineralized under 4% HCl at room temperature with a solid to solvent ratio of 1 g:14 mL for 36 hours. This produced a squashy substance of shells and calcium chloride in the form of a solution. In this demineralization step, CaCO_3 was eliminated in a diluted acidic solution. Next, the protein content of the shells was withdrawn from the main chemical structure during the proteinization step. It was deproteinized by treating the shell compound in 5% concentration of NaOH at 90°C for 24 hours. This solution had a solid to solvent ratio of 1 g:12 mL. It was then dried at 150°C under vacuum pressure, which produced chitin.

To convert chitin to chitosan, chitin undergoes a process that involves a partial removal of the acetyl groups from the chitin structure. Chitin was treated with a 45% concentration of NaOH in a 1g:15mL solid to solvent ratio at 110°C. It was also combined with strong hydroxide at room temperature for 24 hours. This produced chitosan, which was then purified in 2% concentration of acetic and was re-precipitated with 20% concentration of NaOH solution. The chitosan was freeze dried with methanol and after lyophilized under -70°C.

Synthesis of [Bmim]OAc

A 2 L, three necked, round bottom flasks were set up with a hot water bath, a N₂ source, a thermometer, a mechanical stirrer, and a reflux condenser. It should be noted that N₂ (99.999%) was purchased from Beijing Huayuan Gas Chemical Industry Co., Ltd. (Beijing, China). The flask was flushed with N₂ and 151.5 g N-methylimidazole, 100 mL acetonitrile, and 220 g of 1-chlorobutane.

N-Methylimidazole was purchased from Aldrich Chemical Company, Inc. (99%) and was dried over KOH pellets and distilled at 211°C. Acetonitrile was purchased from Merk and was distilled over P₂O₅. 1-Chlorobutane was purchased from Merk and was used as was.

These chemicals were brought to a gentle reflux with a temperature of 75-80°C for 48 hours. The solution was constantly checked to ensure it did not exceed 85°C. After, it was cooled to room temperature. Acetonitrile and excess 1-chlorobutane became a volatile substance and was removed via a liquid nitrogen trap. The solution came out to be 35% 1-chlorobutane by weight, which was determined by gas chromatography, and was stored in a dark flask.

The remaining oil-like solution was re-dissolved in 250 mL dry acetonitrile and added dropwise via cannula to a solution of 1000 mL of dry ethyl acetate and one seed crystal of 1-butyl-3-methylimidazolium chloride were placed in a 2 L, three-necked round bottom flask, which contained a N₂ inlet source and a mechanical stirrer. Ethyl acetate was purchased from Merck and was distilled over P₂O₅. The seed crystal was obtained by dissolving ~1 g of the crude imidazolium salt in 3 mL of acetonitrile. This solution was kept at about 30°C overnight. Spontaneous crystallization was observed when the volatile materials were removed. To determine the morphology of the imidazolium salt, a 150-rpm agitation speed was used.

The imidazolium salt began to crystallize exothermically almost immediately. After the acetonitrile solution was added, the flask was cooled at -30°C for 2 hours. The solution was removed via filtration through a filter cannula, producing a white solid. The solid was then ground then dried under reduced pressure (0.1 mbar, 0.001 mm) at 30°C for 6 hours. 289.5 g of [Bmim]OAc was produced with a purity of 89% and a melting point of $66-67^{\circ}\text{C}$. To obtain these characteristics, differential scanning was performed at a heating rate of $2^{\circ}\text{C}/\text{min}$ from 20°C to 100°C . A conventional melting point apparatus was also used.

Spectral Properties of Chitin

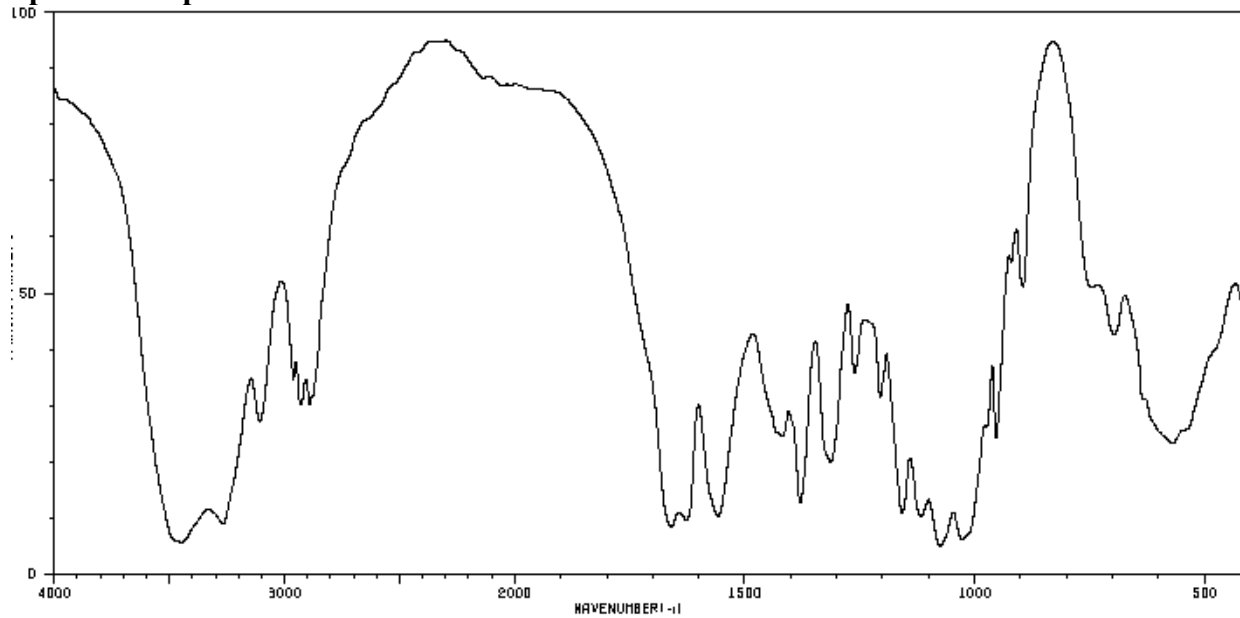


Figure S1: IR spectrum of chitin obtained from crab shells.

The above figure shows the IR spectrum of chitin that was obtained from crab shells.

Spectral Properties of Chitosan

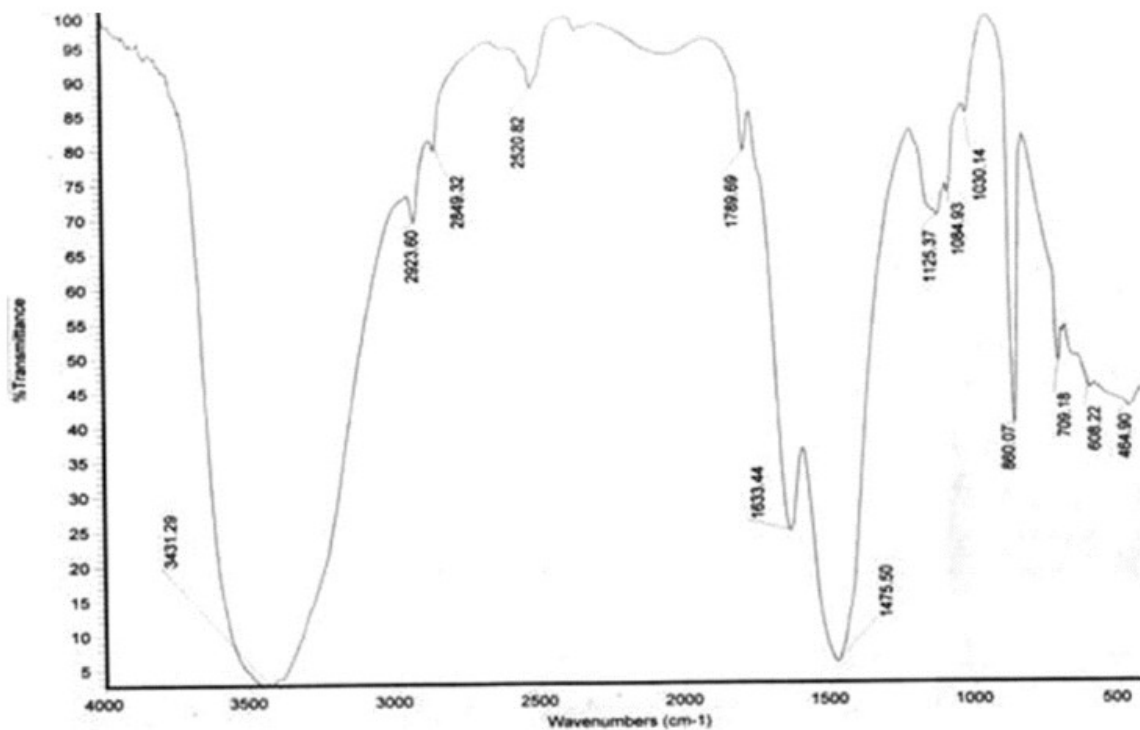


Figure S2: IR Spectrum of chitosan.

The above figure shows the IR spectrum for chitosan, which was obtained from the chitin of crab shells.

Spectral Properties of [Bmim]OAc.

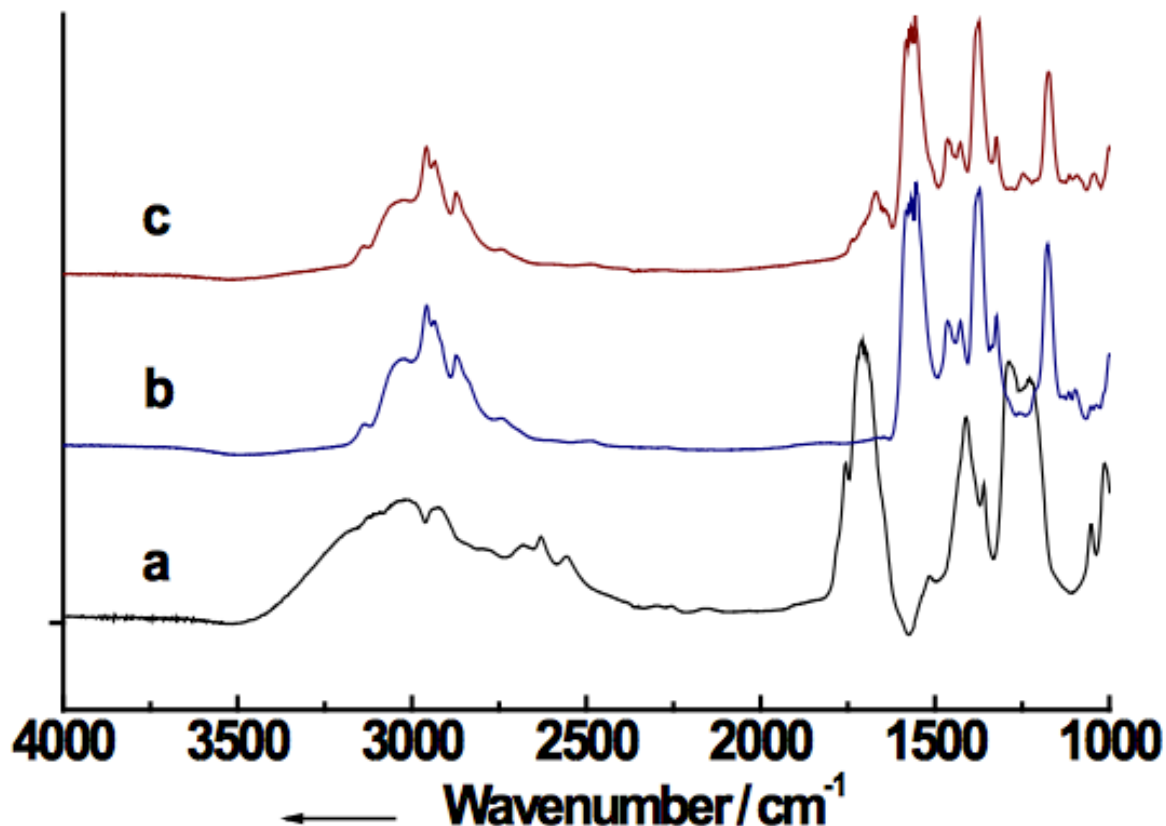


Figure S3: ATR-FTIR spectra of various forms of [Bmim]OAc: pure acetic acid (a), pure [Bmim]OAc at 25°C (b), and [Bmim]OAc at 140°C (c).

The figure above shows various spectral forms of [Bmim]OAc. Spectra b is of most importance since it shows the ATR-FTIR spectrum of [Bmim]OAc around room temperature.

Table S1. Spectral Properties of [Bmim]OAc.

Proton	δ (ppm)	$^3J_{HH}$	δ (ppm) (multiplicity)
1H-s	9.38	7.79	13.6
1H-s	7.84	--	19.6
2H-s	4.18	7.1	32.3
3H-s	3.87	4.07	36.6
2H-m	1.78	--	49.8
6H-m	1.30-1.21	--	122.3
3H-t	0.86	7.3	124.0

The above table is the spectral properties of the ^1H -NMR and ^{13}C -NMR spectra of [Bmim]OAc. ^1H -NMR was conducted under 400 MHz with DMSO- d_6 . ^{13}C -NMR was conducted under 75 MHz with CDCl_3 .

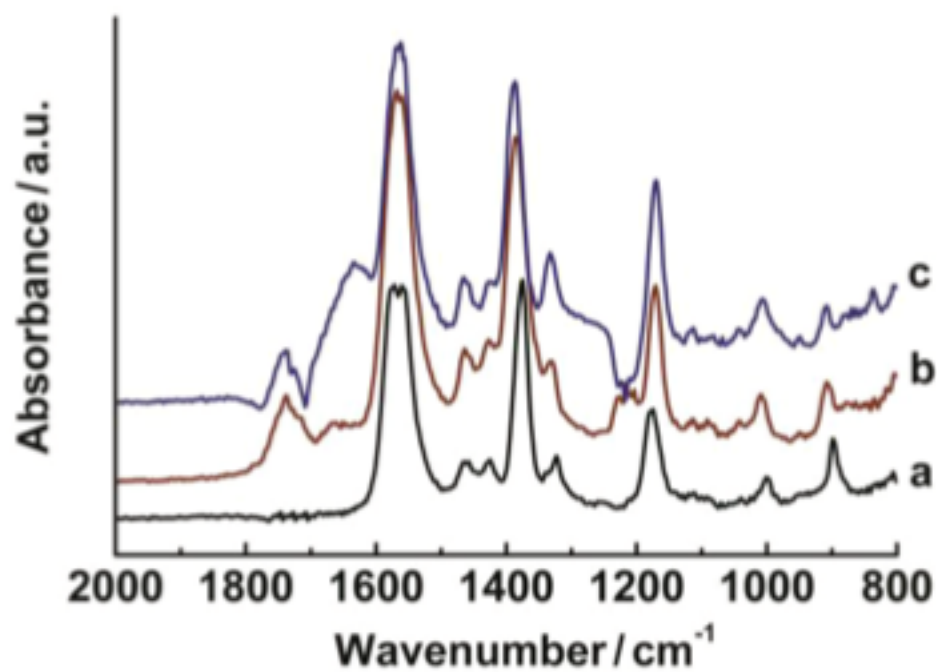


Figure S4. ATR-IR spectra of pure [Bmim]OAc (curve a), [Bmim]OAc containing 9 wt. % chitosan (curve b), and after CO₂ capture at room temperature (curve c).

Bibliography

Griffith, Jeraime, Tom Welton. Synthesis of 1-Hexyl-3-methylimidazolium Chloride. *ChemSpider Synthetic Pages*. **2015**, 786.

Sun, Xiaofu, Chengyi Huang, Zhimin Xue, and Tiancheng Mu. An Environmentally Benign Cycle to Regenerate Chitosan and Capture Carbon Dioxide by Ionic Liquids. *Energy & Fuels*. **2015**, 29.3, 1923-930.

Dias, A. M. A., A. R. Cortez, M. M. Barsan, J. B. Santos, C. M. A. Brett, and H. C. De Sousa. Development of Greener Multi-Responsive Chitosan Biomaterials Doped with Biocompatible Ammonium Ionic Liquids. *ACS Sustainable Chemistry & Engineering*. **2013**, 1.11, 1480-492.