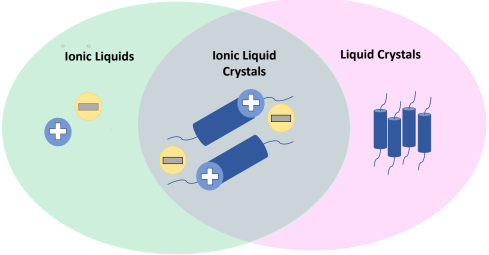
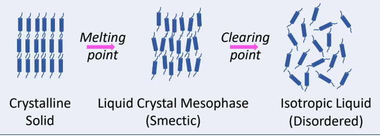
CO_2 Sorption in Ionic Liquid Crystals

Grace Redwine[1,2], Noemi Leick[2], Thomas Gennett[1,2]
[1]Department of Chemistry, Colorado School of Mines, Golden, CO
[2]National Renewable Energy Laboratory, Golden, CO

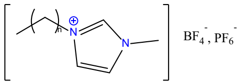
Introduction



Liquid Crystal Phases



Introduction: Ionic liquid crystals (ILCs) have an affinity for certain polarizable gases such as CO_2, due to their similarity to ionic liquids. We investigated three ILCs in the [1-alkyl-3-methylimidazolium$^+$] family: *n*=12,14 with [BF_4^-] and [PF_6^-]: liquid crystalline analogues to ionic liquids with moderate (e.g., 1-2 mol%) CO_2 solubility at atmospheric conditions: [1-butyl-3-methylimidazolium$^+$] with [BF_4^-] and [PF_6^-].



Motivation: While ionic liquids show high CO_2 solubility, regenerating the CO_2 is a high-energy process. Liquid crystals show low CO_2 solubility but have a much lower regeneration energy requirement.

Research Questions: 1. Will ionic liquid crystals uptake CO_2? 2. What are the energy requirements of regenerating CO_2?

Key Findings

1. Will ionic liquid crystals uptake CO_2?
- $C_{12,14}$mim BF_4^- show significant absorption of CO_2 in the isotropic and smectic phases
- C_{14}mim PF_6^- does not show CO_2 absorption

2. What are the energy requirements of regenerating CO_2?
- Regeneration of CO_2 requires heating to the melting point: 27 °C (C_{12}mim BF_4^-) and 41 °C (C_{14}mim BF_4^-). This is significantly less than the heating required to regenerate CO_2 from ionic liquids (>100 ° C). In addition, refrigeration temperatures (0-5 °C) are enough to occlude the CO_2 in the crystalline phase to store.

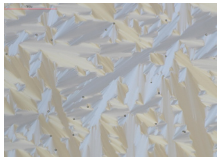
Methods

- Temperature Programmed Desorption (TPD): The TPD system used for this study is a calibrated, custom-built system that is equipped with a Stanford Research System RGA 100 mass spectrometer able to measure mass-to-charge ratios from 1 - 100 amu. *In-situ* CO_2 dosing was performed at 760 torr.
- Thermogravimetric Analysis (TGA): a TA instruments Q600 SDT was used to monitor heat flow and weight fluctuation in samples under continuous flow (100 ml/min) of specified gas.
- Polarized Optical Microscopy (POM): An Olympus BX53-P equipped with a Linkam LTS420 hot stage.
- Differential Scanning Calorimetry: A TA Instruments DSC 25 equipped with a Discovery liquid N2 pump.

Initial Characterization

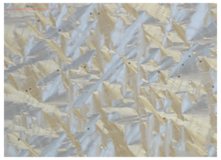
Smectic Phase Shown in Images

C_{14}mim PF_6^-



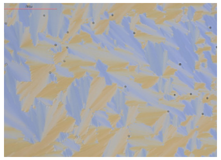
Isotropic → Smectic: **74.7 °C**
Smectic → Crystalline: **64.0 °C**

C_{14}mim BF_4^-



Isotropic → Smectic: **117.0 °C**
Smectic → Crystalline: **40.1 °C**

C_{12}mim BF_4^-



Isotropic → Smectic: **44.7 °C**
Smectic → Crystalline: **26.5 °C**

Experimental

Investigating Diffusivity of CO_2 into C_{14}mim BF_4^-

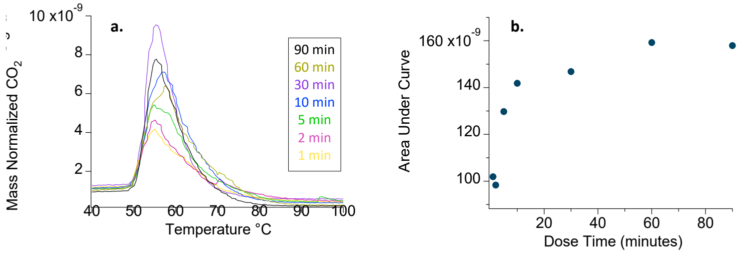


Figure 1. Time-dependent CO_2 diffusion into the isotropic phase of C_{14}mim BF_4^-.
a) Mass normalized signal of CO_2 (m/z 44) vs. temperature, for different dosing durations.
b) Area under the curves from a.) vs. dose time in minutes.

Using TPD to Investigate Sorption of CO_2 into ILCs

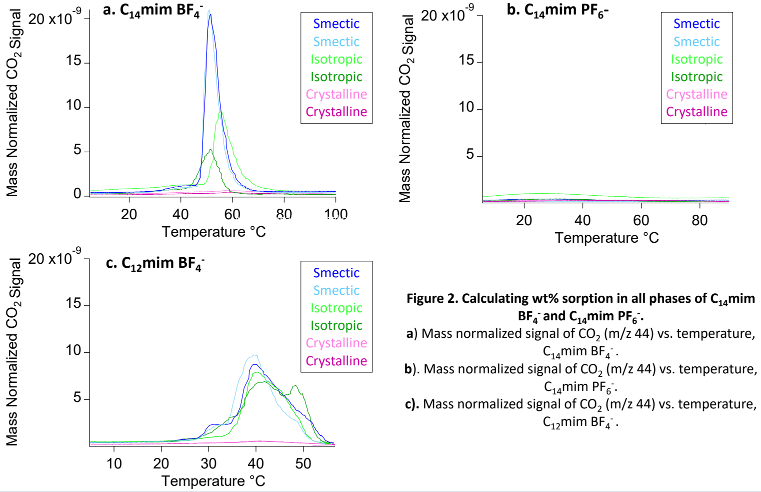


Figure 2. Calculating wt% sorption in all phases of C_{14}mim BF_4^- and C_{14}mim PF_6^-.
a) Mass normalized signal of CO_2 (m/z 44) vs. temperature, C_{14}mim BF_4^-.
b). Mass normalized signal of CO_2 (m/z 44) vs. temperature, C_{14}mim PF_6^-.
c). Mass normalized signal of CO_2 (m/z 44) vs. temperature, C_{12}mim BF_4^-.

Results

Weight Percent of CO_2 in ILCs

C_{14}mim BF_4^-	Phase	Weight Percent CO_2 (%)
	crystalline	0.011
	smectic	0.099
	isotropic	0.062
C_{14}mim PF_6^-	Phase	Weight Percent CO_2 (%)
	crystalline	0.0089
	smectic	0.0023
	isotropic	0.010
C_{12}mim BF_4^-	Phase	Weight Percent CO_2 (%)
	crystalline	0.0081
	smectic	0.11
	isotropic	0.11

Conclusions

Factors known to affect solubility in both ionic liquids and liquid crystals:
Ionic Liquids
- Cation/anion interactions with CO_2[1] and free volume[3,4]

Liquid Crystals
- Phase and free volume[2]

Free volume is the primary factor affecting CO_2 solubility in both[3,4]

Conclusions:
- C_{12}mim BF_4^- shows the highest sorption at 0.12 wt% CO_2 in the isotropic phase vs. C_{14}mim BF_4^- with 0.097 wt% in the smectic phase.
  - *We hypothesize that the increase in chain length affects the free volume of the smectic vs. isotropic phase of C_{14}mim BF_4^-, increasing the latter.*
- The change in anion from BF_4^- to PF_6^- decreased the sorption to an insignificant level more analogous to a physical adsorption onto the material in all phases.
  - *We hypothesize that the change in anion to the larger, less charge dense PF_6^- decreased the attractive forces between CO_2 and the anion.*
- 0.12 wt% of CO_2 in C_{12}mim BF_4^- is small but significant. This is in addition to the room temperature release of CO_2 after only requiring refrigeration temperatures to occlude the CO_2, making ionic liquid crystals promising materials for future research.

Future work:
- Optimize model and calculate diffusion coefficients for ILCs in both liquid phases.
- Incorporate theoretical and computational work to probe differences between the three systems: free volume, attractive and repulsive forces, chain length dynamics.
- Investigate these systems on a longer timescale: how long is CO_2 retained in these ILCs at temperatures above 0 °C and below the melting points?
- Determine the potential of using these ILCs for H_2 storage applications.

References

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Acknowledgments

This work was supported by the Hydrogen Materials-Advanced Research Consortium (HyMARC), established as part of the Energy Materials Network under the U. S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Hydrogen and Fuel Cell Technologies Office.

ACS FALL 2022
Sustainability in a Changing World
August 21 - 25, 2022
Chicago, IL & Hybrid
NREL/PO-5900-83801