

# PROBLEM BASED LEARNING, POLYMER MEMBRANES, AND IONIC LIQUIDS



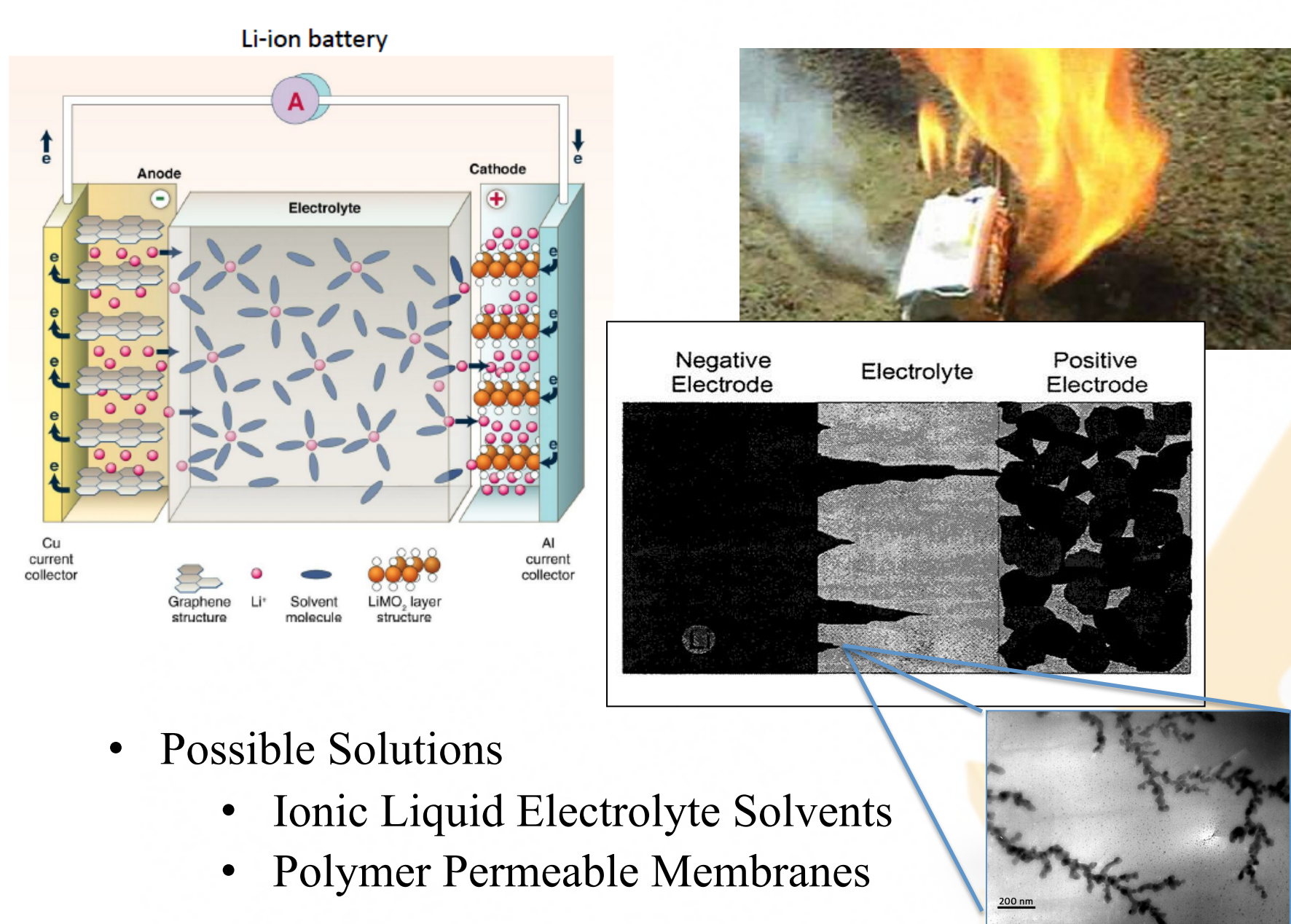
Dr. Joan Brennecke, Dr. Aruni Desilva, Dr. William Phillip,  
Jacob Weidman, Dan Fagnant, & Thomas C. Adams



Chemical and Biomolecular Engineering, University of Notre Dame

## Introduction

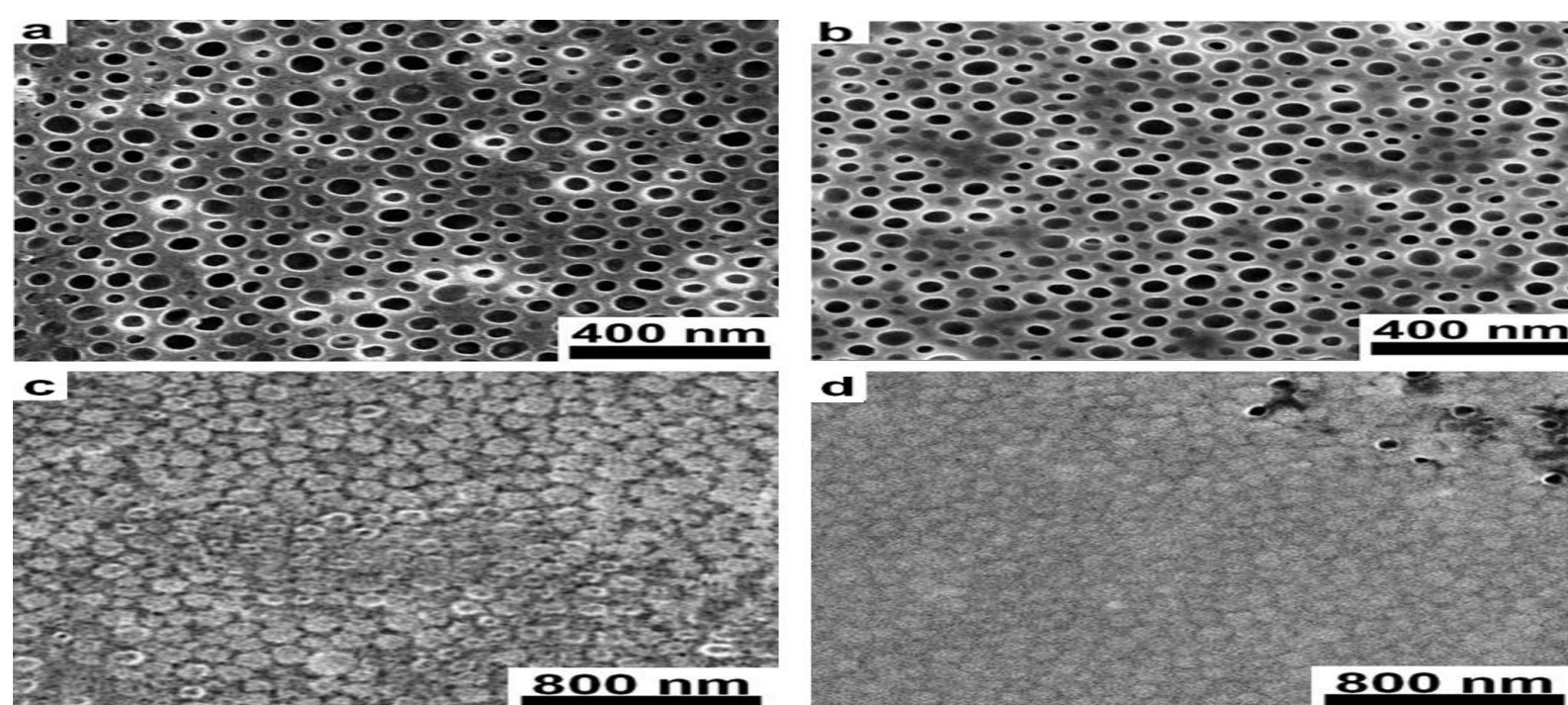
- Renewable energy has many challenges
  - Solar – Only during daylight hours
  - Wind – Only when the wind blows
  - Electric Cars – Batteries can be dangerous
- Storage is a necessity - Batteries need to be safer
- Lithium Ion Batteries
  - Dendrite growth can cause shorts / fires
  - Organic solvents are flammable



- Possible Solutions
  - Ionic Liquid Electrolyte Solvents
  - Polymer Permeable Membranes

## Problem

- Wetting membranes with ionic liquids cause swelling
- Need to predict permeable membrane diameter
  - Must be big enough for lithium ions to pass
  - Must be small enough to block dendrite growth
- Attempt to find a predictor of swelling effects

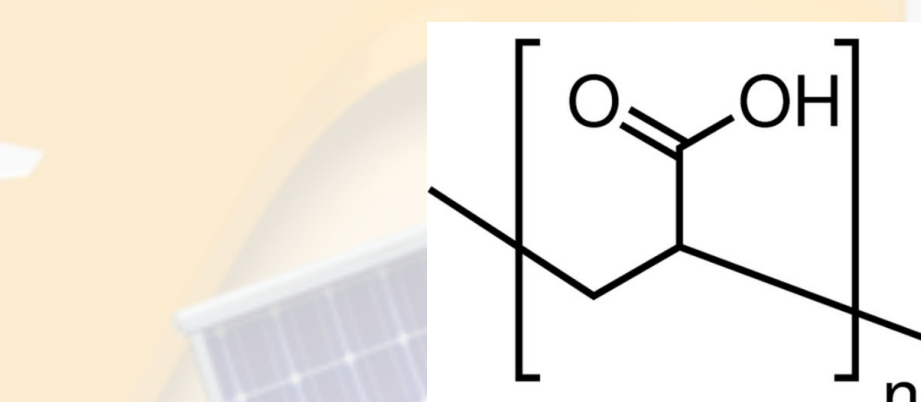


- Kamlet-Taft parameters ( $\alpha$ ,  $\beta$ , and  $\pi$ ) predict hydrogen bonding and polarities of the ionic liquids, which may affect the swelling of polymer membrane

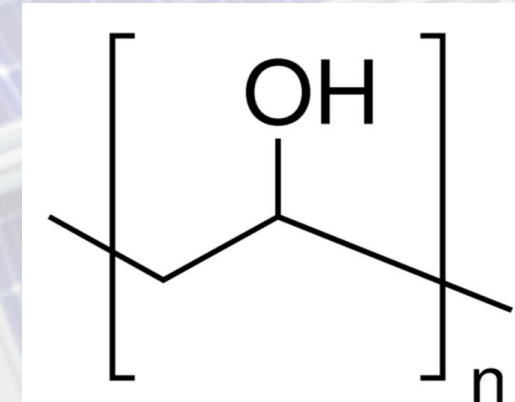


## Materials and Methods

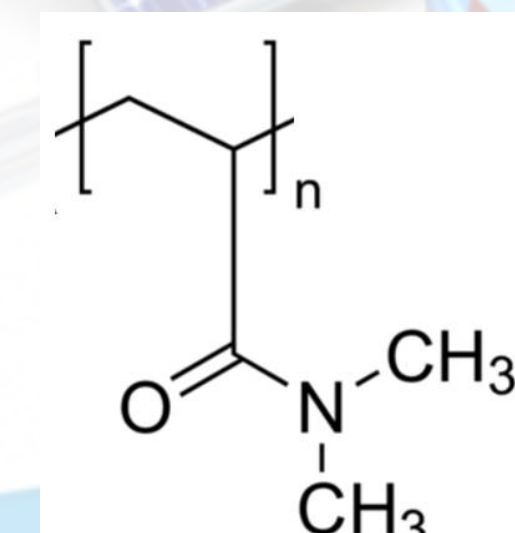
- To calculate Kamlet-Taft Values
  - Dilute dye in ionic liquids
    - Reichardt's Dye (30)
    - 4-nitroaniline
    - N, N-diethyl-4-nitroaniline
  - 250  $\mu\text{M}$  / L
  - Run UV-Vis scan to find maximum absorbance
  - Calculate  $E_N^T$  – normalized polarity based on max
  - Calculate Kamlet-Taft Values of  $\alpha$ ,  $\beta$ , and  $\pi^*$ 
    - $\alpha$  – Hydrogen Bond Donor – Acidity
    - $\beta$  – Hydrogen Bond Acceptor – Basicity
    - $\pi$  – Dipolarity / Polarizability Ratio
  - Soak samples of Emim[ $\text{Tf}_2\text{N}$ ] and Hmim[ $\text{Tf}_2\text{N}$ ] in:
    - Poly (Acrylic Acid) – PAA



- Poly (Vinyl Alcohol) – PVA



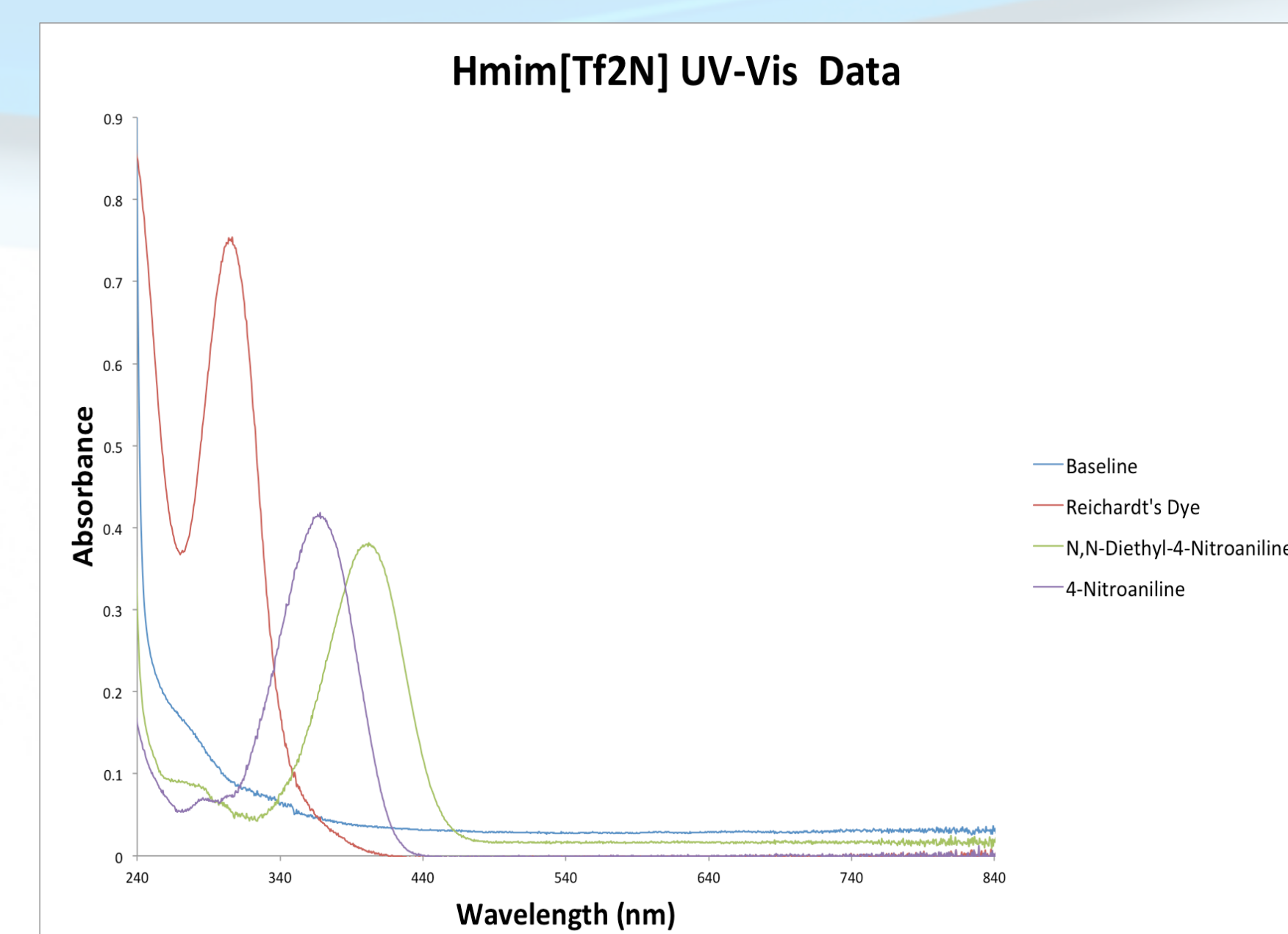
- Poly (Dimethylacrylamide) – PDMA



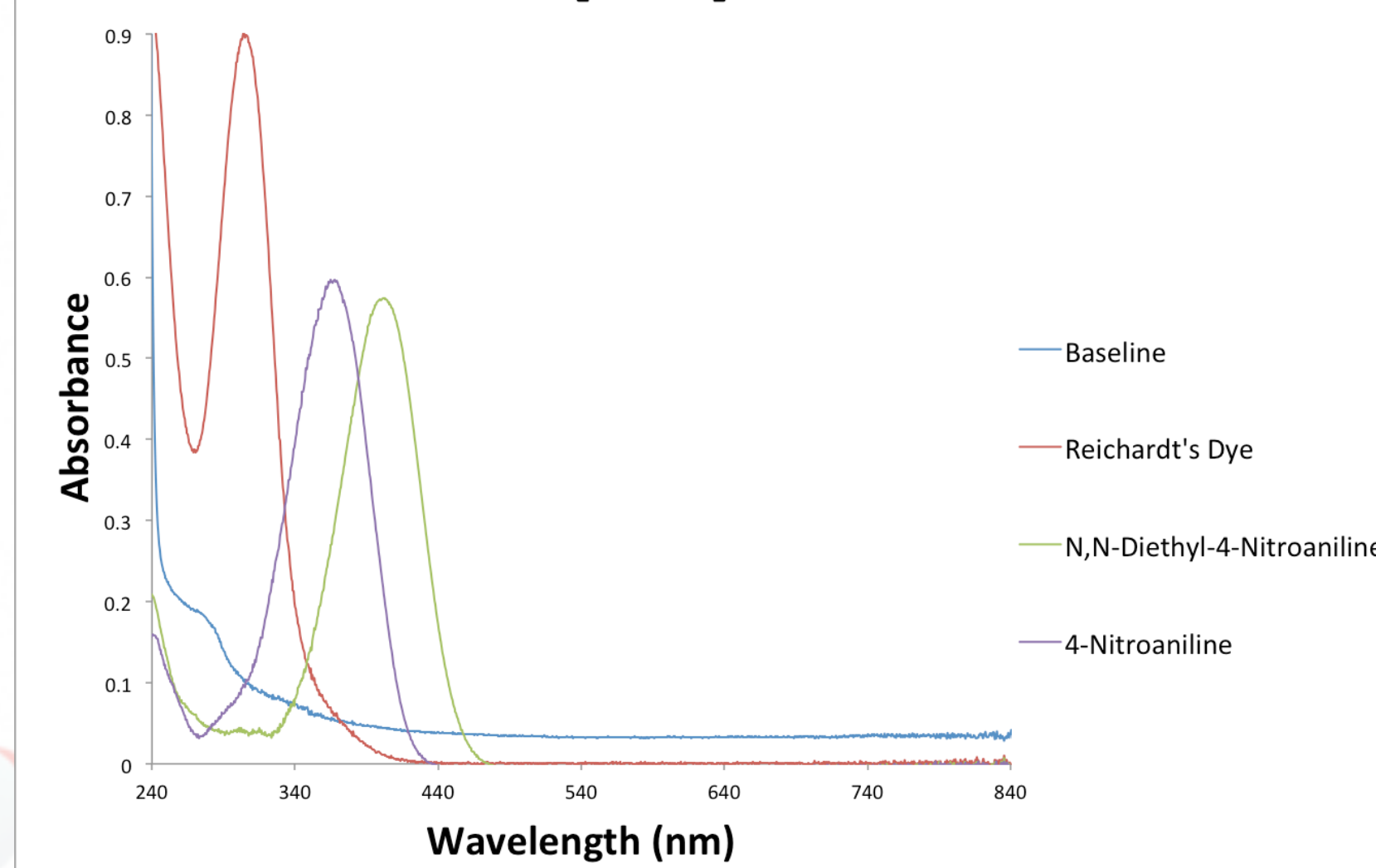
- Determine effects of ionic liquids on polymer membranes

## Results

- UV-Vis Scan confirmed published Kamlet-Taft values for Emim[ $\text{Tf}_2\text{N}$ ] and Hmim[ $\text{Tf}_2\text{N}$ ]



Emim[ $\text{Tf}_2\text{N}$ ] UV-Vis Data



- Subtle differences in Kamlet-Taft values (published):

Ionic Liquid	Abbreviation	Alph	Beta	PI*
1-Hexyl-3-methylimidazolium bis(trifluoromethanesul)	[C6C1im][NTf2]	0.65	0.26	0.97
1-Hexyl-3-methylimidazolium chloride	[C6C1im]Cl	0.48	0.94	1.02
1-Hexyl-3-methylimidazolium bromide	[C6C1im]Br	0.45	0.74	1.09
1-Butyl-3-methylimidazolium bis(trifluoromethanesul)	[C4C1im][NTf2]	0.72	0.24	0.9
1-Ethyl-3-methylimidazolium bis(trifluoromethanesul)	[C2C1im][NTf2]	0.71	0.23	0.98
1-Octyl-3-methylimidazolium bis(trifluoromethanesul)	[C8C1im][NTf2]	0.6	0.29	0.96

- Differences in membrane diameters as well:

	A	B	C	D
1 Poly(acrylic acid)	PAA MW	(Diameter (nm) in emim)	(Diameter (nm) in hmim)	
2	130	3789	4542	
6 Poly(vinyl alcohol)	PVA MW			
7	40	3316	3850	
11 Poly(dimethylacrylamide PDMA MW				
12	76	4565	5177	

- Hmim[ $\text{Tf}_2\text{N}$ ] has a higher  $\beta$  value
- Hmim[ $\text{Tf}_2\text{N}$ ] has a slightly larger diameter
- However both Emim[ $\text{Tf}_2\text{N}$ ] and Hmim[ $\text{Tf}_2\text{N}$ ] have very similar  $\pi^*$  values
- Perhaps one could look at swelling effects of Hmim[Cl] or Hmim[Br] due to the variation of Kamlet-Taft values

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- If  $\beta$  correlates to an increase in diameter than Hmim[Cl] should have the largest diameter
- However, if  $\pi^*$  correlates to an increase in diameter than Hmim[Br] should have the largest diameter

## Conclusions

Hydrogen Bonding or Dipolarity / Polarizability may actually determine the swelling effects of ionic liquids. However, more data is needed. One could try wetting the polymer membranes with Hmim[Br] or Hmim[Cl] to determine if either  $\beta$  or  $\pi^*$  have a greater correlation. Lastly, this research can be used to model real-world challenges, and strategies to solve them. In an effort to prepare students for college and / or career, Tom Adams will present these results to his high school students. Students will follow this curriculum unit outline.

Day	Lesson
1	<ul style="list-style-type: none"> <li>Entry Event 1 – ND Energy Presentation – Dr. Brennecke</li> <li>Knows / Need to Knows</li> <li>Reflection – Engineering Design – Literacy Task</li> </ul>
2	<ul style="list-style-type: none"> <li>Entry Event 2 – Lithium Battery Youtube Videos</li> <li>Standards – NGSS – Engineering and Design</li> <li>Reflection – Engineering Design – Literacy Task</li> </ul>
3	<ul style="list-style-type: none"> <li>Brainstorm / Project Outline</li> <li>Entry Event 3 – Youtube – Electrolyte Dough</li> <li>Scaffolding 1 – Al / Cu Electrolyte Battery Design</li> <li>Reflection – Engineering Design – Literacy Task</li> </ul>
4	<ul style="list-style-type: none"> <li>Make Electrolyte Dough / Aluminum Can Batteries</li> <li>Scaffolding 2 – Salts – Can Salt Exist as a Liquid?</li> <li>Reflection – Engineering Design – Literacy Task</li> </ul>
5	<ul style="list-style-type: none"> <li>Entry Event 4 – Ionic Liquids</li> <li>Scaffolding 3 – Lithium Battery Design</li> <li>Scaffolding 4 – Dendrite Growth – Fire</li> <li>Scaffolding 5 – Polymer Membranes</li> <li>Reflection – Engineering Design – Literacy Task</li> </ul>
6	<ul style="list-style-type: none"> <li>Entry Event 5 – Predicting Swelling Effects</li> <li>Scaffolding 6 – Kamlet-Taft Values</li> <li>Scaffolding 7 – Hydrogen Bonding</li> <li>Reflection – Engineering Design – Literacy Task</li> </ul>
7	<ul style="list-style-type: none"> <li>Modeling with Notre Dame RET Data</li> <li>Write Quadratic Regressions in Excel</li> <li>Find Max Absorbance Based on Equations</li> <li>Reveal Kamlet-Taft Values</li> <li>Reflection – Engineering Design – Literacy Task</li> </ul>
8	<ul style="list-style-type: none"> <li>Entry Event 6 – Membrane / IL Solvent Data</li> <li>Make Observations and Determine Correlations</li> <li>Reflection – Engineering Design – Literacy Task</li> </ul>
9	<ul style="list-style-type: none"> <li>Create Abstract for Poster Session – Literacy Task</li> <li>Create Poster</li> <li>Reflection – Engineering Design – Literacy Task</li> </ul>
10	<ul style="list-style-type: none"> <li>Finish Culminating Products</li> <li>Practice Presentation – Peer Reviewed</li> </ul>
11	<ul style="list-style-type: none"> <li>Poster Session</li> </ul>

Possible collaboration with ND Remote Labs

## Literature Cited

- Ab Rani, M. A., Ab-Rani, M. A., Ab Rani, A., Brant, L., Crowhurst, A., Dolan, M., et al. (2011). Understanding the polarity of ionic liquids. PCCP. Physical Chemistry Chemical Physics, 13(37), 16831-40.
- Lee, J., Lee, S., & Ruckes, J. (2008). Solvent polarities and Kamlet - Taft parameters for ionic liquids containing a pyridinium cation. The Journal of Physical Chemistry.B, 112(5), 1473-1476.
- Reichardt, C. (2005). Polarity of ionic liquids determined empirically by means of solvatochromic pyridinium N-phenolate betaine dyes. Green Chemistry, 7(5), 339-351.
- Spange, S., Spange, R., & Lungwitz, A. (2014). Correlation of molecular structure and polarity of ionic liquids. Journal of Molecular Liquids, 192, 137-143.
- Zhang, Y., Zhang, C., Shi, J., & Brennecke, E. (2014). Refined method for predicting electrochemical windows of ionic liquids and experimental validation studies. The Journal of Physical Chemistry.B, 118(23), 6250-6255.